Stable Hydroxycarbonium Ions Derived from Stereoisomeric Spirocyclopropane-anthrones

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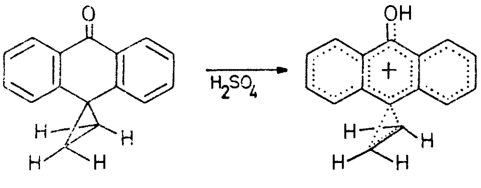
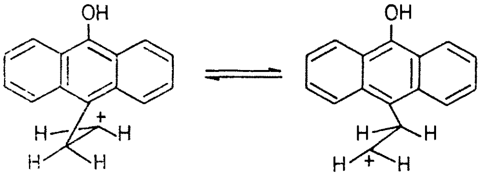
Summary Protonation of stereoisomeric spirocyclopropane-anthrones in 96% D_2SO_4 led to stable hydroxycarbonium ions whose n.m.r. spectra and retention of stereochemistry upon deprotonation were consistent with static bridged ions rather than equilibrating open-ring mixtures.

PROTONATION of spiro[anthrone-10,1′-cyclopropane] (I) in concentrated sulphuric acid was reported to result in the formation of a symmetrical hydroxycarbonium ion (II) in which the charge delocalization extends over the cyclopropane ring.[1,2]

Although bridged structure (II) is compatible with the electron release from the spirocyclopropane group in the solvolysis of β-(9-anthryl)-ethyl systems,[3,4] such ions can, in principle, exist as an equilibrium mixture of open ring classical structure, (III) $\rightleftharpoons$ (IV).



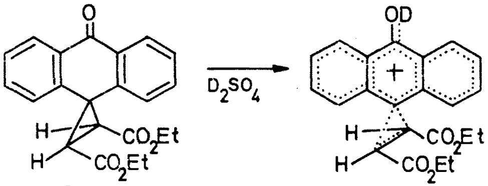
(I) (II)



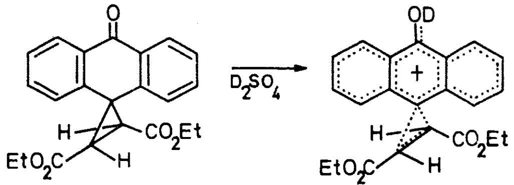
(III) (IV)

We outline our initial results on the structure and reactivity of hydroxycarbonium ions derived from stereoisomeric spirocyclopropane-anthrones which show that these ions exist as static bridged systems rather than as equilibrium mixtures of open-ring ions.

cis- and *trans*-2′,3′-Dimethoxycarbonylspiro[anthrone-10,1′-cyclopropane] (V) and (VI)[5] dissolved readily in 96% D_2SO_4 at room temperature to give lemon-yellow stable solutions. The n.m.r. spectra of the respective *cis*- and *trans*-hydroxycarbonium ions are compared with their neutral precursors in the Table. Since the n.m.r. spectra show that (VII) and (VIII) are different species, no *cis–trans* isomerization has occurred. Failure to detect stereochemical changes upon protonation of these isomers clearly removes the possibility of having an equilibrium mixture of two classical ions similar to (III) $\rightleftharpoons$ (IV).



(V) (VII)



(VI) (VIII)

60 MHz N.m.r. spectra (δ *p.p.m.*)

Compound	$-CH_3$	$-CH_2-$	Cyclopropane	Aromatic
(V) ($CDCl_3$[a])	1·14	4·16	3·12	7·08—8·52
(VII) (D_2SO_4[b])	1·35	4·75	4·10	7·30—9·0
(VI) ($CDCl_3$)	1·07	4·08	3·49	7·24—8·42
(VIII) (D_2SO_4)	1·39	4·40	4·30	7·40—8·95

[a] Values in $CDCl_3$ reported relative to internal Me_4Si.

[b] Values in D_2SO_4 reported relative to internal CH_2Cl_2 as secondary reference, $\delta = 5{\cdot}30$.

As for (I)→(II), one may interpret the paramagnetic shift of 0·98 and 0·81 p.p.m. for the cyclopropane protons of (VII) and (VIII) relative to (V) and (VI) respectively as being consistent with increased electron deficiency in the cyclopropane ring caused by participation in charge delocalization in the hydroxycarbonium ions. The relationship between chemical shift and extent of delocalization is somewhat less significant in the case of (VII) and (VIII) because of possible perturbations induced through protonation of the ethoxycarbonyl groups.

Extended delocalization is supported, however, by changes in the u.v.–visible absorption spectra of (VII) and (VIII) on going from ethanolic to H_2SO_4 solutions. On protonation, the absorption maxima of (V) and (VI) underwent bathochromic shifts of about 920 Å from 2680 to 3600 and from 2650 to 3570 Å respectively. On the other hand, the corresponding maximum of anthrone was shifted to red in H_2SO_4 only 820 Å from 2680 to 3500 Å. The additional 100 Å shift to longer wavelengths caused by the presence of the spirocyclopropane group in (VII) and (VIII) supports the idea of extended π-delocalization with participation from the three-member ring.

Quenching the acidic solutions of either (VII) or (VIII) with absolute ethanol resulted in almost quantitative recovery of the respective neutral precursors (V) and (VI) without stereochemical alterations.† This tends to confirm the state character of bridged ions (VII) and (VIII).

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† N.m.r. analyses of purposely prepared *cis–trans* mixtures show that any isomerization in excess of 2% could have been detected.

[1] L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, 1965, **87**, 3506.
[2] M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 1735.
[3] L. Eberson, J. P. Petrovich, R. Baird, D. Dykes, and S. Winstein, *J. Amer. Chem. Soc.*, 1965, **87**, 3504.
[4] R. Leute and S. Winstein, *Tetrahedron Letters*, 1967, 2475.
[5] N. Filipescu and J. W. Pavlik, *J. Chem. Soc.*, in the press.