Photochemical Synthesis of *NNN′N′*-Tetramethylmethanediamine

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Summary Ultraviolet irradiation of carbon tetrachloride solutions of dimethylamine provides an easy, high-yield synthesis of the unusual photoproduct *NNN′N′*-tetramethylmethanediamine.

CHEMICAL and photochemical interactions of amines and polyhalogenocarbons have been given mechanisms in which both ionic and radical intermediates have been separately and jointly implicated.[1] Furthermore, product mixtures are typically complex, with composition strikingly dependent on variations in reaction conditions. In the course of photochemical studies of amines, we have discovered an anomalous photochemical reaction of dimethylamine (**1**) in polychlorocarbons: the high-yield photosynthesis of *NNN′N′*-tetramethylmethanediamine (**2**) as the dominant nitrogen-containing volatile product.

Solutions of (**1**) (2—200 mmol; 1·0 M) in carbon tetrachloride were irradiated under argon at 300 nm and 35°. Efficient destruction of dimethylamine was accompanied by formation of a white precipitate, which was identified by Volhard titration and n.m.r. spectroscopy as dimethylamine hydrochloride (**3**). The liquid phase contained, in addition to solvent, chloroform, methylamine, and one photoproduct which was isolated by preparative g.l.p.c. (alkali-treated Carbowax 20M) and identified by comparison with authentic material as *NNN′N′*-tetramethylmethanediamine (**2**).

$$\underset{(\mathbf{1})}{\mathrm{Me_2NH}} \xrightarrow[\mathrm{CCl_4}]{h\nu} \underset{(\mathbf{2})}{\mathrm{(Me_2N)_2CH_2}} + \underset{(\mathbf{3})}{\mathrm{Me_2NH_2Cl}} + \mathrm{CHCl_3} + \mathrm{MeNH_2}$$

In a typical experiment, 100 mmol of (**1**) gave 22 mmol of (**2**), 32 mmol of (**3**), and 25 mmol of chloroform. As diamine (**2**) was also shown to be somewhat photolabile, optimum yields of (**2**) were achieved at *ca.* 50% conversion of (**1**), with slight diminution thereafter. Methylamine yields were small.

Ground-state syntheses of diamines of the type $R_2N[CH_2]_nNR_2$ from secondary amines and dihalogenated hydrocarbons are known,[2] and (**2**) has been synthesized by condensation of (**1**) with formaldehyde.[3] The photochemical synthesis, however, is drastically different. Solvent labelling experiments indicate no incorporation of solvent into photoproduct (**2**). Thus a minimum 3:1 stoicheiometry for conversion of (**1**) into (**2**) is required, and the isolable yields of (**2**) are *ca.* 65—70%. Similar yields were obtained in a variety of polyhalogenocarbon solvents but longer irradiation times were required.

The one literature precedent for formation of (**2**) from (**1**) is a reference to unpublished studies of the mercury-sensitized decomposition of gaseous dimethylamine.[4] Diamine (**2**) is also produced in 1% yield in photolysis of tetramethyltetrazene (**4**)[4] and in 2—4% yield during autoxidation of tetrakis(dimethylamino)ethylene (**5**).[5] Although the precise mechanistic origins of (**2**) are unclear, the intermediacy of dimethylamino-radicals is implicated by formation of (**2**) from (**4**) and (**5**) as well as (**1**). A free-radical mechanism for the (**1**) → (**2**) transformation is supported by the zero-conversion quantum yields for disappearance of (**1**) ($\Phi = 4{\cdot}7$ mol einstein^{-1}) and for appearance of (**2**) ($\Phi = 1{\cdot}2$). Polymerization, however, was very minor. The intermediacy of *N*-chlorodimethylamine (**6**), an *a priori* possibility in view of occurrence of chloroamines in reactions of other amines and carbon tetrachloride,[6] was shown to be of minor importance by photochemical and dark control experiments with independently prepared[7] (**6**).

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