Synthesis and ^{13}C Nuclear Magnetic Resonance Spectrum of 1-(2,3-Diphenylcycloprop-2-enylidenemethyl)-2,3-diphenylcyclopropenium Perchlorate

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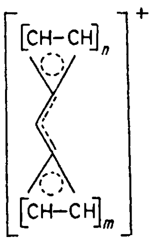
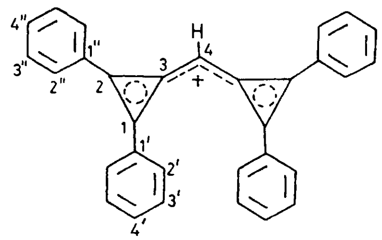
Summary The title compound, a stable salt of a new carbocation, has been synthesized and shown by ^{13}C n.m.r. spectroscopy to have a dipolar structure.

Syntheses of new conjugated cationic species of type (I) ($m=n=3$;[1] $m=1$, $n=3$[2]) have recently been reported. We now report on the synthesis and properties of the 1-(2,3-diphenylcycloprop-2-enylidenemethyl)-2,3-diphenylcyclopropenium ion (II), the smallest-ring analogue ($m=n=1$) of the cation (I), which was obtained in the course of our synthetic study on a series of polymethylenebis(diphenylcyclopropenium) dications.[3]

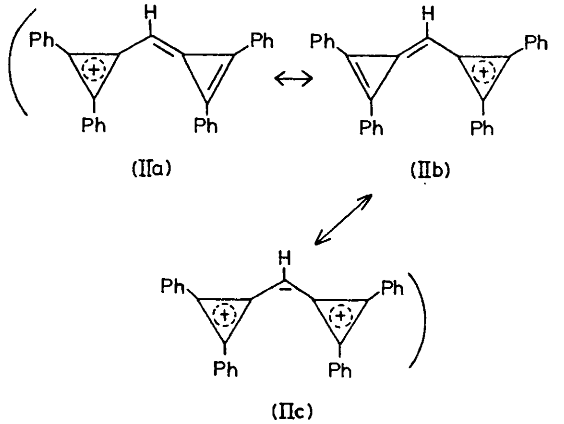
Reaction of 1,5-diphenylpenta-1,4-diene with phenylchlorocarbene generated from phenylchlorodiazirine gave the dicyclopropylmethane (III) (59%), which was then dehydrochlorinated with KOBu^t in tetrahydrofuran to afford bis(2,3-diphenylcycloprop-2-enyl)methane† (IV) as white needles (89%); m.p. 118·0—118·6 °C; ν_{max} (KBr) 1815w, 1490s, 1440s, 750s, and 680s cm^{-1}; δ (CDCl$_3$) 1·92 (2H, t, CH$_2$), 2·23 (2H, t, $>$CH–), 7·33 (12H, m, *m*-,*p*-H), and 7·70 (8H, m, *o*-H).

Hydride abstraction of (IV) with trityl perchlorate (2 equiv.) in acetonitrile did not give the dication (V), but yielded the perchlorate† of the monocation (II) as yellow crystals by subsequent deprotonation; m.p. 227·0—228·0 °C (decomp.); ν_{max} (KBr) 1830m, 1490s, 1440vs, 1380vs, 1090vs, 765s, and 680s cm^{-1}; λ_{max} (MeCN) 243 (log ϵ 4·45), 269 (4·51), and 353 (4·77) nm; δ (CD$_3$CN) 6·52 (1H, s, vinylic H) and 7·33—8·33 (20H, m, ArH). Compound (II) is stable


(I)



(II)



(IIa) (IIb) (IIc)

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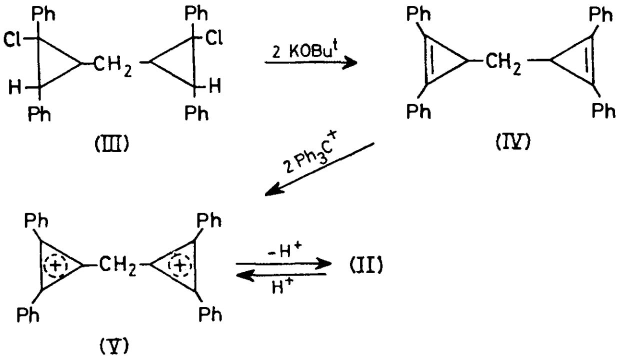
† Satisfactory elemental analyses have been obtained.

in air and soluble only in polar solvents, *e.g.*, MeCN, CH_2Cl_2, or 0·1N HCl. In spite of its highly strained structure, the pK_R^+ value of (II) was found to be 7·23 ± 0·10 (determined spectrophotometrically in 23% EtOH), indicating that its electronic stability was comparable with that of the cation (I) with $m=n=3$ (pK_R^+ 7·49[1b]). In the n.m.r. spectrum taken in CF_3CO_2H the vinylic proton at δ 6·52 disappears presumably owing to the rapid proton-exchange process which occurs in the equilibrium between (II) and (V). When CF_3SO_3H is added (*ca.* 4%), the equilibrium is shifted towards (V), as shown by the appearance of a singlet at δ 6·19 (2H) and a hypsochromic shift of the u.v. maximum to 313 nm (log ε 4·78).



The ^{13}C n.m.r. spectrum of (II) measured in CD_3CN showed the following signals: δ (p.p.m. from Me_4Si) 144·0(s), 145·0(s) (C-1, C-2; charge density +0·1833); 148·4(s) (C-3; +0·1955); 68·6 (d) (C-4; −0·2632); 122·6(s), 123·0(s) (C-1′, C-1″; −0·0106); 133·4(d), 134·4(d) (C-2′, C-2″; +0·0166); 130·5(d), 131·0(d) (C-3′, C-3″; −0·0007); and 135·7(d), 136·4(d) (C-4′, C-4″; +0·0134). Assignments were made by comparison with the spectrum of the diphenylcyclopropenium ion and with the calculated charge density‡ of (II) given in parentheses. The planarity of this cyclopropenium system is clearly demonstrated by the appearance of C-1, C-2, and phenyl carbons in sets of pairs of signals. It should also be noted that the C-4 carbon appears at unusually high field, δ 68·6. This remarkable chemical shift is attributable to the considerable amount of negative charge residing on this carbon, which is in agreement with the calculated result. This finding thus illustrates the significant contribution of the dipolar structure (IIc) to the resonance hybrid of (II).§

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‡ Calculated by the HMO method ($\beta_{1,3}=\beta_{2,3}=\cdots=0{\cdot}9$; $\beta_{C-Ph}=0{\cdot}8$).

§ This type of polarization seems to be a characteristic feature of the cation (I), since the chemical shift of the corresponding central carbon was also found to be at a remarkably high field [δ 100·1 (M. Oda, personal communication)] in the 8-cyano derivative of (I) with $m=n=3$, [see ref. 1(a)].

[1] (a) T. Otomo, M. Oda, and Y. Kitahara, *Chem. Comm.*, 1971, 114; (b) Y. Kayama, M. Oda, and Y. Kitahara, *Chem. Letters*, 1973, 1169.
[2] M. Oda, K. Tamate, and Y. Kitahara, *Chem. Comm.*, 1971, 347.
[3] Unpublished work.