The Structures of Chlorofenchenephosphonic Acid and Chlorobromofenchene

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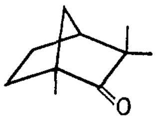
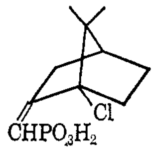
The reactions of pentahalophosphorus with carbonyl compounds have been the subject of a large number of investigations.[1] Recent studies by Newman and coworkers have indicated a number of mechanistic complexities.[2] There may, in fact, be more than one pathway available for these reactions. At least some reaction products are formed *via* α-halocarbonium ions,[2b,3] while in other studies[2a,c] it has been argued that these species are not intermediates. Subtle solvent and temperature effects render the reactions sensitive to experimental conditions.[2]

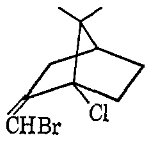
Many years ago, Gardner and Cockburn[4a] reported that reaction between fenchone (**1**) and phosphorus pentachloride affords a *phosphorus*-containing substance, a dibasic acid, $C_{10}H_{14}ClPO(OH)_2$, which they named chlorofenchenephosphonic acid. It was felt that a determination of the structure of this substance would aid in understanding the reactions between pentahalophosphorus and carbonyl compounds; in addition, it was of interest to examine a curious reaction of the phosphonic acid, in which it was reported[4b] that when the sodium salt of the acid was treated with bromine water, a compound $C_{10}H_{14}ClBr$, chlorobromofenchene, was formed. We report at this time spectral evidence supporting structure **2** for the phosphonic acid and **3** for the chlorobromide. The nuclear magnetic resonance (nmr) spectrum of the phosphonic acid consists of a doublet of triplets centered at τ 4.67, (J = 17 and 2.4 cps, respectively) and complex multiplet absorption from τ 7.5 to 9.1; the ratio of the low-field (olefinic) absorption to the aliphatic absorption is 1:13. The 17-cps coupling constant is of the magnitude to be expected for phosphorus–hydrogen couplings through two bonds.[5] The 2.4-cps coupling of the vinyl proton to the two allylic methylene protons in **2** is also of the correct order of magnitude, but the configuration about the double bond cannot be assigned from the nmr data.[6] The nmr spectrum of the chlorobromide is, likewise, consistent with **3**. Its nmr spectrum consists of a triplet at τ 3.73 (J = 2.6 cps), two singlets at τ 8.94 and 9.10, and a complex multiplet from τ 7.2 to 8.8, relative areas 1:3:3:7, respectively. These are assigned respectively to the single vinyl proton, the two nonequivalent methyl groups, and the remaining aliphatic protons in 3. The infrared spectrum supports the structural assignment, with maxima at 6.04 and 3.26 μ (vinyl) and a doublet at 7.24 and 7.31 μ (*gem*-dimethyl). The bridgehead location of the chlorine atom in **3** is consistent with its unreactivity toward hot ethanolic silver nitrate.[4b] Since the nmr spectra of the phosphonic acid and the bromochloride are similar in the aliphatic region, and since the vinyl–allylic coupling is of the same magnitude in both compounds, and also from chemical reasoning (*vide infra*), it is concluded that no skeletal rearrangement occurs during the brominolysis. Support for this contention was obtained by conversion of indene-2-phosphonic acid[7] (**4**) to 2-bromoindene[8] (**5**) in high yield under the same conditions used to convert **2** to **3**.



1



2



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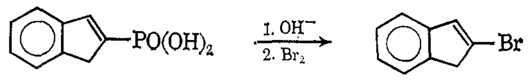
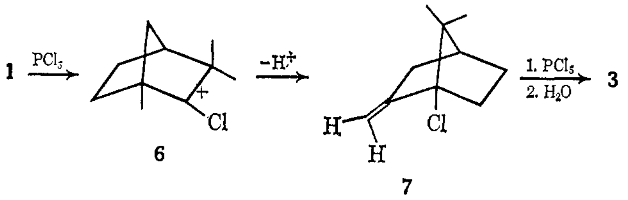


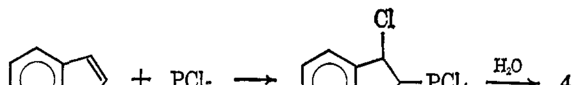
4 **5**

Discussion

The following sequence leading to formation of **2** is suggested.



The α-chlorocarbonium ion **6** is almost certainly the initial intermediate.[2b,3] Formation of **7** from **6** is straightforward and reminiscent of many cationic transformations in the fenchyl and camphyl series.[9] The formation of α,β-unsaturated phosphonic acids from the reaction between olefins and phosphorus pentachloride by a sequence of addition, hydrolysis, and elimination (**7** → **3**) has been known for many years. The formation of indene-2-phosphonic acid **4** is representative.[7]



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[1] T. L. Jacobs, *Org. Reactions*, **5**, 20 (1949).

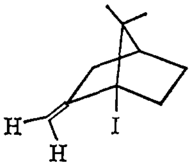
[2] (a) M. S. Newman and G. Kaugars, *J. Org. Chem.*, **31**, 1379 (1966); (b) M. S. Newman and B. C. Ream, *ibid.*, **31**, 2175 (1966); (c) M. S. Newman and B. C. Ream, *ibid.*, **31**, 3861 (1966).

[3] The reaction of trimethylacetaldehyde with phosphorus trichloride dibromide (PCl_3Br_2) in methylene chloride affords both 1,1-dibromoneopentane and 2,3-dibromo-2-methylbutane as primary products (unpublished experiments by Mr. O. R. Thomas).

[4] (a) J. A. Gardner and G. B. Cockburn, *J. Chem. Soc.*, **71**, 1156 (1897); (b) J. A. Gardner and G. B. Cockburn, *ibid.*, **73**, 704 (1898).

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 349; G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3557 (1966).

[6] The nmr spectrum of i in the olefinic region consists of triplets at τ 4.72 and 4.89 (J = 2.3 and 2.0 cps, respectively), indicating that *cis* and *trans* vinyl–allylic couplings are about equal in this system (unpublished experiments of Mr. J. N. Cawse).



i

[7] E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930).

[8] Dutch Patent 92,148 (Sept 15, 1959); see *Chem. Abstr.*, **55**, 17577 (1961).

[9] J. L. Simonsen, "The Terpenes," Vol. II, 2nd ed, Cambridge, Cambridge University Press, 1949.

The formation of vinyl bromides **3** and **5** from **2** and **4**, respectively, is undoubtedly related to the facile alkaline decomposition of dibromophosphonic acids to vinyl bromides, first discovered by Conant and coworkers[10] in 1924 and recently reinvestigated by Kenyon and Westheimer.[11] The latter investigators found that the reaction is completely stereospecific, and hence, *if* the present reaction goes by way of the sodium salt of the dibromophosphonic acid, the configuration about the double bond must be the same in **2** and **3**.

Experimental Section[12]

Chlorofenchenephosphonic acid (**2**) was prepared according to the procedure of Gardner and Cockburn.[4a] Indene-2-phosphonic acid (**4**) was synthesized by the method of Bergmann and Bondi.[7]

Chlorobromofenchene (**3**).—This compound was prepared by a variation on the method of Gardner and Cockburn.[4b] A suspension of 1.25 g (0.005 mole) of chlorofenchenephosphonic acid (**2**) in 50 ml of water containing 1 drop of phenolphthalein solution was neutralized with dilute base. Dropwise addition of saturated bromine water was accompanied by immediate decolorization and separation of a milky precipitate. Addition of bromine water was continued until a light orange color persisted. The mixture was then treated with sodium bisulfite solution and extracted with ether. The ether solution was washed with water and dried over sodium sulfate. Distillation of the ether afforded 1.15 (92%) of **3**, homogeneous by vpc (15% SE-30 on Fluoropack 80, 3-ft column, 170°).

2-Bromoindene (**5**).—This compound was prepared in 85% yield from indene-2-phosphonic acid (**4**) in the same manner as chlorobromofenchene. Its melting point of 34–36° compares with a literature[8] value of 38–39°. Its nmr spectrum consists of a complex aromatic multiplet from τ 2.6 to 3.1, a triplet at τ 3.22 (J = 1.7 cps), and a doublet at τ 6.59 (J = 1.7 cps), relative areas 4:1:2, respectively.

Registry No.—**2**, 10485-07-1; **3**, 10485-08-2; **5**, 10485-09-3.

Acknowledgment.—This research was supported by the Petroleum Research Fund of the American Chemical Society. We thank Dr. T. W. Rave for a helpful discussion.

[10] J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, **42**, 830 (1920).

[11] G. L. Kenyon and F. H. Westheimer, *ibid.*, **88**, 3561 (1966).

[12] Nmr spectra were measured on a Varian A-60A spectrometer relative to tetramethylsilane (τ 10.00) as external standard. Vapor phase chromatography (vpc) was carried out on a Varian Aerograph model A-90P. Infrared spectra were measured in carbon tetrachloride on a Perkin-Elmer Model 237 spectrophotometer.

Transannular Cyclization Reactions in Medium-Sized Ring Amino Alcohols

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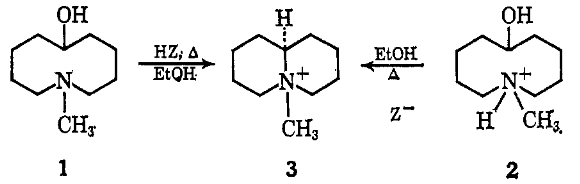
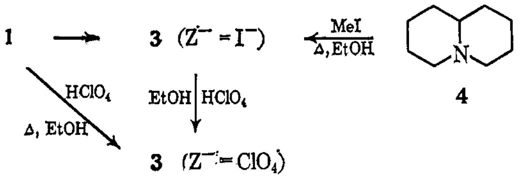
While investigating possible transannular[2] cyclization reactions with olefinic amine oxides contained in medium-sized ring systems, we had occasion to attempt a dehydration of N-methyl-1-azacyclodecan-6-ol (**1**) by conventional procedures. In no instance during the latter treatment were we able to isolate the anticipated olefin, but instead products produced from a novel and rapid transannular cyclization reaction (eq 1). Compound **1** yielded normal salts (**2**) as



(1)

$Z^- = ClO_4^-, I^-$, picrate

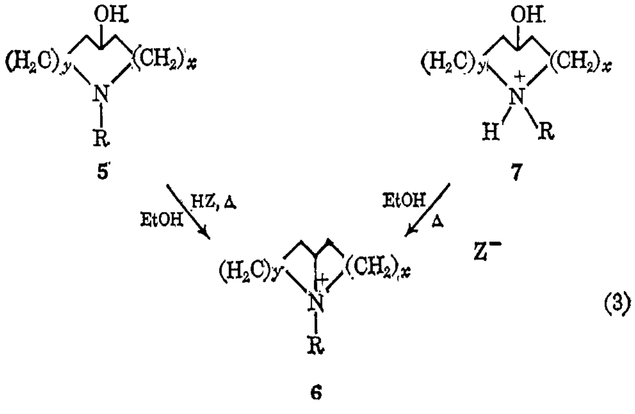
ascertained by infrared and elemental analysis, which upon heating in ethanol also resulted in the cyclization products, **3** (eq 1). Unequivocal structure proof of **3** was obtained by the treatment of quinolizidine[3] (**4**) with methyl iodide[4] producing **3** ($Z^- = I^-$) identical (mixture melting point, infrared, and nmr) with the compound produced upon treatment of **1** with hydrogen iodide in refluxing ethanol (eq 2). In addition, **3**



(2)

($Z^- = I^-$), obtained from **4**, when treated with excess perchloric acid yielded the perchlorate, **3** ($Z^- = ClO_4^-$), identical (mixture melting point and infrared) with the product obtained from **1** when treated with perchloric acid in refluxing ethanol (eq 2).

An obvious extension of this type of transannular cyclization reaction to other medium-sized ring systems was undertaken for the purpose of determining the generality of the reaction. Accordingly, the amino alcohols, **5a** and **b**, were prepared and upon direct treatment with monoprotic acids in refluxing ethanol resulted in the formation of **6a** and **b**, as a consequence of transannular cyclization reactions (eq 3). The



(3)

a, $x = y = 2$; R = cyclohexyl
b, $x = 2$; $y = 3$; R = methyl
$Z^- = ClO_4^-, I^-$, picrate

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[1] Taken in part from the Ph.D. thesis of D. Lohner, Adelphi University, 1966.

[2] For a recent review, see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

[3] N. J. Leonard, A. S. Hay, R. W. Fulmer, and V. W. Gash, *J. Am. Chem. Soc.*, **77**, 439 (1955).

[4] The product from the reaction of quinolizidine (**4**) with methyl iodide, **3** ($Z^- = I^-$), was shown to be the *trans* isomer by comparison with an authentic sample graciously supplied by K. Winterfield.