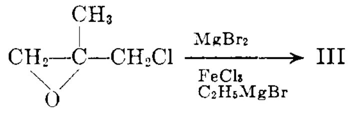
urethane, m.p. 130.0–130.5°, *anal.* C, 78.75; H, 5.55; N, 4.41 and a *p*-nitrobenzoate, m.p. 102.0–102.5°, *Anal.* C, 67.38; H, 4.59; N, 4.84.

Cyclopropyl acetates may also be prepared by the addition of iodomethylzinc iodide to enol esters.[9] In this way 1-methylcyclopropyl acetate was formed in low yield from isopropenyl acetate. Hydride reduction and gas chromatographic purification gave a colorless liquid, b.p. 103°, which was assigned the structure III on the basis of infrared and NMR spectrum and its ready conversion by alkali to methyl ethyl ketone.

Cottle[1,2] prepared cyclopropanol from epichlorohydrin, magnesium bromide, ferric chloride, and ethylmagnesium bromide. The mechanism of this conversion is obscure and its applicability to the preparation of other cyclopropanols has never been tested. We have found that III can conveniently be prepared in 35% yield by this method from 2-methylepichlorohydrin.



These results make it clear that cyclopropanols are stable molecules, readily prepared and purified. Extension of these methods to the preparation of other cyclopropanols of interest is being investigated.

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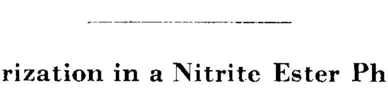
(10) National Science Foundation Cooperative Fellow, 1959–60.

Epimerization in a Nitrite Ester Photolysis

Sir:

An elegant method for functionalizing an "unactivated" aliphatic site was recently reported by Barton, Beaton, Geller, and Pechet.[1] The method involves photochemical rearrangement of a nitrite ester to an oximino alcohol, and its power as a synthetic tool has been convincingly demonstrated.[2,3]



In connection with research in the caryophyllene-humulene field we have been investigating the constitution of "α"-caryophyllene alcohol[4] and have used the nitrite reaction as a degradative step. We have encountered in our work a case in which the *C—O bond undergoes a change of configuration* in the course of the nitrite→oximino alcohol transformation. Because of the significance of this finding to those who may use the nitrite reaction in synthesis or in structural studies we wish to report relevant experiments that establish this configurational change, even though we are not ready to propose complete structures for our compounds.

"α"-Caryophyllene alcohol (henceforth abbreviated "α"-alcohol; $C_{15}H_{26}O$, m.p. 118.5–119.5°[5]; 3,5-dinitrobenzoate, m.p. 176.5–177°) was prepared as reported[4a] and was oxidized (97%) to a ketone $C_{15}H_{24}O$ (m.p. 40.5–41.5°; 2,4-dinitrophenylhydrazone m.p. 158.5–159°). This ketone responded negatively to several tests for enolizable hydrogens, and its infrared band at 1742 cm.$^{-1}$ (carbon tetrachloride) indicates a strained carbonyl comparable to that in a five-membered ring. Reduction of the ketone with sodium in 2-propanol regenerated "α"-alcohol (87%), whereas hydrogenation (platinum/ethyl acetate/perchloric acid) gave in about equal amounts "α"-alcohol and a liquid, isomeric alcohol (designated *epi*-"α"-alcohol) whose 3,5-dinitrobenzoate has a m.p. of 129.5–130.5°. The epimeric alcohols are readily separated by chromatography and can be differentiated by infrared spectroscopy. Oxidation of *epi*-"α"-alcohol with chromium trioxide reformed the original ketone (80%). These experiments show that "α"-alcohol and *epi*-"α"-alcohol are epimeric secondary alcohols.

Nitrosation of *epi*-"α"-alcohol (sodium nitrite in acetic acid) gave the crude *epi*-nitrite as a liquid [ν (carbon tetrachloride) 1642, 1621, 915 cm.$^{-1}$] from which *epi*-"α"-alcohol could be regenerated by saponification. Irradiation of this *epi*-nitrite in benzene with a mercury lamp gave an oximino alcohol $C_{15}H_{25}O_2N$ (m.p. 226.5–227° dec., ν (potassium bromide) 3500, 1632 cm.$^{-1}$; yields, 50–60%). Acid hydrolysis of the oxime provided the corresponding keto alcohol $C_{15}H_{24}O_2$ [m.p. 98.5–

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(1) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960).

(2) D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **82**, 2641 (1960); D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **83**, 750 (1961).

(3) An alternate photolytic pathway has been discovered for the case of steroid C-17β nitrites (C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto, and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961)).

(4) Y. Asahina and T. Tsukamoto, *J. Pharm. Soc.* (*Japan*), **484**, 463 (1922); (b) J. Bell and G. G. Henderson, *J. Chem. Soc.*, 1971 (1930); (c) D. H. R. Barton, T. Brunn, and A. S. Lindsey, *J. Chem. Soc.*, 2210 (1952); (d) D. H. R. Barton and A. Nickon, *J. Chem. Soc.*, 4665 (1954); (e) S. Dev, *Current Sci.* (*India*), **20**, 296 (1951).

(5) Satisfactory analyses were obtained for all compounds whose melting points are reported here.

99.5°; ν (carbon tetrachloride) 3636, 3350, 1733 cm.$^{-1}$; no aldehydic H *via* infrared or NMR]. That the same carbon skeleton is in hand was shown by Wolff-Kishner reduction of the keto alcohol to *epi*-"α"-alcohol (85%), identified by infrared as well as by melting point, mixture melting point, and infrared of the derived 3,5-dinitrobenzoate.

Similar nitrosation of "α"-alcohol gave the corresponding nitrite [ν (carbon tetrachloride) 1650, 1623, 928 cm.$^{-1}$] as a low-melting solid (m.p. 25–26°) which reverts to "α"-alcohol on saponification. Irradiation of this nitrite produced the *same oximino alcohol* (yields, 40–67%) as was obtained from the *epi*-series. Identification was secured by melting point, mixture melting point, and infrared, and also by hydrolysis to the same keto alcohol obtained before.

These transformations establish that in the photo-rearrangement of "α"-caryophyllene alcohol nitrite the C—O bond undergoes change from its original configuration to the *epi*-configuration.

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