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Reactions of the Carbanions of Substituted 2-Cyanopropionamides and 2-Cyanothiopropionamides: *O*- and *S*-Methylation with Methyl Trifluoromethanesulfonate

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ABSTRACT: *α-Carbanions of the substituted 2-cyanopropionamides 5 (X = O) and 2-cyanothiopropionamides* **5** *(X = S) react with trifluoromethanesulfonic acid to give the C-protonated systems* **11**, *while methylation with methyl trifluoromethanesulfonate results in O- or S-methylation to give* **12** *(X = O or S). The X-ray crystal structure of* **12c**, *an example of O-methylation, is presented.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:644–650, 1999

INTRODUCTION

We have previously reported [1] the preparation and some properties of the phosphonium zwitterionic system **1**. We have also subsequently demonstrated that such compounds are useful precursors for the preparation of a number of novel compounds and that they also undergo some interesting reactions with isocyanates and isothiocyanates involving rearrangement of the initially formed *N*-anionic intermediates.

Reaction of the zwitterionic system **1** with alkyl halides and similar alkylating agents, as anticipated, resulted in *C*-alkylation to give chiral phosphonium salts [2]. Thus, for example, reaction of **1a** (Alk = Pr^i; Alk′ = Et) with 4-nitrobenzyl bromide gave **2a** (Alk = Pr^i; Alk′ = Et), while methylation with methyl trifluoromethanesulfonate gave **3a** (Alk = Pr^i, Alk′ = Et) (Scheme 1). Due to their proximity to the chiral center in these phosphonium salts, the protons in the P-methylene groups and the two methyls in each isopropyl group in these compounds are nonequivalent in the ^{1}H NMR spectrum.

The reaction of **1** with isocyanates and isothiocyanates was also observed. However, although the reactions of carbanions with isocyanates and isothiocyanates have been known for many years as a route to monosubstituted amides and thioamides

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[3], the carbanionic species **1** behave in a novel way leading to the formation of carbamates **5** via rearrangement of the initially formed nitrogen anions **4** [4–9] (Scheme 2). The structures of these carbamates **5** were established by X-ray crystallography [5–7].

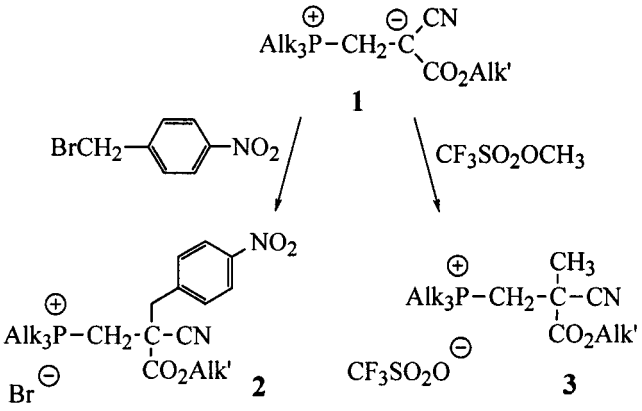
This type of behavior can be viewed overall as the effective insertion of RCNX (X = O, S) into a carbon-carbon bond and appears to have wide applicability. Thus, for example, we have recently shown that the carbanions **7** derived from the cyano ester **6** also undergo reaction with ArCNO, with rearrangement of the initially formed *N*-anion, to give the carbamates **9** (Scheme 3) [9].

Such behavior is, however, limited to anions that do not contain other acidic protons, because if these are present, self-protonation of the *N*-anion **8** can occur before rearrangement, leading to the formation of an *N*-monosubstituted amide.

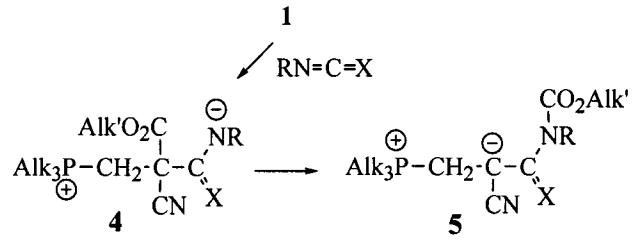
RESULTS AND DISCUSSION

Because of the ready formation of the carbanionic species **5** and **9**, these systems provide a convenient model for investigating the reaction of the α-carbanions of *N,N*-disubstituted amides with electrophilic compounds. There appear to have been relatively few studies on the reactions of such carbanions. Alkylation of several *N,N*-dialkylacetamides at the α-carbon via carbanion intermediates has been reported [10,11]. Due to extensive delocalization of the anionic charge in the zwitterionic system **5**, such systems are relatively weak nucleophiles in comparison with the starting zwitterion **1** and do not undergo reaction with aryl isocyanates, methyl iodide, or 4-nitrobenzyl bromide at room temperature. However, reaction can be achieved with powerful electrophilic agents. So, for example, reaction of **5** (X = O, S) with trifluoromethanesulfonic acid gave the corresponding protonated systems **11** (X = O or S), while methylation with methyl trifluoromethanesulfonate resulted in *X*-alkylation to give **12** (X = O or S) (Scheme 4) rather than a *C*-alkylation product, as observed in the reaction of **1a** described earlier.

The structures of **11** and **12** were determined by NMR spectroscopy, and, for **12c** (R = m-MeC_6H_4, Alk = Pr^i, Alk′ = Me, X = O), the configuration was determined by X-ray analysis (see Figure 1). It is in-



SCHEME 1



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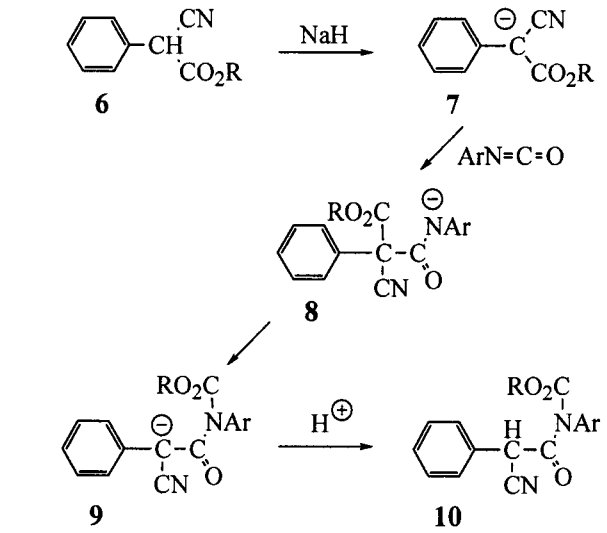

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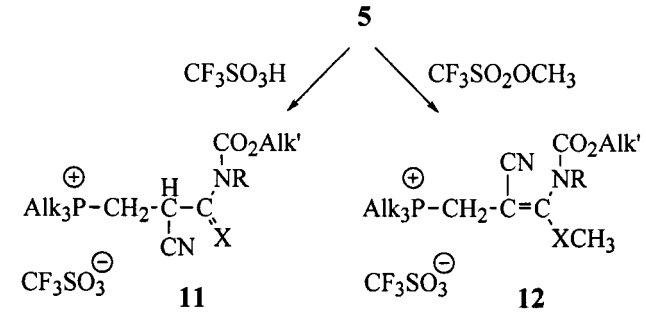

SCHEME 4

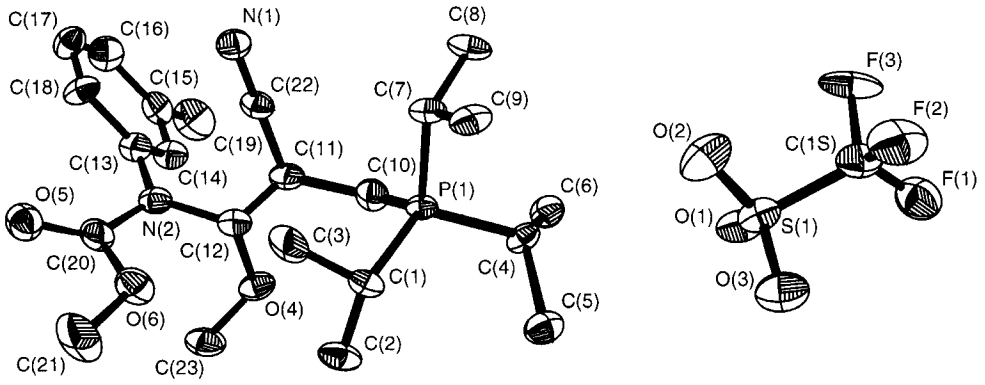

FIGURE 1 The X-ray crystal structure of **12c** showing 50% ellipsoids.

teresting to note that the reactions with methyl trifluoromethanesulfonate led to the formation of only one isomer, with a *trans* arrangement of the CN and XMe groups. Bond lengths and bond angles for **12c** are listed in Tables 1 and 2 using the numbering indicated in Figure 1. The thermodynamic stability of the *Z*-isomers of **12** appears to be high, and no isomerization to the corresponding *E*-isomer or the corresponding *C*-alkylated system was achieved by heating a solution of **12c** in deuteriochloroform at 100°C for 10 hours in a sealed capillary.

The preference for *X*-alkylation in **5** (X = O or S) with methyl trifluoromethanesulfonate would appear to be related to the presence of both the cyano and NC=X groups adjacent to the carbanionic center because *O*-methylation was also observed in the reaction of **9** with methyl trifluoromethanesulfonate. It is also interesting to note that the alkylation of cyanoacetamides was reported to result in the formation of analogous α-alkoxyenamines [12].

The dependence of the position and intensity of the IR band of the CN group on its chemical environment is well known, and we previously commented on the increased intensity and the shift to lower wavenumbers relative to those of the starting cyanoacrylates ($\bar{\nu}_{CN}$ 2200–2250 cm^{-1}) [6] as evidence for extensive delocation of the anionic charge in the zwitterionic systems **1**. The IR spectral data for the CN group of some of the compounds that were prepared in the course of our studies are given in Tables 1 and 2. The compounds in these tables can be divided into three groups: those in which the CN group is adjacent to a carbanionic center as in **5** (Table 1); those in which it is attached to a C=C bond as in **12** (Table 2); and those in which it is attached to an sp^3-carbon (Table 1). For the first group of compounds, we again see the characteristic increase in intensity and shift to lower wavenumbers for the CN band ($\bar{\nu}_{CN}$ 2185 ± 5 cm^{-1}) previously observed in **1**. It is clear that this effect is associated with conjugation between the CN group and the adjacent anionic charge in **5**. A similar interaction also appears to occur in **12**, the second group of compounds, where the CN group is also attached to an sp^2 carbon ($\bar{\nu}_{CN}$ 2223 ± 3 cm^{-1}), although here the increase in intensity and shift to lower wavenumbers is less marked. However, in the third group of compounds, those shown in the lower half of Table 1, where the CN group is attached to a saturated sp^3 carbon, this conjugation effect is no longer possible, and accordingly the position ($\bar{\nu}_{CN}$ 2250 ± 5 cm^{-1}) and intensity of the CN bands are comparable to those observed in other compounds containing nonconjugated CN groups. Further work is continuing.

TABLE 1 Infrared Absorption Bands of the C≡N Group[a]

Compound	$\bar{\nu}_{CN}$ *(cm⁻¹)*
i-$Pr_3P^+CH_2C^-$(CN)C(O)N(m-ClC_6H_4)COOEt **5b**	2180 (vs)
i-$Pr_3P^+CH_2C^-$(CN)C(O)N(p-$O_2NC_6H_4$)COOEt **5d**	2185 (vs)
i-$Pr_3P^+CH_2C^-$(CN)C(S)N(Ph)COOEt **5e**	2190 (vs)
i-$Pr_3P^+CH_2CH$(CN)COOEt $CF_3SO_2O^-$	2256 (w)
i-$Pr_3P^+CH_2C$(CN)(COOEt)($CH_2C_6H_4NO_2$-p) Br^-	2245 (w)
PhC(CN)($CH_2C_6H_4NO_2$-p)C(O)N(Ph)COOMe	2250 (w)

[a]Samples run in KBr discs; (vs), very strong; (w), weak.

EXPERIMENTAL

NMR spectra were recorded on a Bruker (AMX-400) spectrometer, ^1H (400.26 MHz), ^{13}C (100.68 MHz), and ^{31}P(162.02 MHz), (δ ppm, internal reference = TMS, $CDCl_3$ and 80% H_3PO_4 for ^1H, ^{13}C, and ^{31}P spectra respectively). IR spectra were recorded on a Carl Zeiss M-82 spectrometer. The carbamates were prepared as previously described [7]. The reactions were performed under a nitrogen atmosphere.

TABLE 2 Infrared, ^{31}P, and ^{1}H NMR Data for Compounds **12**[a]

						IR $\bar{\nu}$ cm^{-1}		
Ar	*Alk*	*Alk′*	*X*	$\delta(^{31}P)$	$\delta(^{1}H)$ ppm	*C=C*	*C=O*	*CN*
12a Ph	Pr^i	C_2H_5	O	45.30	1.31 t(3H, J_{HH} = 7.2Hz, CH_3CH_2); 1.46 dd (18H, J_{HP} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 2.90 m (3H, $CHCH_3$); 3.51 d (2H, J_{HP} = 12.5 Hz, CH_2-P); 3.93 s (3H, CH_3O); 4.34 q (2H, J_{HP} = 7.2 Hz, CH_2CH_3); 7.27–7.41 m (5H, C_6H_5)	1640	1750	2225
12b m-ClC_6H_4	Pr^i	C_2H_5	O	45.68	1.33 t (3H, J_{HH} = 7.2 Hz, CH_3CH_2); 1.46 dd (18H, J_{HP} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 2.88 m (3H, $CHCH_3$); 3.48 d (2H, J_{HP} = 12.5 Hz, CH_2-P); 3.90 s (3H, CH_3O); 4.35 q (2H, J_{HH} = 7.2 Hz, CH_2CH_3); 7.17–7.35 m (4H, C_6H_4)	1650	1765	2225
12c m-MeC_6H_4	Pr^i	CH_3	O	47.61	1.54 dd (18H, J_{HP} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 2.35 s (3H, $CH_3C_6H_4$); 3.06 m (3H, J_{HH} = 7.2 Hz, $CHCH_3$); 3.74 d (2H, J_{HP} = 12.6 Hz, CH_2-P); 3.87 s (3H, CH_3O); 3.94 s (3H, CH_3O); 7.17–7.35 m (4H, C_6H_4)	1650	1750	2225
12d m,p-$Cl_2C_6H_3$	Pr^i	C_2H_5	O	45.54	1.32 t (3H, J_{HH} = 7.2 Hz, CH_3CH_2); 1.47 dd (18H, J_{HP} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 2.87 m (3H, $CHCH_3$); 3.52 d (2H, J_{HP} = 12.4 Hz, CH_2-P); 3.91 s (3H, CH_3O); 4.35 q (2H, J_{HH} = 7.2 Hz, CH_2CH_3); 7.19–7.50 m (3H, C_6H_3)	1645	1755	2220
12e p-$NO_2C_6H_4$	Pr^i	C_2H_5	O	47.74	1.36 t (3H, J_{HH} = 7.2 Hz, CH_3CH_2); 1.58 dd (18H, J_{HP} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 3.08 m (3H, $CHCH_3$); 3.79 d (2H, J_{HP} = 12.8 Hz, CH_2-P); 4.01 s (3H, CH_3O); 4.45 q (2H, J_{HH} = 7.2Hz, CH_2CH_3); 7.79 d (2H, J_{HH} = 9.2 Hz, C_6H_4); 8.31 d (2H, J_{HH} = 9.2 Hz, C_6H_4)	1652	1755	2220
12f Ph	Pr^i	C_2H_5	S	48.70	1.31 t (3H, J_{HH} = 7.2Hz, CH_3CH_2); 1.59 dd (18H, J_{Hp} = 16.2 Hz, J_{HH} = 7.2 Hz, CH_3CH); 2.43 s (3H, CH_3S); 3.20 m (3H, $CHCH_3$); 3.86 d (2H, J_{HP} = 12.2 Hz, CH_2-P); 4.35 q (2H, J_{HH} = 7.2 Hz, CH_2CH_3); 7.30–7.50 m (5H, C_6H_5)	1580	1758	2224

[a]IR spectra were obtained in KBr discs, NMR spectra were obtained in $CDCl_3$ solution.

General Procedure for the Methylation of Carbamates **5** ($X = O, S$)

To a stirred suspension of the appropriate zwitterion **5** (0.1 g, 0.25 mmol) in dry benzene at room temperature was added dropwise a slight excess of methyl trifluoromethanesulfonate. After the mixture was stirred at room temperature for 1 hour, the solvent was pumped off, and the residue was dissolved in THF (5 mL). The resulting solution was then placed in a refrigerator at $-10°C$ to effect crystallization. Crystals of the corresponding methylated systems **12** were obtained in high yield (typically ca. 90%). The IR spectra of **12** showed bands for the CN, C=C, and CO ester groups, and the C=O amide groups when present. The ^{1}H-NMR spectra were also consistent with the proposed structures (see Table 2). For yields, melting points, and elemental analysis data for compounds **12**, see Table 3.

TABLE 3 Yields, Melting Points, and Elemental Analyses for Compounds **12**

	Yield (%)	m.p. (°C)	Molecular Formula Molecular Weight	Elemental Analysis	Calcd.	(%)	Found	(%)
12a	93	105–108	$C_{24}H_{36}F_3N_2O_6PS$	C	49.32	C	49.30
			568	H	6.16	H	6.15
				N	4.79	N	4.77
				P	5.31	P	5.39
12b	93	84–86	$C_{24}H_{35}ClF_3N_2O_6PS$	C	47.8	C	48.03
			602.5	H	5.81	H	5.97
				N	4.65	N	4.56
				P	5.52	P	5.63
				Cl	5.88	Cl	5.94
12c	92	125–127	$C_{24}H_{36}F_3N_2O_6PS$	C	50.7	C	50.59
			568	H	6.34	H	6.51
				N	4.93	N	4.82
				P	5.46	P	5.49
12d	93	92	$C_{24}H_{34}Cl_2F_3N_2O_6PS$	C	45.21	C	46.21
			637	H	5.34	H	5.39
				N	4.40	N	4.04
				P	4.87	P	4.76
				Cl	10.83	Cl	10.53
12e	93	155	$C_{24}H_{35}F_3N_3O_8PS$	C	46.98	C	46.72
			613	H	5.71	H	5.77
				P	5.06	P	5.07
				N	6.85	N	6.79
12f	93	64–65	$C_{24}H_{36}F_3N_2O_5PS_2$	C	50.32	C	50.70
			584	H	6.16	H	6.50
				N	4.79	N	4.94
				P	5.31	P	5.47
				S	10.96	S	10.84

TABLE 4 Crystal and Structure Refinement Data for **12c**

Empirical Formula	$C_{24}H_{36}F_3N_2O_6PS$
Formula Weight	568.58
Temperature	158(2) K
Wavelength	0.71073 Å
Crystal System	Orthorhombic
Space Group	$P2_12_12_1$
Unit Cell Dimensions	$a = 8.083(2)$ Å $\alpha = 90°$ $b = 8.293(2)$ Å $\beta = 90°$ $c = 41.361(13)$ Å $\gamma = 90°$
Volume, Z	2772.7(12) Å^3, 4
Density (Calculated)	1.362 Mg/m^3
Absorption Coefficient	0.235 mm^{-1}
F(000)	1200
Crystal Size	0.3 × 0.3 × 0.2 mm
θ Range for Data Collection	2.50 to 28.07°
Limiting Indices	$-10 \le h \le 4$, $9 \le k \le 10$, $-47 \le l \le 54$
Reflections Collected	3481
Independent Reflections	3481 ($R_{int} = 0.0000$)
Absorption Correction	None
Refinement Method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	3459/0/343
Goodness-of-Fit on F^2	1.026
Final R Indices [$I > 2\sigma(I)$]	$R1 = 0.0662$, $wR2 = 0.1657$
R Indices (All Data)	$R1 = 0.0767$, $wR2 = 0.1874$
Absolute Structure Parameter	0.0(2)
Largest Diff. Peak and Hole	0.642 and −1.019 eÅ^{-3}

Reaction of **5e** *with Trifluoromethanesulfonic Acid*

To a stirred solution of **5e** (R = p-$NO_2C_6H_4$, Alk = Pr^i, Alk′ = C_2H_5, X = O, 0.05 g, 0.11 mmol) in $CDCl_3$ (1.5 mL) at 0°C was added dropwise trifluoromethanesulfonic acid (0.017 g, 0.11 mmol). The ^{1}H NMR spectra recorded after 15 minutes showed signals for a PCH_2CH group confirming the formation of the *C*-protonated system **11e**.

To a stirred solution of **5e** (0.1 g, 0.22 mmol) in CH_2Cl_2 (5 mL) at room temperature was added dropwise a solution of trifluoromethanesulfonic acid (0.033 g, 0.22 mmol) in CH_2Cl_2 (2 mL). After the mixture was stirred for 15 minutes the solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (2 mL). Addition of hexane (10 mL) to this solution at 0°C resulted in the formation of a colorless precipitate of **11e**, which was filtered off and dried in vacuo. Yield: 0.12 g (88%), m.p. 115–119°C, ^{1}H NMR ($CDCl_3$): 1.15 t (3H, J_{HH} = 7.2 Hz, $C\underline{H}_3CH_2$); 1.51 m (18H, $C\underline{H}_3CH$); 2.89 m (1H, CH_A-P); 3.06 dm (3H, J_{HP} = 19.6 Hz, J_{HH} = 7.2 Hz, $C\underline{H}CH_3$); 3.25 m

TABLE 5 Bond Lengths (Å) for **12c**

S(1)–O(1)	1.433(4)	N(2)–C(12)	1.424(6)
S(1)–O(3)	1.436(4)	N(2)–C(13)	1.435(6)
S(1)–O(2)	1.440(4)	C(1)–C(3)	1.533(7)
S(1)–C(1S)	1.809(7)	C(1)–C(2)	1.538(7)
P(1)–C(10)	1.826(4)	C(4)–C(5)	1.515(7)
P(1)–C(7)	1.828(4)	C(4)–C(6)	1.517(7)
P(1)–C(1)	1.828(4)	C(7)–C(8)	1.531(6)
P(1)–C(4)	1.838(5)	C(7)–C(9)	1.531(6)
F(1)–C(1S)	1.349(7)	C(10)–C(11)	1.498(6)
F(2)–C(1S)	1.324(6)	C(11)–C(12)	1.361(6)
F(3)–C(1S)	1.349(6)	C(11)–C(22)	1.421(6)
O(4)–C(12)	1.338(5)	C(13)–C(14)	1.378(7)
O(4)–C(23)	1.446(6)	C(13)–C(18)	1.398(7)
O(5)–C(20)	1.195(6)	C(14)–C(15)	1.393(7)
O(6)–C(20)	1.348(6)	C(15)–C(16)	1.399(8)
O(6)–C(21)	1.441(7)	C(15)–C(19)	1.512(7)
N(1)–C(22)	1.164(6)	C(16)–C(17)	1.382(8)
N(2)–C(20)	1.382(6)	C(17)–C(18)	1.379(7)

TABLE 6 Bond Angles (degrees) for **12c**

O(1)–S(1)–O(3)	115.1(3)	C(12)–C(11)–C(22)	116.1(4)
O(1)–S(1)–O(2)	115.1(3)	C(12)–C(11)–C(10)	122.5(4)
O(3)–S(1)–O(2)	115.0(3)	C(22)–C(11)–C(10)	121.3(4)
O(1)–S(1)–C(1S)	104.0(2)	O(4)–C(12)–C(11)	119.4(4)
O(3)–S(1)–C(1S)	102.8(3)	O(4)–C(12)–N(2)	120.0(4)
O(2)–S(1)–C(1S)	102.3(3)	C(11)–C(12)–N(2)	120.4(4)
C(10)–P(1)–C(7)	111.2(2)	C(14)–C(13)–C(18)	121.0(5)
C(10)–P(1)–C(1)	109.8(2)	C(14)–C(13)–N(2)	118.4(4)
C(7)–P(1)–C(1)	108.8(2)	C(18)–C(13)–N(2)	120.6(4)
C(10)–P(1)–C(4)	107.6(2)	C(13)–C(14)–C(15)	120.9(5)
C(7)–P(1)–C(4)	106.0(2)	C(14)–C(15)–C(16)	118.3(5)
C(1)–P(1)–C(4)	113.4(2)	C(14)–C(15)–C(19)	119.7(5)
C(12)–O(4)–C(23)	120.2(4)	C(16)–C(15)–C(19)	122.1(5)
C(20)–O(6)–C(21)	116.6(5)	C(17)–C(16)–C(15)	120.1(5)
C(20)–N(2)–C(12)	119.2(4)	C(18)–C(17)–C(16)	121.8(5)
C(20)–N(2)–C(13)	123.3(4)	C(17)–C(18)–C(13)	117.9(5)
C(12)–N(2)–C(13)	117.5(4)	O(5)–C(20)–O(6)	125.3(5)
C(3)–C(1)–C(2)	111.7(4)	O(5)–C(20)–N(2)	125.8(5)
C(3)–C(1)–P(1)	112.5(3)	O(6)–C(20)–N(2)	108.9(4)
C(2)–C(1)–P(1)	111.2(3)	N(1)–C(22)–C(11)	178.6(5)
C(5)–C(4)–C(6)	110.7(5)	F(2)–C(1S)–F(3)	106.9(5)
C(5)–C(4)–P(1)	116.0(4)	F(2)–C(1S)–F(1)	106.7(5)
C(6)–C(4)–P(1)	113.1(3)	F(3)–C(1S)–F(1)	106.4(5)
C(8)–C(7)–C(9)	112.3(4)	F(2)–C(1S)–S(1)	112.3(4)
C(8)–C(7)–P(1)	111.8(3)	F(3)–C(1S)–S(1)	111.7(4)
C(9)–C(7)–P(1)	110.6(3)	F(1)–C(1S)–S(1)	112.5(4)
C(11)–C(10)–P(1)	116.3(3)		

(1H, CH_B-P); 4.37 m (2H, $\underline{CH_2}CH_3$); 5.56 m (1H, CHCN); 7.59 d (2H, J_{HH} = 9.0 Hz, C_6H_4); 8.23 d (2H, J_{HH} = 9.0 Hz, C_6H_4).

^{13}C NMR ($CDCl_3$): 13.64 s ($\underline{C}H_3CH_2$); 15.73 d (CH_2-P, J_{CP} = 45.3 Hz); 16.18 d ($\underline{C}H_3CH$, J_{CP} = 3.1 Hz); 20.12 d ($\underline{C}HCH_3$, J_{CP} = 40.4 Hz); 64.83 s ($O\underline{C}H_2CH_3$); 116 d (CN, J_{CP} = 1.8 Hz); 124.41 d ($C_6\underline{H}_4$); 129.67 d ($\underline{C}HCN$, J_{CP} = 8.5 Hz); 142.46 s (C_6H_4); 147.65 s (C-NO_2); 152,43 s (C(O)N); 165,09 d (C(O)), J_{CP} = 7.6 Hz).

^{31}P NMR ($CDCl_3$): 44.1 ppm

IR (KBr): $\bar{\nu}$ 1745 (CO), 2245 (CN) cm^{-1}

Anal. found, (%): C, 45.83; H, 5.48; N, 6.60; P, 5.05; S, 5.33; Calcd for $C_{23}H_{33}F_3N_3O_8PS$(%): C, 46.08; H, 5.51; N, 7.01; P, 5.18; S, 5.34.

Reaction of **1a** *with Methyl Trifluoromethanesulfonate*

To a stirred solution of 1a (Alk = Pr^i; Alk′ = Et, 0.2 g, 0.7 mmol) in CH_2Cl_2 (3 mL), methyl trifluoromethanesulfonate (0.12g, 0.74 mmol) was added dropwise. The solvent was evaporated in vacuo, and the resulting colorless oil was reprecipitated as an oil from CH_2Cl_2 by addition of hexane. Removal of volatile components in vacuo gave a viscous oil that exhibited only one signal in the ^{31}P NMR spectrum. This material was subsequently identified as the phosphonium salt **3a**.

^{31}P NMR: 44.1 ppm; ^{1}H NMR ($CDCl_3$): 1.89 d (3H, $^3J_{HP}$ = 2.4 Hz, CH_3CCN) (see Ref. [6]).

X-Ray Structure Determination of **12c** (*R = m-MeC_6H_4, Alk = Pr^i, Alk′ = Me, X=O*)

Data were collected with an automated four-circle Siemens P3/PC diffractometer (158 K, Mo Kα-radiation, graphite monochromator, $\theta/2\theta$-scan). Crystallographic details are given in Table 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques with anisotropic approximation for nonhydrogen atoms. The hydrogen atoms were included into the refinement in geometrically calculated positions (riding model) with fixed isotropic thermal parameters. An absorption correction was not necessary and therefore not applied. The absolute structure was determined by Flack parameter refining, which became equal to 0.0(2). The calculations were performed using SHELXTL PLUS (PC Version 5.0) programs [13]. The atom labeling scheme is given in Figure 1, and selected bond lengths and angles are given in Tables 5 and 6. Full atomic coordinates, bond distances and angles, and anisotropic temperature factors have been deposited with the Cambridge Crystallographic Data Center.

REFERENCES

[1] Gololobov, Yu. G.; Kolomnikova, G. D.; Krylova, T. O. Tetrahedron Lett 1994, 35, 1751.

[2] Krylova, T. O.; Kolomnikova, G. D.; Petrovskii, P. V.; Gololobov, Yu. G. Izvest Akad Nauk Ser Khim 1994, 1641; Russ Chem Bull 1994, 43, 1553.

[3] Boyd, R. N.; Leshim, R. J Amer Chem Soc 1953, 75, 2762.

[4] Gololobov, Yu. G.; Kolomnikova, G. D.; Krylova, T. O. Izvest Akad Nauk Ser Khim 1995, 186; Russ Chem Bull 1995, 44, 181.

[5] Krylova, T. O.; Shishkin, O. V.; Struchkov, Yu. T.; Kolomnikova, G. D.; Gololobov, Yu. G. Zhur Obshch Khim 1995, 65, 1393; J Gen Chem 1995, 65, 1275.

[6] Gololobov, Yu. G.; Pinchuk, V. A.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. Phosphorus, Sulfur, Silicon Relat Elem 1996, 115, 19.

[7] Gololobov, Yu. G.; Kardanov, N. A.; Khroustalyov, V. N.; Petrovskii, P. V. Tetrahedron Lett 1997, 38, 7437.

[8] Gololobov, Yu. G.; Petrovskii, P. V. Izvest Akad Nauk Ser Khim, 1996, 2377; Russ Chem Bull 1996, 45, 2258.

[9] Gololobov, Yu. G.; Galkina, M. A.; Kuzminseva, I. Yu.; Petrovskii, P. V. Izvest Akad Nauk Ser Khim, 1998, 1878; Russ Chem Bull 1998, 47, 1832.

[10] Needles, H. L.; Whitfield, R. E. J Org Chem 1966, 31, 989.
[11] Crouse, D. N.; Seebach, D. Chem Ber 1968, 101, 3113.
[12] Ahlbrecht, H.; Vonderheid, C. Chem Ber 1973, 106, 2009.
[13] Sheldrick, G. M. SHELXTL PC, version 5.0. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.