

### 3,4-Benzotropone: Generation, Spectroscopic Characterization, and Reactions

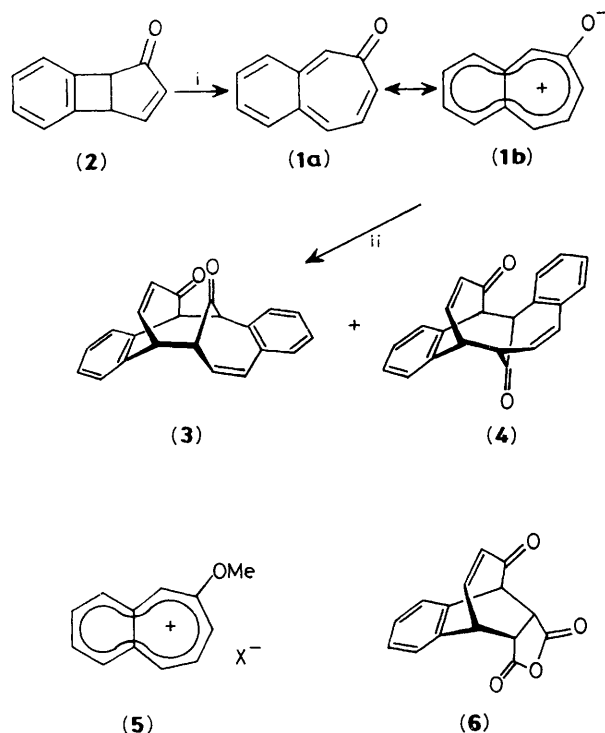
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3,4-Benzotropone (**1**) is generated by irradiating 3a,7b-dihydrocyclopenta[*a*]cyclobutabenzen-1-one (tricyclo[5.4.0.0<sup>2,6</sup>]undeca-1(7),3,8,10-tetraen-5-one) (**2**) in a rigid medium at low temperature or by thermolysing (**2**) at 220 °C; its spectral and chemical properties are described.

3,4-Benzotropone (**1**) is of considerable interest in theoretical<sup>1</sup> and preparative<sup>2</sup> organic chemistry. Ten  $\pi$ -electron peripheral conjugation is expected to give some aromatic character to (**1**) and also to modify the reactivity of the *o*-quinodimethane system. Despite extensive studies on troponoid compounds,

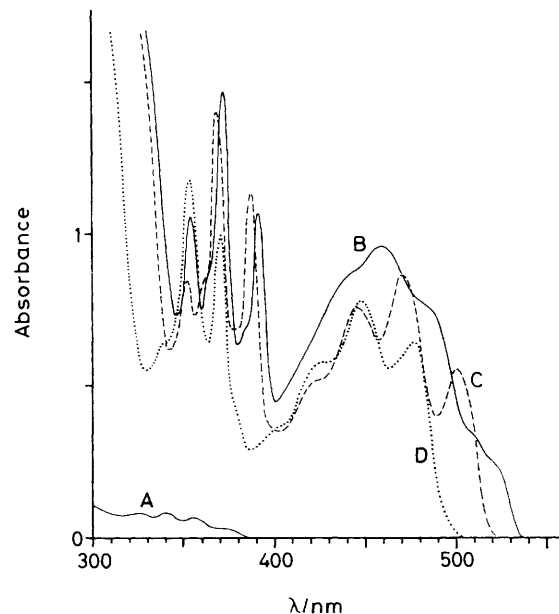
however, information on *o*-quinoidal 3,4-benzotropones is surprisingly scarce and only a few derivatives have been reported so far, *viz.*, the chemical trapping of dibenzotropones by Bauld<sup>3</sup> and the photochemical generation of 7-phenoxy-3,4-benzotropone by Chapman.<sup>4</sup> In this Commun-



**Scheme 1.** Conditions: i, irradiation (>300 nm) in EPA at 77 K or in  $\text{CFCl}_3\text{-CF}_2\text{BrCF}_2\text{Br-CHCl}_3$  at  $-155^\circ\text{C}$ ; ii,  $>-100^\circ\text{C}$ .

ication we report the preparation and characterization of parent (1).

Irradiation of a dilute solution of compound (2)<sup>†</sup> in EPA (a 5:5:2 mixture of ether, isopentane, and ethanol) with a high-pressure mercury lamp through Pyrex at 77 K led to the development of a strong absorption in the range 300–550 nm (spectrum B in Figure 1). The generated orange species was stable in a rigid EPA glass at 77 K ( $-196^\circ\text{C}$ ) and also in a fluid EPA solution at  $-130^\circ\text{C}$ , but was consumed rapidly at  $-78^\circ\text{C}$ . The decay of the absorption followed second-order kinetics and, from the resultant photolysate, two  $[\pi_8 + \pi_{10}]$  dimers, (3) and (4), were isolated in almost equal amounts in a combined yield of 80%. Thus we conclude that the photolysis of (2) in EPA at 77 K led to the practically quantitative formation of (1). The molar absorptivity of (1) at 458 nm was estimated to be *ca.* 2500 and the rate constant for the dimerization of (1) was  $12 \pm 3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $-78^\circ\text{C}$ . Photochemically, (1) appeared to be stable at least in the EPA glass at 77 K and showed no tendency to revert to (2). When the glass was thawed below  $-130^\circ\text{C}$  and refrozen at 77 K, the spectrum changed significantly in shape, presumably as a result of the solvation of the newly generated polar (1) by the reorientation of solvent molecules (spectrum C). If resonance form (1b) is a major contributor to the structure of (1), then (1) should be readily protonated.<sup>‡</sup> This was indeed the case. Thus, the spectrum (D) which was recorded after irradiating



**Figure 1.** Absorption spectral change observed upon irradiation of (2) in EPA or in 1% trifluoroacetic acid-EPA at 77 K with a high-pressure mercury lamp through Pyrex (A: before irradiation. B: after irradiation,  $\lambda_{\text{max}}/\text{nm}$  353, 372, 392, 438sh, 458, 482sh, 506sh, 518sh) and upon subsequently thawing the mixture below  $-130^\circ\text{C}$  and refreezing it at 77 K (C: in EPA,  $\lambda_{\text{max}}/\text{nm}$  352, 368, 387, 425sh, 444, 471, 501. D: in 1% trifluoroacetic acid-EPA,  $\lambda_{\text{max}}/\text{nm}$  354, 371, 427sh, 448, 477).

(2) in 1% trifluoroacetic acid-EPA at 77 K, thawing the mixture below  $-130^\circ\text{C}$ , and refreezing it at 77 K was quite similar to that reported for (5), though the initial spectrum before the thaw was virtually identical with that observed in the absence of the acid.

The compound (2) exhibits a carbonyl absorption at  $1688 \text{ cm}^{-1}$  in a  $\text{CFCl}_3\text{-CF}_2\text{BrCF}_2\text{Br-CHCl}_3$  (25:25:4) glass at  $-155^\circ\text{C}$ . Irradiation of the glass (>300 nm) led to disappearance of the above absorption and growth of new absorption bands at 1594, 1538, 1506, and  $1438 \text{ cm}^{-1}$ . Interestingly tropone also exhibits four absorption bands in a somewhat higher wavenumber region.<sup>6</sup> When the starting (2) was labelled with  $^{18}\text{O}$ , these bands were shifted to 1592, 1536, 1492, and  $1434 \text{ cm}^{-1}$ , respectively. Thus the third band at  $1506 \text{ cm}^{-1}$  may be assigned to a vibration involving primarily the C=O stretching mode while the other three bands are of principally C=C stretching character. Tropone exhibits a C=O stretching vibration at  $1553 \text{ cm}^{-1}$  under the same recording conditions. The unusually low C=O stretching frequency of (1) is noteworthy, though it may be premature to refer that simply to the contribution from the resonance form (1b).<sup>7</sup>

The clean photo-valence isomerization of (2) to (1) presently observed is exceptional for a bicyclo[3.2.0]hepta-3,6-dien-2-one derivative.<sup>8</sup> Photolysis of (2) in methanol at ambient temperature afforded only small amounts of (3) and (4), indicating that the clean photo-transformation of (2) to (1) specifically took place in a rigid medium at low temperature.

The generation of (1) from (2) was thermally effected also. Thus, upon heating a mixture of (2) and maleic anhydride (10 mol. equiv.) in benzene at  $220^\circ\text{C}$  for 55 h, the  $[\pi_2 + \pi_8]$  adduct (6) was produced in 52% yield [64% by g.l.c., 85% conversion of (2)]. Below  $200^\circ\text{C}$ , (2) virtually remained unconsumed.

<sup>†</sup> The compound (2) was prepared by the addition of benzyne to cyclopenten-2-one acetal followed by hydrolysis and subsequent dehydrogenation of the resultant ketone with dichlorodicyanobenzoquinone (DDQ). Satisfactory spectral and analytical data were obtained for all new isolable compounds.

<sup>‡</sup> We thank a referee for suggesting this possibility.

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