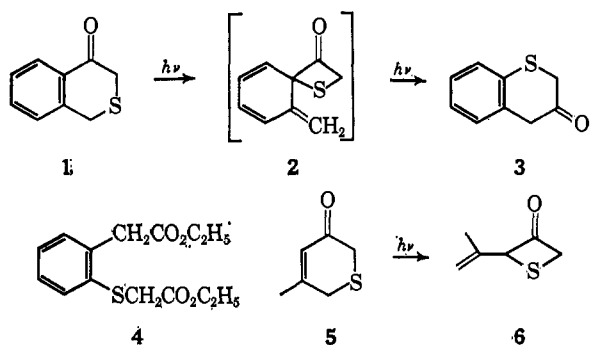boxylation. Photolysis of 1 under similar conditions in a Rayonet reactor, 3500-A source,[6] resulted in very slow decomposition to polymeric material, indicating excitation of only the long-wavelength band is not sufficient for the reaction.

We believe that the initial photoproduct is the triene 2 which undergoes a further photochemically induced rearrangement to 3. In an effort to obtain evidence for the intermediacy of 2 in the reaction, 5[4,7] was irradiated under similar conditions in the hope of isolating 6, which should not undergo further photochemical rearrangement if excitation of the triene system is responsible for further photochemical rearrangement of 2. Photolysis[1] of 5 in cyclohexane produced 6[8] in 30% yield. This observation and the appearance of an absorption band at 1770 cm^{-1} in the infrared spectrum of a solution of 1 in cyclohexane which had been photolyzed for a short period of time suggest that 2 is a reasonable intermediate in the formation of 3.

8-Methyl-, 7-methoxy-, 3-methyl-, and 3,3-dimethyl-isothiochroman-4-one also undergo this photochemical rearrangement in yields varying from 20 to 40%.[9]

(6) The Southern New England Ultraviolet Co., Middletown, Conn.
(7) $\lambda_{max}^{isooctane}$ 231.5 mμ (ϵ 9340), 270 (302), 347 (97.8).
(8) $\nu_{max}^{CCl_4}$ 1780, 1641, 1448, 1397, 1374, 1168, 1127, 910 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 245 mμ (ϵ 912), 330 (166); nmr: δ 4.1 (2 H, broad singlet, -SCH$_2$C(=)-), 1.85 (3 H, broad singlet, CH$_3$-), 5.0, 5.1, 5.25 (3 H, broad singlets, CH$_2$=C< and >CCH(S-)CO-).
(9) This research has been supported by National Science Foundation Grant No. GP-5761.
(10) Alfred P. Sloan Fellow, 1963-1967.

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Received February 27, 1967

Inhibited Pseudo-Rotation in a Cyclic Monoalkylphosphorane[1]

Sir:

Methyl ethylene phosphate undergoes hydrolysis, both to open the ring and to lose the methoxyl group, at a rate about a million times as great as that for trimethyl phosphate.[2] The driving force for the rapid reactions is presumably ring strain.[3] However, to explain the unexpected rapid hydrolysis of the ester group *external* to the ring in methyl ethylene phosphate and various other cyclic compounds[2,4-6] we recently

(1) This research was supported by the National Science Foundation under Grant GP-2098.
(2) F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 1773 (1963).
(3) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963); D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).
(4) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

postulated[7] that the hydrolysis of phosphate esters may, and in some cases must, proceed with pseudo-rotation[8,9] of trigonal-bipyramidal intermediates. In contrast to methyl ethylene phosphate, the methyl ester of the five-membered cyclic phosphinic acid hydrolyzes at a rate comparable to that of the ester of diethylphosphinic acid.[6,10] This fact can be explained by postulating that, in analogy with the known chemistry of the alkylfluorophosphoranes,[11] oxygen atoms preferentially occupy the apical, and alkyl groups the equatorial positions in the trigonal-bipyramidal intermediates formed during hydrolysis. Under these assumptions, the hydrolysis of the ester of the cyclic phosphinic acid is slow, despite the presumed strain in the ring, because, in order to form a trigonal-bipyramidal intermediate, an alkyl group must be forced into an unfavorable axial position, or else the ring angle must be expanded to 120°. Both kinetic[4,7] and X-ray crystallographic[12] evidence as well as theory[8] argue against this latter choice. The chemistry of phostonates[7] can also be rationalized on the assumption of preferential placement of alkyl groups in equatorial positions in trigonal-bipyramidal intermediates in hydrolysis. Ramirez and his co-workers[13] have prepared many cyclic phosphoranes, including[14] I, where an alkyl group is part of a five-membered ring system. According to our postulates,[7] this compound should exist preferentially in a structure where the alkyl group is equatorial, and where therefore the methoxyl groups occupy different positions. However, the nmr spectrum of I, determined at room temperature,[14] shows only one kind of methoxyl group.

We now report that, at low temperatures, the nmr spectrum of I corresponds to that expected for the structure as shown. At room temperature, the three
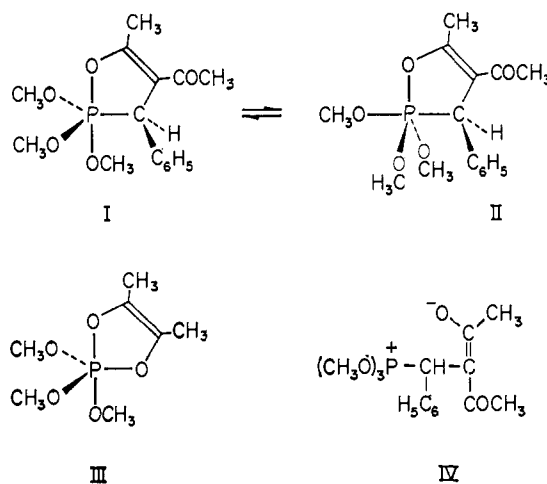
(5) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).
(6) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431 (1966).
(7) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966).
(8) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(9) D. Hellwinkel, *Ber.*, **99**, 3628, 3660 (1966), has demonstrated similar pseudo-rotations for pentaarylphosphoranes by stereochemical studies.
(10) G. Aksnes and K. Bergesen, *Acta Chim. Scand.*, **20**, 2508 (1966).
(11) E. Muetterties and R. A. Schonm, *Quart. Rev.* (London), **20**, 245 (1966); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **4**, 496 (1965).
(12) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965).
(13) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).
(14) F. Ramirez, O. P. Madan, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965).
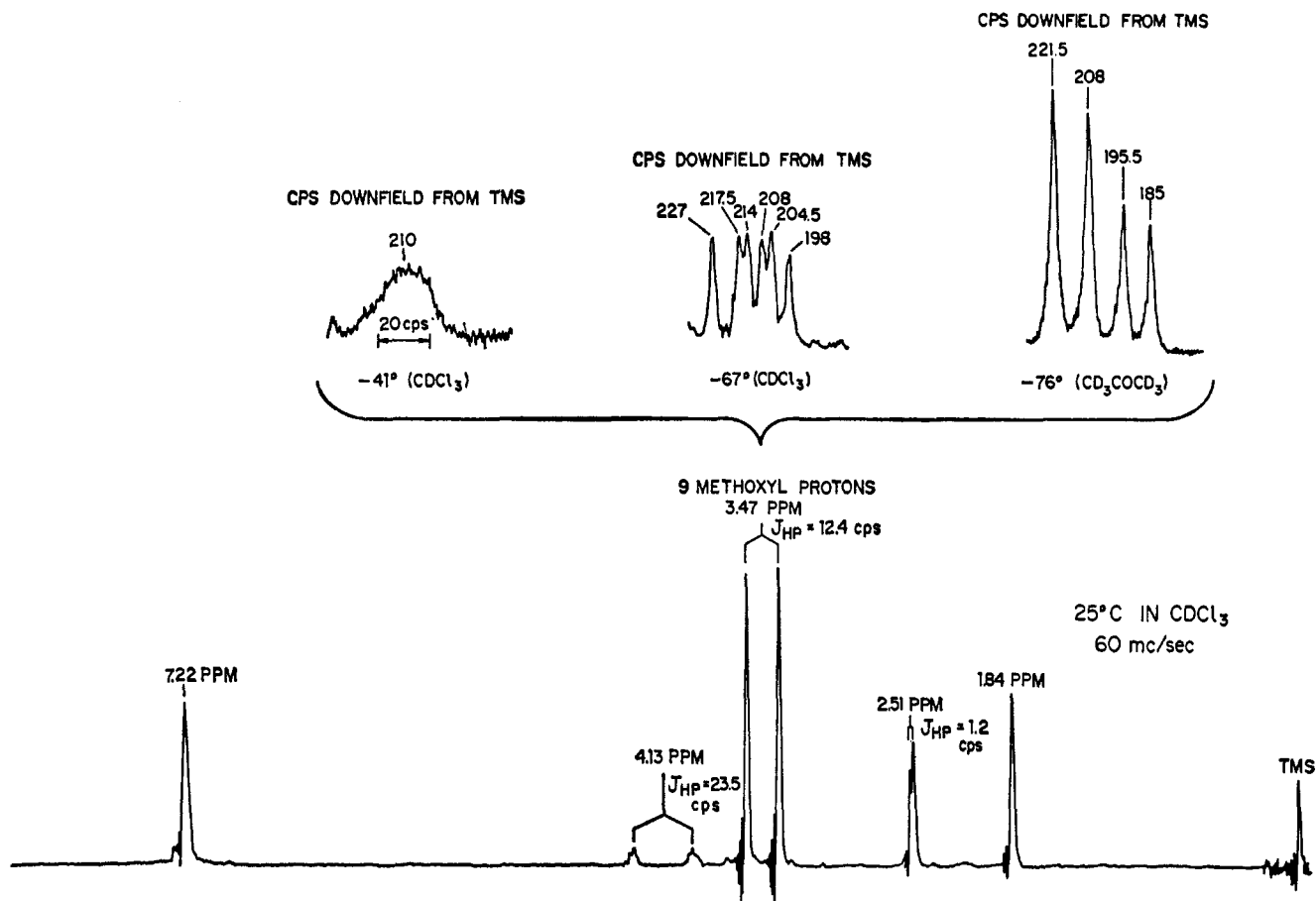
Figure 1. The proton nmr spectrum, at 60 Mc, for I at 25, −41, and −67° in deuteriochloroform, and −76° in deuterioacetone.

methoxyl groups appear as a doublet; the signal is split by ^{31}P with J = 12.5 cps. In either deuteriochloroform or in deuterioacetone, the doublet observed at room temperature collapses, at about −40°, to a broad band, and at −65° this band is again resolved (Figure 1). In deuterioacetone, the nmr spectrum of the methoxyl groups shows two separate doublets, with J = 13.5 and 10.5 ppm and with integrated intensities of 1:2, corresponding to one apical and two equatorial methoxyl groups, whereas in deuteriochloroform the spectrum shows three partially separated doublets, two with J = 13 and one with J = 10 cps. These again correspond to one apical and two equatorial methoxyl groups. Since the two equatorial methoxyl groups in I differ in their relationship to the phenyl ring, it is the acetone spectrum, rather than that in chloroform, that is somewhat unexpected. In contrast to I, the pentaoxyphosphorane III shows only one kind of methoxyl groups (a sharp doublet, J = 13 cps) all the way down to −100°. For III, pseudo-rotation necessarily generates unstrained structures with apical oxygen atoms; the equivalence of positions in this compound resembles that[8,11] of PF_5.

The low-temperature nmr spectra in Figure 1 show that I is stable with equatorial alkyl group. The constancy of the average chemical shift for the methoxyl groups and of the coupling constants shows that, at high temperature, exchange occurs among equivalent structures. Pseudo-rotation about an equatorial methoxyl group as pivot will convert I to II; two methoxyl groups of II are equivalent, and the pseudo-rotation from II to I can utilize a different methoxyl group as pivot than that for its formation. Further pseudo-rotations can complete the exchange process. Although II is energetically unfavorable with respect to I, its formation in minute amount and reversion to I is apparently sufficiently rapid at room temperature to catalyze the exchange of the methoxyl groups; II functions as does the boat form of cyclohexane in the interconversion of equivalent chair forms. An alternative mechanism for exchange of the methoxyl groups allows the opening of the five-membered ring[15] to form IV, followed by mixing of the methoxyl groups by rotation and reclosure of the ring. Even if such a mechanism is operative, it does not in any way affect the conclusion that, at low temperatures, the structure of I is frozen as drawn, that pseudo-rotation is inhibited, and that in derivatives of phosphorane alkyl groups preferentially occupy equatorial and oxygen atoms apical positions. But the explanation involving ion pairs is relatively unlikely. First, the enolate ion in IV must be more stable than the corresponding enolate in an ion pair derived from III; if the formation of ion pairs were the only mechanism for exchange, I should undergo the reaction more readily, rather than less readily, than III. But further, the temperature at which the doublet for I coalesces is about −41° in deuteriochloroform and −37° in deuterioacetone, but about −60° in deuteriotoluene. If the exchange among the methoxyl groups occurred by way of an ion pair, this exchange should prove more facile, rather than less facile, in the more

(15) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, 85, 3252 (1963).

polar solvents. Further studies of these spectra are in progress.

The experiments were carried out with a Varian A-60 nmr spectrometer, equipped with a Varian Associates V-6031B variable low-temperature probe.

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Contact and Solvent-Separated Ion Pairs of Carbanions. III. Reactivities in Proton-Abstraction Reactions

Sir:

It was recently shown[1] that changes in the absorption spectra of solutions of carbanions and radical ions upon varying the solvent composition and temperature could be interpreted in terms of two kinds of ion pairs, *i.e.*, contact and solvent-separated ion pairs. We have now studied the reactivity behavior of these species in proton-abstraction reactions and have made a number of interesting observations.

Alkali salts of the fluorenyl carbanion were allowed to react with 1,2- or 3,4-benzofluorene in dioxane, tetrahydrofuran, or 1,2-dimethoxyethane as solvent. The progress of the reaction was followed spectrophotometrically, and the rate constants were calculated from the initial slopes of the recorder tracings. In a number of instances a flow system was used, but even then some of the reactions were too rapid to obtain accurately the initial slopes. In these cases calculation of the rate constants was based on the half-life of the reaction. Although this will somewhat affect the accuracy of the data, the differences between the observed second-order rate constants for the various systems are large enough to justify a comparison. The results are reported in Table I.

The data for fluorenyllithium show a strong dependence of the rate constants on the carbanion concentration in all three solvents. The same is true of fluorenylsodium in dioxane. This suggests the presence of unreactive aggregates, $[F^-,M^+]_n$, in these solutions, and the kinetic measurements lead to an average aggregation number of 5 or even higher. This strong association, even in solvents like THF and DME, is surprising since no such association was observed for the less charge delocalized polystyryl salts in either THF or dioxane.[2] It is likely that the association of the fluorenyl salts is favored by the planar structure of the carbanion. This may lead to a sandwich-type aggregate in which many ion pairs are stacked up

$$\begin{array}{c} | \oplus | \oplus | \oplus \\ \ominus \quad \ominus \quad \ominus \end{array}$$
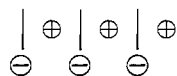
An additional attractive force, particularly important for the lithium salts, may result from a tendency of the counterion to complex with the highly polarizable π cloud of the fluorenyl ring.

(1) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965); **88**, 307 (1966).

(2) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

Table I. Observed Rate Constants for the Reaction Fluorenyl⁻,M⁺ + 1,2- or 3,4-Benzofluorene at 25°

Solvent	[F⁻,M⁺] × 10⁻⁵, M	k_{obsd}, M⁻¹ sec⁻¹	Solvent	[F⁻,M⁺] × 10⁻⁵, M	k_{obsd}, M⁻¹ sec⁻¹
F⁻,Li⁺ + 3,4-Benzofluorene			F⁻,Li⁺ + 1,2-Benzofluorene		
THF	370	2.86	THF	40	1.6
	140	3.16		4.7	12.3
	61	5.0		4.2	19.9
	26.8	9.2		0.67	51.6
	10.8	29.0	DME	15.0	6.8
	3.3	60.0		4.5	14.4
	1.36	158.0		0.9	103
F⁻,Na⁺ + 1,2-Benzofluorene					
Dioxane	42	183	THF	32	3800
	20	294		1.5	3960
	8.1	660		1.3	3500
	2.8	1660	DME	24	~80,000
	1.2	4200		22	~80,000
				0.92	~50,000
F⁻,Cs⁺ + 1,2-Benzofluorene			F⁻,N⁺Bu₄ + 1,2-Benzofluorene		
Dioxane	46	860	THF	43	800
	11	1300		46	700
	2.8	1560	DME	35	810
THF	42	960		35	930
	43	1080	F⁻,Na⁺ + 1,2-Benzofluorene		
	1.9	1570	in THF + CH₃O(CH₂CH₂O)₄CH₃		
				40	650
				40	575

Aggregation persists, at least for the lithium salts, even in THF and DME, where the ion pairs are solvent separated. This suggests that in the solvent-separated ion pair of fluorenyllithium the counterion is not fully surrounded by solvent molecules, since aggregation would then be sterically unfavorable and expected to be less than for the poorly solvated fluorenylcesium. Apparently, the lithium ion assumes a new average position in the solvent-separated ion pair; away from the carbanion but yet still close to the π-electron cloud of the ring system (see Figure 1). Such a position, made possible because of increased association with solvent molecules, would also lead to the observed red shift in the spectrum as compared to the contact ion pair and would at the same time energetically be favorable because of π complexing. Rate measurements with dioxane solutions of fluorenyllithium containing varying quantities of dimethyl sulfoxide again point to strong association of both contact and solvent-separated ion pairs in these systems. This type of association may well be responsible for the large discrepancies observed in the values for proton-transfer rate constants in solutions of fluorenyllithium in dimethyl sulfoxide,[3] in which different techniques and different carbanion concentrations were used.

Another interesting observation concerns the role of the counterion in proton-abstraction reactions. At low concentrations (*i.e.*, under conditions where aggregation vanishes), fluorenylsodium is as reactive or even more so in dioxane than in THF, while a strong increase in the rate constant is observed in DME. In the first two solvents the sodium salt is a contact ion pair, while in DME it is essentially solvent separated. Hence, less energy is needed in the latter case to transfer

(3) J. I. Brauman, D. F. McMillen, and Y. Kanazawa, *J. Am. Chem. Soc.*, **89**, 1728 (1967); C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 1730 (1967).