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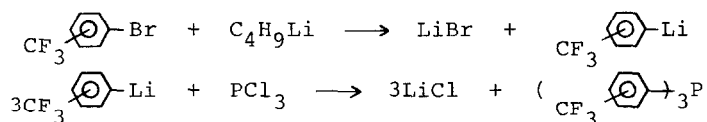
SHORT COMMUNICATION

THE SYNTHESIS OF TRIS-(TRIFLUOROMETHYLPHENYL) PHOSPHINES AND
PHOSPHINE OXIDES

KALATHIL C. EAPEN* and CHRIST TAMBORSKI

Air Force Materials Laboratory, Wright Patterson Air Force Base,
Ohio (45433) U.S.A.

This paper describes the synthesis of three isomeric tris-(trifluoromethylphenyl)phosphines $(2,3,4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ (I, II, III) and their oxides, $(2,3,4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{PO}$ (IV, V, VI). The phosphines were prepared through the reaction of the appropriate 2,3, or 4-trifluoromethylphenyllithium and PCl_3 .



During the course of isolating $(4\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ (III) from the reaction mixture, it was noted that the product was air sensitive and was slowly converting to the phosphine oxide VI. If a nitrogen atmosphere was used, only the desired phosphine III could be isolated. This oxygen sensitivity was unexpected in view of the ease of synthesis and stability of the hydrocarbon analog $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ (VII) as well as the perfluorinated aromatic phosphine $(\text{C}_6\text{F}_5)_3\text{P}$ [1]. The other two isomers $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ (I) and $(3\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ (II) did not show any significant air sensitivity during the period of isolation from their reaction mixtures.

*National Research Council Senior Postdoctoral Associate 1976-1978. Present address: University of Dayton Research Institute, 300 College Park, Dayton, Ohio U.S.A.

A qualitative evaluation of the oxidative stabilities of the three phosphines I, II and III was determined by exposing each of the pure phosphines to atmospheric air and analyzing by gas chromatography for the formation of the oxide as a function of time. The $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ when left exposed to air at ambient temperature for 4 months showed 8% of the phosphine I converted to the oxide IV. The phosphine II, under the same conditions was converted in 71% to the oxide V while the phosphine III was totally converted to the oxide VI in only one month. In contrast, the $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P(VII)}$ under the same conditions showed no oxidation to the phosphine oxide. These observations towards atmospheric oxidation demonstrate that the introduction of a CF_3 - group into the phenyl ring, e.g., the phosphines I, II and III reduce their oxidative stability and suggest that these phosphines are more basic than their non-fluorinated analogs. A convincing explanation for this observation is not readily apparent in view of the reported [2] net electron withdrawing effect of the CF_3 and must await detailed quantitative investigation. The above observation however is noteworthy for those investigators concerned with studies regarding the electronic effects of a CF_3 substitution. From our investigation the following order of oxidative stability of the phosphines was determined as $\text{I} > \text{II} > \text{III}$.

The required oxides IV and V were prepared by oxidation of the phosphine with m-chloroperbenzoic acid. The oxide VI was prepared as described above by air oxidation of the phosphine. The infrared spectra of the phosphine and phosphine oxide show an absorption at $1400\text{-}1442\text{ cm}^{-1}$ which has been attributed [3,4] to the $\text{P-C}_6\text{H}_5$ absorption band. The phosphine oxides have an absorption at about 1200 cm^{-1} which may be due to the P=O stretching vibration [4,5,6]. This assignment however is not certain in our compounds due to the strong C-F absorptions in the same region. The mass spectra of all the phosphines I, II and III and phosphine oxides IV, V and VI (by chemical ionization) show the molecular ions at 466 and 482 respectively. The $(\text{M-F})^+$ at 477 and 463 as well as the $(\text{M-C}_6\text{H}_4\text{CF}_3)^+$ at 321 and 337 for the phosphines and phosphine oxides respectively are the prominent fragments observed.

EXPERIMENTAL

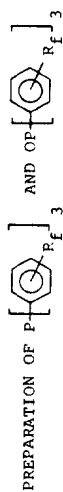
General Comments

All new compounds prepared were characterized by NMR (^{19}F and ^1H), IR, MS (chemical ionization) and elemental analysis. All melting points are uncorrected. Gas chromatography analysis was performed on a Hewlett-Packard Model 700 instrument using 6 ft. or 12 ft. stainless steel column (1/4 in. diam.) packed with 10% SE30 on Chromosorb W.

General Method for the Synthesis of tris-(trifluoromethylphenyl) phosphines

In a dry four-necked 500 ml reaction flask fitted with two addition funnels, a sealed stirrer and a thermometer was placed the appropriate bromobenzotrifluoride (0.08 mole) in anhydrous diethyl ether (100 ml). n-Butyllithium (0.075 mole) was placed in one addition funnel while in the other funnel freshly distilled PCl_3 (0.025 mole) dissolved in anhydrous diethyl ether (25 ml) was placed. Dry nitrogen was passed through the flask which was cooled to $\sim 0\text{--}5^\circ$ with an ice bath. The $\text{C}_6\text{H}_5\text{Li}$ was added dropwise during 20 min. while keeping the reaction temperature between $0\text{--}5^\circ$. A mild exotherm was noted and the contents become colored from red to reddish brown. The contents were stirred for an additional 30 min. Hydrolysis of an aliquot sample and G.C. analysis indicated complete conversion to the organolithium reagent. The PCl_3 -diethyl ether solution was slowly added during 1 h. An exothermal reaction was observed. The reaction temperature was maintained at $\sim 5^\circ$ by controlling the rate of addition. The reaction mixture became turbid, deposited solids and the color changed to a yellow and finally orange. After addition of the PCl_3 solution, the contents were stirred for an additional 3 h. and finally hydrolyzed with 6NHCl (100 ml). The diethyl ether layer was phase separated, dried over a molecular sieve and the solvent evaporated under vacuum to yield the crude phosphine product. Purification of the phosphine was done by recrystallization or column chromatography. See Table I.

TABLE I



R _f	YIELD (%)	METHOD OF PURIFICATION	M. P. (°C)	ELEMENTAL ANALYSIS		IR ABSORPTIONS (cm ⁻¹)		NMR- ¹ H & ¹⁹ F CHEM. SHIFT	
				[FOUND] C, H, P	[EXPECTED]	P-Ph	⁴ P=O	Ph-H δ (TMS)	CF ₃ δ (CFCl ₃)
<u>PHOSPHINES</u>									
2-CF ₃ [I]	88	A	174-175	54.42, 2.65, 6.72 54.08, 2.58, 6.65		1440	--	6.9, m 7.4, m 7.7, m	58.0, d (J=55 Hz)
3-CF ₃ ^{1,2} [II]	71	B	--	54.85, 2.68, 6.34 54.08, 2.58, 6.65		1410	--	7.5, m	63.4, s
4-CF ₃ ² [III]	67	D	78-80	53.79, 2.70, 6.40 54.08, 2.58, 6.65		1400	--	7.6, m	63.6, s
<u>PHOSPHINE OXIDES</u>									
2-CF ₃ [IV]	71	E	247-248	52.25, 2.26, 6.05 52.28, 2.48, 6.43		1442	1231	7.1-7.4, m 7.5-7.8, m	55.8, s
3-CF ₃ [V]	95	F	103-104	52.03, 2.24, 6.19 52.28, 2.48, 6.43		1423	1194	7.5-8.1, m	63.5, s
4-CF ₃ ³ [VI]	21	F	191-193	52.34, 2.89, 5.84 52.28, 2.48, 6.43		1403	1199	7.8, m	63.9, s

1. Liquid boiling above 340°/atm B.P. not determined.

2. Some oxidation was observed during isolation.

3. Isolated during preparation of the phosphine.

4. Spectra taken as KBr wafer except II which was measured as neat liquid.

A. Recrystallized from benzene-petroleum ether. B. Column chromatography on alumina using petroleum ether as eluent.

D. Column chromatography on silica using petroleum ether as eluent followed by recrystallization from ethanol. E. Recrystallization from acetone-hexane. F. Recrystallization from hexane.

Synthesis of tris-(2-trifluoromethylphenyl)phosphine oxide

In a three necked flask fitted with a water condensor, thermometer and an addition funnel was placed $(2\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$ (1.86g., 0.004 mole) dissolved in benzene (10 ml). The contents were stirred at room temperature while m-chloro-perbenzoic acid (0.78g., 0.0045 mole) in benzene (20 ml) was added in small portions during 20 min. A mild exotherm was noted and a white solid started to deposit. Stirring was continued for an additional 18 h. and then the reaction mixture filtered and the crude product was collected. The crude product was stirred with aqueous Na_2CO_3 solution to remove any m-chlorobenzoic acid. The remaining solid was recrystallized to obtain the pure phosphine oxide. See Table I.

Synthesis of tris-(3-trifluoromethylphenyl)phosphine oxide

The method and quantity of reactants used was identical to the preparation of the 2-isomer. The only difference was that no solid was deposited on addition of the peracid. The clear solution obtained at the end of 5 h. of stirring was extracted with aqueous Na_2CO_3 and the solvent removed by evaporation leaving the crude product. See Table I.

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