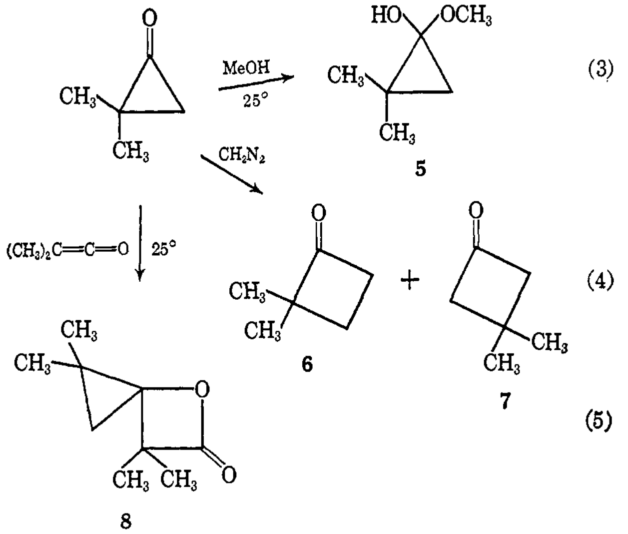
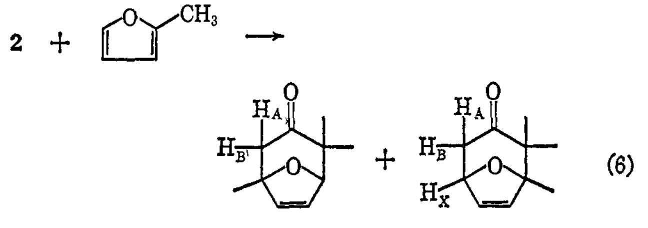
and affords the hemiketal **5** in nearly quantitative yield.[13]



Treatment of **2** with excess diazomethane (eq 4) affords the cyclobutanones **6** and **7** in the ratio 25:75, confirming earlier predictions that cyclopropanones are enormously more reactive than cyclobutanones in an uncatalyzed ring expansion with diazomethane.[14–17]

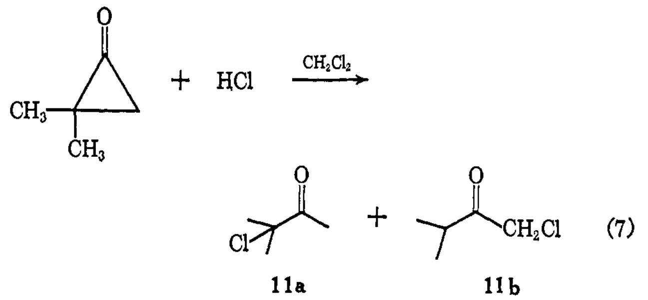
Compound **2** reacts with dimethylketene at room temperature to yield the novel cycloadduct **8** (eq 5). Compound **8** possesses the following properties: mass spectrum, *m/e* 154 (molecular ion, 1.1%), 110 (loss of CO_2, 9.5%), 70 ($(CH_3)_2C{=}C^+{=}O$, 100%), 56 ($(CH_3)_2C^+{=}CH_2$, 20%); infrared, $\lambda_{max}^{CCl_4}$ 5.47 μ; nmr **AB** quartet centered at 0.67 ppm (J = 7 cps), four three-proton singlets at 1.38, 1.29, 1.25, and 1.10 ppm.

The reaction of cyclopropanones with 1,3-dienes is predicted to occur in a concerted manner to yield 1,4–1,3 adducts.[18] The addition of **2** and 2-methylfuran yields a mixture of the 1,4–1,3 adducts **9** and **10** in the ratio 58:42, a result not inconsistent with a concerted mode of addition.

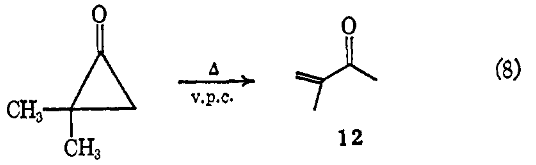


Compounds **9** and **10** were shown to be isomeric by mass spectrometry (molecular ion, *m/e* 166 common to both); infrared of both compounds possesses $\lambda_{max}^{CCl_4}$ 1720 cm^{-1}; nmr of **9** shows a simple **AB** quartet centered at 2.35 ppm (J = 15 cps) while **10** shows an **ABX** spectrum, the **AB** portion centered at 2.40 ppm, X centered at 4.85 ppm (J_{AB} = 15.2 cps, J_{AX} = 4.7 cps, J_{BX} = 1.3 cps).

Treatment of **2** with dry HCl leads to the unexpected result that the two isomeric α-chloro ketones **11a** and **11b** are produced in the rate 40:60 (~60% over-all yield).



Attempts to collect **2** by preparative vpc lead to formation of methyl isopropenyl ketone (**12**).



Cyclopropanone itself is available from the reactions of diazomethane and ketene.[15,17,19] The preparation and reactions of other cyclopropanones is under vigorous study in our laboratory.

Acknowledgments. The authors are indebted to the National Science Foundation (Grant NSF-GP-4280) and the Air Force Office of Scientific Research (Grant AFOSR-1000-66) for their generous support of this work.

[13] Compound **5** possesses molecular weight of 116 (mass spectrum) and its nmr shows an AB quartet centered at 0.58 ppm, J = 5 cps.

[14] J.-M. Conia and J. Salaun, *Bull. Chem. Soc. France*, 1957 (1964); M. D. Owen, G. R. Ramage, and J. E. Simonsen, *J. Chem. Soc.*, 1213 (1938).

[15] P. Lipp and R. Koster, *Ber.*, **64**, 2823 (1931).

[16] D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

[17] A. S. Kende, Ph.D. Dissertation, Harvard University, 1956.

[18] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

[19] W. B. Hammond and N. J. Turro, unpublished results. The greater ease of handling **2** compared to **1** encourages us to feel that cyclopropanone itself may be a tractable organic compound.

[20] National Science Foundation Predoctoral Fellow, 1964–1966.

[21] Fellow of the Alfred P. Sloan Foundation.

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The Photochemical 1,3 Addition of Alcohols to Benzenes[1]

Sir:

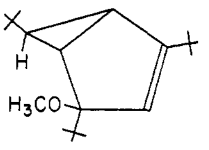
We wish to report a new photochemical reaction, the formation of alkoxy[3.1.0]bicyclohexenes by 1,3 addition of alcohols to benzene and alkylbenzenes. In the case of 1,3,5-tri-*t*-butylbenzene, the quantum yield for this addition reaction in methanol is severalfold greater than that for the isomerization observed[2] in hydrocarbon solutions. Furthermore, the bicyclic ether is formed to the exclusion of the isomeric hydrocarbons. The structure of the product (I) suggests that it is formed by addition[3] of methanol to 1,2,4-tri-*t*-butylbenzvalene[4] (II) or an excited state closely resembling it. It is reasonable to conclude that the same intermediate is formed in hydrocarbon solvents and is the precursor

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

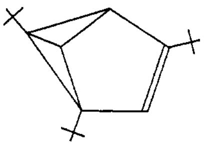
[2] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

[3] Related photochemical additions of alcohols to conjugated dienes are discussed by W. G. Dauben and W. T. Wipke, "Organic Photochemistry," Butterworths, London, 1965, p 539.

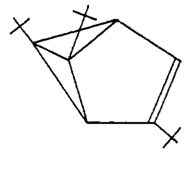
[4] Following the suggestion of J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966), we are renaming benzvalene as tricyclo[3.1.0.0^{2,6}]hex-3-ene to accord with IUPAC rules. Compound III was previously[2] called 2,5,6-tri-*t*-butyltricyclo[2.1.0.0^{5,6}]hex-2-ene.



I



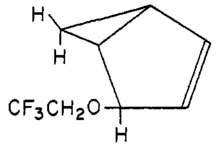
II



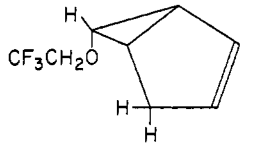
III

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 ($\sim$0.02 *M*) at 2537 A (4-w Germicidal lamp, Corning 7910 filter) and room temperature results in its disappearance with a quantum yield of 0.15. The only product detectable by nmr, either initially or after 90% conversion, is the adduct I, a white solid, mp 35°, recrystallizable from methanol. It has been characterized as 4-methoxy-2,4,6-tri-*t*-butyl[3.1.0]bicyclohex-2-ene (I) on the basis of the following properties: the ultraviolet spectrum shows only end absorption above 2000 A (ϵ_{2200} 2500). The nmr spectrum[7] exhibits singlets of 9 H (*t*-butyl) at τ 8.87, 9.04, and 9.10 and of 3 H (OCH_3) at τ 7.02 and multiplets of 1 H at τ 5.24, 8.31, 8.86, and 9.27. The latter can be assigned[8] to positions 3, 5, 1, and 6 (*endo*), respectively, on the basis of their chemical shifts and coupling constants ($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 (ϕ_{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} $\sim$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, $\sim$8.1, $\sim$8.3, 9.06, and 10.10 and a quartet of two protons (OCH_2CF_3) at τ 6.13. The appearance of only two olefinic protons, coupled with 5.5 cps, and of the two high-field protons (*gem*-cyclopropyl, J = 4 cps) leads to the conclusion that the product is 4-trifluoroethoxy-[3.1.0]bicyclohex-2-ene. The nmr spectrum of V consists of multiplets of one proton each centered at τ 4.41, 4.53, 8.03, and 8.26, two nonidentical protons at τ 7.5, and a proton at τ 6.5 partially obscured by the characteristic quartet of the OCH_2CF_3 protons centered at τ 6.46. As with IV, there are only two olefinic protons, coupled with 5.6 cps, indicating that this compound is also a bicyclohexenyl ether. The absence of the high-field protons suggests that the alkoxyl group is on the cyclopropane ring. By double resonance, the proton at τ 6.5 is shown to be strongly coupled ($J \sim 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.

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Received April 15, 1966

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**,