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NOVEL REACTION OF BENZOPHENONE WITH HEXAMETHYLPHOSPHORIC TRIAMIDE: FORMATION OF 1,1,2,2-TETRAPHENYLETHANE

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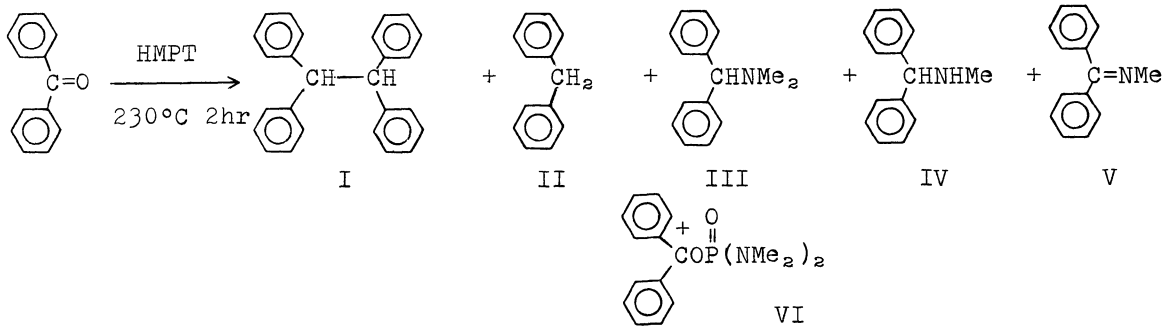
Upon thermal treatment with hexamethylphosphoric triamide benzophenone afforded 1,1,2,2-tetraphenylethane (I) by formally deoxygenative condensation together with diphenylmethane (II), benzhydryldimethylamine (III), benzhydrylmethylamine (IV), and benzophenone methylimine (V).

Recently Monson and collaborators reported an intriguing chemistry in which cycloalkanones were converted by treatment with hexamethylphosphoric triamide (HMPT) into pyridine derivatives *via* 1-dimethylaminocycloalkenes.[1] They were successful in explaining the reaction by assuming a cationic species derived from the enamines. With this in mind it was hoped that the reaction of benzophenone, a representative non-enolizable ketone, with HMPT might lead to yet unexplored mode of reaction since enamine formation is unlikely in the case of benzophenone. This proved to be the case, and 1,1,2,2-tetraphenylethane (I) was produced by reductive condensation of benzophenone together with several nitrogen-containing compounds.

Benzophenone (2 g; 11 mmol) was dissolved in 10 ml of HMPT and the solution was heated at 230°C under nitrogen atmosphere for 2 hr with concomitant evolution of dimethylamine. The reaction mixture was distilled under diminished pressure. A mixture of II[2] (63 mg; 3%), III[3] (204 mg; 9%), IV[4] (23 mg; 1%), and V[5] (265 mg; 12%) distilled at 100—130°C/2 mmHg,[6] and a higher boiling mixture of octamethyl pyrophosphoramide[7] and I[8] (232 mg after recrystalization from n-hexane; 13%) came out at 100—160°C/0.4 mmHg. The structure of these products were all confirmed by the spectral data as well as direct comparison with each authentic



specimen。

Previously we reported the reaction of HMPT with alcohols, dehydration of which are difficult or impossible stereochemically。[9] For example, II and III were formed by the reaction of benzhydrol with HMPT, and benzhydryl tetramethylphosphorodiamidate was established as an intermediate for the reaction of benzhydrol。 In the present case the actual mechanism for the formation of the compounds (I)—(V) is not understood yet. However, we feel that a cationic species such as VI might play some role as a precursor in the reaction on the analogy of the results in the case of alcohols。

The investigation aimed at the mechanistic details is under way.[10]

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