15 min. The reaction was decomposed with sodium hydroxide–sodium borohydride[23a] and worked up in the usual manner.[5] The crude product was acetylated with acetyl chloride–pyridine to give 900 mg (92%) of acetate ester. Vpc analysis (300 ft × 0.01 in. DC-550 silicone column, 115°, 30 psig) gave a mixture of two esters, retention time 30.0 min (87%) and 34.5 min (13%). Neither ester was shown by comparative vpc to be *exo*-5-acetoxy-*syn*-7-*tert*-butylnorbornene-2 (**11**), retention time 27.5 min (from hydroboration of **1**). A pure sample of the major ester was separated by preparative vpc (10 ft × 0.375 in. 20% FFAP column, 170°, 110 ml/min) and was shown by nmr to be *endo*-5-*tert*-butyl-*anti*-7-acetoxynorbornene-2 (**10**).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.68; H, 9.57. Nmr ($CDCl_3$) δ 5.96 (m, 2, HC=CH), 4.26 (m, 1, J = 5 Hz, HCO), 2.50–2.88 (m, 2, >CH), 2.03 (s, 3, CH_3CO), 1.60–1.88 (m, 2, exo $>CH_2$), 0.95 (s, 1, endo $>CH_2$), 0.80 [s, 9, $(CH_3)_3C$].[31]

(31) The position and stereochemistry of the *anti*-7-acetoxy group was established by comparative nmr with other acetoxynorbornenes.[11]

The reaction of the 7-*tert*-butyldiene with mercury(II) trifluoroacetate in benzene-d_6 was studied by nmr.[24] The spectrum of the diene was immediately replaced by that of the exo,cis mercuration adduct of the anti double bond: δ 5.80 (dq, 2, HC=CH), 4.85 (d, 1, HCO, J = 8 Hz), 2.93 (m, 2, >CH), 2.30 (d, 1, HgCH, J = 8 Hz), 2.20 (s, 1, HC-*tert*-Bu), 0.86 [s, 9, $(CH_3)_3C$]. An identical experiment with norbornadiene gave the following nmr spectrum: δ 6.00 (dq, 2, HC=CH), 4.88 (d, 1, HCO, J = 8 Hz), 2.90 (m, 2, >CH), 2.18 (d, 1, HCHg, J = 10 Hz), 1.50 (s, 2, $>CH_2$). Both spectra were unchanged after 24 hr at room temperature.[32]

Registry No.—**1**, 32640-82-7; **2**, 32640-83-8; **3**, 32640-84-9; **4**, 32640-85-0; **5**, 32670-72-7; **10**, 32640-90-7; **11**, 32640-91-8; **12**, 32640-86-1; **12** (tosylate), 32640-87-2; exo,cis mercuration adduct of the anti double bond, 32640-89-4; adduct of norbornadiene and mercury(II) trifluoroacetate, 32640-88-3.

(32) The authors thank Dr. R. L. Hartgerink for these nmr measurements.

Notes

Formation of (Alkoxymethylene)dimethylimmonium Halides in the Reactions of Triphenylphosphine Dihalides with Alcohols in Dimethylformamide

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The reaction of triphenylphosphine dihalides with alcohols to give halides[1] is a useful synthetic procedure.[2] The reaction mechanism in acetonitrile has been proposed as shown in eq 1.[3] The reaction may also pro-

$$R_3PX_2 + R'OH \xrightarrow{\text{fast}} R_3\overset{+}{P}OR' + \overset{-}{X}HX \xrightarrow{\text{slow}} R_3P{=}O + R'X + HX \quad (1)$$

ceed satisfactorily when dimethylformamide (DMF) is used as the solvent.[1,2] We report here a second pathway followed by this reaction when done in DMF.

When *N*-benzoyl-*N*-methyl-4-hydroxyadamantan-1-amine[4] (**1**) is allowed to react with triphenylphosphine dibromide in DMF at ice-bath temperatures, a crystalline precipitate forms. The spectral and analytical properties of this relatively stable product were not consistent with the expected bromide structure **4**. Instead, elemental analysis showed that, in addition to bromine, the empirical formula had also gained the elements of C_3H_6N. The nmr spectrum suggested that part of this gain could be accounted for by two methyl groups attached to a heteroatom such as nitrogen. The infrared spectrum showed the absence of an OH bond and a new strong absorption band at 1710 cm^{-1}. These data suggested that the product had structure **2a**, an (alkoxymethylene)dimethylimmonium bromide. Structure **2** is, in fact, an immomium ether halide, a structural type for which considerable precedent exists.[5] For example, an analogous structure has been assigned to the salts obtained from the reaction of dimethylformiminium chloride with either *tert*-butyl alcohol or dimethylbenzylcarbinol, although the products were characterized by elemental analyses only.[5c] Related structures have frequently been postulated[6] and occasionally isolated[7] as intermediates in Vilsmeyer formylation reactions.

Consistent with structure **2a** was the observation that the compound was water soluble and was rapidly hydrolyzed, giving formate ester **3** as the product. The structure of **3** was apparent from the elemental analyses and the infrared spectrum (ester carbonyl at 1730 cm^{-1}), as well as the fact that it underwent further hydrolysis under alkaline conditions to give the starting alcohol **1**. The latter result shows that the configuration of the oxygen substituent in **1** has been retained throughout these transformations.

An (alkoxymethylene)dimethylimmonium iodide intermediate (**2b**) also formed when iodine was used in the reaction instead of bromine. Formate ester **3** was also obtained from this intermediate upon hydrolysis.

An intermediate of the above type apparently formed when the diol 1-benzoyl-1-methyl-4,6-dihyroxyadaman-

(1) G. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

(2) *Cf.* L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 1247–1249.

(3) G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.*, 2509 (1964).

(4) M. E. Herr, R. A. Johnson, H. C. Murray, L. M. Reineke, and G. S. Fonken, *J. Org. Chem.*, **33**, 3201 (1968).

(5) *Cf.* (a) R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 179 (1961); (b) F. H. Suydam, W. E. Greth, and N. R. Langerman, *J. Org. Chem.*, **34**, 292 (1969); (c) Z. Arnold, *Collect Czech. Chem. Commun.*, **26**, 1723 (1961).

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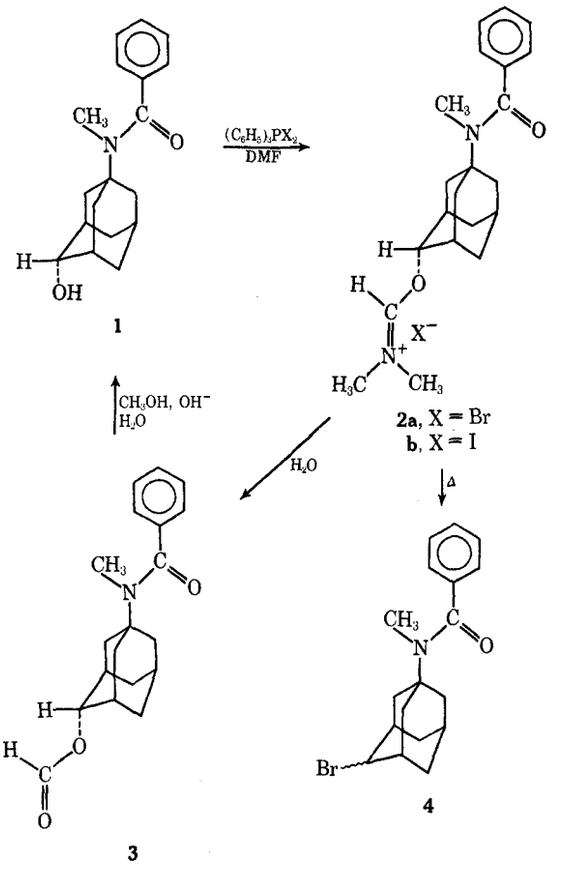
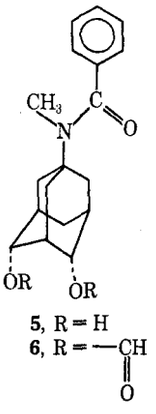
(7) *Cf.* G. Ferré and A.-L. Palomo, *Tetrahedron Lett.*, 2161 (1969).

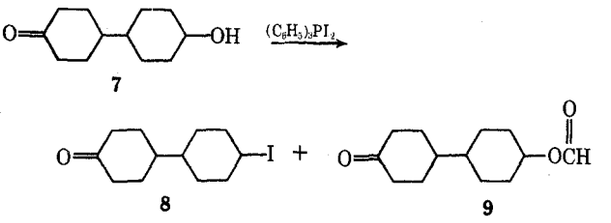


tan-1-amine (**5**) was allowed to react with triphenylphosphine dibromide in DMF. The product actually isolated from work-up of the reaction, which involved aqueous conditions, was the diformate ester **6**. Saponification of **6** gave starting diol **5**.

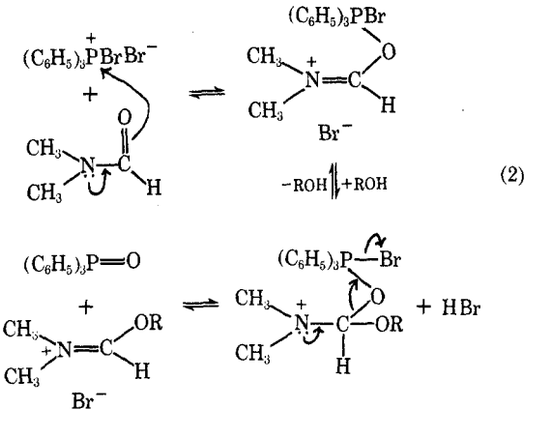


Conversion of the salt **2a** to bromide **4** was attempted by refluxing in toluene, but it remained unchanged. However, when fused at its melting point, **2a** was converted into **4** in good yield. Thin layer chromatographic analysis of **4** showed it to consist of two components, suggesting that a mixture of epimeric C-4 bromides had been obtained.

Attempts to isolate intermediates such as **2** from reaction of triphenylphosphine dihalides with other alcohols under the same conditions have not been successful. In still another case, the reaction of 4-(4′-hydroxycyclohexyl)cyclohexanone (**7**)[8] with triphenylphosphine diiodide, both the iodide **8** and the formate **9** were detected among the reaction products.



It seems plausible that a mechanism similar to that postulated for the formation of the Vilsmeyer reaction intermediates[6] is involved here also. Such a sequence is shown in eq 2. It may be noted that no inversion of



the alcohol configuration is required by this mechanism. We have not studied the effect of other variables on this reaction.

Experimental Section

4-(*N*-Benzoyl-*N*-methyl-1-aminoadamantoxymethylene)dimethylimmonium Bromide (2a).—A mixture of 28.5 g of *N*-benzoyl-*N*-methyl-1-adamantanamin-4α-ol (**1**), 150 ml of dimethylformamide, and 27.5 g of triphenylphosphine in a nitrogen atmosphere and with ice cooling was stirred and treated dropwise with 16.0 g of bromine during 15 min. During this addition, the original solids dissolved and a precipitate separated. The product was recovered by filtration, washed quickly with ether and placed in a vacuum desiccator, yield 33.34 g, mp 187–192° dec. For analysis a sample was recrystallized from methylene chloride–hexane: mp 195–198° dec; ir (Nujol) 1710 (CH=N), 1650 cm^{-1} (amide); nmr ($CDCl_3$) δ 10.35 (s, 1, N=CHO), 7.33 (s, 5, C_6H_5), 5.55 (m, 1, CHOC=N), 3.64 (s, 3, C=NCH_3), 3.29 (s, 3, C=NCH_3), 2.81 (s, 3, NCH_3).

Anal. Calcd for $C_{21}H_{29}N_2O_2Br$: C, 59.85; H, 6.94; N, 6.65; Br, 18.97. Found: C, 59.46; H, 6.77; N, 6.63; Br, 19.45.

***N*-Benzoyl-*N*-methyl-1-adamantanamin-4α-ol Formate (3).**—The compound **2a** (1.5 g) was dissolved in 10 ml of water; crystals began to separate almost immediately; and, after 1 hr, these were collected, washed with water, and dried, yield 1.04 g, mp 93–95°. The analytical sample obtained from aqueous acetone melted at 95–97°: ir (Nujol) 1730 (formate), 1630 cm^{-1} (amide); nmr ($CDCl_3$) δ 8.08 (s, 1, HC=O), 7.35 (s, 5, C_6H_5), 5.1 (m, 1, CHO–), 2.83 (s, 3, NCH_3).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.60; H, 7.36; N, 4.27.

Hydrolysis to *N*-Benzoyl-*N*-methyl-1-adamantanamin-4α-ol (1).—A sample of the formate ester **3** was heated with methanol and 10% aqueous sodium hydroxide to give **1** identical in all respects with authentic material.

(8) G. S. Fonken, M. E. Herr, and H. C. Murray, U. S. Patent 3,281,330 (Oct 25, 1966).

N-Benzoyl-*N*-methyl-1-adamantanamine-4α,6α-diol Diformate (6).—A mixture of 3.01 g of *N*-benzoyl-*N*-methyl-1-adamantanamine-4α,6α-diol (5), 20 ml of dimethylformamide, and 5.5 g of triphenylphosphine under nitrogen was stirred in an ice bath and treated dropwise with bromine until an orange color persisted. After 1 hr, the mixture was diluted with water and extracted with methylene chloride; the extract was washed with 5% sodium bicarbonate solution and dried (Na_2SO_4). The solvent was removed and the residue was recrystallized from acetone–water: yield 1.20 g; mp 142–144°; ir (Nujol) 1730 (formate), 1630 cm^{-1} (amide); nmr ($CDCl_3$) δ 7.96 (s, 2, HC=O), 7.25 (s, 5, C_6H_5), 5.08 (m, 2, CHO–), 2.79 (s, 3, NCH_3).

Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.31; H, 6.64; N, 4.56.

Hydrolysis to *N*-Benzoyl-*N*-methyl-1-adamantanamine-4α,6α-diol (5).—A sample of the diformate ester 6 was converted to the free diol by warming in methanol and 10% aqueous sodium hydroxide solution. This product was identical in all respects with compound 5.

4-(*N*-Benzoyl-*N*-methyl-1-aminoadamantoxymethylene)dimethylimmonium Iodide (2b).—When iodine was substituted in place of bromine in the above reaction with 1, the product isolated was the iodide salt 2b: mp 150° dec; ir (Nujol) 1695 (CH=N), 1640 cm^{-1} (amide).

Anal. Calcd for $C_{21}H_{29}N_2O_2I$: C, 53.85; H, 6.24; N, 5.98; I, 27.10. Found: C, 53.82; H, 6.22; N, 5.82; I, 27.00.

N-Benzoyl-*N*-methyl-4ϵ-bromo-1-adamantanamine (4).—The compound 2a, 5.59 g, was heated in an oil bath at 200–205° for 15 min. The mixture was cooled, treated with 25 ml of water, and extracted with methylene chloride; the extract was washed with water and dried (Na_2SO_4); the extract residue was chromatographed over 200 g of Florisil by the gradient elution method with 4 l. of solvent SSB containing increasing proportions of acetone from 0 to 25%; cuts of 70 ml each were collected. Residues from fractions 15–20 contained the C_4-bromo product 4. Tlc of this material on a silica gel microplate developed ten times with 10% acetone in Skellysolve B showed this to be a mixture of 4α- and 4β-bromo compounds. A sample recrystallized from ether–pentane melted at 96–99°.

Anal. Calcd for $C_{18}H_{22}NOBr$: C, 62.07; H, 6.37; N, 4.02; Br, 22.95. Found: C, 62.38; H, 6.36; N, 4.19; Br, 22.81.

Reaction of 4-(4′-Hydroxy)cyclohexylcyclohexanone (7) with Triphenylphosphine Diiodide.—Triphenylphosphine (5.80 g, 0.022 mol) and 4-(4′-hydroxy)cyclohexylcyclohexanone (7)[8] (3.92 g, 0.020 mol) were dissolved in dimethylformamide (55 ml). Iodine crystals (5.06 g, 0.020 mol) were added to the solution over a period of 20 min at room temperature. After stirring at room temperature for 5 hr, the solution was light yellow. Methanol (5 drops) was added, causing most of the color to disappear. The solution was poured into water (300 ml) and the resulting cloudy mixture was extracted with ether (five 60-ml portions). The ether solution was washed with 5% $NaHCO_3$ solution (100 ml) and with water, then dried over $MgSO_4$. The dry ether solution was concentrated under reduced pressure, giving a mixture of liquid and crystals. This mixture was lixiviated with Skellysolve B (four times) and the solution was concentrated under reduced pressure. The residue was passed through silica gel (300 g) in 1:1 ethyl acetate–Skellysolve B, separating the products (fractions 1 and 2) from triphenylphosphine oxide. The presence of a formate ester (9) in the product mixture (fraction 2) was suggested by spectral evidence (a signal at δ 8.00 in the nmr and a band at 1720 cm^{-1} in the ir spectrum). Hydrolysis (5 ml of 5% $NaHCO_3$ plus 50 ml of CH_3OH) of the product mixture (fractions 1 and 2, reflux for 20 min) caused disappearance of one product (on tlc) and appearance of starting keto alcohol 7, some of which crystallized and was recovered. The remaining product mixture was chromatographed on silica gel (300 g, 3.5 cm column) packed with 20% ethyl acetate in Skellysolve B. Elution with the same solvent (335-ml fractions) gave fraction 1, crystalline triphenylphosphine, identified by ir spectrum; fraction 2, triphenylphosphine and an olefinic component, δ 7.3 and 5.65, respectively, in the nmr spectrum; fraction 3, olefinic component plus 4-(4′-iodo)cyclohexylcyclohexanone; fraction 4, 4-(4′-iodo)cyclohexylcyclohexanone (8), δ 4.84 in the nmr for ICH, 0.551 g of viscous oil.

Registry No.—DMF, 68-12-2; 2a, 32653-72-8; 2b, 32653-73-9; 3, 32653-74-0; 4α, 32653-75-1; 4β, 32653-76-2; 6, 32653-77-3; 8, 32670-59-0.

Transannular Reactions of Heptamethylenimine Derivatives

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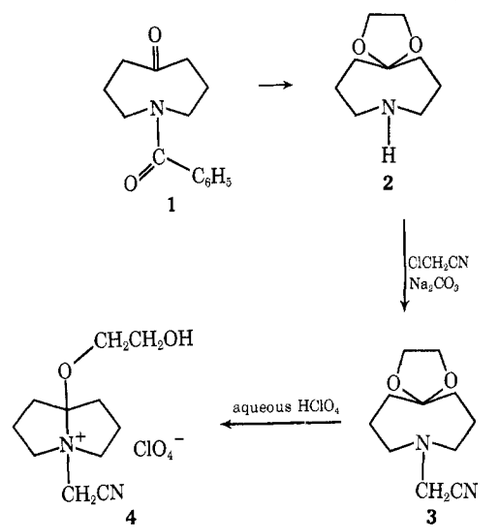
Microbial oxygenation of *N*-benzoylheptamethylenimine has provided a source of the 5-oxo derivative 1, which can be modified to molecules that undergo transannular reactions.[1] Described below are two additional, unusual transannular reactions encountered in work with compounds derived from 1.

Interception of Ketal Hydrolysis by Transannular Amine.—A large variety of nucleophiles other than water participate in reactions with acetals and ketals. Under anhydrous conditions, the acid-catalyzed exchange with alcohols is well known,[2] while other reports have demonstrated reaction with hydride,[3] Grignard reagents,[3b,4] imide nitrogen,[5] and amine nitrogen.[6] Participation of oxygen[7] and sulfur[8] in the hydrolysis of acetals has also been observed.

With the exception of the unusual example cited above, amine ketals generally form stable acid salts[9] under anhydrous conditions. We have hydrolyzed several amine ketals with no apparent anomalies.[1] However, when the amine ketal 3, prepared from 1 *via* 2



(1) R. A. Johnson, M. E. Herr, H. C. Murray, and G. S. Fonken, *J. Org. Chem.*, **33**, 3187 (1968).

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(4) (a) M. R. Kulibekov, *Dokl. Akad. Nauk Azerb. SSR*, **20**, 15 (1964); *Chem. Abstr.*, **61**, 10579*h* (1964); (b) R. A. Mallory, S. Rovinski, and I. Scheer, *Proc. Chem. Soc.*, 416 (1964); R. A. Mallory, S. Rovinski, F. Kohen, and I. Scheer, *J. Org. Chem.*, **32**, 1417 (1967); (c) D. Lednicer, *ibid.*, **29**, 2480 (1964).

(5) H. E. Johnson and D. G. Crosby, *ibid.*, **27**, 2077 (1962).

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