The Photochemistry of Cyclononatetraenide and Bicyclo[4,3,0]nonatriene

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Summary Cyclononatetraenide ion experiences enhanced basicity on irradiation, and the structures of photoproducts of bicyclo[4,3,0]nonatriene have been determined.

CYCLO-OCTATETRAENE DIANION[1] experiences enhanced basicity on irradiation, and it was shown that this result could be interpreted in terms of π-energy changes, obtained through simple Hückel Molecular Orbital (HMO) calculations,[2] for protonation of the anion in its ground or excited state. It was predicted that cyclononatetraenide (I), too, should become more basic when photoexcited, and I now report that this is indeed the case.

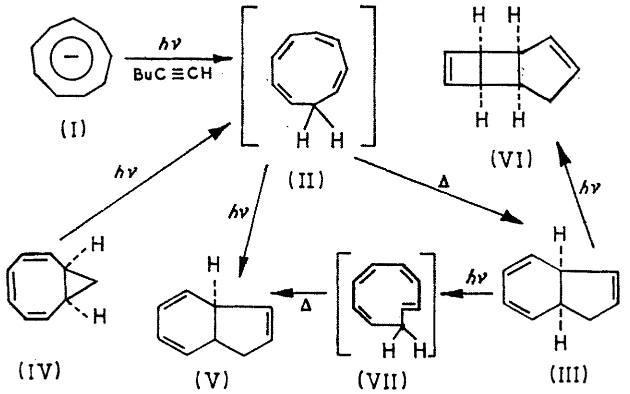
The enhancement of basicity of (I) on photoexcitation could not have been predicted by arguments based on u.v. spectral shifts[3] for the anion and its conjugate acid, cyclononatetraene (II). In addition, charge distribution arguments[4] cannot be employed because of the high symmetry of (I).

The prediction and observation of the increased basicity of photoexcited (I) parallels the photochemistry[1] of cyclo-octatetraene dianion. That the predictive method[1] employed is successful for both anions (each a system that could not be studied either by measuring u.v. shifts or by charge distribution calculations) strongly suggests that determining π-energy changes calculated from simple HMO methods is a useful method for predicting or explaining photochemical enhancements of basicity for anions whose conjugate acid is either unknown or too unstable to isolate, or for highly symmetric systems. This treatment is readily extended to include other photochemical acid–base systems. The observation that (I), like cyclo-octatetraene dianion, becomes more basic on irradiation suggests that this is a general phenomenon for cyclic aromatic species. For example, it has been reported[5] that benzene becomes more basic on photoexcitation.

That (I) becomes more basic when irradiated has been determined by its reaction with acids too weak to protonate it in the dark. When (I) is irradiated in the presence of hex-1-yne and the reaction is monitored by g.l.c. analysis of hydrolysed portions, (III) and several other photoproducts are observed. These other compounds are identical with those obtained from photolysis of either (III)[6] or bicyclo[6,1,0]nonatriene (IV). Photolysis of (IV) results in its rapid conversion into (III), presumably *via* (II) in a photochemically allowed process.[7] These results imply that excited (I) abstracts a proton from hex-1-yne to give (II) which then closes thermally[7] to give (III). That protonation of (I) by hex-1-yne did occur in the *excited* state was also demonstrated by the generation of

(III) and of butylacetylide in the reaction mixture.† The absence of (III) and of butylacetylide in a dark reaction control indicates that no proton transfer occurs in the dark. That (I) does not yield the photo-products of (III) on hydrolysis when (I) is photolysed under aprotic conditions was demonstrated by the absence of these compounds when no weak acid was present during photolysis. The products thus observed when (I) is irradiated in the presence of hex-1-yne must therefore be those of either (II) or (III).

Of the two major photo-products of (III), one can be shown to be *trans*-bicyclo[4,3,0]nonatriene (V). This previously unreported compound has been characterized by its spectral properties [n.m.r.: multiplet δ 5·68—6·50 (6 protons), multiplet 2·53—3·03 (1 proton), multiplet 1·38—2·50 (3 protons); u.v.: λ_{max} 260 nm. (ϵ 3500); m.s.: *m/e* 118], by its ready oxidation to indene by molecular oxygen, and by identity of the hydrogenated photo-product with authentic *trans*-bicyclo[4,3,0]nonane.[1] The structure of the other major photo-product of (III) is inferred to be (VI) from its spectral data [n.m.r.: multiplet δ 5·34—6·00 (4 protons), multiplet 1·15—2·50 (6 protons); u.v.: end-absorption only; m.s.: *m/e* 118].



The origin of the photo-products of (III) in the irradiation of (I) in the presence of weak acids can be envisaged as a protonation of excited (I) to give (II) which then closes thermally to give (III). The photolysis of (III) can be explained in terms of a conrotatory ring opening[7] to give *cis,cis,cis,trans*-cyclononatetraene (VII) which then closes thermally to yield (V). Alternatively, the production of (VI) could arise directly *via* a conrotatory closure of excited (II) although the short lifetime of (II) renders this pathway unlikely. In an independent route, excited (III) can close in a disrotatory manner to give (VI).

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† Photolysis and control reaction mixtures were worked up by the addition of these solutions to dry, neat methyl iodide in a nitrogen atmosphere. In experiments where hex-1-yne was converted into butylacetylide, hept-2-yne was produced in this work-up. The products studied were isolated by preparative g.l.c. using a 6 ft. × 0·25 in. 5% Carbowax 20M on 80-100 Chromosorb column.

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[4] For example, see W. Meier, D. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, 1962, **45**, 2628.

[5] For example, see J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron, Suppl.*, 1963, **2**, 65.

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[7] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

[8] M. Tichý, F. Šipoš, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1966, **31**, 2889, and catalytic hydrogenation.