<u>Tetrakis(2,2,3,3-tetrafluoropropoxy)methylphosphorane (IIIb)</u> was obtained in 72% yield, $\delta P = -48$ ppm. PMR spectrum in CD_3CN: 1.90 d (PCH_3, 3H, $^2J_{PCH} = 16$; s in the $^1H-\{^{31}P\}$ DNMR spectrum, $\omega = 40477.621$ Hz), 4.46 m ($POCH_2$, 8H, $^3J_{FH} = 13.5$, $^3J_{PH} = 6$, $^4J_{FH} = 1$; br.t in the $^1H-\{^{31}P\}$ DNMR spectrum), 6.32 t.t (CHF_2, 4H, $^2J_{FH} = 52.5$, $^3J_{FH} = 4.7$). Found: C, 26.79; H, 2.57%. Calculated for $C_{13}H_{15}F_{16}O_4P$: C, 26.85; H, 2.65%.

<u>Tetrakis(1,1,5-trihydroperfluoropentyloxy)methylphosphorane (IIIc)</u> was obtained in 68% yield, bp 130-135°C (0.04 mm), $\delta P = -49$ ppm. PMR spectrum in 1:1 CCl_4 + 50% CD_3CN: 1.80 d ($P-CH_3$, 3H, $^2J_{PCH} = 17$), 4.40 br.t.d ($POCH_2$, 8H, $^3J_{FH} = 13$, $^3J_{PH} = 6$), 6.10 t.t (CHF_2, 4H, $^2J_{PCH} = 50.5$, $^3J_{FH} = 5$). Found: C, 26.09; H, 1.77%. Calculated for $C_{21}H_{15}F_{32}O_4P$: C, 25.97; H, 1.54%.

<u>Bis(2,2,2-trifluoroethoxy)methylphosphonate (IV)</u> was obtained from 0.011 mole salt (Ia) and 0.012 mole 2-propanol in 89% yield, bp 75-77°C (10 mm), $\delta P = 33$ ppm. PMR spectrum in CCl_4: 1.52 d ($P-CH_3$, 3H, $^2J_{PCH} = 18.5$; s in the $^1H-\{^{31}P\}$ DNMR spectrum, $\omega = 40480.908$ Hz), 4.36 two d.q ($POCH_2$, 4H, $^3J_{PH} \approx {}^3J_{FH} = 9$; two q in the $^1H-\{^{31}P\}$ DNMR spectrum). Found: C, 23.12; H, 2.77%. Calculated for $C_5H_7F_6O_3P$: C, 23.07; H, 2.69%.

The ^1H and $^1H-\{^{31}P\}$ NMR spectra were taken on a Varian HA 100D spectrometer at 100 MHz for (Ia), (Ic), (IIIa), (IIIb), and (IV) and on a Tesla BS 467A spectrometer at 60 MHz for (Ib) and (IIIc). The $^{31}P-\{^1H\}$ NMR spectra were taken on an RYa-2303 spectrometer at 8 MHz by E. I. Gol'dfarb, to whom the authors are sincerely grateful.

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REACTION OF PHENYLSULFENYL CHLORIDE WITH C-(N,N-DIMETHYLAMINO)-METHYLENE-P-PHENYLPHOSPHINE

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PhSCl adds regiospecifically to the P=C double bond in C-(N,N-dimethylamino)-methylene-P-phenylphosphine to give $PhP(SPh)_2$ and Cl_2CHNMe_2.

Regitz [1] and Schmidtpeter [2] have shown that sulfenyl chlorides add at the P=C bond of 1,2,3-diazaphospholes to give unstable addition products with sulfur-carbon and phosphorus-chlorine bonds. The regiospecificity of the addition of sulfenyl chlorides to these dicoordinated phosphorus compounds corresponds to the polarization of the P=C bond arising due to the difference in the electronegativities of the component atoms. C-dialkylaminophosphaalkenes have opposite polarization of the P=C double bond [3], which, in turn, may lead to reverse addition in the reaction of sulfenyl chlorides with such phosphaalkenes.

In order to check this hypothesis, we carried out the reaction of C-(N,N-dimethylamino)methylene-P-phenylphosphine (I) with phenylsulfenyl chloride (II). Completion of this reaction requires a (I):(II) mole ratio equal to 1:2.

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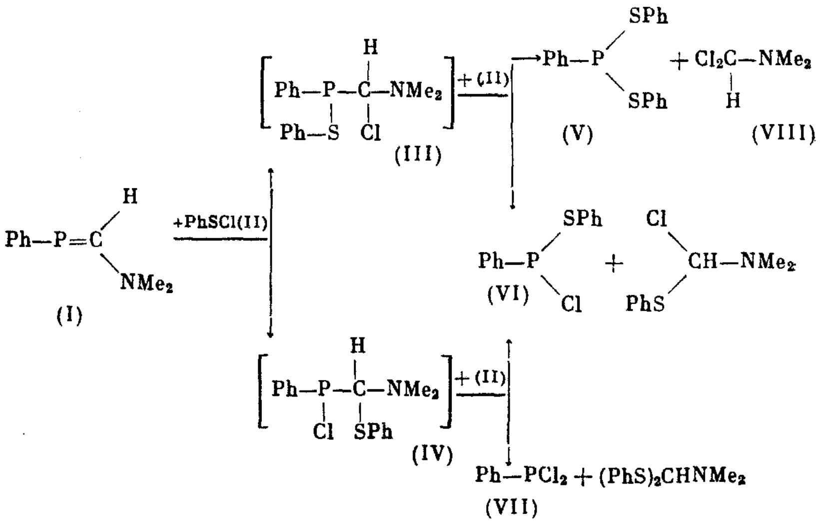

We have found that the reaction does not stop at the addition of one mole of (II) and proceeds with complete cleavage of the P-C bond in (I). The major phosphorus-containing product of this reaction is bis(phenylthio)phenylphosphinite (V). Phenyldichlorophosphine (VII) is the product of the reverse addition of the sulfenyl chloride but was not detected even in the ^{31}P NMR spectra of the reaction mixtures. (Phenylthio)phenylchlorophosphine (VI) was noted in the spectra of the reaction mixtures but only in small amounts. The ^{31}P NMR signal for (VI) is found at 141.9 ppm [4,5]. The (V):(VI) ratio in the reaction mixtures ranges from 6:1 to 7:2 as indicated by ^{31}P NMR spectroscopy. Product (VI) may be obtained either from intermediate (III) with a P-S fragment upon reverse addition of a second molecule of (II) or from intermediate (IV) with a P-Cl fragment by an addition scheme differing from that in the initial step for the addition of sulfenyl chloride (II). N,N-Dimethylamino(dichloro)methane (VII) was isolated as the only nitrogen-containing compound in this reaction.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a Bruker M-250 spectrometer. All the operations were carried out in argon.

A sample of 2.2 g (0.012 mole) (I) was added to 6.4 g (0.052 mole) phenylsulfenyl chloride (II) in 15 ml acetonitrile at 0°C. The crystalline precipitate formed upon completion of the exothermal reaction was filtered off and recrystallized from acetonitrile. The yield of N,N-dimethylamino(dichloro)methane (VIII) was 1.25 g (73%), mp 140°C (sealed capillary) [6]. Distillation of the filtrate gave 2.04 g (47%) (V), bp 146-147°C (0.01 mm) [7]. ^{31}P NMR spectrum: $\delta = 90.0$ ppm [7]. Found: P, 8.80%. Calculated for $C_{18}H_{15}PS_2$: P, 9.51%.

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