CHEMISTRY LETTERS, pp. 889-892, 1978. Published by the Chemical Society of Japan

BIS(FLUOROALKOXY)TRIPHENYLPHOSPHORANES : PREPARATION AND REACTIONS

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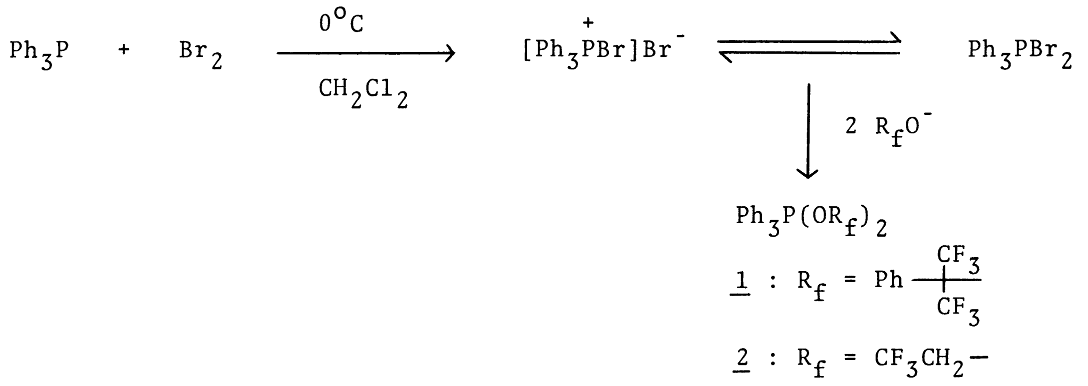
Bis(fluoroalkoxy)triphenylphosphoranes were prepared by the replacement of bromines of triphenylphosphine dibromide by fluoroalkoxides [$C_6H_5C(CF_3)_2ONa$, and CF_3CH_2ONa]. Alcohols and carboxylic acids readily reacted with $Ph_3P(OCH_2CF_3)_2$ to form corresponding 2,2,2-trifluoroethyl ethers and esters, respectively. $Ph_3P[OC(CF_3)_2C_6H_5]_2$, however, was so stable that it did not undergo reactions with these hydroxyl compounds.

There are active research interests in the preparation and reactions of pentacoordinated phosphorus compounds.[1)] Reported synthetic routes for phosphoranes so far include i) the condensation of trivalent phosphorus compounds with quinones, α-diketones or carboxylic acids,[2-4)] and ii) the oxidative addition of peroxycompounds to phosphines.[5-9)] As for the utilization of phosphoranes for synthetic reactions, no reports have appeared except those used them for dehydration leading to heterocycles.[8-11)]

In consideration of the electronic effects of ligands, fluoroalkyl or fluoroalkoxy groups having a strong electron-withdrawing effect, are expected to stabilize the phosphoranes. Recently, Schmutzler and co-workers[10)] have reported the preparation of pentakis(hexafluoroisopropoxy)phosphorane, of which, however, no reactions are mentioned.

In this paper, we wish to report a convenient method for the preparation of bis(fluoroalkoxy)triphenylphosphoranes and some reactions of bis(2,2,2-trifluoroethoxy)-triphenylphosphorane with alcohols and carboxylic acids. The preparation of bis-(fluoroalkoxy)triphenylphosphoranes, 1 and 2, was performed by the replacement of bromines of triphenylphosphine dibromide by fluoroalkoxide ions.



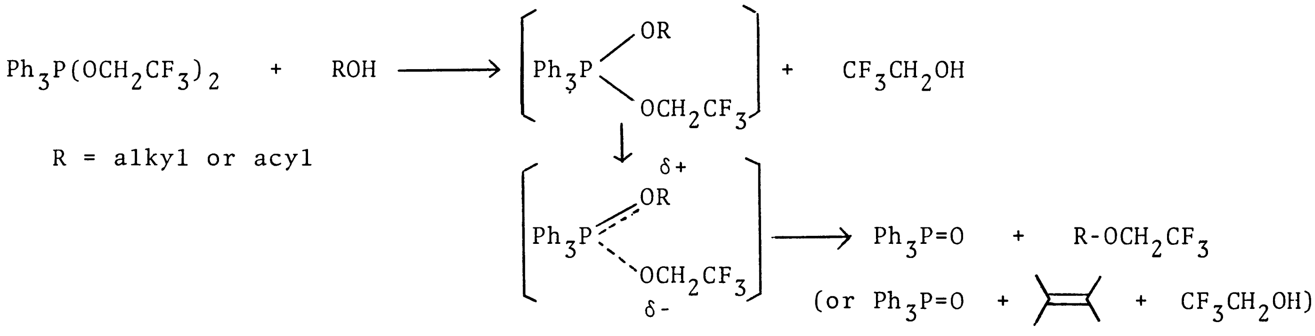
$$Ph_3P + Br_2 \xrightarrow[CH_2Cl_2]{0^\circ C} [Ph_3\overset{+}{P}Br]Br^- \rightleftharpoons Ph_3PBr_2$$

$$[Ph_3\overset{+}{P}Br]Br^- \xrightarrow{2\ R_fO^-} Ph_3P(OR_f)_2$$

$\underline{1}$: $R_f = Ph-C(CF_3)_2-$

$\underline{2}$: $R_f = CF_3CH_2-$

The compound 1 was very stable crystals and it was not attacked by nucleophiles. In contrast, the compound 2 was so unstable that it could not be isolated, though various attempts were made. The presence of 2 in CH_2Cl_2 solution, however, was evident from its ^{19}F nmr spectra (see the experimental below). Further, we found that 2 in the solution is very susceptible to the attack of O-nucleophiles such as alcohols and carboxylic acids, affording 2,2,2-trifluoroethyl ethers and esters in good yields, respectively. With cyclic alcohols such as cyclohexanol or borneol, however, dehydration giving olefins preferentially proceeded (Table 1). The reaction mechanism is speculated as follows.



The difference of these reactivities is probably ascribed to the bulkiness or to the strong negativity of $OC(CF_3)_2Ph$ group compared with those of OCH_2CF_3 group. In conclusion, the phosphoranes which carries weakly negative fluoroalkoxyl groups, such as 2, are found to be useful reagents for the preparation of fluoroalkyl ethers and esters.

EXPERIMENTAL

Phosphorane 1 Into a mixture of triphenylphosphine (10 mmol), sodium α,α-bis(trifluoromethyl)benzyloxide (20 mmol) and methylene chloride (40 ml), bromine (10 mmol) was added slowly at 0 °C. After 1 h of stirring at that temperature, the precipitates (NaBr) were removed by filtration and the solvent was evaporated in

Table 1 Preparation of CF_3CH_2 ethers and esters.

ROH or RCO_2H	Product	Yield e) (%)	b.p. (°C/mmHg) [m.p. (°C)]	^{19}F nmr f) ($J_{CF_3-CH_2}$) [ppm (Hz)]
n-$C_5H_{11}OH$	n-$C_5H_{11}OCH_2CF_3$ a)	68	135.5 - 136.5	72.8 (8.1)
n-$C_8H_{17}OH$	n-$C_8H_{17}OCH_2CF_3$ d)	77	164.5 - 165.5	73.5 (9.0)
$PhCH_2OH$	$PhCH_2OCH_2CF_3$ d)	84	74 - 76/11	72.4 (9.0)
$PhCH_2CH_2OH$	$PhCH_2CH_2OCH_2CF_3$ d)	70	193 - 194	72.5 (8.1)
	CH_2=CHPh	11	144.5 - 145.5	
$C_6H_{13}CH(Me)OH$	$C_6H_{13}CH(Me)OCH_2CF_3$ d)	72	178 - 179	72.8 (8.5)
PhCH(Me)OH	$PhCH(Me)OCH_2CF_3$ d)	59	171 - 172	74.8 (9.6)
cyclohexanol	cyclohexene	71	82 - 83	
borneol	camphene	61	[51 - 52]	
$PhCO_2H$	$PhCO_2CH_2CF_3$ b)	82	77/13	72.8 (8.4)
n-$C_3H_7CO_2H$	n-$C_3H_7CO_2CH_2CF_3$ c)	85	111 - 112	73.8 (8.9)
n-$C_4H_9CO_2H$	n-$C_4H_9CO_2CH_2CF_3$ c)	80	138.5 - 140	73.9 (8.7)

a) C. B. Beard, et al., J. Org. Chem., 38, 3673 (1973). b) E. J. Bourne, et al., J. Chem. Soc., 3268 (1958). c) J. Radwell, et al., J. Chem. Eng. Data, 6, 282 (1961). d) Structures of these products are established from spectral data and C and H elemental analysis. e) Yields are those of the products actually isolated. f) See Note 12.

vacuo yielding crude solid. Recrystallization from CCl_4 gave 1 in a yield of 84%, m.p. 124 - 126 °C. ^{19}F nmr ($CDCl_3$) : δ 68.2 (s)12); ^1H nmr : δ 7.85 (m, 15H), 7.45 (m, 10H). Anal. Calcd for $C_{36}H_{25}O_2PF_{12}$: C, 57.76; H, 3.37%. Found : C, 58.50; H, 3.82%.

Phosphorane 2 Sodium 2,2,2-trifluoroethoxide was used instead of sodium α,α-bis(trifluoromethyl)benzyloxide in the above reaction and worked up similarly. As 2 is extremely hygroscopic, it was unable to isolate it in pure form, while the solution in CH_2Cl_2 was stable enough. ^{19}F nmr ($CDCl_3$) : δ 72.5 (t, $J_{CF_3-CH_2}$= 9.0 Hz); ^1H nmr : δ 2.87 (q of d, 4H, J_{OCH_2-P}= 4.2 Hz), 7.27-7.57 (m, 15H). The yield determined by ^{19}F nmr using benzotrifluoride as a standard was 95%.

2,2,2-Trifluoroethyl ethers Into a solution of 2, obtained from triphenylphosphine (10 mmol), sodium 2,2,2-trifluoroethoxide (20 mmol) and bromine (10 mmol) in CH_2Cl_2 (20 ml), benzyl alcohol (10 mmol) was added at room temperature. After removing the solvent, the residual oily materials were distilled under vacuum to yield 2,2,2-trifluoroethyl benzyl ether in an 84% yield, b.p. 74 - 76 °C/11 mmHg. ^{19}F nmr : δ 72.4 ($J_{CF_3\text{-}CH_2}$ = 9.0 Hz). ^{1}H nmr : δ 3.60 (q, 2H), 4.33 (s, 2H), 7.10-7.30 (m, 5H). Anal. Calcd for $C_9H_9OF_3$: C, 56.84; H, 4.77%. Found : C, 56.76; H, 4.86%.

Other reactions between 2 and alcohols were carried out in a similar way (Table 1).

2,2,2-Trifluoroethyl esters Benzoic acid (10 mmol) was used as above reaction, and the reaction mixture was worked up similarly. Distillation in vacuo gave 2,2,2-trifluoroethyl benzoate in an 82% yield, b.p. 77 °C/ 13 mmHg. Lit (Table 1, b) : b.p. 83 °C/ 19 mmHg. ^{19}F nmr : δ 72.8 (t, $J_{CF_3\text{-}CH_2}$ = 7.5 Hz). The ^{1}H nmr : δ 4.55 (q, 2H), 7.03-8.03 (m, 5H).

Reactions with other carboxylic acids were carried out in a similar way (Table 1).

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12. All the ^{19}F nmr chemical shifts throughout this article are given in δ ppm from int. CCl_3F.

(Received June 16, 1978)