the vicinal coupling constants for the cyclopropyl ring protons of *cis-* and *trans*-1-(benzenesulfonyl)-2-phenylcyclopropane have been previously reported,[3] but no detailed analysis of the four spin cyclopropyl ring system was presented. In the present work, the chemical shifts and coupling constants of the cyclopropyl ring protons of **6** were determined from 60 and 100 MHz nmr spectra by iterative calculations using the program LAOCN3 (Table I). The values of the coupling constants definitely establish the configuration of **6** as trans.

TABLE I

NMR ($CDCl_3$) ASSIGNMENTS FOR THE CYCLOPROPYL RING PROTONS OF 6

	Chemical shift, δ^a	Coupling constant, Hz
H_1	1.50	$J_{1,2} = -5.72$, $J_{1,3} = 8.35$, $J_{1,4} = 6.71$
H_2	1.89	$J_{2,3} = 5.40$, $J_{2,4} = 9.87$
H_3	2.77	$J_{3,4} = 4.44$
H_4	2.89	

[a] Recorded in parts per million downfield from tetramethylsilane.

Experimental Section[9]

2-((β-Chlorophenethyl)sulfonyl)thiophene (**4**).—In a 500-ml, three-neck flask equipped with a magnetic stirrer, a thermometer, a nitrogen inlet, and a reflux condenser fitted with a calcium chloride drying tube were placed 21.97 g (0.12 mol) of 2-thiophenesulfonyl chloride, 12.50 g (0.12 mol) of styrene, 0.16 g (1.2 mmol) of anhydrous cupric chloride, 0.25 g (1.8 mmol) of triethylamine hydrochloride, and 4.80 g of acetonitrile. The system was flushed with nitrogen, and the reaction mixture was heated at 95° for 2 hr. The reaction mixture was diluted with methanol (40 ml), and a crystalline solid formed immediately. The solid was filtered off, washed with water, and vacuum dried to give 32.40 g (93% yield) of crude sulfone as a slightly yellow solid, mp 90–92°. The crude sulfone was recrystallized from 180 ml of methanol to give 22.28 g of 2-((β-chlorophenethyl)sulfonyl)thiophene as small white needles, mp 92–93°. A 7.9-g second crop was also obtained.

Anal. Calcd for $C_{12}H_{11}ClO_2S_2$: C, 50.25; H, 3.87; Cl, 12.36; S, 22.36. Found: C, 50.31; H, 3.78; Cl, 12.40; S, 22.72.

2-(*trans*-β-Styrylsulfonyl)thiophene (**5**).—In a set-up as described above were placed 14.30 g (0.05 mol) of **4** and 300 ml of benzene. The system was swept with nitrogen. To the benzene solution, 7.50 g (0.075 mol) of triethylamine were added dropwise, with stirring. The reaction mixture was allowed to stir for 15 min and then filtered to remove the triethylamine hydrochloride which precipitated. The triethylamine hydrochloride was washed with several portions of benzene. The benzene was removed *in vacuo* from the combined filtrates, leaving a pale yellow solid. The solid was recrystallized from approximately 100 ml of absolute ethanol to give 10.09 g (81% yield) of 2-(*trans*-β-styrylsulfonyl)thiophene as small, slightly yellow needles, mp 97–99°.

Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 5.03; S, 25.60. Found: C, 57.97; H, 5.09; S, 25.65.

2-((*trans*-2-Phenylcyclopropyl)sulfonyl)thiophene (**6**).—In the usual set-up were placed 3.28 g (0.013 mol) of **5**, 4.00 g (0.019 mol) of trimethylsulfonium iodide, and 75 ml of dimethyl sulfoxide. The system was swept with nitrogen. To this solution, a solution of 2.20 g (0.019 mol) of potassium *tert*-butoxide in 25 ml of dimethyl sulfoxide was added dropwise, with stirring. After the addition was complete, the reaction mixture was allowed to stir for 0.5 hr, and then diluted to approximately 700 ml with water. A white solid separated which was filtered off, air dried, and recrystallized from 50 ml of 95% ethanol to give 2.89 g (84% yield) of 2-((*trans*-2-phenylcyclopropyl)sulfonyl)thiophene, mp 116–118°.

Anal. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58; S, 24.26. Found: C, 58.89; H, 4.70, S, 24.34.

Registry No.—**4**, 34566-07-9; **5**, 34566-08-0; **6**, 34566-09-1.

Acknowledgment.—The author wishes to thank Dr. Thomas E. Evans of the Dow Analytical Laboratory for obtaining and interpreting the nmr spectra.

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[9] All melting points are uncorrected. The nmr spectral data were recorded on a Varian HA-100 spectrometer with tetramethylsilane as an internal standard. The microanalyses were performed by the Dow Analytical Laboratory.

Intermolecular Exchange in Methylphosphonic Difluoride–Amine Complexes *via* a Fluorine Bridged Dimer

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A few fluorophosphoranes, *e.g.*, $(CH_3)_3PF_2$ and $(CH_3)_2PF_3$, have recently been shown to undergo a temperature and concentration dependent intermolecular exchange *via* a fluorine bridged dimer.[1,2] Earlier, a similar process had been postulated to explain the exchange in, *e.g.*, SF_4, ClF_3, and BrF_3.[3] The purpose of this note is to report evidence which appears to support not only the formation of a labile complex between methylphosphonic difluoride (I) and amines, but also intermolecular exchange of fluorines in the complex *via* an analogous process.

Results and Discussion

The normal proton spectrum of I in benzene shows a doublet of triplets ($J_{P-H} = 19.3$, $J_{F-H} = 6.1$ Hz). When triethylamine is added to I, the doublet of triplets collapses to a doublet and the J_{P-H} value remains unchanged at 19.3 Hz regardless of amine concentration. The interaction of I and several secondary and tertiary amines was studied by measuring the pmr peak width at half-height of the methyl resonance of the protons on I. The extent of the amine interaction with I was dependent upon amine basicity and, to some extent, on the size of the alkyl or aryl groups on the amine nitrogen (Figure 1). Decoupling the fluorine nuclei of I resulted in the collapse of the pmr spectrum to a doublet similar in peak width to that caused by the more basic amines used in the investigation. The ability of primary amines to collapse the pmr spectrum of I could not be studied, since amide formation was quite rapid under our experimental conditions.

The normal ^{19}F nmr spectrum of I in benzene at 25° shows a doublet, each peak of which is split into a quartet by the methyl protons ($J_{P-F} = 1102$, $J_{F-H} = 6.1$ Hz). Upon the addition of small quantities of triethylamine (100:1, mole ratio of I to amine), the splitting of

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(1) T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Amer. Chem. Soc.*, **92**, 5759 (1970).

(2) H. Dreeskamp and K. Hildenbrand, *Z. Naturforsch. B.*, **26**, 269 (1971).

(3) E. L. Muetterties snd W. D. Phillips, *J. Amer. Chem. Soc.*, **79**, 322 (1957); **81**, 1084 (1959).

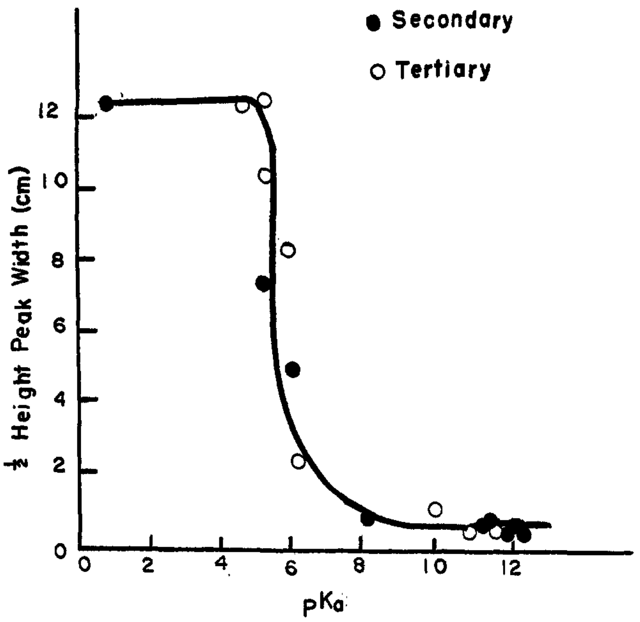


Figure 1.—The effect of amine basicity on the pmr spectral collapse in benzene solution of the methyl protons of methylphosphonic difluoride: methylphosphonic difluoride 2.2×10^{-3} mol, all amines 5.5×10^{-4} mol, 0.5 ml of benzene.

the doublet by the methyl protons was no longer apparent and the doublet had a smaller J_{P-F} value. Further additions of triethylamine caused the J_{P-F} value to decrease until a 1:1 molar ratio of I to triethylamine was reached; the spectrum then showed a single resonance.

The ^{31}P nmr spectrum of I shows a triplet, each peak of which is split into a quartet. On the addition of small quantities of triethylamine (100:1, mole ratio of I to amine), only a very broad signal could be observed. Cooling this same sample to −20° caused the slight reappearance of the triplet. An attempt was made to observe this temperature dependence in the pmr spectrum.

Raising the temperature of a 50:1 molar ratio of I and triethylamine from 33 to 100° caused no change in the J_{P-H} value; no line broadening was observed. Since the proton and ^{19}F spectra of I were only partially collapsed by the interaction of I with 4-phenylpyridine, the effect of temperature on the interaction of I and this amine was investigated. Raising the temperature from 10 to 73° of a benzene solution containing 0.006 mol of I and 0.001 mol of 4-phenylpyridine resulted in an increased collapse of the methyl resonance. However, the doublet of triplets was still in evidence, and the J_{P-H} value remained constant at 19.3 Hz. A similar temperature change had no effect on the proton spectrum of I in the absence of amine.

The spectral changes observed are consistent with an exchange phenomenon which is dependent upon amine basicity and also suggest a slight temperature dependence for the interaction. The loss of P–F coupling in the amine complex while the P–H coupling remains intact suggests that P–F bonds are broken in the exchange process. A similar loss of P–F coupling with retention of the P–H coupling has also been observed in the exchange of fluorines in $(CH_3)_3PF_2$.[1]

To test the possibility that the exchange in the amine complex was a heterolytic P–F bond cleavage, we attempted to trap exchanging fluoride anions. The ^{19}F nmr spectrum of I (0.004 mol) and triethylamine (0.004 mol) in benzene (0.5 ml) was taken to ensure that collapse had occurred. Triethylammonium tosylate (0.001 mol) was added and the ^{19}F spectrum was observed for 24 hr to ascertain if triethylammonium fluoride (II) was being produced by reaction 1. No evidence for the formation of II was observed. Furthermore, no evidence for the formation of IV (eq 2) was

$$\underset{\text{I}}{CH_3POF_2} + Et_3NH^+OTs^- \xrightleftharpoons{Et_3N:} \underset{\text{II}}{Et_3NH^+F^-} + CH_3POFOTs \qquad (1)$$

$$\underset{\text{I}}{CH_3POF_2} + \underset{\text{III}}{CH_3POCl_2} \xrightleftharpoons{Et_3N:} \underset{\text{IV}}{2CH_3POFCl} \qquad (2)$$

obtained when an equimolar mixture of I and III was allowed to react in the presence of triethylamine, even when the concentration of the amine was four times that of I.[4]

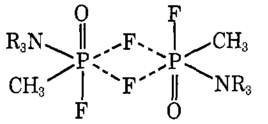
An attempt was also made to observe amide formation from I, and 12 different secondary amines under conditions where collapse of the methyl resonance in the pmr spectrum was observed. There was no evidence of amide formation.

Several reports have indicated that dissociation into ions does not take place when some phosphorus V fluorides are complexed with amines.[5,6] In our studies, if heterolytic P–F bond cleavage were responsible for the observed spectral changes, then one would expect to see some evidence for it through amide formation or the formation of II. In addition to these data, we have observed that fluoride ion will displace chloride ion from III when NaF is added to a solution of III in DMF. Consequently, if heterolytic P–F bond cleavage were taking place, one would also expect to see some evidence for it in the formation of IV. Furthermore, no collapse of the pmr spectrum is observed when methylphosphonothioic difluoride (V) is mixed with amines under our experimental conditions. However, upon addition of excess I to the above, collapse of both I and V can be observed in the pmr spectrum (eq 3 and 4). These

$$\underset{\text{V}}{CH_3PSF_2} + \text{Amine} \longrightarrow \text{No apparent effect} \qquad (3)$$

$$\underset{\text{V}}{CH_3PSF_2} + \underset{\text{I}}{CH_3POF_2} + \text{Amine} \longrightarrow \text{Collapse of both difluorides} \qquad (4)$$

data, in conjunction with the loss of P–F coupling while the P–H coupling remains intact, suggest that the transition state for the exchange in the amine complex with I is similar to the bridged species VI shown below.



VI

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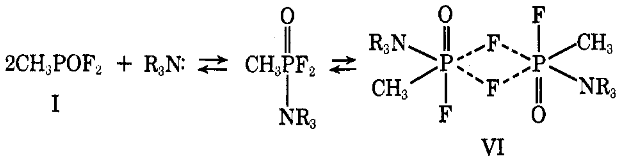
[4] An equimolar mixture of pure methylphosphonic difluoride and methylphosphonic dichloride was observed for 7 days at room temperature. No evidence for halide exchange was observed. B. M. Zeffert, P. B. Coulter, and H. Tannenbaum, *ibid.*, **82**, 3843 (1960).

[5] F. N. Teble and E. L. Muetterties, *Inorg. Chem.*, **6**, 129 (1967).

[6] L. Lunazzi and S. Brownstein, *J. Magn. Resonance*, **1**, 119 (1969).

The lack of formation of IV in eq 2 and the stability of IV to reaction conditions may simply indicate that the mixed bridge is relatively unstable.[7] Some additional support for this view comes from the inability of chloride ion to readily displace fluoride ion from I in the presence of amine under our reaction conditions.

Our data support a labile complex between I and amines and also an exchange phenomenon; however, it does not appear that the complex is undergoing an intramolecular exchange. The results of our work seem to be best explained by rapid intermolecular exchange of fluorine *via* the fluorine bridged dimer shown in eq 5.



(5)

Experimental Section

Materials.—Methylphosphonic dichloride[8] and methylphosphonic difluoride[9] were prepared, distilled, and stored under dry nitrogen. The methylphosphonothioic difluoride was obtained from Ash-Stevens, Inc., under Contract No. DAAA15-69-C-0584. All amines were obtained from commercial sources and dried over CaO before use. Thiophene-free benzene from Mallinckrodt Chemical Works was distilled and dried over molecular seives.

Triethylammonium tosylate was prepared by adding triethylamine (0.1 mol) to toluenesulfonic acid (0.1 mol) dissolved in 50 ml of benzene. The solution was dried over anhydrous $MgSO_4$ and decanted into a dry flask, and the solvent was removed. The nmr spectrum of the solid which remained indicated that it was the desired tosylate. The compound was used without further purification.

Instruments.—The proton nmr spectra were recorded at 60 MHz using a Varian A-60D nmr spectrometer. The ^{19}F and ^{31}P studies were carried out at 94.1 and 40.5 MHz, respectively, using a Varian HA-100 nmr spectrometer. These spectra were obtained in the unlocked (HR) mode using the V-3507 unit to sweep the field.

Registry No.—I, 22382-13-4.

[7] Methylphosphonic chlorofluoride (IV) is stable to our reaction conditions.

[8] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

[9] T. P. Dawson and K. C. Kennard, *J. Org. Chem.*, **22**, 1671 (1957).

Radiation-Induced and Electrochemical Formation of 3-Substituted 4,4-Dimethyl-γ-butyrolactone from α,β-Unsaturated Ester

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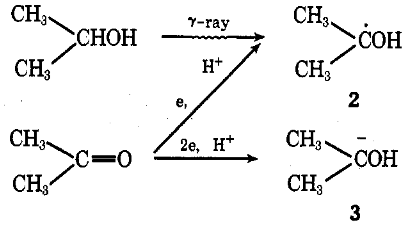
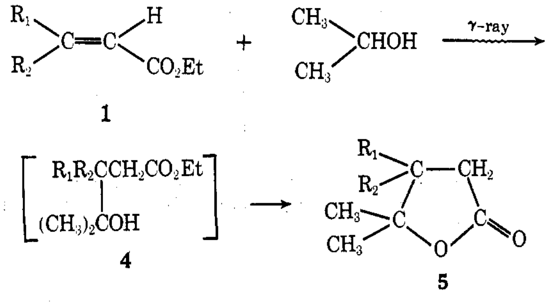
It has been previously reported[1] that radiation and ultraviolet-induced addition reactions of various alcohols to ethyl crotonate gave the corresponding 3-methyl-4-alkyl-substituted γ-butyrolactones. In the present paper, the radiation-induced addition reactions of 2-propanol and electrochemical reductive addition reactions of acetone to α,β-unsaturated esters are reported.

Since it is known that radiolysis of 2-propanol produces α-hydroxy radical **2**,[2-4] and electroreduction of acetone in a protic solvent gives radical **2** or anion **3**,[5-8] both addition reactions are expected to give the



identical products. In the present work, it was found that substituted γ-butyrolactones were obtained in fairly good yields by using such simple procedures.

Irradiation of α,β-unsaturated ester **1a-e** in a tenfold excess of 2-propanol with ^{60}Co γ-rays gave the corresponding 3-substituted 4,4-dimethyl-γ-butyrolactone **5a-e**.



a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = R_2 = CH_3$
d, $R_1 = H$; $R_2 = CO_2Et$
e, $R_1 = CO_2Et$; $R_2 = H$
f, $R_1 = C_6H_5$; $R_2 = H$

The yield of lactones, conversion of α,β-unsaturated esters, and *G* values of lactone formation and ester consumption are listed in Table I. *G* values were calculated from the low-conversion linear part of the curve which was obtained from the plot of the yield of lactone and the conversion of ester against the irradiation time.

Ethyl acrylate (**1a**) produced no lactone, probably because it easily polymerized by radical initiation. This is indicated by its high value of $G(-\mathbf{1a})$.

Reactivity of the α,β-unsaturated ester toward the intermediate radical **6** seems to control the yield of lactone. A reactive ester such as **1a** proceeds predominantly in eq 2 to give a polymer, but in a less reactive ester an intermediate radical **6** may preferentially

[1] M. Tokuda, Y. Yokoyama, T. Taguchi, A. Suzuki, and M. Itoh, *J. Org. Chem.*, in press.

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