

PHOTOCHEMICAL BEHAVIOR OF DIBENZODERIVATIVES
OF TROPONE, TROPILIDENE AND HEPTAFULVENE (1)

Jan Kopecký and Joan E. Shields

Institute of Industrial Hygiene and Occupational Diseases
Prague, Czechoslovakia⁺

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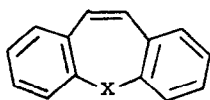
Boston College
Department of Chemistry
Chestnut Hill, Massachusetts, USA⁺

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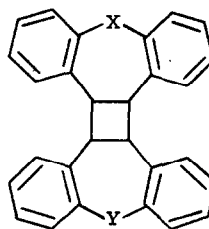
In connection with our interest in the synthesis of some 10 π -electron systems, we have investigated the photochemical behavior of 2,3,6,7-dibenzo derivatives of tropone (Ia), tropilidene (Ib) and heptafulvene (Ic). These compounds are promising starting materials for the photochemical synthesis of pseudoaromatic compounds. A recent publication (2), describing the photodimerization of 2,3,6,7-dibenzotropone (Ia) prompts us to report our results in this area.

Irradiation (3) of Ia in a variety of solvents afforded dimer IIa, $C_{30}H_{20}O_2$, m.p. 237-238° dec. Polarity of the solvents was apparently not critical; the best yields (90- 95%) of dimer were obtained, however, when the reaction was carried out in isopropanol. No photoreduction products were observed. This suggests that the lowest triplet state of dibenzotropone has π, π^* rather than n, π^* character (4). A similar conclusion was reached from singlet-triplet absorption measurements and MO-arguments (5).

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- Ia, X = C=O
 Ib, X = CH₂
 Ic, X = C=CH₂



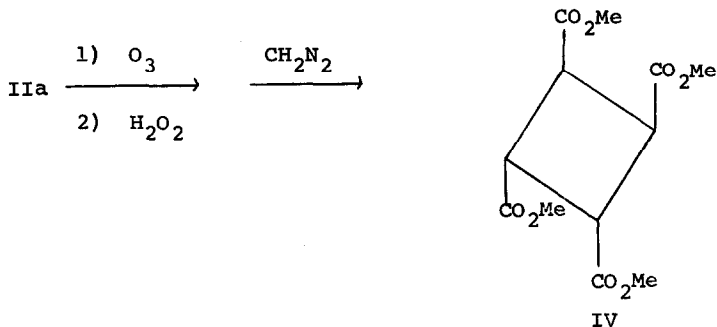
- IIa, X = Y = C=O
 IIb, X = Y = CH₂
 IIc, X = Y = C = CH₂
 IIId, X = C = O, Y = CH₂
 IIe, X = C = O, Y = C = CH₂

Similarly, 2,3,6,7-dibenzotropolidene (Ib) underwent dimerization in cyclohexane solution to IIb, C₃₀H₂₄, m.p. 341-2° (6), in 80% yield. Aluminum isopropoxide reduction of diketone IIa afforded an authentic sample of IIb, indicating that IIa and IIb possess the same stereochemistry about the cyclobutane ring.

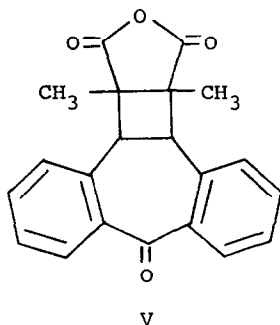
Attempts to effect the dimerization of 2,3,6,7-dibenzoheptafulvene (Ic) in the absence of a photosensitizer were unsuccessful. However, irradiation of Ic in the presence of an excess of dibenzotropone (Ia) in cyclohexane solution, afforded a mixture (separable by chromatography on silica gel) of 26% of dimer IIa, 18% of dimer IIc, C₃₂H₂₄, m.p. 247.5-248.5° and 40% of the 1 : 1 adduct IIe, C₃₁H₂₂O, m.p. 217-218°. The yield of photodimer IIc can be improved at the expense of the formation of IIe by use of equimolar amounts of Ia and Ic. Treatment of IIa with methylenetriphenylphosphorane gave, after chromatography on neutral alumina, comparison samples of IIc and IIe. Spectral comparison and mixture melting points showed that they are identical with the photo products. The synthesis of IIc and IIe from the ketone dimer IIa established that these compounds possess the same stereochemistry about the cyclobutane ring.

Competition between mixed addition and dimerization was also found when a cyclohexane solution containing Ia and Ib was irradiated. Chromatographic separation of the reaction product afforded the dimers IIa (50% yield) and IIb (25% yield) in addition to the 1 : 1 adduct IIId, C₃₀H₂₂O, m.p. 300-301° (9% yield).

Stereochemistry of the various cyclobutane derivatives was assigned as trans from the results of ozonolysis of IIa. A suspension of the dimer in 90% aqueous acetic acid was ozonized (7) at 25° for 24 hours. Subsequent oxidative decomposition with hydrogen peroxide and esterification with diazomethane afforded 18% yield of cis,trans,cis-1,2,3,4-tetracarboxymethoxycyclobutane (IV) (8). The identity of IV has been established by comparison (mp, nmp, infrared spectra and tlc mobility) with authentic material (9).



The formation of 1 : 1 adducts (IIId and IIe) with dibenzotropone (Ia) led us to investigate photochemical cycloadditions to Ia. It has been found that Ia undergoes light-induced cycloaddition to dimethylmaleic anhydride in the presence of benzophenone at -75°. The reaction product consists of the known (10) photodimer of dimethylmaleic anhydride and the cycloadduct V, C₂₁H₁₆O₄, m.p. 297-298° (57% yield). The nmr spectrum of V showed a multiplet of eight aromatic protons centered at τ 2.5, two cyclobutane protons at τ 5.4 and six methyl protons at τ 8.5.



Further studies dealing with the photocycloaddition reactions of dibenzo derivatives of tropone, tropilidene and heptafulvene are still in progress.

REFERENCES

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3. Irradiations were carried out at $20 \pm 5^{\circ}$ (unless otherwise specified) using a Phillips 125 W high pressure lamp and a Solidex glass filter. All solutions were flushed with Argon for 15 minutes before irradiation.
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6. Elemental analyses and nmr spectra (determined in CDCl_3 at 60 Mc) of all new compounds were consistent with the proposed structures.
7. A Welsbach Model T-408 laboratory ozonator was employed with a flow rate of 3.0 grams per hour.
8. C.W. Griffin, A.F. Velluro and K. Furukawa, J.Am.Chem.Soc. 83, 2725 (1961).
9. An authentic sample of the ester was kindly furnished by Professor Griffin.
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