A Photochemical Synthesis of Benzocyclopropenone

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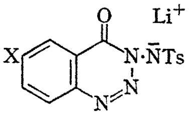
ALTHOUGH benzocyclopropenes have been isolated and are moderately stable, the more strained but electronically more stabilized derivative, benzocyclopropenone (IVa), has remained elusive.[1] We report studies of the photochemical decomposition of lithium 3-*p*-tolyl sulphonylamino-1,2,3-benzotriazin-4(3*H*)-one (Ia), which, together with those of the accompanying communication,[2] implicate (IVa) as a ground-state intermediate.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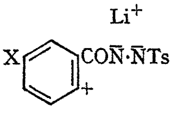
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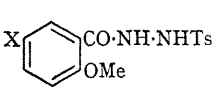
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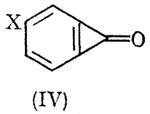
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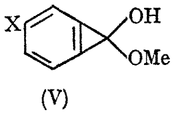
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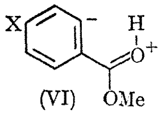
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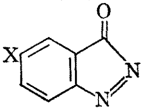
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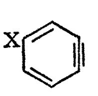
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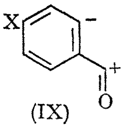
(IX)

(a)X=H; (b)X=Cl Ts=p-Me·C_6H_4·SO_2

The precursor 3-*p*-tolylsulphonylamino-1,2,3-benzotriazin-4(3*H*)-one, m.p. 204—206° (decomp.) and the 6-chloro-analogue, m.p. 170—172° (decomp.), were prepared in nearly quantitative yield by the diazotization of the corresponding anthranilic acid toluene-*p*-sulphonohydrazides.[3] Treatment with lithium hydride in tetrahydrofuran or lithium methoxide in methanol provided solutions of the requisite salts (Ia, b) from which, after a long time at 30—40°, the parent acids could be recovered quantitatively by acidification. Nitrogen was rapidly eliminated by u.v. excitation (Hanovia 450 w lamp, Pyrex filter) of a solution (λ_{max} 320 nm.) of (Ia) (0·5%) in methanol at 40° to give lithium toluene-*p*-sulphonate (92%), methyl benzoate (52%), and *o*-methoxybenzoic acid toluene-*p*-sulphonohydrazide (8%), m.p. 178—180° (decomp.) Photolysis of (Ib) in the same manner provided lithium toluene-*p*-sulphonate (90%), methyl *p*-chlorobenzoate (42%),[†] and 5-chloro-2-methoxybenzoic acid toluene-*p*-sulphonohydrazide (6%), m.p. 154—155° (decomp.).

The appearance of the *p*-chlorobenzoate ester in the latter case demands the intervention of an intermediate with the symmetry of a benzocyclopropenone. A mechanistic suggestion for this transformation may involve the addition of methanol to (IVb) leading to a hemiacetal (Vb) which undergoes Favorskii ring-opening to yield the ester. From strain relief considerations, the uncatalysed acetalization of benzocyclopropenone should be more exothermic than that of diphenylcyclopropenone.[4] The geometry of the prototropic rearrangement of (Vb) requires a transition state close to (VIb) where the inductive stabilization of the developing carbanionic centre by the chloro-substituent is greatest. Such thermodynamic control provides for the predominant formation of the observed *para*-isomer.[‡] The absence of the methanolysis product (methyl *m*-chlorobenzoate) of 6-chloroindazolone[5] (VIIb) argues against its intermediacy in the decomposition of (Ib) but the isolation of (IIIb) suggests the interposition of a *dipolar* intermediate (II) which collapses to (IVb).

The thermolysis of (Ia) in refluxing triglyme (220°) containing anthracene affords triptycene (30%), which may result from the decarbonylation of (IVa) to give benzyne (VIIIa). A concerted thermal expulsion of CO from (IVa) is orbital-symmetry-forbidden, which suggests that the 1,3-dipole (IXa) intervenes in the fragmentation of (IVa).[6] In

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[†] No *meta*-isomer was detected by i.r. analysis.

[‡] Similar arguments have been advanced in explanation of isomer ratios obtained in the addition of nucleophiles to substituted dehydrobenzenes. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, pp. 134—150.

fact, the photolysis of (Ib) in benzene at 40° provides a small amount (*ca.* 5%) of *p*-chlorobenzophenone.

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[2] J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, following Communication.

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[4] A. W. Krebs, *Angew. Chem.*, 1965, **77**, 10.

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