Table I. Deuterium Isotope Effects on Dipole[a] Moments

Molecule	Dipole moment, D.	Deuterium isotope effect
CH_3F	1.847	. . .
CD_3F	1.858	+0.011
$CH_3C\equiv CH$	0.780	. . .
$CH_3C\equiv CD$	0.767	−0.013
$CD_3C\equiv CH$	0.784	+0.004
$CD_3C\equiv CD$	0.772	−0.008
$CH_3CH_2CH_3$	0.085	. . .
$CH_3CD_2CH_3$	0.095	+0.010
$CD_3CH_2CD_3$	0.076	−0.009

[a] Estimated accuracy is ±0.001 D.

sumption of a constant direction[4] for the isotope effect is correct. If the direction of the total dipole moment in methyl fluoride is taken to be such that the methyl group is at the positive end, the isotope shifts observed indicate that the methyl group in methylacetylene is also at the positive end of the molecule, but that the methyl groups in propane are at the negative end. The results for methylacetylene are in accord with the accepted idea that methyl groups are electron releasing when bonded to a carbon involved in a π system, whereas the propane results indicate a small electron-withdrawing effect for methyl groups in ordinary saturated systems lacking polar constituents. The fact that the inductive effect of a methyl group in a saturated system might be different from that for a methyl group involved in a π system is not unexpected in view of the difference in "hybridization" involved. Some indication that this might be the case has already been found[5] from kinetic effects. In systems where there is considerable deviation from conventional bond angles, as in methylcyclopropane, or when a highly electronegative group is present, the conclusions reached here do not apply since the methyl group is very likely electron donating in these cases.

(5) (a) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **86**, 1161 (1964); (b) R. C. Fort and P. von R. Schleyer, *ibid.*, **86**, 4194 (1964); (c) H. O. Holtz and L. M. Stock, *ibid.*, **87**, 2404 (1965).

(6) A. P. Sloan Fellow.

(7) American Chemical Society Petroleum Research Fund Fellow, 1963-1964.

(8) We wish to thank Professor John I. Brauman for helpful discussions.

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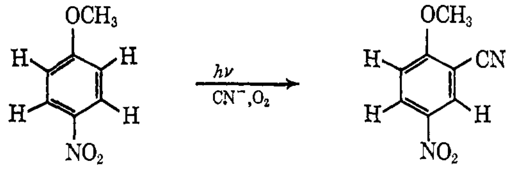
Received April 9, 1966

Photoinduced Substitution. III. Replacement of Aromatic Hydrogen by Cyanide[1,2]

Sir:

We have observed that cyanide reacts with photoexcited 4-nitroanisole in aqueous solution in the presence of oxygen to give 2-cyano-4-nitroanisole. The net effect is replacement of an aromatic hydrogen atom by the cyanide group. This reaction provides a new method for preparing aromatic nitriles and demonstrates a new mode by which nucleophiles may attack aromatic nitro compounds.[3]



I II

The initial experiments were carried out in a nitrogen atmosphere. In a typical case a solution of 0.5 g of 4-nitroanisole and 2.0 g of potassium cyanide in 100 ml of *t*-butyl alcohol and 400 ml of water was flushed with nitrogen and irradiated[4] for 3 hr. Conventional isolation procedures afforded 85 mg of a compound (III) melting at 224.5–225.5° and 35 mg of a compound (II) melting at 127.5–128°. The elemental analysis and spectral data indicated that III was a dicyanodimethoxyazoxybenzene (probably the 3,3′-dicyano-4,4′-dimethoxy isomer). Compound II was identified as 2-cyano-4-nitroanisole by its melting point,[5] elemental analysis, and nmr and infrared spectra. In addition, acid hydrolysis of II yielded 2-methoxy-5-nitrobenzoic acid, which did not depress the melting point of an authentic sample.

On the assumption that II and III arose from a common intermediate, III, by some type of disproportionation reaction, and II, by oxidation by trace amounts of oxygen in the system, we repeated the experiment (1.5-hr irradiation) with air as the sweep gas in place of nitrogen. The yield of II increased markedly (133 mg total) at the expense of III (none was isolated). A similar experiment with oxygen in place of air afforded 229 mg (39%) of II. Still better results were obtained when the irradiation time was reduced. Thus 10-min irradiation of a solution of 4-nitroanisole (100 mg) and potassium cyanide (400 mg) in 20 ml of *t*-butyl alcohol and 450 ml of water in the presence of oxygen gave 21.5 mg of 4-nitroanisole and 61.2 mg (67% based on nitroanisole consumed) of 2-cyano-4-nitroanisole.

Additional information was gained from spectral and kinetic studies on dilute aqueous solutions of 4-nitroanisole (1×10^{-4} *M*). The data are consistent with sequence 1, in which the major events leading to II are (a) absorption of light by 4-nitroanisole, (b) addition of cyanide to electronically excited 4-nitroanisole,[6] and (c) oxidation of the intermediate adduct by molecular oxygen. An alternate pathway involving absorption of light by a ground-state complex of cyanide and 4-nitroanisole is considered unlikely since the ultraviolet absorption spectrum of 4-nitroanisole is not influenced by addition of potassium cyanide to the solution, even at a concentration of 0.1 *M* cyanide.

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(1) Part II: R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Am. Chem. Soc.*, **87**, 2945 (1965).

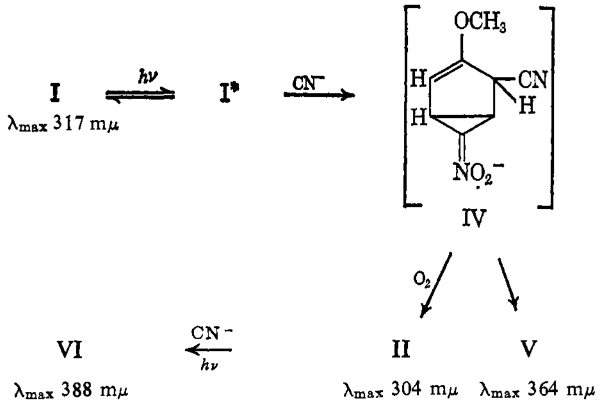
(2) This investigation was supported by a Public Health Service Fellowship (5-F1-GM-25, 182) from the National Institute of General Medical Science.

(3) Pyridine and 4-methylpyridine displace nitrite from excited 4-nitroanisole. Hydroxide ion behaves similarly and, in addition, attacks at the ether function to give 4-nitrophenol (see ref 1). For other photoinduced nucleophilic substitution reactions see E. Havinga and R. D. DeJongh, *Bull. Soc. Chim. Belges*, **71**, 803 (1962); D. F. Nijhoff and E. Havinga, *Tetrahedron Letters*, **47**, 4199 (1965); R. O. DeJongh and E. Havinga, *Rec. Trav. Chim.*, **85**, 275 (1966).

(4) A General Electric 1200-w low-pressure lamp was used, and the light was filtered through Pyrex to remove radiation below 290 mμ. The major bands were at 313 and 366 mμ. See ref 1 for details.

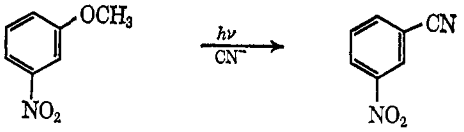
(5) Reported values are 126° (J. Blanksma, *Chem. Weekblad*, **5**, 793 (1908)) and 130° (H. P. Baudet, *Rec. Trav. Chim.*, **43**, 709 (1924)).

(6) The structure postulated for the intermediate adduct, IV, is based on (a) the valence bond formulation for the excited state of a nitroaromatic proposed by H. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **85**, 922 (1963), and (b) the fact that CN is *meta* to nitro in the final product.



It was found that II as well as I underwent a photoinduced reaction with cyanide ion. Pseudo-first-order kinetics were obtained for both the reaction of II (followed spectrophotometrically by the increase in absorbance at 385 mμ) and the reaction of I (followed spectrophotometrically by the decrease in absorbance at 335.5 mμ, the isosbestic point for conversion of II to VI). Under the same conditions of irradiation (1×10^{-4} *M* nitro compound, 4×10^{-3} *M* CN^-, 25°, Pyrex filter) I reacted 16 times faster than II ($t_{1/2}$ = 50 and 815 sec for I and II, respectively). This factor is sufficiently great that a high conversion of I to II may be realized before II reacts further. Formation of II in these experiments was confirmed by both spectral and chromatographic data. When the irradiation of I was carried out in the absence of oxygen, a maximum developed at 364 mμ and no maximum appeared at 304 mμ, the region in which II absorbs.

With a good departing group *meta* to the nitro group, direct displacement by cyanide may occur. For example, it was found that irradiation of a solution of 100 mg of *m*-nitroanisole and 400 mg of sodium cyanide for 10 min in 20 ml of *t*-butyl alcohol and 450 ml of water afforded 32 mg of *m*-nitrobenzonitrile and 28 mg of unreacted *m*-nitroanisole. Oxygen was not necessary for this reaction.



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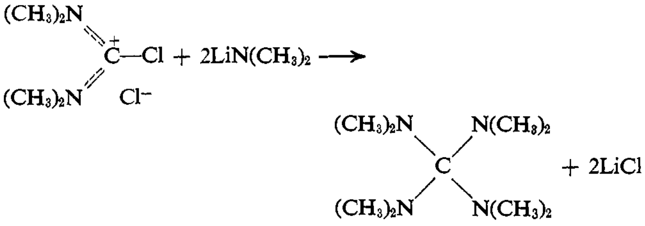
Received April 1, 1966

Preparation of Tetrakis(dimethylamino)methane

Sir:

We wish to report the synthesis and characterization of tetrakis(dimethylamino)methane, the first tetraminomethane described in the literature. Although the silicon,[1] germanium,[2] and tin[3] analogs have been described, there was some doubt as to whether the carbon derivative could exist. The potential guanidinium precursors are generally quite stable and steric crowding of the four dialkylamino groups would tend to destabilize the tetramine (covalent radii for C, 0.77 A; Si, 1.17 A).

The tetrakis(dimethylamino)methane is prepared in 70% yield by allowing tetramethylchloroformamidinium chloride[4] to react with a slurry of lithium dimethylamide in benzene at room temperature for several hours. The tetramine is a readily sublimable, hygroscopic solid, mp 122.5–124.5° (from *n*-pentane). Its structural assignment is based on its origin, molecular weight, nmr spectrum, and elemental analysis. *Anal.* Calcd for $C_9H_{24}N_4$: C, 57.4; H, 12.8; N, 29.8; mol wt, 188. Found: C, 57.4; H, 12.8; N, 29.4; mol wt, 189 ± 3 (cryoscopy in benzene). The nmr spectrum (benzene solvent, TMS internal standard) exhibited a sharp singlet at τ 7.39.



Experiments are in progress to elucidate the chemistry of the tetraminomethanes.

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(1) H. Breederveld and H. I. Waterman, *Research* (London), **5**, 537 (1952).

(2) H. Anderson, *J. Am. Chem. Soc.*, **74**, 1421 (1952).

(3) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1962).

(4) H. Eilingsfeld, G. Neubauer, M. Seefelder, and H. Weidinger, *Ber.*, **97**, 1232 (1964).

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Received April 18, 1966