

Fig. 1.—pH dependence of τ^{-1} . All concentrations are total concentrations; temperature $10 \pm 1^\circ$, ionic strength 0.1 (KNO_3). Curve 1, \square , $8 \times 10^{-5} M$ model imidazole, $2.3 \times 10^{-5} M$ phenol red; curve 2, \triangle , $8 \times 10^{-5} M$ CT, $4.6 \times 10^{-5} M$ phenol red; curve 3, \circ , $8 \times 10^{-5} M$ CGN, $4.6 \times 10^{-5} M$ phenol red; curve 4, ∇ , $8 \times 10^{-5} M$ TPCK-CT (94.5% inactive), $4.6 \times 10^{-5} M$ phenol red; and curve 5, \diamond , $8 \times 10^{-5} M$ DIP-CT, $4.6 \times 10^{-5} M$ phenol red.

respectively, for the proteins, to be compared with $k_{13} = 7 \times 10^8$ and $k_{31} = 1.4 \times 10^8 M^{-1} \text{sec}^{-1}$ for model imidazole. These results suggest that the "available" imidazole groups of these proteins experience relatively slight environmental restrictions.

The "available" concentration of imidazole groups in CT is twice the total protein concentration as expected from titration data.² The L-1-tosylamido-2-phenylethyl chloromethyl ketone derivative of CT (TPCK-CT) has only one "available" imidazole group by the present method of analysis, in agreement with other evidence indicating that the catalytic-site imidazole in TPCK-CT is eliminated.³

The relaxation time profiles in the several variables were identical for diisopropylphosphorylchymotrypsin (DIP-CT) and TPCK-CT when corrected for a CT impurity of 5.5% in our TPCK-CT samples. This suggests that the DIP group blocks indicator attack on imidazole, consistent with a close approach of the imidazole and serine groups at the catalytic site. Since TPCK-CT has lost the protonic processes of the catalytic-site imidazole, it is possible that this group is also not free for protonic reactions in DIP-CT. By these tests TPCK-CT and CT differ only in the concentration of "available" imidazole groups. Rejecting accidental compensation, it is possible to conclude that both imidazoles of CT are essentially identical in behavior with the single "available" imidazole group of TPCK-CT and, consequently, that the catalytic-site imidazole group shows no special ionization properties.

The behavior of chymotrypsinogen (CGN) is peculiar and will require additional study. The intercept on a τ^{-1} vs. CGN concentration plot is identical with that ob-

tained for CT, TPCK-CT, and DIP-CT. This suggests that the rate constants for "available" imidazoles are the same for CGN as for the other proteins. If so, the "available" imidazole concentration in CGN is about 1.5 (rather than 2 or 1) times the total protein concentration.

The effects of substrates and competitive inhibitors on the rate constants and "available" imidazole concentrations are currently being investigated. We have found that $2 \times 10^{-3} M$ indole increases τ by 38% when total $[\text{CT}] = 10^{-4} M$. Indole is a competitive inhibitor having a dissociation equilibrium constant of $7.0 \times 10^{-4} M$. The increase in τ expected if indole binding prevents the direct transfer reaction at one of the two CT imidazoles can be calculated to be 37%. Consequently, it appears that the binding of indole causes some type of protective infolding of one imidazole group, reducing its "available" concentration. This finding strongly suggests that the binding of substrate side chains, through changes in folding, exerts direct control on a functional group participating in acylation or deacylation. The method is thus able to provide detailed information about the catalytic process even at this early stage of development.

DIP-CT and TPCK-CT were prepared from Worthington α -CT, and Worthington CGN was used.

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Phenylbis(dimethylamino)fluorophosphonium Phenylpentafluorophosphate¹

Sir:

A recent report² on some aryldialkylaminotrifluorophosphoranes, ArPF_3NR_2 , led us to include this type of compound in a general study of five-coordinate stereochemistry, conducted by means of F^{19} n.m.r. spectroscopy.³ Both the F^{19} and P^{31} n.m.r. spectra for any R_2PF_3 species, except the perfluoroalkyl derivatives, $(\text{R}_f)_2\text{PF}_3$, could be interpreted in terms of a trigonal bipyramidal arrangement of the ligands around the phosphorus atom, the fluorine atoms occupying the two axial and one equatorial positions.

Among a number of alkyl- (aryl-) dialkylaminotrifluorophosphoranes, which we have investigated, one clearly stands out with respect to an unusual transformation occurring upon storage of this compound. Phenyl dimethylaminotrifluorophosphorane, $\text{C}_6\text{H}_5\text{PF}_3\text{N}(\text{CH}_3)_2$, not previously reported, was prepared using the method of the Russian workers,² via $\text{C}_6\text{H}_5\text{PF}_3\text{H}$ and $\text{C}_6\text{H}_5\text{PF}_3\text{Cl}$, the latter being allowed to react with dimethylamine. We have also obtained the compound less expediently by the reaction of phenyl dimethylaminochlorophosphine with arsenic or antimony tri-

(1) Phosphorus-Fluorine Chemistry. XI. For X in this series see: R. Schmutzler, *Z. Naturforsch.*, in press.

(2) Zh. M. Ivanova and A. V. Kirsanov, *Zhur. Obshch. Khim.*, **32**, 2592 (1962).

(3) (a) E. L. Muettterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muettterties, K. J. Packer, W. Mahler, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) R. Schmutzler, *Angew. Chem.*, **76**, 570 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3**, 513 (1964).

(4) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, in press.

(2) M. A. Marini and C. Wunsch, *Biochemistry*, **2**, 1454 (1963).

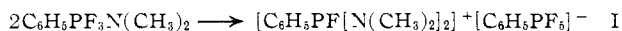
(3) G. Schoellmann and E. Shaw, *ibid.*, **2**, 252 (1963).

fluoride,^{3c} or by the reaction of phenyltetrafluorophosphorane with dimethylamine.⁵

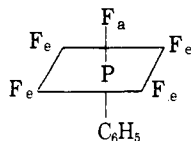
Freshly distilled $C_6H_5PF_3N(CH_3)_2$ [b.p. 88° (6.5 mm.)] is a mobile liquid, typically covalent and well-soluble in nonpolar solvents. Its P^{31} n.m.r. spectrum consists of a doublet ($J_{P-F_{eq}} = 963$ c.p.s.) of triplets ($J_{P-F_{ax}} = 821$ c.p.s.), chemical shift (relative to an external 85% H_3PO_4 reference) $+53.6$ p.p.m. When a sample of this compound was allowed to stand at room temperature over prolonged periods (*i.e.*, several weeks) the P^{31} (and F^{19}) n.m.r. spectrum indicated formation of new phosphorus-containing species at the expense of $C_6H_5PF_3N(CH_3)_2$. This change was observed independently of the origin of the sample of $C_6H_5PF_3N(CH_3)_2$ but was most rapid for the product obtained by dimethylaminolysis of $C_6H_5PF_4$.⁵ In the latter case, after standing for three weeks, the liquid $C_6H_5PF_3N(CH_3)_2$ had completely solidified to a crystalline solid which was soluble only in polar solvents, such as acetonitrile or dimethyl sulfoxide. Formation of a salt-like product is thus suggested, and it could be shown that the molar conductance at 0.5° of a $0.009 M$ solution of the product in acetonitrile is increased about two orders of magnitude over the conductance of the pure solvent (965.6×10^{-6} vs. 11.87×10^{-6} ohm $^{-1}$ cm. $^{-1}$ for pure CH_3CN).⁶

According to the chemical analysis no change in elemental composition has occurred during the conversion. *Anal.* Calcd. for $C_{16}H_{22}F_6N_2P_2$: C, 45.9; H, 5.3; N, 6.7; P, 14.8. Found: C, 46.0; H, 5.7; N, 7.0; P, 15.1.

It is therefore proposed that the following conversion with formation of two new phosphorus-containing species has taken place.



The evidence obtained, especially from the P^{31} and H^1 n.m.r. measurements, is fully consistent with the above formulation, and the following octahedral arrangement for $[C_6H_5PF_5]^-$ may reasonably be considered



The P^{31} n.m.r. spectrum of I in acetonitrile showed that the original $C_6H_5PF_3N(CH_3)_2$ had completely disappeared, and the following signals were observed: a 1-1 doublet to low field of the H_3PO_4 reference ($J_{P-F} = 1037$ c.p.s., $\delta = -56.0$ p.p.m.) is owing to the fluorophosphonium cation, $[C_6H_5PF\{N(CH_3)_2\}_2]^+$. A doublet at high field is attributed to coupling between the central phosphorus and the axial fluorine atom ($J_{P-F_{ax}} = 697$ c.p.s.); each of the components is further split into a quintet by coupling between phosphorus and the four equivalent fluorine atoms in equatorial positions ($J_{P-F_{eq}} = 816$ c.p.s.). These values compare reasonably well to J_{P-F} in PF_6^- (710 c.p.s.). Most significantly, the P^{31} chemical shift for $[C_6H_5PF_5]^-$ was found to have the very high positive value of $+136.0$ p.p.m.,

(5) R. Schmutzler and G. S. Reddy, to be published.

(6) This measurement was obtained with the kind assistance of Mr. N. C. D. Carey of this laboratory.

only slightly lower than for PF_6^- ($+143.7$ p.p.m.⁷). This finding is in accord with the decrease in symmetry in going from PF_6^- to $[C_6H_5PF_5]^-$.

The F^{19} n.m.r. spectrum of I is also consistent with the proposed structure, a doublet with $J_{P-F} = 1046$ c.p.s., $\delta = +86.7$ p.p.m. (relative to an internal $CFCl_3$ reference) being observed for the cation. A doublet of doublets ($J_{P-F_{eq}} = 818$ c.p.s.), and a doublet of quintets ($J_{P-F_{ax}} = 690$ c.p.s., $J_{F_{ax}-F_{eq}} = 41$ c.p.s.), is owing to the $[C_6H_5PF_5]^-$ anion. The latter pattern is comparable, for instance, to that of F_5P -base adducts,⁸ or of the $[TiF_5(ROH)]^-$ anion.⁹

The identity of the cationic species, $[C_6H_5PF\{N(CH_3)_2\}_2]^+$, is well established from the F^{19} and P^{31} n.m.r. spectra.¹⁰ Additional information is provided by the H^1 n.m.r. spectrum of I in acetonitrile, which consists in the aliphatic region of a basic doublet due to spin-spin coupling between phosphorus and the protons of the $(CH_3)_2N$ groups ($J_{P-H} = 11.6$ c.p.s.), each component being further split into a doublet by coupling with the single fluorine atom in the cation and the $(CH_3)_2N$ groups ($J_{F-H} = 3.14$ c.p.s.), δ (relative to an internal $Si(CH_3)_4$ standard) $= -2.73$ p.p.m. Finally, integration of the H^1 n.m.r. spectrum confirms the unchanged composition, $C_8H_{11}F_3NP$ ($H_{arom.}:H_{aliph.} = 10:12$).

Hexacoordinate phosphorus species are noteworthy for their paucity, and, in fact, there are no other well-established precedents but the long known PF_6^- and PCl_6^- (in $PCl_4+PCl_6^-$).¹¹ The near identity of the P^{31} chemical shifts for PF_6^- and for our $[C_6H_5PF_5]^-$ suggests similar geometry in both cases. Also, the stability of $[C_6H_5PF_5]^-$ in solutions is comparable to that of PF_6^- , and solutions of I in acetonitrile could be kept unchanged over periods of several months, as followed by the F^{19} or P^{31} n.m.r. spectrum.

It must be noted that the above type of isomerization of an aryldialkylaminotrifluorophosphorane has been established, thus far, only for $C_6H_5PF_3N(CH_3)_2$. There are indications that $C_6H_5PF_3NC_5H_{10}$ ($C_5H_{10}N =$ piperidyl) and $CH_3PF_3N(CH_3)_2$ undergo a similar transformation, but it is of interest that the very closely related $C_6H_5PF_3N(C_2H_5)_2$, under exactly identical conditions as for $C_6H_5PF_3N(CH_3)_2$, remained completely unchanged, as shown by the observation of its refractive index and F^{19} n.m.r. spectrum over more than 6 months. Apparently there are especially favorable circumstances energetically for the formation of the solid $[C_6H_5PF\{N(CH_3)_2\}_2][C_6H_5PF_5]$.

Acknowledgment.—The author is grateful to Professor H. J. Emeléus, F. R. S., for his interest. Deutscher

(7) We have consistently obtained a value of $+143.7$ p.p.m. for the P^{31} chemical shift of hexafluorophosphates, independent of the cation. The reported value [$+118$ p.p.m.: H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954)] appears to be too low.

(8) (a) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960); (b) E. L. Muetterties in "Advances in the Chemistry of Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, p. 509; (c) F^{19} n.m.r. spectroscopic evidence for $[RPF_4]^-$ has been obtained in the system $RPF_4-(CH_3)_2SO$: K. J. Packer and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3035 (1963), and E. L. Muetterties, personal communication.

(9) R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).

(10) A first fluorophosphonium salt, $[FPCl_3][SbCl_6]$, has just been reported: J. K. Ruff, *ibid.*, **2**, 813 (1963).

(11) A potentially hexacoordinate phosphorus species has been obtained recently by the reaction of trimeric phosphonitrilic chloride with catechol and triethylamine, but no P^{31} n.m.r. data are available owing to the poor solubility of the product: H. R. Alcock, *J. Am. Chem. Soc.*, **85**, 4050 (1963), and personal communication.

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The Photolysis of Spiro[2.5]octa-1,4-dien-3-one in Ethyl Ether. A Note on the Mechanism of Photolysis of 2,5-Cyclohexadienones¹

Sir:

Photolyses of crossconjugated cyclohexadienones in solution have led to rearranged products whose structures suggested that their mode of formation involved ionic intermediates.² However, it has been postulated^{2a,3} that radical intermediates might well precede the product-determining ionic intermediates, although the necessity for this added mechanistic complication has not been accepted universally.⁴ We now report a novel photochemical reaction of a 2,5-cyclohexadienone which requires the postulation of radical intermediates to explain adequately the results.

The substrate, spiro[2.5]octa-1,4-dien-3-one (I), was prepared according to the procedure of Baird and Winstein^{5,6} and was crystallized at low temperatures before photolysis. The photolysis of I in ethyl ether with a Hanovia 450-watt high pressure mercury arc with a Pyrex filter was followed by ultraviolet spectra of aliquots withdrawn during the reaction. The dienone has λ_{\max} 261 m μ ^b and new maxima appeared at 225 and 280 m μ while the peak at 261 m μ diminished. When the source was turned off during photolysis, the relative peak heights in the ultraviolet spectrum did not change for an indefinite period, and on reillumina-

TABLE I

PHOTOLYSIS OF SPIRO[2.5]OCTA-1,4-DIEN-3-ONE (I)

Runs	1 ^a	2 ^a	3 ^a	4 ^a	5 ^b
Dienone I, moles $\times 10^{3c}$	1.3	1.7	2.3	2.5	0.22
Concn. of I in ether, moles/l. $\times 10^{3c}$	4.1	5.4	7.6	1.6	0.64
Products, mole % based on I					
<i>p</i> -Ethylphenol (II)	50	30	10	20	53
Acetal (III)	<i>d</i>	4	2.2	3.8	<i>d</i>
IV + V ^e	21	28	18	16	17.5 ^f
Polymeric and unidentified photoproducts	<i>d</i>	<i>d</i>	71	59	<i>d</i>

^a Yields determined by weighing of isolated material. ^b Yields determined by g.l.c. ^c Based on ultraviolet spectrum of ethereal solution and ϵ at 261 m μ of 23,000.^b ^d Undetermined. ^e Combined yield of unseparated mixture of IV and V. ^f Analysis by g.l.c. indicates mixture of 37% IV and 63% V.

(1) Part III of a series: The Photochemistry of Unsaturated Ketones. Part II: D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Letters*, No. 22, 1375 (1964). Part I: D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, No. 27, 1911 (1963).

(2) For reviews, see (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); (b) O. L. Chapman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 323-420.

(3) H. E. Zimmerman in ref. 2b, pp. 183-208.

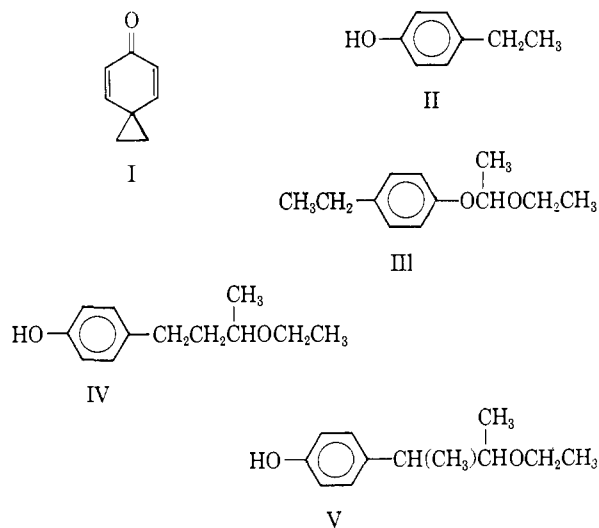
(4) See ref. 2b and G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

(5) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963); **79**, 4238 (1957).

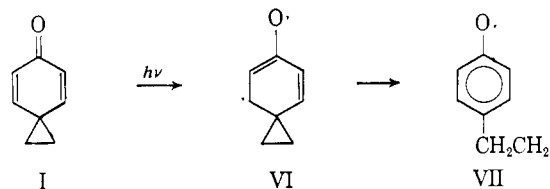
(6) We are indebted to Professor Winstein and Dr. Baird for detailed procedures for the preparation of I prior to their full publication.

tion the reaction resumed at an unchanged rate. A control sample of dienone in ether which was not irradiated showed no change. All evidence indicates that other thermal reactions of the dienone,⁵ not initiated by photolysis, were not competing with the photochemical reaction.

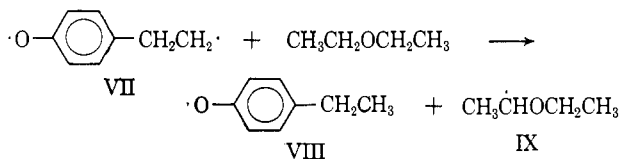
The products were isolated by column chromatography on silica gel and molecular distillation and are given with yields in Table I. The structures of III, IV, and V (mixture of diastereomers) were elucidated by analysis of n.m.r. and mass spectra and were confirmed by independent synthesis.⁷ Isolation of reduc-



tion products and incorporation of ether into the products necessitate postulation of radical intermediates in this reaction. The exact modes of formation of III, IV, and V are unknown, but preliminary mechanistic suggestions seem appropriate. Excitation of I appears to give diradical VII either directly or *via* VI.⁸ Ring opening of VI to VII⁹ is anticipated not



only because of the formation of the benzene ring but also by analogy with the model cyclopropylcarbonyl radical.¹⁰ The reactive primary radical VII would most likely abstract an α -hydrogen from ether to give



(7) Details will be given in the full paper. Satisfactory elemental analyses have been obtained for all new compounds.

(8) The cyclopropane ring is favorably situated geometrically to interact directly with the π -system in I, as has been noted in the ultraviolet spectrum of I.⁵

(9) Ring opening has been observed in the vapor-phase photolysis of acetylcyclopropane: J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(10) (a) D. I. Schuster, Ph. D. Dissertation, California Institute of Technology, 1961; (b) R. Breslow in "Molecular Rearrangements," Vol. 1, P. De Mayo, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 291-294.