DECOMPOSITION OF 2-PYRAZOLINES

By
PAUL OTIS SANDERFER

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
August, 1965

ACKNOWLEDGMENTS

The author wishes to extend his thanks to his research director, Dr. W. M. Jones, for his invaluable guidance and encouragement throughout the progress of this work and the preparation of this dissertation. He wishes also to thank the other members of his committee, Dr. G. B. Butler, Dr. W. S. Brey, Dr. J. F. Helling and Dr. T. O. Moore, for their kind assistance.

Special thanks go to the author's wife, Miriam, for typing this dissertation and for having the patience and understanding which made this task so much easier.

The National Science Foundation provided a portion of the financial assistance for this research.

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I. INTRODUCTION

Numerous investigators have studied the condensation of substituted diazomethanes with olefins, especially the olefins of the α, β unsaturated carbonyl type, under quite varied conditions (1,2). This type reaction at low temperatures leads to the general class of heterocyclic compounds known as pyrazolines. The route of addition for the diazomethane to α, β unsaturated carbonyl compounds is shown in Figure 1.

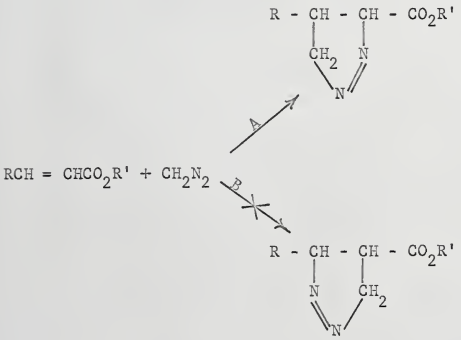
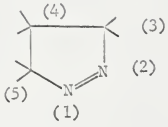
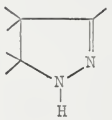


Fig. 1. - Route of Addition of Diazomethane to α, β Unsaturated Carbonyl Compounds (3).

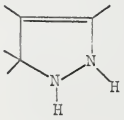
There are three possible isomeric forms of these compounds I, the 1-pyrazoline; II, the 2-pyrazoline; III, the 3-pyrazoline.



I



II



III

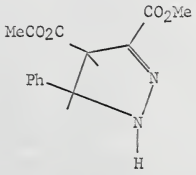
The subsequent discussion in this dissertation will deal exclusively with forms I and II.

Von Auwers and Konig (4) have reported that the initial product of the reaction is I and if one of the substituents on position 3 is hydrogen and the other a group which can conjugate with a double bond ($\rangle$C=O, Ph, -COOR, etc.) then I, either under reaction conditions or by treatment with mineral acids, tautomerizes to the more stable isomer II.

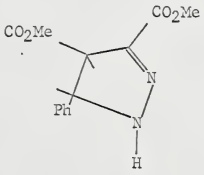
Perhaps the most widely studied reaction of this class of compounds has been their thermal decomposition. Upon heating at or above the melting point, pyrazolines decompose to produce nitrogen gas, olefinic compounds and substituted cyclopropanes. This decomposition has stimulated much interest (1-20).

The conversion of 1-pyrazolines to cyclopropanes and olefinic materials has received quite an intensive study with numerous reports related to its stereospecificity and its proposed path of decomposition (1,4-15).

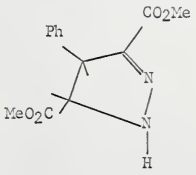
The 2-pyrazoline structure has not received such a concentrated study. Jones (5,15) began such a study. The initial step was to study the stereochemistry of the decomposition of three 2-pyrazolines IV, V and VI. The mechanism of the thermal decomposition has long been presumed to proceed via the 1-pyrazoline followed by loss of nitrogen (1,5,7,15).



IV



V



VI

Jones (15) found that IV and V gave predominately the cyclopropane isomer in which the ester groups were trans and VI gave predominately the cis isomer. These results were very easily explained by the presumed initial tautomerization of the 2-pyrazoline to the thermodynamically favored 1-pyrazoline followed by a stereospecific loss of nitrogen as proposed in Figure 2. This line of reasoning also explained the results of von Auwers (17) who found that the decomposition of 3,4-dicarbomethoxy-2-pyrazoline gave 33% trans-1,2-dicarbomethoxycyclopropane and 2% of the cis isomer. The predominance of the trans isomer over the cis in the case of von Auwer, the stereochemistry of the decomposition of IV, V and

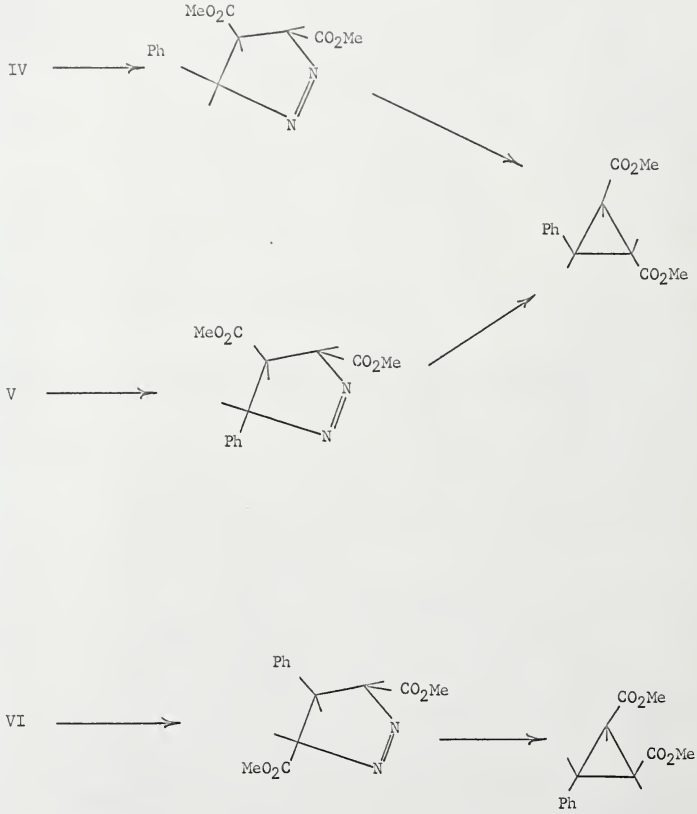
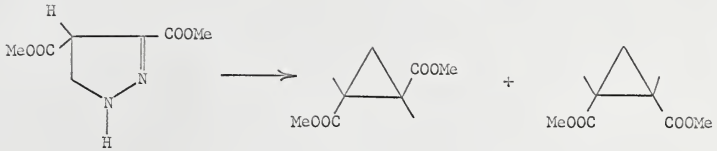
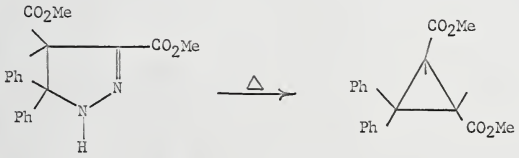


Fig. 2.- Suggested Path for the Decomposition of Three 2-Pyrazolines.



33% 2%

VI from Jones's work, and the report by van Alphen (18) that the decomposition of 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline, VII,



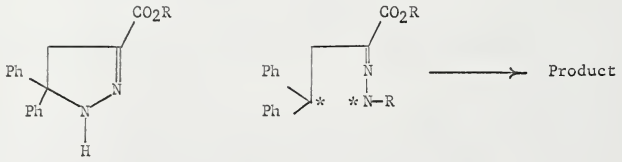
VII trans

gave predominately the trans cyclopropane has been taken as presumptive evidence for the intermediacy of the 1-pyrazoline in these reactions (1,15,20).

In an attempt to further elucidate the mechanism of these conversions, Baarda (21) undertook a kinetic study of the conversion of certain 2-pyrazolines to cyclopropanes. To briefly summarize his results, he found 1) 5,5-diphenyl-2-pyrazolines underwent abnormally rapid decompositions relative to the 5-carboalkoxy-2-pyrazolines; 2) with added base, the decompositions fit the rate expression:

Rate = k_1 (2-Pyrazoline) + k_2 (2-Pyrazoline)(Base); and 3) the thermal decomposition of the 2-pyrazolines under study without added base and in hydrocarbon solvents showed first-order kinetics. From these results, he concluded that the proposed 2-pyrazoline ⟶ 1-pyrazoline reaction scheme was not general and he postulated various possible alternatives.

One alternative suggestion was cleavage of the carbon-nitrogen single bond (C_5-N_1) to give an open intermediate which then could proceed to products. One such scheme is shown in the following equation.



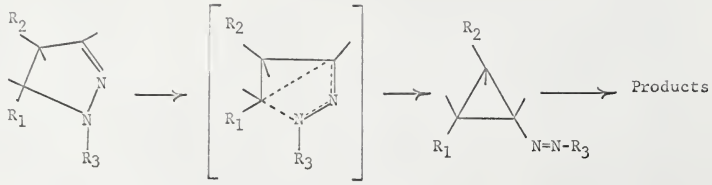
This path was particularly attractive in view of the extremely rapid decomposition rate of the 5,5-diphenyl-2-pyrazolines and the observed first-order kinetics. If an open intermediate of this type were involved, then substitution of phenyl groups at the 5 position would obviously stabilize any type of intermediate that developed. Also, the ring opening would involve only the pyrazoline and if this were the slow step (or rapid step followed by unimolecular decomposition), it would show first-order kinetics.

In order to test the possibility of rapid cleavage of the C_5-N_1 bond, the optically active 5-phenyl-5-(p-methylphenyl)-3-carbomethoxy-2-pyrazoline was synthesized and subjected to partial decomposition. The unreacted starting material was recovered and found to have lost none of its optical activity. This definitely excluded rapid cleavage of the carbon-nitrogen single bond as racemization of the active center would have taken place.

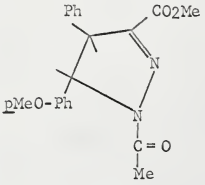
Slow cleavage of the carbon-nitrogen single bond was also eliminated. It was felt that if any open intermediate could form in the case of the 1-hydrogen-2-pyrazoline, it could form much more easily in the case of the 1-acetyl-2-pyrazoline. Therefore, the above optically active 2-pyrazoline was acylated and then subjected to the identical decomposition conditions as used for the parent compound. This reaction was continued over a period of time equivalent to several half-lives of the unacylated compound. Under these conditions, again, no racemization was observed. Only unreacted starting material was isolated.

Apparently from these data, total cleavage of the C_5-N_1 bond was not the reaction path.

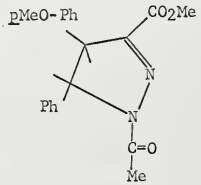
A second alternative reaction route which would explain the lack of racemization at C_5, the first-order kinetics and the abnormal rate of decomposition of the 5,5-diphenyl-2-pyrazolines, was formulated. If there were a concerted bond formation between C_3 and C_5 along with the cleavage of C_5 and N_1, then each of the above results could be rationalized as shown in the following equation.



This possibility was tested in the following way. If the cyclopropylazo intermediate were formed, if R_1 and R_2 were distinguishable and if the intermediate could attain equilibrium with the starting 2-pyrazoline, then it should be possible to observe a scrambling of the positions of R_1 and R_2 in the original 2-pyrazoline. Investigating this possibility, Pyron* prepared 4-phenyl-5-(p-methoxyphenyl)-3-carbomethoxy-2-pyrazoline and 4-(p-methoxyphenyl)-5-phenyl-3-carbomethoxy-2-pyrazoline and acylated both compounds to give VIII and IX. These compounds were then subjected to the same conditions required to decompose the parent compounds. Again, no



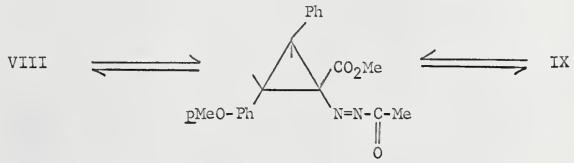
VIII



IX

*Unpublished observations, R. S. Pyron.

intermixing was observed (there was quantitative recovery of the starting material), thus excluding concerted bond formation and



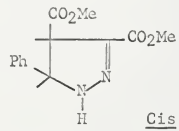
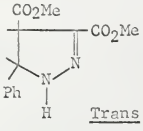
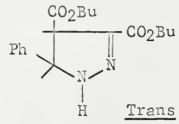
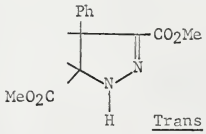
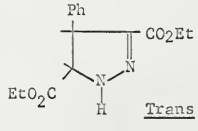
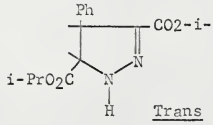
collapse of the pyrazoline ring system.

Having excluded the obvious possible alternatives and since much of the published evidence (1,5,15,17,18) for the 2-pyrazoline ⟶ 1-pyrazoline route for the thermal decomposition in the melt had resulted from stereochemical studies, an attempt was made to gain more insight into the "new mechanism" by studying the stereochemistry of the cyclopropane products formed under the same conditions in which the "new mechanism" was thought to be operating. A number of pyrazolines were synthesized and decomposed both in the melt and in solution. The results, summarized in Table 1, showed only slight differences in the stereochemistry of the products resulting from the melt or solution decomposition. Thus, these results suggested that the same mechanism was operating in each case.

Since the melt decomposition was believed to involve 2-pyrazoline ⟶ 1-pyrazoline tautomerization, it was therefore decided to very carefully re-examine Baarda's arguments to determine

TABLE 1

PERCENT OF THE CIS-ISOMER (TWO ESTER GROUPS CIS) RESULTING FROM THE THERMAL DECOMPOSITION OF SELECTED 2-PYRAZOLINES IN TETRAGLYME AND IN THE MELT

2-Pyrazoline	% Cis in Solution at 230°	% Cis in Melt at 230°
 Cis	48%	39%
 Trans	25%	16%
 Trans	15%	23%
 Trans	80%	71%
 Trans	75%	80%
 Trans	71%	85%

whether they could be made consistent with the 2-pyrazoline ⟶ 1-pyrazoline scheme.

The purpose of the remainder of this dissertation is to report the re-examination of these arguments and to show that they are all consistent with the proposed 2-pyrazoline ⟶ 1-pyrazoline scheme.

II. INSTRUMENTATION AND TECHNIQUE

The decomposition of the 2-pyrazolines used in this study is easily followed due to the fact that nitrogen gas is lost quantitatively during the course of the reaction. Therefore, the progress of the reaction was assessed by the collection of the evolved gas over mercury in a constant temperature burette calibrated in 0.1 ml. increments. The gas entered through a three-way stopcock at the top of the burette and atmospheric pressure was obtained at each reading by means of a leveling bulb.

The decomposition was carried out in a cylindrical vessel 19.5 cm. tall and 4 cm. in diameter fitted with 29/42 ball joints as shown in Figure 3. A side-arm nitrogen bubbler was permanently attached about 40 mm. from the bottom of the vessel. The tip of the bubbler extended down inside the vessel to a point such that it would be about half the height of a column of 50 ml. of solvent. The bubbler was attached to a three-way stopcock which could seal the vessel from the atmosphere.

A nitrogen exit tube was permanently attached near the neck of the flask and was attached to the burette by a capillary side arm, tygon tubing, a three-way stopcock connected to a vacuum pump and more tygon tubing.

Fig. 3.- Photograph of the Kinetic Reaction Vessel Showing the Nitrogen Bubbler and the Pellet-Dropping Assembly.

At the top of the reaction vessel was attached a section of glass which held the sample. This section was not in the bath. The sample, a pellet for the solid samples and a glass tray for the oil samples, was placed on a hinged glass plate which was held in place by a glass bar with a magnet sealed in the opposite end. This section was then sealed by a glass stopper held in place by a clamp, as were all joints in the system.

When the sample to be decomposed was to be introduced into the solvent, an external magnet was used to slide the glass bar back, thus releasing the trap and allowing the sample to drop into the solvent.

The solvent was stirred by a teflon-coated magnetic stirring bar which was controlled, when the vessel was suspended in the constant temperature bath, by a variable chuck magnetic stirring motor.

The constant temperature bath was GE SF 1017 silicone oil. The temperature of the bath was maintained to an accuracy of 0.01° by a Sargent Model S Thermonitor.

The general procedure used in carrying out each decomposition may be outlined as follows:

1. The reaction vessel was rinsed several times with acetone and allowed to dry thoroughly.
2. A 50 ml. sample of hexadecane, which had been previously distilled and stored over molecular sieves, was pipetted into the flask.
3. The sample was placed on its hinged trap door.

4. The whole reaction vessel was assembled and the nitrogen bubbler and exit tube connected. The system was now sealed from the atmosphere except for the stopcock at the top of the burette which was still open to the atmosphere.
5. Nitrogen gas, purified by bubbling through wash bottles filled with Fieser's solution (see Experimental), lead acetate, concentrated sulfuric acid, the sodium ketyl of benzophenone in xylene, and paraffin oil, was then allowed to bubble through the solvent and the rest of the system thence into the air for 30-45 minutes. The solvent was stirred continuously during this period.
6. The system was then closed and evacuated until bubbles no longer came out of the solvent.
7. The evacuation was stopped and nitrogen gas again was bled into the system. This procedure insured an atmosphere of nitrogen throughout the system.
8. The reaction vessel was then suspended in the oil bath and the temperature allowed to become constant again. The bubbling of nitrogen gas through the vessel was continued for a time after the vessel had been placed in the bath.
9. The nitrogen bubbler was sealed for the duration of the reaction.
10. Stirring of the solvent was continuous from this point to the end of the reaction period.

11. The system was then closed to the atmosphere.

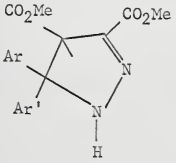
12. The solid pellet or tray of oil, weighed to the nearest 0.1 mg., was dropped into the hot solvent. The time observed for the dissolving of the sample did not exceed 30 seconds. The procedure of Overberger (22) was followed for solid samples in which V_∞ was taken as the calculated volume of nitrogen converted to the temperature and pressure of the collecting burette and zero time was the time of introduction of the sample. This procedure was checked and found to be quite accurate.

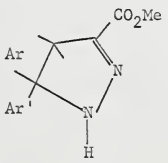
For runs made with the oil materials, the actual observed t_∞ volume reading was taken as V_∞ because the exact purity of the oil was unknown.

The actual burette readings were taken as V_t.

III. RESULTS AND DISCUSSION

One of the strongest arguments that was presented for the "new mechanism" was the very rapid rate of decomposition of 5,5-diaryl-2-pyrazolines. In an attempt to elucidate the role of the aryl groups at the 5 position of the 2-pyrazoline, two series (XI-XIV) and (XV-XVIII) of 5,5-diaryl-2-pyrazolines were prepared. The series differed only in the substituent at the 4 position.





XI	Ar=Ar'=Ph	XV	Ar=Ar'=Ph
XII	Ar=Ph;Ar'=p-Me-Ph	XVI	Ar=Ph;Ar'=p-Me-Ph
XIII	Ar=Ar'=p-Me-Ph	XVII	Ar=Ar'=p-Me-Ph
XIV	Ar=Ar'=p-Cl-Ph	XVIII	Ar=Ar'=p-Cl-Ph

The 2-pyrazolines were prepared by adding the diaryldiazomethanes to dimethyl maleate (XI-XIV) and to methyl acrylate (XV-XVIII).*

*For elaboration, see the Experimental.

These compounds were subjected to kinetic decomposition in approximately 0.01 molar hexadecane solution in the presence of added tri-n-propylamine. The kinetics were followed by the evolution of nitrogen gas and the rates were found to follow a first-order kinetic plot. Some typical plots of these data are shown in Figures 4-7. The temperature was held constant at 135° for each run in order that there would be no ambiguity involved in drawing comparisons between the various observed rates. The results of the decompositions are summarized in Tables 2-3.

It will be noted that electron-donating substituents slightly retarded the rate whereas electron-attracting substituents slightly increased the rate. These results suggest a slow formation of the 1-pyrazoline by a process, for example, such as outlined below where there is a rapid equilibrium setup prior to the rate-determining step.

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{\ominus} + BH^{\oplus} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A'H + B \xrightarrow{k_3} \text{Product}$$

AH = 2-Pyrazoline

B = Base

A'H = 1-Pyrazoline

This process is described by the expression $\frac{d(\text{Product})}{dt} = k_3(A'H)$. If k_2 is the slow step and using the "steady-state" assumption, the total rate expression develops into equation 1, where K is the

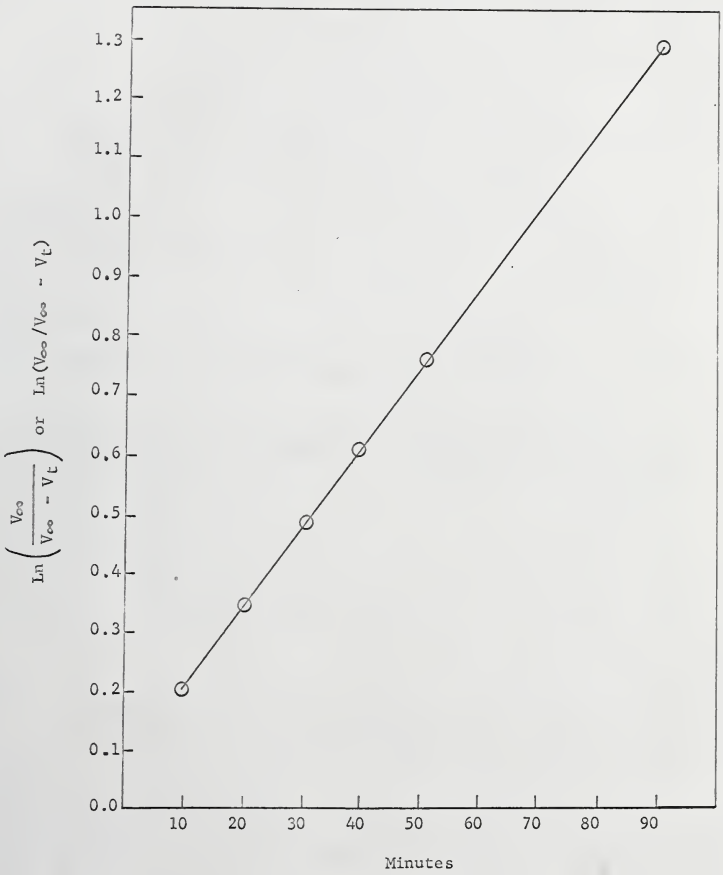


Fig. 4. - The First-Order Plot of the Data Obtained from the Decomposition of 1.87 x 10^{-3} Mole of 5,5-(4,4'-Dimethyldiphenyl)-3-Carbomethoxy-2-Pyrazoline in the Presence of 2.11 x 10^{-3} Mole of Tri-n-propylamine in 50 ml. of Hexadecane at 135°.

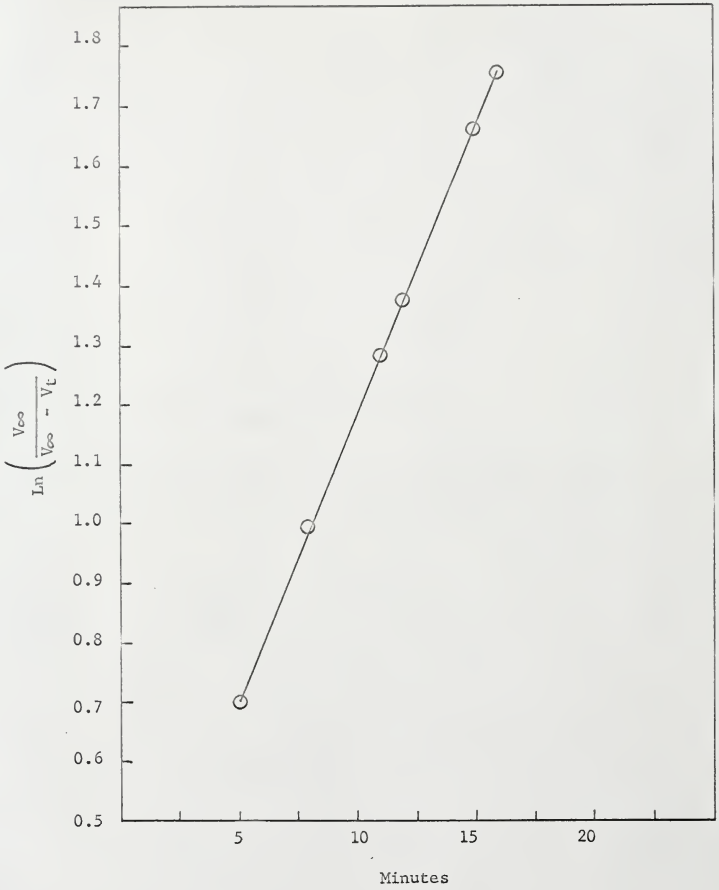


Fig. 5. - The First-Order Plot of the Data Obtained from the Decomposition of 2.59 x 10^{-3} Mole of 5,5-(4,4'-Dichlorodiphenyl)-3-Carbomethoxy-2-Pyrazoline in the Presence of 2.11 x 10^{-3} Mole of Tri-n-propylamine in 50 ml. of Hexadecane at 135°.

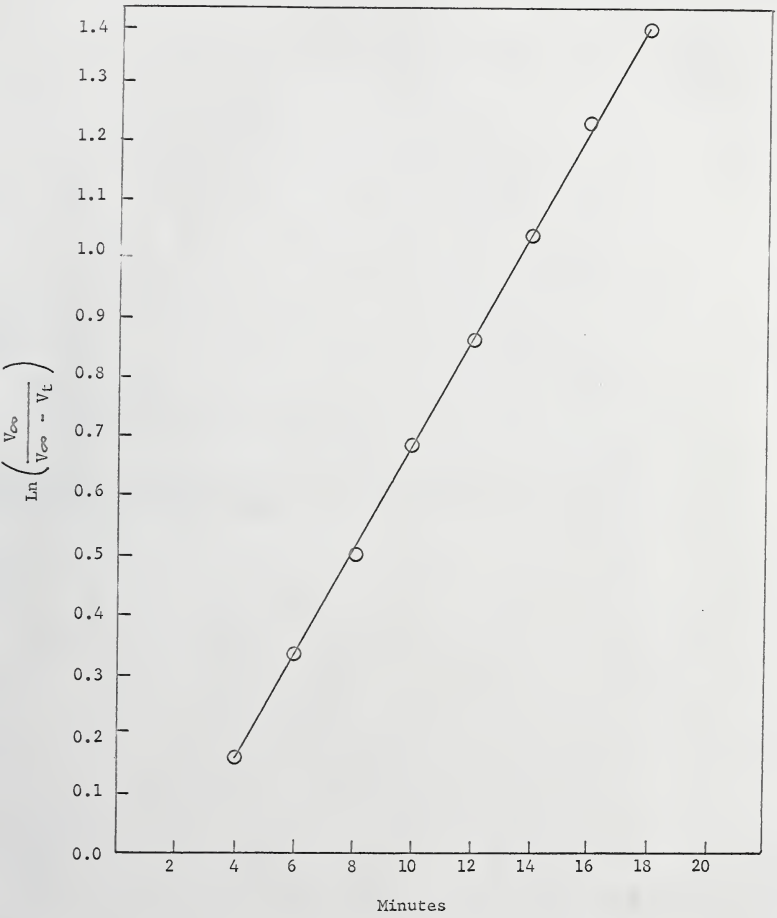


Fig. 6. - The First-Order Plot of the Data Obtained from the Decomposition of 2.0 x 10^{-3} Mole of 5,5-Diphenyl-3,4-Dicarbomethoxy-2-Pyrazoline in the Presence of 2.11 x 10^{-3} Mole of Tri-n-propylamine in 50 ml. of Hexadecane at 135°.

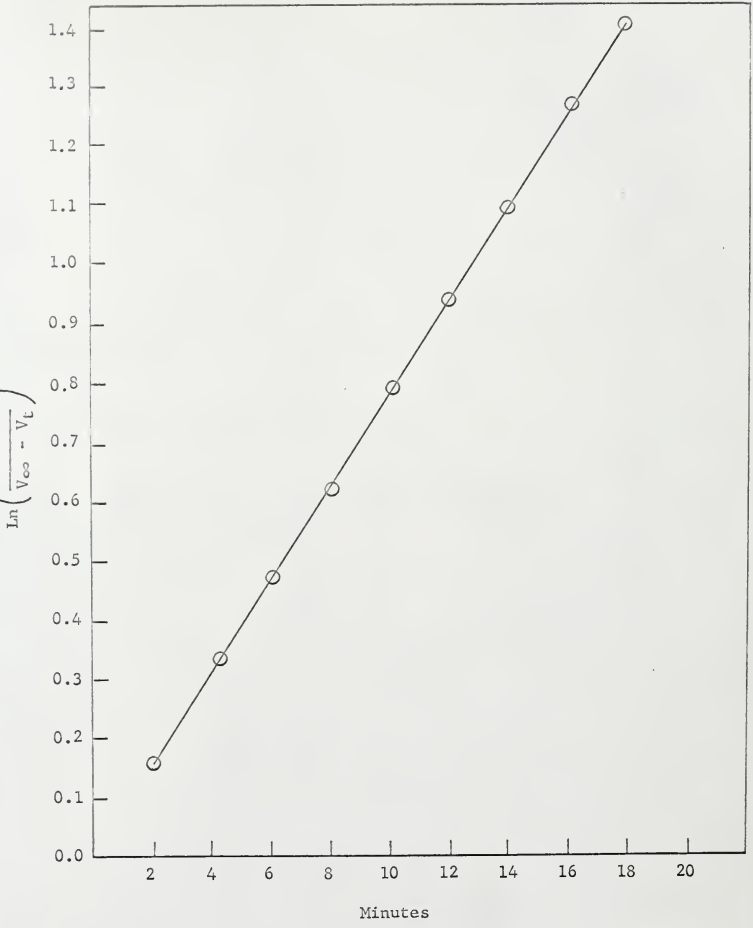
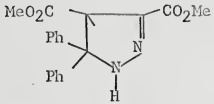
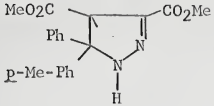
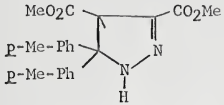
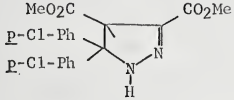


Fig. 7. - The First-Order Plot of the Data Obtained from the Decomposition of 2.19 x 10^{-3} Mole of 5,5-(4,4'-Dimethyldiphenyl)-3, 4-Dicarbomethoxy-2-Pyrazoline in the Presence of 2.11 x 10^{-3} Mole of Tri-n-propylamine in 50 ml. of Hexadecane at 135°.

TABLE 2

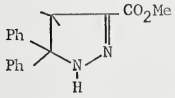
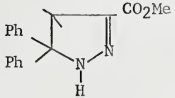
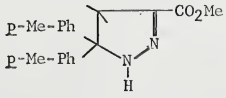
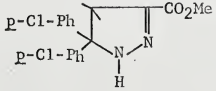
RATES OF DECOMPOSITION OF 5,5-DIARYL-3,4-DICARBOMETHOXY-2-PYRAZOLINES IN HEXADECANE

Reactant	Experimental Temperature	Base* Concentration Mole/50 ml.	Observed k(sec^{-1})	Relative Rates
	135°	2.11×10^{-3}	$1.67 \pm 0.00 \times 10^{-3}$	1.3
	135°	2.11×10^{-3}	$1.51 \pm 0.01 \times 10^{-3}$	1.2
	135°	2.11×10^{-3}	$1.32 \pm 0.01 \times 10^{-3}$	1
	135°	2.11×10^{-3}	$8.31 \pm 0.00 \times 10^{-3}$	6.3

*Tri-n-propylamine

TABLE 3

RATES OF DECOMPOSITION OF 5,5-DIARYL-3-CARBOMETHOXY-2-PYRAZOLINES IN HEXADECANE

Reactant	Experimental Temperature	Base* Concentration Mole/50 ml.	Observed k(sec^{-1})	Relative Rates
	135°	2.11×10^{-3}	$0.277 \pm 0.00 \times 10^{-3}$	1.2
	135°	2.11×10^{-3}	$0.253 \pm 0.02 \times 10^{-3}$	1.1
	135°	2.11×10^{-3}	$0.230 \pm 0.01 \times 10^{-3}$	1
	135°	2.11×10^{-3}	$1.67 \pm 0.00 \times 10^{-3}$	7.3

*Tri-n-propylamine

equilibrium constant for the formation of $A^{\ominus}$. From this expression

$$\frac{d(\text{Product})}{dt} = k_2K(AH)(B) \qquad (1)$$

the effect of substituents upon the rate can be explained by the manner in which the substituents change the equilibrium constant (electron-donating substituents would decrease K whereas electron-attracting substituents would increase K) since the effect on K should be greater than the effect on k_2.

Since the suggested rate expression included a base term, the dependency of the decompositions on base concentration was checked. As would be predicted for a reaction first order in a catalyst, it was found that a plot of $k_{obs.}$ versus the base concentration gave a straight line (see Figures 8-11). Surprisingly however, it was also noted that, in most of the cases, the intercept of the line at $k_{obs.} = 0$ was not the origin (as would be predicted by equation 1). Furthermore, it was found that the plots passed through the base coordinate at essentially the same point which corresponded to a base concentration of minus 0.01 molar. This behavior requires the relationship shown in equation 2 which is most readily interpreted

$$k_{obs.} = k(\text{Base}) + k' \qquad (2)$$

as a decomposition mechanism in competition with the added base-induced mechanism. The nature of this competitive mechanism was of

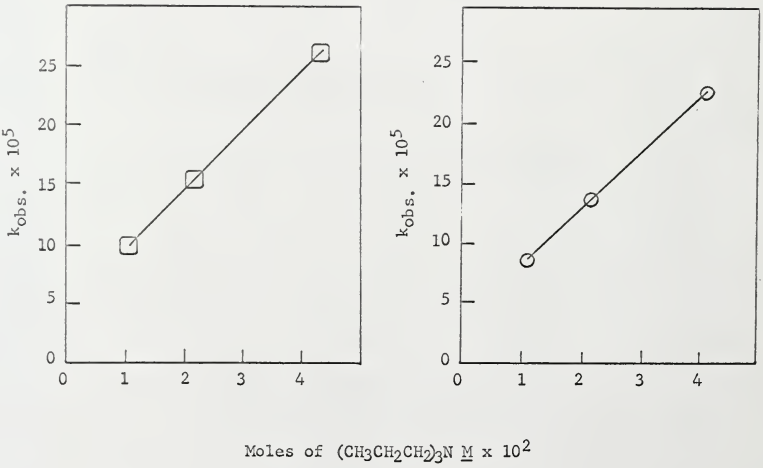


Fig. 8. - Plots of the Observed First-Order Rate Constants Versus Base Concentration for the 5-Phenyl-5-(4-Methylphenyl)-3-Carbomethoxy-2-Pyrazoline (□) and 5,5-(4,4'-Dimethyldiphenyl)-3-Carbomethoxy-2-Pyrazoline (○).

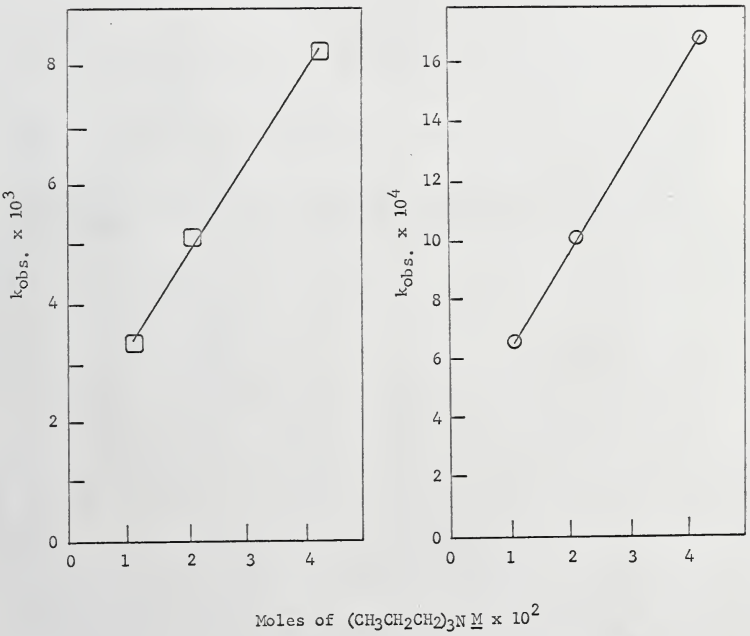


Fig. 9. - Plots of the Observed First-Order Rate Constants Versus Base Concentration for the 5,5-(4,4'-Dichlorodiphenyl)-3,4-Dicarbomethoxy-2-Pyrazoline (□) and 5,5-(Dichlorodiphenyl)-3-Carbomethoxy-2-Pyrazoline (○).

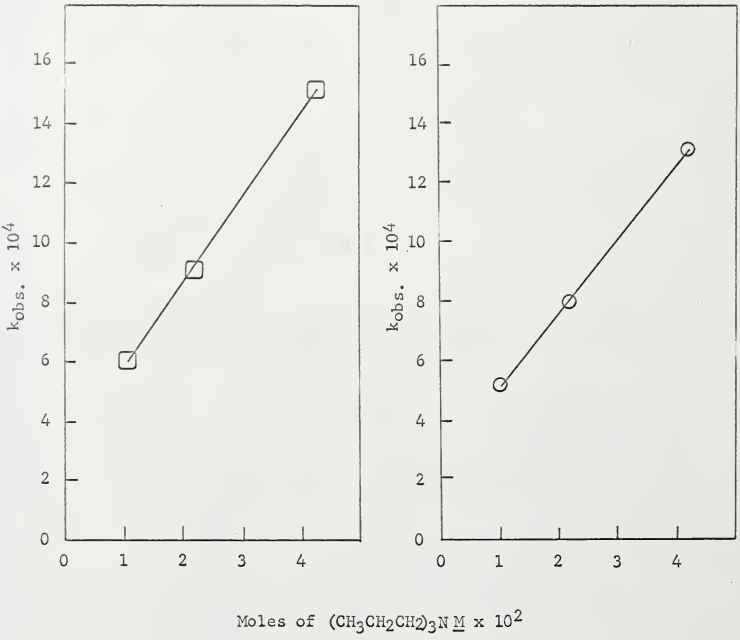


Fig. 10. - Plots of the Observed First-Order Rate Constants Versus Base Concentration for the 5-Phenyl-5-(4-Methylphenyl)-3,4-Dicarbomethoxy-2-Pyrazoline (□) and 5,5-(4,4'-Dimethyldiphenyl)-3,4-Dicarbomethoxy-2-Pyrazoline (○).

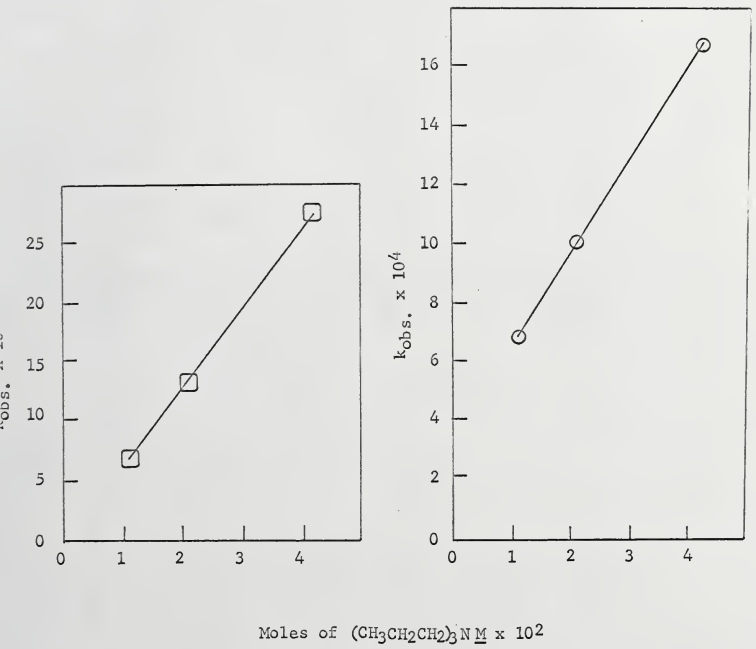


Fig. 11. - Plots of the Observed First-Order Rate Constants Versus Base Concentration for the 5,5-Diphenyl-3-Carbomethoxy-2-Pyrazoline (□) and 5,5-Diphenyl-3,4-Dicarbomethoxy-2-Pyrazoline (○).

some interest, especially in view of Baarda's general "new mechanism" conclusions. However, a close examination of the kinetic data suggested that this competitive mechanism was probably no more than a simple competitive 2-pyrazoline to 1-pyrazoline conversion probably catalyzed by a basic surface of the reaction vessel. Thus, it was found that the plots of $k_{obs.}$ versus base gave values for k' that followed essentially the same order with changes in the pyrazoline structure as did the values of k. (These results are summarized in Table 4.) In fact, the ratio of k/k' was nearly constant from one compound to the next. This observation was certainly suggestive of similar mechanisms in the two reactions. Since this competitive reaction was probably no more than a surface-catalyzed reaction due, quite possibly, to base from the previous run being adsorbed to the surface of the reaction flask, it was not surprising that there were slight variations in the k/k' ratio.

These observations were all consistent with the 2-pyrazoline $\longrightarrow$ 1-pyrazoline tautomerization scheme but a problem was encountered when Baarda's results were checked. It was found that for Baarda's work, a plot of $k_{obs.}$ versus the base concentration did not give a straight line. However, his results were found to fit an expression of the type shown in equation 3. This type of correlation

$$\frac{1}{k_{obs.}} = \frac{1}{Base} + k'' \qquad (3)$$

arises directly from the following reaction scheme if two criteria

TABLE 4

DATA CALCULATED FROM THE PLOT OF $K_{OBS.}$ VERSUS BASE CONCENTRATION FOR XI-XVIII

	Base Concentration at $k_{obs.} = 0$	k	k'	$\frac{k}{k'}$
XIV	1.0×10^{-2}	1.50×10^{-1}	1.50×10^{-3}	100
XI	1.0×10^{-2}	3.00×10^{-2}	3.00×10^{-4}	100
XVIII	0.9×10^{-2}	3.20×10^{-2}	2.88×10^{-4}	111
XII	1.0×10^{-2}	2.67×10^{-2}	2.67×10^{-4}	100
XIII	0.9×10^{-2}	2.67×10^{-2}	2.40×10^{-4}	111
XV	0	6.67×10^{-3}	through zero	
XVI	1.0×10^{-2}	5.00×10^{-3}	5.00×10^{-5}	100
XVII	0.9×10^{-2}	5.00×10^{-3}	4.50×10^{-5}	111

are met. First, a competitive reaction must not be important.

$$\text{2-Pyrazoline + Base} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{1-Pyrazoline + Base} \xrightarrow{k_2} \text{Products}$$

$$\frac{\text{Rate}}{\text{(2-Pyr.)}} = \frac{k_1 k_2 (\text{Base})}{k_{-1}(\text{Base}) + k_2} = k_{\text{obs.}} \qquad (4)$$

$$\frac{1}{k_{\text{obs.}}} = \frac{1}{k_1(\text{Base})} + \frac{k_{-1}}{k_1 k_2} \qquad (5)$$

Second, the reversal of 1-pyrazoline to 2-pyrazoline must be competitive with loss of nitrogen. An examination of Baarda's experimental conditions shows that both of these criteria could be fulfilled. Thus, Baarda's studies were run with base concentrations varying from 0.1 to 0.48 molar (in contrast to 0.01 to 0.042 molar in the present study). At these concentrations, the competitive surface reaction would account for less than 10% (down to about 1%) of the total reaction. Furthermore, the higher base concentrations would promote reversal of the 1-pyrazoline to the 2-pyrazoline without appreciably affecting the 1-pyrazoline to cyclopropane conversion.

Thus, all of these observations are quite consistent with the 2-pyrazoline $\longrightarrow$ 1-pyrazoline conversion. In fact, the present study with low base concentrations points strongly toward this proposed reaction path.

A striking comparison which appeared during the course of this work was the observation that between corresponding members of the two 5,5-diaryl-2-pyrazoline series under study (i.e., 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline and 5,5-diphenyl-3-carbomethoxy-2-pyrazoline, etc.) the ratio of their respective observed rate constants was nearly constant. For example, the observed rate constants (these constants are for runs with 2.11×10^{-2} mole of base added) for XI, XII, XV and XVI were 1.67, 1.51, 0.277 and 0.253×10^{-4} sec^{-1} respectively. The ratios of XI to XV and XII to XVI were 6.02 and 5.99 respectively (for comparison between the remaining members of the two series see Table 5). The 5,5-diaryl-3,4-dicarbomethoxy-2-pyrazoline series had the faster observed rate constants. This can be explained easily using the proposed reaction scheme. The 4-carbomethoxy group is an electron attractor and in the five-membered pyrazoline ring system it increases the initial equilibrium constant K which causes an increase in the rate. The parallelism between the two series also suggested that the same mechanism was being followed in each series.

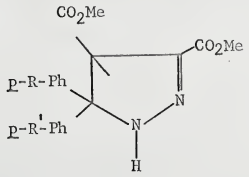
These results and observations are therefore consistent with the proposed 2-pyrazoline $\longrightarrow$ 1-pyrazoline conversion and suggest that for the decomposition of 5,5-diaryl-2-pyrazolines the rate-determining step is the formation of the 1-pyrazoline.

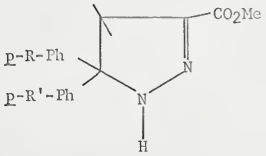
The above suggestion that formation of the 1-pyrazoline is the slow step for the 5,5-diaryl-2-pyrazolines presented a major problem. This problem centered around the evidence of Jones (5a)

TABLE 5

COMPARISON OF THE OBSERVED RATE CONSTANTS BETWEEN LIKE MEMBERS OF THE TWO SERIES OF COMPOUNDS

Substituent	$\frac{k_{obs.}\ (XI\text{-}XIV)}{k_{obs.}\ (XV\text{-}XVIII)}$ Respectively
R=R'=H	6.02
R=H;R'=Me	5.99
R=R'=Me	5.74
R=R'=Cl	4.99





that in the melt the rate-determining step for the decomposition of 5-carboalkoxy-2-pyrazolines was the formation of the 1-pyrazoline as shown in Figure 12. In other words, if the rate-determining steps in each case were the same, why did the 5,5-diaryl-2-pyrazolines undergo such an abnormally rapid decomposition relative to the 5-carboalkoxy-2-pyrazolines? Jones found that starting from either XX or XXI as pure material and effecting partial decomposition in the melt followed by recovery of the starting material, gave only the pure 2-pyrazoline with which he had started. If the slow step of the decomposition shown in Figure 12 had been the decomposition of the 1-pyrazoline, then it would have been possible to establish an equilibrium between the 2-pyrazoline and the 1-pyrazoline. This possibility would have resulted in a scrambling of the two ester groups because in the 1-pyrazoline they would have been equivalent. Since no scrambling of the ester groups was observed, the slow step of the decomposition was indicated to be the formation of the 1-pyrazoline.

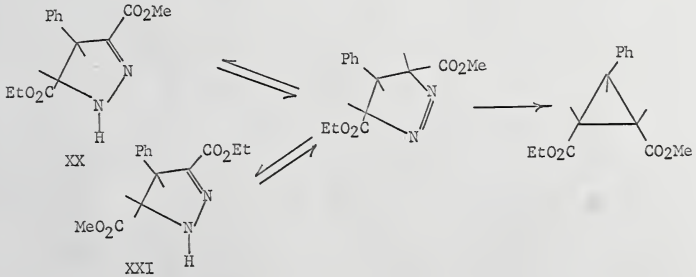


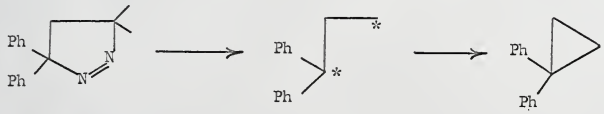
Fig. 12. - Reaction Scheme Taken from an Investigation of W. M. Jones.

Baarda (21) in some of his investigations found that the rate of decomposition of 5-carboalkoxy-2-pyrazolines in solution was much less than the 5,5-diphenyl-2-pyrazolines. These results for the 5,5-diphenyl-2-pyrazolines and the 5-carboalkoxy-2-pyrazolines place one or more of the following requirements on the mechanism: 1) either the two phenyl groups accelerate the formation of the 1-pyrazoline, or 2) the 5-carboalkoxy group must decelerate the rate of formation of the 1-pyrazoline, or 3) whereas the rate-determining step for the decomposition of the 5-carboalkoxy-2-pyrazoline in the melt is the formation of the 1-pyrazoline, the rate-determining step in solution is the decomposition of the 1-pyrazoline.

In view of the kinetic data discussed thus far and the pK_a's of analogous carboxylic acids, the first of these three possibilities seems highly unlikely. For example, the pK_a for diphenylacetic acid is 3.94 whereas the pK_a for malonic acid is 2.85. Since the same factors probably operate in the 2-pyrazoline system as in the example acids (i.e., inductive effects), then the 5-carboalkoxy group would be expected to exert a stronger influence upon the N_1 hydrogen atom than the diaryl substituents. Thus, the diaryl substituents on C_5 must exert their rate-increasing powers in some step other than the formation of the 1-pyrazoline.

The second requirement could pertain due, possibly, to some sort of special stabilization of the 2-pyrazoline relative to the 1-pyrazoline in the 5-carboalkoxy case caused by intramolecular hydrogen bonding of the ester group with the hydrogen atom attached

to the nitrogen atom. However, this possibility was made unlikely by the observations of Pyron* that the thermal decomposition of 5-phenyl-2-pyrazolines was also extremely slow. Thus, all the previous evidence suggests that, indeed, the slow step in the case of the 5-carboalkoxy-2-pyrazoline is the decomposition of the 1-pyrazoline, or in other words, substitution of two phenyl groups on C_5 accelerate the decomposition of the 1-pyrazoline. This latter statement is intuitively obvious since any type of intermediate formed by the loss of nitrogen from the 1-pyrazoline (7,14) would be stabilized by the two aromatic rings.

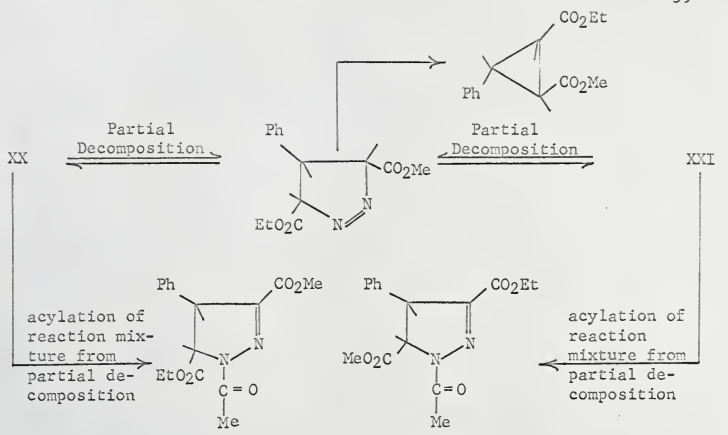


An attempt to check this extremely attractive possibility experimentally was carried out again by synthesizing both XX and XXI and subjecting each pure compound to partial decomposition in solution in the presence of added base. Each 2-pyrazoline was dissolved in 50 ml. of decalin to which 0.3 ml. of triisoamylamine had been added. This solution was heated at 150° until 50% of the

*Unpublished observations, R. S. Pyron.

calculated volume of nitrogen had been evolved. Numerous attempts were made to isolate the 2-pyrazoline from the decalin solution but each one met with failure until finally a procedure was developed for preparing the acetyl derivatives in decalin solution. Acetyl chloride proved to be utterly useless for this reaction but acetic anhydride catalyzed by a few drops of sulfuric acid and heat performed the desired operation nicely.

The infrared spectrum of the pure acetyl derivatives, which were prepared directly from the pure 2-pyrazolines, offered a very nice diagnostic tool for identifying the two isomeric compounds. A peak at 11.4 μ for the 5-carboethoxy isomer and at 12.6 μ for the 5-carbomethoxy isomer proved to be present only in the spectrum of each compound respectively. When either of the two pure mixed-ester 2-pyrazolines (XX or XXI) was partially decomposed, acylated, and the resulting product isolated, the infrared spectrum of the product indicated the presence of both acetyl derivatives by the presence of both analytical peaks (11.4 μ and 12.6 μ). Blanks showed that no isomerization of the 2-pyrazoline occurred during the acylation reaction. These results indicated that in solution the 5-carboalkoxy-2-pyrazoline attained an equilibrium with its 1-pyrazoline and as a result, a mixture of isomers was isolated from the partial decomposition experiments as shown by the following reaction scheme. These results differed completely from the work of Jones (5a) in the melt, and constituted evidence for the proposed change in the rate-determining step for the 5-carboalkoxy-2-pyrazolines.



This above conclusion was confirmed by a kinetic study of the decomposition of a 5-carboalkoxy-2-pyrazoline. Using 4-phenyl-3-carboethoxy-5-carbomethoxy-2-pyrazoline, XXI, as the sample, such a study was undertaken. In this case, the temperature of the constant temperature bath was increased from 135° (for 5,5-diaryl-2-pyrazolines) to 160° in order to get a measurable rate of nitrogen evolution. Also, tri-n-propylamine was replaced by triisoamylamine because the 160° bath temperature was above the boiling point of tri-n-propylamine. All other conditions and procedures were the same as those used in the kinetic decomposition of the 5,5-diaryl-2-pyrazolines.

If the rate-determining step in the thermal decomposition in solution of the 5-carboalkoxy-2-pyrazolines is actually the decomposition of the corresponding 1-pyrazoline, then the rate of the reaction should be independent of the concentration of added base.

The results of the base-catalyzed decomposition are summarized in Table 6.

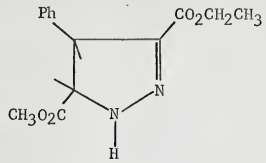
As can readily be seen from Table 6, the rate of nitrogen evolution from 4-phenyl-3-carboethoxy-5-carbomethoxy-2-pyrazoline under the above conditions is completely independent of the amount of base added to the reaction mixture. These observations lend more support to the proposed mechanistic path and explain the abnormally rapid rate of the 5,5-diphenyl-2-pyrazolines.

One final question that needs to be considered is the first-order kinetics for decomposition of 2-pyrazolines reported by Baarda. However, in light of the previous discussion on the surface-catalyzed reaction, this was probably simply a result of a surface-catalyzed 2-pyrazoline to 1-pyrazoline conversion. Before it was recognized that this might be a simple surface reaction, an attempt was made to check the generality of the first-order kinetics in the absence of base. Several 5-phenyl and 5-carboalkoxy-2-pyrazolines were synthesized and decomposed kinetically. There was no generality to the observations of first-order kinetics in the absence of base. In fact, the results could not be reproduced from one run to the next. In retrospect, these anomalies probably resulted from different preparations of the reaction vessel. This was not investigated further.

In conclusion, all major areas of disagreement with the 2-pyrazoline $\longrightarrow$ 1-pyrazoline tautomerizations which were proposed by Baarda have been shown to be completely consistent with and suggestive of such a proton transfer mechanism. The kinetics and

TABLE 6

RATES OF DECOMPOSITION OF 4-PHENYL-3-CARBOETHOXY-5-CARBOMETHOXY-2-PYRAZOLINE IN HEXADECANE

Reactant	Experimental Temperature	Base* Concentration Mole/50 ml.	Observed $k(sec^{-1})$	Relative Rates
	160°	6.91×10^{-4}	1.76×10^{-5}	1.00
	160°	1.38×10^{-3}	1.84×10^{-5}	1.04

*Triisoamylamine

base dependence studies of the 5,5-diaryl-2-pyrazoline series elucidated the role of the aryl groups at C_5 and pinpointed the rate-determining step for these compounds. The work with the mixed ester 3,4-dicarboalkoxy-2-pyrazolines confirmed a change in the rate-determining step from the melt to solution decomposition. The general reaction scheme as outlined below is the reaction path now proposed for the base-catalyzed decomposition of 2-pyrazolines. For the 5,5-diaryl-2-pyrazolines the formation of the 1-pyrazoline is the slow step (or k_2 is slow), whereas for the 5-carboalkoxy-2-pyrazoline the

$$\text{2-Pyrazoline + Base} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{2-Pyrazoline}^{\ominus}) + \text{H}^{\oplus}\text{ Base} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$

$$\text{1-Pyrazoline + Base} \xrightarrow{k_3} \text{Products}$$

decomposition of the 1-pyrazoline (k_3 is slow) is the rate-determining step. An activation energy versus reaction coordinate diagram (Figure 13) summarizes these considerations.

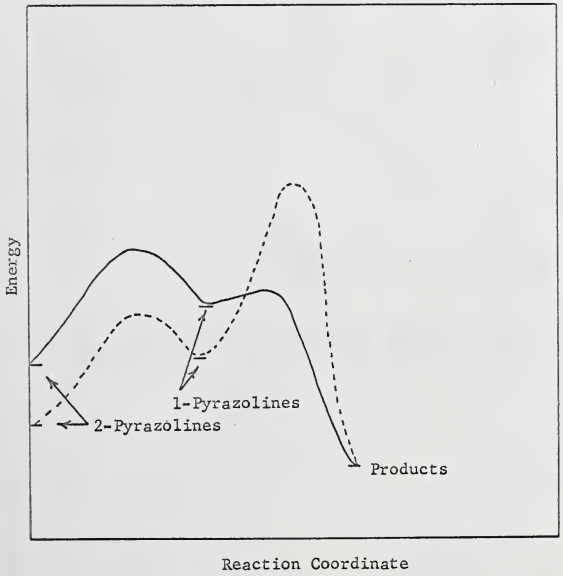


Fig. 13. - An Activation Energy Diagram for the Decomposition of 5,5-Diaryl-2-Pyrazolines (———) and 5-Carboalkoxy-2-Pyrazolines (------) in Hexadecane in the Presence of Added Base.

IV. SUMMARY

A kinetic study of the base-catalyzed thermal decomposition of 2-pyrazolines in solution was undertaken to elucidate further the mechanism of their decomposition. The initial task was to determine the role of aromatic substitution at C_5 in the over-all mechanism and to evaluate the work of Baarda in terms of the published mechanistic suggestions. These suggestions were to the effect that the 2-pyrazoline initially tautomerizes to the 1-pyrazoline which then loses nitrogen.

The present study did, in fact, elucidate the role of aromatic substituents on C_5. It also revealed that the base-catalyzed decompositions exhibit first-order kinetics. All of Baarda's evidence suggesting that the 2-pyrazoline $\longrightarrow$ 1-pyrazoline tautomerization was not operative was shown to be entirely consistent with such a mechanism. Finally, a mechanism was proposed. This mechanism, including conversion to cyclopropane products, is illustrated in Figure 14.

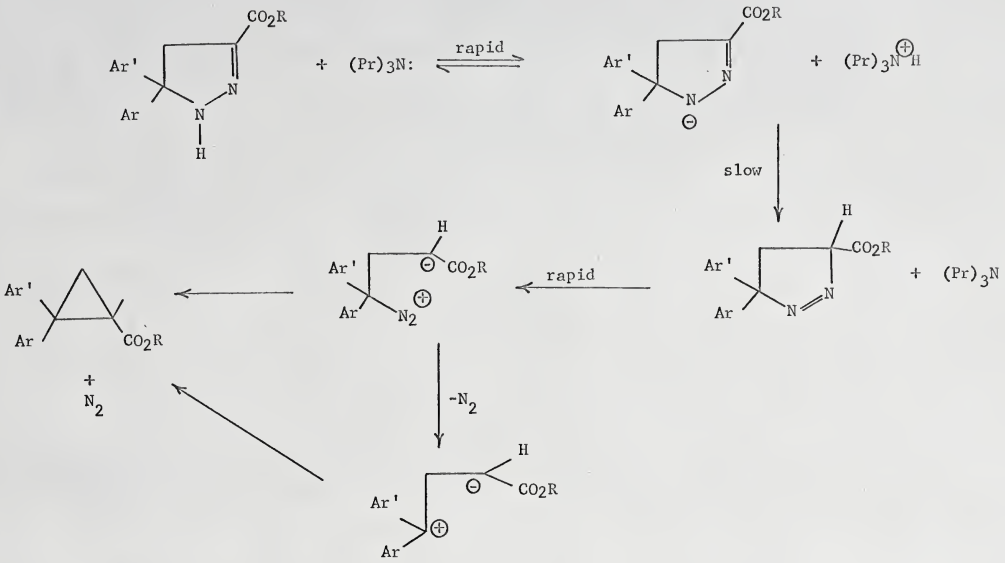


Fig. 14. - A Proposed Mechanism for the Base-Induced Thermal Decomposition of 5,5-Diaryl-3-Carboalkoxy-2-Pyrazolines.

V. EXPERIMENTAL

Infrared spectra were run on a Perkin-Elmer Model 137B Infracord Spectrophotometer. Ultraviolet spectra were run on a Cary Model 14 Spectrophotometer. Compound analyses were performed by Galbraith Laboratories, Incorporated, Knoxville, Tennessee. All melting points were taken on a Thomas-Hoover melting point apparatus and were uncorrected. All boiling points also were uncorrected.

The vapor-phase chromatographic analyses were run on an Aerograph Hy-Fi Model 600-B vapor-phase chromatograph using a hydrogen flame ionization detector. The Minneapolis-Honeywell recorder was equipped with a disc chart integrator.

Elemental analyses for the 2-pyrazolines which were oils were taken on the respective acetyl derivatives.

General procedure followed for the melt and solution decompositions used for the stereochemical studies.* - The melt decompositions were run in a 13 x 120 mm. test tube which was attached to a water-filled burette. An amount of sample was chosen so that about 50 ml. of nitrogen was evolved. The test tube was immersed in an oil bath heated to 230°. The sample remained in the bath until gas was no longer evolved. The resulting oil was then dissolved in ether

*The results from these decompositions are summarized in the Introduction.

and analyzed by vapor-phase chromatography. The retention times were compared to those of pure samples of cis and trans 3-phenyl-1, 2-dicarbomethoxy-cyclopropane which were prepared respectively by decomposition in the melt of 4-phenyl-3,5-dicarbomethoxy-2-pyrazoline and 5-phenyl-3,4-dicarbomethoxy-2-pyrazoline. The ratio of integrated intensities of the two peaks gave the percentage composition of each component.

For pyrazoline esters other than the dimethyl esters, the oil resulting from the decomposition of the pyrazoline was hydrolyzed in methanolic potassium hydroxide, acidified with hydrochloric acid and reacted with excess diazomethane, prepared by the method of DeBoer and Backer (23). This procedure converted all cyclopropanes to the dimethyl esters.

The solution decompositions were run at 230° in a 200 ml. round-bottomed flask in which the pyrazoline sample was dissolved in tetraglyme which had been purified by reaction with calcium hydride followed by distillation from lithium aluminum hydride.

Work-up involved the addition of water to the tetraglyme solution. This procedure caused the products to form an oil which could be separated easily from the tetraglyme-water solution. Analysis for the cyclopropane products was carried out in the same manner as for the melt decompositions. All cyclopropane esters were converted to the methyl esters, as described above, for analytical purposes.

Preparation of ethyl diazoacetate. - The method of Searle (24) was followed in the preparation of the diazoacetic ester. This

compound was potentially explosive, therefore much care was used in handling it.

A solution of 140 g. (1.0 mole) of ethyl glycinate hydrochloride in 250 ml. of water was mixed with 600 ml. of methylene chloride in a two-liter three-necked round-bottom flask fitted with a stirrer, dropping funnel, thermometer, and nitrogen inlet tube, and cooled to -5°. The flask was flushed with nitrogen and an ice-cold solution of 83 g. (1.2 moles) of sodium nitrite in 250 ml. of water was added with stirring. The temperature was lowered to -9° and 95 g. of 5% sulfuric acid was added from the dropping funnel during a period of about 3 minutes. The temperature rose to a maximum of $+1^{\circ}$ with the cooling bath at -23°. The reaction terminated within 10 minutes when heat was no longer evolved.

The reaction mixture was transferred to an ice-cold two-liter separatory funnel, and the yellow-green methylene chloride layer was run into one-liter of cold 5% aqueous sodium bicarbonate solution. The aqueous layer was extracted once with 75 ml. of methylene chloride. The methylene chloride and sodium bicarbonate solutions were returned to the separatory funnel and shaken until no trace of acid remained, as shown by indicator paper. The yellow organic layer was separated and dried for 5-10 minutes over 15 g. of anhydrous sodium sulfate. The dried ethyl diazoacetate solution was filtered and the methylene chloride removed on a rotary evaporator at room temperature. The yield of the yellow diazoacetic ester was 100 g. (88%). This product was pure enough for preparative work.

Preparation of 4-phenyl-3,5-dicarboethoxy-2-pyrazoline. - The procedure of Buchner (25) was followed with a slight modification. Twenty-five grams (0.219 mole) of ethyl diazoacetate was mixed with 37 g. (0.21 mole) of ethyl cinnamate and a pinch of hydroquinone added. This mixture was heated overnight on a steam bath. The resulting orange oil was poured into a crystallizing dish and scratched to induce crystallization. This procedure produced an oily, yellow solid which was filtered and recrystallized from hot methanol. Yield: 33 g. (0.114 mole; 54%) of white crystals, m.p. 75-77°, reported m.p. 79° (25). Significant absorptions in the infrared spectrum (Nujol) were at 2.99, 5.80, 5.90, 6.42 and 6.85 μ.

Preparation of methyl glycinate hydrochloride. - Following the method of Curtius and Goebel (31), 100 g. (1.33 moles) of glycine was added to a large excess of methanol. This mixture was heated to reflux and dry hydrogen chloride gas, made by dropping commercial concentrated hydrochloric acid into stirred concentrated sulfuric acid, was bubbled into the methanol. When all of the glycine had dissolved, the reaction was complete. The hot solution was then poured into a beaker and allowed to cool, thereby precipitating the crude hydrochloride. This solid was filtered from the methanol solution and recrystallized several times from methanol. The yield was 125 g. (1.0 mole; 75%) of white needles, m.p. 175-176°, reported m.p. 175° (31).

Preparation of methyl diazoacetate. - This diazoacetic ester was prepared in the same manner as the ethyl ester, following the procedure of Searle (24). One hundred twenty-six grams (1 mole) of

methyl glycinate hydrochloride was diazotized with sodium nitrite and sulfuric acid.

Following the usual work-up, 100 g. (1 mole; 100%) of the yellow diazo compound was obtained. This liquid was stored in a brown bottle in the refrigerator until needed. The infrared spectrum (plates) had significant peaks at 3.28, 4.7, 5.9 and 6.95 μ. The ultraviolet spectrum gave $\lambda_{max.}$ in cyclohexane at 244 mμ (ϵ 1.06 x 10^4).

Preparation of 4-phenyl-3,5-dicarbomethoxy-2-pyrazoline. - Following the same procedure as used in the preparation of 4-phenyl-3,5-dicarboethoxy-2-pyrazoline, 32 g. (0.32 mole) of methyl diazoacetate and 51 g. (0.315 mole) of methyl cinnamate were mixed together along with a pinch of hydroquinone. This mixture was then heated overnight on a steam bath. The resulting oil was worked up in the usual way. Yield: 48 g. (0.184 mole; 58%) of white needles, m.p. 106°, reported m.p. 107° (26). Significant absorptions in the infrared spectrum (Nujol) were at 3.0, 5.79, 6.46 and 6.88 μ.

Preparation of 4-phenyl-3,5-dicarboisopropoxy-2-pyrazoline. - Five grams (0.021 mole) of 4-phenyl-2-pyrazoline-3,5-dicarboxylic acid, prepared by the alkaline hydrolysis of the corresponding dimethyl ester, was dissolved in ether and mixed with excess dimethyldiazomethane, prepared by the silver oxide oxidation of acetone hydrazone (27). After all bubbling had ceased, the ether was removed under reduced pressure. The resulting yellow oil was distilled at 60°/2 mm. The infrared spectrum (plates) of the residue,

a brown oil, boiling above 60°/2 mm. indicated the presence of a 2-pyrazoline ester by peaks at 2.95, 2.78, 2.83, 6.40 and 6.88 μ.

Preparation of phenyldiazomethane. - Phenyldiazomethane was prepared by the method of Staudinger and Gaule (28) using red, rather than yellow, mercuric oxide. The crude mixture was found to contain about 30% phenyldiazomethane by titration of 2 ml. of the diazo solution with a standard solution of maleic anhydride. This crude solution was used without further purification since the primary contaminant was benzaldehyde azine which would not be expected to interfere with the desired reactions.

Preparation of cis-5-phenyl-3,4-dicarbomethoxy-2-pyrazoline. - Following the procedure of Jones (5b), 8.2 g. (0.058 mole) of dimethyl fumarate and a pinch of hydroquinone were dissolved in 130 ml. (approximately 0.059 mole as standardized with maleic anhydride) of ethereal phenyldiazomethane. The red solution was placed in the refrigerator until the color had been discharged. During this time, a white solid precipitated which was then filtered and recrystallized from methanol. Yield: 5.4 g. (0.038 mole; 65%) of white needles, m.p. 132-133°, reported m.p. 130-132° (5b). Significant absorptions in the infrared spectrum (Nujol) were at 2.98, 5.80, 5.91, 6.45 and 6.90 μ.

Preparation of trans-5-phenyl-3,4-dicarbomethoxy-2-pyrazoline. - Following the same procedure used for the preparation of cis-5-phenyl-3,4-dicarbomethoxy-2-pyrazoline, 8.2 g. (0.058 mole) of dimethyl maleate and a pinch of hydroquinone were dissolved in 130 ml. (approximately 0.059 mole as standardized with maleic anhydride)

of ethereal phenyldiazomethane. This solution was placed in the refrigerator until the red diazo color had disappeared. The solvent was then removed under reduced pressure giving rise to a yellow oil which resisted all attempts at crystallization. Significant absorptions in the infrared spectrum (plates) were at 2.97, 5.70, 5.80, 6.43 and 6.97 μ.

Preparation of trans-5-phenyl-3,4-dicarbobutoxy-2-pyrazoline. - Following the same procedure as used in the preparation of cis-5-phenyl-3,4-dicarbomethoxy-2-pyrazoline, 10 g. (0.044 mole) of di-n-butyl maleate and a pinch of hydroquinone were dissolved in an ether solution of phenyldiazomethane of approximately equimolar concentration. The usual work-up gave a yellow oil which resisted all attempts at crystallization. Absorptions in the infrared spectrum (plates) which indicated the presence of the 2-pyrazoline were at 2.98, 5.75, 5.85, 6.43 and 6.88 μ.

Preparation of 4-phenyl-3-carbomethoxy-5-carboethoxy-2-pyrazoline.* - Following the procedure of Buchner and von der Heide (30), 45 g. (0.395 mole) of ethyl diazoacetate was added to 48 g. (0.297 mole) of methyl cinnamate. To this mixture a pinch of hydroquinone was added. The mixture was then placed on a steam bath for 24 hours. During this period, there was some visible decomposition of the diazo compound. At the end of the reaction time, the resulting orange oil was poured into a beaker and washed with pentane. The

*For a discussion concerning the structures of this compound and its isomer, see references 5a and 29.

remaining oil was dissolved in a small amount of ethyl ether and cooled in dry ice. During cooling, a yellow oily solid formed which was filtered and recrystallized from ethyl ether to give 41.4 g. (0.150 mole; 50%) of a white solid, m.p. 74-76°, reported m.p. 76° (30). The significant absorptions in the infrared spectrum (potassium bromide) were at 2.99, 5.78, 5.95, 6.57, 13.3 and 14.3 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 288 mμ (ϵ 1.30 x 10^4).

Preparation of 4-phenyl-3-carboethoxy-5-carbomethoxy-2-pyrazoline. - Again, following the procedure of Buchner and von der Heide (30), 50 g. (0.50 mole) of methyl diazoacetate was added to a mixture of 81 g. (0.460 mole) of ethyl cinnamate and a pinch of hydroquinone. This mixture was then placed on a steam bath and heated for 28 hours. Also during this time, there was visible gas evolution. At the end of this time, the solution was a deep orange color. The solution was poured into a crystallizing dish while still hot and a small amount of ether added. The oil dissolved in the ether. The solution was stirred and at the same time the vessel was scratched to induce crystallization. Crystallization took place rapidly giving an oily yellow solid which was filtered and recrystallized from hot methanol. This procedure yielded 83 g. (0.30 mole; 65%) of white crystals, m.p. 105-107°, reported m.p. 107° (30). The significant absorptions in the infrared spectrum (potassium bromide) were at 2.99, 5.79, 5.95, 6.53, 13.3 and 14.3 μ. The ultraviolet spectrum gave λmax. in 2-propanol at 288 mμ (ϵ 1.44 x 10^4).

Preparation of benzophenone hydrazone. - Following the procedure of Grasley,* 400 g. (2.18 moles) of commercial benzophenone was added to 200 g. (6.25 moles) of anhydrous hydrazine. This mixture was then dissolved in 400 ml. of absolute ethanol and the solution was then refluxed for 17 hours. Following the reflux period, the solution was poured into a beaker and allowed to cool, depositing large needle-shaped crystals. The solid was filtered from the solution and washed several times to remove the excess hydrazine. The solid was then recrystallized repeatedly from absolute ethanol. Yield: 420 g. of white needles, m.p. 97-99°, reported m.p. 99° (32). The significant absorptions in the infrared spectrum (potassium bromide) were at 2.85, 2.99, 6.20, 6.31, 6.40, 6.69, 6.92, 12.82, 13.00, 14.21 and 14.39 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 273 mμ (ϵ 1.16 x 10^4).

Preparation of diphenyldiazomethane. - Following the general procedure as outlined by Miller (33), 26 g. (0.132 mole) of benzophenone hydrazone was dissolved in 400 ml. of ether. To this solution, 15 g. anhydrous sodium sulfate and 20 ml. of ethanol saturated with potassium hydroxide were added with stirring. The stirring was continued for 3 hours during which time 70 g. (0.323 mole) of red mercuric oxide (commercial N.F. IX) was added in small portions. There was ample evidence of reaction, for upon addition of the mercuric oxide, the oxide lost its red color and a deep purple solution was formed.

After the reaction period, the purple solution was filtered

*Unpublished observations, M. H. Grasley.

and the solvent removed under reduced pressure giving rise to a purple oil which sometimes, upon standing in the refrigerator, did form low-melting crystals. Significant absorptions in the infrared spectrum (plates) were at 4.90, 6.29, 6.71, 6.94, 13.39 and 14.42 μ. The ultraviolet spectrum gave λ max. in cyclohexane at 282 mμ (ϵ 3.78 x 10^4).

Preparation of 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline. - Using the procedure of van Alphen (18), approximately equimolar amounts of diphenyldiazomethane (25 g., 0.129 mole) and dimethyl maleate (18.6 g., 0.129 mole) were dissolved in ether and allowed to stand at room temperature until the loss of the red color was complete. Upon removal of the solvent, the remaining oil completely solidified, m.p. 120-145° dec. This solid was recrystallized from methanol giving 30.1 g. (70%) of white crystals, m.p. 141-142° dec., reported m.p. 142° dec. (18). The significant absorptions in the infrared spectrum (potassium bromide) were at 2.98, 5.70, 5.88 and 6.32 μ. The ultraviolet spectrum gave λ max. in methanol at 297 mμ (ϵ 1.16 x 10^4).

Preparation of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline. - The general procedure followed was that of Jones, Glenn and Baarda (34). The flask used in the reaction was soaked in a saturated solution of trisodium phosphate for several days and then washed with distilled water.

A mixture of 5.71 g. (0.064 mole) of cold triethylamine, 5.5 g. (0.064 mole) of cold, freshly distilled methyl acrylate and 11.3 g. (0.058 mole) of diphenyldiazomethane was added to 100 ml. of

cold technical pentane. The mixture was stirred until it was homogeneous and then placed in the refrigerator overnight or until the red diazo color was discharged. Upon discharge of the red color, a large amount of white solid precipitated. This solid was filtered from the solution and recrystallized from methanol several times. Yield: 13 g. (0.046 mole; 80%) of white crystals, m.p. 138-140° dec., reported m.p. 138-139° dec. (34). Significant absorptions in the infrared spectrum (potassium bromide) were at 2.95, 5.88 and 6.38 μ. The ultraviolet spectrum gave λ max. in methanol at 298 mμ (ϵ 1.05 x 10^4).

Preparation of 4,4'-dimethylbenzophenone hydrazone. - This compound was prepared by a slight adaptation of the method used by Baltzly, et al. (35).

Fifty grams (0.238 mole) of 4,4'-dimethylbenzophenone was dissolved in 120 ml. of 1-butanol in a 500 ml. round-bottom flask equipped with a reflux condenser. After all the solid ketone had dissolved, 30 ml. (0.798 mole) of 85% hydrazine hydrate was added. The solution turned bright yellow upon the addition of the hydrazine hydrate. The solution was then refluxed for 18 hours. At this time, the alcohol solution was set aside to cool overnight. During this time, white crystals were deposited on the sides and bottom of the flask. The mixture was filtered and the white solid recrystallized from absolute ethanol. Recrystallization gave 40 g. (0.174 mole; 73.1%) of white crystals, m.p. 107-108°, reported m.p. 108-110° (35). The infrared spectrum (potassium bromide) gave peaks at 2.90, 3.0, 6.2, 6.35 and 6.61 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 264 mμ (ϵ 1.48 x 10^4).

Preparation of 4,4'-dimethyldiphenyldiazomethane. - This diazo compound was prepared by the method of Miller (33). Thirty grams (0.132 mole) of 4,4'-dimethylbenzophenone hydrazone, prepared by the method of Baltzly, et al. (35), was mixed with 20 g. of anhydrous sodium sulfate in a one-liter three-necked flask equipped with a mechanical stirrer. To this mixture, 400 ml. of anhydrous ethyl ether was added along with 17 ml. of saturated alcoholic potassium hydroxide solution. After the hydrazone had dissolved, 70 g. (0.323 mole) of red mercuric oxide was added slowly over a period of 1 hour. The mixture was then stirred for 5 more hours. The solution was a very deep purple. The purple ether solution was filtered and the spent mercuric oxide-sodium sulfate mixture was washed several times with small portions of ethyl ether. These washings were filtered and added to the first solution. The ether was then removed by vacuum distillation yielding 23 g. (0.104 mole; 78.8%) of a purple solid, m.p. 100-101°, reported m.p. 101° (36). Significant absorptions in the infrared spectrum (potassium bromide) were at 4.91, 6.26, 6.63, 12.32 and 14.25 μ. The ultraviolet spectrum gave λ max. in cyclohexane at 286 mμ (ϵ 5.58 x 10^3).

Preparation of 5,5-(4,4'-dimethyldiphenyl)-3,4-dicarbomethoxy-2-pyrazoline. - In a 250 ml. Erlenmeyer flask prepared in the same manner as for the preparation of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline, 5.6 g. (0.955 mole) of triethylamine and 8 g. (0.0555 mole) of dimethyl maleate were mixed with 100 ml. of anhydrous ether and set in the refrigerator to cool. Upon cooling, 11 g. (0.050 mole) of 4,4'-dimethyldiphenyldiazomethane was added and the solution

returned to the refrigerator. The solution remained in the refrigerator until the diazo color was discharged, whereupon the solvent was removed under reduced pressure giving rise to a brown oil which crystallized when dissolved in a small amount of methanol, cooled to dry ice temperature, and the vessel scratched with a glass rod. The resulting solid was filtered and then recrystallized from methanol, again with cooling and scratching the vessel. Yield: 6 g. (30%) of a white powder, m.p. 50-52° dec. This compound was not stable enough at room temperature to obtain a good analysis. Significant absorptions in the infrared spectrum (potassium bromide) were at 2.95, 5.73, 5.89, 6.40 and 12.25 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 298 mμ (ϵ 1.42 x 10^4).

Preparation of 5,5-(4,4'-dimethyldiphenyl)-3-carbomethoxy-2-pyrazoline. - In a 250 ml. Erlenmeyer flask prepared as described in the preparation of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline, 5.6 g. (0.055 mole) of triethylamine and 4.7 g. (0.055 mole) of methyl acrylate were mixed with 100 ml. of technical pentane and brought to 0°, whereupon 11 g. (0.050 mole) of 4,4'-dimethyldiphenyldiazomethane was added and the solution returned to the refrigerator until the red diazo color had disappeared. Then the solvent was removed under reduced pressure giving rise to a yellow oil which resisted all attempts to induce crystallization. Significant absorptions in the infrared spectrum (plates) which indicated that the 2-pyrazoline was indeed present were at 2.95, 5.89, 6.41 and 12.25 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 298 mμ. This oil was used in the subsequent kinetic decompositions, without further

purification. For each decomposition, the oil contained 85-95% of the 2-pyrazoline as calculated from the observed volume of nitrogen evolved.

Preparation of 4-methylbenzophenone. - Following the procedure of Hughes, Ingold and Taher (37),* a mixture of 190 g. (1.36 moles) benzoyl chloride, 145 g. (1.09 moles) of anhydrous aluminum trichloride and one liter of carbon disulfide was heated on the steam bath under reflux conditions for 2 hours and then cooled. After the addition of 150 g. (1.63 moles) of toluene, the heating was continued for 4 hours. The solution was then cooled and added to ice water. The filtered carbon disulfide solution was washed with successive amounts of dilute hydrochloric acid, water, saturated sodium bicarbonate solution and water. Then the solution was dried over anhydrous sodium sulfate and distilled.

When all the carbon disulfide had been removed, the residue was cooled and filtered. The resulting solid was recrystallized from pentane. Yield: 147 g. (0.75 mole; 55%) of a white solid, m.p. 55-56°, reported m.p. 57° (39). Significant absorptions in the infrared spectrum (potassium bromide) were at 6.05, 6.23, 6.91, 12.71, 13.65 and 14.34 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 257 mμ (ϵ 1.52 x 10^4).

Preparation of 4-methylbenzophenone hydrazone. - Utilizing the procedure of Baltzly, et al. (35), 34 g. (0.174 mole) of 4-methylbenzophenone and 15 ml. of 85% hydrazine hydrate were dissolved in

*See also reference No. 38.

100 ml. of 1-butanol and refluxed for 2 days. At the end of this time, the solution was poured into a beaker and cooled in dry ice to precipitate the hydrazone. When the solid had precipitated, the solution was filtered and the solid recrystallized several times from absolute ethanol. Yield: 20 g. (0.095 mole; 55%) of white crystals, m.p. 86-87°, reported m.p. 80-81° (39). The melting point of this material was depressed by addition of the starting ketone. The significant absorptions in the infrared spectrum (potassium bromide) were at 2.91, 3.01, 6.22, 6.36, 6.65, 6.97, 12.17, 13.00 and 14.40 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 273 mμ (ϵ 1.30 x 10^4).

Preparation of phenyl-p-tolyl-diazomethane. - Following the outline of Baltzly, et al. (35), 8 g. (0.038 mole) of 4-methylbenzophenone hydrazone was dissolved in 50 ml. of anhydrous ether. Five grams of anhydrous sodium sulfate and 8 ml. of saturated ethanolic potassium hydroxide were added with stirring. The stirring was continued as 16 g. (0.076 mole) of red mercuric oxide was added in small portions over a period of 1 day. The solution was a deep purple color at the end of the reaction period. The solution was then filtered and the solvent removed under reduced pressure giving 7 g. (0.037 mole; 88%) of a purple solid, m.p. 54-55° dec., reported 52-55° dec. (40). Significant absorptions in the infrared spectrum (potassium bromide) were at 4.89, 6.62, 12.30, 13.37 and 14.40 μ. The ultraviolet spectrum gave λmax. in cyclohexane at 278 mμ (ϵ 1.54 x 10^4).

Preparation of 5-(4-methylphenyl)-5-phenyl-3,4-dicarbomethoxy-2-pyrazoline. - In 220 ml. of anhydrous ether, 11.7 g. (0.0564 mole) of phenyl-p-tolyl-diazomethane was mixed with 8.1 g. (0.0564 mole) of dimethyl maleate, a small amount of triethylamine and a pinch of hydroquinone. This solution was put in the refrigerator until the diazo color had been discharged. Then the solvent was removed under reduced pressure giving rise to a yellow oil. Significant absorptions in the infrared spectrum (plates) which indicated the presence of the 2-pyrazoline were at 2.99, 5.85, 6.39, 12.12, 12.95 and 14.42 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 295 mμ. This oil was used in subsequent kinetic determinations without further purification. For each decomposition, the oil contained from 85-95% of the 2-pyrazoline as calculated from the observed volume of nitrogen evolved.

Preparation of 5-(4-methylphenyl)-5-phenyl-3-carbomethoxy-2-pyrazoline. - In 150 ml. of anhydrous ether, 8 g. (0.038 mole) of phenyl-p-tolyl-diazomethane, 3.3 g. (0.038 mole) of methyl acrylate, 2 ml. of triethylamine and a pinch of hydroquinone were mixed and the solution set in the refrigerator until the diazo color disappeared. Then the solvent was removed under reduced pressure yielding a yellow oil which failed to crystallize. Significant absorptions in the infrared spectrum (plates) which indicated the presence of the 2-pyrazoline were at 2.96, 5.90, 6.42, 12.20, 12.92 and 14.35 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 292 mμ. This oil was used in subsequent kinetic determinations without further purification. For each decomposition, the oil contained 85-95% of the

2-pyrazoline as calculated from the observed volume of nitrogen evolved.

Preparation of 1,1-(4,4'-dichlorodiphenyl)-2,2-dichloroethene. - One mole (335 g.) of 4,4'-dichlorodiphenyltrichloroethane (DDT) was mixed with 67 g. (1.3 moles) of potassium hydroxide dissolved in absolute ethanol and refluxed for 4 hours. At the end of this time, a yellowish solid had precipitated and the solution was a dark brown. The solution was filtered and set aside to cool. The residual yellow solid was washed with ethanol which removed the color and left a white powder. This solid proved to be potassium chloride.

The washings and the original ethanol solution were combined and allowed to cool further, whereupon a heavy mass of crystals was deposited in a short time. The solution was filtered and the solid was recrystallized from ethanol. Yield: 161 g. (0.51 mole; 51%) of yellow crystals, m.p. 87-89°, reported m.p. 89° (41). Significant absorptions in the infrared spectrum (potassium bromide) were at 6.30, 6.40, 6.71, 12.05 and 12.55 μ. The ultraviolet spectrum gave $\lambda_{max.}$ in 2-propanol at 223 mμ (ϵ 2.54 x 10^4) and 247 mμ (ϵ 2.65 x 10^4).

Preparation of 4,4'-dichlorobenzophenone. - This ketone was prepared by the nitric acid oxidation of 1,1-(4,4'-dichlorodiphenyl)-2,2-dichloroethene. This was the method as used by Backeberg and Marais (42). In a typical run, 2 g. (0.0063 mole) of the olefin was dissolved in 20 ml. of glacial acetic acid and 10 ml. of fuming nitric acid (sp. gr. 1.51) was added. The solution was then heated

on a steam bath in the hood for 2-2.5 hours. Almost immediately upon addition of heat to the vessel, the red-brown fumes of nitrogen dioxide were observed and the solution itself was a reddish color.

At the end of the heating period, the red solution was poured into water, covered and set in the refrigerator to cool. A white powder formed upon contact with the water.

Also, one of the side products formed upon the addition to water was a very powerful lachrymator, and care was taken to filter the solution in the hood.

The cold water solution was filtered and the white powder recrystallized from absolute ethanol. Yield: 1.5 g. (0.006 mole; 95%) of white flakes, m.p. 144-146°, reported m.p. 145-146° (42). Significant absorptions in the infrared spectrum (potassium bromide) were at 6.08, 6.35, 6.75 and 12.02 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 264 mμ (ζ 2.73 x 10^4).

Preparation of 4,4'-dichlorobenzophenone hydrazone. - This compound was prepared using a slight modification of the method of Szmant and McGinnis (43).

Twenty-one grams (0.0837 mole) of 4,4'-dichlorobenzophenone, prepared by the nitric acid oxidation of 1,1-dichloro-2,2-(4,4'-dichlorodiphenyl)-ethene (42) was added to 25 g. (0.742 mole) of 95% anhydrous hydrazine in 250 ml. of 95% ethanol. The solution was allowed to reflux in a one-liter round-bottom flask equipped with a Soxhlet extractor for 2 days. The extraction thimble was filled with 20 g. of calcium oxide that had been previously heated at 110° in an oven for 2 days. After the reflux period, some of the solvent was

removed by applying a slight vacuum to the reaction vessel. The solution was then poured into water and allowed to stand. A white precipitate formed and was collected by filtration. Recrystallization from 95% ethanol gave 17 g. (0.0642 mole; 76.7%) of white crystals, m.p. 90-93°, reported m.p. 92-93° (43). The reported color was yellow but the melting point and infrared spectrum indicated that this was the hydrazone. Significant absorptions in the infrared spectrum (potassium bromide) were at 2.91, 3.01, 6.31 and 6.75 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 273 mμ (ϵ 5.42 x 10^3).

Preparation of 4,4'-dichlorodiphenyldiazomethane. - This compound was prepared according to the general procedure of Miller (33). Five grams (0.0189 mole) of 4,4'-dichlorobenzophenone hydrazone, prepared by the method of Szmant and McGinnis (43), was dissolved in 100 ml. anhydrous ethyl ether and 10 g. of anhydrous sodium sulfate added to the solution, followed by 5 ml. of a saturated alcoholic potassium hydroxide solution. Fifteen grams (0.0693 mole) of red mercuric oxide was added slowly. This mixture was placed in a 500 ml. flask equipped with a mechanical stirrer. The mixture was then stirred for 3 days at room temperature. The ether solution was reddish-purple. This solution was filtered and evaporated to dryness giving a reddish-purple solid. Recrystallization from pentane gave 4 g. (0.0141 mole; 74.6%) of red needles, m.p. 68-70°, reported m.p. 70° (36). Significant absorptions in the infrared spectrum (potassium bromide) were at 4.88, 6.35, 6.73, 12.2 and 12.3 μ. The ultraviolet spectrum gave λ max. in cyclohexane at 288 mμ (ϵ 1.56 x 10^4).

Preparation of 5,5-(4,4'-dichlorodiphenyl)-3,4-dicarbomethoxy-2-pyrazoline. - In a typical run, 1 g. (0.0038 mole) of 4,4'-dichlorodiphenyldiazomethane was added to 0.55 g. (0.0038 mole) of dimethyl maleate in 20 ml. of anhydrous ether. To this solution, 1 ml. of triethylamine and a pinch of hydroquinone were added and the total solution placed in the refrigerator until the red diazo color had been discharged. The solvent was then removed under reduced pressure giving rise to a yellow oil which failed to crystallize. Significant absorptions in the infrared spectrum (plates) which indicated the presence of the 2-pyrazoline were at 2.98, 5.79, 5.88, 6.40 and 12.10 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 298 mμ. This oil was used without further purification in the subsequent kinetic runs. For each decomposition, the oil contained from 85-95% of the 2-pyrazoline as calculated from the observed volume of nitrogen evolved.

Preparation of 5,5-(4,4'-dichlorodiphenyl)-3-carbomethoxy-2-pyrazoline. - In a typical run, 1.8 g. (0.0069 mole) of 4,4'-dichlorodiphenyldiazomethane and 0.53 g. (0.0069 mole) of methyl acrylate were added to a cold solution of 25 ml. of anhydrous ether, 2 ml. of triethylamine and a pinch of hydroquinone. This solution was then placed in the refrigerator until the red diazo color disappeared. The usual work-up gave a yellow oil which failed to crystallize. Significant absorptions in the infrared spectrum (plates) which indicated the presence of the 2-pyrazoline were at 2.97, 5.89, 6.40 and 12.09 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 297 mμ. This oil was used without further purification in the

subsequent kinetic runs. For each decomposition, the oil contained 85-95% of the 2-pyrazoline as calculated from the observed volume of nitrogen evolved.

Preparation of 5,5-(4,4'-dimethyldiphenyl)-3,4-dicarbomethoxy-1-acetyl-2-pyrazoline. - The solid (0.6 g., 0.0016 mole) prepared by the reaction of 4,4'-dimethyldiphenyldiazomethane and dimethyl maleate was dissolved in acetic anhydride and 3 drops of concentrated sulfuric acid were added. The solution was swirled and then heated a short time on a steam bath. The hot solution was allowed to cool and then was poured into cold water. An oil immediately separated upon contact with the water. Solid sodium bicarbonate was added with stirring until the bubbling ceased. The solution was washed with ether and the ether solution was dried over anhydrous sodium sulfate. The ether was removed under reduced pressure giving rise to a white solid, m.p. 143-146°, after recrystallization from methanol. The significant absorptions in the infrared spectrum (potassium bromide) were at 5.70, 5.83, 5.92 and 6.29 μ with the absence of a peak in the 2.8-3.1 μ region indicating no nitrogen-hydrogen bond. The ultraviolet spectrum gave λ max. in 2-propanol at 281 mμ (ϵ 1.27 x 10^4).

Anal. Calcd. for $C_{23}H_{24}N_2O_5$: C, 67.23; H, 5.92; N, 6.86. Found: C, 67.50; H, 6.01; N, 6.90.

Preparation of 5,5-(4,4'-dimethyldiphenyl)-3-carbomethoxy-1-acetyl-2-pyrazoline. - The oil from the reaction of 4,4'-dimethyldiphenyldiazomethane and methyl acrylate was dissolved in 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added.

The usual work-up afforded a white solid, m.p. 152-153.5°, after recrystallization from methanol. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.82, 5.91 and 6.29 μ with no peak in the 2.8-3.1 μ region. The ultraviolet spectrum gave λ max. in 2-propanol at 279 mμ (ϵ 1.25 x 10^4).

Anal. Calcd. for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 8.00. Found: C, 72.01; H, 6.44; N, 8.16.

Preparation of 5-phenyl-5-p-tolyl-3,4-dicarbomethoxy-1-acetyl-2-pyrazoline. - The oil from the reaction of phenyl-p-tolyl-diazomethane and dimethyl maleate was dissolved in 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added. The usual work-up gave a white solid, m.p. 132-134°, after recrystallization from methanol. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.76, 5.81, 5.91, 6.32 and 6.88 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 278 mμ (ϵ 1.26 x 10^4).

Anal. Calcd. for $C_{22}H_{22}N_2O_5$: C, 66.99; H, 5.62; N, 7.10. Found: C, 66.81; H, 5.60; N, 7.02.

Preparation of 5-phenyl-5-p-tolyl-3-carbomethoxy-1-acetyl-2-pyrazoline. - The oil from the reaction of 4-methylphenyl-phenyl-diazomethane and methyl acrylate was dissolved in 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added. The usual work-up afforded a white solid, m.p. 138-140°, reported m.p. 138-140° (21), after recrystallization from methanol. The infrared spectrum (potassium bromide) gave peaks at 5.80, 5.92 and 6.29 μ with no peak in the 2.8-3.1 μ region. The ultraviolet spectrum gave

λ max. in methanol at 278 mμ (ϵ 1.34 x 10^4) (21).

Anal. Calcd. for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.48; H, 5.78; N, 8.43.

Preparation of 5,5-(4,4'-dichlorodiphenyl)-3,4-dicarbomethoxy-1-acetyl-2-pyrazoline. - The oil from the reaction of 4,4'-dichlorodiphenyldiazomethane and dimethyl maleate was dissolved in 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added. The usual work-up gave a white solid, m.p. 174-175.5°, upon recrystallization from methanol. The infrared spectrum (potassium bromide) showed peaks at 5.76, 5.81, 5.91, 6.29 and 6.70 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 266 mμ (ϵ 1.74 x 10^4).

Anal. Calcd. for $C_{21}H_{18}Cl_2N_2O_5$: C, 56.14; H, 4.04; Cl, 15.78; N, 6.24. Found: C, 56.22; H, 4.17; Cl, 15.81; N, 6.12.

Preparation of 5,5-(4,4'-dichlorodiphenyl)-3-carbomethoxy-1-acetyl-2-pyrazoline. - The oil from the reaction of 4,4'-dichlorodiphenyldiazomethane and methyl acrylate was dissolved in 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added. The usual work-up gave a white solid, m.p. 183-185°, after recrystallization from methanol. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.74, 5.99 and 6.29 μ with no peak in the 2.8-3.1 μ region. The ultraviolet spectrum gave λ max. in 2-propanol at 277 mμ (ϵ 1.74 x 10^4).

Anal. Calcd. for $C_{19}H_{16}Cl_2N_2O_3$: C, 58.33; H, 4.12; Cl, 18.12; N, 7.16. Found: C, 58.53; H, 4.38.

The major portion of this sample was lost in an accident at

Galbraith Laboratories. Only enough material for the carbon and hydrogen determinations was recovered.

Isolation of 2,2-diphenyl-cyclopropanecarboxylic acid. - Following the procedure of Baarda (21), the residue from reduced-pressure removal of the solvent from a spent kinetic reaction mixture from the decomposition of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline was hydrolyzed with methanolic potassium hydroxide. The usual work-up procedure gave 0.455 g. (0.00668 mole; 83%) of a white solid, m.p. 170-172°, reported m.p. 169-171° (44).

Isolation of 2-phenyl-2-p-tolyl-cyclopropanecarboxylic acid. - This acid was isolated in the same manner as the 2,2-diphenyl-cyclopropanecarboxylic acid. The usual work-up gave 0.340 g. of a crude solid. Recrystallization of this solid from ether/pentane gave 0.110 g. (0.0044 mole) of a white solid, m.p. 144-152°, reported m.p. 145-153° (21). The wide range was due possibly to a mixture of cis and trans isomers. The infrared spectrum (potassium bromide) gave significant peaks at 3.2-3.9 (broad), 5.9, 6.68, 6.95, 13.32, 13.9 and 14.40 μ. The ultraviolet spectrum gave $\lambda_{max.}$ in 2-propanol at 229 mμ (ϵ 1.99 x 10^4).

Isolation of 2,2-(4,4'-dimethyldiphenyl)-cyclopropanecarboxylic acid. - This acid was isolated in the same manner as 2,2-diphenyl-cyclopropanecarboxylic acid. The usual work-up gave 0.123 g. (0.00463 mole) of a white solid, m.p. 153-154.5°. Significant absorptions in the infrared spectrum (potassium bromide) were at 3.3-4 (broad), 5.9, 6.65, 12.4 and 12.95 μ. The ultraviolet spectrum gave $\lambda_{max.}$ in 2-propanol at 228 mμ (ϵ 1.79 x 10^4).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.16; H, 6.93.

Isolation of 2,2-(4,4'-dichlorodiphenyl)-cyclopropanecarboxylic acid. - This acid was isolated in the same manner as 2,2-diphenyl-cyclopropanecarboxylic acid. The usual work-up gave 0.200 g. (0.000652 mole) of white crystals, m.p. 171-172°, reported m.p. 170.5-171° (45). Significant absorptions in the infrared spectrum (potassium bromide) were at 3.2-3.92 (broad), 5.90 and 6.69 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 232 mμ (ϵ 2.22 x 10^4).

Anal. Calcd. for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94; Cl, 23.09. Found: C, 62.47; H, 4.07; Cl, 23.20.

Isolation of 3,3-(4,4'-dimethyldiphenyl)-1,2-dicarbomethoxycyclopropane. - The solvent from a spent reaction mixture from the kinetic decomposition of 5,5-(4,4'-dimethyldiphenyl)-3,4-dicarbomethoxy-2-pyrazoline was removed under reduced pressure leaving a solid residue. The residue was recrystallized from methanol. Yield: 0.422 g. (0.00125 mole) of white needles, m.p. 142.5-144.5°. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.76, 6.68, 6.98 and 13.77 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 228 mμ (ϵ 1.47 x 10^4).

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.49; H, 6.57.

Isolation of 3,3-diphenyl-1,2-dicarbomethoxycyclopropane. - This ester was isolated in the same manner as for 3,3-(4,4'-dimethyldiphenyl)-1,2-dicarbomethoxycyclopropane. Recrystallization of the residue gave 0.376 g. (0.00121 mole; 68%) of white solid, m.p. 174-176°,

reported m.p. 174-174.5° (15). A mixed melting point with an authentic sample gave no depression of the melting point. The infrared spectrum (potassium bromide) gave peaks at 5.77, 6.67, 6.95, 13.38 and 14.38 μ.

Isolation of 3,3-(4,4'-dichlorodiphenyl)-1,2-carbomethoxycyclopropane. - This ester was isolated in the same manner as for the 3,3-(4,4'-dimethyldiphenyl)-1,2-dicarbomethoxycyclopropane. Recrystallization from methanol gave 0.480 g. (0.00126 mole) of white crystals, m.p. 151-153°. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.76, 6.68, 6.98, and 13.77 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 232 mμ (ϵ 2.33 x 10^4).

Anal. Calcd. for $C_{19}H_{16}Cl_2O_4$: C, 60.18; H, 4.25. Found: C, 59.98; H, 4.05.

Isolation of 3-phenyl-3-p-tolyl-1,2-dicarbomethoxycyclopropane. - This cyclopropane was isolated in the same manner as the 3,3-(4,4'-dimethyldiphenyl)-1,2-dicarbomethoxycyclopropane. Recrystallization from methanol gave 0.347 g. (0.00107 mole) of white crystals, m.p. 134-136°. Significant absorptions in the infrared spectrum (potassium bromide) were at 5.73, 6.68, 6.95, 13.33, 13.9 and 14.37 μ. The ultraviolet spectrum gave λ max. in 2-propanol at 226 mμ (ϵ 8.27 x 10^3).

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.22. Found: C, 73.90; H, 6.20.

Preparation of 4-phenyl-3-carboethoxy-5-carbomethoxy-1-acetyl-2-pyrazoline. - One gram (0.00362 mole) of the 4-phenyl-3-

carboethoxy-5-carbomethoxy-2-pyrazoline, prepared by the reaction of methyl diazoacetate with ethyl cinnamate, was added to 5 ml. of acetic anhydride to which 1 drop of concentrated sulfuric acid had been added. This mixture was placed in a flask and heated on the steam bath for about 10 minutes. The solution thus obtained was cooled and poured into water. Solid sodium bicarbonate was added in portions until all bubbling had ceased. Then the solution was washed with ethyl ether. The ether solution was dried over anhydrous sodium sulfate. The ether solution then was evaporated to dryness, giving a white solid. Recrystallization of the solid from 95% ethanol gave 0.9 g. (0.00283 mole; 78.2%) of white crystals, m.p. 105-108°. The significant absorptions in the infrared spectrum (potassium bromide) were at 5.7, 5.8, 5.9 and 12.6 μ. The ultraviolet spectrum gave λmax. in 2-propanol at 276 mμ (ϵ 1.63 x 10^4).

Anal. Calcd. for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.20; H, 5.71; N, 8.90.

Preparation of 4-phenyl-5-carboethoxy-3-carbomethoxy-1-acetyl-2-pyrazoline. - This compound was prepared by the same method used to prepare 4-phenyl-3-carboethoxy-5-carbomethoxy-1-acetyl-2-pyrazoline. The usual work-up gave a clear oil which resisted all attempts at crystallization. This procedure gave 0.9 g. (0.00283 mole; 78.2%) of the oil. Significant absorptions in the infrared spectrum (plates) were at 5.7, 5.8, 5.92 and 11.4 μ. The ultraviolet spectrum gave λmax. in 2-propanol at 275 mμ (ϵ 1.66 x 10^4).

In comparison with the infrared spectrum of the 4-phenyl-3-carboethoxy-5-carbomethoxy-1-acetyl-2-pyrazoline, it was found that

the spectra were quite similar except at 11.4 and 12.6 μ. The 11.4 μ peak was found only with the 5-carboethoxy isomer and the 12.6 μ peak only with the 5-carbomethoxy isomer. The presence of these peaks served as an analytical tool in subsequent reactions.

Anal. Calcd. for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.19; H, 5.75; N, 8.79.

Partial decomposition of 4-phenyl-3-carboethoxy-5-carbomethoxy-2-pyrazoline. - A sample of the 2-pyrazoline (0.6435 g., 0.00233 mole) was dissolved in 50 ml. of decalin in which 0.3 ml. of triisoamylamine had been mixed. This solution was placed in a constant temperature oil bath at 150° until 50% of the calculated amount of nitrogen had been evolved. The solution was then removed from the bath and allowed to cool, whereupon 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid were added. The liquids formed a two-phase mixture which was heated overnight at 60°. The two layers were then separated and the anhydride layer worked up in the usual manner. This work-up gave 0.3 g. (0.00094 mole; 81%) of a yellow oil. The infrared spectrum (plates) of this material gave peaks at 3.38, 5.78, 5.80, 5.95, 11.4 and 12.6 μ. The appearance of both peaks at 11.4 and 12.6 μ indicated a mixture of the two acetyl derivatives.

Partial decomposition of 4-phenyl-5-carboethoxy-3-carbomethoxy-2-pyrazoline. - A sample of the 2-pyrazoline (0.6537 g., 0.00236 mole) was dissolved in 50 ml. of decalin in which 0.3 ml. of triisoamylamine had been mixed. This solution was placed in a constant temperature bath at 150° until 50% of the calculated amount

of nitrogen had been evolved. The same work-up procedure used for the acylation of the reaction mixture from the partial decomposition of 4-phenyl-3-carboethoxy-5-carbomethoxy-2-pyrazoline was followed here. Yield: 0.3 g. (0.00094 mole; 80%) of a yellow oil. The infrared spectrum (plates) gave peaks at 3.38, 5.78, 5.95, 11.4 and 12.6 μ. The appearance of both peaks at 11.4 and 12.6 μ indicated a mixture of the two acetyl derivatives.

Purification of the nitrogen gas bubbled through the hexadecane prior to a kinetic run. - A system similar to that described by Fieser (46) was used to purify the nitrogen gas which was bubbled through the hexadecane solvent as part of the preliminary treatment for a kinetic run. This system consisted of a series of wash bottles containing, respectively, Fieser's solution (47), saturated lead acetate solution, concentrated sulfuric acid, the metal ketyl from benzophenone and sodium in xylene and a final bottle of paraffin oil.

Preparation of Fieser's solution (47). - This solution contained alkaline sodium hydrosulfite with sodium anthraquinone B-sulfonate added as a catalyst. The solution was prepared by dissolving 20 g. of potassium hydroxide in 100 ml. of water and adding 2 g. of sodium anthraquinone B-sulfonate and 15 g. of sodium hydrosulfite to the warm solution. The mixture was stirred until a clear, blood-red solution was obtained.

Preparation of the metal ketyl of benzophenone and sodium. - Five grams of sodium was covered with xylene and 5 g. of potassium dropped onto the sodium. The metals were pushed together with a glass rod until they alloyed and became a liquid. This liquid was

transferred by pipette, under a layer of solvent, to a suitable amount of xylene in the wash bottle. Ten grams of benzophenone was added and the bottle sealed at the top. The solution turned a very bright blue. Prior to each use, the solution had to be shaken vigorously.

Purification of hexadecane. - Eastman practical hexadecane was distilled under reduced pressure and stored under argon and over Linde 3 A molecular sieves. B.p.$_{4.0\ mm.}$ 133.2-134°.

Purification of methyl acrylate, tri-n-propylamine, triethylamine, triisoamylamine and dimethyl maleate. - Each of these liquids was distilled at atmospheric pressure and middle cuts taken. Methyl acrylate, b.p. 79.5-80.5°, reported b.p. 80.5° (48); tri-n-propylamine, b.p. 154-156°, reported b.p. 156° (49); triisoamylamine, b.p. 235-237°, reported b.p. 237° (50); triethylamine, b.p. 88-89°, reported b.p. 89.5° (51); dimethyl maleate, b.p. 203-205°, reported b.p. 205° (52).

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BIOGRAPHICAL SKETCH

Paul Otis Sanderfer was born in Union City, Tennessee, on March 1, 1937. In 1955, he graduated from Union City High School and entered Union University. From that institution he received the degree of Bachelor of Science and entered the Graduate School at the University of Florida in 1959. During his graduate work at the University of Florida he has held a graduate assistantship and an interim instructorship in the Department of Chemistry.

Mr. Sanderfer is married to the former Miriam Watt and is the father of a son, Van. He is a member of the American Chemical Society, Gamma Sigma Epsilon and Alpha Tau Omega.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 14, 1965

Ernest H. Cox
Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

Chairman