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THE TRICYCLOPROPYLCYCLOPROPENYL CATION

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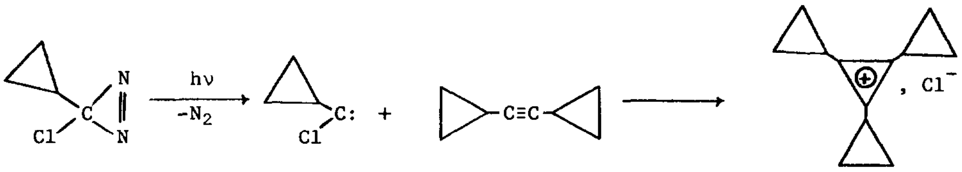
Summary: The preparation and properties of the tricyclopropylcyclopropenyl cation are described.

Since the initial preparation of a cyclopropenyl cation,[1] many aryl, alkyl, and heteroatomic-substituted derivatives of this simplest cyclic aromatic system have been synthesized.[2] Of particular interest are the intrinsic stability of the parent ion and the relative stabilities of its substituted derivatives. On the pK_R+ scale,[3] it is clear that arylcyclopropenyl cations are generally less stable than alkyl-substituted varieties,[3-5] while the latter are less stable than dialkylaminocyclopropenyl cations.[2d,5]

Consider the pK_R+ values of the triphenylcyclopropenyl (3.1)[3] and cyclopropyldiphenylcyclopropenyl (5.04)[5,6] cations. Naive extrapolation of the enhanced stability associated with a single cyclopropyl for phenyl exchange suggests that the tricyclopropylcyclopropenyl cation (I) should exemplify the most stable class of all-hydrocarbon cyclopropenium ions yet reported. An attempt to prepare I by reaction of cyclopropylmagnesium bromide with dicyclopropylcyclopropenone (followed by HBF_4/Ac_2O) led only to an intractable product.[5] However, our recent development of the intermolecular chemistry of cyclopropylchlorocarbene[7] points the way to a simple and successful synthesis of I.

A solution of cyclopropylchlorodiazirine[7,8] in dicyclopropylacetylene[9] was photolyzed (Pyrex filter, 20°) for 30-40 min with a focussed Osram 200W XE mercury lamp; eq. (1).[10] The precipitated white solid, I, was filtered under nitrogen, triturated with ether, and reprecipitated from cold, dry acetonitrile solution by the addition of ether.

Analytically pure (C, H, Cl) I, mp 89-90°, is insoluble in hexane, benzene, ether, and CCl_4, somewhat soluble in $CHCl_3$, and soluble in acetone, acetonitrile, DMSO, and water. I is moderately hygroscopic, and yellows perceptibly upon storage at ambient temperature. Treatment of I with $AgBF_4$ in CH_3CN solution gives an instantaneous precipitate of AgCl; I, BF_4^- can be re-



I

(1)

covered from the filtrate (see below).

Tricyclopropylcyclopropenylium chloride showed λ_{max} 210 (ϵ 22,900, H_2O, pH 3.7) and ν_{max} 3080, 3010, 1425 cm^{-1} (KBr). The latter band is the most intense absorption in the ir spectrum, and may be associated with the cyclopropenium ring.[2b,3,5] The ^1H nmr spectrum (D_2O/DSS) consisted of two complex multiplets centered at δ2.4 (3 methine protons) and δ1.6 (12 methylene protons). The ^{13}C nmr spectrum (D_2O/external TMS) displayed 3 lines at δ168.3 (C^+), 14.59 and 7.51 ppm. The ^1H and ^{13}C nmr spectra of I, Cl^- and I, BF_4^- were identical. The pK_R+ of I, determined titrimetrically in 1:1 CH_3CN/0.05N aqueous NaCl solution,[3,5] was 9.4±0.3 for three measurements on two lots of I, Cl^-.

Tricyclopropylcyclopropenyl cation (pK_R+ 9.4) is thus readily prepared via eq. (1). It is, as anticipated, considerably more stable on the pK_R+ scale than triphenylcyclopropenyl cation (pK_R+ 3.1)[3] or trimethylcyclopropenyl cation (pK_R+ 7.4).[4] The superior cyclopropenium ion stabilizing ability of cyclopropyl vs. alkyl substituents[4,5] is conjugative in origin,[5] as is also clear from our observation of a distinct λ_{max} (210 nm) for I; tri-n-propylcyclopropenyl cation (pK_R+ 7.2) shows only end absorption down to 185 nm.[3] The observed pK_R+ of I (9.4) is close to that predicted by additive extrapolation of the ΔpK_R+ for cyclopropyldiphenylcyclopropenyl[5] vs. triphenylcyclopropenyl[3] cations [3x(5.04-3.1) + 3.1 ~ 8.9].[11] Whether the total cyclopropyl stabilization is indeed equally tripartite, and what this might imply about the conformational preferences of I in solution, are matters under current investigation.

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(10) Photolysis was carried only to low conversion (~28% diazirine decomposition, based upon manometric determination of the evolved nitrogen). Continued irradiation led to yellowing of the solid product. Typical photolyses employed ~2 mmol of the diazirine in 2 ml of the acetylene, and gave ~70 mg of I (~60% yield based on decomposed diazirine).

(11) The effects of anion variation (Br^-, BF_4^-, Cl^-) are ignored in this obviously crude comparison.

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