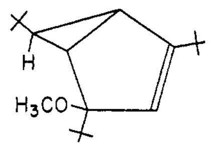
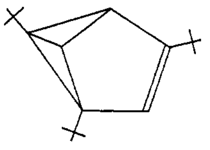
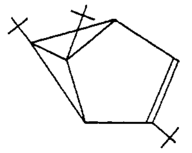


I



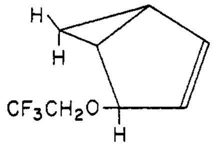
II



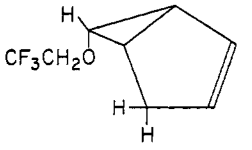
III

of the 1,3,6-tri-*t*-butylbenzvalene[4,5] (III) and 1,2,4-tri-*t*-butylbenzene isomers.[2] The lower quantum yields observed in the hydrocarbon solutions indicate that the intermediate returns in large part to 1,3,5-tri-*t*-butylbenzene.

Although benzene does not appear to react in this manner with methanol, it does yield two adducts (IV and V) upon photolysis in trifluoroethanol.[6] The nature of these products suggests that the reaction follows a similar course.



IV



V

Irradiation of 1,3,5-tri-*t*-butylbenzene in methanol solution (~0.02 *M*) at 2537 A (4-w Germicidal lamp, Corning 7910 filter) and room temperature results in its disappearance with a quantum yield of 0.15. The only product detectable by nmr, either initially or after 90% conversion, is the adduct I, a white solid, mp 35°, recrystallizable from methanol. It has been characterized as 4-methoxy-2,4,6-tri-*t*-butyl[3.1.0]bicyclohex-2-ene (I) on the basis of the following properties: the ultraviolet spectrum shows only end absorption above 2000 A (ϵ_{2200} 2500). The nmr spectrum[7] exhibits singlets of 9 H (*t*-butyl) at τ 8.87, 9.04, and 9.10 and of 3 H (OCH_3) at τ 7.02 and multiplets of 1 H at τ 5.24, 8.31, 8.86, and 9.27. The latter can be assigned[8] to positions 3, 5, 1, and 6 (*endo*), respectively, on the basis of their chemical shifts and coupling constants ($J_{1,3} = 1.5$, $J_{1,5} = 5.7$, $J_{1,6} = 4.6$, and $J_{5,6} = 2.7$ cps). Both the stereochemistry of the proton at C-6 and the absence of this resonance in the adduct from CH_3OD are consistent with addition to a benzvalene-like structure.

Photolysis of benzene in trifluoroethanol under similar conditions yields as the principal products IV and V in a ratio of about 2:1 ($\phi_{\text{total}} = 0.05$). They are readily isolated by gas chromatography (retentions relative to mesitylene on QF1 at 50°: V = 0.95, IV = 1.38). Their ultraviolet absorptions are similar: no maximum above 2000 A (ϵ_{2200} ~3000). The infrared spectrum of IV shows strong C–H vibrations at 3.27 and 3.41 μ and a double bond vibration at 6.27 μ; the corresponding values for V are 3.28, 3.43, and 6.22 μ. The nmr spectrum of IV shows multiplets of one proton each centered at τ 3.71, 4.58, 5.55, ~8.1, ~8.3, 9.06, and 10.10 and a quartet of two protons (OCH_2CF_3) at τ 6.13. The appearance of only two olefinic protons, coupled with 5.5 cps, and of the two high-field protons (*gem*-cyclopropyl, J = 4 cps) leads to the conclusion that the product is 4-trifluoroethoxy-[3.1.0]bicyclohex-2-ene. The nmr spectrum of V consists of multiplets of one proton each centered at τ 4.41, 4.53, 8.03, and 8.26, two nonidentical protons at τ 7.5, and a proton at τ 6.5 partially obscured by the characteristic quartet of the OCH_2CF_3 protons centered at τ 6.46. As with IV, there are only two olefinic protons, coupled with 5.6 cps, indicating that this compound is also a bicyclohexenyl ether. The absence of the high-field protons suggests that the alkoxyl group is on the cyclopropane ring. By double resonance, the proton at τ 6.5 is shown to be strongly coupled (J ~ 7 cps) to each of the τ 8 bridgehead protons and is therefore in the *exo* position on the cyclopropane ring. The conclusion that V is 6-*endo*-trifluoroethoxybicyclo-[3.1.0]hex-2-ene is further supported by the similarity in nmr spectrum with those of the methyl and hexyl ethers reported[9] by Schöllkopf and Paust. The stereochemistry of V is again that which would be expected from addition to a benzvalene-like structure.

The alcohol additions reported here bear at least a superficial resemblance to the previously reported[10] additions of olefins to benzene. The relationship between these reactions and the nature of the intermediates is under investigation.[10a]

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[5] Since solutions of III in methanol are stable at room temperature and photolyze predominantly to 1,2,4-tri-*t*-butylbenzene, it may be concluded that III is not formed during the photolysis of 1,3,5-tri-*t*-butylbenzene in this solvent.

[6] Two products, not yet fully characterized, are also formed from 1,3,5-tri-*t*-butylbenzene in this solvent.

[7] 100-Mc spectra taken in CCl_4 solution with a Varian HA-100 spectrometer. We thank Miss Gail Norman for these spectra.

[8] The spectral data are also consistent with an isomer in which the *t*-butyl group is at C-3 instead of C-2. Thermal decomposition of the adduct at 200° to 1,3,6-tri-*t*-butylfulvene provides evidence that the *t*-butyl groups are not on adjacent carbon atoms. Characterization of this fulvene will be reported later.

[9] U. Schöllkopf and J. Paust, *Ber.*, **98**, 2221 (1965); U. Schöllkopf, personal communication.

[10] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2066 (1966).

[10a] NOTE ADDED IN PROOF. Methoxy derivatives analogous to IV and V are formed by irradiation of benzene in methanol containing a trace of hydrochloric acid.

[11] Student Aide, A.C.M. Argonne Semester Program.

Louis Kaplan, James S. Ritscher,[11] K. E. Wilzbach
Chemistry Division, Argonne National Laboratory
Argonne, Illinois

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The Photoisomerization of Dibenzobicyclo[2.2.2]octatrienes

Sir:

Recently, Zimmerman and Grunewald[1] reported the photoisomerization of bicyclo[2.2.2]octa-2,5,7-triene ("barrelene") to tricyclo[3.3.0.0^{2,8}]octa-3,6-diene ("semibullvalene"). We have independently observed this rearrangement in the photolysis of a number of dibenzobicyclo[2.2.2]octatrienes.

Irradiation of an acetone solution of dibenzobicyclo-[2.2.2]octatriene (**1a**)[2] with a Philips HPK 125 high-pressure mercury lamp (Pyrex filter) gave dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**2a**) in 85% yield.[3] The nmr spectrum of this product was identical with that reported for **2a** obtained by dimerization of benzocyclobutadiene.[4] Further structure proof was ob-

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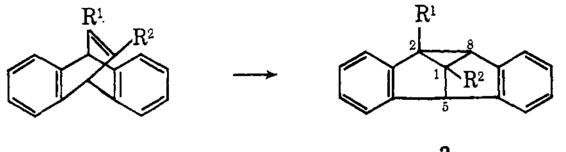
[1] H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).

[2] S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960).

[3] All compounds reported here gave satisfactory elemental analyses.

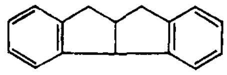
[4] G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**,

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**.



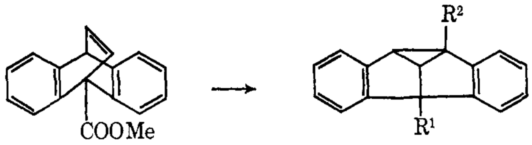
1 **2**

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.

Engelbert Ciganek
Contribution No. 1202, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

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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.

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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[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.