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STABILIZATION OF A NAPHTHOCYCLOBUTADIENE BY HALO GROUPS

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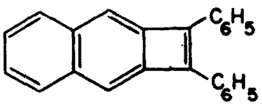
The hydrocarbon 1,2-diphenylnaphtho[b]cyclobutadiene (I)[1] represents the only known example of an isolable compound containing a cyclobutadiene nucleus which has only one pair of neighboring carbons fused to an aromatic system, and which is not stabilized by metal complexing.[2] The stability of I is attributable not only to a relatively low π-bond order for the 2a-8a bond, but also to conjugative stabilization of the entire system by the phenyl substituents.[3] Significantly, several attempts to prepare the isomeric 3,8-diphenylnaphtho[b]cyclobutadiene (II) have afforded only polymer, although the generation of II in these reactions was confirmed by trapping it with 1,2-diphenylisobenzofuran to afford the crystalline adduct III.[4] The phenyl substituents of II must add little resonance stabilization to the naphthocyclobutadiene system since, as in 1-phenylnaphthalene, they are twisted considerably out of the plane of the naphthalene ring. We now wish to report the isolation of a derivative of II which is stabilized by bromo substituents.

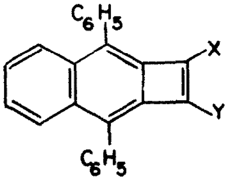
Bromination of 3,8-diphenylnaphtho[b]cyclobutene (IV)[4a] with N-bromosuccinimide afforded the following bromides or their mixtures, depending upon the reaction conditions used: 1-bromo-3,8-diphenylnaphtho[b]cyclobutene (V, m.p. 143-144°), 1,1-dibromo-3,8-diphenylnaphtho[b]cyclobutene (VI, m.p. 174-175°), 1,2-dibromo-3,8-diphenylnaphtho[b]cyclobutene (VII, m.p. 198.5°), 1,1,2,2-tetrabromo-3,8-diphenylnaphtho[b]cyclobutene (VIII, m.p. 222-223°).[5,6] The structures assigned to these bromides were supported by their reactions with silver trifluoroacetate, followed by water: V, VI, VII and VIII gave, respectively, 3,8-diphenylnaphtho[b]cyclobuten-1-ol (IX, m.p. 206-207°), 3,8-diphenylnaphtho[b]cyclobuten-1-one (X, m.p. 205°), 3,8-diphenylnaphtho[b]cyclobutene-1,2-diol (XI, m.p. 205-209°), and 3,8-diphenylnaphtho[b]cyclobutene-1,2-dione (XII, double m.p. 238° and 248°).[7] The latter hydrolysis products were further interrelated by the following reactions: chromic acid oxidation of alcohol IX gave ketone X; zinc-ammonium chloride reduction of diketone XII gave hydroxyketone XIII (m.p. 226°), which was also obtained from ketone X by N-bromosuccinimide bromination to bromoketone XIV (m.p. 190-191°), followed by reaction of XIV with silver trifluoroacetate and then water. Hydroxyketone XIII and bromoketone XIV showed strong carbonyl absorption (at 5.70 and 5.60 μ, respectively) and therefore did not spontaneously enolize to the corresponding cyclobutadienoid tautomers.

In accord with earlier reports,[4] we have been unable to isolate 3,8-diphenylnaphtho[_b_]cyclobutadiene (II), generated either from dibromide VII and zinc or from monobromide V and potassium _t_-butoxide. Similarly, 1-bromo-3,8-diphenylnaphtho[_b_]cyclobutadiene (XV) could not be isolated when either dibromide VI or dibromide VII was treated with potassium _t_-butoxide; the initial generation of XV in these reactions was confirmed by trapping it with 1,3-diphenylisobenzofuran to give adduct XVI, m.p. 276.5°. In contrast, the reaction of tetrabromide VIII with activated zinc dust for 10-15 seconds in boiling benzene solution afforded (40% yield) stable orange-yellow crystals of 1,2-dibromo-3,8-naphtho[_b_]cyclobutadiene (XVII), m.p. 162-165° (dec.). The structure of XVII was in accord with the following reactions: (a) XVII added bromine readily to regenerate tetrabromide VIII in high yield; (b) XVII was reduced catalytically in the presence of palladium and triethylamine to hydrocarbon IV; (c) XVII added 1,3-diphenylisobenzofuran to afford the colorless adduct XVIII, m.p. 320°.

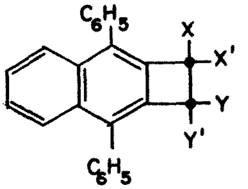
Further attempts to ascertain the minimal substitution necessary for the stabilization of the naphtho[_b_]cyclobutadiene system are in progress.



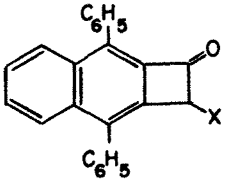
I



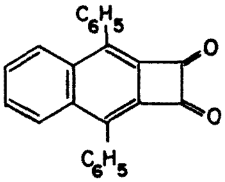
XVII: X = Y = Br
XV: X = H; Y = Br
II: X = Y = H



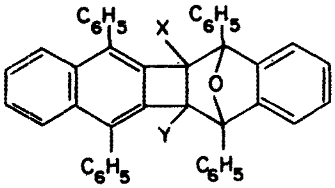
IV: X = X' = Y = Y' = H
V: X = X' = Y = H; Y' = Br
VI: X = X' = H; Y = Y' = Br
VII: X = Y = H; X' = Y' = Br
VIII: X = X' = Y = Y' = Br
IX: X = X' = Y = H; Y' = OH
XI: X = Y = H; X' = Y' = OH



X: X = H
XIII: X = OH
XIV: X = Br



XII



XVIII: X = Y = Br
III: X = Y = H
XVI: X = Br; Y = H

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3. Calculations by A. G. Anastassiou, quoted in Chem. and Eng. News, 42, No. 3, 37 (1964).

4. (a) C. D. Nenitzescu, M. Avram, I. G. Dinulescu and G. Mateescu, Ann., 653, 79 (1962).

   (b) M. Avram, I. G. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu and C. D. Nenitzescu, Chem. Ber., 97, 372 (1964).

5. Elemental analyses and spectral properties of all new compounds are in accord with the assigned structures. In view of the relative importance of dibromide XVII its analysis is presented here: Calcd. for $C_{24}H_{14}Br_2$: C, 62.38; H, 3.04; Br, 34.58. Found: C, 62.49; H, 3.10; Br, 34.72.

6. The only bromination product of IV reported previously (Ref. 4a) was dibromide VII. The melting point (145°) ascribed to VII in this earlier report is very close to that found by us for the monobromide V.

7. The stereochemistry at C-1 and C-2 in VII and XI is as yet uncertain.