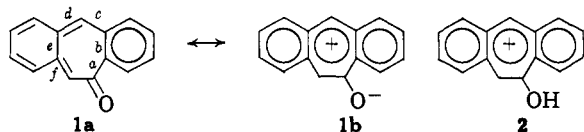


Dibenzo[*b,e*]tropone and Its Conjugate Acid

Sir:

We wish to report on the generation and trapping of dibenzo[*b,e*]tropone (1) and on the synthesis and some properties of its stable conjugate acid (2). Dibenzo[*b,e*]tropone (hereafter referred to as [*b,e*]) is of interest



because it possesses the unstable *o*-xylene structural moiety in its most stable neutral canonical form. It may therefore be expected to incorporate more than the other dibenzotropones of the zwitterionic "ylium oxide" form, in which the benzenoid character of the *o*-xylylene moiety is at least formally restored. HMO calculations of the carbonyl π bond order (p_{CO}) and of the charge density on the carbonyl oxygen (q_O) are listed in Table I for [*b,f*], [*b*], [*b,e*], and tropone.¹

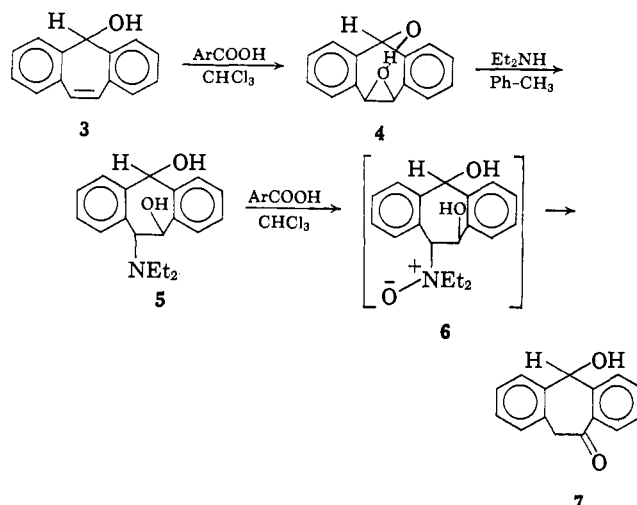
Table I

Compound	p_{CO}	q_O
[<i>b,f</i>]	0.638	-0.636
[<i>b</i>]	0.581	-0.680
[<i>b,e</i>]	0.533	-0.730
Tropone	0.535	-0.734

Particularly noteworthy is the near-equivalence of p_{CO} and q_O for [*b,e*] and tropone. It appears that the localizing effect of a benzo substituent attached to the *b* bond is almost exactly compensated for by the delocalizing effect of a benzo substituent at the *e* bond (see 1a).

The key compound in the synthesis is the hydroxy ketone 7, obtained in a three-step sequence starting with the commercially available 3 (see Scheme I).²

Scheme I



Reaction of 3 with *m*-chloroperbenzoic acid in chloroform (0–5°, 24 hr) gives the epoxide 4 in 65% yield (mp 124–126°).³ The nmr spectrum consists of an aromatic proton multiplet at *ca.* τ 2.7 (eight protons), an AB quartet ($J_{AB} = 12.3$ cps, two protons) centered

(1) All β 's were taken as equal and $\alpha_o = \alpha + \beta$ was assumed.

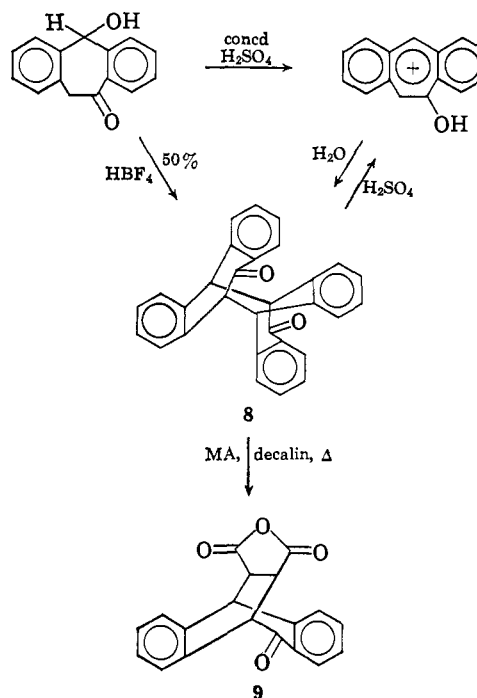
(2) Aldrich Chemical Co.

(3) Satisfactory elemental analyses were obtained for all compounds in this synthesis.

at τ 4.87, and a singlet at τ 5.62 (two protons). The singlet is assigned to the protons α to the epoxide function; the AB protons are those attached to and α to the oxygen atom. The *cis* configuration is assigned on the basis of the lack of effect of dilution on the hydrogen-bonded hydroxyl stretch (3440 cm^{-1}). A similar *cis*-directing effect has been observed for hydroxyl in the reactions of olefins with methylene-transfer agents.⁴ Diethylamine opens the oxirane ring (refluxing toluene, 5 hr), furnishing amine 5 in 73% yield (mp 209–210°). Although too insoluble for nmr analysis, the latter compound is satisfactorily identified by its very strong hydroxyl stretch, its elemental analysis, and its mass spectrum (m/e 279, P – 18, dehydration). Conversion of the amine to its N-oxide (*m*-chloroperbenzoic acid, chloroform, 0–5°, 8 hr) results, after alkaline work-up, in spontaneous Cope elimination of the oxide, giving the hydroxy ketone directly (80%, mp 149°). The infrared spectrum of the latter (THF) shows strong carbonyl (1680 cm^{-1}) and hydroxyl (3400 cm^{-1}) absorptions. An intense m/e 206 (P – 18, dehydration) peak appears in the mass spectrum. This dehydrated species is very likely [*b,e*].

Some aspects of the chemical behavior of [*b,e*] are illustrated in Scheme II. Dissolution of the hydroxy ketone (7) in concentrated sulfuric acid gives the red conjugate acid of [*b,e*], identified by its nmr spectrum,

Scheme II

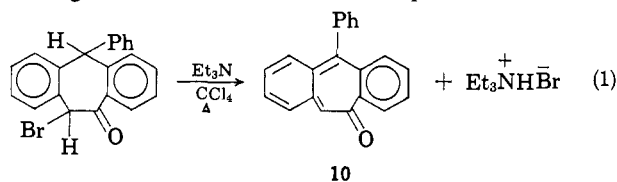


which consists of a low-field singlet at τ 0.67 (one proton) and a complex multiplet between τ 1.2 and 2 (nine protons). HMO calculations indicate the doubly benzylic position to be highly electron deficient, and far more so than any of the other proton-bearing positions. When the aforementioned solutions are made alkaline at –20°, the free tropone [*b,e*] is liberated, as indicated by the orange coloration imparted to a supernatant ether layer. However, the color fades so rapidly that no physical data could be obtained on free [*b,e*]. The product obtained upon work-up of the two-phase

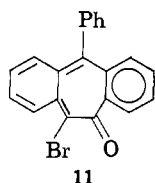
(4) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964).

system is the dimer **8** ($\nu_{C=O}$ 1670 cm^{-1} ; mp 350° dec; m/e 412).^{5,6} The dimer is obtained directly by warming the hydroxy ketone in 50% aqueous fluoroboric acid. The conjugate acid of [b,e] can be regenerated by warming the dimer in concentrated sulfuric acid (60°, 15 min). Refluxing the dimer in decalin with maleic anhydride gives the Diels–Alder adduct **9** in good yield. Thus, at elevated temperatures the dimer is in equilibrium with the monomeric [b,e].

Substituted tropone **10** was sought in an effort to obtain a stable neutral derivative of [b,e], as shown in (1). The reaction mixtures exhibited the expected low-frequency carbonyl absorption in the infrared (1623 cm^{-1}) and gave a Diels–Alder adduct with dimethyl acetylenedicarboxylate. However, all attempts to isolate **10** gave only intractable mixtures, presumably resulting from air oxidation. Tropone **11** behaved



similarly ($\nu_{C=O}$ 1645 cm^{-1}).



Acknowledgment. We wish to thank the Welch Foundation for support of this research.

(5) The stereochemistry of the dimer has not been investigated.

(6) Elemental analyses of the dimer have the correct carbon:hydrogen ratio, but the percentages of each were consistently low, presumably because of the difficulty in achieving complete combustion of the dimer.

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Bicyclo[6.2.0]deca-1,3,5,7-tetraene

Sir:

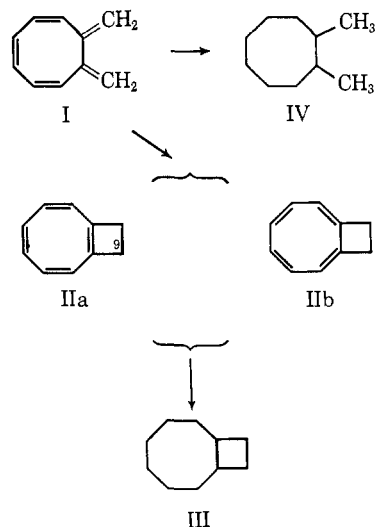
We describe the synthesis of bicyclo[6.2.0]deca-1,3,5,7-tetraene (II), a substance containing fused cyclooctatetraene and cyclobutene rings.

7,8-Dimethylenecycloocta-1,3,5-triene (I)¹ was irradiated in methanol with a medium-pressure Hanovia mercury vapor lamp (2 amp, 125 w) for 2 hr at room temperature. Chromatography on silicic acid gave II as a yellow liquid in ca. 10% yield as sole product isolated. Substance II was relatively stable in solution, but decomposed rapidly in the neat state at room temperature.

The structural assignment II was based on the spectral properties. The mass spectrum had a molecular ion at m/e 130 and a base peak at m/e 129. The ultraviolet spectrum (EtOH) showed end absorption only (no $\lambda_{\text{max}} > 215 \mu$), like cyclooctatetraene itself.²

(1) (a) J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 508 (1966); (b) F. A. L. Anet and B. Gregorovich, *Tetrahedron Letters*, 5961 (1966).

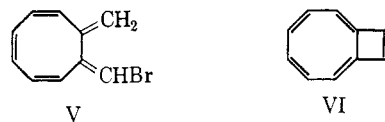
(2) See A. C. Cope and C. G. Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948); B. Ekström, *Chem. Ber.*, **92**, 749 (1959).



The infrared spectrum (neat) exhibited maxima at 3010 (s), 2920 (s), 2870 (s), 1635 (m), 1620 (m), 1445 (m), 1430 (m), 795 (s), 785 (s), 760 (vs), and 685 (s) cm^{-1} . The nmr spectrum (CCl_4 , 100 Mc/sec) showed a complex multiplet (6 H) at τ 4.38–4.72 assigned to the olefinic protons and a singlet (4 H) at τ 7.62 assigned to the allylic protons.

The structure of II was confirmed by hydrogenation in methanol over platinum, whereby 3.9 molar equiv of hydrogen was absorbed. The resulting bicyclo[6.2.0]deca-1,3,5,7-tetraene (III) (presumably the *cis* isomer) was a colorless liquid, homogeneous by glpc; mass spectrum, molecular ion peak at m/e 138; nmr spectrum, broad band at τ 7.7–8.7, no olefinic or methyl protons. Under the same hydrogenation conditions, substance I absorbed 4.8 molar equiv of hydrogen and yielded 1,2-dimethylcyclooctane (IV),³ homogeneous by glpc; mass spectrum, molecular ion peak at m/e 140; nmr spectrum, broad band (14 H) at τ 8.2–8.7 assigned to the ring protons, signals at τ 9.11 and 9.18 (6 H) assigned to the methyl protons.

Irradiation of 7-methylene-8-bromomethylenecycloocta-1,3,5-triene (V)⁴ also led to II, but the 9-bromo derivative of II could not be isolated from this reaction. Preliminary experiments designed to convert II to the fully conjugated bicyclo[6.2.0]deca-1,3,5,7,9-pentaene (VI)⁵ have so far not met with success.



The transformation of I to II is an example of the now well-established photochemical cyclization of conjugated dienes to cyclobutenes.⁶

(3) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **74**, 179 (1952).

(4) Compound V was prepared from 1,2-bisbromomethylcyclooctatetraene^{1a} in almost quantitative yield by treatment with potassium *t*-butoxide in ether.

(5) See A. Rosowsky, H. Fleischer, S. T. Young, R. Partsch, W. H. Saunders, and V. Boekelheide, *Tetrahedron*, **11**, 121 (1960).

(6) See R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962); K. J. Crowley, *Proc. Chem. Soc.*, 334 (1962).

(7) CSIRO Overseas Postgraduate Fellow.

(8) Imperial Chemical Industries Fellow.

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