tion chromatography. The first fraction (orange needles) was azobenzene, the second (yellow crystals) was azoxybenzene, and the third (white crystals) was diphenylamine. Identification of the products was made on the basis of their mp and comparison of their ir and nmr spectra with those of the authentic samples.

The procedures for other runs were essentially similar to that described above. When the two reactants were mixed at 35°, nitrogen evolved instantaneouly. Benzene was always one of the products formed, but its amount was not always determined.

Esr Measurement of Diphenylnitroxide Radical. A benzene solution (1.1 g) of nitrosobenzene (0.02 g) was cooled to 0° in an esr tube, and before it solidified a benzene solution (0.45 g) of phenylhydrazine (0.03 g) was added. Its esr spectrum was determined at 0° with a JES-PE esr spectrometer. The signals of diphenylnitroxide radical were observed,[10] and did not change as long as the mixture was kept as solid at 0°. When it was warmed up and melted, the signals of the radical disappeared ($g = 2.0057$, $a^N = 10.0$ G). When a benzene solution of nitrosobenzene or that of phenylhydrazine was subjected to esr measurements, no esr signals were observed. Only when the two solutions were mixed, were esr signals of diphenylnitroxide radicals observed.

Reaction between Diphenylnitroxide and Phenylhydrazine. A methanol solution (25 ml) of diphenylnitroxide (0.4 g, 2.3 mmol) was cooled to −5°, and then a methanol solution (3 ml) of phenylhydrazine (0.1 g, 0.92 mmol) was added to the cooled solution. The dark red solution became yellow with evolution of some nitrogen. After the mixture was warmed to and allowed to stand at room temperature for 1 hr, the solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography (alumina). The first fraction eluted with hexane–benzene (3:2) was rechromatographed with hexane, and the first fraction eluted was identified as diphenylamine by comparison of its ir spectrum with that of an authentic sample; yield, 0.046 g (0.12 mol/mol of Ph_2NO used).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—Phenylhydrazine, 100-63-0; nitrosobenzene, 586-96-9; *p*-nitrosotoluene, 623-11-0; *p*-dimethylaminonitrosobenzene, 138-89-6; diphenylnitroxide, 712-51-6.

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Intramolecular Migration of the Pentafluorophenyl Group under Acidic Conditions

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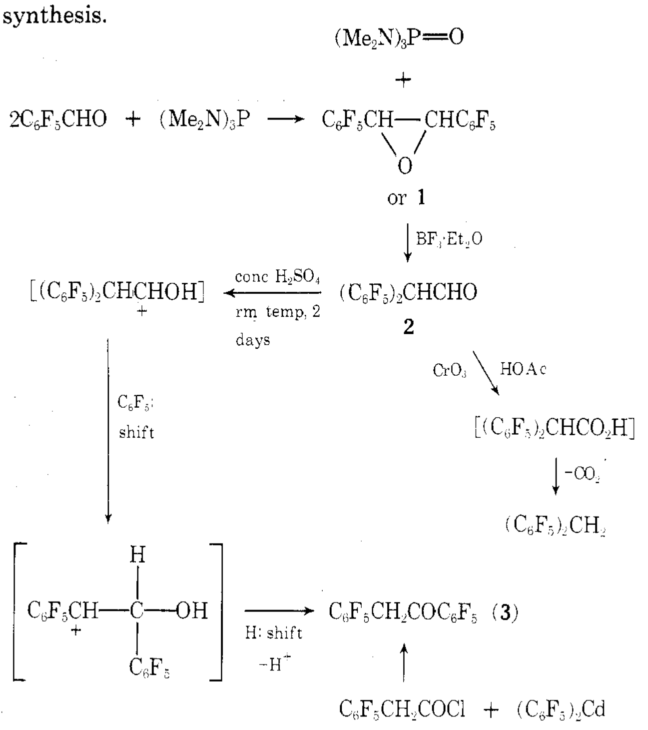
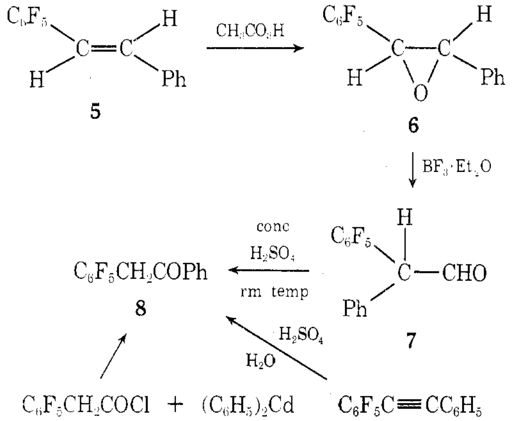
Acid-catalyzed skeletal rearrangements involving the 1,2 shift of aryl groups are well known. Phenyl groups containing electron-attracting substituents generally migrate much more slowly than phenyl, if at all. One might anticipate that the moderately electron-withdrawing pentafluorophenyl group[2a] would cause considerable deactivation in such reactions. To our knowledge, acid-catalyzed rearrangements involving intramolecular 1,2 migration of the C_6F_5 group have not been reported. We describe here a series of interrelated reactions in which we observed such aryl participation.

Pentafluorobenzaldehyde reacted rapidly with tris(dimethylamino)phosphine (hexamethylphosphorus triamide) to give a mixture of diastereomeric stilbene oxides.[2b] This mixture or the pure *trans*-stilbene oxide (**1**), obtained by peroxidation of the olefin,[3] reacted with boron trifluoride etherate to form the isomeric decafluorodiphenylacetaldehyde (**2**) by migration of the C_6F_5 moiety. Compound **2** was oxidized by Jones reagent to the diphenylacetic acid which rapidly lost CO_2 to form decafluorodiphenylmethane. When treated with concentrated H_2SO_4, **2** slowly underwent a reverse, 1,2-pentafluorophenyl shift *via* the unstable cation **4**,[4] to give the isomeric ketone (**3**), whose structure was confirmed by independent synthesis.



In order to compare the relative migratory aptitudes of the phenyl and pentafluorophenyl groups, the unsymmetrical stilbene **5**, prepared by Wittig syntheses ($C_6F_5CH_2Br$ and PhCHO or $PhCH_2Br$ and C_6F_5CHO), was converted to the epoxide **6**, which was isomerized to the diphenylacetaldehyde **7**. Compound **7** was characterized by its infrared spectrum and 2,4-dinitrophenylhydrazone. The latter reaction provides no information on which aryl group migrated. However, on standing with concentrated H_2SO_4 at room temperature, **7** was readily transformed into the ketone **8** in a 95% conversion with no evidence of the presence of its isomer, $PhCH_2COC_6F_5$. Also, compound **8** readily formed a 2,4-dinitrophenylhydrazone, showed carbonyl absorption around 1700 cm^{-1}, and was in all respects identical with an authentic sample (*cf.* isomer, Experimental Section). This observation demonstrated the strong preference of C_6H_5 over C_6F_5 migration in such 1,2 shifts. Ketone **8** was also prepared by two alternate routes, one of which has been reported previously.[5] These results are in marked contrast to the overwhelming migratory preference of C_6F_5 over C_6H_5 in 1,2 shifts in alkaline medium.[6] In the latter case, the pentafluorophenyl ring stabilizes the developing negative charge in the transition state.



Experimental Section

Decafluorostilbene Oxides.[7] To a stirred solution of pentafluorobenzaldehyde (19.6 g, 0.1 mol) in 20 ml of dry benzene was added dropwise 9.5 g (0.0583 mol) of hexamethylphosphorus triamide[8] dissolved in 5 ml of anhydrous ether. The temperature was regulated below 36° during addition. After 45 min, addition was complete and the reaction mixture was heated at 50° for 1 hr and cooled. The solvents were removed by flash evaporation, water and ether were added to the residue, and the ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Ether was removed by flash evaporation and the residual oil was triturated with ethanol. Thin layer chromatography showed the presence of two components. The mixture of oxides was crystallized from ethanol: mp 164–176°; calcd mass spectrum 376, found 376.

Decafluorodiphenylacetaldehyde[9] **(2).** To a solution of 8.5 g of decafluorostilbene oxides in 60 ml of benzene and 20 ml of anhydrous ether was added 2 ml of freshly distilled boron trifluoride etherate. The mixture was shaken and left at room temperature for 1 min. Water (100 ml) was added and the mixture shaken. The two layers were separated and the aqueous layer was extracted with benzene. The combined organic layers were dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated and triturated with ethanol to remove any unreacted epoxide. The alcoholic solution was evaporated to give a semisolid material, which could not be distilled or crystallized: ir (CCl_4) 1710 cm^{-1} (s). Further purification was effected by adsorption over neutral alumina and elution with anhydrous ether. A mass spectrum of this sample revealed a peak at 376; 2,4-dinitrophenylhydrazone melted at 227°.

Attempted Oxidation of 2. To 5 g of impure aldehyde **2**, dissolved in acetone, was added slowly a solution of Jones reagent (13.4 g of CrO_3, 11.5 ml of concentrated H_2SO_4, and 33.5 ml of water). After addition was complete, excess reagent was destroyed by adding isopropyl alcohol. The reaction mixture was poured into water and the aqueous solution extracted with three 100-ml portions of ether. The combined ether layers were washed with water and then with a 10% solution of potassium carbonate. Acidification of the aqueous layer failed to give a solid. The ether layer, after drying over $MgSO_4$, gave, on concentration, a solid which melted at 61°, identical with an authentic sample of decafluorodiphenylmethane: mp[10] 62°.

Reaction of 2 with Concentrated H_2SO_4. A sample of **2** (7.52 g, 0.02 mol) was mixed with 10 ml of concentrated H_2SO_4 and the mixture set aside for 2 days at room temperature. The mixture was then poured into water and extracted with ether, and the ether layer was washed with a dilute solution of sodium bicarbonate and dried over anhydrous $MgSO_4$. Ether was removed by flash evaporation and the residual oil distilled (72°, 2 Torr; 7.2 g, 96% yield). The ir spectrum was identical with that of an authentic sample of decafluorodesoxybenzoin (**3**).[11]

Decafluoro-*trans*-stilbene.[12] In a 100-ml round-bottomed flask were placed triethyl phosphite (8.3 g, 0.05 mol) and pentafluorobenzyl bromide (13 g, 0.05 mol). A condenser was attached and the mixture was heated gently for 1 hr. At 130–140°, ethyl bromide was evolved. The internal temperature reached 210° at the end of 1 hr. The product was cooled and dissolved in 100 ml of dry 1,2-dimethoxyethane. Pentafluorobenzaldehyde (9.8 g, 0.05 mol) and 50% sodium hydride (2.4 g, 0.05 mol) were added to the phosphonate solution and the mixture was heated slowly to 85°. After heating for 0.5 hr, the mixture was cooled and dissolved in a large excess of water. The precipitated stilbene was filtered, dried, and purified by sublimation: mp 101° (lit.[3,13,14] mp 96.5–97.5°, 101.5–103.5°, 101°); yield 11.3 g (63%).

Pentafluoro-*trans*-stilbene (5). (a) From Pentafluorobenzyl Bromide and Benzaldehyde. The procedure was the same as that described for decafluoro-*trans*-stilbene: mp 137° (lit.[15] 139–140°); yield 60%.

b. From Benzyl Chloride and Pentafluorobenzaldehyde. The procedure was the same as above: mp 139°, mixture melting point not depressed.

Epoxidation of Stilbenes. (a) Decafluoro-*trans*-stilbene Oxide (1). The procedure of House and Rief[9b] was employed. Decafluoro-*trans*-stilbene (10.8 g, 0.03 mol) in 45 ml of methylene chloride was epoxidized with 6.5 ml of 40% peracetic acid to give 11 g (96%) of **1**: mp 166°. *Anal.* Calcd for $C_{14}H_2OF_{10}$: C, 44.41; H, 0.53. Found: C, 44.5; H, 0.57.

(b) Pentafluoro-*trans*-stilbene Oxide (6). The procedure was the same as described above: mp 112°; yield 75%. *Anal.* Calcd for $C_{14}H_7OF_5$: C, 58.74; H, 2.44. Found: C, 58.69; H, 2.40.

Pentafluorodiphenylacetaldehyde (7). The same procedure as for the isomerization of decafluorostilbene oxide to compound **2** was used: bp 97° (2 Torr); calcd mass spectrum 286, found 286; ir $\nu_{C=O}$ 1715 cm^{-1}; 2,4-dinitrophenylhydrazone melted at 185°.

Reaction of 7 with Concentrated H_2SO_4. A sample of **7** (5.72 g, 0.02 mol) was mixed with 10 ml of concentrated H_2SO_4 and set aside at room temperature for 2 days. After work-up (as described earlier for **2**), a solid, mp 117°, was isolated (yield 5.4 g, 95%). The melting point was not depressed when mixed with compound **8**, but was depressed when mixed with benzyl pentafluorophenyl ketone. Compound **8** gave a 2,4-dinitrophenylhydrazone which melted at 174°.

Preparation of Desoxybenzoins. The procedure was the same as that used for pentafluoroacetophenone.[16]

(a) Decafluorodesoxybenzoin (3). Compound **3** was prepared from pentafluorophenylacetyl chloride and bis(pentafluorophenyl)cadmium: bp 71–74° (2–3 Torr), ir $\nu_{C=O}$ 1740 cm^{-1} (s). *Anal.* Calcd for $C_{14}H_2OF_{10}$: C, 44.41; H, 0.53. Found: C, 44.48; H, 0.52. This compound failed to form a 2,4-dinitrophenylhydrazone.

(b) Pentafluorobenzyl Phenyl Ketone (8). Compound **8** was prepared from pentafluorophenylacetyl chloride and diphenylcadmium: mp 118° (lit.[11] mp 118–120°); ir $\nu_{C=O}$ 1700 cm^{-1} (s); nmr 7.8 ppm (5 H), phenyl protons, and a triplet at 4.36 ppm (methylene protons split by ortho fluorines). *Anal.* Calcd for $C_{14}H_7OF_5$: C, 58.74; H, 2.44. Found: C, 58.6; H, 2.39. 2,4-Dinitrophenylhydrazone mp 174°.

(c) Benzyl Pentafluorophenyl Ketone. This compound was prepared from phenylacetyl chloride and bis(pentafluorophenyl)cadmium: mp 54° (lit.[17] mp 52–56°); ir $\nu_{C=O}$ 1713 cm^{-1}; nmr 7.16 ppm (5 H), phenyl protons, and a singlet at 4.05, methylene protons. This compound failed to form a 2,4-dinitrophenylhydrazone.

Registry No.—**1**, 52438-84-3; *cis*-**1**, 52393-42-7; **2**, 52438-80-9; **2** 2,4-DNPH, 52393-43-8; **3**, 24043-89-8; **5**, 19292-25-2; **6**, 52393-44-9; **7**, 52393-45-0; **7** 2,4-DNPH, 52393-46-1; **8**, 34073-32-0; **8** 2,4-DNPH, 52555-18-7; pentafluorobenzaldehyde, 653-37-2; decafluoro-*trans*-stilbene, 14992-40-6; pentafluorobenzyl bromide, 1765-40-8; benzaldehyde, 100-52-7; benzyl chloride, 100-44-7; pentafluorophenylacetyl chloride, 832-72-4; bis(pentafluorophenyl)cadmium, 15989-98-7; diphenylcadmium, 2674-04-6; benzyl pentafluorophenyl ketone, 52393-47-2; phenylacetyl chloride, 103-80-0.

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Cleavage by Acid of the Phosphorus–Carbon Bond in Cyclic Phosphines Containing a β-Carbonyl Group[1]

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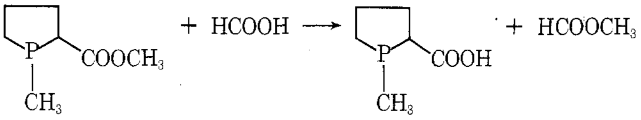
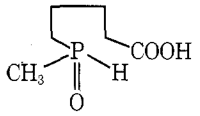
The C–P bond of simple phosphines is known to withstand the conditions of the common organic reactions. However, we have found that the bond is rendered sensitive to cleavage by an acidic medium when a β-carbonyl group is present. This reaction was encountered in an attempt to effect the conversion of methyl 1-methyl-2-phospholanecarboxylate[2] (**1**) to the acid (**2**) by HCl-catalyzed transesterification with formic acid[3] (91%). The crystalline solid that was obtained in 71% yield had properties quite unlike those expected for **2**. Through a combination of spectral techniques, it was established to have the ring-opened structure **3**.



1 **2**

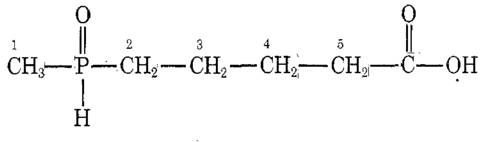


3

The product, which by analysis differed from the expected structure **2** by the elements of H_2O, had infrared spectral bands for a strongly hydrogen-bonded carboxylic acid group, showing that the expected transesterification had occurred. However, there were also P–H (2375 cm^{-1}) and P=O (1100 cm^{-1}) stretching bands, and this suggested the presence of phosphorus in the secondary phosphine oxide function. The P–H bond was also apparent in the ^{1}H nmr spectrum; a peak appeared at 9.98 ppm in H_2O that was removed on running the sample in D_2O. This proton had been coupled with the P-CH$_3$ group, for this latter signal, which in H_2O was a doublet of doublets (J_{PCH} = 14, J_{HPCH} = 2 Hz), lost the smaller coupling after D exchange. The peak at 9.98 ppm is half of the P–H signal; the other half is obscured by the H_2O signal. However, in $CDCl_3$ both halves were visible, with δ 7.62 and J_{PH} = 476 Hz. The shift and coupling constant are in line with those known for other secondary phosphine oxides (*e.g.*, for Me$_2$PHO,[4] δ 7.5, J_{PH} = 490; for Et$_2$PHO,[4] δ 7.2, J_{PH} = 468; for 3,4-dimethyl-3-phospholene oxide (**4**), which was available from previous work,[5] δ 7.97, J_{PH} = 490 Hz).

The proton-decoupled ^{31}P nmr signal (δ −31.8 in $CHCl_3$, −38.2 in H_2O) was also in the region expected for secondary phosphine oxides (*e.g.*, for Et$_2$PHO,[4] δ −41.0 and −47.7; for the phospholene oxide **4**, δ −39.8 and −44.4). Replacement of the proton with deuterium introduces a valuable structure diagnostic effect; the phosphorus singlet is split to a 1:1:1 triplet with a characteristic coupling (for **3**, *J* = 73 Hz; other secondary phosphine oxides gave similar values [4]).

The ^{13}C nmr spectrum also proved the secondary phosphine oxide structure. Carbons attached to phosphoryl groups have large (60–100 Hz) coupling constants,[6] and are readily recognized. For **3**, there would be two such signals of roughly equal intensity and these were observed at δ 13.0 with J_{PC} = 64 Hz (C-1) and δ 29.0 with J_{PC} = 65 Hz (C-2). The complete assignment is shown below.

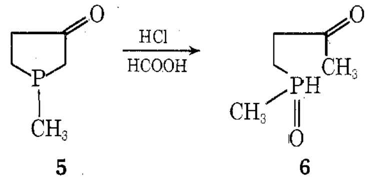


$$\overset{1}{CH_3}-\underset{H}{\overset{O}{\overset{\|}{P}}}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{O}{\overset{\|}{C}}-OH$$

δ:	13.0	29.0	21.2	26.1	34.3	179.0
J_{PC}:	64	65	<2	10	s	s

C-5 is easily recognized since it should be quite similar in position to the α-carbon of pentanoic acid (δ 34.5).[7] The assignment of C-3 and C-4 rests first on a coupling effect with ^{31}P; it is known that in aliphatic tertiary phosphine sulfides and oxides, $^3J_{PC}$ exceeds $^2J_{PC}$,[8] and since this should prevail also in secondary oxides, C-4 is the signal with J_{PC} = 10 Hz. Chemical shift relations support this assignment. Thus, C-4 should have a shift much like that of the β-carbon of pentanoic acid, since phosphorus groups are known to exert only a slight effect on a carbon in this position.[8] The C-4 shift of 26.1 ppm corresponds well to that of the β carbon of pentanoic acid (δ 25.2).[7] C-3 is upfield of C-4 because it undergoes γ-shielding effects[8] with both CH$_3$ and O on phosphorus.

The generality of the cleavage process was tested with another β-carbonyl phosphine, compound **5**, which was available from previous work.[9] The HCl–formic acid treatment should produce structure **6**, and the product obtained had spectral properties (see Experimental Section) that confirmed this expectation. The product was a noncrystallizing oil, and complete characterization was not possible. There is no doubt, however, that the ring cleavage occurred, and that secondary phosphine oxide **6** was formed.



5 **6**

The mechanism of the cleavage of these β-carbonylphosphines presumably involves attack of water on the proton-