N^1, N^3–Me). ^{19}F NMR spectrum (δ, ppm, acetone): 3.0 s, 9.5 s (1:2). ^{13}C NMR spectrum (δ, ppm, J, Hz, MeOH): 160.0 (C^4), 157.5 [$C(O)CF_3$, J_{C-F} = 38], 150.1 (C^2), 145.0 (C^6), 123.3 (CF_3, J_{C-F} = 291.0), 116.0 [$C(O)CF_3$, J_{C-F_3} = 291.0], 100.0 (C^5), 66.2 [$C(CF_3)_2$, J_{C-F} = 31], 37.2 (N^1–Me), 28.1 (N^3–Me).

5-(1-Methoxycarbonyl-1-trifluoroacetamido-2,2,2-trifluoroethyl)-1,3-dimethyluracil (XI) was obtained under the same synthetic conditions as (X) from 1.4 g 1,3-dimethyluracil in 10 cm^3 $CHCl_3$ and 2.6 g (III); yield 3.76 g (XI). ^1H NMR spectrum (δ, ppm, acetone-d_6): 11.2 bs (1H, NH), 7.7 s (1H, C^6–H), 3.8 s (3H, OMe), 3.5 s, 3.25 (6H, N^1–Me, N^3–Me). ^{19}F NMR spectrum (δ, ppm, acetone): 1.9 s, 2.8 s (1:1).

CONCLUSIONS

1. 4-Aminopyrimidines react with hexafluoroacetone to give pyrimidooxazines and pyrimidooxadiazines.

2. An account is given of the C^5 aminoalkylation of 1,3-dimethyluracil by the trifluoroacetylimines of hexafluoroacetone and of the methyl ester of trifluoropyruvic acid.

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CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.

11.* α-POLYFLUOROALKYLBENZYLDICHLOROPHOSPHATES AS PHOSPHORYLATING AGENTS IN THE CATALYTIC PHOSPHORYLATION OF PRIMARY POLYFLUOROALKANOLS

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We have shown previously that on heating, α-polyfluoroalkylbenzyldichlorophosphates alkylate polyfluorinated alcohols of different structures, including primary polyfluoroalkanols, with the formation of the corresponding unsymmetrical polyfluorinated ethers [2]

$$RC_6H_4CHR_FOPOCl_2 + R_F'CH_2OH \xrightarrow{T°C} RC_6H_4CHR_FOCH_2R_F'$$

Alkylation proceeds at temperatures of 100-160°C, depending on the structure of the initial benzyldichlorophosphate, it being impossible to detect the formation of phosphorylation products under these conditions [2].

However, when one considers that phosphorylation of polyfluorinated primary alcohols by the acid chloride of pentavalent phosphorus is catalyzed by certain metal salts [3], it might

*For previous communication, see [1].

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TABLE 1. Catalytic Phosphorylation of Primary Polyfluoroalkanols by α-Polyfluoroalkylbenzyldichlorophosphates

R	R_F	R_F'	Catalyst*	Reaction temperature, °C	Reaction time, h	Yield, %
H	CF_3	CF_3	$CaCl_2$	120	1,0	80
H	CF_3	C_3F_7	$CaCl_2$	120	1,5	78
H	CF_3	C_4F_9	$CaCl_2$	120	2,0	80
H	CF_3	$CF_3OCF_2CF_2$	$CaCl_2$	120	1,25	85
H	CF_3	CF_3CH_2	$CaCl_2$	120	0,5	91
H	CF_3	CF_3CH_2	Mg	90	1,0	84
m-CH_3	CF_3	C_4F_9	$CaCl_2$	120	1,0	71
m-CF_3	CF_3	C_4F_9	$CaCl_2$	120	3,0	72
m-CF_3	CF_3	C_4F_9	Mg	120	1,0	76
m-NO_2	CF_3	CF_3	$CaCl_2$	120	3,0	75
H	C_3F_7	C_4F_9	Mg	120	4,0	76
H	C_3F_7	$CF_3CH_2CH_2$	Mg	120	0,5	82

*0.025 mole catalyst to 1 mole $RC_6H_4CHR_FOPOCl_2$.

be expected that α-polyfluoroalkylbenzyldichlorophosphates too would be able, in the presence of a catalyst, to act as phosphorylating agents toward these alcohols under defined temperature conditions.

In fact, α-polyfluoroalkylbenzyldichlorophosphates (I)-(V) react, at temperatures not above 120°C, with primary polyfluoroalkanols (VI)-(XI) in porportions of 1:2.2 in the presence of anhydrous $CaCl_2$ or magnesium metal forming phosphorylation products exclusively – bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates (XII)-(XXI).

$$\underset{\text{(I)—(V)}}{RC_6H_4CHR_FOPOCl_2} + 2\underset{\text{(VI)—(XI)}}{R_F'CH_2OH} \xrightarrow[-HCl]{\text{Cat, T°C}} \underset{\text{(XII)—(XXI)}}{RC_6H_4CHR_FOP(O)(OCH_2R_F')_2}$$

R = H, $R_F = CF_3$ (I); R = *m*-CH_3, $R_F = CF_3$ (II); R = *m*-CF_3, $R_F = CF_3$ (III); R = = *m*-NO_2, $R_F = CF_3$ (IV); R = H, $R_F = C_3F_7$ (V); $R_F' = CF_3$ (VI); C_3F_7 (VII); C_4F_9 (VIII); $CF_3OCF_2CF_2$ (IX); CF_3CH_2 (X); $CF_3CH_2CH_2$ (XI); R = H, $R_F = R_F' = CF_3$ (XII); R = H, $R_F = CF_3$, $R_F' = C_3F_7$ (XIII); R = H, $R_F = CF_3$, $R_F' = C_4F_9$ (XIV); R = H, $R_F = CF_3$, $R_F' = CF_3OCF_2CF_2$ (XV); R = H, $R_F = CF_3$, $R_F' = CF_3CH_2$ (XVI); R = *m*-CH_3, $R_F = CF_3$, $R_F' = C_4F_9$ (XVII); R = *m*-CF_3, $R_F = CF_3$, $R_F' = C_4F_9$ (XVIII); R = *m*-NO_2, $R_F = R_F' =$ = CF_3 (XIX); R = H, $R_F = C_3F_7$, $R_F' = C_4F_9$ (XX); R = H, $R_F = C_3F_7$, $R_F' =$ = $CF_3CH_2CH_2$ (XXI).

The conditions for the catalytic phosphorylation of the primary polyfluoroalkanols by α-polyfluoroalkylbenzyldichlorophosphate and the yields of phosphorylation products are set out in Table 1.

Here, it proved that in the series of 1,1-dihydroperfluoroalkanols $CF_3(CF_2)_nCH_2OH$ [alcohols (VI)-(VIII), where n = 0, 2, 3, respectively] the rate of the catalyzed phosphorylation fell somewhat with increased chain length of the perfluoroalkyl radical, and in the series of ω-trifluoromethylalkanols $CF_3(CH_2)_nCH_2OH$ [alcohols (VI), (X), and (XI), where n = 0, 1, 2, respectively], on the other hand, the rate of the catalytic phosphorylation increased considerably with increase in chain length.

The dependence of the rate of the catalytic phosphorylation on the structure of the polyfluoroalkyl radical R_F in these two types of alcohol $R_F'CH_2OH$ runs parallel to the change in electron-acceptor properties of the radical, in particular: $CF_3(CF_2)_n$ (n > 0) > CF_3 [4] ≫ $CF_3(CH_2)_n$ (n > 0) [5].

Replacement of the terminal trifluoromethyl group in 1,1-dihydroperfluorobutan-1-ol (VII) by a trifluoromethoxy group [alcohol (IX)] also leads to some increase in the catalytic phosphorylation rate and this too can be attributed to the slight reduction in the electron-acceptor properties of CF_3O in comparison with CF_3 [6].

The results obtained provide evidence that for the case of primary polyfluoroalkanols of normal structure one of the basic factors which determine their reactivity in catalytic phosphorylation is the electron-acceptor property of the phosphorus-containing radical.

TABLE 2. Bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates $RC_6H_4CHR_FOP(O)(OCH_2R_F')_2$

Compound	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %				Formula	Calculated, %				$^{31}P-\{^1H\}$ NMR spectra (δ, ppm)*
				C	H	F	P		C	H	F	P	
(XII)	90–91(1)	1,3923	1,4874	34,3	2,4	40,7	7,3	$C_{12}H_{10}F_8O_4P$	34,3	2,4	40,7	7,4	−2,60s
(XIII)	107,5–108(0,2)	1,3650	1,5902	30,9	1,7	52,0	4,9	$C_{16}H_{10}F_{17}O_4P$	31,0	1,6	52,1	5,0	−2,86s
(XIV)	130–132(2)	1,3588	1,6341	30,0	1,4	54,8	4,2	$C_{18}H_{10}F_{21}O_4P$	30,0	1,4	55,4	4,3	−2,67s
(XV)	99–100(0,05)	1,3588	1,5915	29,5	1,5	49,6	–	$C_{16}H_{10}F_{17}O_6P$	29,5	1,6	49,5	–	−2,81s
(XVI)	115–116(0,2)	1,4043	1,4441	37,3	3,1	38,1	6,9	$C_{14}H_{14}F_8O_4P$	37,5	3,2	38,2	6,9	−2,48s
(XVII)	114–116(0,1)	1,3629	1,6103	31,0	1,7	54,1	3,9	$C_{19}H_{12}F_{21}O_4P$	31,1	1,6	54,3	4,2	−2,63s
(XVIII)	119–120(0,1)	1,3517	1,6805	29,0	1,3	57,9	–	$C_{19}H_9F_{24}O_4P$	29,0	1,2	57,8	–	−2,48s
(XIX)	155–156(1)	1,4207	1,5870	31,0	1,9	36,8	6,7	$C_{12}H_9F_9NO_6P$	31,0	2,0	36,8	6,7	−2,78s
(XX)	106–107(0,05)	1,3470	1,6810	29,4	1,3	58,2	3,5	$C_{20}H_{10}F_{25}O_4P$	29,3	1,2	57,9	3,8	−2,71s
(XXI)	136–137(0,1)	1,3945	1,4539	37,4	3,2	42,8	5,4	$C_{18}H_{18}F_{13}O_4P$	37,5	3,2	42,9	5,4	−1,47s

*In CCl_4 solution.

It has been established that although both magnesium metal and anhydrous $CaCl_2$ are quite active catalysts for the phosphorylation of primary polyfluoroalkanols by α-polyfluoroalkylbenzyldichlorophosphates, magnesium proves to be considerably more effective and as a result the reaction can be completed in a shorter time, or at a lower temperature, when using magnesium.

Thus, depending on the reaction conditions – temperature and the presence or absence of catalyst – α-polyfluoroalkylbenzyldichlorophosphates can act selectively on the same substrate, in particular on polyfluoroalkylated primary alcohols, as alkylating and as phosphorylating agents: In the latter case the appropriate phosphorylation reactions provide a simple and effective method for the synthesis of a series of bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates.

The phosphates (XII)-(XXI) are colorless, mobile liquids, freely soluble in organic solvents and insoluble in water. The constants for the bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates which we prepared, together with the results of elemental analysis and ^{31}P NMR data are given in Table 2.

The initial α-polyfluoroalkylbenzyldichlorophosphates (I), (III), and (V) were prepared by known methods [7], and α-trifluoromethyl-m-methylbenzyldichlorophosphate (II) and α-trifluoromethyl-m-nitrobenzyldichlorophosphate (IV) were prepared from the corresponding substituted 2,2,2-trifluoroacetophenones by the following route:

$$\underset{\text{(XXII), (XXIII)}}{m\text{-}RC_6H_4COCF_3} \xrightarrow{NaBH_4} \underset{\text{(XXIV), (XXV)}}{m\text{-}RC_6H_4CH(OH)CF_3} \xrightarrow{\text{cat., } POCl_3,\ 120^\circ} \underset{\text{(II), (IV)}}{m\text{-}RC_6H_4CH(CF_3)OPOCl_2}$$

R = CH_3(II), (XXII), (XXIV); NO_2 (IV), (XXIII), (XXV).

EXPERIMENTAL

A Bruker WP-200SY instrument was used to obtain PMR and ^{19}F NMR spectra using TMS and CF_3COOH respectively as internal and external standards. ^{31}P NMR spectra were run on a Bruker HX-90 instrument in impulse mode with noise suppression of the spin–spin interactions of the phosphorus nuclei with protons; the internal standard was 85% H_3PO_4. IR spectra were recorded on a UR-20 instrument.

3'-Methyl-2,2,2-trifluoroacetophenone (XXII). A solution of 108 g (0.9 mole) CF_3COOLi in 300 ml dry THF was added to a solution of Grignard reagent, prepared from 171 g (1 mole) m-bromotoluene and 26.4 g (1.1 mole) Mg in 0.5 liter dry ether cooled to −10°C, slowly over a period of 2 h, and the mixture then heated at bp for 2 h. After standing overnight it was treated in the usual manner and the product distilled in vacuum collecting the fraction with bp 50-80°C/10 mm. The distillate was dissolved in an equal volume of dry pentane and passed through a column of Al_2O_3 (2 g Al_2O_3 per g distillate) using pentane as eluent, the solvent distilled off and the residue fractionated in vacuum using a Widmar column to yield 130.0 g (77%) (XXII), bp 73.5-74.5°C/20 mm, n_D^{20} 1.4634, d_4^{20} 1.2341. Found, %: C 57.1; H 3.7; F 30.2. $C_9H_7F_3O$. Calculated, %: C 57.4; H 3.8; F 30.3. IR spectrum (ν, cm^{-1}): 1719 (C=O).

3'Nitro-2,2,2-trifluoroacetophenone (XXIII). To 67.3 g (0.386 mole) 2,2,2-trifluoroacetophenone, cooled to −5°C, was added 120 ml concentrated H_2SO_4 dropwise over 0.5 h followed by a mixture of 32 ml concentrated HNO_3 and 48 ml concentrated H_2SO_4 dropwise over 1.5 h. The mixture was stirred for 1 h at 0°C, poured onto 0.8 kg ice, extracted with 4 × 150 ml ether and the extract washed with 20 ml water and 2 × 20 ml saturated $NaHCO_3$ and dried over anhydrous $MgSO_4$. The solvent was removed and the residue distilled in vacuum collecting the fraction with bp 88-90°C/3 mm. The distillate was kept for 2 days at ~0°C and recrystallized three times from a mixture of ether and hexane. Yield 44.7 g (53%) (XXIII), mp 58-59°C. Found, %: C 43.7; H 1.9; F 26.0; N 6.2. $C_8H_4F_3NO_3$. Calculated, %. C 43.8; H 1.8; F 26.0; N 6.4. IR spectrum (ν, cm^{-1}): 1365, 1565 (NO_2), 1750 (C=O). The mother liquor after separating (XXIII) was evaporated and the 2.3 g residue chromatographed on 50 g Al_2O_3 and eluted with hexane; 0.2 g 2'-nitro-2,2,2-trifluoroacetophenone, n_D^{20} 1.4840 (see [8]).

m-Methyl-α-trifluoromethylbenzyl Alcohol (XXIV). To a solution of 120.7 g (0.64 mole) (XXII) in 360 ml methanol cooled in ice was added dropwise a solution of 12.2 g (0.32 mole) $NaBH_4$ in 120 ml water and the solution stirred 5 h at ~20°C and left overnight. The excess $NaBH_4$ was decomposed with 30% H_2SO_4 and the mixture diluted with an equal volume of water and extracted with 4 × 300 ml ether. The usual treatment yielded 114.1 g (94%) (XXIV), bp 111-112°C/27 mm, n_D^{20} 1.4644, d_4^{20} 1.2507. Found, %: C 57.0; H 5.1; F 30.0. $C_9H_9F_3O$. Calculated, %: C 56.8; H 4.8; F 30.0.

m-Nitro-α-trifluoromethylbenzyl Alcohol (XXV). A similar preparation to the foregoing, using 10 g (45.7 mmoles) (XXIII) and 0.87 g (22.9 mmoles) $NaBH_4$ yielded 9.0 g (89%) (XXV). mp 53-54°C (ether–petroleum ether). Found, %: C 43.0; H 2.8; N 6.6. $C_8H_6F_3NO_3$. Calculated, %: C 43.4; H 2.7; N 6.3. IR spectrum (ν, cm^{-1}): 1373, 1555 (NO_2).

m-Methyl-α-trifluoromethylbenzyldichlorophosphate (II). A mixture of 9.5 g (0.05 mole) (XXIV), 15.3 g (0.1 mole) $POCl_3$, and 0.14 g (1.26 mmoles) anhydrous $CaCl_2$ was heated 4 h at 120°C, the excess $POCl_3$ distilled out in vacuum and the residue fractionated in vacuum. Yield 11.4 g (74%) (II), bp 90-91°C/1 mm, n_D^{20} 1.4746, d_4^{20} 1.4338. Found, %: C 35.3; H 2.5; Cl 23.1; F 19.0; P 10.1. $C_9H_8Cl_2F_3O_2P$. Calculated, %: C 35.2; H 2.6; Cl 23.1, F 18.6; P 10.1. PMR spectrum (CCl_4, δ, ppm, J, Hz): 2.326 s (3H, CH_3), 5.882 dq (1H, CH, J_{H-F} = 6.0, J_{H-P} = 14.0), 7.04-7.33 m (4H, C_6H_4). ^{19}F NMR spectrum (CCl_4, δ, ppm, J, Hz): 1.181 d (CF_3, J_{H-F} = 6.1). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): 7.04 s.

m-Nitro-α-trifluoromethylbenzyldichlorophosphate (IV). A mixture of 14.5 g (65.6 mmoles) (XXV), 30.2 g (197 mmoles) $POCl_3$, and 0.182 g (1.64 mmoles) anhydrous $CaCl_2$ was heated 17 h at 120°C, the excess $POCl_3$ distilled out in vacuum and the residue fractionated in vacuum. Yield 12.4 g (56%) (IV), bp 132.5-133°C/1 mm, n_D^{20} 1.5005, d_4^{20} 1.5974. Found, %: C 28.4; H 1.5; Cl 20.7; N 4.2; P 8.8. $C_8H_5Cl_2F_3NO_4P$. Calculated, %: C 28.4; H 1.5; Cl 21.0; N 4.1; P 9.2. PMR spectrum (CCl_4, δ, ppm, J, Hz): 6.280 dq (1H, CH, J_{H-F} = 5.8, J_{H-P} = 14.2), 7.68-8.44 m (4H, C_6H_4). ^{19}F NMR spectrum (CCl_4, δ, ppm, J, Hz): 1.002 d (CF_3, J_{H-F} = 5.8). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): 8.04 s.

Bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates. A mixture of 0.003-0.03 mole α-polyfluoroalkylbenzyldichlorophosphate, 2.2-multiple quantity of polyfluorinated primary alcohol, and 0.075-0.75 mmole of appropriate catalyst was heated for several hours at the required temperature and the bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates (XII)-(XXI) isolated by distillation in vacuum; constants are set out in Table 2.

CONCLUSIONS

α-Polyfluoroalkylbenzyldichlorophosphates react, in the presence of catalytic quantities of certain metals or their salts, with polyfluorinated primary alcohols with the formation of phosphorylation products [bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl)phosphates] exclusively.

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