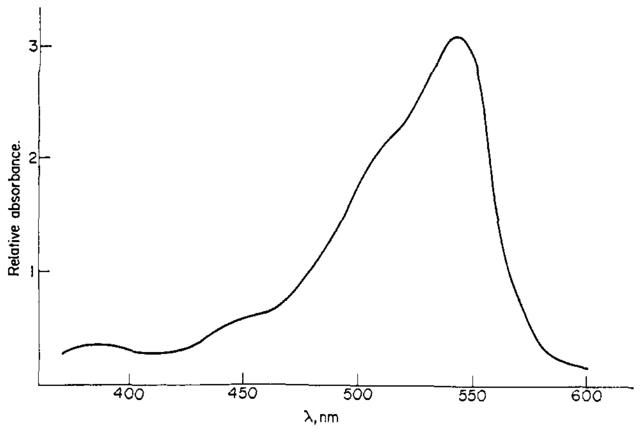
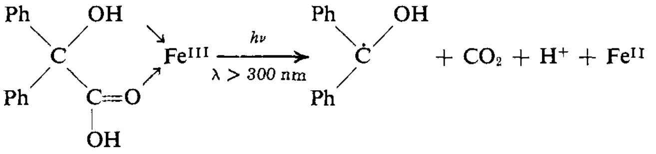


Figure 2. Flash photolysis spectrum obtained from a solution in ethanol of uranyl perchlorate (2×10^{-3} *M*) and benzilic acid (2×10^{-3} *M*).

To ascertain the time scale of production of $Ph_2\dot{C}OH$ we have also flash photolyzed with light of $\lambda > 300$ nm solutions of benzilic acid and various perchlorates, including those of Fe^{III}, U^{VI}, V^{V}, and Cu^{II} (all at 2×10^{-3} *M* concentration). The optical spectrum obtained spectrographically with U^{VI} 1 μsec after the flash (1.1 kJ, ~25 μsec) shown in Figure 2 (λ_{max} 542 ± 3 nm) is identical with that given by Porter and Wilkinson.[10] The other metal ions behaved similarly. Benzilic acid alone gave no transient absorption when flashed with light of $\lambda > 300$ nm and addition of 10^{-2} *M* naphthalene, which would have quenched any process of abstraction by benzophenone impurity[10] in the benzilic acid, was without effect on any of these systems.

In both the esr and flash photolysis experiments the substrate is subjected to oxidative decarboxylation by the complexed oxidant, *e.g.*



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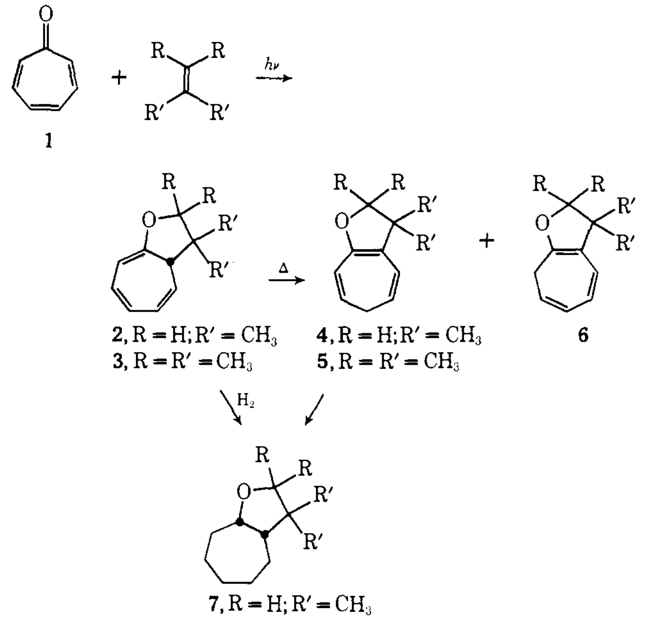
Photochemical 8 + 2 Cycloadditions of Tropone

Sir:

The thermal cycloaddition of tropone to various unsaturated molecules gives, depending on the nature of the addend and on reaction conditions, products resulting from 6 + 4, 4 + 2, and 8 + 2 addition processes,[1] all of which are predicted to be symmetry allowed by the now well-known orbital symmetry selection rules.[2] Tropone has been reported to undergo photochemical dimerization to afford, in acetonitrile, a mixture of 6 + 4, 6 + 2, and 4 + 2 dimers,[3] and in aqueous sulfuric acid, a low yield of the anti 6 + 6 dimer.[4] The 6 + 4 dimer, at least, seems to be the result of a nonconcerted, multistep process and the Woodward–Hoffmann rules of course do not apply to this and other two-step processes. We report here the *photochemical* 8 + 2 addition of tropone to simple olefins, which leads to products of the 8-oxabicyclo-[5.3.0]decane type.



Irradiation of tropone (**1**, 0.02 mol, Pyrex filter, acetonitrile solvent) for 3 hr in the presence of a tenfold excess of isobutene gave 35–40% of a 1:1 adduct, **2**, bp 44–45° (0.2 mm). Compound **2** exhibits infrared bands at 1634 (m) and 1070 (s) cm^{-1}, indicative of a vinyl ether linkage; the nmr spectrum (CCl_4) includes signals at τ 3.72 (2 H, m, H-4, H-5), 4.26 (2 H, m, H-3, H-6), 4.77 (1 H, 2 d, $J = 10.1$, $J' = 3.0$ Hz, H-2), 5.88 (1 H, 2 d, $J = 3.0$, $J' = 2.2$ Hz, H-7), 6.36 (2 H, s, $-OCH_2$), and 8.74 and 8.88 (3 H each, s, $-CCH_3$). The chemical-shift assignments and couplings were verified by double resonance experiments and by comparison with the spectrum of the thermal adduct of tropone and diphenylketene, whose structure is analgous to that of **2**.[5] Adduct **2** exhibits $\lambda_{max}^{CH_3OH}$ 279 nm (ϵ 3400), in agreement with expectation for a fused cycloheptatriene chromophore, and a mass spectral parent ion at *m/e* 162 (relative intensity 40) as well as major fragment ions at 147 (100), 119 (62), 107 (48), 91 (95), and 77 (82). Heating **2** to 180° under nitrogen, or simply gas chromatography on a column at 200°, caused isomerization *via* 1,5-sigmatropic shifts of hydrogen to the air- and heat-sensitive isomers **4** and **6** (3:1 ratio). Compound **4** showed ir_{max}^{film} 1640 and 1029 cm^{-1}; nmr (CCl_4) τ 4.08 and 4.12 (2 H, 2 d,

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(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(3) (a) A. S. Kende, *J. Amer. Chem. Soc.*, 88, 5026 (1966); (b) A. S. Kende and J. E. Lancaster, *ibid.*, 89, 5283 (1967).

(4) T. Mukai, T. Tezuka, and Y. Akasaki, *ibid.*, 88, 5025 (1966).

(5) (a) Nmr data at 100 MHz are given for the tropone–diphenylketene adduct by C. Jutz, J. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, 22, 1809 (1966). However, the structure assigned by these authors was later shown to be incorrect; see (b) R. Gompper, A. Studemeer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968). Furthermore, the spectrum we obtain for this adduct exhibits couplings significantly different from those published by Jutz, *et al.*, and closely resembles the spectra of 2 and 3.

J = 9.9 and 9.6 Hz, H-2 and H-6), 4.7–5.3 (2 H, two overlapping pairs of triplets, J = 9.6 and 9.9, J' = 6.8 Hz, H-3 and H-5), 5.97 (2 H, s, $-\text{OCH}_2$), 7.66 (2 H, t, J = 6.8 Hz, H-4 and H-4′), and 8.87 (6 H, s, $-\text{C(CH}_3)_2$); $\text{uv}_{\text{max}}^{\text{CH}_3\text{OH}}$ 280 nm (ϵ 3100); mass spectral parent ion at *m/e* 162 (37) and fragment ions at 147 (79), 119 (40), 107 (52), 91 (42), 78 (100), and 69 (45). Irradiation of the τ 7.66 triplet in the nmr spectrum causes collapse of the two pairs of triplets at 4.7–5.3, leaving two doublets at 4.69 and 4.92, J = 9.6 and 9.9 Hz, respectively. The tropone–diphenylketene adduct undergoes a similar rearrangement to a product whose nmr spectrum quite closely resembles that of **4**, and to which an analogous structure was assigned on the basis of spectral and chemical evidence.[6] Compound **6**, not obtained pure, showed nmr signals at 4.1–4.3 and 4.8–5.0 (4 H, m), 5.96 (2 H, s), 7.28 (2 H, d, J = 6.1 Hz), and 8.95 (6 H, s), and $\nu_{\text{max}}^{\text{film}}$ 1636 and 1056 cm^{-1}. The position of the methylene group is assigned as depicted above on the basis of relative thermodynamic stabilities of substituted cycloheptatrienes; see ref 1b, footnotes 10 and 11.

Hydrogenation of **2** and of **4** over palladium/charcoal led to the uptake, in both cases, of ~98% of 3 mol of hydrogen and to the isolation of the same saturated bicyclic ether **7**: $\text{ir}_{\text{max}}^{\text{film}}$ 1055 and 1080 (s) cm^{-1}; nmr (CCl_4) τ 5.98 (1 H, m, H-1), 6.60 (2 H, AB, $\Delta\nu_{\text{AB}}$ = 12.5, J = 8.1 Hz, $-\text{OCH}_2-$), 7.6–8.8 (11 H, m), and 9.06 and 9.12 (3 H each, s, $-\text{C(CH}_3)_2-$); parent ion *m/e* 168*. Both **2** and **4** were unreactive to *N*-phenylmaleimide and tetracyanoethylene at 25–50°; heating **4** with an excess of either reagent at 100° led only to gums and recovered dienophile.

In similar fashion, irradiation of tropone in excess tetramethylethylene gave 40–45% of adduct **3**, bp 56–57° (0.2 mm). Compound **3** showed $\text{ir}_{\text{max}}^{\text{film}}$ 1636 and 1070 cm^{-1}; nmr (CCl_4) τ 3.78 (2 H, m), 4.30 (2 H, m), 4.79 (1 H, 2 d, J = 9.3, J' = 2.9 Hz, H-2), 5.93 (2 d, J = 2.9, J' = 2.3 Hz, H-1), and 8.77, 8.88, 8.92, and 9.00 (3 H, each, s, CCH_3); *m/e* 190 (26, parent), 175 (69), 161 (100), 106 (55), 91 (31), and 78 (86); uv_{max} 278 nm (ϵ 2600). Thermolysis of **3**, either in glass, or on gas-chromatography columns, gave as sole product the isomer **5**: $\text{ir}_{\text{max}}^{\text{film}}$ 1610, 1190, and 1050 cm^{-1}; nmr (CCl_4) τ 3.98 and 4.01 (1 H, each, 2 d, J = 9.8 and 9.3 Hz, H-2 and H-6), 4.6–5.2 (2 H, 2 d of t, H-3 and H-5), 7.69 (2 H, t, J = 7.0 Hz, H-4, H-4′), and 8.70 and 8.92 (6 H each, s, CCH_3); uv_{max} 281 nm (ϵ 3600); *m/e* 190 (84, parent), 175 (44), 174 (100), 159 (30), 106 (75), and 90 (48); uv_{max} 281 nm (ϵ 3600).

Irradiation of tropone with excess 1,1-dichloroethylene produced an unstable adduct which lost hydrogen chloride readily; neither the adduct nor its transformation product could be isolated pure. From irradiation of tropone with 1,1-diphenylethylene, tetrachloroethylene, cyclopentene, and diphenylacetylene, only unchanged **1** and tarry materials were obtained. However, irradiation of tropone in excess cyclopentadiene gave adduct **8**: bp 56–58° (0.4 mm) (41%); ir (film) 1638 ($-\text{OC}{=}\text{C}$), 1180 and 1078 (C—O) cm^{-1}; nmr (CCl_4) τ 3.5–4.5 (4 H, m, H-3, 4, 5, 6), 4.4 (2 H, narrow m, cyclopentene vinyls), 4.8 (1 H, 2 d, J = 9.5, J' = 2.6 Hz, H-2), 5.8 (1 H, m, H-1), 6.4–7.1 (2 H, m, methines), and 7.2–7.4 (2 H, m, $-\text{CH}_2$); *m/e* (parent) 172. The alternative 8 + 4 structure can be ruled out, since the signals for the cyclopentene vinyl and the bridge methylene hydrogens of such an adduct would be expected to appear at significantly lower and higher levels, respectively, than is observed for **8**.[7]

Mixtures of **1** with isobutene and tetramethylethylene underwent no reactions when stored in the dark. Irradiation of a tropone–isobutene mixture containing sufficient fluorenone to absorb ≥80% of the incident light resulted in formation of **2** at a rate only slightly less than that in the direct irradiation. These results favor the intermediacy of a tropone triplet excited state in the 8 + 2 additions observed here. It follows from the observed orientation in the adduct from isobutene that the first step in the process is bonding of the tropone oxygen atom to the terminal methylene group of the olefin. This argues that the reactive triplet in these additions is n → π^* in nature, since 2 + 2 additions of saturated ketones and certain α,β-unsaturated ketones to olefins to give oxetanes, a process in which the reactive site is the carbonyl oxygen, is known to proceed *via* ketone n → π^* triplets.[8] Experiments designed to more clearly delineate the scope of the addition and the nature of the reactive excited state are in progress.

Acknowledgment. I thank Otto Gansow for performing the double resonance experiments.

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[6] A. S. Kende, *Tetrahedron Lett.*, 2677 (1967); the mechanistic speculations in this paper are incorrect, as they were based on the erroneous structure originally assigned by Jutz, *et al.*,[5a] to the primary adduct.

[7] Dr. A. S. Kende has isolated an 8 + 2 adduct of tropone and furan, whose structure is evident from its nmr spectrum (private communication fom Dr. Kende).

[8] (a) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 23 (1968); (b) D. R. Arnold, *ibid.*, **6**, 301 (1969).

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Probable Formation of 13-Atom Polyhedral Complexes Containing $\text{B}_{10}\text{C}_2\text{H}_{12}^{2-}$ and Cobalt

Sir:

Previously, the largest known polyhedral carborane derivatives were icosahedral, 12-atom species typified by the $\text{B}_{10}\text{C}_2\text{H}_{12}$ carboranes and transition metal derivatives of the $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ dicarbollide ions.[1] We now wish to report the probable formation of 13-atom polyhedral complexes apparently generated with formal Co(III), π-bonded C_5H_5^-, and the $\text{B}_{10}\text{C}_2\text{H}_{12}^{2-}$ ion[2–4] formed by electron addition to 1,2-$\text{B}_{10}\text{C}_2\text{H}_{12}$. The inclusion of the transition metal atom into the $\text{B}_{10}\text{C}_2\text{H}_{12}^{2-}$ ion presumably completes a 13-atom polyhedron; Figure 1. The $\text{B}_{10}\text{C}_2\text{H}_{12}^{2-}$ ion was produced by the reduction of 1,2-$\text{B}_{10}\text{C}_2\text{H}_{12}$ at room temperature with 2 equiv of sodium in tetrahydrofuran with a

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[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

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[3] L. Zakharkin, V. Kalinin, and L. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 2310 (1967).

[4] V. Stanko, Yu. V. Gol'tyapin, and V. Brattsev, *Zh. Obsch. Khim.*, **39**, 1175 (1969).