was distilled out at room temperature and the amine was isolated as described in the photoreduction by (+)-2-butylamine, leading to 1.52 g (77% recovery) of (+)-N,N-dimethyl-2-butylamine, $\alpha^{20.6}$ (obsd) +15.10° (1 dm), neat. Purification on an Aerograph Autoprep 700, 20% Carbowax 20 *M* on 60–80 Chromosorb W (column 90°, detector 180°, collector 120°, injector 20°) led to no significant change in rotation. Rotation of the amine initially was $\alpha^{24.5}$ (obsd) +14.91°.

Photochemical Conversions of 3*H*-Pyrazoles to Cyclopropenes and 1,2-Diazabicyclo[2.1.0]pent-2-enes[1]

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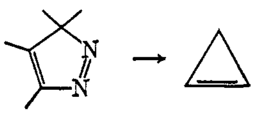
Abstract: A series of six alkyl-substituted 3*H*-pyrazoles has been irradiated with ultraviolet light. In all cases nitrogen elimination occurs and cyclopropenes are formed in variable yields. Using filtered light, ring opening was found to precede nitrogen elimination, and the corresponding diazoalkenes were formed. On irradiation of three fully alkylated 3*H*-pyrazoles isomerization to 1,2-diazabicyclo[2.1.0]pent-2-enes competes with nitrogen elimination. The extent of photoisomerization is solvent and temperature dependent. In all cases the isomerization was found to be fully reversible.

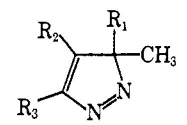
Pyrolysis of pyrazolines has long been known as one of the more versatile syntheses of cyclopropanes.[2–4] More recently it has been observed that nitrogen elimination from the heterocycles can be effected advantageously under photochemical conditions.[3] Several years ago it occurred to us that the reaction might be extended to the 3*H*-pyrazole system (I) which may serve as a convenient precursor of cyclopropenes. In two preliminary communications we have reported that certain 3*H*-pyrazoles can indeed be converted in satisfactory yields to cyclopropenes when illuminated with ultraviolet light.[5,6] Since then other papers have appeared reporting similar reactions.[7,8] It is the purpose of this contribution to give a more detailed account of the scope of the reaction and to report some findings of mechanistic implications. In addition, a novel photoisomerization of 3*H*-pyrazoles to 1,2-diazabicyclo[2.1.0]pent-2-enes and its thermoactivated reversal will be included in the discussion.

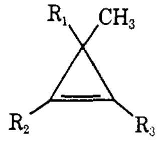

I

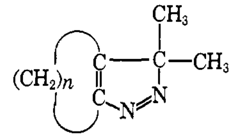
Results and Discussion

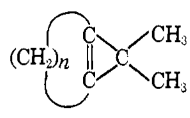
The 3*H*-pyrazole derivatives II–VII used in this study were synthesized by several new methods developed in this laboratory and described elsewhere.[9,10]

The photolyses were carried out in Pyrex reaction vessels thus eliminating irradiation with shorter wavelength than 300 mμ. When alkanes or toluene were used as solvents, nitrogen evolution was usually rapid and cyclopropenes VIII–XIII were formed in yields ranging from fair to good. Products were characterized either by direct comparison with samples previously prepared by different methods (VIII and IX) or by elemental analysis, spectral data, and further chemical transformations. The infrared spectra of X–XIII show the characteristic cyclopropene ring vibrations at 1740, 1860, 1840, and 1740 cm^{-1}, respectively.[11] Here, as in previous examples the strong dependence of this frequency on the double bond substitution type is apparent as well as the additional effect caused by a distortion of the "natural" cyclopropene bond angles caused by ring fusion in XII and XIII. The nuclear magnetic resonance spectra show signals for the methyl groups of X–XIII with the expected chemical shifts (listed in Experimental Section). The structure assignment of X is corroborated by the long-


II, $R_1 = R_3 = CH_3$; $R_2 = H$
III, $R_1 = R_2 = R_3 = CH_3$
IV, $R_1 = CH_3$; $R_2 = H$; $R_3 = C_6H_5$
V, $R_1 = OCH_3$; $R_2 = R_3 = CH_3$


VIII, $R_1 = R_3 = CH_3$; $R_2 = H$
IX, $R_1 = R_2 = R_3 = CH_3$
X, $R_1 = CH_3$; $R_2 = H$; $R_3 = C_6H_5$
XI, $R_1 = OCH_3$; $R_2 = R_3 = CH_3$


VI, *n* = 5
VII, *n* = 4


XII, *n* = 5
XIII, *n* = 4

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[1] Supported by grants from the National Science Foundation, GP-1076 and GP-4212.

[2] T. L. Jacobs in "Heterocyclic Compounds," Vol. 5, R. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp 45 ff.

[3] T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962).

[4] W. M. Jones, *ibid.*, **80**, 6687 (1958); **81**, 5153 (1959); **82**, 3136 (1960).

[5] G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 399 (1963).

[6] G. L. Closs and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3904 (1963).

[7] G. Ege, *Tetrahedron Letters*, 1665 (1963).

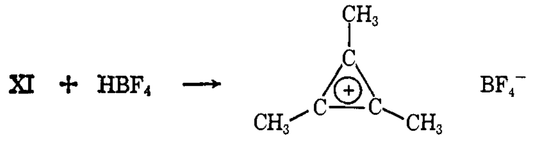
[8] R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).

[9] G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).

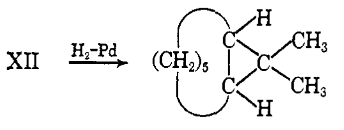
[10] G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).

[11] *Cf.* G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 70 (1966).

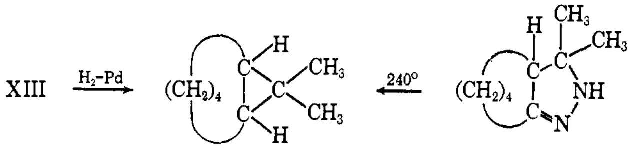
range coupling constant of 0.7 Hz between the vinyl proton and the geminal dimethyl group, and by the ^{13}C–H coupling constant of 220 Hz for the vinyl proton. Both values agree well with those observed in similar cyclopropenes.[12,13] Upon addition of strong acids, the trimethylmethoxycyclopropene XI is easily converted to trimethylcyclopropenium salts. The tetrafluoroborate XIV dissolves in water without decomposition and shows a single nmr peak at τ 7.05. The bicyclic cyclopropenes XII and XIII were catalytically hydrogenated and gave the corresponding bicyclic hydrocarbons XV and XVI in good yield. For comparison, 7,7-dimethylnorcarane (XVI) was synthesized by pyrolysis of the pyrazoline XVII and was found identical in all properties with the hydrogenation product from XIII.



XIV

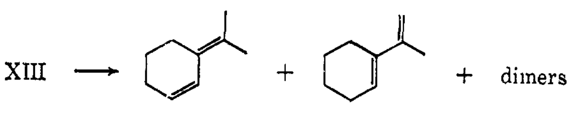


XV

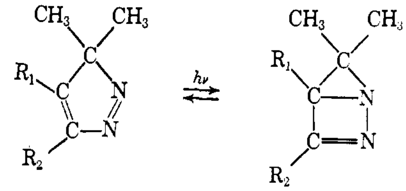


XVI XVII

The stabilities of the newly synthesized cyclopropenes vary with structure. While XI and XII are stable at room temperature, X polymerizes slowly, and XIII decomposes rapidly at temperatures above −40° to 3-isopropylidenecyclohexene, 1-isopropenylcyclohexene, and a mixture of dimers which was not further investigated. Because of the low thermostability all spectral investigations and the catalytic hydrogenation were carried out at temperatures below −40°. Also, separation of XIII from the tricyclic heterocycle XVIIIc, formed as a by-product and discussed below, was not possible because of the low thermostability.



Although the over-all transformation of 3*H*-pyrazoles to cyclopropenes appears to be a simple nitrogen elimination, the actual reaction sequence is complex and is influenced by substituents, solvents, and temperature. The fully alkylated derivatives, III, VI, and VII, undergo a reversible side reaction which is competing with nitrogen elimination. Thus if either of these 3*H*-pyrazoles is irradiated in methylene chloride at −50° or lower temperature little or no nitrogen evolution is observed. Examination of the reaction mixture by nmr at low temperature reveals that the starting material has been converted to a photoisomer. On warming to room temperature the spectrum of the initial 3*H*-pyrazole is regenerated in a dark reaction. On the basis of spectral data and the facile reversibility of the reaction it is suggested that the photoisomers are derivatives of the 1,2-diazabicyclo[2.1.0]pent-2-ene skeleton XVIII, a valence bond tautomer of 3*H*-pyrazole. This structure assignment is most strongly supported by the chemical shifts of the methyl groups of the photoisomers XVIIIa–c. Thus the tetramethyl derivative XVIIIa has three magnetically different methyl groups attached to saturated carbon atoms and one which is located on a double bond as evidenced by singlets at τ 8.97, 8.69, 8.61, and 8.19, respectively. Similarly the geminal methyl groups in VI and VII become magnetically nonequivalent in the respective photoisomers causing signals at τ 8.90 and 8.62 in XVIIIb and at 8.92 and 8.65 in XVIIIc. All three compounds show strong bands in the infrared spectrum between 1604 and 1608 cm^{-1}, compatible with the presence of a nitrogen-substituted C=N double bond in a four-membered ring. A maximum at 219 mμ (heptane) in the ultraviolet spectrum of XVIIIa is not unexpected for a chromophore consisting of an aziridine ring conjugated with a carbon–nitrogen double bond. Finally, cryoscopic measurements in benzene showed that the photoisomer XVIIIa has the same molecular weight as the corresponding 3*H*-pyrazole.



XVIIIa, $R_1 = R_2 = CH_3$
XVIIIb, $R_1 = R_2 = (CH_2)_5$
XVIIIc, $R_1 = R_2 = (CH_2)_4$

The partition of the reaction between the photoisomerization path and nitrogen elimination from VII was studied at low temperature where the rate of the back-reaction of the photoisomerization is negligible. As Table I shows, the fraction of isomerization *vs.* nitrogen evolution is a function of solvent with nitrogen elimination favored in nonpolar media. Photo-

Table I. Solvent Dependence of Product Distribution on Photolysis of VII

Solvent	Temp, °C	Product distribution,[a,b] % XIII	XVIIIc
n-Pentane	−60	70	30[c]
Cyclopropane	−60	70	30
Butadiene	−57	40	60
Dimethoxyethane	−59	25	75
Tetramethylsilane	−55	5	95
Methylene chloride	−60	0	100
Methanol	−58	0	100

[a] Determined from integrated intensities of methyl resonances in nmr spectra. [b] Probable accuracy ±5%. [c] Determined from volume of nitrogen evolution.

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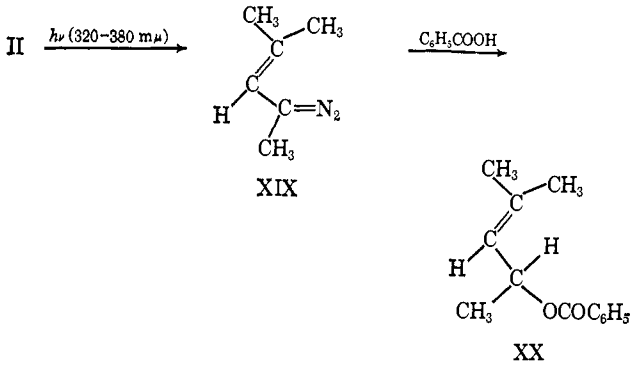
(12) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).
(13) G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

sensitizers such as benzophenone, acetophenone, and anthracene had no noticeable effect on the distribution of products.

The reversion of the photoisomers to the 3*H*-pyrazole system was studied on the tetramethyl derivative XVIIIa. The reaction was followed by either ultraviolet spectroscopy by observing the appearance of the band at 352 mμ in the corresponding 3*H*-pyrazole III, or by nmr recording the changes in the methyl resonance region. It was found that the reaction follows first-order kinetics and that the rate is somewhat solvent dependent. For example, the unimolecular rate constant in methylene chloride at 35° is 3.3×10^{-4}, while the rate in ethanol is 1.6×10^{-4} sec^{-1}. Clean kinetics in dilute solution in methylene chloride were only obtained on degassed solutions, otherwise a peculiar autocatalytic effect was accelerating the reaction by approximately a factor of 10. In all cases studied, the reversal to the 3*H*-pyrazole was quantitative.

The photoisomerization process seems to be restricted to the fully alkylated 3*H*-pyrazoles. Thus, even at very low temperature no evidence for photoisomer formation was obtained on the photolysis of II, IV, or V.

All of the 3*H*-pyrazoles studied developed a transient red color during photolysis suggesting the intermediacy of a diazo compound. Evidence for this type of intermediate was obtained when trimethyl-3*H*-pyrazole (II) was irradiated using a filter eliminating both the visible and the ultraviolet light below 320 mμ (Corning 7-60 and 7-37). Under those conditions II was converted to the diazoalkene XIX in 50% yield. Characterization of XIX is based upon its electronic spectrum ($\lambda\lambda_{\max}$ 279 and 522 mμ (ϵ 7000 and 23) and the diazo stretching vibration in the infrared spectrum (2035 cm^{-1}). Furthermore, reaction with benzoic acid gave the allylic ester XX, identical in all properties with a sample synthesized by an independent method. Similarly, the filtered irradiation of III and IV was shown to give the corresponding diazoalkenes in better than 50% yield. In the case of the tetramethyl derivative III, ring opening to the diazoalkene is accompanied by photoisomerization to XVIIIa, and high yields of the diazo compound can only be obtained at temperatures where the reversal of the photoisomerization is relatively fast. As has been reported previously,[9] photolysis of the diazoalkenes in Pyrex leads to the formation of the corresponding cyclopropenes.



The experimental observations on the irradiation of 3*H*-pyrazoles suggest a reaction scheme as summarized in Figure 1. Under the conditions employed in this study the 3*H*-pyrazoles are excited mainly *via* absorption by the low-energy and low-intensity band at approximately 350 mμ, and presumably associated with an $n-\pi^*$ transition of the nonbonding electrons on the azo group. With the data at hand it cannot be decided whether both reaction paths, isomerization (path A) and ring opening (path B), branch out from the same excited state or whether the product partition is preceded by a partitioning into two excited states. The absence of any noticeable effect of photosensitizers on the product ratio seems to suggest a single excited state, or at least excited states of the same multiplicity. The difference in polarity of the diazoalkene and the photoisomers is sufficient to attribute the change in product ratio with different solvents to a conventional solvent effect. No explanation can be offered why photoisomerization has been observed only on fully alkylated 3*H*-pyrazoles. It is worth pointing out that the isomerization has recently found its analogy in the carbocyclic series with the photoisomerization of cyclopentadiene to bicyclo[2.1.0]pent-2-ene.[14] Although it has been shown that loss of nitrogen can occur in two steps (B and C) requiring two separate excitations, it cannot be excluded that part of the reaction proceeds in a single step (D). The latter mechanism may be of greater importance when higher energy irradiation is used under which conditions little of the diazoalkenes are observable.[15] Either reaction path should lead to vinyl carbenes as the immediate precursors of cyclopropenes. So far, evidence for vinylcarbenes as reaction intermediates has been circumstantial and is mostly based on the fact that other reactions formally leading to vinylcarbenes such as based induced pyrolysis of α,β-unsaturated tosylhydrazones and several α eliminations give cyclopropenes as final products.[9,16]

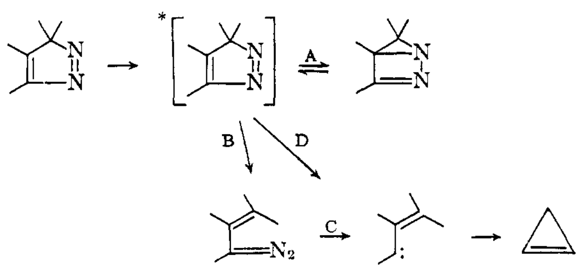


Figure 1.

Experimental Section

All boiling points and melting points are uncorrected. The nmr spectra were recorded on Varian A-60 and DP-60 spectrometers. Unless otherwise stated, the spectra were measured in carbon tetrachloride solution with tetramethylsilane as internal standard. Chemical shifts are reported in τ units, with the number in parenthesis indicating the number of protons causing the signal. The letter immediately following the parenthesis designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; m, unresolved multiplet. Infrared spectra were obtained on a Beckman IR-7 instrument and ultraviolet spectra were recorded on a Cary 14 spectrophometer.

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(14) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 848 (1966).

(15) The lower steady-state concentration of diazoalkene observable on irradiation with light below 300 mμ may also be due to a faster photolysis rate of the diazoalkenes which have a high intensity absorption band at approximately 280 mμ.

(16) The phenylvinylcarbene derived from IV has recently been characterized by its low-temperature esr spectrum demonstrating a triplet ground state: G. L. Closs and L. R. Kaplan, unpublished work.

3,3-Dimethyl-4,5-cyclohepteno-3*H*-pyrazole (VI). The tosylhydrazone of 2-isopropylidenecycloheptanone[17] was prepared by adding tosylhydrazide (18.6 g, 0.1 mole) to the solution of 2-isopropylidenecycloheptanone (15.2 g, 0.1 mole) in methanol (30 ml) at 45°. The tosylhydrazone was allowed to crystallize at 0°. Recrystallization from methylene chloride gave the pure tosylhydrazone (19.0 g, 60%) melting at 171–172°.

Anal. Calcd for $C_{17}H_{24}N_2O_2S$: N, 8.74. Found: N, 8.76

Sodium methoxide (4 0 g, 0.074 mole) was added at 0° to a slurry of the tosylhydrazone (23.0 g, 0.072 mole) in methanol (90 ml). After stirring for 1 hr, the solvent was evaporated under vacuum at 20°, and the solid residue was dried (0.1 mm) for 20 hr. The sodium salt was then slowly heated to 130° (0.1 mm), and the volatile products were condensed in a Dry Ice trap. The decomposition was complete after 2 hr. The distillate was fractionated and the fraction boiling at 61–63° (0.025 mm) (7.9 g, 68%) was collected; nmr spectrum: 7.1 (2) m; 7.8 (2) m, 8.3 (6) m, and 8.8 (6) s; ultraviolet spectrum: $\lambda\lambda_{max}$ 274 mμ (ϵ 3530) and 347 mμ (ϵ 300).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.11; H, 9.82; N, 17.07. Found: C, 73.30; H, 9.68; N, 17.01

3,3-Dimethyl-4,5-cyclohexeno-3*H*-pyrazole (VII). Tosylhydrazide (37.2 g, 0.2 mole) was added to a solution of 2-isopropylidenecyclohexanone[18] (27.6 g, 0.2 mole) in methanol (80 ml) at 45°. The mixture was kept at this temperature for 25 min and was then cooled to 0° and pentane (80 ml) added. The precipitate was filtered and recrystallized from methylene chloride–pentane. The pure tosylhydrazone (38.0 g, 61%) melted at 164–165°.

Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.71; H, 7.24; N, 9.14. Found: C, 62.73; H, 7.19; N, 9.17.

The sodium salt of the tosylhydrazone (10.5 g, 0.034 mole) was prepared from sodium methoxide (2.0 g, 0.037 mole) in methanol (50 ml) followed by evaporation of the solvent *in vacuo*. The solid residue was heated for 1 hr to 90° and for another hour to 140° while allowing the pyrolysate to distil into a Dry Ice trap (0.2 mm). Fractionation of the distillate and collection of the fraction boiling at 48–50° (0.025 mm) gave 3,3-dimethyl-4,5-cyclohexeno-3*H*-pyrazole (3.9 g, 76%); nmr spectrum: 7.2 (2) m, 7.8 (2) m, 8.2 (4) m, and 8.78 (6) s; ultraviolet spectrum: $\lambda\lambda_{max}$ 272 mμ (ϵ 3350) and 346 mμ (ϵ 345).

Anal. Calcd for $C_9H_{14}N_2$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.64; H, 9.49; N, 18.38.

Photolysis Equipment. A. Experiments with unfiltered light were carried out in a cyclindrical reaction vessel consisting of concentrical Pyrex tubes. The inner part contained the cooling liquid; the outer, about 0.5-cm wide, contained the reaction mixture. A 550-w Hanovia high-pressure mercury lamp was placed in the center of the vessel. In experiments run below room temperature methanol was used as the cooling liquid and was circulated through a heat exchanger cooled with Dry Ice–acetone.

B. Experiments in which filters were employed were run on an optical bench arrangement consisting of an Osram 500-w mercury high-pressure lamp, a 7-cm diameter quartz lens, filter plates, and a reaction cell. The cell was constructed out of a 7-cm diameter Pyrex tube, one end of which was closed with a quartz plate. A Pyrex separation divided the cell into two chambers. The chamber containing the quartz window (1-cm long) had three openings for mechanical stirrer, thermometer, and gas connection tube. The second chamber in back of the reaction vessel was used for circulation of the cooling liquid.

C. Small scale irradiations were advantageously carried out in standard 5-mm nmr tubes. For temperature control the tubes were fitted with a Pyrex jacket through which methanol was circulated as a cooling liquid, using a small circulating pump and copper tubing as a heat exchanger. During the experiment, the jacketed tube was placed approximately 1 cm away from a 550-w Hanovia high-pressure mercury lamp.

1,3-Trimethylcyclopropene. 3,3,5-Trimethyl-3*H*-pyrazole[10] (2.0 g, 18 mmoles) was irradiated in *n*-heptane (100 ml) at 10° using apparatus A. The nitrogen evolution was monitored and was complete after 40 min. Trimethylcyclopropene was enriched by fractional distillation, collecting a fraction (4.9 g) from 30 to 96°. An analysis of this material by infrared (1768 cm^{-1}), using a pure sample of 1,3,3-trimethylcyclopropene[9] for comparison, showed this fraction to contain 0.97 g (65%) of trimethylcyclopropene. A second fractionation gave pure material (bp 43°), identical in all properties with a sample prepared by a previously described method.[9]

1,2,3,3-Tetramethylcyclopropene. 3,3,4,5-Tetramethyl-3*H*-pyrazole[10] (0.97 g, 7.8 mmoles) was irradiated in toluene (60 ml) at 40° using apparatus A. Nitrogen evolution was slow and required 6 hr to be 95% complete. The reaction mixture was fractionated on a spinning-band column giving a fraction (0.55 g, 74%) boiling between 67 and 69° of better than 95% pure tetramethylcyclopropene. The spectral properties of this material were identical with those of a sample of tetramethylcyclopropene prepared by a previously described method.[19]

1,2,3-Trimethyl-3-methoxycyclopropene. 3,4,5-Trimethyl-3-methoxy-3*H*-pyrazole[10] (1.4 g, 10 mmoles) was irradiated in *n*-pentane (100 ml) at −20°. Nitrogen evolution was complete after approximately 20 min. The pentane was removed under reduced pressure, and the residue was distilled at room temperature into a flask cooled with Dry Ice–acetone (0.74 g, 65%). The compound was found to be unstable when exposed to moist air; infrared spectrum: ring vibration at 1860 cm^{-1}; nmr: 7.14 (3) s, 8.3 (6) s, and 8.75 (3) s.

Trimethylcyclopropenium Fluoroborate. 3,4,5-Trimethyl-3-methoxy-3*H*-pyrazole[10] (1.4 g, 10 mmoles) was irradiated in *n*-pentane (100 ml) as described above. The reaction mixture was cooled to −20° and a mixture of 48% fluoroboric acid (3.2 g, 20 mmoles) and acetic anhydride (20.6 g, 200 mmoles) was added under vigorous stirring. The mixture was kept at this temperature for 2 min, and then anhydrous ether (400 ml) was added. Stirring was continued at −20° for 2 hr. The precipitate was then allowed to settle, and the solvent was decanted. Washing with anhydrous ether (100 ml) and drying under vacuum gave the trimethylcyclopropenium fluoroborate as a white powder (1.4 g, 82%, mp 132–134°). The material can be recrystallized to give long colorless needles by dissolving it in acetone and leaving it in a covered vessel containing ether; nmr: (acetonitrile) 7.05 (s).

Anal. Calcd for $C_6H_9BF_4$: C, 42.91; H, 5.41. Found: C, 42.85; H, 5.70.

1-Phenyl-3,3-dimethylcyclopropene. 3,3-Dimethyl-5-phenyl-3*H*-pyrazole[10] (2.4 g, 15 mmoles) was dissolved in *n*-pentane (140 ml) and irradiated at 0° in apparatus A. Nitrogen evolution was complete after 20 min. The solvent was removed under vacuum. Attempts to distil the residue at reduced pressure resulted in decomposition of the material. Purification was accomplished by chromatography on Florisil and elution with *n*-pentane. The major fraction after removal of solvent was 1-phenyl-3,3-dimethylcyclopropene (1.0 g, 50%), a colorless oil, better than 90% pure as determined by its nmr spectrum. The compound polymerizes rapidly in the condensed phase at room temperature; infrared spectrum: ring vibration at 1740 cm^{-1}; nmr: 2.3–2.6 (6) m and 8.62 (6) d (0.7 Hz).

8,8-Dimethylbicyclo[5.1.0]octene-Δ-1,7. 3,3-Dimethyl-4,5-cyclohepteno-3*H*-pyrazole (1.15 g, 7 mmoles) in *n*-pentane (100 ml) was irradiated at 15° in apparatus A. Nitrogen evolution was complete after 5 hr. The reaction mixture was fractionated, collecting the fraction boiling at 55–56 (12 mm) (5.9 g 84%); infrared spectrum: ring vibration at 1840 cm^{-1}; nmr: 7.4–8.6 (10) m and 8.85 (6) s.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.95; H, 11.82.

The stability of the cyclopropene was tested by heating a solution of the hydrocarbon in fluorotrichloromethane to 100° for 10 hr. No change was observed in the nmr spectrum.

Hydrogenation of 8,8-Dimethylbicyclo[5.1.0]octene-Δ-1,7. The olefin (1.4 g, 10.2 mmoles) was hydrogenated in ether (10 ml) with palladium (5%) on charcoal catalyst (0.1 g) at 0°. The hydrogen consumption was 94% of the theoretical volume. After removing the solvent, the residual oil was distilled over a short Vigreux column. The fraction collected at 68–69° (20 mm) (1.2 g) was further purified by glpc on a 5-ft column containing silicon oil SF-96 on Firebrick, yielding a pure sample of 8,8-dimethylbicyclo[5.1.0]octane; nmr: 7.9–9.5 (12) m and 9.0 (6) s.

Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.53; H, 13.39.

Irradiation of 3,3-Dimethyl-4,5-cyclohexeno-3*H*-pyrazole (VII). A. In *n*-Pentane at −20°, Followed by Work-up above Room Temperature. 3*H*-Pyrazole VII (1.5 g, 10 mmoles) was irradiated in *n*-pentane (100 ml) at −20° using apparatus A. Nitrogen elimination (95% of theoretical) was completed after 40 min. After

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[17] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

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removal of the solvent the residue was distilled under vacuum using a small Vigreux column. Two fractions were collected: (a) 20° (0.2 mm) (0.25 g) and (b) 91° (0.2 mm) (1.0 g). Glpc analysis on a Carbowax 20M column showed fraction b to be a mixture of two components, present in a ratio of 4.3:1. The major component was trapped and shown to be 3-isopropylidenecyclohexene; nmr: 3.89 (1) doublet (10.5 Hz) of triplets (1.7 Hz), 4.50 (1) doublet (10.5 Hz) of triplets (3.7 Hz), 7.5–8.7 (6) m, 8.3 (6) narrow multiplet; infrared spectrum: 1682 and 1642 cm^{-1}; ultraviolet spectrum: λ_{max} (methanol) 241 mμ (ϵ 21,400).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.50; H, 11.65.

The minor component was trapped from the glpc and was shown to be 1-isopropylcyclohexene;[20] nmr: 4.2 (1) m, 5.2 (2) m, 7.6–8.1 (4) m, 8.16 (3) m, 8.1–8.7 (4) m; infrared: 1608 and 1636 cm^{-1}.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.54; H, 11.63.

Fraction b showed two peaks in the glpc analysis and a very complex nmr spectrum.

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.01; H, 11.36.

B. In Pentane–Ether at −65° Followed by Hydrogenation. 3*H*-Pyrazole VII (0.5 g, 3.4 mmoles) was irradiated in a mixture of *n*-pentane–ether, 65:35 (10 ml) at −65°. Nitrogen evolution ceased after 140 min after 55% of the theoretical volume had evolved. The solution was transferred into a hydrogenation apparatus without allowing it to warm up, and palladium (5%) on charcoal (50 mg) was added. Hydrogen consumption began after warming to −40° and was complete after 2 hr. After removing the solvent, the residue was analyzed by glpc on a QF-1 column. Only one major peak was observed. The material was trapped and was found to be identical in all spectral properties and glpc retention time with a sample of 7,7-dimethylbicyclo[4.1.0]-hexane.

C. In Cyclopropane at −60° Followed by Spectral Identification of 7,7-Dimethylbicyclo[4.1.0]heptene-Δ-1,6 (XIII). 3*H*-Pyrazole VII (0.073 g, 0.48 mmole) was dissolved in an nmr tube in cyclopropane (1 ml) at −40° and was irradiated at −60° using apparatus C. Nitrogen evolution ceased after 2 hr (7.5 ml, approximately 65% of the theoretical amount). The tube was then transferred to a precooled probe of the DP-60 nmr spectrometer, and the spectrum was determined at −55°. Besides the cyclopropane proton resonance which served as the standard (τ 9.80) the spectrum showed resonances attributable to the cyclopropene XIII (70%) and the photoisomer XVIIIc 30%. No other peaks were visible. After subtracting the resonances of XVIIIc the positions of the cyclopropene resonances were 7.7 (4) m, 8.3 (4) m, and 8.79 (6) s. On warming the solution to −35° these peaks were diminishing in intensities and were replaced by a rather complex spectrum.

In a separate experiment, a solution of the 3*H*-pyrazole VII in cyclopropane was irradiated in a low-temperature infrared cell at −60°. Determination of the infrared spectrum after 2 hr of irradiation showed a medium intensity band at 1740 cm^{-1} which on warming to −35° disappeared and is attributed to the ring vibration of the cyclopropene ring in XIII.

D. In Methylene Chloride at −60° Followed by Spectral Identification of the Photoisomer XVIIIc. 3*H*-Pyrazole VII (0.085 g, 0.57 mmole) was dissolved in an nmr tube in methylene chloride (1 ml) and was irradiated at −60° using apparatus C. Nitrogen evolution was negligible and the irradiation was discontinued after 2 hr. The sample was transferred into a precooled probe of the nmr spectrometer without warming. The spectrum was determined at −60°: 7.7–8.4 (8) broad multiplet, 8.65 (3) s, and 8.92 (3) s. The solution was allowed to warm to 0° and was held at this temperature for 1 hr. The nmr spectrum was now identical with that obtained from a sample of 3*H*-pyrazole VII. The solvent was evaporated and the infrared spectrum of the residue was identical with that of VII. In a separate experiment a solution of VII was irradiated as described above and the resulting solution was transferred at low temperature (below −30°) into a low-temperature infrared cell. A strong band at 1608 cm^{-1} is attributed to the C=N stretching vibration. This band disappeared on warming to 0°.

E. In Various Solvents at Low Temperature. 3*H*-Pyrazole VII (0.3–0.5 mmole) was irradiated in an nmr tube in solvents listed in Table I at temperatures ranging from −55 to 60° using apparatus C. In each case the product analysis was performed by nmr as described above by integrating the methyl resonances of XIII and XVIIIc, with the exception of the irradiation in *n*-pentane where the nitrogen evolution was used for analysis. The results are given in Table I.

7,7-Dimethylbicyclo[4.1.0]heptane (XVI). 2-Isopropylidenecyclohexanone[18] (5.5 g, 0.04 mole) in methanol (2.5 ml) was added slowly to a solution of hydrazine (6 g, 0.18 mole) in water (3.5 ml) and methanol (2.5 ml). The mixture was heated to 80° for 20 min and after adding sodium carbonate solution (30%) was extracted with ether. The ether extract was dried over potassium carbonate, and the solvent was evaporated. The residue was fractionated collecting a fraction at 98–100° (4.0 mm) of pyrazoline XVII (4.7 g, 78%), which was used for pyrolysis without any further purification.

The pyrazoline (1.5 g, 0.01 mole) was mixed together with powdered potassium hydroxide and palladium on charcoal and was heated to 240°. The distillate of the pyrolysis was fractionated on a small Vigreux column, collecting a fraction boiling at 52° (20 mm) (0.95 g). Unsaturated by-products were removed by ozonolysis at −70° in methanol followed by fractional distillation yielding pure 7,7-dimethylbicyclo[4.1.0]heptane (0.65 g, 52%); nmr: 8.3–9.0 (8) m, 9.10 (3) s, 9.13 (3) s, and 9.5 (2) m.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.22; H, 12.81.

Irradiation of 3,3-Dimethyl-4,5-cyclohepteno-3*H*-pyrazole (VI) in Methylene Chloride at −60°. 3*H*-Pyrazole VI (0.048 g, 0.29 mmole) in methylene chloride (1 ml) was irradiated in an nmr tube at −60° using apparatus C. No measurable nitrogen evolution was observed and irradiation was discontinued after 2 hr. The nmr tube was transferred to the precooled probe of the DP-60 nmr spectrometer, and the spectrum was recorded at −55°: 7.7 (2) m, 8.4 (8) m, 8.62 (3) s, and 8.90 (3) s. On warming the solution to 0°, the resonances diminished in intensity and were replaced by the spectrum of VI. After evaporation of the solvent, the residue showed an infrared spectrum identical with that of a sample of the 3*H*-pyrazole VI.

In a separate experiment, the low-temperature irradiation was followed by the recording of the infrared spectrum at −50°. A strong band at 1604 cm^{-1} is attributed to the C=N stretching vibration of the photoisomer. On warming this band disappeared and was replaced with a band at 1651 cm^{-1} (N=N stretching, of VI).

Irradiation of 3,3,4,5-Tetramethyl-3*H*-pyrazole (III) in Methylene Chloride at −60°. 3*H*-Pyrazole III (0.05 g, 0.4 mmole) in methylene chloride (1 ml) was irradiated in an nmr tube at −60° using apparatus C for 1 hr. No measurable evolution of nitrogen was observed. The nmr spectrum was recorded at −60°: 8.19 (3) s, 8.61 (3) s, 8.69 (4) s, and 8.97 (3) s. After warming to room temperature for 12 hr the spectrum of III was regenerated: 7.76 (3) q, 1.2 Hz; 8.22 (3) q, 1.2 Hz; and 8.79 (6) s. The infrared spectrum of the photoisomer (XVIIIa) was obtained by irradiating a 20 mole % solution of III at −60° as described above: 1604 cm^{-1} (C=N stretching); this band disappeared on warming and was replaced by a band at 1662 cm^{-1} (N=N stretching of III).

The rate of the reversal of the photoisomerization of III was studied by nmr in the following manner. The photoisomer was produced as described above in 5% solution in methylene chloride (1 ml) in an nmr tube. The sample was then inserted into the nmr probe which was temperature regulated to 35 ± 0.5°. The reaction was followed by integrating the areas under the methyl resonances of the photoisomer and the 3*H*-pyrazole and computing the fraction of photoisomer remaining The reaction was followed to approximately two half-lifes. The average first-order rate constant from two runs was 3.25×10^{-4} sec^{-1}.

Determination of the rate of the reversal of the photoisomerization by ultraviolet spectroscopy was carried out in the following manner. The photoisomer was prepared as described above in an nmr tube using either ethanol or *n*-heptane as a solvent. The solutions were then diluted to 10^{-3} *M* and transferred into a ultraviolet absorption cell, which was thermostated at 35° in a Cary 14 spectrophotometer. Optical densities were recorded at 340 mμ where the photoisomer showed no absorption. The average first-order rate constants in 95% ethanol and in *n*-heptane at 35° were 1.56×10^{-4} and 2.7×10^{-4} sec^{-1}.

2-Methyl-4-diazo-2-pentene from 3,3,5-Trimethyl-3*H*-pyrazole. 3*H*-Pyrazole II (0.777 g, 7.0 mmoles) was dissolved in methylene chloride (60 ml) and was irradiated at −42° using apparatus B equipped with Corning filter 7-60. Nitrogen evolution was very slow and after 95 min the irradiation was discontinued. A sample of the intensely red colored solution was examined by nmr: 8.06

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(3) s, 8.15 (3) m, and 8.30 (3) m as the major peaks; ultraviolet spectrum: $\lambda\lambda_{max}$ 279 mμ (ε 7000) and 522 mμ (ε 29) (the extinction coefficients are based on an estimated 60% conversion); infrared spectrum: 2035 cm^{-1} (C=N=N). Part of the reaction mixture was added to an ethereal solution of benzoic acid. Nitrogen was evolved and the solution decolorized. The mixture was washed with sodium bicarbonate and water. After evaporation of the solvent, the residue was distilled under vacuum (60° (0.5 mm)). The distillate gave infrared and nmr spectra identical with those obtained from a sample of 2-methyl-4-benzoyloxy-2-pentene.

2-Methyl-4-benzoyloxy-2-pentene. 2-Methyl-2-penten-4-ol (12 g, 0.12 mole) was allowed to react with benzoyl chloride (16.8 g, 0.12 mole) in pyridine (100 ml) at 0° for 40 min. The reaction mixture was poured on ice, extracted with ether, and dried over sodium sulfate. Distillation yielded a fraction (13.35 g) boiling at 60–80° (0.025 mm) consisting mainly of benzoate. Repeated distillation over a column gave a pure sample boiling at 62° (0.05 mm).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.84. Found: C, 76.26; H, 7.84.

1-Phenyl-1-diazo-3-methyl-2-butene from 3,3-Dimethyl-5-phenyl-3*H*-pyrazole. 3*H*-Pyrazole IV (1.27 g, 7.4 mmoles) in methylene chloride (100 ml) was irradiated at −40° using apparatus B equipped with Corning filter 7-37. No nitrogen evolution was detected. After 80 min, the irradiation was discontinued, and a sample of the solution was analyzed by nmr: 2.7 (5) (m), 7.98 (3) m, and 8.22 (3) m. Based on an integration of the nmr peaks conversion to the diazo compound was 86%; ultraviolet spectrum: $\lambda\lambda_{max}$ 292 mμ (ε 18,000) and 522 mμ (ε 56) (the extinction coefficients are based on the conversion as determined by nmr); infrared spectrum: 2035 cm^{-1} (C=N=N).

The Stereoselective Rearrangements of Conformationally Mobile Epoxides[1a]

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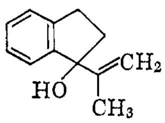
Abstract: The syntheses and structural assignments of *erythro-* and *threo-*1-methyl-1-(hydroxyindanyl)oxirane are described. The course of the rearrangements of each of these isomers to 1- and 2-tetralone derivatives utilizing homogeneous (boron trifluoride) and heterogeneous (alumina) catalyses have been examined. The latter effects the arrangements in a stereoselective manner lending support to an earlier suggestion that such reactions proceed through conformationally immobile surface absorbed transition states.

As part of a study of ring expansion reactions,[2,3] we have examined the acid-catalyzed rearrangements of the diastereomeric epoxy alcohols derived from the oxidation of 1-isopropenyl-1-indanol (**1**).



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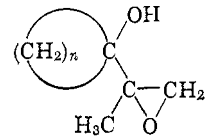
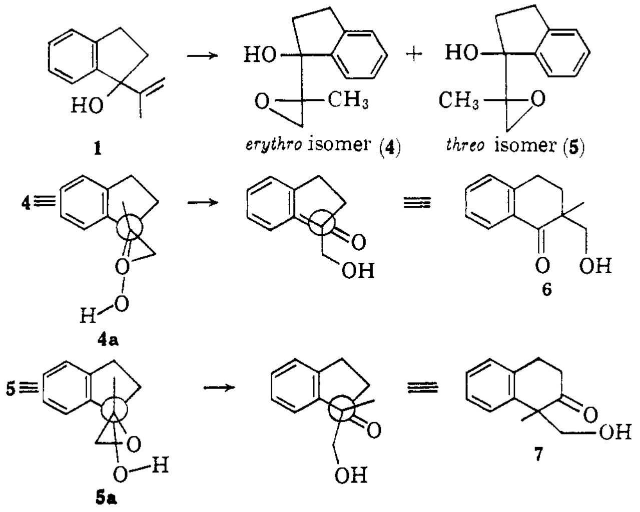


2, *n* = 4
3, *n* = 5

Our interest in this system stemmed from a mechanistic proposal[3] that the alumina-catalyzed ring enlargement of the unsubstituted analogs **2** and **3** proceeded through a transition state in which both oxygen atoms were attached to the surface of the catalyst.

The *erythro-* and *threo-*epoxy alcohols (**4** and **5**) appeared to be particularly suited to demonstrate the stereochemical implications derived from such a conformationally rigid transition state. Adsorption of *both* oxygen atoms onto a surface infers that these atoms are mutually eclipsed (or nearly eclipsed) to allow maximum approach of the nonbonded electrons to the electrophilic surface. Ring opening and rearrangement of these "eclipsed" surface adsorbed conformations (**4a** and **5a**) should then proceed by preferential migration of the group which is held *anti* (methylene in **4a**; aryl in **5a**) to the epoxide oxygen. These processes are depicted in Scheme I.

Scheme I



In contrast, stereochemical predictions based on adsorption of the epoxide oxygen atom alone are less evident. An inspection of models suggests that aryl

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(2) C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, 29, 3320 (1964).

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