Benzocyclopropenone

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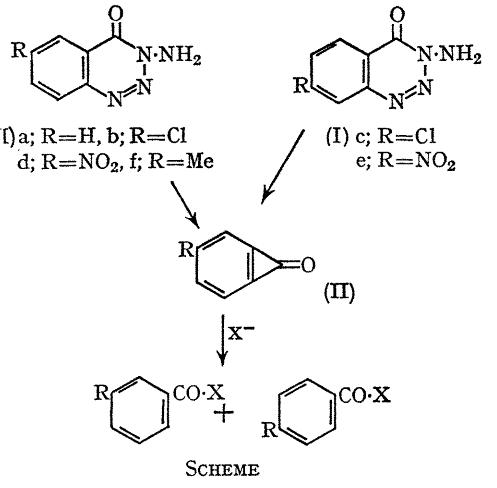
Summary Benzocyclopropenones are shown to be reactive intermediates in the oxidation of 3-aminobenzotriazin-4-ones.

BENZOCYCLOPROPENONE (IIa) has been suggested as an intermediate in the thermal and mass-spectral fragmentation of several aromatic compounds, such as phthalic anhydride and indanetrione,[1] but it has not hitherto been reported in chemical reactions in solution in spite of its interest as a potential homoaromatic system (III). The oxidation of 3-amino-1,2,3-benzotriazin-4-one (Ia) seemed to offer a mild route to benzocyclopropenone, by analogy with the generation of benzyne by oxidation of 1-aminobenzotriazole.[2] Evidence for the intermediacy of benzocyclopropenone in the oxidation of the aminotriazinone (Ia) is presented, based on the following premise: a substituted triazinone (I) should lead to the formation of an unsymmetrical benzocyclopropenone (II), which can then react with a nucleophile, X^-, to give two derivatives of benzoic acid, in one of which the carbonyl group has rearranged (See Scheme).



SCHEME

The results of several experiments are given in the Table. The aminotriazinones (I) in dry methanol or dichloromethane were added to a solution of lead tetra-acetate in the same solvent at 20°. A gas was immediately evolved and the oxidation appeared to be complete within a few seconds. In the experiments done in dichloromethane, water (as moist ether) was added as soon as gas evolution had ceased.

TABLE

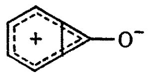
Oxidation of aminotriazinones (I) *in methanol*

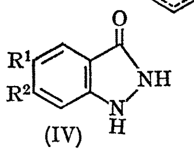
Triazinone	Products (%)
(Ia)	Methyl benzoate (77)
(Ib)	[a] Methyl *m*-chlorobenzoate (58) Methyl *p*-chlorobenzoate (11)
(Ic)	[a] Methyl *p*-chlorobenzoate (68) No methyl *m*-chlorobenzoate detectable
(Id)	[b] Methyl *m*-nitrobenzoate (59) Methyl *p*-nitrobenzoate (13)
(Ie)	[b] Methyl *m*-nitrobenzoate (7) Methyl *p*-nitrobenzoate (73)
(If)	[b] Methyl *m*-toluate (57) Methyl *p*-toluate (9)

Oxidation of aminotriazinones (I) *in dichloromethane*

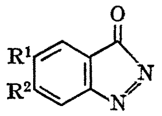
Triazinone	Trap	Products (%)
(Ib)	H_2O	[c] *m*-Chlorobenzoic acid (1) *p*-Chlorobenzoic acid (15)
(Ic)	H_2O	[c] *m*-Chlorobenzoic acid (0·2) *p*-Chlorobenzoic acid (21)

[a] Analysed by high-resolution i.r. spectroscopy.
[b] Analysed by g.l.c.
[c] Separated by column chromatography.

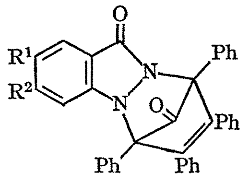

(III)



(IV)



(V)



(VI)

There is thus clear evidence for rearrangement in the oxidation of the aminotriazinones (Ib—If), the rearrangement being greater in the cases of the 6-chlorotriazinone (Ib) and the 6-nitrotriazinone (Id), as would be expected for inductive stabilization of the developing carbanion. The yields of unrearranged products (Table) are not significant, however, because there is another intermediate in the oxidations, namely the corresponding indazolone (V), which could be detected and preferentially removed as the tetracyclone adduct (VI). Compound (V) is formed by an independent pathway and is not a precursor of the benzocyclopropenone, because it never leads to rearrangement products. This was shown in a separate series of experiments in which the indazolones were generated by oxidation of the corresponding indazolinones[3] (IV); these oxidations, in methanol, gave exclusively the unrearranged methyl esters by direct nucleophilic attack of methanol on the indazolone.

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[1] R. F. C. Brown and R. K. Solly, *Austral. J. Chem.*, 1966, **19**, 1045; E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.

[2] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 1964, 296.

[3] E. F. Ullman and E. A. Bartkus, *Chem. and Ind.*, 1962, 93.

[4] M. S. Ao, E. M. Burgess, A. Schauer, and E. A. Taylor, preceding Communication.