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The Reactions of Several Carbonyl Compounds with Hexamethylphosphoric Triamide

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Synopsis. Non-enolizable carbonyl compounds were found to undergo intriguing reaction upon heating with hexamethylphosphoric triamide; benzophenone gave 1,1,2,2-tetraphenylethane and benzophenone methylimine, while fluorenone afforded 9-methylfluorene, 9-dimethylaminofluorene, and fluorene. In contrast, anthrone, an enolizable compound, was completely recovered unchanged under the the same reaction conditions.

Hexamethylphosphoric triamide (HMPT), an excellent dipolar aprotic solvent,[1] has also been widely utilized as a reagent in organic synthesis.[2] In line with this tendency, Monson and his co-workers reported an intriguing chemical process in which cycloalkanones were converted by thermal treatment with HMPT into pyridine derivatives *via* 1-dimethylaminocycloalkenes.[2g] They were successful in explaining the reaction by assuming a cationic species derived from the enamines.

With this in mind, we hoped that the reaction of non-enolizable carbonyl compounds with HMPT might lead to a yet unexplored mode of reaction, since enamine formation is unlikely in this case. This proved to be the case, and 1,1,2,2-tetraphenylethane was obtained from benzophenone, and 9-methylfluorene from fluorenone.

Upon thermal treatment with HMPT at 230—240 °C for 2 hr, benzophenone afforded 1,1,2,2-tetraphenylethane (**1**) by a formally deoxygenative condensation, together with diphenylmethane (**2**), benzhydryldimethylamine (**3**), and benzophenone methylimine (**4**), as is shown in Table 1. On the other hand, a similar treatment of fluorenone gave mainly the reduction product, fluorene (**5**), together with 9-methylfluorene (**6**) and 9-dimethylaminofluorene (**7**). All these compounds gave satisfactory spectral data, and **1**,[3] **4**,[4] and **6**[5] were identical with the authentic specimens independently prepared. In the case of benzaldehyde, a complex mixture containing at least eleven products resulted, from which bibenzyl (**8**), benzyldimethylamine (**9**), and dibenzylmethylamine (**10**) were isolated.

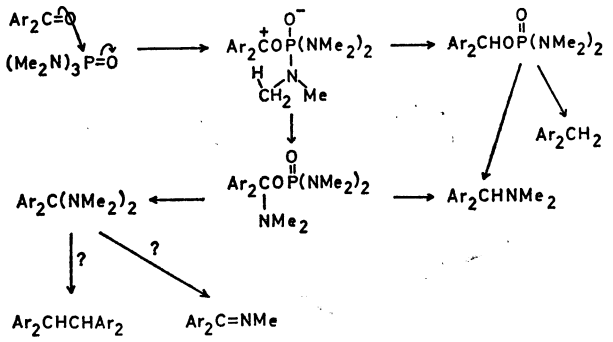
Furthermore, xanthone was converted to xanthene in a 47% yield, but anthrone, an enolizable compound, was completely recovered under these conditions, in accordance with the fact that phenol was converted only slightly to phenyl tetramethylphosphorodiamidate[6] by treatment with HMPT for 5 hr.

When an equimolar mixture of benzophenone and HMPT was heated at 230—240 °C for 2 hr, both the benzophenone and the HMPT were fully consumed. In this case, benzophenone methylimine (**2**) was obtained in a 49% yield after the vacuum distillation of the reaction mixture, although trace amount of **2** and **3** were included as impurities.

Additionally, as is shown in Table 1, the reaction of deoxybenzoin and benzopinacol with HMPT gave peculiar compounds (Runs 7 and 8). In both examples, a cleavage of the central C-C bond of the starting materials took place, although the detailed mechanism is yet unclear.

An inspection of the results listed in the Table (Runs 1 to 4) and the results for the corresponding alcohols[7] indicates that a mechanism similar to that of the reaction of alcohols with HMPT might operate also in the reaction of non-enolizable carbonyl compounds with HMPT, though including some different factors.

Thus, we tentatively propose Scheme 1 with regard to the first step of the reaction.



Scheme 1.

Since benzophenone methylimine (**4**) which had been independently prepared was unchanged even if it was treated with HMPT at 230—240 °C for 2 hr, **4** was the final product in this reaction. The presumed intermediate, an aminal, was prepared in the case of benzaldehyde[8] and was treated *without* a solvent at 230—240 °C, affording only a trace amount of bibenzyl, while the starting material was almost entirely recovered. The detailed mechanism for the formation of the peculiar products, such as **1**, **4**, **7**, and **8**, is not yet understood.

The formation of 2,3,5,6-tetraphenylpyridine (**11**) from deoxybenzoin was well explained by Monson's mechanism.[2g] The compound (**11**) was identical with an authentic specimen independently prepared.[9]

Finally an additional observation might be noted. Throughout Runs 1—3 and 5—7, octamethylpyrophosphoramide[10] was formed.

Experimental

All the temperatures are uncorrected. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The mass spectra were taken by using a Hitachi RMS-4 mass spectrometer. The NMR spectra were obtained on an EM-360

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Table 1. The reaction with HMPT

Run	Substrate	Products (%)
1	Benzophenone	$Ph_2CHCHPh_2$(13), Ph_2CH_2(3), Ph_2CHNMe_2(9), $Ph_2C{=}NMe$(12)
2	Benzaldehyde	$PhCH_2CH_2Ph$(1), $PhCH_2NMe_2$(11), $(PhCH_2)_2NMe$(8), etc.
3	Fluorenone	fluorene(68), 9-methylfluorene(6), 9-dimethylaminofluorene(13)
4	9-Fluorenol	fluorene(11), 9-methylfluorene(1), 9-dimethylaminofluorene(35)
5	Xanthone	xanthene (47, based on unrecovered xanthone) xanthone was recovered in 52%.
6	Anthrone	no reaction
7	Deoxybenzoin	$PhCH{=}C(NMe_2)Ph$(34), $PhCONMe_2$(13), 2,3,5,6-tetraphenylpyridine(3)
8	Benzopinacol	$Ph_2CHCHPh_2$(15), Ph_2CH_2(4), Ph_2CHNMe_2(49), $Ph_2C{=}NMe$(7)

spectrometer, TMS being chosen as the internal standard.

Starting Materials. The benzophenone, benzaldehyde, fluorenone, xanthone, and anthrone were commercially-available products. The following compounds were prepared by the reported method; 9-fluorenol,[11] deoxybenzoin,[12] and benzopinacol.[13]

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

General Procedure for the Reaction with HMPT. The substrate (0.01 mol) was dissolved in HMPT (10 ml) and heated at 230—240 °C under N_2 for 2 hr. The reaction mixture was then distilled under reduced pressure. After the HMPT had been distilled off at 110—115 °C/15 mmHg, the residue was separated to a single product by a combination of vacuum distillation, column chromatography, and preparative glc.

Preparation of Benzophenone Methylimine (4).[14] A mixture of benzophenone dichloride (6 g, 0.025 mol) and 30% aqueous methylamine (60 ml) was stirred for 4 hr. After an additional methylamine solution (20 ml) had been added and stirring had been continued for 1 hr, the organic material was extracted with ether and dried (Na_2SO_4). The removal of the ether and distillation at 133—135 °C/5 mmHg gave 4.3 g (88%) of benzophenone methylimine, which was identical with the product of the reaction of benzophenone with HMPT.

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