

m.p. 145–163° dec. Alternatively, to a solution of silver perchlorate in thiophene was added methyl iodide, and the reaction mixture was treated as above. *Anal.* Calcd. for $C_6H_7SPF_6$: C, 24.7; H, 2.9; S, 13.2; PF_6 , 59.6; mol. wt., 244. Found: C, 24.8, 24.9; H, 2.9, 3.0; S, 14.3, 15.0; PF_6 , 59.3, 59.4; mol. wt. 247. The ultraviolet absorption spectrum showed: $\lambda_{max}^{H_2O}$ 225 (log E 3.49), 269 $m\mu$ (2.75); since hexafluorophosphate anion does not absorb in the 200–400 $m\mu$ region, the spectrum is that of the thiophenium cation. The infrared spectrum included peaks at λ_{max}^{KBr} 3.2 (assigned to the onium methyl C–H) and 14.0 μ (aromatic C–H out-of-plane vibration).²

The n.m.r. spectrum (DCO_2D) shows a singlet at δ 3.28³ which we ascribe to the S–CH₃ hydrogens and a singlet with a slightly broadened base at δ 7.65 (ring hydrogens) present in the ratio 4:3. A weak band at δ 3.24 also appears and must be due to the methyl deuteroformate formed by alkylation of the solvent by the thiophenium salt. In repetitive scans of the sample this band showed increasing intensity and the bands at δ 7.15 and 2.80 decreased (but retained their relative intensities); at the same time, the characteristic multiplet of thiophene centered around δ 6.9 (barely distinguishable from noise in the first spectrum of the series) became more pronounced.

Hydrogenation of I over palladium yielded a tetrahydro derivative whose infrared spectrum was identical with that of the sulfonium fluorophosphate prepared from thiophane, methyl iodide, and sodium hexafluorophosphate. *Anal.* Calcd. for $C_6H_{11}SPF_6$: C, 24.3; H, 4.5. Found: C, 24.1, 23.9; H, 4.5, 4.5.

Acknowledgment.—This work was supported in part by an institutional grant to New York University from the American Cancer Society. We wish to thank Mr. John Olsen for technical assistance.

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 75.

(3) Since tetramethylsilane reacted with the methylthiophenium ion, chemical shifts were determined with reference to the methyl peak of DCO_2CH_3 and corrected to a TMS internal standard.

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Selective Reduction of Polyhalogenated Olefins with Sodium Borohydride

Sir:

We wish to report that the reaction of polyhalogenated olefins with sodium borohydride in diglyme at 0° provides a selective reduction of vinylic halogen to yield monohydropolyhalogenated olefins.¹

In this way 1,2-dichlorohexafluorocyclopentene has been converted in a yield of 88% to 1-hydro-2-chlorohexafluorocyclopentene, b.p. 77.5° (746 mm.), n_D^{20} 1.3432, C=C at 1635 cm^{-1} .³ The proton magnetic

(1) In contrast to the formation of olefins in these reactions, Wartik and Pearson² found that the sodium borohydride reduction of vinyl bromide and allyl bromide yielded dialkylboranes.

(2) T. Wartik and R. K. Pearson, *J. Inorg. Nucl. Chem.*, **5**, 250 (1958).

(3) J. A. Sedlak, Ph.D. Thesis, Ohio State University, 1960, reports b.p. 75.2–76.9°, C=C 1637 cm^{-1} .

resonance spectrum⁴ exhibited a complex multiplet at τ 3.50 in agreement with the structure containing a vinylic proton. In a similar manner, 1,2-dichlorotetrafluorocyclobutene was converted in 83% yield to 1-hydro-2-chlorotetrafluorocyclobutene, b.p. 59.5° (744 mm.), n_D^{20} 1.3463, C=C 1596 cm^{-1} , vinyl proton multiplet at τ 3.33,⁵ and octafluorocyclopentene was converted in 73% yield to 1-hydroheptafluorocyclopentene, b.p. 45.5° (748 mm.), n_D^{20} 1.297, C=C 1695 cm^{-1} , vinyl proton multiplet at τ 4.07.⁶ When 1-chloroheptafluorocyclopentene was subjected to the reduction reaction, 1-hydro-2-chlorohexafluorocyclopentene was obtained in 88% yield by the preferential reduction of vinylic fluorine.

The smooth reduction of these olefins by borohydride contrasts with similar reported reductions with lithium aluminum hydride. Tatlow and co-workers⁷ have reported that the reduction of decafluorocyclohexene with lithium aluminum hydride yielded a mixture of eight reduction products formed by vinylic reduction and subsequent rearrangements of the starting olefin and the reduced olefins. Similarly, Sedlak³ has reported that reduction of 1,2-dichlorohexafluorocyclopentene with lithium aluminum hydride yielded only uncharacterized high boiling material and no simple reduction products. In comparison, the mild reduction observed with sodium borohydride provides a convenient route to polyfluorinated olefins containing vinylic hydrogen. Examination of the scope of this reaction is continuing.

The number of hydrides of the borohydride ion active in the reduction reaction has been found in these examples to be dependent upon the substituents on the olefinic bond. The mole ratio of borohydride to olefin required to effect optimum conversion of the olefin to the monoreduction product was found to be 1:1 for the olefins containing the $-CCl=CCl-$ grouping, 1:2 for the $-CF=CF-$ grouping, and 1:3 for the $-CF=CCl-$ grouping. When the mole ratio of borohydride to olefin exceeded these ratios, the yield of the monoreduction product decreased.

The following procedure is typical. In a four-necked flask was placed 25 ml. of dry diglyme (distilled from $LiAlH_4$) and 22.8 g. (100 mmoles) of 1-chloroheptafluorocyclopentene. This mixture was cooled to 0° and 34.3 ml. of 0.97 M sodium borohydride (33.3 mmoles) in diglyme was added dropwise⁸ keeping the temperature below 5°. After the addition of the borohydride was completed, the reaction mixture was stirred at 0° for an additional 0.5 hr. and then cautiously

(4) The proton magnetic resonance spectra were obtained with a Varian A60 spectrometer. The spectra were run on the pure liquids containing tetramethylsilane as an internal standard. In all cases, the proton resonance was observed as a complex multiplet due to coupling with the fluorines. The reported values are the center position of these multiplets.

(5) J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963), reported b.p. 53.8–54° (625 mm.), n_D^{20} 1.3452, C=C 1587 cm^{-1} .

(6) R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 281 (1963), report b.p. 46°, C=C 1696 cm^{-1} .

(7) D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *ibid.*, 4828 (1963).

(8) During the addition of the borohydride solution 12 mmoles (corrected to S.T.P.) of hydrogen was evolved. The source of this hydrogen is not readily apparent but was observed in all these reactions and was most pronounced in the reaction of the olefins containing the $-CCl=CCl-$ grouping (33 mmoles of H_2 was evolved when 100 mmoles of 1,2-dichlorohexafluorocyclopentene was treated with 100 mmoles of $NaBH_4$ solution). The large amounts of hydrogen evolved cannot be due to the scavenging of water by active hydride in the reaction mixture since, in several different reactions, the amount of hydrogen evolved increased in a progressive manner as the reaction was scaled up in size.

hydrolyzed by the addition of water.⁹ After complete hydrolysis, the reaction mixture was poured into 50 ml. of ice-water and the organic layer was separated. Gas chromatographic analysis of the organic phase on a silicone rubber column showed the presence of 88 mmoles (88%) of 1-hydro-2-chlorohexafluorocyclopentene, 4 mmoles (4%) of 1,2-dihydrohexafluorocyclopentene, and 4 mmoles (4%) of unreacted 1-chloroheptafluorocyclopentene. The 1-hydro-2-chlorohexafluorocyclopentene was isolated by fractionation in a 36-in. spinning-band column.

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(9) In this reaction only 4 mmoles of hydrogen (corrected to S.T.P.) was evolved on hydrolysis. In the reactions of the olefins containing the $-\text{CF}=\text{CF}-$ and the $-\text{CCl}=\text{CCl}-$ groupings, much larger amounts of hydrogen were generated on hydrolysis, and the addition of water should be carried out cautiously.

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A New C-D Ring Cleavage of Dihydrocorynantheine Derivatives. The Partial Synthesis of the Dihydroburnamicine Ring System¹

Sir:

Several examples of 2-acylindole alkaloids have recently been found and a 2-acylindole alkaloid has been suggested as an intermediate in the biogenesis of echitamine.²⁻⁴ We wish to report a new C-D ring cleavage of dihydrocorynantheine which produces the 2-acylindole chromophore and has been used in the partial synthesis of dihydroburnamicine.

The action of lead tetraacetate in benzene solution transforms dihydrocorynantheine to the expected 7-acetoxy-7H-dihydrocorynantheine, m.p. 180–181°, in 23% yield based on unrecovered dihydrocorynantheine.⁵ The acetoxyindolenine afforded the corresponding N_b-methiodide, I, m.p. 206° dec., upon exposure to methyl iodide. Hydrolysis of 7-acetoxy-7H-dihydrocorynantheine methiodide in refluxing aqueous acetic acid containing sodium acetate afforded in 55% yield the 2-acylindole compound II, obtained in two crystalline modifications from ether solution. One form melted at 153–155° (needles) and the other form (prisms) had m.p. 208–209°; they had identical infrared spectra in chloroform solution.

The structure of II is supported by the following observations. The ultraviolet spectrum in ether solutions shows normal 2-acylindole absorption [$\lambda_{\text{max}}^{\text{ether}}$ 307 m μ (ϵ 14,800)] which was changed to normal indole absorption by the addition of acetic acid. In ethanol solution the compound shows only the absorption expected for a normal indole and α -methoxymethylene-carbonyl chromophores. This striking solvent effect

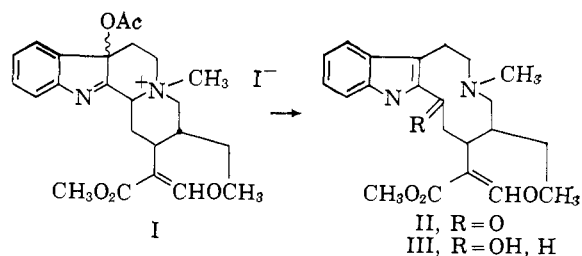
(1) The authors gratefully acknowledge financial support from the National Science Foundation (Grant GP-252) and the National Institutes of Health (Grant NB 03232-03).

(2) M. F. Bartlett and W. I. Taylor, *J. Am. Chem. Soc.*, **85**, 1203 (1963).

(3) U. Renner, D. A. Prins, A. L. Burlingame, and K. Bieman, *Helv. Chim. Acta*, **46**, 2186 (1963); M. P. Cava, S. K. Talapatra, J. A. Weisbach, B. Douglas, and G. O. Dudek, *Tetrahedron Letters*, No. 2, 53 (1963).

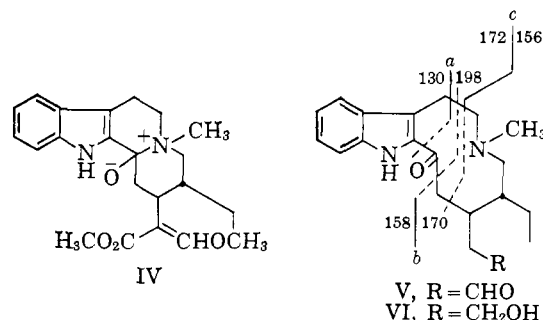
(4) G. F. Smith, *Chem. Ind. (London)*, 1120 (1961).

(5) N. Finch, C. Gemedon, I. Hsu, and W. I. Taylor, *J. Am. Chem. Soc.*, **85**, 1520 (1963).



is ascribed to the formation of an ionic species such as IV in polar solvents. The infrared spectrum (chloroform solution) of II has a strong band at 1640 cm^{-1} consistent with the 2-acylindole structure. The n.m.r. spectrum of II exhibits a sharp signal at τ 8.36 attributed to the N-methyl group. That the N-methyl group should appear at such high field is not unexpected since the N-methyl group of protopine appears τ 8.08.⁶ Compound III has a $\text{p}K_{\text{a}}$ of 9.02 (50% aqueous methanol) which is very close to that reported for burnamicine.²

The 3-keto compound, III, was quite resistant to reduction with sodium borohydride in aqueous methanol. This inertness is ascribed to the formation of the ionic species IV in polar solvents. In accord with this hypothesis, II is smoothly reduced to the corresponding alcohol, III, m.p. 179–180°, in 1,2-dimethoxyethane. The alcohol shows the expected infrared and ultraviolet spectra and its n.m.r. spectrum shows the N-methyl group shifted downfield to τ 7.76.



Saponification and acid-catalyzed hydrolysis of the 2-acylindole III was accompanied by decarboxylation to give in 60% yield the ketoaldehyde V which was used without deliberate purification. The infrared spectrum in chloroform solution showed absorption at 1720 and 1640 cm^{-1} . The ketoaldehyde was converted in 50% yield to dihydroburnamicine⁷ VI by the action of sodium borohydride in aqueous methanol. The dihydroburnamicine obtained in this manner melted at 101–103° after crystallization from benzene. The crystalline material retains benzene which is shown by combustion analysis and its n.m.r. spectrum. The benzene is removed by extended drying at 80° under reduced pressure. The ultraviolet spectrum in ether shows 2-acylindole absorption [λ_{max} 307 m μ (ϵ 13,900)] changed to a normal indole spectrum upon addition of acetic acid. The ultraviolet spectrum in ethanol

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, No. 339.

(7) A direct comparison of our material with the reduction product of authentic burnamicine was not possible since no burnamicine remained from structural studies.² We wish to thank Dr. Taylor for a helpful discussion of this problem. It is not certain that dihydroburnamicine prepared from dihydrocorynantheine has the same absolute configuration at C-15 as authentic burnamicine but biogenetic considerations suggest that this should be the case.