Generation and Thermal Bond Relocation of the Cyclononatetraenyl Cation

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Summary 9-Chloro-*cis*^{4}-cyclononatetraene undergoes rapid solvolytic rearrangement to *exo*-1-chloro-*cis*-8,9-dihydroindene, *via* the cyclononatetraenyl cation.

The *cis*^{4}-cyclononatetraenyl cation (**1**) is an interesting 8π monocycle, since its dimensions are such as to allow planar as well as puckered geometries. Recently Schleyer, Boche, and their co-workers[1] presented evidence, based on rate data and deuterium labelling experiments, that thermolysis of *anti*-9-chlorobicyclo[6,1,0]nona-2,4,6-triene in aqueous acetone proceeds by what appears to be (**1**). We now report on the ready solvolytic generation of (**1**) from 9-chloro-*cis*^{4}-cyclononatetraene (**2a**).[2]

9-Chloro-*cis*^{4}-cyclononatetraene (**2a**) rearranges cleanly and irreversibly to *exo*-1-chloro-*cis*-8,9-dihydroindene (**3a**) on mild heating in $CDCl_3$, the conversion being characterized by $t_{\frac{1}{2}}(0°)$ *ca.* 70 min ($\Delta F^{\ddagger}$ *ca.* 21 kcal mol^{-1}). The same bond relocation (**2a**) $\rightarrow$ (**3a**)† also obtains in SO_2 although far more rapidly, *e.g.*, $t_{\frac{1}{2}}(-66°) < 10$ min, ($\Delta F^{\ddagger} < 15$ kcal mol^{-1}).‡ The greatly enhanced rate of this conversion in the more ionizing medium (SO_2) raised the question of whether rearrangement here might not be chiefly activated by initial ionization of (**2**). In order to test this possibility it was necessary to assess the thermal fate of appropriately labelled (**2**). We therefore prepared the monodeuterio-compound (**2b**) by exposing *anti*-9-chloro-

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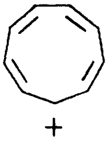
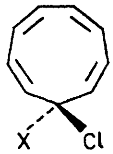
† (**3**) was characterized by (i) its n.m.r. spectra in SO_2 and $CDCl_3$ which were identical with those given by authentic (**3a**) in these solvents and (ii) through its conversion into a known[2] (i.r., n.m.r., m.p.) cycloadduct on treatment with 4-phenyl-1,2,4-triazoline-3,5-dione.

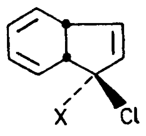
‡ This value must be regarded as maximal for it was estimated on the basis of the time lapse between dissolution of (**2**) in SO_2 at $-66°$ and n.m.r. analysis of the resulting solution at the same temperature.

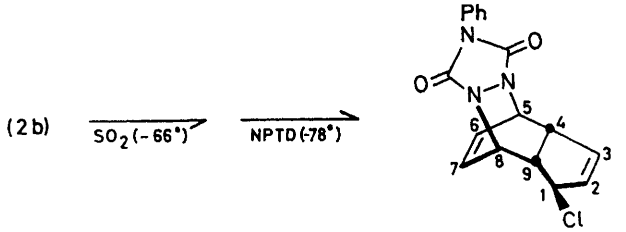
syn-9-deuteriobicyclo[6,1,0]nona-2,4,6-triene to sensitized radiation at *ca.* −60°.§ Dissolution of (**2b**) in SO_2 at *ca.* −66° followed by rapid replacement of this solvent by CH_2Cl_2 at the same temperature and subsequent treatment of the resulting solution with 4-phenyl-1,2,4-triazoline-3,5-dione (NPTD) at −78° produced the cycloadduct (**4**): m.p. 206·5—207·5°; *m/e* 328 (M^+); ν_{CO} (KBr) 1705 cm^{-1}; n.m.r. ($CDCl_3$; 60 MHz) τ 2·57 (5H, s, Ph), 3·63 (1·76H, t, 6- + 7-H) 4·20 (1·76H, s, 2- + 3-H), 4·85 (0·89H, m, 5- or 8-H), 5·00 (0·91H, m, 8- or 5-H), 5·52 (0·88H, m, 1-H), 6·1—6·5 (0·89H, m, 4-H), and 6·5—7·0 (0·90H, m, 9-H). The n.m.r. data clearly require that the deuterium label in (**4**) be distributed equally among its nine carbon centres. Further, control experiments involving analogous work-up procedures established that (i) in $CDCl_3$, rearrangement of (**2b**) to the dihydroindene skeleton occurs entirely without scrambling of the label, *i.e.*, the product here contains the intact CDCl function shown in (**3b**) and (ii) exposure of (**3b**) to SO_2 within the temperature range of −66 to −20° activates only localized deuterium scrambling whereby the label in (**4**) is now associated exclusively with C-1 and C-3. We therefore conclude that the complete scrambling of the label effected on dissolution of (**2b**) in SO_2 at −66° is best and perhaps uniquely rationalized in terms of initial ionization of (**2**) to the cyclononatetraenyl cation, and suggest the sequence of steps shown in the Scheme for the overall conversion of (**2**) into (**3**) in this medium.¶


(1)

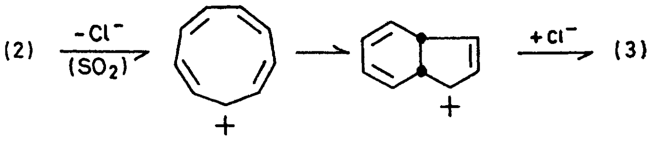

(2)

a; X = H
b; X = D


(3)



(4)



Scheme

The ease with which (**1**) materializes from (**2**) is remarkable in view of its rapid subsequent rearrangement. This seemingly anomalous behaviour is perhaps best understood in terms of the di-allylic nature of chloride (**2**) and its consequent rapid ionization to (**1**) through an obviously "early" transition state. In turn, the thermal lability of the resulting monocyclic carbonium ion is undoubtedly due to its being a $4n$–π system, *i.e.*, to its inability effectively to delocalize charge without developing the antiaromatic character accompanying a D_{9h} geometry. In fact, the resistance of this molecule to the development of antiaromaticity will most likely be shown in the form of in-plane or out-of-plane distortions, the latter being more likely from considerations of skeletal strain. Whatever their nature, however, the geometrical constraints imposed on this molecule are such as to allow for complete equivalence of the various carbon centres during its brief existence. Finally, there is a striking difference in thermal stability between (**1**) [$t_{\frac{1}{2}}(-66°) < 10$ min] and its $4n + 2$ analogue, *i.e.*, the cyclononatetraenyl anion,[3] which has been reported[3b] effectively to resist rearrangement even on prolonged heating at 163°. Irrespective of this comparison the lability of (**1**) is sufficiently pronounced as to be clearly indicative of antiaromaticity.

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§ The photolysis temperature employed here was substantially lower than that described previously[2] in order to ensure the complete absence of (**3b**) in the photolysate.

For an even distribution of the label among the nine carbon centres, each must be associated with 11·1% D and 88·9% H. The observed quantities thus correspond to the following degree of scrambling: C-1 (99%), C-2, C-3 (101%), C-4 (98%), C-5 or C-8 (100%), C-6, C-7 (101%), C-8 or C-5 (98%), and C-9 (99%). The even distribution of the deuterium label in (**4**) is also indicated by the fact that its i.r. spectrum is virtually superimposable with that of its non-deuteriated counterpart but differs considerably from that displayed by the adduct specifically deuteriated at C-1.[2]

¶ Significantly, we find *anti*-9-chlorobicyclo[6,1,0]nona-2,4,6-triene to be inert in SO_2 at −20°. The low solvolytic reactivity of this substance compared to (**2**) is consistent with the earlier findings concerning its solvolytic thermolysis.[1]

[1] J. C. Barborak, T. M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, 1971, **93**, 279.

[2] A. G. Anastassiou and E. Yakali, *J. Amer. Chem. Soc.*, 1971, **93**, 3803.

[3] (a) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 5194; (b) E. A. LaLancette and R. E. Benson, *ibid.*, 1969, **87**, 1941.