Fragmentation of Cyclic α-Carbonylazo-compounds. New Routes to Benzocyclobutenedione and to Biphenylene

By D. L. Forster, T. L. Gilchrist, C. W. Rees,* and E. Stanton

(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary Benzocyclobutenedione and biphenylene are formed in high yield by the vapour phase pyrolysis of Diels–Alder adducts of phthalazine-1,4-dione and indazol-3-one, respectively.

Cyclic α-carbonylazo-compounds, which can readily be generated in solution by oxidation of the corresponding cyclic hydrazides, are labile species which polymerise on attempted isolation but which add rapidly to conjugated dienes to form stable Diels–Alder adducts.[1] We have studied the vacuum pyrolysis of the cyclopentadiene and butadiene adducts of several α-carbonylazo-compounds in an attempt to generate the α-carbonylazo-compounds in the vapour phase, and to promote their unimolecular fragmentation.

The cyclopentadiene adduct (**1**), m.p. 230° (decomp.), of phthalazine-1,4-dione, was prepared by the lead tetraacetate oxidation of 2,3-dihydrophthalazine-1,4-dione in the presence of cyclopentadiene.† The adducts (**2**),[2] m.p.

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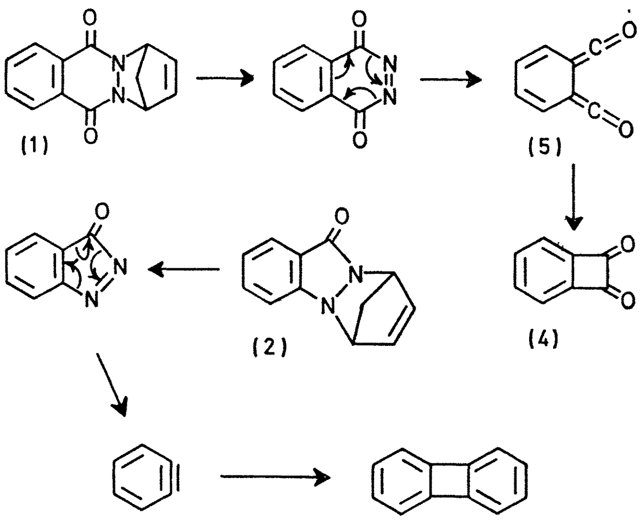
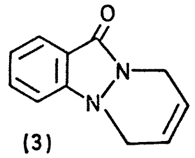
† Satisfactory analytical and spectral data have been obtained for the new compounds reported.

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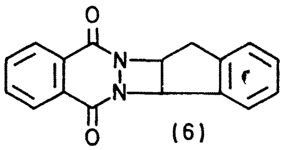
(6)

93—94°, and (**3**),[2] m.p. 114—115°, from indazol-3-one, were similarly prepared by the oxidation of 2,3-dihydroindazol-3-one, or, better, by oxidation of 3-amino-1,2,3-benzotriazin-4-one,[3] in the presence of the appropriate diene.

The adduct (**1**) was pyrolysed by sublimation through a 15 × 1 cm tube at 500° and 0·01 mmHg. The pyrolysate was pure benzocyclobutenedione (**4**) (88%), m.p. 130—132° (from cyclohexane). The adduct (**2**) similarly gave, at 400° and 0·04 mmHg, pure biphenylene (63%). When the butadiene adduct (**3**) was pyrolysed at 610°, the pyrolysate consisted of starting material (50%) and biphenylene (80% based on starting material consumed).

Pyrolysis of the cyclopentadiene adduct (**1**) represents a useful synthetic route to benzocyclobutenedione.[4] The process can be rationalised as a retro-Diels–Alder reaction followed by nitrogen extrusion from phthalazine-1,4-dione. An allowed $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$-fragmentation would give the bis-keten (**5**) which could then close to give benzocyclobutenedione.

An analogous fragmentation of the indazolone adducts (**2**) and (**3**) results in the loss of both nitrogen and carbon monoxide, with the formation of benzyne and hence biphenylene.

The fragmentation is not confined to diene adducts: the cycloadduct (**6**)[5] of phthalazine-1,4-dione and indene fragments at 500° and 0·02 mmHg to give benzocyclobutenedione (64%) and indene.

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[1] E. Fahr and H. Lind, *Angew. Chem. Internat. Edn.*, 1966, **5**, 372.

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

[3] J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc.* (*C*), 1971, 981.

[4] For other routes to benzocyclobutenedione, see (a) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076; (b) R. F. C. Brown and R. K. Solly, *Chem. and Ind.*, 1965, 1462.

[5] O. L. Chapman and S. J. Dominianni, *J. Org. Chem.*, 1966, **31**, 3862.