residual yellow oil was chromatographed on 50 g. of alumina. This led to 90 mg. of IVa, m.p. and m.m.p. 145–146° on crystallization from petroleum ether, and 14 mg. of IIa, m.p. and m.m.p. 150–152° on crystallization from the same solvent.

A similar reduction of 210 mg. of Ib with 837 mg. of hydride yielded 58 mg. of IVb, m.p. and m.m.p. 144–146° on crystallization from petroleum ether.

The infrared and p.m.r. spectral properties of all products were identical with those of samples described above.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Stereochemistry of the Formation and Decomposition of 1-Pyrazolines[1]

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Thermal decomposition of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**) proceeds with loss of geometry to give, in addition to unsaturated products, both 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) and 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**). Light-induced decomposition of the same 1-pyrazoline results in stereospecific formation in high yield of 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**), together with some methyl tiglate. Formation of the latter compound arises from a formal reversal of the addition of diazomethane to an unsaturated ester. 3-Carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) behaves analogously to pyrazoline (**7**).

Addition of diazomethane to double bonds activated by a suitable electron-withdrawing group, followed by thermal decomposition of the resulting pyrazolines, is an established route to cyclopropanes,[3-5] although the synthetic utility of the method is hampered by extensive formation of unsaturated compounds in the pyrolysis step.[3-13] von Auwers and König studied the stereochemistry of the preparation of cyclopropanes by this method, and concluded that when the intermediate pyrazolines are 1-pyrazolines, the cyclopropanes formed retain the geometry of the initial olefins.[14,15] Recent studies have focused on the more complex problem of the stereochemistry of cyclopropane formation in cases where the intermediate pyrazoline is a conjugated 2-pyrazoline.[16-18] The explanation advanced for the results of these studies is based on the assumption that 1-pyrazolines indeed decompose with retention of geometry, as reported by von Auwers and König.[15] However, major errors in the analytical results of von Auwers and König in other cases have been demonstrated,[8,9] so re-investigation of their results with presently available analytical tools probably is advisable.

Stereochemistry of 1-Pyrazoline Formation.—Formation of 1-pyrazolines by the addition of diazomethane to double bonds "activated" by electron-withdrawing groups is often described as a *cis* addition,[3-5] but only one study of this point has been made.[14] In this study the stereochemistry of the reaction was examined by the addition of diazomethane to pairs of isomeric α,β-unsaturated esters. The first pair, dimethyl citraconate and dimethyl mesaconate, on treatment with diazomethane gave two liquid 1-pyrazolines, presumably *cis*-3,4-dicarbomethoxy-3-methyl-1-pyrazoline (**1a**) and *trans*-3,4-dicarbomethoxy-3-methyl-1-pyrazoline (**2a**), respectively. These pyrazolines had identical physical constants,[14] but they were reported to give different products on pyrolysis.[15] 3,4-Dicarbomethoxy-4-methyl-2-pyrazoline (**3**) was obtained from both esters.[14] In the case of the other ester pair, treatment of dimethyl dimethylmaleate with diazomethane gave a low-melting 1-pyrazoline, supposedly *cis*-3,4-dicarbomethoxy-3,4-dimethyl-1-pyrazoline (**4**), while dimethyl dimethylfumarate and diazomethane yielded a liquid 1-pyrazoline reported to be *trans*-3,4-dicarbomethoxy-3,4-dimethyl-1-pyrazoline (**5**). Steric structures were not determined experimentally; *cis* addition was assumed because stereospecific *trans* addition could not be envisioned. No examination of the degree of stereospecificity was made. Similarly, addition of diphenyldiazomethane to dimethyl citraconate[19] and to dimethyl mesaconate[19,20] has also been reported to produce different pyrazolines (**1b** and **2b**).

In the present work addition of diazomethane to methyl angelate and to methyl tiglate produced 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) and 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**), respectively. These were shown to be different by their n.m.r. spectra (Fig. 1), and by

(1) (a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., Sept. 11–16, 1960; *cf.* Abstracts of Papers, p. 96 P. (b) Portions of the present work dealing with the formation and photolysis of pyrazolines have appeared as a brief communication [K. L. Rinehart, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960)]. (c) The earliest brief description of the present results including pyrolyses is that of D. Wedegaertner, University of Illinois Organic Seminar Abstracts, Summer Session (June 22), 1960, p. 1.

(2) (a) Lubrizol Fellow, 1959–1960; National Science Foundation Predoctoral Fellow, 1960–1961. (b) Alfred P. Sloan Foundation Fellow.

(3) T. L. Jacobs, in R. Elderfield, ed., "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 45 ff.

(4) B. Eistert, in "Neuere Methoden der Präparativen Organischen Chemie," Zweite Unveränderte Auflage, Verlag Chemie, Berlin, 1945, pp. 388–392.

(5) A. N. Kost and V. V. Ershov, *Uspekhi Khim.*, **27**, 431 (1958).

(6) D. E. Applequist and D. E. McGreer, *J. Am. Chem. Soc.*, **82**, 1965 (1960).

(7) K.-D. Grundmann and R. Thomas, *Ber.*, **93**, 883 (1960).

(8) D. E. McGreer, *J. Org. Chem.*, **25**, 852 (1960).

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

(10) G. Nominé and D. Bertin, *Bull. soc. chim. France*, 550 (1960).

(11) R. F. Rekker, J. P. Brombacher and W. Th. Nauta, *Rec. trav. chim.*, **73**, 417 (1954).

(12) H. L. Slates and N. L. Wendler, *J. Am. Chem. Soc.*, **81**, 5472 (1959).

(13) E. N. Trachtenberg and G. Odian, *ibid.*, **80**, 4015 (1958).

(14) K. von Auwers and F. König, *Ann.*, **496**, 27 (1932).

(15) K. von Auwers and F. König, *ibid.*, **496**, 252 (1932).

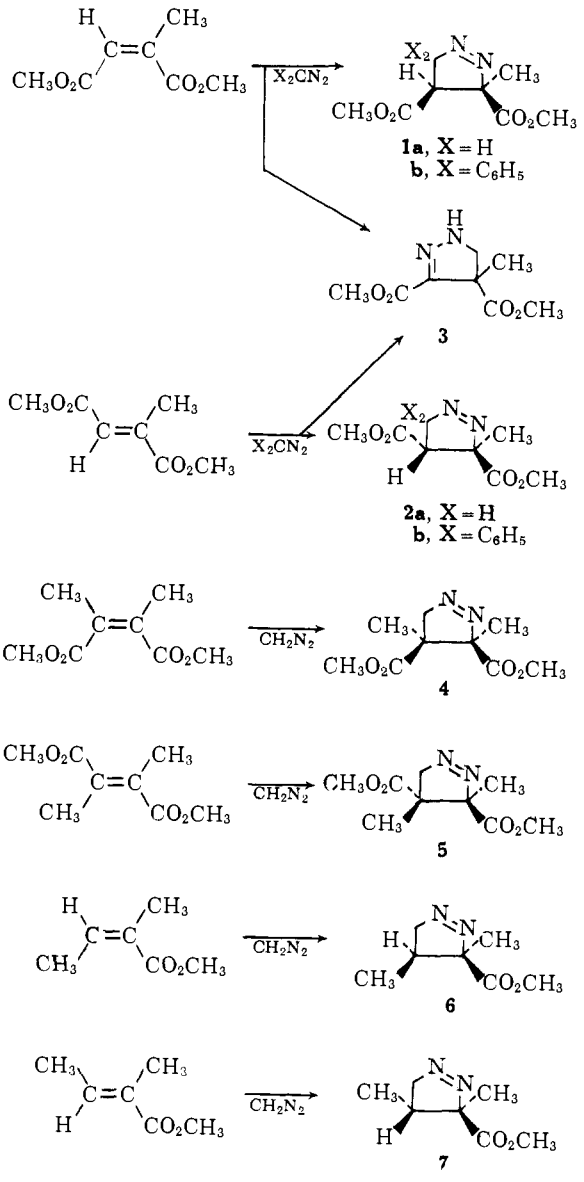
(16) W. M. Jones, *J. Am. Chem. Soc.*, **80**, 6687 (1958).

(17) W. M. Jones, *ibid.*, **81**, 5153 (1959).

(18) W. M. Jones, *ibid.*, **82**, 3136 (1960).

(19) W. M. Jones and W.-T. Tai, *J. Org. Chem.*, **27**, 1030 (1962).

(20) J. van Alphen, *Rec. trav. chim.*, **62**, 334 (1942).



1a, X = H
b, X = C_6H_5

3

2a, X = H
b, X = C_6H_5

4

5

6

7

their infrared spectra, which had bands at 1737 and 1734 cm.$^{-1}$, respectively, due to saturated ester carbonyl,[21] and at 1545 and 1540 cm.$^{-1}$, respectively, due to N=N.[9,22-25] The infrared spectra resemble one another in other respects, but they are clearly due to different compounds.[26] That neither pyrazoline **6** nor **7** is a 2-pyrazoline is shown by the lack of N–H stretch in the infrared spectra, and by the ultraviolet spectra, which showed λ_{max} 322 mμ (ϵ 212) in each case,[27] and by

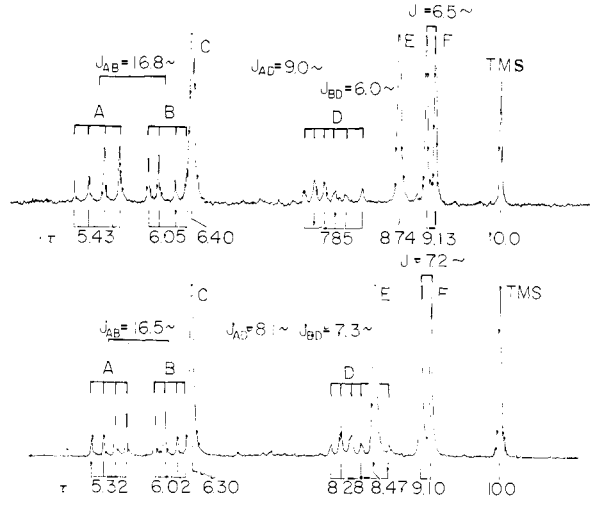


Fig. 1.—N.m.r. spectra of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**) (top) and 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) (bottom) in carbon tetrachloride at 60 Mc.

the incompatibility of the n.m.r. spectra with such structures. That neither pyrazoline **6** nor **7** is a 4-carbomethoxy-3,4-dimethyl-1-pyrazoline, which would result from the unexpected α-addition[28] of diazomethane is also shown by the n.m.r. spectra. α-Addition has been observed in the addition of diphenyldiazomethane to nitroölefins,[29,30] and in the addition of diazomethane to vinyl butyl ether.[31] In the n.m.r. spectrum of either pyrazoline **6** or **7** (Fig. 1) the two four-peak groups, A and B, are due to the C-5 hydrogen atoms, which split one another, and are also split by the C-4 hydrogen atom to give a typical[32,33a] ABX spectrum. The sharp peak C is due to the ester methyl group, while the complex multiplet D results from the C-4 hydrogen atom, which is split by the two C-5 hydrogen atoms and also by the C-4 methyl group. The sharp singlet E is due to the unsplit C-3 methyl group, and the doublet F is due to the C-4 methyl group, split by the C-4 hydrogen atom. The values observed for the coupling constants between the C-5 hydrogen atom and the C-4 hydrogen atom are reasonable[33b] for the assignments made.

The assignments of geometry to pyrazolines **6** and **7** are based on the n.m.r. spectra, and on the results of the light-induced decompositions, which are discussed later. The C-4 hydrogen atom of

(21) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 179.

(22) G. P. Mueller and B. Riegel, *J. Am. Chem. Soc.*, **76**, 3686 (1954).

(23) J. A. Moore, *J. Org. Chem.*, **20**, 1607 (1955).

(24) R. Wiechert and E. Kaspar, *Ber.*, **93**, 1710 (1960).

(25) J. A. Moore, W. F. Holton and E. L. Wittle, *J. Am. Chem. Soc.*, **84**, 390 (1962).

(26) These spectra may be seen in the Ph.D. thesis submitted by T. V. Van Auken to the University of Illinois, available from University Microfilms.

(27) (a) Ultraviolet spectra of only three other 1-pyrazolines have been reported. These had λ_{max} at 320 mμ[11] and at 329 mμ.[23,25b] Azomethane has λ_{max} at 340 mμ [H. C. Ramsperger, *J. Am. Chem. Soc.*, **50**, 123 (1928)]; (b) C. G. Overberger and J.-P. Anselme, *ibid.*, **84**, 869 (1962).

(28) The term "α-addition" is used to indicate addition of diazomethane in such a manner that the new carbon–carbon bond forms at the α-carbon of the unsaturated compound, while β-addition indicates addition in the reverse manner. β-Addition is usually observed [see R. J. Landborg, Ph.D. Thesis, State University of Iowa, 1960].

(29) W. E. Parham, C. Serres and P. R. O'Connor, *J. Am. Chem. Soc.*, **80**, 588 (1958).

(30) W. E. Parham, H. G. Braxton, Jr., and P. R. O'Connor, *J. Org. Chem.*, **26**, 1805 (1961).

(31) I. A. D'yakonov, *Zhur. Obshchei Khim.*, **17**, 67 (1947); *cf. C. A.*, **42**, 902h (1948).

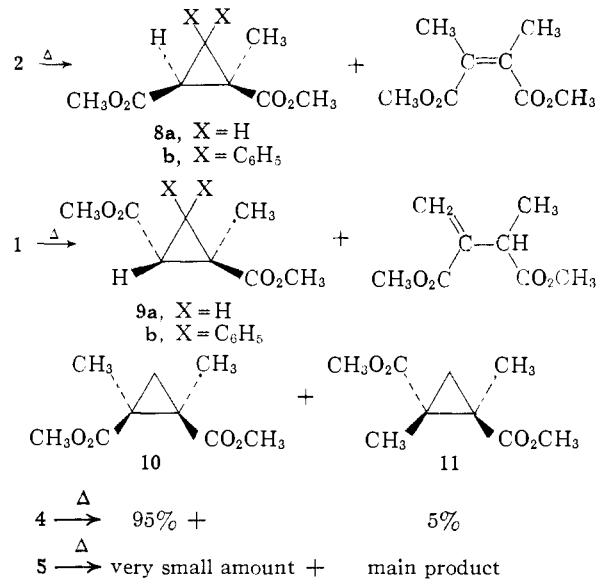
(32) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 132.

(33) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959; (a) p. 90; (b) p. 85.

pyrazoline **7** appears at lower field than does that of pyrazoline **6** because of the unshielding effects of the adjacent *cis*-carbomethoxy group.

The methyl angelate used to prepare pyrazoline **6** was found by gas chromatography to contain 3–4% of methyl tiglate. If addition of diazomethane were a nearly stereospecific process, then pyrazoline **6** would contain about 3% of pyrazoline **7**. The infrared spectrum of pyrazoline **7** shows a band at 1125 cm.$^{-1}$ having ϵ 10.5. (For comparison, the ester carboxyl band of pyrazoline **7** at 1737 cm.$^{-1}$ has ϵ 34.3.) This band is not present in the infrared spectrum of pyrazoline **6**. Calculations indicate that 5% of pyrazoline **7** in pyrazoline **6** should be detectable by means of this band, but since it does not appear at all in the spectrum of pyrazoline **6**, no more than 2% of pyrazoline **7** could have been formed by addition of diazomethane to methyl angelate. Thus the reaction must be at least 98% stereospecific. It is probably completely so. This is in better agreement with the molecular mechanism proposed by Huisgen, Stangl, Sturm and Wagenhofer for this reaction,[34] than with an ionic mechanism.[4,35]

Thermal Decomposition of 1-Pyrazolines.—The formation of cyclopropanes by the thermal decomposition of 1-pyrazolines has been generally accepted as a stereospecific reaction proceeding with retention of geometry,[3,4,16–18] and has been mentioned as having "been clearly shown to occur stereospecifically."[18] Nevertheless, like the formation of 1-pyrazolines, the stereochemistry of this reaction has been examined in only one study.[15] von Auwers and König reported that on thermal decomposition *trans*-3,4-dicarbomethoxy-3-methyl-1-pyrazoline (**2a**) gave *trans*-1,2-dicarbomethoxy-1-methylcyclopropane (**8a**) as the main product, along with a very small amount of dimethyl β-methylitaconate.[15] Similarly, the isomeric *cis*-3,4-dicarbomethoxy-3-methyl-1-pyrazoline (**1a**) was reported to produce mainly *cis*-1,2-dicarbomethoxy-1-methylcyclopropane (**9a**) and a small amount of dimethyl dimethylmaleate. The results described for the 3,4-dicarbomethoxy-3,4-dimethyl-1-pyrazolines (**4** and **5**) were comparable.[15] Thermal decomposition of the *trans*-pyrazoline **5** was reported to give *trans*-1,2-dicarbomethoxy-1,2-dimethylcyclopropane (**10**) as the main product, along with a small amount of *cis*-1,2-dicarbomethoxy-1,2-dimethylcyclopropane (**11**). In the case of the *cis*-pyrazoline **4** the amounts were reversed, 5% of the *trans*-cyclopropane **10** and 95% of the *cis*-cyclopropane **11** being formed.[36] von Auwers and König also reported that 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**) on pyrolysis formed a mixture consisting of 77% methyl 2,3-dimethyl-2-butenoate (**15**) and 23% 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**).[15] The geometry of cyclopropane **14** was assigned only by analogy with the results just mentioned.



Thermal decomposition of *cis*-pyrazoline **1b** has been reported[19,20] to produce *trans*-cyclopropane **9b**, while *trans*-pyrazoline **2b** has been reported[20] to form the same compound. The structure of compound **9b** was established by a negative bromine test,[19] a negative permanganate test,[20] and failure of the corresponding acid to crystallize,[19] even when seeded with the crystalline acid corresponding to cyclopropane **8b**.[19]

In the present study the mixture formed by thermal decomposition of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) has been shown by gas chromatography to consist of four products—methyl 2,3-dimethyl-3-butenoate (**12**), 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**), 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) and methyl 2,3-dimethyl-2-butenoate (**15**)—in the ratio 0.15:1.22:1.00:1.16. Thermal decomposition of the *cis*-pyrazoline **7** formed the same compounds in the ratio 0.24:0.70:1.00:3.73. Pyrolysis of these pyrazolines, then, in contrast to the results of von Auwers and König, proceeds with loss of geometry, although there is a slight degree of stereoselectivity: 1.22:1.00 in favor of the *trans*-cyclopropane **13** from the *trans*-pyrazoline **6**, and 1.00:0.70 in favor of the *cis*-cyclopropane **14** from the *cis*-pyrazoline **7**. Esters **12**, **13**, **14** and **15** were shown to be stable under the reaction conditions.

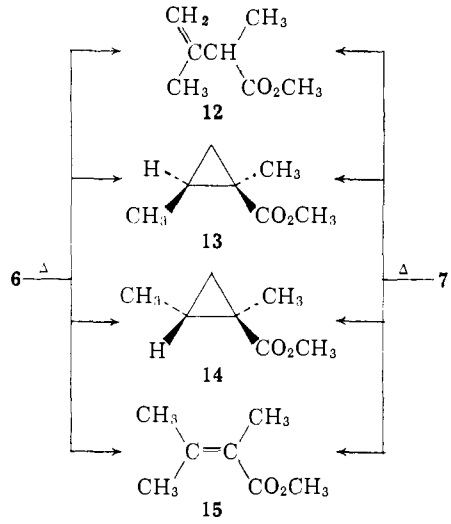
The structures of the unsaturated esters **12** and **15** were established by their infrared and n.m.r. spectra, and by comparison with authentic samples. Ester **12** showed absorption at 1737 (unconjugated ester), 1645 (double bond) and 898 cm.$^{-1}$ (CH_2=). The n.m.r. spectrum of this compound showed peaks at τ[37] 5.21, 6.42, 6.94 (quartet, J = 7 c.p.s.), 8.28 and 8.78 (doublet, J = 7 c.p.s.) due, respectively, to the terminal methylene group, the ester methyl group, the α-hydrogen atom (split by the 2-methyl group), the 3-methyl group and the 2-methyl group (split by the α-hydrogen atom). Ester **15** showed infrared absorption at 1710 (conjugated ester) and 1638 cm.$^{-1}$, and λ_{max} 221 mμ

(34) R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).

(35) W. G. Young, L. J. Andrews, S. L. Lindenbaum and S. J. Cristol, *J. Am. Chem. Soc.*, **66**, 810 (1944).

(36) Preliminary results by the present authors tend to substantiate the results reported by von Auwers and König[15] for the pyrolysis of the 3,4-dicarbomethoxy-3,4-dimethyl-1-pyrazolines.

(37) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).



(ε 8350), which is characteristic of a trisubstituted α,β-unsaturated ester.[38,39] The n.m.r. spectrum showed only three peaks at τ 6.37, 8.00 and 8.19, the last two having an area ratio of 1:2. The peak at τ 6.37 is due to the ester methyl group, while the peak at τ 8.00 results from the 3-methyl group *cis* to the carbomethoxy group. The large peak at τ 8.19 is due to the 2-methyl group and the 3-methyl group *trans* to the carbomethoxy group combined.[40] Authentic samples of esters **12** and **15**, prepared by the Reformatsky reaction of methyl α-bromopropionate with acetone followed by dehydration of the resulting hydroxy ester with phosphorus oxychloride and pyridine, showed identical gas chromatographic retention times, and identical spectral properties with the unsaturated esters obtained from thermal decomposition of pyrazolines **6** and **7**.

Cyclopropanes **13** and **14** were identified by their infrared, ultraviolet and n.m.r. spectra. In the infrared these compounds had carbonyl absorption at 1720 cm.$^{-1}$, but no double bond in the 1700–1600 cm.$^{-1}$ region. In the ultraviolet they had only end absorption. No absorption due to vinyl hydrogen atoms appeared in the n.m.r. spectra (Fig. 2), but in the region of τ 8.7 to 9.8 appeared cyclopropane hydrogen atoms split into a complex pattern and partly obscured by absorption due to methyl groups. That these compounds are different is clearly shown by their different infrared[26] and n.m.r. spectra, and by their different gas chromatographic retention times. Geometric assignments were made on the basis of competitive saponifications in which the less hindered carbomethoxy group of ester **14** was consumed more rapidly than that of ester **13**.[44]

(38) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3331 (1955).
(39) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).
(40) This assignment is preferred rather than the alternative assignment of the τ 8.00 peak to the 2-methyl group, and the τ 8.19 peak to both the 3-methyl groups because the vinyl methyl groups of 3-methyl-2-butenoate appear at τ 7.92 and 8.16,[41] and those of methyl angelate appear at τ 8.02 and 8.11,[41-43] while those of methyl tiglate appear at τ 8.18 and 8.22.[41-43]
(41) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2886 (1960).
(42) R. R. Frazer, *Can. J. Chem.*, **38**, 549 (1960).
(43) K. L. Rinehart, Jr., and T. V. Van Auken, unpublished results.
(44) The geometries of *cis-trans*-acid pairs have been established by their relative rates of esterification.[45,46]

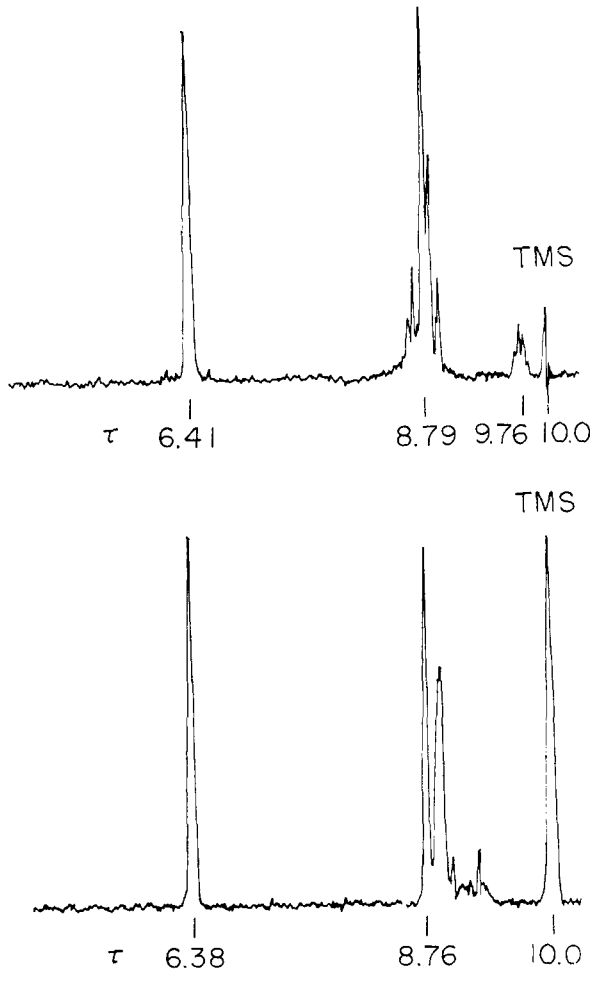
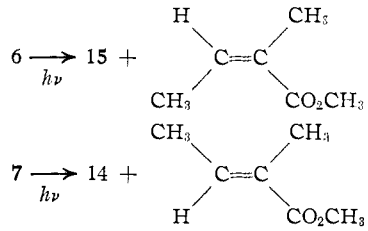


Fig. 2.—N.m.r. spectra of 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) (top) and 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**) (bottom) in carbon tetrachloride at 60 Mc.

In light of our discovery that 1-pyrazolines undergo pyrolysis without stereospecificity, it is perhaps appropriate to examine evidence relating to pyrolyses of 2-pyrazolines and the rule proposed by Jones[16-18] that "the geometrical configuration of the primary cyclopropane resulting from the decomposition of a 2-pyrazoline is determined by the relative thermodynamic stabilities of the intermediate 1-pyrazolines." In propounding this rule and in using it to make configurational assignments for cyclopropanes, it was assumed from the work of von Auwers and König[15] that 1-pyrazolines decompose stereospecifically to cyclopropanes. As the present results demonstrate that pyrolysis of 1-pyrazolines may proceed with loss of geometry, the rule cannot be considered to have general validity. The geometry of the predominant cyclopropane formed may be determined in the transition of the 2-pyrazoline to an intermediate 1-pyrazoline, but it may also be determined in the decomposition of the intermediate 1-pyrazoline. Individual cases thus warrant closer inspection.

(45) J. J. Sudborough and L. L. Lloyd, *J. Chem. Soc.*, **73**, 81 (1898).
(46) J. J. Sudborough and D. J. Roberts, *ibid.*, **87**, 1940 (1905).

Photolysis of 1-Pyrazolines.—Although 2-pyrazolines do not produce cyclopropanes when irradiated with ultraviolet light,[47,48] 1-pyrazolines under these conditions produce cyclopropanes in high yield.[1,48] Significantly, under these conditions decomposition occurs stereospecifically.[1] Irradiation with ultraviolet light of pyrazoline **7** produced principally the corresponding cyclopropane **14** in 63 to 76% yield. The major side



product was identified by its gas chromatographic retention time and infrared spectrum as methyl tiglate, the compound from which pyrazoline **7** was prepared. When pyrazoline **7** itself was injected into the gas chromatograph, pyrolysis took place in the injection port, and the products of thermal decomposition were eluted. No methyl tiglate was observed, so this ester must be a product of the light-induced decomposition rather than an impurity present in the pyrazoline. Small amounts of the isomeric cyclopropane **13** and/or the unsaturated ester **12**,[49] and of the unsaturated ester **15** were also found in the product mixture.[50] These may be due to the presence of a small amount of 4-carbomethoxy-*cis*-4,5-dimethyl-2-pyrazoline (**16**) in the product mixture. Pyrolysis of this 2-pyrazoline in the injection port of the gas chromatograph would result in the same products as the corresponding 1-pyrazoline **7**. The results of several irradiations of pyrazoline **7** are shown in Tables I and II. Light-induced decomposition

TABLE I

PHOTOLYSIS OF 3-CARBOMETHOXY-*cis*-3,4-DIMETHYL 1-PYRAZOLINE (**7**) AS THE NEAT LIQUID

Run	Time, hr.	Temp.,[a] °C.	Yield,[b] %	Product ratios[c,d] 12 + 13	Me Tig	14	15
1	24	..	77	0.1	1.0	4.5	0.2
2	36	25	103	.1	1.0	3.4	.2
3	132	18	106	.2	1.0	3.6	.1
4	42	..	98	.1	1.0	2.7	.3

[a] Temperature of cooling water coming from reactor. [b] Assumes product mixture has the composition $C_7H_{12}O_2$; yields greater than 100% probably indicate presence of undecomposed pyrazoline. [c] Ratio of areas of gas chromatographic peaks without correction for relative thermal conductivities. [d] Me Tig = methyl tiglate; other compounds pictured in text.

of pyrazoline **6**, either as the neat liquid or in a dilute solution of pentane, gave similar results. Cyclopropane **13** was produced in 72% yield by irradiation of pyrazoline **6** as the neat liquid.

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

(48) K. Kocsis, P. D. Ferrini, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960).

(49) The cyclopropyl ester **13** and the unsaturated ester **12** could not be separated on a didecyl phthalate column, which was the most convenient column for analysis of the other compounds in the mixture.

(50) Our previously reported[1b] observation that side products could be completely eliminated by using lower temperatures has not proved reproducible.

TABLE II

PHOTOLYSIS OF 3-CARBOMETHOXY-*cis*-3,4-DIMETHYL-1-PYRAZOLINE (**7**) IN VARIOUS SOLVENTS

Run	Time,[a] hr.	Solvent	ε[b]	g. 7 / g. sol.	Product ratios[c,d] 12 + 13	Me Tig	14	15
1	72	Pentane	1.844	0.0188	0.2	1.0	4.4	0.2
2	120			.159	3.3	1.0	84.0	0.1
3	98	Cyclo-	2.023	.136	..	1.0	3.5	..
4	82	hexane		.0178	..	1.0	3.2	..
5	96			.32	0.1	1.0	3.3	0.1
6	6	Dioxane	2.209	.0619	.1	1.0	3.4	.1
7	136			.0521	.1	1.0	3.6	.1
8	25	Cyclo-	2.220	.329	.2	1.0	3.6	.1
9	80	hexene[e]		.303	.2	1.0	3.7	.1
10	20			.125	.2	1.0	3.9	.2
11	..			.124	.4	1.0	7.3	.3
12	82			.0266	..	1.0	3.3	..
13	45			....	0.4	1.0	9.0	0.6
14	63	Benzene	2.284	.0559	.1	1.0	3.3	.1
15	86	Acetone	20.70	.0821	.4	1.0	5.4	.2
16	148			....	.5	1.0	9.5	.3
17	20	Methanol	32.63	.137	.2	1.0	3.7	.2
18	86	Aceto-						
		nitrile	37.5	.0925	.4	1.0	5.6	.4

[a] Variations in time are due to age and distance of sunlamp. [b] Dielectric constant; from J. A. Riddick and E. E. Toops, Jr., in Weissberger, "Technique of Organic Chemistry," Vol. III, Interscience Publishers, Inc., New York, N.Y., 1955, pp. 48, 52, 72, 86, 90, 126, 136, 224. [c] Ratio of areas of gas chromatographic peaks without correction for relative thermal conductivities. [d] As in Table I. [e] No bicyclo[2.1.0]heptane was observed in the photolyses with cyclohexene.

Methyl angelate, the principal side product, was identified by its gas chromatographic retention time and infrared spectrum.

Irradiation of pyrazoline **7** in a variety of solvents of different polarity (Table II) failed to alter greatly the ratio of cyclopropane to methyl tiglate.

The predominant formation of cyclopropane **14** and methyl tiglate from pyrazoline **7** and of cyclopropane **13** and methyl angelate from pyrazoline **6** supports the structural assignments made for these pyrazolines. If these pyrazolines had the opposite geometries to those assigned, then both the addition of diazomethane to the unsaturated ester and the formation of the photolysis products would have to be stereospecific *trans* processes. This seems very unlikely.

The synthetic value of this method of decomposing 1-pyrazolines has been illustrated recently by the preparation of a number of steroidal cyclopropanes in high yield.[48] Some of these cannot be prepared in reasonable yield by thermal decomposition of the same pyrazolines.[51,52]

Mechanistic Considerations.—Both ionic[4,35] and diradical[5,47,53,54] mechanisms have been proposed earlier for the thermal decomposition of 1-pyrazolines. These proposals were made on the assumption that cyclopropanes are formed with retention of geometry by the reaction, and some modification is necessary in light of the present findings.

The previously proposed[4,35] ionic mechanism shown in Fig. 3 can accommodate our results if

(51) A. Wettstein, *Helv. Chim. Acta*, **27**, 1803 (1944).

(52) A. Sandoval, G. Rosenkranz and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 2383 (1951).

(53) D. E. McGreer, Ph.D. Thesis, Univ. of Illinois, 1959, p. 22.

(54) W. I. Awad, S. M. Abdel, R. Omran and M. Sobhy, *J. Org. Chem.*, **26**, 4126 (1961).

changed slightly. Rotation about the former C-3; C-4 bond must take place in either intermediate **18** or **19** before cyclopropane is formed.[55] The possibility that the pyrazolines themselves isomerize is excluded, since the infrared spectrum of pyrazoline **7**, after partial pyrolysis, showed no bands attributable to pyrazoline **6**. The zwitterion **19** is a resonance form of the singlet diradical **20**, and analogs of both forms lead to the expectation that this species should cyclize immediately. A primary carbonium ion would react vigorously with a carbanion, and geminate radial pairs[56] are known to couple very rapidly.[57] Thus, it does not seem likely that loss of geometry would take place in step c alone,[58] although rotation in a singlet diradical species has been suggested to explain the thermal isomerization of cyclopropane-d_2.[59] Loss of geometry could take place prior to the formation of species **19**, however, by rotation of the diazonium ion **18**. Step b involves the formation of a primary carbonium ion from the corresponding diazonium ion. This has been estimated[60] to have an energy of activation of 3–5 kcal./mole. If the negative charge in the diazonium species **18** is delocalized into the ester group so that C-3 is essentially planar, then rotation about the C-3;C-4 bond might compete with loss of nitrogen. This rotation involves consecutive eclipsed interactions of methyl–carbomethoxy and methylenediazonium–methyl. The barrier to rotation through these conformations should be greater than the 4.4–6.1 kcal./mole estimated[61,62] for the eclipsed methyl–methyl interaction in butane. Thus loss of nitrogen should be slightly favored over rotation, and some degree of stereoselectivity would be expected. Step d offers the possibility of an N type displacement of the diazonium group by backside attack of the C-3 carbanion. This should involve a lower energy of activation than step b, but a considerably higher entropy factor, since exact orientation about the C-4;C-5 bond is required.

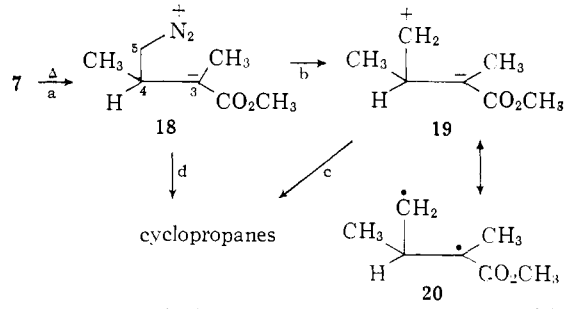
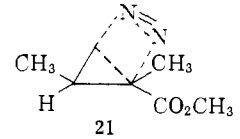


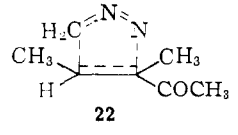
Fig. 3.—Possible ionic mechanism of thermal decomposition.

If the diradical species **20** were in the triplet state, it would not be a resonance form of zwitterion **19**. Intermediates of this type have been suggested to account for the lack of stereospecificity observed in the addition of methylene to olefins in both the vapor phase,[63] and in solution.[64] A diradical species analogous to the diazonium ion **18** might also be considered as a possible intermediate in the thermal decomposition of 1-pyrazolines, but this is unlikely since in azo compounds apparently both carbon–nitrogen bonds break simultaneously.[65]

When larger groups are present, any of these routes would predict an increase in stereoselectivity as a result of more hindered rotation. This was observed by von Auwers and König.[15] Similarly, stereoselectivity should be reduced or lost when the pyrazoline is modified in such a way as to increase the stability, and hence the life-time, of the intermediates involved. This could explain the loss of stereoselectivity observed[16–18,27b] in 2-pyrazolines having phenyl groups in the 3- and 5-positions, if geometry is being lost in the decomposition of the 1-pyrazoline rather than conversion of the 2-pyrazoline to the 1-pyrazoline.

It is of some interest to examine the possible routes of thermal decomposition in view of the much greater stereospecificity of photolytic decomposition. Photolysis would be expected to lead to a higher energy intermediate than pyrolysis, so that an excited singlet might be formed by the former, and a ground-state singlet might be formed by the latter (but not the reverse). However, the stereochemistry observed is contrary to this supposition. An attractive alternative route for the photolysis of 1-pyrazolines involves a molecular mechanism with a transition state such as **21**. Stereospecific regeneration of methyl tiglate and methyl angelate could then be ex-



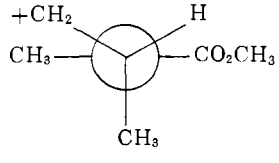


(55) Unsaturated ester formation is not discussed since the principal point under study is the retention or loss of geometry in the cyclopropanes. Unsaturated ester formation by either an ionic route (proton or hydride transfer) or by a radical mechanism does not contribute to this point.

(56) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960).

(57) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 76ff.

(58) If rotation took place partially in species **18**, so that **19** were formed in a conformation such as **19a**, from which ring closure is not possible without further rotation, then completion of loss of geometry might take place in the zwitterion **19**.



19a

(59) (a) B. S. Rabinovitch and D. W. Setser, *J. Am. Chem. Soc.*, **83**, 750 (1961); (b) E. W. Schlag and B. S. Rabinovitch, *ibid.*, **82**, 5996 (1960).

(60) A. Streitwieser and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

(61) K. Ito, *ibid.*, **75**, 2430 (1953).

(62) K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940).

(63) (a) F. A. L. Anet, R. F. W. Bader and A.-M. Vander Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960); (b) R. M. Etter, H. S. Skovronek and P. S. Skell, *ibid.*, **81**, 1008 (1959); (c) H. M. Frey, *ibid.*, **82**, 5947 (1960); (d) D. B. Richardson, M. C. Simmons and I. Dvoretzky, *ibid.*, **82**, 5001 (1960).

(64) K. R. Kopecky, G. S. Hammond and P. A. Leermakers, *ibid.*, **83**, 2397 (1961).

(65) (a) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 3628 (1955); (b) C. G. Overberger and A. V. DiGiulio, *ibid.*, **81**, 2154 (1959); (c) S. Seltzer, *ibid.*, **83**, 2625 (1961).

plained through a similar transition state (**22**). The possibility that these unsaturated esters were formed by loss of the elements of diazomethane as nitrogen and methylene in two steps was also considered. A photolysis of pyrazoline **7** in cyclohexene, designed to trap any methylene formed, gave no bicyclo[2.1.0]heptane, but this is not regarded as definitive.

From the present data and from earlier results of others, no definitive choice can be made among these mechanistic possibilities.

Experimental[66]

3-Carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (6).—A solution of 11 g. (0.26 mole) of diazomethane[68] and 3.3 g. (0.029 mole) of methyl angelate [prepared by the method of Dreiding and Pratt[69]; b.p. 124–127°, n^{25}D 1.4294 (lit.[69] b.p. 124.2°, n^{25}D 1.4303), which was shown by gas chromatography (4-ft. didecyl phthalate column, 110°) to contain 3% methyl tiglate] in 400 ml. of ether was allowed to stand for 4 days. Excess diazomethane was destroyed by addition of formic acid. Then the solution was washed with saturated bicarbonate solution and water, and dried over magnesium sulfate. Removal of solvent under vacuum gave 3.6 g. of crude pyrazoline. Fractionation of this through a Holzman semi-microcolumn[70] gave 2.0 g. (47%) of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**), b.p. 54–55° (0.5 mm.), n^{25}D 1.4509; λ_{max} 235 mμ (ε 72), 233 mμ (ε 213). The compound showed infrared absorption at 1737 (unconj. ester) and 1545 cm.$^{-1}$ (N=N), while no absorption appeared in the 3600–3100 and 1700–1600 cm.$^{-1}$ regions. The n.m.r. spectrum is shown in Fig. 1.

Anal. Calcd. for $C_7H_{12}N_2O_2$: C, 53.82; H, 7.74; N, 17.93. Found: C, 53.89; H, 7.77; N, 17.92.

3-Carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (7).—A solution of 16.8 g. (0.4 mole) of diazomethane[65] and 14.8 g. (0.148 mole) of tiglic acid in 700 ml. of ether was allowed to stand for 5 days. The reaction mixture was worked up in the same manner as for pyrazoline **6**, leaving 22 g. of crude pyrazoline. Distillation through a Holzman semi-microcolumn[70] gave 14.4 g. (62%) of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**), b.p. 72–73° (1.5 mm.), n^{25}D 1.4561 [lit.[14] b.p. 80–82° (2 mm.)]. Redistillation through the same column gave an analytical sample, b.p. 98–101° (11 mm.), n^{25}D 1.4546, λ_{max} 323 mμ (ε 212). The infrared spectrum showed absorption at 1734 (unconj. ester) and 1540 cm.$^{-1}$ (N=N), with no absorption in the 3600–3100 and 1700–1600 cm.$^{-1}$ regions. The n.m.r. spectrum is shown in Fig. 1.

Anal. Found: C, 54.03; H, 7.89; N, 17.73.

Methyl 2,3-Dimethyl-3-butenoate (12) and Methyl 2,3-Dimethyl-2-butenoate (15). A. From the Reformatsky Reaction.—A solution of 150 g. (2.58 moles) of acetone and 95 g. (0.58 mole) of methyl α-bromopropionate, n^{25}D 1.4482 (lit.[71] n^{20}D 1.4463), in 500 g. of dry benzene was added during 1.5 hours to 38 g. (0.58 mole) of zinc in 550 ml. of dry benzene heated at reflux. Heating and stirring were continued for 3 hours. The mixture was cooled, and then stirred for 1 hour with 750 ml. of 12 *N* sulfuric acid. The layers were separated and the aqueous layer was extracted twice with benzene. The original organic layer was washed successively with water, saturated sodium bicarbonate solution, and water, and then dried over magnesium sulfate. Solvent was removed under vacuum. Distillation of the residue through a 3-ft. Podbielniak column[72] gave 30 g. (34%) of the hydroxy ester, n^{25}D 1.4260, which showed infrared bands at 3520 (OH), and 1735 and 1718 cm.$^{-1}$ (carbonyl of hydroxy ester[73]), and gave only one peak on gas chromatography (4-ft. didecyl phthalate and 4-ft. silicone grease columns).

To a solution of 28.6 g. (0.198 mole) of the hydroxy ester in 710 g. of pyridine, cooled to 5°, 155 g. of phosphorus oxychloride was added. The mixture stood for 10 hours, and then was heated on the steam-bath for 4 hours. After cooling the solution was poured into ice and water. The resulting mixture was extracted with hexane, and the hexane extracts were washed with 2 *N* hydrochloric acid and water, and dried over magnesium sulfate. Removal of solvent under vacuum left a residue of 20.2 g., which was shown by gas chromatography (4-ft. didecyl phthalate column) to contain 3.2 g. (13% yield) of methyl 2,3-dimethyl-3-butenoate (**12**) and 11.5 g. (46% yield) of methyl 2,3-dimethyl-2-butenoate (**15**). Analytical samples were obtained by gas chromatography. Methyl 2,3-dimethyl-3-butenoate (**12**) showed infrared absorption at 1737 (saturated ester), 1645 (double bond) and 898 cm.$^{-1}$ (CH_2=), and n.m.r. absorption at τ[37] 5.21, 6.42, 6.94 (quartet, J = 6.9 c.p.s.), 8.28 and 8.78 (doublet, J = 6.9 c.p.s.) (assignments in discussion).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44. Found: C, 65.59; H, 9.43.

Methyl 2,3-dimethyl-2-butenoate (**12**) had n^{25}D 1.4439,[74] λ_{max} 221 mμ (ε 8350), infrared absorption at 1710 (conj. ester) and 1638 cm.$^{-1}$ (double bond), and n.m.r. absorption at τ 6.40, 8.02 and 8.21 (assignments in text).

Anal. Found: C, 65.33; H, 9.49.

B. From Pyrazoline Decompositions.—Methyl 2,3-dimethyl-2-butenoate (**15**), formed in the pyrazoline decompositions described later, was isolated by gas chromatographic collection (4-ft. didecyl phthalate column). It showed infrared, ultraviolet and n.m.r. spectra, and gas chromatographic retention time identical with those of the authentic sample just described.

Methyl 2,3-dimethyl-3-butenoate (**12**), also formed in the pyrazoline decompositions described later, was isolated by gas chromatographic collection (8-ft. silicone grease column). It was identified by an infrared spectrum, and by a gas chromatographic retention time identical with those of the authentic sample decribed previously, and by an n.m.r. spectrum of a mixture of methyl 2,3-dimethyl-3-butenoate (**12**) and 1-carbomethoxy-*trans*-2,3-dimethylcyclopropane (**13**) obtained by gas chromatographic collection (4-ft. didecyl phthalate column). The ultraviolet spectrum of this mixture showed only end absorption.

Identification of 1-Carbomethoxy-*trans*-1,2-dimethylcyclopropane (13) and 1-Carbomethoxy-*cis*-1,2-dimethylcyclopropane (14). A. Isolation.—1-Carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**), obtained from the pyrazoline decomposition mixtures by gas chromatographic collection (8-ft. silicone grease column, 4-ft. didecyl phthalate column), had n^{25}D 1.4289. It showed infrared absorption at 1720 cm.$^{-1}$ (saturated ester) with no bands in the 1700–1600 cm.$^{-1}$ region, and showed only end absorption in the ultraviolet. The n.m.r. spectrum is shown in Fig. 2.

(66) Gas chromatographic analyses were carried out on an F and M Gas Chromatograph, model 202, and on a Perkin-Elmer vapor fractometer, model 154b, using helium as the carrier gas, and firebrick as the liquid phase support. Ultraviolet spectra were measured in 95% ethanol on a Cary recording spectrophotometer, model 14M. Infrared spectra were determined in carbon tetrachloride on a Perkin-Elmer spectrophotometer, model 21B, with sodium chloride optics. N.m.r. spectra were measured in carbon tetrachloride with a Varian high-resolution spectrometer (model V4300B with super stabilizer) at 60 Mc. using tetramethylsilane as an internal standard. Refractive indices are corrected[67] to 25°. We are indebted to Mr. J. Nemeth, Mrs. A. Bay, Mrs. E. J. Corey and Miss J. Liu for the microanalyses, to Mr. J. Chiu and Miss C. Juan for the ultraviolet spectra, and to Mr. O. W. Norton for the n.m.r. spectra, and to Mr. W. O. Dalton, Mr. R. H. Johnson, Mr. D. W. Vittum, Jr., Mr. P. McMahon and Mrs. M. D. Verkade for the infrared spectra.

(67) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 135.

(68) F. Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943); see footnote 3.

(69) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **76**, 1902 (1954).

(70) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(71) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

(72) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

(73) (a) N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Petersen, *J. Am. Chem. Soc.*, **74**, 4070 (1952); (b) S. Searles, M. Tamres and G. M. Barrow, *ibid.*, **75**, 71 (1953); (c) H. B. Henbest, G. D. Meakins and T. I. Wrigley, *J. Chem. Soc.*, 2633 (1958).

(74) A. M. Gakhokidze, *Zhur. Obshchei Khim.*, **17**, 1327 (1947), reported the improbably high n^{25}D 1.4881 for this ester, prepared by an unspecified method.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.57; H, 9.44. Found: C, 65.41; H, 9.47.

1-Carbomethoxy-*trans*-1,2-dimethylcyclopropane, obtained from the pyrazoline decomposition product mixtures by gas chromatographic collection (8-ft. silicone grease column), had $n^{25}D$ 1.4218, showed infrared absorption at 1720 cm.$^{-1}$ (saturated ester) with no bands in the 1700–1600 cm.$^{-1}$ region, and showed only end absorption in the ultraviolet. The n.m.r. spectrum is shown in Fig. 2.

Anal. Found: C, 65.86; H, 9.50.

B. Competitive Saponifications. I.—A solution of *ca.* 100 mg. of a mixture of 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**) and 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) in 2 ml. of absolute methanol was shown by gas chromatography (4-ft. didecyl phthalate column) to contain the two compounds in the ratio 0.77:1.00:**13**:**14**. To this solution 3 ml. of 0.1 *N* aqueous potassium hydroxide was added, and the mixture was heated under reflux for 18 hours. It was then diluted with 50 ml. of water, and extracted repeatedly with ether. The ether extracts were dried, and examined by gas chromatography (2-m. didecyl phthalate column), which showed the compound ratio to be 1.86:1.00:**13**:**14**. After concentration of the ether extracts to about half their original volume, re-examination by gas chromatography (4-ft. didecyl phthalate column) showed the compound ratio to be 1.74:1.00:**13**:**14**.

II.—A solution of 193 mg. of a mixture of methyl 2,3-dimethyl-3-butenoate (**12**), 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**), 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) and methyl 2,3-dimethyl-2-butenoate (**15**) in 1 ml. of methanol was shown by gas chromatography (8-ft. silicone grease column) to contain these compounds in the ratio 0.68:1.90:1.00.1.26. To this solution 4 ml. of 1 *N* potassium hydroxide was added, and the solution was heated under reflux for 18 hours. It was diluted with 50 ml. of water, and extracted repeatedly with ether. The ether extracts were dried, and examined by gas chromatography (8-ft. silicone grease column), which showed the four compounds to be in the ratio 0.18:3.12:1.00:3.26.

III. **Control.**—A solution of 0.2 ml. of a mixture of the four compounds used in run II above in 4 ml. of absolute methanol was shown by gas chromatography (4-ft. silicone grease column) to contain these compounds in the ratio 0.45:1.91:1.00:1.57:**12**:**13**:**14**:**15**. This solution was poured into 50 ml. of water, and the mixture was extracted repeatedly with ether. The ether extracts were dried and re-examined by gas chromatography (4-ft. silicone grease column), which showed the compounds to be in the ratio 0.38:1.94:1.00:1.35:**12**:**13**:**14**:**15**.

Thermal Decomposition of 3-Carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (7).—Heating of 0.815 g. of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline at 155–165° for 148 hours under nitrogen gave 0.557 g. (83%) of a mixture of esters. The infrared spectrum of this mixture showed that no pyrazoline remained. Gas chromatographic analysis (8-ft. silicone grease column) showed it to consist of esters **12**, **13**, **14** and **15** in the ratio 0.24:0.70:1.00:3.73:**12**:**13**:**14**:**15**.

Thermal Decomposition of 3-Carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (6).—Heating of 0.620 g. of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) at 155–165° for 31 hours under nitrogen gave 0.557 g. (109%) of a mixture of esters. The infrared spectrum of this mixture showed that no pyrazoline remained. Gas chromatographic analysis (8-ft. silicone grease column) showed the mixture to consist of esters **12**, **13**, **14** and **15** in the ratio 0.15:1.22:1.00:1.16:**12**:**13**:**14**:**15**.

Simultaneously with this pyrolysis, 0.549 g. of a mixture of these four esters was heated under similar conditions. Before heating, gas chromatography showed the mixture to consist of the four esters in the ratio 0.47:1.41:1.00:1.43:**12**:**13**:**14**:**15**. After heating, the residue, which weighed 0.520 g. (95%), was found to contain the same four compounds in the ratio 0.44:1.33:1.00:1.46.

Photolysis of 3-Carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (7).—Results of photolyses of 3-carbomethoxy-*cis*-3,4-dimethyl-1-pyrazoline (**7**) as the neat liquid, and in various solvents, are recorded in Tables I and II. Usually the neat liquid or solution was placed in a quartz test-tube, and cooled either by an internal cold-finger condenser, or by a quartz cooling-jacket surrounding the test-tube. Irradiation was carried out with a GE sunlamp. Progress of the reaction was followed by gas chromatography (didecyl phthalate column), with disappearance of the peaks due to esters **13** and **15** (formed by pyrolysis of the pyrazoline in the injection port) indicating that the reaction was complete. In the neat liquid studies the reaction was also followed by infrared spectroscopy using the carbonyl bands.

Results were not always uniform. This is in part due to change in the output of ultraviolet light as the sunlamp aged, and in part due to failure to standardize the distance between the sample and the sunlamp.

Photolysis of 3-Carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (6). A. In Pentane.—In a quartz test-tube equipped with a cold-finger condenser extending to the bottom of the test-tube 98.2 mg. (0.629 mmole) of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) in 5 ml. of pentane was irradiated with a GE sunlamp for 31 hours. Gas chromatography (4-ft. didecyl phthalate column) showed methyl angelate, 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**) and/or methyl 2,3-dimethyl-3-butenoate (**12**), methyl tiglate, 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) and methyl 2,3-dimethyl-2-butenoate (**15**) in the ratio 1.00:8.77:0.24:1.06:0.18.

B. As the Neat Liquid.—In the reactor just described 984 mg. (6.30 mmoles) of 3-carbomethoxy-*trans*-3,4-dimethyl-1-pyrazoline (**6**) was irradiated with a GE sunlamp for 43 hours. Gas chromatography of the resulting mixture, which weighed 652 mg. (81%), showed it to consist of methyl angelate, 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**), methyl tiglate and 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) in the ratio 1.00:21.3:0.4:1.7. No methyl 2,3-dimethyl-2-butenoate (**15**) was found. The infrared spectrum of cyclopropane **13**, obtained by gas chromatographic collection from this reaction mixture, showed no bands due to ester **12**. Possibly the formation of methyl tiglate and 1-carbomethoxy-*cis*-1,2-dimethylcyclopropane (**14**) is due to photolytic isomerization of methyl angelate and 1-carbomethoxy-*trans*-1,2-dimethylcyclopropane (**13**), or to the presence of 3-carbomethoxy-*cis*-dimethyl-1-pyrazoline (**7**).

Isolation and Identification of Methyl Tiglate and Methyl Angelate.—Methyl angelate and methyl tiglate were isolated by gas chromatography (didecyl phthalate column from the product mixtures obtained by photolysis of pyrazolines **6** and **7**, respectively. Both unsaturated esters showed infrared spectra and gas chromatographic retention times identical with authentic samples. The collected sample of methyl tiglate was also identified by its ultraviolet spectrum, λ_{max} 210 mμ, which was identical with that of the authentic sample.

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