3 - acetoxy - 7α - fluoro - 1,3,5(10) - estratriene - 6,17-dione. The orientation and configuration of the substituents at C-6 and C-7 of X point to the intermediate B′ in the formation of X by bident α-attack of PF on IX.[7a,c]

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SYNTHESIS OF CYCLOPROPENONES BY A MODIFIED FAVORSKII REACTION

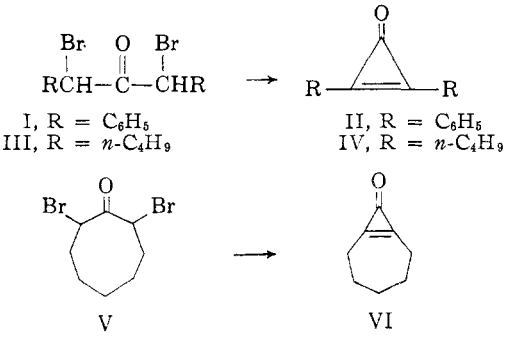
Sir:

The Favorskii reaction of α-haloketones with base has been shown to proceed through an intermediate with the symmetry of a cyclopropanone in at least some cases.[1,2,3] We wish to report[4] that under some conditions a cyclopropanone can be intercepted, when the starting material is a dibromo ketone, by dehydrobromination to the very stable cyclopropenone system. This is much more convenient than the types of syntheses reported previously[5,6,7] for cyclopropenones.

Treatment of α,α'-dibromodibenzyl ketone (I) (either the pure isomer, m.p. 112–114°,[8] or the mixture of *d,l*- and *meso*-compounds, m.p. 79–85°) with excess 20% triethylamine in methylene chloride at room temperature for 30 min. affords 50–60% yields of diphenylcyclopropenone (II),[5,6] best isolated by silica gel chromatography. The reaction also can be applied to the synthesis of cyclopropenones bearing only aliphatic substituents. Thus α,α'-dibromodi-*n*-amyl ketone (III) b.p. 101–106° (0.7 mm.), ($C_{11}H_{20}OBr_2$: C, 40.26; H, 6.14; Br, 48.72. Found: C, 40.46; H, 6.41; Br, 48.42; n.m.r. shows that this is a mixture of the *meso* and *d,l* compounds, with triplets at 5.45 and at 5.60 τ in addition to the other expected peaks), was treated with a 40:1 mixture of chloroform and triethylamine at reflux for 48 hr. A 12% yield of dibutylcyclopropenone (IV) was obtained, b.p. 95–97° (0.3 mm.) ($C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.72; H, 11.27). In the infrared the compound has the expected absorption at 1850 and 1660 cm.$^{-1}$; in the n.m.r. the methylenes attached to the cyclopropene ring are found as a triplet at 7.6 τ, with the remaining protons as a multiplet at 8.6 τ (methylenes) and a triplet at 9.15 τ (methyls).

The reaction can be extended to prepare other dialkylcyclopropenones. Interestingly, it also can be applied to dibromocycloöctanone. When 2,8-dibromocyclooctanone[9] (V) was heated under N_2 at 90° in a closed system with a 50% excess of 5% triethylamine in chloroform a 50% yield of cycloheptenocyclopropenone (VI) was obtained, m.p. 52–53° ($C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.85; H, 8.15). The material sublimes at 45° (1.5 mm.). In the infrared the compound shows the expected strong bands at 1840 and 1640 cm.$^{-1}$, and the n.m.r. spectrum confirms the structure. A four-proton triplet at 7.45 τ is assigned to the methylene groups attached to the ring, while a six-proton multiplet at 8.22 τ is found for the remaining protons. With refluxing aqueous KOH solution this compound affords cycloheptene-1-carboxylic acid, identical with an authentic sample.[9] It is hoped that VI may serve as a source of gas-phase cycloheptyne; in common with other cyclopropenones[5,6,7] VI loses carbon monoxide on pyrolysis, although in the case of VI rather high temperatures (250°) are required. Among other products, a 16% yield of tris-cycloheptenobenzene can be isolated from this pyrolysis, m.p. 184–185° ($C_{21}H_{30}$: C, 89.47; H, 10.48; mol. wt., 282. Found: C, 89.29; H, 10.71; mol. wt., 279, CCl_4 vapor pressure). In the ultraviolet the benzene has λ_{max} 274 mμ (ϵ = 262) while the n.m.r. spectrum shows the expected multiplets centered at 7.30 and 8.45 τ in a ratio of 2:3.

So far we have failed to prepare either unsubstituted cyclopropenone or cyclohexenocyclopropenone by application of our reaction conditions to appropriate haloketones. However, in both of these cases the difficulty might well lie with instability of the desired products rather than any failing of the synthetic method. Accordingly, our procedure promises to be of general use in the preparation of cyclopropenones.



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THE CHEMISTRY OF BLUENSOMYCIN. II. THE STRUCTURE OF BLUENSOMYCIN

Sir:

A previous communication[1] gave the structure of bluensidine, one of the two products obtained by methanolysis of the antibiotic bluensomycin. The identity of the second fragment is now described, and a structure for bluensomycin is proposed.

This second fragment (I) (colorless prisms from methanol–ether, m.p. 108–111°, $[\alpha]^{25}D$ −147° (*c*,1, water), $C_{14}H_{26}O_8N$,[2] one C-CH_3, one N-CH_3 (pK_a' 7.87) and one O-CH_3 group) appeared to be the methyl glycoside of an aminodisaccharide. Acetylation (pyridine–acetic anhydride) gave colorless prismatic needles (II), m.p. 195.5–197°, $[\alpha]^{25}D$ −124° (*c*, 1, $CHCl_3$). Analysis of this neutral product indicated $C_{12}H_{15}O_4(OCOCH_3)_4(N\langle^{CH_3}_{COCH_3}\rangle)(OCH_3)$. A close similarity was found to exist between the properties of II and those reported for methyl pentaacetyldihydrostreptobiosaminide, obtained by several laboratories from the methanolysis of dihydrostreptomycin.[3–6] Since

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(2) G. Stork and I. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960); H. House and W. F. Gilmore, *ibid.*, **83**, 3972, 3980 (1961).

(3) A. W. Fort, *ibid.*, **84**, 2620, 2625 (1962).

(4) Reported in part at the 17th National Organic Symposium, Bloomington, 1961. Support of this work by the National Science Foundation, the Petroleum Research Foundation, and the Sloan Foundation is gratefully acknowledged.

(5) R. Breslow, R. Haynie and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

(6) M. Volpin, Yu. Koreshkov and D. Kursanov, *Izvest. Akad. Nauk*, SSSR, 560 (1959).

(7) R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960).

(8) E. Bourcart, *Chem. Ber.*, **22**, 1368 (1889). In this paper it is reported that treatment of the ketone with ethanolic magnesia yields a compound with empirical formula $C_{18}H_{16}O$, but the product is not described further!

(9) G. Hesse and F. Urbanek, *Chem. Ber.*, **91**, 2733 (1958).

(1) B. Bannister and A. D. Argoudelis, *J. Am. Chem. Soc.*, **85**, 119 (1963)

(2) Analytical values for all the compounds described in this paper were consistent with the indicated formulas.