Insertion of $P(CN)_3$ and $As(CN)_3$ as their Isonitrile Forms into the Dimer of Hexafluorothioacetone

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Reaction of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane with $P(CN)_3$ and $As(CN)_3$ yields stable insertion products, in which the nitriles are rearranged to the corresponding isonitrile structures.

It has been reported that the dimer of hexafluorothioacetone, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane, (**1**), undergoes nucleophilic reaction with amines.[1] It also reacts with alcohols[2] and dienes[3] in the presence of fluoride ion catalyst. In all these reactions the dimer (**1**) dissociates and the end products have only the monomeric unit. We report here our preliminary results from the reaction of (**1**) with various nitriles in the presence of triethylamine as catalyst. For the first time we observe that only one of the C–S bonds in (**1**) is cleaved and an insertion of the C≡N moiety takes place. No reaction is observed when hexafluorothioacetone itself reacts with $P(CN)_3$ or $As(CN)_3$; after two days the unreacted nitriles and (**1**) are recovered.

In a typical experiment, a solution of 0.55 g (0.005 mol) of $P(CN)_3$ in 60 ml dry acetonitrile is cooled to −78 °C and 5.46 g (0.015 mol) (**1**) is injected in one stroke, followed by 2—3 drops of triethylamine. The reaction mixture is allowed to warm to room temperature and stirred for 12 h. The precipitate is recrystallised from 1,1,2-trichlorotrifluoroethane–hexane to yield colourless crystals of (**2**), m.p. 136—138 °C, 3.21 g (53% yield). Compound (**3**), m.p. 113–114 °C, 3.63 g (58% yield) is obtained in a similar way.The structures for the compounds (**2**) and (**3**) are assigned on the basis of i.r., n.m.r. (^{19}F, ^{31}P, ^{13}C), and mass spectra and analytical data.

The mass spectrum for compound (**2**) shows the molecular ion at 1201 (*m/z* calc. for $C_{21}F_{36}N_3PS_6$ 1201). The n.m.r. data are given in Table 1. There is a single resonance at 64.17 p.p.m. (*cf.* $\delta_{P(CN)_3}$ −135.7)[4] in the ^{31}P n.m.r. spectrum. In the ^{19}F n.m.r. spectrum, there are two broad signals at −69.8 and −67.6 p.p.m. The ^{13}C n.m.r. spectrum shows a doublet at δ 162.38 (J 9.0 Hz), which is assigned to the ylide-amino carbon atom.[5] This coupling constant proves that compound (**2**) has an isomerized isonitrile group (P–N=C) with a five-membered ring (A) rather than a six-membered ring (B), with a P–C bond, formed by cycloaddition to an N=C unit. Such an arrangement is expected to give a much larger P–C coupling constant. The assignment is supported by the fact that the product obtained from $P(CN)_3$ with hexafluoroacetone contains a five-membered ring.[5]

The i.r. spectrum shows a strong band at 1605 cm^{-1} which is easily assigned to the C=N stretching frequency. The two septets in the ^{13}C n.m.r. spectrum (see Table 1) are assigned to the $C(CF_3)_2$ carbon atoms, the low field septet being assigned to the carbon atom bonded to two sulphur atoms.[6] The CF_3 groups are magnetically equivalent and give a quartet.

Compound (**3**) also shows the molecular ion at 1244 (*m/z* calc. for $C_{21}F_{36}N_3AsS_6$ 1244). In the ^{19}F n.m.r. spectrum two broad signals were observed at −69.8 and −67.7 p.p.m. The ^{13}C n.m.r. spectrum shows a sharp signal at δ 164.38 for the ylide-amino carbon atom and two septets and a quartet† (see Table 1).

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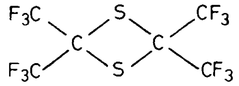
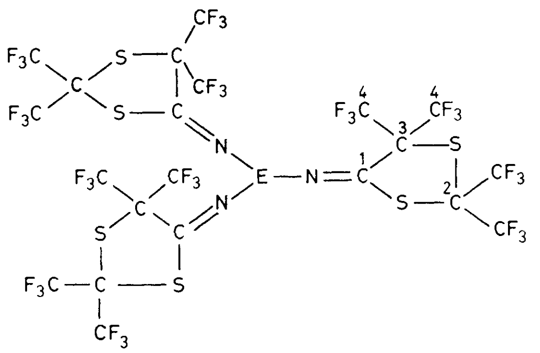
Table 1. ^{31}P, ^{19}F, ^{13}C N.m.r. data for compounds (**2**) and (**3**) (δ in p.p.m., J in Hz, solvent $CFCl_3$).

Compound	δ_P[a]	δ_F[b]	δ_C[c]	
(**2**)	64.17	−69.8 (18F)	162.38	(C-1, d, $^2J_{C-P}$ 9.0)
		−67.6 (18F)	122.2	(C-4, quart., $^1J_{C-F}$ 287.0)
			76.71	(C-2, sept., $^2J_{C-F}$ 32.0)
			67.11	(C-3, sept., $^2J_{C-F}$ 28.0)
(**3**)		−69.8 (18F)	164.38	(C-1, s)
		−67.7 (18F)	121.8	(C-4, quart., $^1J_{C-F}$ 287.0)
			76.6	(C-2, sept., $^2J_{C-F}$ 31.8)
			66.8	(C-3, sept., $^2J_{C-F}$ 28.0)

[a] Ref. external 85% H_3PO_4. [b] Ref. internal $CFCl_3$. [c] Ref. internal Me_4Si.

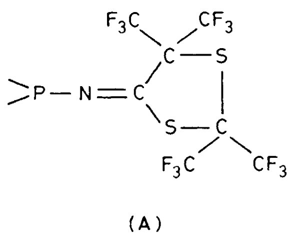


(**1**)

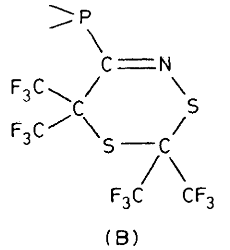


(**2**) E = P

(**3**) E = As



(A)



(B)

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† We cannot rule out a rearranged structure for (**2**) or (**3**) in which nitrogen and sulphur exchange their positions.

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