Thermal Stability of Benzonorbornadienone Hydrazones

By R. S. Atkinson,* A. J. Clark, and R. E. Overill
(*Department of Chemistry, Leicester University, Leicester* LE1 7RH)

Summary The benzonorbornadienone hydrazone (VI) has been prepared and an explanation given for its high thermal stability compared with the parent ketone (III).

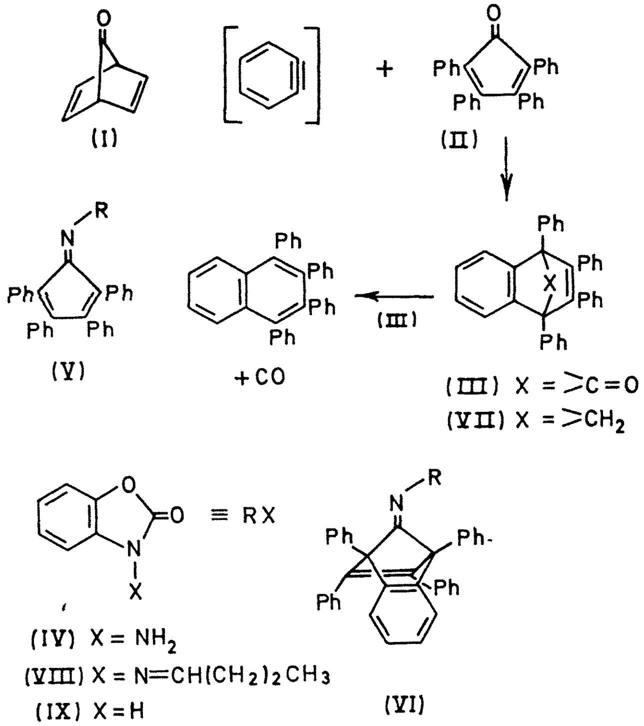
The ready cheletropic elimination of carbon monoxide from norbornadienones (I) precludes their isolation except as metal complexes.[1] Likewise, benzonorbornadienones (III) have not been isolated and addition of benzyne to tetraphenylcyclopentadienone (II) gives 1,2,3,4-tetraphenylnaphthalene with spontaneous elimination of carbon monoxide.[2]

We sought to extend this extrusion reaction to the preparation of isocyanides, noting a dearth of examples of this reaction type in the literature.[3] Thus condensation of 3-aminobenzoxazol-2(3*H*)-one[4] (IV; $X = NH_2$) with (II) gave the corresponding hydrazone (V), m.p. 268—271°. Reaction of this hydrazone with benzyne generated by oxidation of 1-aminobenzotriazole with lead tetra-acetate[5] gave a colourless crystalline product, m.p. 181—184° (52%), formulated on the basis of evidence given below as the benzonorbornadienone hydrazone (VI). The i.r. spectrum showed the presence of the heterocyclic carbonyl group at 1777 cm^{-1} and a band (less than half as intense) at 1660 cm^{-1} ascribable to C=N. In the mass spectrum, the dominant fragmentation is loss of the bridging group (*m/e* 432). A u.v. summation of tetraphenylbenzonorbornadiene (VII)[6] and the butylidene derivative (VIII)[4] gave a curve qualitatively similar to that of the adduct (VI).

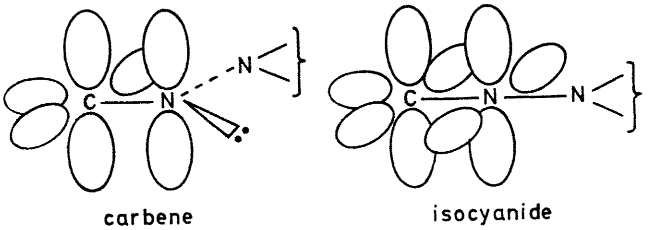
Chemical support for the formulation of (VI) is given by mild acid hydrolysis [acetic acid–1N-HCl (50:1) at room temperature for 1 h] to tetraphenylnaphthalene (80%) and the hydrazine (IV) (37%).

Compared with the thermal instability of benzonorbornadienones, adduct (VI) is remarkably stable; after heating for 1·25 h in boiling decalin (192°), 66% was recovered by crystallisation. The thermal stability of, for example, (VII) can be ascribed to the high energy carbene which would result from extrusion. *N*-Isocyanides, which would be the analogous products from (VI), however, although reactive, are not of comparably high energy content and can be isolated.[7]

This thermal stability may be explained by assuming that in the concerted elimination a colinear geometry is required for R, N, and the bridging carbon in (VI). Only with a linear geometry would efficient stabilisation of the incipient carbene as an isocyanide be possible (Figure).



The linear configuration in (VI) is believed to be the transition state for inversion at the imino-nitrogen[8] and the inversion barrier will be particularly high in the present case because of the benzoxazolinone substituent† (hetero-atom effect). The small angle at the bridge will also result in higher *s* character for the imino-nitrogen lone pair and hence a higher barrier to inversion.



At even higher temperatures (250°) the adduct (VI) is readily decomposed. The products are benzoxazolin-3-(2*H*)-one (IX) and a solid with wide melting range, a band at 2220 cm^{-1} in the i.r. spectrum, and a molecular weight of 457 from the mass spectrum. This result is accommodated by assuming attack of tetraphenylnaphthalene [or unchanged adduct (VI)] on the extruded *N*-isocyanide giving tetraphenylnaphthalene cyanide as a mixture of isomers.

The corresponding adduct to (VI) with a phthalimido-group replacing the benzoxazolinone has also been prepared and shows similar behaviour.

(*Received, March* 22*nd*, 1971; *Com.* **361**.)

---

† This heterocycle retards the inversion rate in aziridines also (see ref. 4).

[1] J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, 1968, **90**, 1656; S. Yankelevitch and B. Fuchs, *Tetrahedron Letters*, 1967, 4945.

[2] G. Wittig and E. Knauss, *Chem. Ber.*, 1958, **91**, 895.

[3] B. P. Stark and A. J. Duke, 'Extrusion Reactions', Pergamon Press, Oxford, 1967.

[4] R. S. Atkinson and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 772.

[5] C. C. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.

[6] H. Gunther, *Chem. Ber.*, 1963, **96**, 1806.

[7] H. Bredereck, B. Föhlisch, and K. Walz, *Angew. Chem.*, 1962, **74**, 388.

[8] H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.