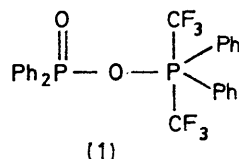


## Reaction of Trifluoroacetic Acid with Chlorodiphenylphosphine

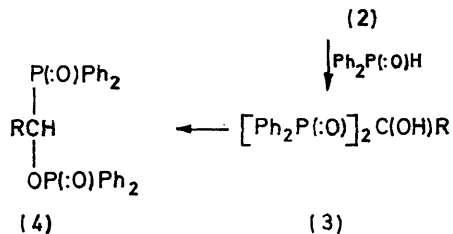
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The reaction of trifluoroacetic acid with chlorodiphenylphosphine at 160–170° gives 1-diphenylphosphinyl-2,2,2-trifluoroethyl diphenylphosphinate together with small amounts of 1-hydroxy-2,2,2-trifluoroethyldiphenylphosphine oxide and diphenyl-2,2,2-trifluoroethylphosphine oxide.

FROM the action of heat on a mixture of trifluoroacetic acid and chlorodiphenylphosphine Sartori and Thomzik<sup>1</sup> isolated a thermally stable compound, m.p. 169.3°, to which they assigned structure (1). Sartori and Hochleitner<sup>2</sup> later obtained spectroscopic evidence which they interpreted as showing that the acylphosphine oxide  $\text{Ph}_2\text{P}(\text{:O})\cdot\text{CO}\cdot\text{CF}_3$  and the phosphine oxide  $\text{Ph}_2\text{P}(\text{:O})\cdot\text{CF}_3$



were intermediates in this reaction. Our previous experience<sup>3,4</sup> with acylphosphine oxides showed them to be extremely susceptible to nucleophilic addition to the carbonyl group, e.g. benzoic anhydride and diphenylphosphine oxide gave the phosphinate (4; R = Ph)

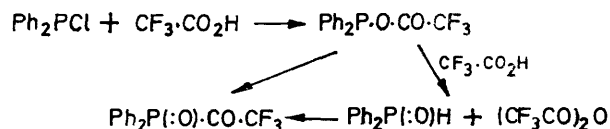


SCHEME

as shown in the Scheme. Equally, structure (1) did not seem to agree with the spectroscopic data reported and we have therefore reinvestigated the reaction of trifluoroacetic acid with chlorodiphenylphosphine.

The major product, m.p. 170–172°, isolated in 92% yield from the reaction of an excess of trifluoroacetic acid with chlorodiphenylphosphine at 160–170°, was identical to that described by Sartori and proved to be the known 1-diphenylphosphinyl-2,2,2-trifluoroethyl di-

phenylphosphinate (4; R = CF<sub>3</sub>) previously obtained<sup>5</sup> from the oxidation of diphenyltrifluoroacetylphosphine. Presumably (4; R = CF<sub>3</sub>) is formed as in the Scheme *via* the dioxide (3; R = CF<sub>3</sub>), the rearrangement being assisted by the strongly electron-attractive CF<sub>3</sub> group.<sup>4</sup> The acylphosphine oxide (2; R = CF<sub>3</sub>) could be formed as shown from trifluoroacetic anhydride and diphenylphosphine oxide or directly from diphenyltrifluoroacetoxyphosphine although this is less probable if the reactions of this phosphine are analogous to those of other acyloxydiphenylphosphines.<sup>3,4</sup>



Minor products, which sublimed out of the mixture during the reaction, were identified as the phosphine oxides  $\text{Ph}_2\text{P}(\text{:O})\cdot\text{CH}(\text{OH})\cdot\text{CF}_3$  and, probably,  $\text{Ph}_2\text{P}(\text{:O})\cdot\text{CH}_2\cdot\text{CF}_3$  (5) on the basis of spectroscopic data (see Experimental section). Speculation on how they are produced would not be justified beyond noting that the reaction mixture is strongly reducing and the formation of the oxide (5) has analogies in the reactions of aldehydes with tetraphenyldiphosphine.<sup>4</sup>

### EXPERIMENTAL

<sup>19</sup>F N.m.r. spectra were determined at 94.1 MHz. Positive chemical shifts are to high field of internal PhCF<sub>3</sub>.

*Reaction of Trifluoroacetic Acid with Chlorodiphenylphosphine.*—Trifluoroacetic acid (25 ml) was added dropwise to chlorodiphenylphosphine (19.7 g) with stirring at 40° under nitrogen. The mixture was kept at 40° for a further 1 h and the excess of trifluoroacetic acid was removed under reduced pressure. The residue was then gradually heated at 0.1 mmHg. At about 100° gas was given off and a white solid sublimed onto the cold surface of the flask. The mixture was kept at 160–170° for 5 h. Crystallisation of the residue from CCl<sub>4</sub> gave 1-diphenylphosphinyl-2,2,2-trifluoroethyl diphenylphosphinate (20.8 g), m.p. 170–172° (lit.,<sup>5</sup> 169–170°). The <sup>1</sup>H and <sup>19</sup>F n.m.r., i.r., and mass spectra were identical with those described<sup>5</sup> for (4; R =

<sup>1</sup> P. Sartori and M. Thomzik, *Z. anorg. Chem.*, 1972, **394**, 157.  
<sup>2</sup> P. Sartori and R. Hochleitner, *Z. anorg. Chem.*, 1974, **404**, 164.

<sup>3</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. (C)*, 1967, 1547.

<sup>4</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. (C)*, 1968, 1700.

<sup>5</sup> E. Lindner, H. D. Ebert, and P. Junkes, *Chem. Ber.*, 1970, **103**, 1364.

CF<sub>3</sub>). The sublimed material (2.3 g) was fractionally crystallised from carbon tetrachloride to give 1-hydroxy-2,2,2-trifluoroethyldiphenylphosphine oxide (0.8 g), m.p. 184—188°,  $\nu_{\max}$  (Nujol) 3060br cm<sup>-1</sup>,  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>CO] 2.33—3.05 (10H, m), 3.20—3.70 (1H, m, exchanges with D<sub>2</sub>O), and 4.98—5.50 (1H, m), <sup>19</sup>F  $\delta$  +5.88 p.p.m. (dd, *J* 10 and 4.4 Hz), *m/e* 221 (highest peak observed), 219, 202, 201, and 183 (Found: C, 55.85; H, 3.85; F, 19.1; P, 10.55.

C<sub>14</sub>H<sub>12</sub>F<sub>3</sub>O<sub>2</sub>P requires C, 56.0; H, 4.0; F, 19.0; P, 10.3%), and a more soluble, hygroscopic, material (0.24 g), probably diphenyl-2,2,2-trifluoroethylphosphine oxide, which was not obtained completely pure, m.p. 131—138°,  $\tau$  (CDCl<sub>3</sub>) 2.07—2.83 (10H, m), 6.77 (2H, dq, *J*<sub>PH</sub> 12.0, *J*<sub>HF</sub> 11.0 Hz), <sup>19</sup>F  $\delta$  -9.14 p.p.m. (dt, *J*<sub>PF</sub> 7.8, *J*<sub>HF</sub> 11.0 Hz), *m/e* 284, 221, 219, 202, 201, and 183.

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