Formation of a Novel Complex between Pyridinium Bis(alkoxycarbonyl)methylides and Diphenylcyclopropenone; Trapping of Pyridinium Bis(alkoxycarbonyl)-methylide Cation Radicals

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Summary Reactions of pyridinium bis(alkoxycarbonyl)-methylides with diphenylcyclopropenone in refluxing acetonitrile produce the corresponding 1:1 complexes (3), e.s.r. analysis of which indicates the presence of radical cations of the ylides (1).

THE chemistry of both cycloimmonium ylides[1] and cyclo-propenones[2] has attracted considerable attention in recent years because of their intriguing chemical and physical properties. Formation of a charge-transfer complex between cyclopropenones and organic compounds has not been reported, although metal[3] or Lewis acid[4] complexes are known. We now report the formation of stable complexes of pyridinium bis(alkoxycarbonyl)methylides with diphenylcylopropenone which serves as the counter-ion pair.

Reaction of pyridinium bis(methoxycarbonyl)methylide (1a) with diphenylcylopropenone (2) in refluxing aceto-nitrile under nitrogen afforded the complex (3a), with elemental and mass spectrometric analyses corresponding to a 1:1 composition, as purple paramagnetic crystals after rapid purification by column chromatography.

TABLE 1. Physical properties of the complexes (3)

	% Yield	M.p./°C	m/e (M^+)	ν_{max} (KBr)/cm^{-1} (C=O)	λ_{max} (CH$_2$Cl$_2$)/nm
(3a)	27	195—196	415	1712, 1681, 1646	338, 576
(3b)	25	154—155	443	1715, 1680, 1640	340, 582

Complex (3a), which appears to be quite stable under normal atmospheric conditions, exhibits a charge-transfer band at λ_{max} (CH$_2$Cl$_2$) 576 nm (KBr pellet: λ_{max} 580 nm). Its i.r. spectrum does not resemble a superposition of the spectra of its components, with a large shift of the ν(C=O) band of (2), suggesting that (3a) is of the inner complex type[5] (Table 1). Thus, we tentatively propose that the complex (3) exists mainly as the ionic complex (4); assignment of a structure including delocalization of the negative charge on the substituent on the ylide carbon atom seems justified[1] and an analogous type of the complex with metal salts have been reported for related compounds.[6]
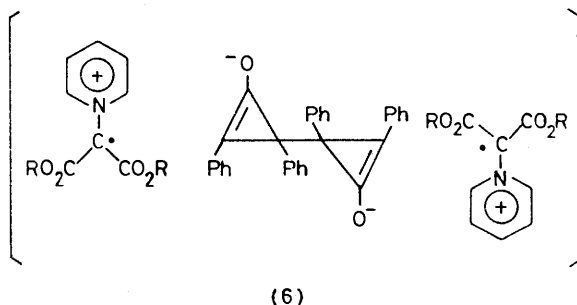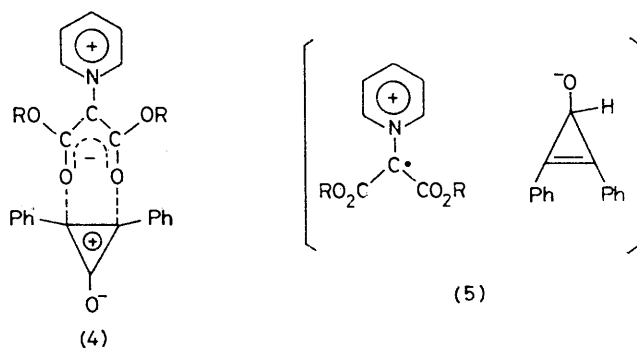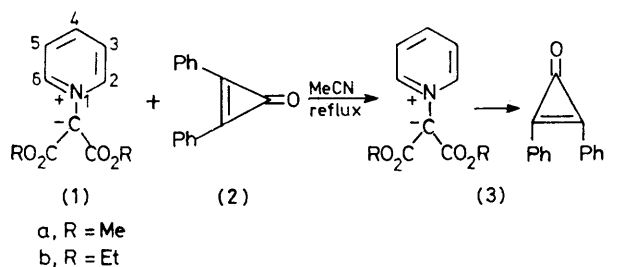
A degassed solution of (3a) in dichloromethane at room temperature shows relatively weak e.s.r. signals, indicating the presence of the cation radical of (1a). A better resolved spectrum was obtained for the complex (3b) [Figure (a)], comprising 76 lines (g 2·0038) whose splittings show the hyperfine couplings of an unpaired electron with the pyridine ring nitrogen and protons as well as the methylene protons of ethoxy groups, the methyl proton splittings being too small to be resolved. Proton and ^{14}N coupling constants resulting from an extensive computer-assisted analysis of the spectrum are shown in the Figure (b) and
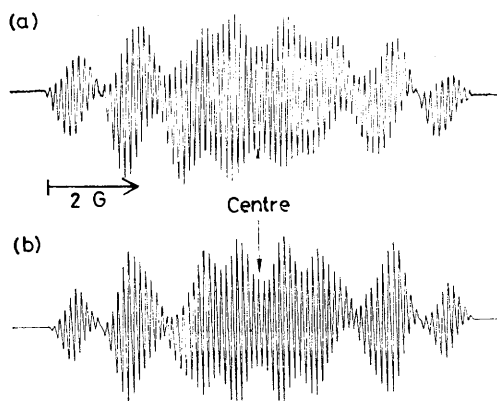
(1) + (2) → (3)

a, R = Me
b, R = Et

(4)

(5)

(6)

(a)

(b)

FIGURE. (a) E.s.r. spectrum of the cation radical of (1b) in CH$_2$Cl$_2$ at room temperature: g 2·0038. (b) Computer-simulated spectrum based upon the parameters given in Table 2. (The computed curve does not account for a slight selective line broadening of the high-field group caused by ^{14}N hyperfine anisotropy.)

Table 2. The assignments in Table 2 were confirmed by the observation of triple signals (1:1:1, $ca.$ 2 G) of equal intensity due to ^{14}N in the e.s.r. spectrum of the complex obtained from the hexadeuteriopyridinium ylide [^{2}H$_5$]-(1b) and (2).† Attempts to observe the counter-anion radical of (2)[7] by e.s.r. spectroscopy failed. The e.s.r. signal probably derives from a complete electron-transfer reaction of (1), but the reason why the counter-anion radical is not detected is not clear. Two of the possible explanations are that the radical cation of (1) exists as the complex (5) derived from the reaction of two molecules of (1) and one molecule of (2) or as a 2:2 complex such as (6).[8]‡

In view of the present results, it appears that nucleophilic additions[9] and 1,3-dipolar reactions[10] of cyclo-immonium ylides with cyclopropenones may proceed by initial formation of a charge-transfer complex§ and that

† The coupling constants compare favourably with theoretical values obtained from simple Hückel M.O. calculations. Further work is in progress on more detailed calculations as well as on the generation of cation (by an independent method) and anion radicals of (1).

‡ The authors are indebted to the referees for this discussion.

§ In fact, a preliminary examination of the fresh reaction mixture of (1a) and (2) showed a charge-transfer band at λ_{max} 800 nm (in addition to that at 576 nm) which was tentatively assigned to the primary molecular complex (3a).

TABLE 2. Hyperfine coupling constants for pyridinium bis-(alkoxycarbonyl)methylide radical cations at room temperature

| Position | Coupling constant/G^a | |
	(1a)[b]	(1b)
N	2·66	1·680
2, 6	1·33	1·183
3, 5	0·30	0·254
4	2·95	2·520
—	0·22 (CO_2Me)	0·130 (CO_2CH_2Me)

[a] 1 G = 10^{-4} T.   [b] Obtained directly from the observed spectrum.

suitably substituted cyclopropenones (or triafulvenes) and cycloimmonium ylides could be used as components for organic conductors.[11]

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