

Photochemistry of Organic Nitrogen Compounds. Part II.¹ The Photolysis of Pyrazolenines *via* Diazo-compounds

By A. C. Day and M. C. Whiting

Evidence is described which throws further light on the mechanism proposed for the photolytic conversion of pyrazolenines into cyclopropenes. The intermediate diazo-compound from the photolysis of 3-(1'-hydroxy-1'-methyl-ethyl)-5,5-dimethylpyrazolenine has been studied spectrophotometrically and by trapping with acetic acid. In the presence of acid, protonation initiates a pinacolic deamination sequence, and a hydroxy-ester and an epoxide are formed in comparable amounts. The epoxide is also a minor product of photolysis in absence of acid.

A one-step synthesis of 5,5-dimethyl-pyrazolenines is described.

THE formation of cyclopropenes by photolysis of pyrazolenines is well established.^{2,3} In connection with other work,⁴ we have studied the photolysis of the pyrazolenine (I); and, whilst our results confirm a brief proposal² that the reaction involves a vinyl-diazo-

alkane, the presence of the hydroxyl group gives our reaction certain additional features.

Addition of 2-diazopropane⁵ to 3-methylbutyn-3-ol

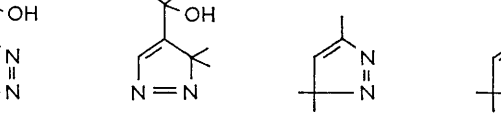
³ (a) G. L. Closs and W. A. Böll, *Angew. Chem. Internat. Edn.*, 1963, **2**, 399; (b) G. Ege, *Tetrahedron Letters*, 1963, 1667; R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1964, **86**, 525.

⁴ A. C. Day and M. C. Whiting, *Chem. Comm.*, 1965, 292; *J. Chem. Soc. (B)*, in preparation.

⁵ A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. (C)*, 1966, 467.

¹ Part I, A. C. Day and M. C. Whiting, *J. Chem. Soc. (C)*, 1966, 464.

² G. L. Closs and W. A. Böll, *J. Amer. Chem. Soc.*, 1963, **85**, 3904.



 (I) (II) (III) (IV)

 (V) (VI) (VII) (VIII)

 (IX) (X) (XI) (XII)

$$\text{MeCH}=\text{CMe}\cdot\text{N}=\text{N}\cdot\text{Me} \quad (\text{IV})$$

$$\text{Me}_2\text{C}=\text{CH}\cdot\text{N}=\text{N}\cdot\text{Me} \quad (\text{V})$$

⁸ R. Hüttel, J. Riedl, H. Martin, and K. Franke, *Chem. Ber.*, 1960, **93**, 1425, and references therein.

A red coloration has previously been observed by Closs and Böll in the irradiation of pyrazolenines, and attributed to an intermediate vinyldiazoalkane, which subsequently loses nitrogen and cyclises.² A point in favour of this proposal is that vinyldiazoalkanes generated by the Bamford-Stevens reaction behave in the same way.⁹ In our case, the evidence that the red intermediate is the diazo-compound (IX) is that (a) the red solutions had λ_{max} (ether) 498 m μ and gave on evaporation a red oil having ν_{max} 2045 cm.⁻¹, (b) the red colour was instan-

¹⁵ "N.M.R. Spectra Catalog," Varian Associates, Palo Alto, California, 1962, vol. 1, Spectrum No. 32.

Org.

taneously destroyed by acid, with evolution of nitrogen, and (c) the reaction with acid gave the expected ester (X). Preparatively, the diazo-compound could be most efficiently trapped by irradiation of the pyrazolenine (I) in 2% ethereal acetic acid. No red colour was observed, the cyclopropene was not formed, and the products were the epoxide (VIII) (35%) and the hydroxy-ester (X) (46%). These were readily separable by distillation. The latter had the expected n.m.r. spectrum containing a complex multiplet (τ 4.75–4.95) for H_A and H_B . This multiplet was much better resolved in the derived diol (XI) (τ_A 5.98; τ_B 4.82; $J_{AB} = 9$ c./sec.). The formation of (VIII), (X), and (XI) is consistent only with pyrazolenine structure (I);* nothing corresponding to the above H_A – H_B couplings would have been observed in products derived from structure (II).

In the early stages of photolyses without added acid, spectra showed an apparent isosbestic point at 388 m μ . This implies that, before any significant decomposition of the diazo-compound has occurred, only two species, pyrazolenine and diazo-compound (IX), are present in more than trace quantities, *i.e.*, any intermediate preceding the diazo-compound must isomerise extremely rapidly: consequently the latter is the first stable photo-product.† The maximum yield of diazo-compound attained during photolysis was usually about 65% (by nitrogen evolution with acid) and occasionally as high as 90–95%. Conversion of the diazo-compound to final products is also mainly a photochemical reaction since, under our conditions, it decomposed photochemically at 35° rather more than three times as fast as it did in the dark at this temperature. The thermal decomposition had a half-life of 60 min. at 35°, and was shown to involve partial reconversion to the pyrazolenine (13%). Thus, photochemical processes account for about 85–90% of the products at this temperature.

Although the diazo-compound (IX) could not be detected spectroscopically in photolyses in acetic acid, this compound is most probably formed transiently as the first step. Whilst having no rigorous evidence for this statement, we consider three points to be in its favour:

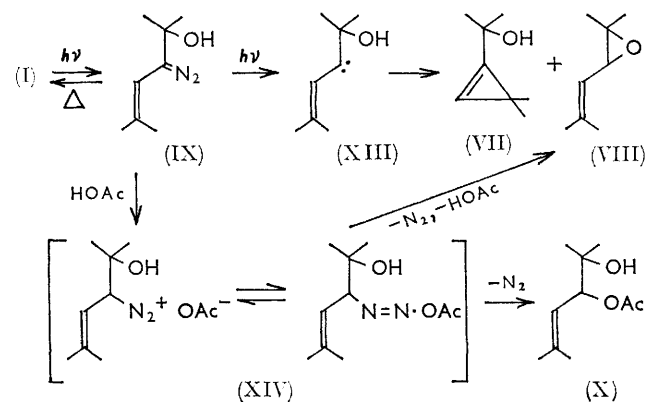
(1) The pyrazolenine was unaffected thermally by 2% ethereal acetic acid.

(2) It is unlikely that the presence of acetic acid (2%) would significantly affect the nature of the excited state. The ultraviolet spectrum of the pyrazolenine was unaffected by acetic acid, except for slight shifts of the kind

found with ethanol (*vide supra*) and attributable ^{13a} in the case of the $n \rightarrow \pi^*$ transition to the decreased polarity of the excited state, *i.e.*, in a protic solvent, hydrogen-bonding stabilises the ground state more than the $n \rightarrow \pi^*$ excited state. Electronically excited molecules often have strikingly different acid-base character from the corresponding ground states;^{13b,17} and, insofar as basicity parallels hydrogen-bonding ability, $n \rightarrow \pi^*$ excitation is expected to decrease the basicity of the pyrazolenine greatly. Possibilities of protonation, etc., of the excited molecule are thus remote: even the ground state of pyrazolenines is virtually non-basic.

(3) When the pyrazolenine (I) was irradiated to maximum concentration of the diazo-compound, then reaction quenched with acetic acid, the products were the cyclopropene (VII) (14%), the epoxide (VIII) (32%), and the acetate (X) (20%). The last two are the sole products of photolyses in acid: the enhanced yield of epoxide is also characteristic of those reactions.

The reactions described in this Paper are most simply explained by the accompanying scheme, in which the diazo-compound (IX) either undergoes carbenoid de-



composition *via* (XIII), or is diverted by protonation to a diazonium acetate. There is ample evidence of the latter reaction^{18,19a,20a} and also for the intermediacy of covalent diazo-esters and diazonium carboxylate ion-pairs in such reactions as the decomposition of *N*-nitroso-amides in non-polar solvents;^{19,21} although it would be sufficient for our reaction to consider only the diazonium ion-pair, we insert the equilibrium at (XIV) in view of White's oxygen-18 studies²¹ and also to allow

* Similar spectroscopic features were shown by the methoxy-alcohol (XII), the product obtained (as expected: cf. ref. 16a) by base-catalysed methanolysis of the epoxide (VIII).

† This conclusion would only be invalid in the fortuitous and unlikely event that a hypothetical intermediate have exactly the same extinction coefficient as the starting material and diazo-compound.

At low temperatures in polar solvents, Closs and Böll² have observed a second photo-isomer of pyrazolenines. This spontaneously reverts to the pyrazolenine at 0°, and so probably represents merely a cul-de-sac in the overall process leading to cyclopropenes.

¹⁶ (a) H. Meerwein, ed E. Müller, "Methoden der Organischen Chemie (Houben-Weyl)," Georg Thieme Verlag, 1965, vol. 6/3, p. 42; (b) H. Söll, *ibid.*, 1958, vol. 11/2, p. 159.

¹⁷ A. Weller in "Progress in Reaction Kinetics," Pergamon, 1961, vol. 1, p. 187; V. G. Krishna and L. Goodman, *J. Amer. Chem. Soc.*, 1961, **83**, 2042; H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, 1965, **30**, 964; E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234; G. Porter and P. Suppan, *Pure and Appl. Chem.*, 1964, **9**, 499; W. Bartok, R. B. Hartman, and P. J. Lucchesi, *Photochem. and Photobiol.*, 1965, **4**, 499.

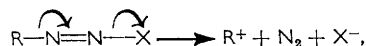
¹⁸ R. Huisgen, *Angew. Chem.*, 1955, **67**, 439; D. Bethell and R. D. Howard, *Chem. Comm.*, 1966, 94, and references therein cited.

¹⁹ R. Huisgen and C. Rüchardt, *Annalen*, 1956, **601**, (a) p. 1, (b) p. 21.

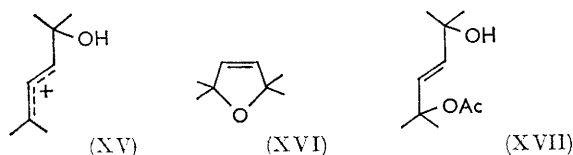
²⁰ H. Zollinger, "Diazo and Azo Chemistry," Interscience, New York, 1961, (a) p. 120, (b) p. 99.

²¹ E. H. White and C. A. Aufdermarsh, *J. Amer. Chem. Soc.*, 1961, **83**, 1179, and earlier Papers.

for the possibility of a concurrent, synchronous fragmentation of the covalent species:



a process important for systems related to secondary, and more stable, carbonium ions.²² Thus, protonation initiates a pinacolic deamination^{16b, 20b, 23} sequence leading to the epoxide (VIII) and the ester (X). Since the epoxide was stable under the reaction conditions, the formation of ester by subsequent reaction of the epoxide with acetic acid is unimportant. The precursor of the epoxide and ester is presumably the allylic carbonium ion (XV): the absence of any product of skeletal rearrangement and the formation of much epoxide are features characteristic of the deamination of 1,2-aminoalcohols when the initial carbonium ion is relatively stable. (Numerous examples are given by Zollinger^{20b} and Söll;^{16b} for similar examples in the reactions of 1,2-glycols see Collins.²⁴) We could not detect the allylic



isomers, (XVI) and (XVII), of our products, and this would seem best explained in the terms used in connection with the decomposition of *N*-nitrosoamides with predominant retention of configuration,^{21, 25} and applied by Ridd²³ to the extensive formation of unrearranged products in the deamination, in acetic acid, of allylic amines²⁶ (cf. also, the formation of unrearranged esters in the reaction of 1-diazobut-2-ene and 3-diazobut-1-ene with 3,5-dinitrobenzoic acid²⁷). Essentially, this explanation is that nitrogen loss is followed so fast by collapse of the carbonium-carboxylate ion-pair that the products are governed to a large extent * by the geometry of the preceding diazo-ester.

In the irradiations in the absence of acid, the epoxide is probably formed by intramolecular insertion in the O-H bond of the carbene (XIII). Proton transfer from tertiary hydroxyl at the diazo-compound stage is much less likely, but cannot be rigorously excluded.

EXPERIMENTAL

A Hanovia 500-w medium-pressure, mercury arc lamp was used for photolysis. Unless otherwise stated, n.m.r. and infrared spectra were determined in carbon tetrachloride, the n.m.r. spectra on a Perkin-Elmer 60 Mc. instrument. N.m.r. spectra are usually reported in the form: τ -value (number of protons, multiplicity, coupling constant in c./sec.); multiplicity is indicated by s, d, t, q, and m (singlet, doublet, triplet, quartet, and multiplet, respectively). M. p.s. were determined on a Kofler hot-stage apparatus. "Light petroleum" refers to the fraction

of b. p. 40–60° unless otherwise stated. The "pentane" used for some irradiations was light petroleum (b. p. 30–40°) washed with concentrated sulphuric acid, fractionated through a column of glass helices, and kept over sodium wire. It had b. p. 35–37° and its ultraviolet absorption in a 1 cm. cell was indistinguishable from the baseline down to 220 m μ ; at 215 m μ it had $E_{1\text{cm.}}$ 0.1. Organic solutions were dried over magnesium or sodium sulphate, and were usually evaporated through a Dufton column. 3-Methylbut-1-yn-3-ol, from Koch-Light Laboratories, was used without further purification.

Preparation of 5,5-Dimethylpyrazolenines.—The acetylene (1 mol.) was treated with 2 mol. of a ca. 0.2 M ethereal solution of 2-diazopropane⁵ in an ice-bath and left to warm up to room temperature overnight. Ether, tetramethylethylene, and dimethylketazine were removed on a rotary evaporator, and the residue was distilled or recrystallised as appropriate.

The 1'-hydroxy-1'-methylethyl-adduct (I) crystallised from light petroleum in 20% yield, m. p. 77–79°. Recrystallised from ether, it had m. p. 79.5–80° (Found: C, 62.25; H, 9.4; N, 18.1. $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$ requires C, 62.3; H, 9.15; N, 18.2%); λ_{max} (hexane) 356 and 245 m μ (ϵ 210 and 1800, respectively), λ_{max} (ethanol) 347 and 254 m μ (ϵ 210 and 2090, respectively); n.m.r. (CDCl_3), τ 8.58 (6H, s), 8.35 (6H, s), 7.33 (one H, removed by D_2O), and 3.40 (one H, s); ν_{max} 1635 and (in Nujol) 3100 cm^{-1} .

No isomeric product (II) (<1%) could be detected in the crystallisation liquors by chromatography.

The reaction of 3-acyloxy-3-methylbut-1-ynes with 2-diazopropane proceeds in much better yield (>50%).⁴ Since the pyrazolenine esters can be hydrolysed to compound (I) in ca. 80% yield⁴ (cf. following preparation), the longer procedure gives an overall yield from 3-methylbut-1-yn-3-ol of ca. 40%.

3-(1'-Ethyl-1'-hydroxypropyl)-5,5-dimethylpyrazolenine (VI). The related acetate⁴ (3.90 g.) in methanol (39 ml.) was treated with 2N aqueous sodium hydroxide (10.5 ml.) and kept in the dark at room temperature for 48 hr. Dilution with water (400 ml.) and continuous extraction with ether for 8 hr. gave the hydroxy pyrazolenine (VI) (2.8 g.). Recrystallised from ether-light petroleum (b. p. 60–80°), the product (2.23 g.) formed needles, m. p. 70–71° (Found: C, 65.5; H, 9.9; N, 15.7. $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}$ requires C, 65.9; H, 10.0; N, 15.4%); λ_{max} (hexane) 355 and 248 m μ (ϵ 240 and 2120, respectively), λ_{max} (ethanol) 346 and 254 m μ (ϵ 230 and 2350, respectively); n.m.r. (CDCl_3), τ 9.18 (6H, t, 7), 8.58 (6H, s), 8.05 (4H, q, 7), 7.56 (one H, removed by D_2O), and 3.35 (one H, s).

Photolysis of Hydroxy pyrazolenine (I).—A (Products). The pyrazolenine (I) (1 g.) in ether (30 ml.) and pentane (150 ml.) was irradiated at reflux under nitrogen in a Pyrex flask. A red coloration developed; irradiation was continued until the solution became colourless again (3 hr.). Removal of the solvents through a Dufton column followed by brief evacuation at 20° gave an oil which was distilled into an ice-cooled receiver to give a mixture (400 mg.) of 1-(1'-hydroxy-1'-methylethyl)-3,3-dimethylcyclopropene (VII) and the epoxide described in B below. The mixture had b. p. 39–44°/9 mm., n_D^{20} 1.4362 (Found: C, 75.7; H,

* But not entirely: cf. White's oxygen-18 study.²¹

²² H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, 496.

²³ J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

²⁴ C. J. Collins, *Quart. Rev.*, 1960, **14**, 357.

²⁵ Cf. E. H. White and J. E. Stuber, *J. Amer. Chem. Soc.*, 1963, **85**, 2168.

²⁶ D. Semenow, Chin-Hua Shih, and W. G. Young, *J. Amer. Chem. Soc.*, 1958, **80**, 5472.

²⁷ D. Y. Curtin and S. M. Gerber, *J. Amer. Chem. Soc.*, 1952, **74**, 4052.

11.5. $C_8H_{14}O$ requires C, 76.1; H, 11.2%). The n.m.r. spectrum was a simple summation of the spectra of the cyclopropene (VII) and the epoxide (VIII) (see below); comparison of the relative intensities of several signals indicated a cyclopropene:epoxide ratio of 60:40. The residue from the distillation was not volatile at 130°/9 mm.

The mixture was treated with alkali in an attempt to hydrolyse the epoxide to the diol (XI) and thus obtain a pure sample of the cyclopropene as the sole, low-boiling product. However, the rate of hydrolysis of the epoxide was too slow for convenience, and the pure cyclopropene was best obtained as follows:

The propionic ester (186 mg., obtained as described elsewhere⁴) of the cyclopropene (VII) was shaken in a sealed tube with 2N aqueous sodium hydroxide (1 ml.) and methanol (1.5 ml.) for 36 hr. After the addition of water, the product was collected with pentane, and distilled to give pure 1-(1'-hydroxy-1'-methyl-ethyl)-3,3-dimethylcyclopropene (VII) (80 mg.), b. p. 44–45°/12 mm., n_D^{25} 1.4324 (Found: C, 75.8; H, 11.4. $C_8H_{14}O$ requires C, 76.1; H, 11.2%); ν_{\max} 1745 cm^{-1} (medium intensity, cyclopropene C=C); n.m.r., τ 8.80 (6H, slightly broader than the τ 8.62 signal), 8.62 (6H, s), 7.57 (one H, removed by D_2O), and 3.21 (one H, multiplet, width at half-height 2.5 c./sec.). Samples of the cyclopropene have been stored at room temperature under nitrogen for several months without detectable decomposition.

B (In presence of acetic acid). The pyrazolenine (2.5 g.) was irradiated as above in ether (250 ml.) containing acetic acid (5 ml.) until the 350 $m\mu$ band disappeared (2 hr.). No red colour was observed. The solution was washed (10% sodium carbonate, then brine), and distilled to give fraction A (0.71 g.), b. p. 40–50°/11 mm., and fraction B (1.40 g.), b. p. 100–101°/11 mm. Fraction A, 4,5-epoxy-2,5-dimethylhex-2-ene (VIII), on redistillation (0.675 g. distillate) had b. p. 41–42°/11 mm., n_D^{22} 1.4413 (Found: C, 76.9; H, 11.6. $C_8H_{14}O$ requires C, 76.1; H, 11.2%); n.m.r., τ 8.80 (3H, s), 8.73 (3H, s), 8.23 (6H, overlapping doublets, $J \sim 1$ c./sec.), 6.86 [one H, doublet ($J = 7$ c./sec.) of multiplets (width at half-height 2–3 c./sec.)], and 5.06 [one H, d ($J \sim 7$ c./sec.) of m ($J \sim 1$ c./sec.)]. Fraction B, 4-acetoxy-5-hydroxy-2,5-dimethylhex-2-ene (X), when redistilled had b. p. 102°/11 mm., n_D^{21} 1.4506 (Found: C, 64.5; H, 9.95. $C_{10}H_{18}O_3$ requires C, 64.5; H, 9.7); n.m.r., τ 8.89 (6H, s), 8.24 (6H, overlapping doublets, $J \sim 1$ c./sec.), 7.99 (3H, s), 7.57 (one H, broad), and 4.80 (s, overlapping a multiplet at slightly higher field, integral = 2H).

C [The diazo-compound (IX)]. (i) The pyrazolenine (100 mg.) was irradiated in 5:1 pentane-ether (18 ml.), as above, and aliquots were taken every 5 min. and investigated spectrophotometrically. The 350 $m\mu$ band ($\epsilon \sim 200$) decreased rapidly in intensity and was barely detectable after 25 min., and a band at 487 $m\mu$ appeared, reaching its maximum intensity in 25 min. and becoming indistinguishable from the baseline in 90–100 min. Decay of the 487 $m\mu$ band gave a good first-order linear logarithmic plot over 4 half-lives: $t_{1/2}$ was 18 min. The spectra showed an apparent isosbestic point at 388 $m\mu$ during the first 25 min. Decay of the 487 $m\mu$ band was accelerated to a small, but real, extent by simultaneous irradiation with the ultraviolet lamp and a 250-w tungsten filament lamp. The magnitude of this effect, and the photochemical half-life given above, depended of course on the scale of the experiment and the geometry of the ensemble (both therefore kept constant in these experiments).

The red oil obtained on evaporation at 0° of a partially photolysed solution had a strong infrared band at 2045 cm^{-1} (diazoalkane), which was still distinct, but weak, in a sample stored neat at 0° overnight.

(ii) As estimated by nitrogen evolution on addition of acetic acid to similar solutions irradiated to maximum intensity of the 487 $m\mu$ band, the diazo-compound had ϵ_{\max} 27 at 487 $m\mu$; maximal yields of diazo-compound calculated from ϵ were 65–95%. (In ether alone, λ_{\max} was 498 $m\mu$.) Titration by Feltzin, Restaino, and Mesrobian's method²⁸ underestimated the diazo-compound ($\epsilon_{\text{apparent}}$ 80) since epoxide formation after protonation consumes no acid.

(iii) After irradiation to maximum concentration of the diazo-alkane, a similar solution was heated under reflux (35°) in the dark. Decay of the 487 $m\mu$ band gave an acceptable first-order plot ($t_{1/2}$ 60 min.), but was not studied beyond 1.2 half-lives. Thermal decay was shown to involve partial reversion (ca. 13%) to the pyrazolenine (I), by increase in the intensity of the 350 $m\mu$ band during decomposition. Other decomposition products were not investigated.

(iv) After irradiation of a solution of the pyrazolenine (1 g.) in ether (100 ml.) to maximum concentration of the diazo-compound (72% yield), an excess of ethereal acetic acid was added. The solution was washed free of acid, dried, and distilled to give a fraction (370 mg.), b. p. 40–50°/10 mm., shown by its n.m.r. spectrum to be a mixture of the cyclopropene (VII) and epoxide (VIII) in the ratio 3:7. The second fraction (243 mg.), b. p. 94–95°/10 mm., was identified as the hydroxy-ester (X) by its infrared and n.m.r. spectra.

4,5-Dihydroxy-2,5-dimethylhex-2-ene (XI).—The hydroxy-ester (X) (1.34 g.), in dry ether (50 ml.), was treated with an excess of lithium aluminium hydride at room temperature for 20 hr., then at reflux for 1 hr. Addition of moist ether followed by aqueous acid, and continuous extraction with ether for 6 hr., gave an oil which was filtered in 1:1 ether-light petroleum through silica gel and distilled. The diol (XI) (0.73 g.) had b. p. 92°(bath)/7 mm., $n_D^{20.5}$ 1.4631 (Found: C, 65.8; H, 11.0. $C_8H_{16}O_2$ requires C, 66.6; H, 11.2%); n.m.r., τ 8.94 (6H, s), 8.29 and 8.24 [6H, doublets ($J \sim 1$ c./sec.)], further fine structure being revealed at high resolution, 6.69 (2H, broad, removed by D_2O), 5.98 (one H, d, 9), and 4.82 [one H, doublet ($J = 9$ c./sec.) of multiplets ($J \sim 1$ c./sec.)].

5-Hydroxy-4-methoxy-2,5-dimethylhex-2-ene (XII).—Treatment of the epoxide (VIII) with a 10% solution of potassium hydroxide in 1:1 methanol-water at 50° overnight, followed by continuous extraction with ether gave the methoxy-alcohol (XII), b. p. 60–70°(bath)/10 mm. (Found: C, 68.2; H, 11.5. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%); n.m.r., τ 8.95 (6H, s), 8.27 (3H, d, ~ 1), 8.19 (3H, d, ~ 1), 7.56 (removed by D_2O), 6.78 (3H, s), 6.42 (one H, d, 10), and 4.98 [one H, doublet ($J = 10$ c./sec.) of multiplets ($J \sim 1$ c./sec.)]; ν_{\max} 2825w and 1090s cm^{-1} (OMe).

Effect of Acid on the Epoxide (VIII).—The epoxide (0.30 g.) was irradiated at reflux in ether (50 ml.) containing acetic acid (1 ml.) for 2 hr. The usual work-up followed by distillation gave recovered epoxide (0.24 g.).

(A. C. D.) THE DYSON PERRINS LABORATORY,
OXFORD UNIVERSITY.

(M. C. W.) DEPARTMENT OF ORGANIC CHEMISTRY,
UNIVERSITY OF BRISTOL.

[6/427 Received, April 5th, 1966]

²⁸ J. Feltzin, A. J. Restaino, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, 1955, **77**, 206.