at δ 2.42 (2 H, singlet, $>\overset{\ulcorner O \urcorner}{C}-CH_2$), 0.88 (3 H, singlet, CH_3), and unresolved absorption in the region 1.1–2.1 (15 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.92; H, 10.99.

Epoxide 15 from *trans*-9-methyl-2-decalone (13) had bp 55° (0.23 mm). Gas chromatographic analysis[29] revealed the presence of 95% **15** and 5% **16**. The product exhibits nmr absorption[29] at δ 2.26 (singlet, 2 H, $>\overset{\ulcorner O \urcorner}{C}-CH_2$), 0.93 (singlet, 3 H, CH_3), and unresolved absorption in the region 1.1–2.1 (15 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.16; H, 11.20.

Epoxidation Studies.—All epoxide mixtures were analyzed by gas chromatography[24] under carefully controlled conditions and it was necessary to use a glass liner in the injection port to prevent rearrangement. Samples of the epoxide mixtures were collected and their infrared spectra were examined to ensure that rearrangement did not occur. The values listed in Table IV are the average values for at least two runs and the results were reproducible to ±2%.

Epoxidation with *m*-Chloroperbenzoic Acid.—To 0.100 g of the appropriate olefin in 2 ml of distilled methylene chloride at 0° was added a 20% excess of *m*-chloroperbenzoic acid in 2 ml of methylene chloride. The reaction mixture was stirred at 0° for 2 hr and the excess per acid was destroyed with 10% sodium sulfite solution. Saturated sodium bicarbonate solution was added and the aqueous layer was separated and extracted with two portions of methylene chloride. The combined organic layers were washed with brine and dried. Removal of the solvent afforded the crude epoxide mixture which was analyzed by gas chromatography.

Similar procedures were used for epoxidations in acetonitrile, ether, and methanol. When methanol was used as the solvent the reaction was carried out to *ca.* 20% completion because the epoxides underwent further reaction. Under these conditions no ring opening of the epoxide occurred.

Epoxidation with Monoperphthalic Acid.—To 0.100 g of the appropriate olefin in 4 ml of ether was added a 10% excess of an ethereal solution of monoperphthalic acid[32] which contained 0.1 g/ml of per acid and the reaction mixture was stirred at room temperature for 20 hr and worked up as above.

(32) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

Epoxidation with Alkaline Hydrogen Peroxide–Benzonitrile.—A solution of 0.100 g of the appropriate olefin, 0.5 ml of methanol, 70 mg of benzonitrile, 15 mg of potassium bicarbonate, and 0.08 ml of 30% hydrogen peroxide was stirred at room temperature for 20 hr and worked up as above. The addition of phosphate ion or changing the base to potassium carbonate had little effect on the stereochemistry of the reaction.

Reaction of *trans*-2-Decalone (1) with Dimethylsulfonium Methylide.—Following the general procedure of Corey and Chaykovsky,[1a] treatment of 10.0 g (66 mmoles) of 1 with dimethylsulfonium methylide from 16.3 g (80 mmoles) of trimethylsulfonium iodide afforded 8.84 g of product, bp 53–55° (0.14 mm). Gas chromatographic analysis[24] revealed the presence of 52% unreacted 1, 21% **2**, and 26% **3**.

Separation of Pure Epoxide 3.—To a solution of 15.0 g of a mixture of epoxides containing 64% **2** and 36% **3** in 340 ml of dimethyl sulfoxide was added a solution of 22.8 g of potassium hydroxide in 68 ml of water. The solution was stirred at room temperature and aliquots were periodically removed and analyzed by gas chromatography. When all of epoxide **2** had reacted (76 hr) the reaction mixture was worked up in the usual manner to afford 0.60 g of pure **3**, bp 56–58° (0.3 mm). The product exhibits nmr absorption at δ 2.37 (singlet, 2 H, $C=CH_2$) and unresolved absorption in the region 0.8 to 2.0 (16 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.42; H, 10.66.

Measurement of Half Band Widths.—All spectra were measured on a Varian A-60 spectrometer at a 0.1-cps sweep time, 50-cycle sweep width, a filter band width of 4 and radio frequency field setting of 0.04. The samples were 10–20% (w/v) in carbon tetrachloride containing 2% TMS as an internal reference. The band widths were measured at half-height to the nearest 0.01 cps and the average deviations are given in Table III.

Registry No.—**4**, 7787-72-6; **10**, 7787-73-7; **14**, 7787-74-8; **2**, 7787-75-9; **11**, 7787-76-0; **15**, 10022-32-9; **3**, 7787-77-1; **7**, 7787-78-2; **8**, 7787-79-3; **12**, 7787-80-6; **16**, 7787-81-7.

Acknowledgment.—We are indebted to the University of Kansas Committee of the American Cancer Society Institutional Research Grant for partial support of this work.

Kinetics of the Base-Induced Conversion of 2-Pyrazolines to Cyclopropanes[1]

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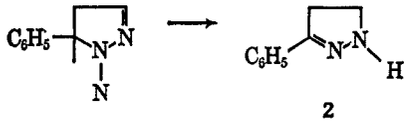
University of Florida, Gainesville, Florida

Received September 28, 1966

A kinetic study of the base-induced thermal conversion of 5,5-diaryl-3-carboalkoxy-2-pyrazolines to cyclopropanes has been made. Electron-donating groups on the aryl rings cause slight rate retardations, and electron-withdrawing groups cause acceleration. Changes in base concentration cause rate changes that are consistent with a mechanism involving slow formation of a 1-pyrazoline followed by rapid loss of nitrogen. Scrambling experiments and the effect of added base on the rate of decomposition of selected 3,5-dicarboalkoxy-2-pyrazolines lead to the conclusion that these, too, decompose *via* the 1-pyrazoline but in this case the slow step is loss of nitrogen.

The mechanism of the thermal conversion of 2-pyrazolines to cyclopropanes[3] has been a subject of interest in these laboratories for some time.[4] However, to date, the direct evidence for the steps involved in this type of conversion is meager. Perhaps the most definitive investigation that has been reported is that of Beech, Turnbull, and Wilson,[5] who studied the effect of various catalysts on the conversion of 3- and 5-phenyl-2-pyrazolines and 3,5-diphenyl-2-pyrazolines to the corresponding cyclopropanes. In addition to finding that basic catalysts were required to effect the conversions, they also noted that 5-phenyl-2-pyrazoline (1) readily underwent conversion to 3-phenyl-2-



1 2

(1) Taken from dissertations submitted by P. O. Sanderfer and D. G. Baarda to the Faculty of the University of Florida, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Alfred P. Sloan Fellow, 1963–1967.

(3) For a review of this area, see T. L. Jocobs in "Heterocyclic Compounds, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957.

(4) *Cf.* W. M. Jones, *J. Am. Chem. Soc.*, **82**, 3136 (1960), and previous papers.

(5) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

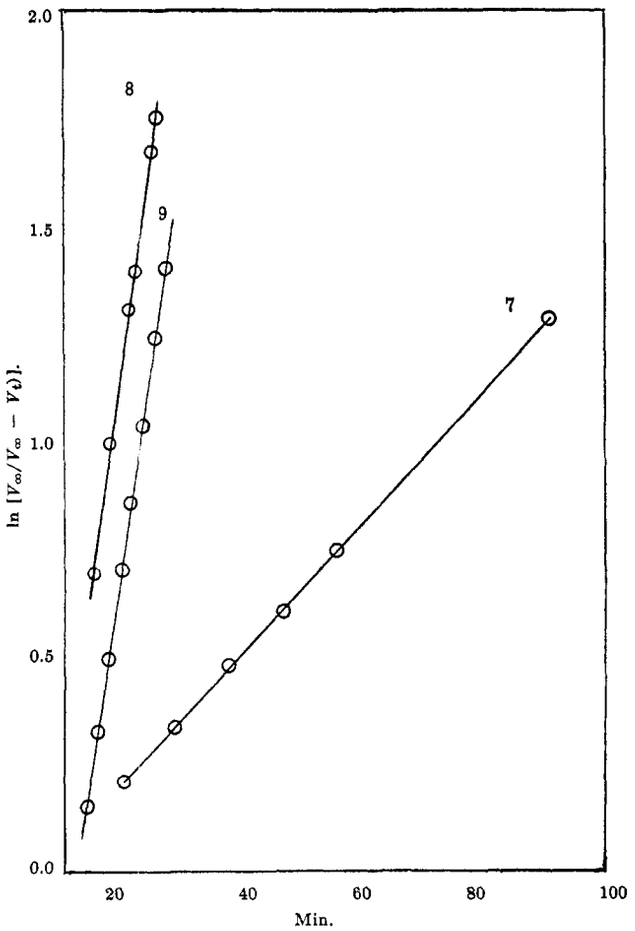
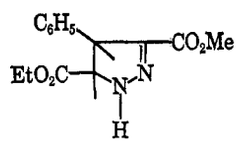


Figure 1.—Plot of ln $[V_\infty/(V_\infty - V_t)]$ *vs.* reaction time in minutes for the reaction of 2-pyrazoline with tri-*n*-propylamine: 9, 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline; 8, 5,5-(4,4′-dichlorodiphenyl)-3-carbomethoxy-2-pyrazoline; 7, 5,5-(4,4′-dimethyldiphenyl)-3-carbomethoxy-2-pyrazoline.

pyrazoline (**2**) under the conditions of their reaction (reflux at 200° with KOH). From these observations, they concluded that the path of the reaction involved loss of nitrogen from an initially formed 1-pyrazoline.[6] Support for this mechanism can be found in the many reports of base catalysis for these conversions[8] and especially in the report of McGreer, Wai, and Carmichael[7] who found that certain 2-pyrazolines were stable up to 500° unless exposed to basic surface.

Finally, we[4] have reported studies on the stereochemistry of the conversion of selected 2-pyrazolines to cyclopropanes where we found that the results could be rationalized by assuming an initial tautomerization of the 2-pyrazoline to the 1-pyrazoline followed by stereoselective[8] loss of nitrogen.

However, in the course of our general investigations on the chemistry of 2-pyrazolines, we noted that, in inert solvents in the presence of base, the rate of decomposition of 2-pyrazolines substituted with two phenyl rings on the 5 carbon appeared to be much faster than analogous 2-pyrazolines substituted on the 5 position with a carboalkoxy group. This qualitative rate difference raised some doubt about the generality of the 1-pyrazoline reaction path for the following reason. In a study that was reported some years ago,[4] it was found that the partial thermal decomposition of **3** and **4** in the melt led to no scrambling of the carbo-



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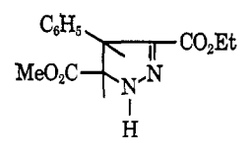

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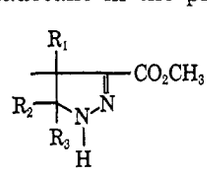
alkoxy groups. To accommodate a 1-pyrazoline mechanism, this observation requires a slow first step. Extrapolation of this conclusion to the 5,5-diaryl-2-pyrazolines would require arguments to explain why substitution of aryl groups on the 5 carbon would give rise to a rather dramatic acceleration in the rate of tautomerization of the 2-pyrazoline to the 1-pyrazoline. Reasons for such an acceleration appeared to us to be so obscure as to suggest either an alternate mechanism[9] for the decomposition of the 5,5-diphenyl-2-pyrazolines or a change in the slow step for the decompositions of **3** and **4** when the reaction medium is changed from the melt to solution.

The purpose of this paper is to report the results of an investigation of these two possibilities.

Results and Discussion

A series of 5,5-diaryl-2-pyrazolines (**5**–**12**) was synthesized by the addition of appropriate diazoalkanes to α,β-unsaturated esters. Their decompositions were carried out in hexadecane in the presence of trialkyl-



5, R_1 = H; R_2 = C_6H_5; R_3 = C_6H_5
6, R_1 = H; R_2 = C_6H_5; R_3 = p-$CH_3C_6H_5$
7, R_1 = H; R_2 = p-$CH_3C_6H_5$; R_3 = p-$CH_3C_6H_5$
8, R_1 = H; R_2 = p-ClC_6H_5; R_3 = p-ClC_6H_5
9, R_1 = CO_2CH_3; R_2 = C_6H_5; R_3 = C_6H_5
10, R_1 = CO_2CH_3; R_2 = C_6H_5; R_3 = p-$CH_3C_6H_5$
11, R_1 = CO_2CH_3; R_2 = p-$CH_3C_6H_5$; R_3 = p-$CH_3C_6H_5$
12, R_1 = CO_2CH_3; R_2 = p-ClC_6H_5; R_3 = p-ClC_6H_5

amines under inert conditions (see the Experimental Section). Although many of these 2-pyrazolines were uncrystallizable oils (**5**, **9** and **11** were crystalline materials, all 2-pyrazolines were characterized by spectra and conversion to solid derivatives) which were too unstable to yield to normal purification methods, they all gave good reproducible first-order kinetic plots and

(6) For discussions of the mechanism and stereochemistry of the thermal conversion of 1-pyrazolines to cyclopropanes, see H. M. Walbrosky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962); F. Impastato, L. Barash, and H. M. Walborsky, *ibid.*, **81**, 1514 (1959); D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *Can. J. Chem.*, **43**, 1389 (1965); D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *ibid.*, **43**, 1398 (1965); D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, **43**, 1407 (1965); R. J. Cawford, R. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965); C. G. Overberger, and J. P. Anselme, *ibid.*, **86**, 658 (1964); T. V. Van Auken, and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).

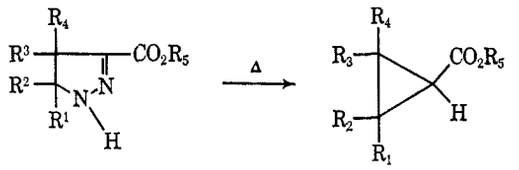
(7) D. E. McGree, W. Wai, and G. Carmichael, *Can. J. Chem.*, **38**, 2410 (1960).

(8) In previous papers on pyrazolines, we have used the word stereospecific where the modern trend [*cf.* H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959), footnote 16, and E. L. Eliel "Stereochemistry of Carbon Compounds," McGraw Hill Book Co., Inc., New York, N. Y., 1962, p 434) would demand the word stereoselective. Since we are in agreement with the current definitions of these terms, we will forthwith change our notation.

(9) For a discussion of various possible alternative mechanisms for the decomposition of 5,5-diphenyl-2-pyrazolines as well as experimental data that excludes these possibilities, see the Ph.D. dissertation of P. O. Sanderfer.[1]

TABLE I

KINETIC DATA FOR THE THERMAL DECOMPOSITION OF 2-PYRAZOLINES



Compd	R_1	R_2	R_3	R_4	R_5	T, °C	10^2 (base)[a]	$k_{obsd} \times 10^3$
5[b]	C_6H_5	C_6H_5	H	H	CH_3	135	4.20	0.28
						135	2.10	0.17
						135	1.05	0.11
6[c]	C_6H_5	p-$CH_3C_6H_5$	H	H	CH_3	135	4.20	0.25
						135	2.10	0.15
						135	1.05	0.097
7[c]	$CH_3C_6H_5$	p-$CH_3C_6H_5$	H	H	CH_3	135	4.20	0.23
						135	2.10	0.14
						135	1.05	0.087
8[c]	p-ClC_6H_5	p-ClC_6H_5	H	H	CH_3	135	4.20	1.7
						135	2.10	1.1
						135	1.05	0.65
9[b]	C_6H_5	C_6H_5	H	CO_2Me	CH_3	135	4.20	1.7
						135	2.10	1.0
						135	1.05	0.67
10[c]	C_6H_5	p-$CH_3C_6H_5$	H	CO_2Me	CH_3	135	4.20	1.5
						135	2.10	0.91
						135	1.05	0.59
11[b]	$CH_3C_6H_5$	p-$CH_3C_6H_5$	H	CO_2Me	CH_3	135	4.20	1.3
						135	2.10	0.79
						135	1.05	0.51
12[c]	p-ClC_6H_5	p-ClC_6H_5	H	CO_2Me	CH_3	135	4.20	8.3
						135	2.10	5.1
						135	1.05	3.3
4[b]	CO_2CH_3	H	C_6H_5	H	CH_2CH_3	160	1.38[d]	0.0176
						160	2.76[d]	0.0184
						160	4.14[d]	0.0187

[a] Tripropylamine was the base used in all cases except 4. [b] Crystalline solid. [c] Oil. [d] Triisoamylamine.

the oils showed on the order of 90% of the calculated gas evolution. The crystalline materials showed essentially quantitative gas evolution. The results are summarized in Table I. Sample plots are pictured in Figure 1. Although it must be kept in mind that the decomposition rates of the unpurified starting 2-pyrazolines are of dubious precision,[10] the trends are consistent with those observed with the crystalline starting materials and are probably reliable.

In general, it was found in the 5,5-diaryl series that electron-withdrawing groups caused rate acceleration whereas electron-donating groups caused rate decreases. For example, crystalline compounds (for which the data are most reliable) **5**, **9**, and **11** showed a small but real rate decrease upon substitution of methyl groups on the *para* positions of the aromatic rings and a larger rate enhancement upon substitution of a carboalkoxy group for a hydrogen on the 4 position of the ring.

These effects are suggestive of a negatively charged transition state which is in accord with a rate-determining formation of a 1-pyrazoline as outlined in eq 1. Either k_1 or k_2 could be the rate-determining step since both transition states would have some negative charge.

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + BA^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A'H + B \xrightarrow{k_3} \text{product} \quad (1)$$

AH = 2-pyrazoline
B = tripropylamine
A'H = 1-pyrazoline

This reaction also requires a kinetic expression that is first order in base. This was confirmed by running the decompositions in the presence of varying concentrations of base. In every case, when the base concentration was varied from 0.01 to 0.042 M good linear relationships were observed between the base concentration and the observed pseudo-first-order rate constant.

Typical plots are pictured in Figure 2.[11]

Thus, the data point to the 2-pyrazoline to 1-pyrazoline mechanism for the decomposition of 5,5-diaryl-2-pyrazolines with the rate-determining step the formation of the 1-pyrazoline, although it must be pointed out

(10) The most likely impurities in the oily pyrazolines are unreacted starting olefin, the azine of the diazomethane used to make the 2-pyrazoline, and triethylamine which had not been removed by the evacuation procedure (see the Experimental Section). A sample 0.553 g of pure 5,5-diphenyl-3,4-dicarbomethoxy-2-pyrazoline was therefore mixed with 0.1 g of dimethyl maleate, 0.1 g of benzalazine, 0.1 g of triethylamine, and 0.4 ml of tri-*n*-propylamine. The mixture was evacuated in the normal way and the kinetics of the mixture were examined. The various impurities had no detectable effect on the reaction rate: $k_{obsd} = 1.66 \times 10^{-3}$ in the presence of the impurities; $k_{obsd} = 1.67 \times 10^{-3}$ in the presence of only the tri-*n*-propylamine.

(11) It is interesting that these linear plots did not go through the origin but, instead, when extrapolated to $k_{obsd} = 0$, they almost invariably crossed the base coordinate at about the same point (*ca.* -10^{-2} M). This phenomenon suggests an effective increase in base concentration and is probably due simply to adsorbed base on the surface of the reaction vessel. The consistency in the intercept of the k_{obsd} *vs.* base plots most likely resulted from the fact that the reaction vessel was cleaned the same way after each run, thus leaving the surface about the same for each new run. These effects were not recognized when the work was underway and have not been thoroughly studied.

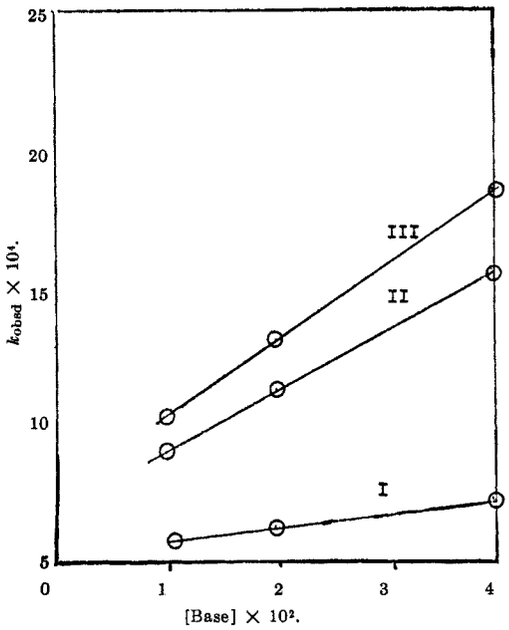


Figure 2.—Representative plots of k_{obsd} *vs.* [tri-*n*-propylamine]: I, 5-phenyl-5-(4-methylphenyl)-3-carbomethoxy-2-pyrazoline; II, 5,5-(4,4′-dimethyldiphenyl)-3,4-dicarbomethoxy-2-pyrazoline; III, 5,5-(4,4′-dichlorodiphenyl)-3-carbomethoxy-2-pyrazoline.

that the data do not exclude the possibility that nitrogen is lost directly from an intermediate anion.

We then turned our attention to the second possible explanation for the rather extreme difference in rates of decomposition of the 5,5-diaryl and 5-carboalkoxy systems: the possibility that, in solution, the 5-carboalkoxy system also decomposes *via* the 1-pyrazoline but, in contrast to the melt and the 5,5-diaryl system, with slow loss of nitrogen from the intermediate. This possibility was approached in two ways. In the first, a study similar to that published for the melt decompositions was carried out. Each of the pure pyrazolines (**3** and **4**) was allowed to decompose in decalin at 150° in the presence of triisoamylamine until about one-half of the calculated nitrogen had been evolved, and the undecomposed starting 2-pyrazoline was then examined for ester scrambling. This was finally accomplished by acylating the crude reaction mixture with acetic anhydride in the presence of a trace of acid (the ester groups were not scrambled by these conditions) and analyzing the resulting N-acylpyrazolines by infrared. It was found that each pyrazoline gave the same mixture of acylpyrazolines. This indicated complete scrambling of the ester groups and suggests a reaction involving initial formation of the 1-pyrazoline followed by a slow decomposition to give the products. This conclusion was supported by studying the effect of base on the rate of the reaction (Table I). As predicted, it was found that the rate of reaction was independent of the concentration of base.

Thus, the difference in rates of decomposition of 5,5-diaryl-2-pyrazolines and 3,5-dicarboalkoxy-2-pyrazolines apparently results simply from a difference in rate-determining step. The apparent incongruity arising from the comparison of the decomposition of the 3,5-dicarboalkoxy-2-pyrazolines in the melt and in basic solution is probably no more than a reflection of the fact that in the melt the base (most likely simply a second molecule of pyrazoline) would be considerably weaker than a tertiary amine. The weaker base would retard reversal of the first step of the reaction (1-pyrazoline returning to 2-pyrazoline) without seriously affecting the rate of loss of nitrogen from the 1-pyrazoline. This could easily change the rate-determining step.

Experimental Section

All analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The melting points were taken in capillary tubes in a Thomas–Hoover melting poing apparatus and were uncorrected. The infrared spectra were run on a Perkin-Elmer Model 137B Infracord Spectrophotometer and the ultraviolet spectra were run on a Cary Model 14 spectrophotometer.

5,5-Diaryl-2-pyrazolines.—The 5,5-diaryl-2-pyrazolines were all prepared in essentially the same way by the method that has been described by Jones, Glenn, and Baarda.[12] In all preparations, an erlenmeyer flask of appropriate size was first soaked in a saturated solution of trisodium phosphate for several days and then rinsed with distilled water. To this was added 100 ml of technical grade pentane. The solvent was cooled in ice and 5.71 g (0.064 mole) of triethylamine, 5.5 g (0.064 mole) of methyl acrylate (or 8.1 g of dimethyl maleate for the 3,4-dicarbomethoxy-2-pyrazolines), and 0.064 mole of the appropriate diphenyldiazomethane were added in that order. The mixture was stirred until it was homogeneous and then placed in the refrigerator overnight or until the red color of the diazomethane had discharged. In some cases, a colorless precipitate formed which could simply be removed and purified by recrystallization, (Table II). In those cases that did not give crystalline products, the solvent and triethylamine were removed from the decolorized solution by first stripping the solvent on a Rotovac followed by evacuation with an efficient pump. The oils were stored under nitrogen until they were used for the kinetic studies. The presence of the 2-pyrazolines in the oils was indicated by the infrared and ultraviolet spectra (Table II), conversion to the crystalline N-acetyl derivatives which were characterized and, finally, from isolation of the cyclopropane product arising from their decompositions (Table III).

In all cases, the amount of gas evolved during the kinetic studies indicated the presence of 85–95% of the desired pyrazoline.

Preparation of the Acetyl Derivatives of 3, 4, 6–8, and 10–12.—The solid or oil (about 0.5 g) isolated from the preparation of the above compounds was dissolved in 5 ml of acetic anhydride and three drops of concentrated sulfuric acid was added. The solution was heated for a short time on a steam bath, cooled, and poured into cold 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 the crude solid acetyl derivatives which were then recrystallized from methanol (see Table IV).

The melting points and analyses are summarized in Table II.

3,5-Dicarboalkoxy-4-phenyl-2-pyrazolines.—The two dicarboalkoxy-4-phenyl-2-pyrazolines were prepared by the method of Buchner and von der Heide.[13] In a typical experiment, 50 g (0.50 mole) of methyldiazoacetate was added to 81 g (0.46 mole) of ethyl cinnamate. To this mixture was added a pinch of hydroquinone and the mixture was heated on a steam cone for 28 hr. The mixture was then poured into a crystallizing dish, a small amount of ether was added, and the mixture was vigorously scratched with a stirring rod. Crystallization took place rapidly giving an oily yellow solid which was filtered and recrystallized from hot methanol to give 83 g (65%) of white crystals, mp 105–107° (lit.[13] mp 107°). The structure of both of the isomeric 2-pyrazolines has been previously established.[14]

Kinetic Studies.—The kinetic studies were carried out in a cylindrical vessel 19.5 cm tall and 4.0 cm in diameter. 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 extend well below the surface of a 50-ml sample of solvent. A nitrogen exit tube

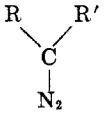
(12) W. M. Jones, T. Glenn, and D. G. Baarda, *J. Org. Chem.*, **28**, 2887 (1963).

(13) See Büchner and von der Heide in footnote *a* of Table II.

(14) W. S. Brey, Jr., and W. M. Jones, *J. Org. Chem.*, **26**, 1912 (1961).

TABLE II

3-CARBOMETHOXY-2-PYRAZOLINES AND ANALYSES OF N-ACYL DERIVATIVES

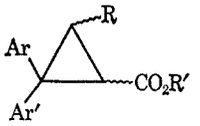


Compd	R	R′	Acceptor olefin	Mp of product, °C	Carbonyl absorptions, μ	Long wavelength max, mμ (ε)	N-Acetyl deriv, mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % Cl	Found, % C	Found, % H	Found, % N	Found, % Cl
3	H	$C_2H_5O_2C$	Methyl cinnamate	74–76[a]	5.78, 5.95	288 (1.30 × 10⁴)[b]	Oil	60.37	5.70	8.80		60.19	5.75	8.7	
4	H	CH_3O_2C	Ethyl cinnamate	105–107[a]	5.79, 5.95	288 (1.44 × 10⁴)[b]	105–108	60.37	5.70	8.80		60.20	5.71	8.9	
5	C_6H_5	C_6H_5	Methyl acrylate	138–140[a] dec	5.88	297 (1.16 × 10⁴)[c]									
6	C_6H_5	*p*-Tolyl	Methyl acrylate	Oil	5.90	292[b,d]	138–140	71.41	5.99	8.33		71.48	5.78	8.4	
7	*p*-Tolyl	*p*-Tolyl	Methyl acrylate	Oil	5.89	298[b,d]	152–153.5	71.98	6.33	8.00		72.01	6.44	8.1	
8	*p*-Cl-C_6H_4	*p*-ClC_6H_4	Methyl acrylate	Oil	5.89	297[b,d]	183–185	58.33	4.12			58.53	4.38		
9	C_6H_5	C_6H_5	Dimethyl fumarate	141–142[a] dec	5.70, 5.88	298 (1.05 × 10⁴)[d]									
10	C_6H_5	*p*-Tolyl	Dimethyl fumarate	Oil	5.85, broad	295[b,d]	132–134	66.99	5.62	7.10		66.81	5.60	7.0	
11	*p*-Tolyl	*p*-Tolyl	Dimethyl fumarate	50–52 dec	5.73, 5.89	298 (1.42 × 10⁴)[c]	143–145	67.23	5.92	7.86		67.50	6.01	6.9	
12	*p*-Cl-C_6H_4	*p*-ClC_6H_4	Dimethyl fumarate	Oil	5.79, 5.88	298[b,d]	174–175.5	56.14	4.04	6.24	5.78	56.22	4.17	6.1	15.8

[a] Lit. mp for **3**, 76°, and **4**, 107° [E. Büchner and C. von der Heide, *Ber.*, **35**, 31 (1902)]; **5**, 138–139° (ref 12); **9**, 142° [C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949)]. [b] Minimum extinction coefficient; assumes oil is pure 2-pyrazoline. [c] Solvent 2-propanol. [d] Solvent methanol.

TABLE III

2,2-DIARYLCYCLOPROPANECARBOXYLIC ACIDS AND ESTERS



Ar	Ar′	R	R′	Registry no.	Mp, °C	Lit. mp, °C	Recrystn solvent	Calcd, % C	Calcd, % H	Calcd, % Cl	Found, % C	Found, % H	Found, % Cl
C_6H_5	C_6H_5	H	H		170–172	169–171[a]	Ether–pentane						
C_6H_5	C_6H_5	CO_2CH_3	CH_3		174–176	174–174.5[b]	Methanol						
C_6H_5	*p*-$CH_3C_6H_4$	H	H		144–152[c]	145–153[d]	Ether–pentane						
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	H	H	10036-84-7	153–154.5		Ether–pentane	81.17	6.81		81.16	6.93	
p-ClC_6H_4	*p*-ClC_6H_4	H	H	10036-84-7	171–172	170.5–171[e]	Ether–pentane	62.56	3.94	23.09	62.47	4.07	23.20
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	CO_2CH_3	CH_3	10036-85-8	142.5–144.5		Methanol	74.54	6.55		74.49	6.57	
C_6H_5	*p*-$CH_3C_6H_4$	CO_2CH_3	CH_3	10036-86-9	134–136		Methanol	74.06	6.22		73.90	6.20	
p-ClC_6H_4	*p*-ClC_6H_4	CO_2CH_3	CH_3	10036-87-0	151–153		Methanol	60.18	4.25		59.98	4.05	

[a] H. M. Walborsky and F. M. Homyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955). [b] W. M. Jones, *ibid.*, **81**, 3776 (1959). [c] Probably a mixture of *cis–trans* isomers. [d] D. G. Baarda, Ph.D. Thesis, University of Florida, 1962. [e] H. Hamada and A. Okamoto, *Botyu-Kagaku*, **18**, 70 (1953).

TABLE IV

Compd	Infrared, cm^{-1}	Ultraviolet λ_{max}, mμ	ε (2-propanol)
3	5.70, 5.8, 5.92, 11.4	275	1.66 × 10⁴
4	5.70, 5.80, 5.90, 12.6	276	1.63 × 10⁴
6	5.80, 5.92, 6.29	274	1.34 × 10⁴
7	5.82, 5.91, 6.29	279	1.25 × 10⁴
8	5.74, 5.99, 6.29	277	1.74 × 10⁴
10	5.76, 5.81, 5.91, 6.32	278	1.26 × 10⁴
11	5.70, 5.83, 5.92, 6.29	281	1.27 × 10⁴
12	5.76, 5.81, 5.91, 6.29	266	1.74 10⁴

at the top of the vessel was connected with tygon tubing to a mercury-filled buret and vacuum pump *via* a three-way stopcock. Samples were introduced by releasing a hinged, glass plate with an external magnet. Solid samples were introduced as weighed, pressed pellets. Oils were introduced in small glass trays. A constant-temperature bath containing GE SR 1017 silicone oil was used. The temperature was held constant (±0.01°) with a Sargent Model S Thermonitor. In a typical run, 50 ml of hexadecane, which had been previously distilled and stored over Linde 3A Molecular Sieves, and a predetermined volume of the amine, which had been distilled (middle cut) and stored over Linde 3A Molecular Sieves, were introduced into the reaction vessel. The system was then thoroughly purged with Linde prepurified nitrogen that was further purified by passing through a series of wash bottles containing Fiesher's solution,[15] lead acetate, concentrated sulfuric acid, and the sodium ketyl of benzophenone in xylene and paraffin oil. The purging precedure which consisted of bubbling the gas through the stirred solvent for 30–45 min followed by evacuation and bleeding in pure nitrogen was independently shown to have no detectable effect on the concentration of the base. The nitrogen flow was then stopped and the reaction vessel was immersed in the constant-temperature bath and allowed to equilibrate. The sample was then introduced by releasing the trap door. The time required for complete solution did not exceed 30 sec. The procedure of Overberger[16] was used for solid samples in which V_∞ was taken as the calculated volume of nitrogen converted to the temperature and pressure of the collecting buret and 0 time was taken as the time of introduction of the sample. This procedure was checked and found to be quite accurate. For runs made with the oils, the actural observed t_∞ volume reading was taken as V_∞.

Product Isolation from Kinetic Runs.—The solvent was removed from each spent kinetic reaction mixture by reduced-pressure distillation. In some cases a solid product was obtained at this point and was simply recrystallized from methanol and characterized either by comparison with known cyclopropanes or by routine methods. Results are summarized in Table III. In those instances where solids were not obtained at this point,

(15) L. F. Fieser, *J. Am. Chem. Soc.*, **46**, 2639 (1924).

(16) See Overberger, *et al.*, in footnote *a* of Table II.

the ester residue was hydrolyzed with methanolic potassium hydroxide and the resulting carboxylic acid was characterized. Properties of the acid are summarized in Table III. In all cases involving 5,5-diarylsubstituted pyrazolines nearly quantitative yields of cyclopropanes were obtained.

Partial Decomposition of 3 and 4.—A sample of each pure 2-pyrazoline (≈0.6 g) 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 about 50% of the calculated amount of nitrogen had been evolved. The solution was then removed from the bath and allowed to cool. Five milliliters 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 was worked up in the usual manner. This work-up gave a pale yellow oil. The infrared spectrum (plates) of this oil gave peaks at 5.78, 5.80, 5.95, 11.4, and 12.6 μ, and was virtually identical with the spectrum of an authentic mixture of the two acetyl derivatives.

The infrared spectrum of the decalin solution remaining showed a single carbonyl peak indicating the possible presence of cyclopropane products.

Removal of the decalin under reduced pressure gave an oil which was hydrolyzed with alcoholic potassium hydroxide at room temperature. Following acidification and reaction of the product with diazomethane, a colorless oil was obtained. The infrared spectrum of this oil was virtually superimposable on the spectrum of a known mixture of *cis*- and *trans*-3-phenyl-1,2-dicarbomethoxycyclopropane.

Registry No.—**3**, 10036-65-4; N-acetyl derivative of **3**, 10036-66-5; **4**, 10036-67-6; N-acetyl derivative of **4**, 10036-68-7; **6**, 10036-69-8; N-acetyl derivative of **6**, 10036-70-1; **7**, 10036-71-2; N-acetyl derivative of **7**, 10036-72-3; **8**, 10036-73-4; N-acetyl derivative of **8**, 10036-74-5; **10**, 10036-75-6; N-acetyl derivative of **10**, 10036-76-7; **11**, 10036-77-8; N-acetyl derivative of **11**, 10036-78-9; **12**, 10036-79-0; N-acetyl derivative of **12**, 10036-80-3; **5**, 10036-81-4; **9**, 10036-82-5.

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Bicyclo[3.3.1]nonanes. II. Synthesis and Reactions of Simple Derivatives

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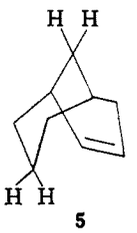
The preparation of numerous bicyclo[3.3.1]nonane derivatives from available starting materials is described. Conversion of 2-N-morpholinobicyclo[3.3.1]nonan-9-one (**2**) to 2-N-morpholinobicyclo[3.3.1]nonane (**3**) and reaction of the latter with hydrogen peroxide gave the N-oxide **4** which on pyrolysis produced bicyclo[3.3.1]non-2-ene (**5**) in good over-all yield. Hydroboration of **5** gave a 2:3 mixture of *exo*-bicyclo[3.3.1]nonan-2-ol (**6**) and *exo*-bicyclo[3.3.1]nonan-3-ol (**7**). Oxidation of **7** produced bicyclo[3.3.1]nonan-3-one (**8**) which on reduction yielded *endo*-bicyclo[3.3.1]nonan-3-ol (**9**). Oxidation of **5** with selenium dioxide gave *exo*-bicyclo[3.3.1]non-3-en-2-ol (**10**), which could be further oxidized with manganese dioxide to bicyclo[3.3.1]non-3-en-2-one (**11**). Reduction of **11** with sodium borohydride produced *endo*-bicyclo[3.3.1]non-3-en-2-ol (**12**); catalytic hydrogenation of **11** gave bicyclo[3.3.1]nonan-2-one (**13**). Ketone **13** could also be synthesized from β-(3-carboxycyclohexyl)-propionic acid (**20**) by pyrolysis of the barium salt or through a Dieckmann condensation of the corresponding diethyl ester.

Although the bicyclo[3.3.1]nonane structure is a potentially interesting framework for the investigation of structure–reactivity relationships, a detailed study of the chemistry of the system has not yet been reported due, in part, to the relative inaccessibility of suitable simple derivatives. As a prelude to a study of the solvolytic reactivity of certain bicyclo[3.3.1]nonane derivatives, we have investigated several synthetic approaches to the parent system and have developed two practical routes which are versatile and adaptable to the synthesis of large quantities of these compounds.

In 1956, Stork and Landesman[2] reported that a high yield of 2-N-pyrrolidinobicyclo[3.3.1]nonan-9-one (**1**) resulted from the reaction of the pyrrolidine enamine of cyclohexanone with acrolein. The ease of formation of the bridged bicyclic compound made it an attractive starting material for the synthesis of other bicyclo[3.3.1]nonane derivatives. Chart I outlines the synthetic routes which we have used to prepare numerous derivatives from the morpholine analog (**2**) of **1**.

Reduction of **2** by the Wolff–Kishner method gave 2-N-morpholinobicyclo[3.3.1]nonane (**3**) in 74% yield. Oxidation of **3** with hydrogen peroxide and pyrolysis of the resulting amine oxide **4** produced bicyclo[3.3.1]-non-2-ene (**5**) in an over-all yield of 51%. Hydroboration of **5** using the procedure of Brown and Subba Rao[3] gave a 3:2 ratio of two isomeric alcohols. These alcohols were separated chromatographically, and the minor component was shown to be the known *exo*-bicyclo[3.3.1]nonan-2-ol (**6**).[4]



5

The major alcohol formed on hydroboration of **5** was identified as *exo*-bicyclo[3.3.1]nonan-3-ol (**7**) (Figure 1) on the basis of its infrared and nuclear magnetic resonance (nmr) spectra and its subsequent reactions. The nmr spectrum of **7** showed a nine-line pattern (A_2B_2X system) centered at τ 5.77 for the carbinyl proton at C-3; the coupling constants were 11.3 and 5.9 cps. These features are characteristic of an axial proton in a rigid cyclohexane ring.[5] Oxidation of **7** gave bicyclo[3.3.1]nonan-3-one (**8**) in good yield. Re-

(1) For the first paper in this series, see J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).

(2) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

(3) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956); *ibid.*, **81**, 6428 (1959).

(4) A. C. Cope, D. L. Nealy, P. Scheiner, and G. Wood, *ibid.*, **87**, 3130 (1965).

(5) F. A. L. Anet, *ibid.*, **84**, 1053 (1962).