Carbonyl Difluoride: a Versatile Fluorinating Reagent

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Carbonyl difluoride is a readily accessible reagent for introducing fluorine into molecules by oxidative addition to the central atom or by displacement of hydrogen from P–H, N–H, or C–H bonds.

Fluorine transfer reagents which are nondestructive and which can be used with a variety of systems are valuable synthetic tools. We now report the first example of COF_2 (**1**)† as a versatile fluorinating agent which can be used at 25 °C to fluorinate oxidatively compounds where the central atom is co-ordinatively unsaturated or to replace P–H, N–H, or C–H bonds with P–F, N–F, or C–F bonds, respectively.[1,2]

Oxidative addition reactions occurred between organophosphines or organophosphites and (**1**) in methylene dichloride at 25 °C, to afford the corresponding difluoro compounds (**2**) and (**3**) [reactions (1) and (2), respectively].

$$\underset{}{R_3P} + \underset{(\mathbf{1})}{COF_2} \xrightarrow[12\ h]{CH_2Cl_2} \underset{(\mathbf{2})}{R_3PF_2} + CO \qquad (1)$$

R (% yield) = Me (72), Bu^n (70), Bu^t (75), Ph (80).

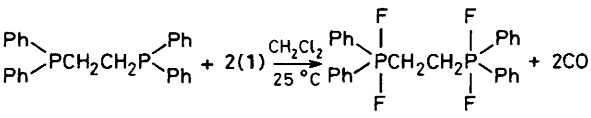
$$(RO)_3P + (\mathbf{1}) \xrightarrow[25\,°C]{CH_2Cl_2} \underset{(\mathbf{3})}{(RO)_3PF_2} + CO \qquad (2)$$

R (% yield) = EtO (72), Bu^{n}O (70).

A single distillation or crystallization gave the pure compounds (**2**) and (**3**) which were identified and characterized by comparing i.r., ^{31}P and ^{19}F n.m.r., and mass spectra with literature values.[3,4]

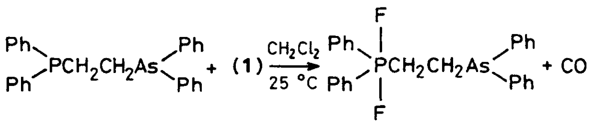
Oxidative fluorination occurred at phosphorus but not at arsenic to form two new fluorophosphoranes (**4**) and (**5**) in high yield [reactions (3) and (4), respectively]. In a typical reaction, 0.79 g $Ph_2PCH_2CH_2PPh_2$ was dissolved in 20—25 ml CH_2Cl_2 in a 50 ml round-bottomed Pyrex flask equipped with a Kontes Teflon-stemmed valve and 10/30 inner joint. COF_2 (2 mmol) was added. The mixture was stirred at 25 °C for 12 h. The volatile materials were pumped off to leave behind a white residue which was purified by Kugelrohr distillation at 100 °C/1 Torr.

In contrast, with 2,8-dioxa-5-aza-1-phosphabicyclo-[3.3.0]octane under similar conditions, oxidative fluorination did not occur but rather the fragments C(O)F and F were added to nitrogen and phosphorus respectively, with concomi-


(3)

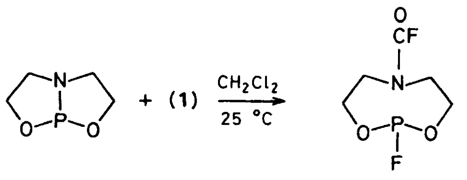
$$Ph_2PCH_2CH_2PPh_2 + 2(\mathbf{1}) \xrightarrow[25\,°C]{CH_2Cl_2} Ph_2PF_2CH_2CH_2PF_2Ph_2 + 2CO \qquad (3)$$

(**4**) 80%


(4)

$$Ph_2PCH_2CH_2AsPh_2 + (\mathbf{1}) \xrightarrow[25\,°C]{CH_2Cl_2} Ph_2PF_2CH_2CH_2AsPh_2 + CO \qquad (4)$$

(**5**) 75%


(5)

(**6**) 70%

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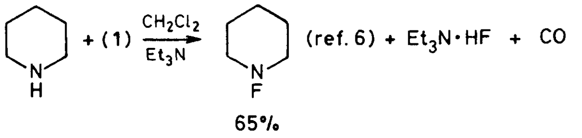
$$(RO)_2P(O)H + (\mathbf{1}) \xrightarrow[CH_2Cl_2]{Et_3N} \underset{(\mathbf{7})}{(RO)_2P(O)F} + CO + Et_3N{\cdot}HF \quad (6)$$

$$R\ (\%\ yield) = Et\ (65),\ Bu^n\ (60)$$

$$Me_2NH + (1) \xrightarrow[Et_3N]{CH_2Cl_2} \underset{45\%}{Me_2NF\ (ref.\ 5)} + Et_3N{\cdot}HF + CO \quad (7)$$



(8)

$$Ph_3CH + (1) \xrightarrow[CH_2Cl_2]{Et_3N} \underset{60\%}{Ph_3CF\ (ref.\ 7)} + CO + Et_3N{\cdot}HF \quad (9)$$

tant nitrogen–phosphorus bond breaking to give (**6**) [reaction (5)]. No CO was produced.

The abstraction of hydrogen was possible when dialkylphosphonates reacted with (**1**) in the presence of triethylamine under analogous conditions to give the phosphorofluoridates (**7**) [reaction (6)], which were characterized by comparison of i.r., ^{31}P and ^{19}F n.m.r., and mass spectral data with literature values.[4]

With dimethylamine [reaction (7)] and piperidine [reaction (8)], (**1**) readily substituted fluorine for hydrogen to form the *N*-fluoro derivatives at 25 °C. Tertiary hydrocarbons were also fluorinated under the same mild conditions [*e.g.*, reaction (9)]. The reaction is currently being extended to other systems which will be reported in due course.

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