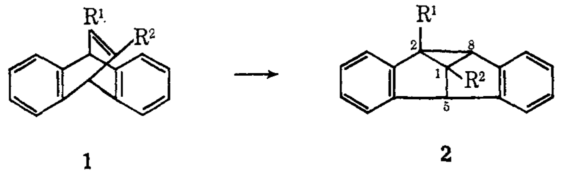
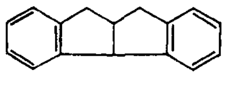
tained by catalytic hydrogenation of **2a** to the known[5] dibenzobicyclo[3.3.0]octadiene (**3**). **2a** was also obtained, albeit at a very slow rate, by the unsensitized photolysis of **1a** in benzene solution, again using a Pyrex filter. Rearrangement of the derivatives **1b–d** to **2b–d**, on the other hand, proceeded fairly rapidly in benzene or cyclohexane solution, using Pyrex vessels and ordinary sunlamps, although for preparative purposes acetone sensitization proved more convenient. Thus, **2b**, mp 98–99°; nmr multiplet at τ 2.6–3.1 (8 H), singlets at τ 4.97 (1 H), 5.51 (1 H), 6.17 (3 H), and 6.32 (3 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 279 mμ (ϵ 1200), 271 (1500), 265 (1400), and 217 (sh, 25,000), was obtained in 96% yield by photolysis of **1b**.[6] Irradiation of **1c**[7] gave **2c**, mp 179–180°; nmr multiplet at τ 2.8–3.3 (8 H) and singlets at τ 4.86 (1 H) and 5.44 (1 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 279 mμ (ϵ 650), 271 (ϵ 890), and 221 (28,000), in 80% yield. **2d**, mp 81.5–82.5°; proton nmr multiplet at τ 2.5–3.2 (8 H) and singlets at τ 5.10 (1 H) and 5.86 (1 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 278 mμ (ϵ 800), 270 (960), 264 (780), and 215 (28,000), was isolated in 74% yield from the photolysis of **1d**.[8] In all three cases, inspection of the nmr spectra of the crude rearrangement products indicated the presence only of the 1,2 isomers **2b–d**.



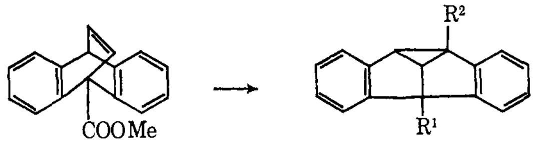
1 2

a, R¹, R² = H
b, R¹, R² = COOMe
c, R¹, R² = CN
d, R¹, R² = CF$_3$
e, R¹=H; R² = COOMe



3

Irradiation of **1e**[9] gave **2e**, mp 169.5–170.5°; nmr multiplet at τ 2.6–3.1 (8 H) and singlets at τ 5.03 (1 H), 6.23 (2 H), and 6.32 (3 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 280 mμ (ϵ 1600), 272 (1900), 266 (1500), and 220 (27,000), in 75% yield. The nmr spectrum of the crude product indicated the presence of less than 5% of other isomer(s) of **2e**. On the other hand, irradiation of 1-methoxycarbonyldibenzobicyclo[2.2.2]octatriene (**4**)[10] gave a mixture of the isomers **5a** and **5b** (ratio 67:33) in 91% yield. Chromatographic separation on Florisil gave **5a**, mp 101–102°; nmr multiplet at τ 2.4–3.1 (8 H), triplet (J = 6.5 cps) centered at τ 5.96 (1 H), singlet at τ 6.20 (3 H), and doublet (J = 6.5 cps) centered at τ 6.92 (2 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 281 mμ (ϵ 1400), 273 (1900), and 219 (26,000), and **5b**, mp 129–130°; nmr multiplets at τ 2.1–2.3 (1 H) and 2.6–3.2 (7 H), doublet (J = 5 cps) centered at τ 5.50 (1 H), multiplet at τ 5.9–6.1 (2 H), and singlet at τ 6.23 (3 H); $\lambda_{\max}^{\mathrm{MeCN}}$ 280 mμ (ϵ 1400), 272 (2100), and 223 (27,000).



4

5a, R¹ = COOMe; R² = H
b, R¹ = H; R² = COOMe

It thus appears that the formation of the dibenzotricyclo[3.3.0.0^{2,8}]octadiene ring system by photolysis of suitable dibenzobicyclo[2.2.2]octatrienes is quite general. The scope of this reaction is under investigation.

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On the Inductive Effect of Methyl Groups Bonded to Saturated Systems[1]

Sir:

It is well established that a methyl group bonded to an unsaturated carbon acts as an electron donor.[2] However, the inductive effect, if any, of a methyl group bonded to a saturated carbon in a system with no polar constituents has not yet been determined. We have recently carried out an investigation by microwave Stark effect measurements of the deuterium isotope effect on molecular dipole moments[3] which gives information bearing on this question. In this study, measurements accurate to 0.001 D. were made for a number of molecules in the ground vibrational state, and deuteration was found to cause a change in the dipole moment of the order of 0.01 D. Among the molecules studied were several in which methyl groups were deuterated. It is reasonable to assume that the direction[4] of the *change* of the dipole moment caused by deuterating a methyl group will be the same for all simple organic molecules. If this assumption is correct, a comparison among molecules of the isotope *shifts* caused by deuteration of methyl groups will determine the relative signs of the direction of the *total* molecular dipole moments. Then if the direction of the total dipole moment for one of the molecules is known for chemical reasons, the direction of the total dipole moment of the other molecules will be determined. Table I lists the results found for methyl fluoride, methylacetylene, and propane. It may be noted that whenever substitution of deuterium on one end of a molecule is found to cause an increase in the dipole moment, substitution at the opposite end is observed to cause a decrease, as would be expected if the as-

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131 (1965); 2a and some of its derivatives have also been prepared recently by S. J. Cristol and B. B. Jarvis, starting from the dibenzobicyclo[3.2.1]octadiene system: S. J. Cristol, private communication.

(5) W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, *J. Chem. Soc.*, 4026 (1957).

(6) O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

(7) C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963).

(8) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961).

(9) Prepared by the addition of methyl propiolate to anthracene.

(10) Prepared by addition of *cis*-1,2-dichloroethylene to 9-methoxycarbonylanthracene followed by dechlorination using a zinc–copper couple. We wish to thank Professor S. J. Cristol and Dr. W. Lim for the details of this dechlorination method.

(1) This research was supported by grants from the National Science Foundation and from the Petroleum Research Fund administered by the American Chemical Society.

(2) For example, C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1965, p 472.

(3) J. S. Muenter and V. W. Laurie, to be published.

(4) Direction is meant in the vector sense.

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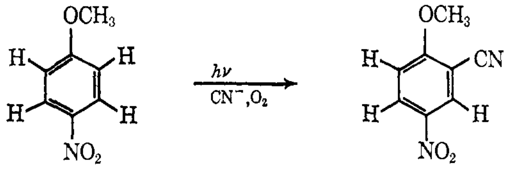
Photoinduced Substitution. III. Replacement of Aromatic Hydrogen by Cyanide[1,2]

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.

(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.