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SYNTHESIS OF 2,2,2-TRISUBSTITUTED 5-TRIFLUOROMETHYL-Δ^4-1,3,4,2-OXADIAZAPHOSPHOLINES AND THEIR POTENTIALITY AS PRECURSORS OF TRIFLUOROACETONITRILE IMINES

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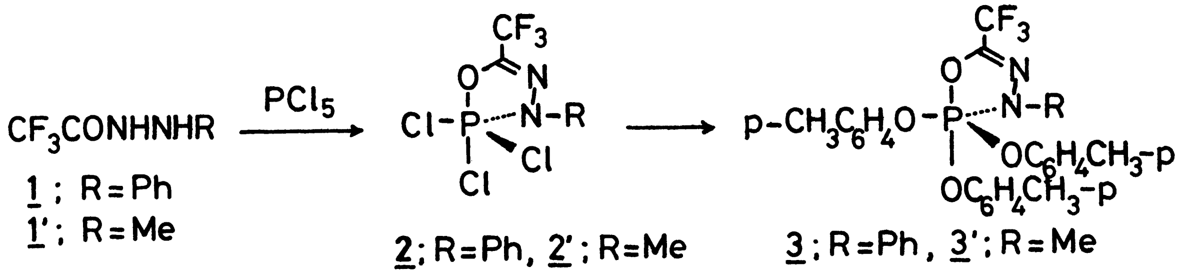
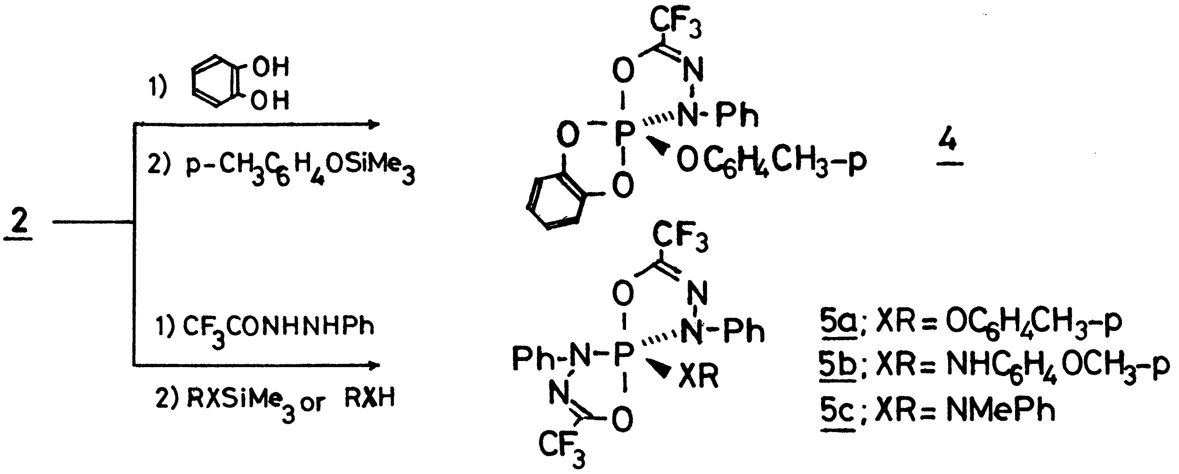
N'-Phenyl- and methyltrifluoroacetohydrazides react with phosphorus pentachloride to give the corresponding 2,2,2-trichloro-3-phenyl- and methyl-Δ^4-1,3,4,2-oxadiazaphospholines, from which various 2,2,2-trisubstituted derivatives are further synthesized. Heating 3-phenyl-2,2,2-tris(p-tolyloxy) analog with an excess of styrene affords 1,5-diphenyl-3-trifluoromethyl-2-pyrazoline, which indicates that the phospholine behaves as a precursor of trifluoroacetonitrile phenylimine.

It is well known that amides can be chlorinated with phosphorus pentachloride to give imidoyl chlorides, and that benzohydrazides can also be converted to benzohydrazidoyl chlorides, precursors of benzonitrile imines.[1) We now wish to report that the reactions of trifluoroacetohydrazides (1 and 1') with phosphorus pentachloride provide, instead of the hydrazidoyl chlorides, the unexpected 2,2,2-trichloro-5-trifluoromethyl-Δ^4-1,3,4,2-oxadiazaphospholines (2 and 2'), a class of pentacovalent phosphorus compounds which have received the structural interest.[2) It is also demonstrated that thus-obtained phospholine degradates on heating to result in the formation of trifluoroacetonitrile imine.

N'-Phenyl- and methyltrifluoroacetohydrazides (1 and 1')[3) reacted with phosphorus pentachloride in toluene at room temperature for 2 h with evolution of hydrogen chloride, giving the corresponding oxadiazaphospholines 2 and 2' in 93 and 90% yields, respectively. The phospholine 2 was then treated with an excess of O-trimethylsilyl-p-cresol in toluene at 110 °C for 4.5 h, affording the 2,2,2-tris-(p-tolyloxy) derivative 3 in 54% yield, while the methyl analog 3' was similarly obtained from 2' only in 16% yield.

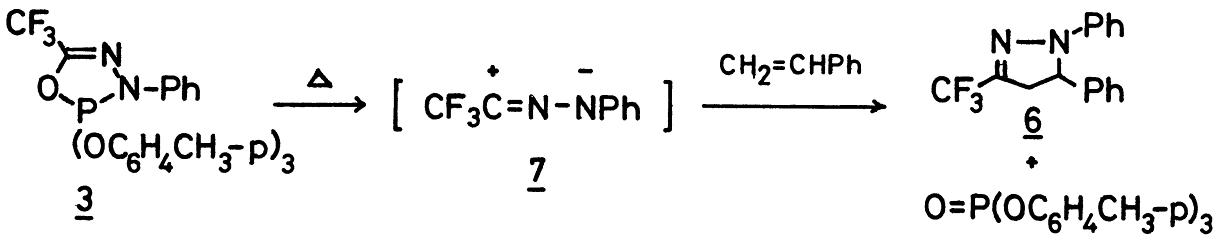


The structure of thus-obtained oxadiazaphospholines (2, 2', 3, 3') was determined by their spectral data, listed in Table 1, and the elementary analyses of 3 and 3'. The phospholines 2 and 2' hydrolyze so easily that the reliable elementary analyses could not be performed. The IR spectrum shows the band due to the carbon-nitrogen double bond in each case. The higher chemical shifts in ^{31}P NMR spectra support the pentacovalent phosphorus structure rather than the phosphonium one.2),4) Each molecule is drawn as a trigonal bipyramid with the phosphorus atom at its center, by analogy with the structure of the related pentacovalent phosphorus compounds with phospholine ring which was determined by X-ray diffraction techniques in the literature.2b)



The reaction of 2 with catechol followed by treatment with O-trimethylsilyl-p-cresol in toluene at 110 °C produced the spirophospholine 4 in 71% yield. The replacement of catechol with O-bis(trimethylsilyl)catechol lowered the yield of 4 to 23%. In the ^{31}P NMR spectrum, a singlet peak appears at δ-43.1, which is considerably deshielded compared with that (δ-69.0) of the tris(p-tolyloxy)phospholine 3.2d)

The preparation of the symmetrical spiro compound from 2 with another molecule of the hydrazide 1 was next investigated. The reaction of 2 with an equimolar ammount of 1 in toluene at 110 °C for 8 h followed by treatment with O-trimethylsilyl-p-cresol for additional 22 h afforded the expected spirophospholine 5a in 50% yield. Treatment with p-anisidine and N-methylaniline in place of silylated p-cresol gave the corresponding spirophospholines 5b and 5c in 52 and 33% yields, respectively. The structure of 5a-c was established by their elemental analyses and spectroscopic properties listed in Table 1. It should be noted that the chemical shifts in the ^{31}P NMR spectra (δ-55.5, -58.5, and -55.5, respectively) of these phospholines 5a-c have no remarkable difference.



It was of particular interest to find that refluxing a solution of 3 and an excess of styrene in xylene for 12 h provided 1,5-diphenyl-3-trifluoromethyl-2-pyrazoline (6) in 73% yield along with 65% of tris(p-tolyl)phosphate. The pyrazoline 6 was identified by its spectral data which were quite consistent with our previously reported values;[5] mp 83.5°C; ^{1}H NMR(CCl_4) δ 2.88(ddq, 1H), 3.60(ddq, 1H), 5.25(dd, 1H), and 6.5-7.5(ar., 10H). These results strongly support the phospholine 3 behaves as a precursor of trifluoroacetonitrile phenylimine (7) which may be liberated on heating and cyclized with styrene to give 6.[6]

Table 1. Physical and Spectral Data of Phospholines 2-5

Phospholine[b]	Bp,°C/mmHg or Mp,°C(Recrys. Solv.)	IR(cm^{-1}) C=N	^{19}F NMR[a] δ[c]	^{31}P NMR[a] δ[c]	^{1}H NMR[a] δ[c]
2	124-126/12	1650		-51.4	7.3(br.s)
2'	77-79/30	1660		-51.1	3.8(d)[d]
3	96-97(hexane)	1648	6.8	-69.0	2.3(s,9H), 6.8(A_2X_2,12H), 7.4(br.s,5H)[d]
3'	100-101(hexane)	1650	6.5	-66.0	2.2(s,9H), 3.6(d,3H), 6.8(A_2X_2,12H)[d]
4	127-129(hexane)	1650	7.2	-43.1	2.3(s,3H), 6.3-7.1(ar.,8H), 7.3(br.s,5H)[d]
5a	137-139(hexane)	1640	7.0	-55.5	2.3(s,3H), 6.9(A_2X_2,4H), 7.2(br.s,10H)[d]
5b	139.5-141.5(hexane)	1640	6.9	-58.5	3.8(s,3H), 5.0(d,1H), 6.9(A_2X_2,4H), 7.4(br.s,10H)
5c	109-110(hexane)	1642	6.7	-55.5	3.1(d,3H), 7.2(s,5H), 7.3(s,10H)

a) Measured in $CDCl_3$ unless otherwise noted. b) Satisfactory analytical data (within ±0.3% for C, H, N) were obtained for all compounds other than 2 and 2'. c) See ref. 7). d) Measured in CCl_4.

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3) The hydrazides 1 and 1' were prepared by trifluoroacetylation of phenylhydazine and methylhydrazine with ethyl trifluoroacetate in 79 and 73% yields, respectively: 1, mp 119-120°C, IR (KBr) 1698 cm^{-1} (C=O), ^{1}H NMR ($CDCl_3$) 6.0(br.s, 1H), 6.6-7.4(ar., 5H), and 8.0(br.s, 1H); 1', mp 58-63°C, IR (nujol) 1680 cm^{-1}(C=O), ^{1}H NMR ($CDCl_3$) 2.7(s, 3H) and 6.2(br., 2H).

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7) The chemical shifts for ^{1}H, ^{19}F, and ^{31}P NMR are all given in δppm downfield from internal tetramethylsilane, external trifluoroacetic acid, and external 85% phosphoric acid, respectively.

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