for an individual acid showed no systematic variation even though the salt concentration varied from about 0.0037*M* to 0.022*M*.

Using the σ values for p-Br, p-NO_2, p-CH_3O, p-CH_3, and H tabulated by McDaniel and Brown[2] the following relation between σ and pK_a for the ionization of substituted benzoic acids in 25% water- 75% methanol by volume at 39.8° was determined using the least squares procedure.

$$pK^x_a = -1.339\,\sigma_x + 5.947$$

This equation can be used to calculate σ values from pK_a's. Inserting the pK_a values of *m*- and *p*-benzoylbenzoic acids, one obtains[9]:

$$\sigma(m\text{-}C_6H_5CO) = +0.343$$

$$\sigma(p\text{-}C_6H_5CO) = +0.429$$

Comparing these with the σ values for *m*- and *p*-acetyl[2] (+0.376 and +0.502, respectively) it is obvious that the benzoyl group is not quite as strong an electron-withdrawing substituent as the acetyl group. This may be due to reduction of the electronegative character of the carbonyl in the benzoyl group by its conjugation with the phenyl ring from which it can withdraw electrons by resonance.

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(9) The constants obtained for acetamino groups using the same equation are σ (p-CH_3CONH) = −0.086 and σ (m-CH_3CONH) = +0.102. The values reported by McDaniel and Brown (Ref. 2) are 0.00 and +0.21 respectively.

Communications TO THE EDITOR

Hydrazine Reduction of α,β-Epoxy Ketones to Allylic Alcohols

Sir:

A preliminary investigation has demonstrated a useful, general, and previously unobserved reductive reaction of hydrazine with α,β-epoxy ketones.[1] The reaction is, in effect, an eliminative Kishner reduction of an α-substituted ketone,[2] *proceeding rapidly at room temperature* with the evolution of nitrogen and formation of an allylic alcohol.

Although optimum conditions remain to be determined, the reduction can be carried out in alcohol solution containing two to three equivalents of hydrazine hydrate and *ca.* 0.2 equivalents of acetic acid. Under these conditions the reaction mixture becomes slightly warm and evolution of nitrogen is effectively complete *in five minutes:* isophorone oxide[3] (89%),[4] 2,3-epoxycyclohexanone[5] (75%), 2,3-epoxybutanone[5a] (50%), glycidaldehyde[6] (20%). A useful alternative procedure, simply treating with excess hydrazine hydrate, can be applied to the reduction of α,β-epoxy ketones only slightly soluble in hydrazine hydrate: 4β,5-epoxy-3-coprostanone[7] (90%), isophorone oxide (69%). However, using this procedure the more soluble epoxy ketones give relatively poor yields: 2,3-epoxycyclohexanone (26%), 2,3-epoxybutanone (5%).

The reaction of hydrazine with α,β-epoxy ketones was investigated when a current study necessitated the preparation of certain sesquiterpenoid precursors containing the $\Delta^{1,2}$-9-octalol system. It was thought that an effective route[8] to this system might be a simple oxidation-reduction sequence starting from the available $\Delta^{1,9}$-2-octalones.[9] The oxidation step, epoxidation of the enone to the epoxy ketone, is an established synthetic method,[10] and the reduction step, the subject of this communication, was therefore first attempted with a known model compound, 4β,5-epoxy-3-coprostanone (I).

A two-phase mixture of I (7 g.) and excess hydrazine hydrate, with no added solvent or base, rapidly evolved a gas (90% yield) on heating to

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(1) The only products isolated from reported reactions of α,β-epoxy ketones with hydrazine itself are of the same type as those obtained from substituted hydrazines, namely pyrazolines and pyrazoles. See T. L. Jacobs, *Heterocyclic Compounds*, Vol. 5, R. C. Elderfield, ed., Wiley, New York, 1957, p. 68.

(2) For a review of the eliminative Kishner reduction of α-substituted ketones see N. J. Leonard and S. Gelfand, *J. Am. Chem. Soc.*, **77**, 3272 (1955).

(3) G. B. Payne, *J. Org. Chem.*, **24**, 719 (1959); R. L. Wasson and H. O. House, *Org. Syntheses*, **37**, 58 (1957).

(4) Yields are based on nitrogen evolution unless otherwise specified. Nitrogen was identified mass spectroscopically and measured volumetrically.

(5) (a) N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, **80**, 5845 (1958); (b) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957).

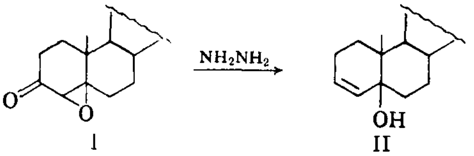
(6) Supplied by Shell Development Co., Emeryville. Calif.; purity not established.

(7) J. I. Shaw and R. Stevenson, *J. Chem. Soc.*, 3549 (1955).

(8) A reasonable but more involved synthesis might be: Δ(1,9)-2-octalone → Δ(1,9)-octalin → Δ(1,2)-9-octalol. See V. Georgian, R. Harrisson, and N. Gubisch, *J. Am. Chem. Soc.*, **81**, 5834 (1959) and G. O. Schenk and O. A. Neumüller, *Ann.*, **618**, 194 (1958).

(9) E. D. Bergmann, *Org. Reactions*, **X**, 179 (1959).

(10) First investigated by E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921). See also refs. 3 and 5 and G. B. Payne, *J. Org. Chem.*, **26**, 250 (1961).



I II

90° for 10 min. followed by refluxing (118°) for a further 15 min. A single crystallization of the crude product from methylbutane at −15° yielded needles of the desired 3-coprosten-5-ol (II) in 68% yield, m.p. 89–91°: analytical sample, m.p. 93.5–94.5°, $[\alpha]_D^{23}$ + 98° (chloroform) (*c* 2.9), $\lambda_{max}^{CS_2}$ 2.75 μ (found: C, 83.58; H, 11.93). The tertiary allylic alcohol II was characterized by its facile dehydration which was readily demonstrated in acidic 95% ethanol (*ca.* 0.05*N* in hydrochloric acid): the characteristic maxima of 3,5-cholestadiene (228, 235, and 242 mμ)[11] appeared in the ultraviolet spectrum and increased in intensity over a period of several hours. Hydrogenation of II with platinum oxide in ethanol proceeded rapidly at room temperature with the uptake of one equivalent of hydrogen and yielded coprostan-5-ol,[12] (99%), m.p. 79–81°, $[\alpha]_D^{23}$ +35° (chloroform) (*c* 3.2), $\lambda_{max}^{CS_2}$ 2.75 μ.

The mild conditions necessary for the rapid succession of steps which presumably involve hydrazone formation, opening of the epoxide and *elimination of nitrogen*[13] were even more strikingly demonstrated when it was found that the reaction of hydrazine with other α,β-epoxy ketones proceeded at room temperature in alcohol solutions in the presence of acetic acid. Preparatively, using these conditions, 1,5,5-trimethyl-2-cyclohexen-1-ol, b.p. 59.0–60.5° (6 mm.), was readily isolated in 66% yield from the reduction of isophorone oxide (10 g.): analytical sample, b.p. 60.5–61.0° (7 mm.), n_D^{27} 1.4653, $\lambda_{max}^{CCl_4}$ 2.8 and 2.9 μ (found: C, 76.87; H, 11.28). Hydrogenation with platinum oxide in ethanol resulted in the uptake of one equivalent of hydrogen and yielded 1,3,3-trimethylcyclohexan-1-ol[14] (78%), m.p. 71.5–72.5°, $\lambda_{max}^{CCl_4}$ 2.8 and 2.9 μ.

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[11] H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

[12] A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 4604 (1957).

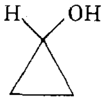
[13] The closely related (but nonreductive) reaction of α-halo ketones with substituted hydrazines also occurs under very mild conditions: V. R. Mattox and E. C. Kendall, *J. Am. Chem. Soc.*, **72**, 2290 (1950).

[14] A. W. Crossley and C. Gilling, *J. Chem. Soc.*, 2218 (1910); K. v. Auwers and E. Lange, *Ann.*, **401**, 303 (1913).

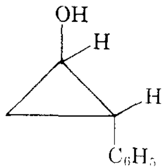
The Synthesis of Cyclopropanols

Sir:

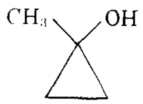
Although cyclopropanol and simply substituted cyclopropanols would be of interest for numerous synthetic and mechanistic studies, no general methods for their preparation are available. Cyclopropanol itself, in very impure form, was prepared by Cottle and co-workers,[1,2] and again in low yield and also impure by Roberts and Chambers,[3] but neither method appeared applicable for the synthesis of substituted cyclopropanols of known structure.[4] We wish to report the synthesis of cyclopropanol (I), *trans*-2-phenylcyclopropanol (II), and 1-methylcyclopropanol (III) by methods which are general enough to be extended to the synthesis of other cyclopropanols.



I



II



III

Our initial interest in the isolation and investigation of cyclopropanols was aroused by the observation that cyclopropanol accumulates during the basic hydrolysis of cyclopropyl acetate,[5] despite its known sensitivity to alkali.[1] Lithium aluminum hydride reduction of the acetate in ether, followed by careful work-up and purification by isolative gas chromatography gave cyclopropanol as a colorless, stable, water-soluble liquid. Its derivatives agreed in melting point with those reported by Cottle.

This method of synthesis was extended to the preparation of II and III. *trans*-2-Phenylcyclopropanecarboxylic acid[6] was converted in good yield to the methyl ketone by reaction with methyllithium[7] and thence to *trans*-2-phenylcyclopropyl acetate with peroxytrifluoroacetic acid.[8] Reaction with lithium aluminum hydride, or better still, with methyllithium, gave II, b.p. 75°/0.2 mm., m.p. 41.5–42.0°. Although II decomposes slowly, its structure was supported by its infrared and NMR spectrum. It readily formed a 1-naphthyl

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[1] J. K. Magrane and D. L. Cottle, *J. Am. Chem. Soc.*, **64**, 484 (1942).

[2] C. W. Stahl and D. L. Cottle, *J. Am. Chem. Soc.*, **65**, 1782 (1943).

[3] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).

[4] At least one natural product contains a cyclopropanol ring. P. Lipp and C. Padberg., *Ber.*, **54**, 1316 (1921).

[5] L. R. Mahoney, Ph.D. Thesis, Iowa State University, 1960.

[6] M. Julia, S. Julia and B. Bémont, Compt. Rend., **245**, 2304 (1957).

[7] C. Tegner, Acta Chem. Scand., **6**, 782 (1952).

[8] W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).