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The Reaction of Alcohols with Hexamethylphosphoric Triamide[1]

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The thermal treatment of 4-homoadamantanol and bicyclo[3.3.1]nonanols with hexamethylphosphoric triamide (HMPT) gave the corresponding olefins in moderate yields. The application of this dehydration method to a system in which olefin formation was regarded as difficult or impossible stereochemically led to various types of reactions, *i.e.*, reduction, substitution, and phosphorodiamidation. Upon being heated in HMPT, 2-adamantanol afforded 2-adamantyl tetramethylphosphorodiamidate, whereas 1-adamantanol was transformed into adamantane *via* 1-adamantyl tetramethylphosphorodiamidate. In the case of allylic or benzylic alcohols, dimethylamino-substituted compounds were obtained. The reduction of the amount of HMPT promoted the formation of an ether, while dibenzhydryl ether was produced exclusively from benzhydrol. The mechanism of these reaction is discussed.

Recently Hexamethylphosphoric triamide (HMPT) has been widely used as a reaction medium because of its excellent properties as a dipolar aprotic solvent.[2] More recently it was found that HMPT behaved as a reagent for dehydrohalogenation,[3a] dehydration,[3b–d] and various types of reactions in organic synthesis.[3e–m]

In line with the interest in the behavior of HMPT as a reagent, we attempted to apply Monson's method[3b–d] for the dehydration of alcohols to bicyclo[3.3.1]-nonane and homoadamantane systems; the corresponding olefins were thus obtained in a moderate yield. However, when this method was extended to a system in which the olefin formation was regarded as difficult judging from the Bredt rule,[4] divergent types of reactions were observed. Among these reactions, in view of the fact that dimethylamino-substituted compounds were obtained from allylic or benzylic alcohols, we investigated the reaction of benzylic alcohols with HMPT in more detail.

This paper will describe the results obtained in the reaction of HMPT (a) with some alicyclic alcohols, and (b) with benzyl alcohols, including (b-1) the effect of the reaction temperature, (b-2) the formation of an ether, and (b-3) the detection of benzylpentamethylphosphoric triamide.

Finally, (c) some mechanistic aspects will be considered particularly, with particular attention being paid to the reaction of benzyl alcohols.

Results and Discussion

The Reaction of Alicyclic Alcohols with HMPT. As shown in Table 1, the dehydration of alcohols took place readily and gave the corresponding olefins in moderate yields. Among these, it should be noted that 4-homoadamantanol is converted to 4-homoadamantene in an excellent yield; this provides the most convenient method yet for the preparation of this cage olefin.[5]

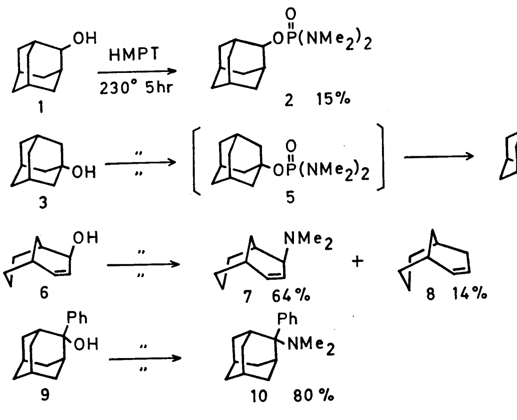
When 2-adamantanol (**1**) was treated with HMPT, 2-adamantyl tetramethylphosphorodiamidate (**2**) could be isolated in a 15% yield, as is shown in Scheme 1.[6] On the other hand, 1-adamantanol (**3**) afforded only the reduction product, adamantane (**4**). When the reaction of **3** with HMPT was followed by glc, combined with MS, however, it was found that 1-adamantyl tetramethylphosphorodiamidate (**5**) was an intermediate leading to the final product, **4**. Compared with the MS spectrum of **2**, that of **5** indicates the base peak at *m/e* 135, corresponding to the adamantyl cation, whereas that of **2** indicates the base peak at *m/e* 151, corresponding to the adamantyloxy cation. This may reflect the more facile formation of adamantane (**4**) from **5** than from **2**.

Table 1. Dehydration of alcohols in HMPT

Alcohol	Olefin	Yied (1%)
4-Homoadamantanol	4-Homoadamantene	91
exo-Bicyclo[3.3.1]nonan -2-ol	Bicyclo[3.3.1]non-2-ene	43
endo-Bicyclo[3.3.1]nonan -2-ol	Bicyclo[3.3.1]non-2-ene	28
Bicyclo[3.3.1]nonane -2,6-diol[a]	Bicyclo[3.3.1]nona-2,6 -diene	35

a) Epimeric mixture; *endo, endo-*, and *endo, exo*-diols.

A similar reaction of *exo*-bicyclo[3.3.1]non-3-en-2-ol (**6**) gave 2-*exo*-dimethylaminobicyclo[3.3.1]non-3-ene (**7**), together with a reduction product, bicyclo[3.3.1]-non-2-ene (**8**). The *exo*-configuration of the dimethylamino group at the 2 position of **7** was established by NMR, which indicated a narrow half-band width of 5.0 Hz assignable to the methine proton at the 2 position.[7] Furthermore, 2-phenyl-2-adamantanol (**9**) gave 2-phenyl-2-dimethylaminoadamantane (**10**) in an 80% yield.



Scheme 1.

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The Reaction of Benzyl Alcohols with HMPT. The fact that dimethylamino-substituted compounds were obtained from allylic or benzylic alcohols such as **6** and **9** prompted us to investigate the reaction of benzyl alcohols with HMPT. The results obtained are listed in Table 2.

TABLE 2. REACTION OF BENZYL ALCOHOLS WITH HMPT

Alcohol	Product	Yield (%)
Benzyl alcohol	Benzyldimethylamine	10
	Dibenzylmethylamine	40
Benzhydrol	Diphenylmethane	8
	Benzhydryldimethylamine	56
Triphenylmethanol	Triphenylmethane	44

Monson and Priest have already reported that benzyl alcohols were converted to the corresponding dimethylamino derivatives.[3f)] However, we could obtain some additional results—that is, the formation of dibenzylmethylamine and two reduction products, diphenylmethane and triphenylmethane.

The Effect of the Reaction Temperature: The reaction of benzyl alcohols with HMPT seems to be highly sensitive to the reaction temperature employed. As is shown in Table 3, dibenzylmethylamine was produced over 215 °C, whereas benzyldimethylamine was a sole product at 200 °C. In the case of benzhydrol, a temperature dependency could be also observed, as is shown Table 4, but it was extremely small as compared with the result in the case of benzyl alcohol. Triphenylmethanol gave only triphenylmethane in the temperature range of 200—230 °C. The formation of reduction products seems to be dependent upon the steric effects; that is, although toluene escaped from detection in the case of benzyl alcohol, the yield of the reduction products increased as the number of phenyl group increased.

TABLE 3. REACTION OF BENZYL ALCOHOL WITH HMPT

Reaction time hr	Reaction temp. °C	Product distribution (%)[a)]	
		$PhCH_2NMe_2$	$(PhCH_2)_2NMe$
1	200	100	—
1	215	85	15
1	230	59	41
5	230	25	75

a) Determined by glc analysis. The yield was almost quantitative except in the case of last run, which is shown in Table 2.

TABLE 4. REACTION OF BENZHYDROL WITH HMPT

Reaction time hr	Reaction temp. °C	Product distribution (%)[a)]	
		Ph_2CH_2	Ph_2CHNMe_2
1	200	6	94
1	215	7	93
1	230	9	91
5	230	11	89

a) Determined by glc analysis. The yield was almost quantitative except in the case of last run, which is shown in Table 2.

The Formation of an Ether: When a series of experiments was performed on the reaction of benzyl alcohol with varying amounts of HMPT, a novel type of reaction was discovered—namely, the formation of an ether.[8)] These data, summarized in Table 5, show that, in the presence of smaller amounts of HMPT, the production of the ether is favored. HMPT was fully consumed when 3 mol of benzyl alcohol was treated with 1 mol of HMPT at 230—240 °C. Since the ratio of benzyldimethylamine (**11**) and dibenzylmethylamine (**12**) was almost unchanged in varying amounts of HMPT, HMPT might be indifferent to the formation of **11** and **12** from the presumed intermediate, benzyl tetramethylphosphorodiamidate (**13**).[3f)]

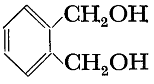
TABLE 5. REACTION OF BENZYL ALCOHOL WITH VARYING AMOUNTS OF HMPT

Molar ratio of benzyl alcohol and HMPT	Product distribution (%)[a)]		
	$PhCH_2NMe_2$	$(PhCH_2)_2NMe$	$(PhCH_2)_2O$
1 : 1	56	39	5
1 : 2/3	55	38	7
1 : 1/3	50	35	15

a) Determined by glc analysis. The yield was almost quantitative.

When 3 mol of benzhydrol was treated with 1 mol of HMPT, dibenzhydryl ether (**14**) was obtained as the sole product in a 71% yield after recrystallization from ethanol.

These results further prompted us to investigate the reaction of phthalyl alcohol (**15**) with HMPT, which was supposed to give rise to intramolecular ether-formation affording phthalan (**16**) (Eq. (1)). Actually, although the yield was far from satisfactory, **16** was obtained in an 8% yield from a mixture of equimolar amounts of **15** and HMPT.



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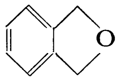
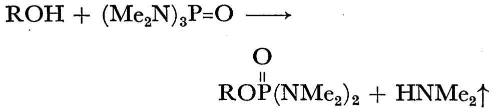


16 (1)

Detection of Benzylpentamethylphosphoric Triamide: When a solution of benzyl alcohol and HMPT was refluxed for 5 hr, a small amount of a new product was detected; this product identified as benzylpentamethylphosphoric triamide (**17**) from the spectroscopic data (see Experimental section). It is highly probable that this compound was formed by the amine-exchange reaction of the benzyldimethylamine produced with HMPT.

Mechanistic Investigations. Intermediacy of Alkyl Tetramethylphosphorodiamidate in the Reaction of Alcohols with HMPT: Concerning the mechanism of the reaction of alcohols with HMPT, Monson and Priest suggested, without rigorous proof, that the initial step of the reaction was the formation of alkyl tetramethylphosphorodiamidate (**18**) (Eq. (2)).[3d)]



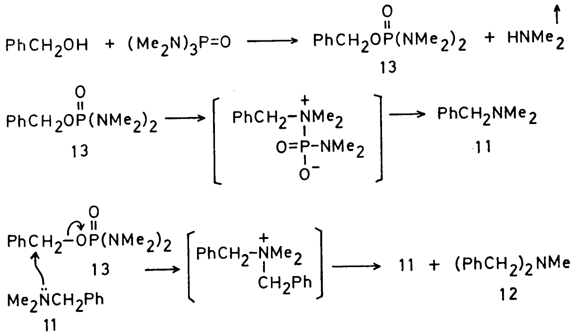
$$ROH + (Me_2N)_3P{=}O \longrightarrow RO\overset{\displaystyle O}{\overset{\|}{P}}(NMe_2)_2 + HNMe_2\uparrow \qquad (2)$$

18

As is shown in Scheme 1, this presumed intermediate was actually isolated by using an adamantanol.

Also, with regard to the mechanism of the reaction of benzyl alcohols with HMPT, Monson and Priest suggested that the benzyl tetramethylphosphorodiamidates initially produced rearranged to benzyldimethylamine (**11**).[3f] In order to establish this mechanism, we prepared benzyl tetramethylphosphorodiamidate (**13**) from sodium benzylate and tetramethylphosphorodiamidic chloride in ether, and thermally treated **13** *without* solvents. The treatment of **13** at 230—240 °C for 1 hr gave **11** and dibenzylmethylamine (**12**) in the same ratio as in the reaction of benzyl alcohol with HMPT. This implies that **13** is actually an intermediateto the two final products, **11** and **12**. According to the Monson mechanism, it is understandable that **11** was produced by the rearrangement of the **13** intermediate. However, it is still not clear how **12** was obtained from **13**. Since Monson did not obtain **12**, we are left with the intriguing question of how **12** was formed from **13**.

The Formation of Dibenzylmethylamine by the Reaction of Benzyl Tetramethylphosphorodiamidate and Benzyldimethylamine: One explanation of the formation of **12** is that the benzyldimethylamine produced (**11**) attacks the benzylic carbon atom of the still-surviving benzyl tetramethylphosphorodiamidate (**13**), which is an intermolecular analogy of the rearrangement of the **13** intermediate (Scheme 2).



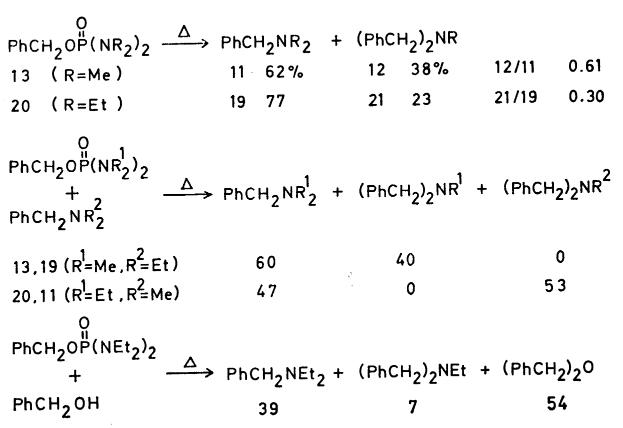
Scheme 2.

In order to test this hypothesis, we investigated the crossed reactions between benzyl tetramethylphosphorodiamidate (**13**) and benzyldiethylamine (**19**)[9] as well as those between benzyl tetraethylphosphorodiamidate (**20**) and benzyl dimethylamine (**11**).[10] It was preliminarily observed that **20** was also thermally converted to benzyldiethylamine (**19**) and dibenzylethylamine (**21**), but the ratio of **21**/**19** was smaller than that of **12**/**11**. In the former case, no crossed reaction was observed, but in the latter case, the crossed reaction did take place and dibenzylmethylamine (**12**) was obtained (Scheme 3).

These observations imply that the rate of the attack of **19** must be slower than that of **11** for steric reasons and also well explain the fact that dibenzhydrylmethylamine is not obtained in the case of benzhydrol.

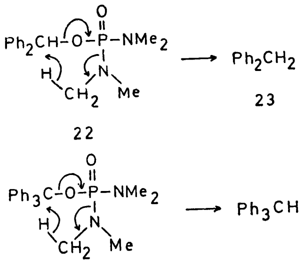
From these results we concluded that **12** was derived from the nucleophilic substitution reaction of **13** by **11** as is shown in Scheme 2.

Additionally, when an equimolar mixture of **20** and benzyl alcohol was treated at 230—240 °C for 1 hr, dibenzyl ether was obtained at the expense of **20**, together with **19** and **21**. (Scheme 3) Therefore, it is highly probable that the ether-formation proceeds by the nucleophilic substitution reaction of **18** by the still-remaining alcohol.



Scheme 3.

Mechanism Concerning the Formation of the Reduction Products: As for the formation of the reduction products, such as diphenylmethane and triphenylmethane, we tentatively propose the mechanism depicted in Scheme 4.



Scheme 4.

When the intramolecular rearrangement occurs, hydrogen from the methyl group attached to nitrogen transfers to the benzylic carbon atom. An attempt to prepare benzhydryl tetramethylphosphorodiamidate (**22**) did not succeed, but instead of **22**, we directly obtained diphenylmethane (**23**) and benzhydryldimethylamine (**24**) in refluxing ether, though the ratio of **23** and **24** was *ca.* 1 : 1, different from the results of the reaction of benzhydrol with HMPT. This explanation can also be extended to the formation of adamantane and bicyclo[3.3.1]non-2-ene from their precurcors. However, these observations can not be explicitly explained at present, and an intermolecular pathway cannot be ruled out.

Experimental

All the temperature are uncorrected. The IR spectra were obtained on a Shimadzu IR-27 spectrophotometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The NMR spectra were obtained on a EM-360 spectrometer, TMS being chosen as the internal standard. The microanalyses were performed by Mrs. Kiyoko Fujimoto.

Hexamethylphosphoric Triamide (HMPT). Commercially-available HMPT was refluxed for 5 hr under N_2 with calcium hydride and then distilled; bp 110—115 °C/15 mmHg.

Starting Materials. The following compounds were prepared according to the reported methods: 4-homoadamantanol,5) *exo*-bicyclo[3.3.1]nonan-2-ol,11) *endo*-bicyclo[3.3.1]-nonan-2-ol,11) bicyclo[3.3.1]nonane-2,6-diol,12) 1-adamantanol,13) 2-adamantanol,14) *exo*-bicyclo[3.3.1]non-3-en-2-ol,11) benzhydrol,15) triphenylmethanol,16) and phthalyl alcohol.17)

Preparation of 2-Phenyl-2-adamantanol. The Grignard reagent prepared from bromobenzene (9.7 g; 0.062 mol) and magnesium (1.5 g; 0.062 atom) in ether (35 ml) was treated with adamantanone (4.5 g; 0.03 mol) in ether (55 ml) and then hydrolyzed with 20% H_2SO_4. The ether layer was separated, combined with an ether extract of the aqueous layer, and dried over Na_2SO_4. The subsequent evaporation of the solvent yielded 4.2 g (63%) of 2-phenyl-2-adamantanol: mp 89.5—90.5 °C, mass spectrum: *m/e* 228 (M^+), NMR ($CDCl_3$): δ 7.1—7.45 (m, 5H), IR (Nujol mull): 3220, 1601, 1008, 697 cm^{-1}. Found: C, 84.38; H, 8.53%. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83%.

General Procedure for Dehydration of Alcohols by HMPT. The substrate (0.01 mol) was dissolved in HMPT (10 ml) and heated at 230—240 °C under N_2 for 5 hr. The reaction mixture was then poured onto water and extracted five times with petroleum ether (bp 40—50 °C). The extract was washed two times with brine and dried over Na_2SO_4. The subsequent evaporation of the solvent gave crude materials. Since 4-homoadamantene5) and bicyclo[3.3.1]non-2-ene11) sublimed during the reaction, they could be obtained in pure form from the sublimates. Bicyclo[3.3.1]nona-2,6-diene was purified by distillation; bp 60—65 °C/20 mmHg (lit,18) 51—51.5 °C/15 mmHg).

Thermal Reaction of Alcohols with HMPT. The treatment was essentially the same as was been described above. The reaction mixture was poured onto water and extracted five times with benzene. The extract was washed two times with brine and dried (Na_2SO_4). After the evaporation of the solvent, a crude material was obtained; this material was purified by a combination of column chromatography and preparative glc.

2-Adamantyl Tetramethylphosphorodiamidata (2): Mp 51.5—53 °C (from *n*-hexane), mass spectrum: *m/e* 286 (M^+), 151 (100%), 135, NMR (CCl_4): δ 2.59 (d, J_{PH} 9.0 Hz, 12H), 4.19—4.60 (b, 1H), IR (Nujol mull): 1290, 1195, 999, 988, 750 cm^{-1}. Found: C, 58.70; H, 9.62; N, 9.59%. Calcd for $C_{14}H_{27}N_2O_2P$: C, 58,72; H, 9.50; N, 9.78%.

*2-*exo*-Dimethylaminobicyclo[3.3.1]non-3-ene (7)*: Mass spectrum: *m/e* 165 (M^+), NMR (CCl_4): δ 2.20 (s, 6H), 2.68 (m, 1H, $W_{1/2}$ 5.0 Hz), 5.87 (m, 2H), IR (liquid film): 1180, 1040, 1000, 720 cm^{-1}. Found: C, 80.21; H, 11.46; N, 8.73%. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48%.

2-Phenyl-2-dimethylaminoadamantane (10): Mp 109.5—111 °C, mass spectrum: *m/e* 255 (M^+), NMR ($CDCl_3$): δ 1.36—1.79 (m, 10H), 1.82 (s, 6H), 2.17—2.42 (b, 1H), 2.40—2.78 (b, 3H), 7.02—7.26 (m, 5H), IR (Nujol mull): 1491, 755, 703 cm^{-1}. Found: C, 84.65; H, 10.11; N, 5.55%. Calcd for $C_{12}H_{25}N$: C, 84.65; H, 9.87; N, 5.48%.

Reaction of Benzyl Alcohols with HMPT. The procedure was the same as that described above. The products were identified by comparison with the reported spectral data (Sadtler Standard Spectra, The Aldrich Library of IR Spectra).

Formation of Dibenzhydryl Ether (14) by the Reaction of Benzhydrol with HMPT: A mixture of 1.84 g (0.01 mol) of benzhydrol and 0.6 g (0.003 mol) of HMPT was heated at 230—240 °C for 1 hr under N_2. The usual work-up and recrystallization from ethanol gave 1.25 g (71%) of dibenzhydryl ether (**14**): mp 107—108 °C (lit,19) 109 °C), mass spectrum: no parent, *m/e* 167 (100%), NMR (CCl_4): δ 5.33 (s, 2H), 7.30 (m, 20H), IR (Nujol mull): 1050 cm^{-1}.

Formation of Phthalan (16) by the Reaction of Phthalyl Alcohol (15) with HMPT: A mixture of 1.38 g (0.01 mol) of phthalyl alcohol and 1.79 g (0.01 mol) of HMPT was heated for 1 hr according to the procedure described above. Column Chromatography (Al_2O_3, *n*-hexane: benzene=4: 1) of the crude material afforded 0.1 g (8%) of phthalan (**16**):20) mass spectrum: *m/e* 120 (M^+), 91 (100%), NMR (CCl_4): δ 5.0 (s, 4H), 7.13 (s, 4H), IR (liquid film): 3030, 1040, 900, 740 cm^{-1}.

Isolation of Benzylpentamethylphosphoric Triamide (17) in the Reaction of Benzyl Alcohol with HMPT: The procedure was as has been described above except that the reaction time was 5 hr. The benzene extract was evaporated; subsequent column chromatography of the residue afforded 3% of benzylpentamethylphosphoric triamide, together with benzyldimethylamine and dibenzylmethylamine. **17**: mass spectrum: *m/e* 255 (M^+), 211, 120 (100%), NMR (CCl_4): δ 2.47 (d, J_{PH} 7.8 Hz, 3H), 2.62 (d, J_{PH} 10.2 Hz, 12H), 4.15 (d, J_{PH} 9.0 Hz, 2H), 7.2—7.4 (m, 5H), IR (liquid film): 1600, 1500, 1300, 1200, 980, 775, 740, 700 cm^{-1}.

Preparation of Benzyl Tetramethylphosphorodiamidate (13). To 2.16 g (0.02 mol) of benzyl alcohol dissolved in 40 ml of anhydrous ether, we added 0.48 g (0.02 mol) of sodium hydride. The mixture was stirred and refluxed for 2 hr. To the suspention of sodium benzylate in ether we then slowly added tetramethylphosphorodiamidic chloride.21) The mixture was stirred and refluxed overnight. The precipitates were removed by filtration, and the organic layer was washed two times with brine and dried (Na_2SO_4). The subsequent evaporation of the solvent, followed by distillation at 140—145 °C/5 mmHg, yielded 3.8 g (79%) of benzyl tetramethylphosphorodiamidate (**13**)22): mass spectrum: *m/e* 242 (M^+), 151 (40%), 91 (100%), NMR (CCl_4): δ 2.53 (d, J_{PH} 9.6 Hz, 12H), 4.85 (d, J_{PH} 9.6 Hz, 2H), 7.30 (s, 5H), IR (liquid film): 1305, 1200, 990, 750, 700 cm^{-1}.

Preparation of Benzyl Tetraethylphosphorodiamidate (20). The procedure described above was followed, but we used tetraethylphosphorodiamidic chloride23) instead of tetramethylphosphorodiamidic chloride. Thus, 2.8 g (94%) of the pure material was obtained after decolorizing with active carbon. **20**: mass spectrum: *m/e* 298 (M^+, feeble), 91 (100%), NMR (CCl_4): δ 1.06 (t, 12H), 3.02 (d of quartet, J_{PH} 12.6 Hz, 8H), 4.87 (d, J_{PH} 7.8 Hz, 2H), 7.30 (s, 5H), IR (liquid film): 1235, 1010 cm^{-1}. Found: C, 60.54; H, 9.38; N, 9.38%. Calcd for $C_{15}H_{27}N_2O_2P$: C, 60.37; H, 9.12; N, 9.38%.

Thermolysis of 13 and 20. The substrate (0.002 mol) was heated for 1 hr at 230—240 °C under N_2. During the period of the reaction, an insoluble oily layer appeared; upon cooling, it solidified to a gummy, crystalline mass. This phenomenon was also observed upon the reaction of benzyl alcohol with HMPT. This compound was identical with bisdimethylammonium dihydrogen pyrophosphate, $(Me_2NH_2)_2H_2P_2O_7$, which Monson and Priest have reported on.3f) The upper layer was immediately subjected to glc analysis; the products shown in Scheme 3 were observed in the specified ratio.

Thermal Reaction between 13 and 19, as well as between 20 and 11. Benzyldimethylamine (**11**)10) and benzyldiethylamine (**19**)9) were prepared according to the reported methods. Each equimolar mixture of the substrates was treated by the procedure described above. The reaction mixture was immediately subjected to glc analysis. The relative ratios are shown in Scheme 3.

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6) A high-molecular-weight product was also obtained (272 mg from 800 mg of 2-adamantanol); it was considered to be di(2-adamantyl) dimethylphsophorodiamidate judging from its NMR and IR data. Moreover, its precise structure was not confirmed. An intractable tarry matter was also formed.

7) This deduction is in accordance with the report by Garbisch that, for 6-substituted 1-phenylcyclohexene, the C-6 substituent may be considered to have preference for the equatorial position for the $W_{1/2}$ of C-6 proton bands$>$15 Hz, and to have preference for the axial position for the $W_{1/2}$ of C-6 proton bands$<$13 Hz; see E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249 (1962).

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