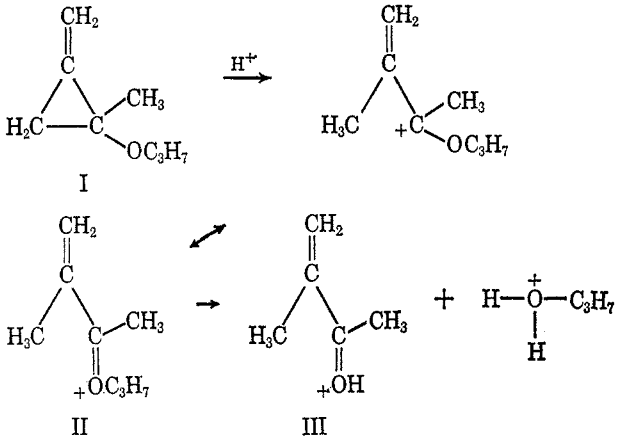
droxyl group.[3] We now report still another approach to stable ions, the protonolysis of appropriately substituted cyclopropanes[4] in 96% sulfuric acid.[2,7]

The nmr spectrum of 2-isopropoxy-2-methyl-1-methylenecyclopropane (I)[8] in 96% sulfuric acid exhibits two slightly broadened singlets at τ 3.22 and 3.49 (two protons, vinyl), a septet centered at τ 4.70 ($J = 6.0$ cps, one proton geminal to oxygen), a sharp singlet at τ 7.43 (methyl group geminal to oxygen), a slightly broadened singlet at τ 8.35 (three protons, allylic methyl), and a doublet centered at τ 8.75 ($J = 6.0$ cps, six protons, isopropyl). As the solution aged (several hours), the spectrum gradually changed. Two singlets emerged at τ 3.08 and 3.35 as the τ 3.22 and 3.49 signals diminished in intensity. Similarly, as the septet at τ 4.70 vanished, another appeared at τ 5.27 ($J = 6.0$ cps) and the singlet at τ 8.35 became replaced by one at τ 8.30. The doublet at τ 8.75 disappeared as a new one grew in at τ 8.94. The methyl signal at τ 7.43 remained unchanged in chemical shift. This transition from one simple spectrum to another equally clean pattern suggested a discrete chemical change as opposed to the indiscriminate destruction of the initially formed ion.



Spectral data first cited are those predicted for ion II, and those obtained from the aged solution are consistent with III and the conjugate acid of isopropyl alcohol in equimolar quantities. These suspicions were confirmed by quenching an aged solution with cold water and extracting the product into carbon tetrachloride. Its nmr spectrum proved to be essentially identical with data reported for 2-methyl-1-buten-3-one.[9] Moreover an equimolar mixture of this substance with isopropyl alcohol gave an nmr spectrum in sulfuric acid which is identical with that of an aged solution of I in sulfuric acid.

It is noteworthy that the spectral changes described occur only slowly and are due primarily to hydrolysis rather than polymerization. The half-life of II is not less than 30 min at 42°. The stability of this ion (II) relative to that of others possessing terminal double bonds[7,10] is perhaps not surprising in view of the extent to which charge is delocalized.

Evidence in hand is insufficient to permit a choice of mechanism for the protonolysis. Reaction could involve a direct attack of proton on the cyclopropane ring or, perhaps more likely, attack on the double bond. The latter would probably not produce a fully developed, rather high energy cyclopropyl ion[11] but would instead involve synchronous rearrangement to II.

The behavior of 2-methoxy-2-methyl-1-methylenecyclopropane in sulfuric acid was examined and found to be similar to that of I. The most notable difference was the diminished half-life of its primary ion.

Experimental Section

Sulfuric Acid Solutions.—Solutions were prepared at concentrations of approximately 10% by volume in reagent grade 96% sulfuric acid. Spectra were obtained with a Varian A-60 nmr spectrometer using standard sample tubes at ambient temperature (~42°). Sodium 3-trimethylsilyl-1-propanesulfonate was used as an internal standard (accepted value τ 9.92).

Acknowledgment.—The authors are indebted to the Robert A. Welch Foundation for the financial support of this study.

[3] For leading references, see C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

[4] The acid-catalyzed solvolysis of cyclopropanes has been rather extensively studied[5,6] but not as a means for preparing stable ions.

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[6] R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964), and references cited therein.

[7] The use of sulfuric acid is described by N. C. Deno, "Progress in Physical Organic Chemistry," Vol. II, Interscience Publishers, Inc. (John Wiley and Sons, Inc.), New York, N. Y., 1964, p 129; N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

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[10] T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964).

[11] The mode of addition of hydrogen bromide to methylenecyclopropane [B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962)] is suggestive of an intermediate cyclopropyl ion. However, the solvent employed was nonpolar and a four-center transition state could therefore be involved.

Ultraviolet Spectral Studies of Conjugation in Esters of Acylphosphonic Acids[1]

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The ultraviolet absorption spectra of I–VIII (Table I) provide evidence for a moderately strong conjugative interaction between phosphorus of the phosphoryl group and carbon of the adjacent carbonyl group. The $n \rightarrow \pi^*$ band in analogous aliphatic aldehydes and the $^1A \rightarrow {}^1L_a$ band ($\pi \rightarrow \pi^*$) in the related *para*-substituted benzaldehydes were compared with the same bands in the respective compounds I–VIII.

There was recently reported convincing ultraviolet spectral evidence for $d\pi$–$p\pi$ bonding in tri-2-pyrryl-, 2-(1-methylpyrryl)-, 2-thienyl-, 2-furylphosphine oxides, phosphine oxides, and phosphonium salts which possess a number of *para* substituents on aromatic rings.[2] The remarkably low-range frequencies for infrared absorption (10–15 cm^{-1} less than that for the C=O in corresponding aldehydes) of the carbonyl group in acylphosphonates[3,4] suggests that the carbon–

[1] We gratefully acknowledge support of this work by the Public Health Service (Grant No. GM 10367-04).

[2] C. E. Griffin, R. P. Peller, K. R. Martin, and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).

[3] K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).

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TABLE I

ULTRAVIOLET SPECTROSCOPIC DATA FOR ALDEHYDES AND ACYLPHOSPHONATES[a]

RCHO		RC(O)P(O)(OR′)$_2$				
R	λ_{max}, mμ (log ϵ_{max})	Compound	R	R′	λ_{max}, mμ (log ϵ_{max})	Δλ
CH_3[b]	290.0 (1.23)	I	CH_3	C_2H_5	334 (1.72)	44
C_2H_5[c]	292.5 (1.32)[d]	II	C_2H_5	C_2H_5	340 (1.85)	47.5
i-C_3H_7[e]	290.0 (1.19)[f]	III	Cyclopentyl	C_2H_5	340 (1.79)	50
		IV	Cyclohexyl	C_2H_5	345 (1.73)	55
C_6H_5[g]	241.0 (4.15)	V	C_6H_5	C_2H_5	258 (4.05)	17
p-ClC_6H_4[g]	253.0 (4.28)[f]	VI	p-ClC_6H_4	C_2H_5	268 (4.10)	15
p-$CH_3C_6H_4$[g]	251.0 (4.18)	VII	p-(t-C_4H_9)C_6H_4	C_2H_5	271 (4.06)	20
p-$CH_3OC_6H_4$[h]	265.0 (4.27)[f]	VIII	p-$CH_3OC_6H_4$	CH_3	295 (4.01)	30

[a] All spectra were recorded in cyclohexane unless otherwise noted. [b] A. Kirrman and J. Cantacuzene, *Compt. Rend.*, **248,** 1968 (1959). [c] Shell Development Co., API Research Project No. 44, Vol. I, 1949, p 329. [d] Spectrum recorded in i-C_8H_{18}. [e] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3131 (1953). [f] Spectrum recorded in n-C_6H_{14}. [g] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **36,** 1362 (1958). [h] J. C. Dearden and W. F. Forbes, *ibid.*, **37,** 1305 (1959).

oxygen bond has a greater degree of single-bond character in the ground state. The virtually constant infrared stretching frequency of the P→O linkage and the approximately 24-cm^{-1} shift toward a lower frequency of the C=C linkage when vinylphosphonates are compared with allylphosphonates suggests a three-atom conjugate system.[5] The approximately 33-cm^{-1} shift toward a lower frequency of the C=O linkage when it is conjugated with a C=C linkage[5] demonstrates the greater conjugating ability of the carbonyl bond in comparison to the phosphoryl bond.

The $n \rightarrow \pi^*$ band in I–IV underwent an average bathochromic shift of 49 mμ. This result suggests overlap of the π^* orbital on carbon with an empty d orbital on phosphorus. In analogy, stabilization of the excited state of an $n \rightarrow \pi^*$ transition in axial α-halocyclohexanones is attributed to overlap of the π^* orbital on carbon with an empty s orbital of relatively low energy from the electronegative halogen.[6] The bathochromic shift of the $n \rightarrow \pi^*$ band in axial α-halocyclohexanones with respect to cyclohexanone is approximately equal to 25 mμ.[6] The bathochromic shift of the same band in acrolein with respect to propionaldehyde is approximately equal to 37.5 mμ.[7]

The $^1A \rightarrow {}^1L_a$ band in the yellow compounds V–VIII underwent a bathochromic shift of 17 to 30 mμ. Stabilization of the excited state in these $\pi \rightarrow \pi^*$ transitions is likely due to extended conjugation. Electronic excitation would produce an excited electron which probably is partially delocalized over the P→O group perhaps through vacant d orbitals on phosphorus. The corresponding aldehydes of VI–VIII possess $^1A \rightarrow {}^1L_b$ transitions in the 275–290-mμ region. The shoulders at 278 and 286 mμ in the spectrum of benzaldehyde very probably correspond to the $^1A \rightarrow {}^1L_b$ transition since they are in the same wavelength region as are the $^1A \rightarrow {}^1L_b$ transitions in the other three corresponding aldehydes. However, in the *para*-disubstituted compounds V–VIII the $^1A \rightarrow {}^1L_b$ transition is apparently hidden beneath the $^1A \rightarrow {}^1L_a$ transition. Each of the compounds V–VIII has one massive band with no discernible shoulders in the 250–300-mμ region. On the basis of the large extinction coefficients for each of these large bands the maximum of each band undoubtedly represents a $^1A \rightarrow {}^1L_a$ transition. Figure 1 has spectra of I, VII, and VIII.

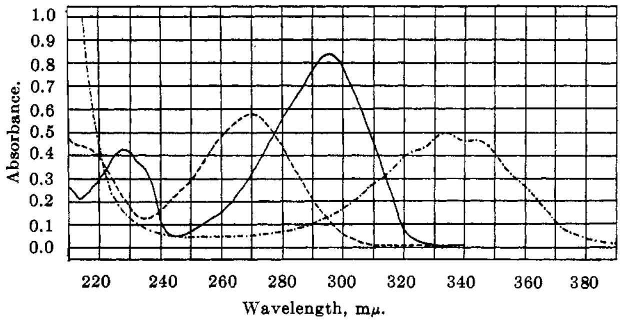

Figure 1.—Ultraviolet spectra of I (-·-·-·), 948 × 10^{-5} *M;* VII (- - - -), 5.11 × 10^{-5} *M;* and VIII (———), 8.10 × 10^{-5} *M;* all spectra recorded in cyclohexane at 25°.

Dipole moment measurements and nmr data do not confirm the existence of a preferred conformation for acylphosphonates.[8] In view of the ultraviolet data, the extent of pπ–dπ bonding in acylphosphonates is apparently far less sensitive to rotation around the bond axis than pπ–pπ bonding such as in acyclic α-diketones,[9] a close analogous system. The formation of pπ–dπ bonds in sulfones, for example, is not as dependent upon steric restraints (as with pπ–dπ bonding in many cases) because of the geometry and large number of the 3d orbitals.[5] In compounds of the type R_3PO it has been pointed out that some interaction of 3d orbitals with a π orbital of the chromophoric R group is possible whatever the orientation of the chromophore plane with respect to the rest of the molecule.[10] A preferred conformation due to pπ–dπ bonding in acylphosphonates may result in some cases, but it does not appear likely to be an imposition from dπ–pπ orbital overlap alone.

Experimental Section

All ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer using quartz cells and spectral grade cyclohexane as solvent. The acylphosphonates were obtained by methods developed in this laboratory.[3,8] Repeated distillation was used to purify all compounds needed. Tlc on a 0.25 mm thickness of silica gel with acetone–chloroform in the volume ratio of 1:9 showed only one spot after development

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(5) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962.

(6) E. L. Eliel, N. L. Allinger, S. K. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 151.

(7) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

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(9) N. J. Leonard and E. R. Blout, *J. Am. Chem. Soc.*, **72,** 484 (1950), and references therein.

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with iodine vapor for each of the compounds examined. The compounds listed in Table I gave the corresponding R_f values: I (0.39), II (0.36), III (0.42), IV (0.38), V (0.40), VI (0.38), VII (0.39), and VIII (0.34).

The Addition Reactions of Aldehydes, Alcohols, and Ethers to Perfluorocyclobutene

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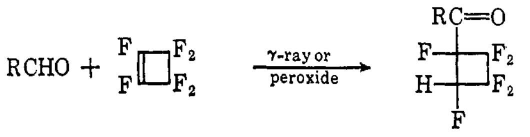
Earlier reports have described the radiation- or peroxide-induced addition reactions of aldehydes,[2] alcohols,[3,4] and ethers[5,6] to chlorofluoroethylenes, 1,2-dichlorotetrafluorocyclobutene, and 1,2-dichlorohexafluorocyclopentene to yield the corresponding 1:1 adducts and the dehydrochlorinated 1:1 adducts. In this paper, these addition reactions were extended further to perfluorocyclobutene to prepare the new ketones, alcohols, and ethers containing 2-hydroperfluorocyclobutyl group, which are the interesting intermediates in the syntheses of the derivatives of polyfluorocyclobutane and polyfluorocyclobutene.

The addition reactions were carried out under irradiation of γ-ray. The same products were obtained in the peroxide-induced addition reaction using *t*-butyl perbenzoate as a catalyst as in the irradiation-induced addition.

Addition Reactions of Aldehydes.—The general reaction is shown in eq 1. The irradiation conditions and yields[7] for each run are listed in Table I.

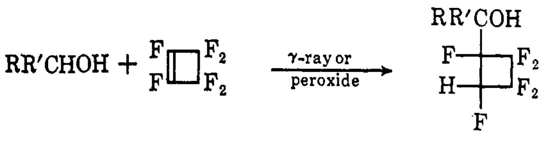


(1)

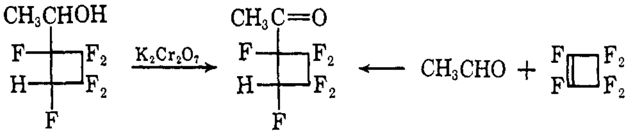
The gas chromatogram of the 1:1 adducts exhibited the presence of *cis* and *trans* form in the 2-hydroperfluorocyclobutyl group. The two stereoisomers were separated by using a preparative gas chromatograph. The physical properties of the 1:1 adducts, 2-hydroperfluorocyclobutyl alkyl ketones, and their 2,4-dinitrophenylhydrazones are shown in Table II.

The distinct difference of the physical properties is found between isomer A and B. While the isomer A has a lower boiling point by about 10° and a smaller retention time compared with isomer B, the melting point of the 2,4-dinitrophenylhydrazone of the isomer A is higher than that of the corresponding isomer B. The specific gravity and refractive index of the isomer A are smaller than those of the isomer B. The infrared spectra of the isomer A showed the C=O absorption band at 1731-1735 cm^{-1}, and those of isomer B at 1739-1742 cm^{-1}. In the proton nmr spectra, absorption bands of the proton in the cyclobutyl group of the isomer A showed a rather simple multiplet due to the coupling with fluorines (τ 4.34-4.38). On the other hand, the corresponding absorption bands of the isomer B exhibited the complicated multiplet (τ 4.61-4.64).

Addition Reactions of Alcohols.—The general reaction is shown in eq 2. The irradiation conditions and yields for each run are listed in Table III. The gas chromatograms of the 1:1 adducts obtained from ethanol and 1-propanol consisted of four peaks, showing the presence of two stereoisomers (*trans* and *cis*) and conformers (*trans* and *gauche*). Their assignment to the A and B isomers was done by comparison of the infrared spectra and retention times (gas chromatogram) of the oxidation products of each stereoisomer with those of the corresponding 1:1 adducts obtained in the addition of aldehydes (for example, eq 3). During the oxidation of each stereoisomer of methyl- or ethyl(2-hydroperfluorocyclobutyl)carbinol with potassium dichromate, no conversion occurred between isomers A and B, yielding only the corresponding pure stereoisomers of the ketone.

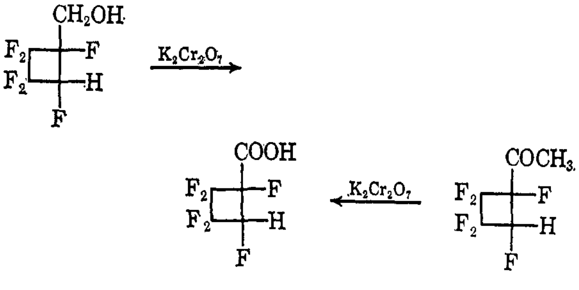


(2)



(3)

The assignment of stereoisomers of the 1:1 adduct of methanol was attempted as shown in eq 4. Though each isomer of the carbinol was converted to the corresponding carboxylic acid with potassium dichromate, oxidation of 2-hydroperfluorocyclobutyl methyl ketone was rather difficult, yielding only a small amount of the carboxylic acid which was found to be a mixture of both stereoisomers. An attempt to oxidize the 1:1 adduct of 2-propanol to get the carboxylic acid was also unsuccessful. Therefore the stereoisomers of 1:1 adducts from methanol and 2-propanol were assigned to isomers A and B from the proton nmr spectra of the acetate of the 1:1 adducts. The physical properties of 2-hydroperfluorocyclobutylalkylcarbinols are shown in Table IV.



(4)

Addition Reactions of Ethers.—While the addition of tetrahydrofuran gave only the 1:1 adduct, dioxane and diethyl ether produced both the 1:1 adduct and

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[1] On leave from the Central Research Laboratory of Showa Denko Co., Tokyo, Japan.

[2] H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962); *Kogyo Kagaku Zasshi*, **65**, 1992 (1962).

[3] H. Muramatsu, *J. Org. Chem.*, **27**, 2325 (1962).

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[5] H. Muramatsu, K. Inukai, and T. Ueda, *ibid*, **29**, 2220 (1964).

[6] H. Muramatsu and K. Inukai, *ibid.*, **30**, 544 (1965).

[7] Throughout this manuscript, the yields in the addition reactions were based on the amounts of perfluorocyclobutene.