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PHOTOREACTIONS OF TETRAFLUORODIPHOSPHINE WITH ALKYNES

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SUMMARY

The reactions of tetrafluorodiphosphine with several alkynes in the gas phase and under UV irradiation were studied. Simple addition products were obtained in substantial yield from CF_3CCH, CF_3CCCH_3, and CF_3CCCF_3. Methyl substituted alkynes gave little volatile product while ethyne and diphenyl ethyne gave no volatile addition products. Non-volatile byproducts were obtained, probably polymers, in substantial quantity in the latter instances. Volatile products were characterized by IR and NMR spectra and by mass spectrometry.

INTRODUCTION

We have previously reported that tetrafluorodiphosphine, P_2F_4, adds to carbon-carbon double bonds under UV irradiation to give bidentate phosphine ligands [1-3]. Coordination chemistry of two of these has also been reported [4-7]. We now report the results of our continuing work with this free-radical precursor in its reactions with a variety of alkynes. In general one anticipates addition similar to that observed for the alkenes except that steric effects may differ, two mole addition is possible, and cis/trans isomers may be observed in the product mix.

EXPERIMENTAL

Standard high vacuum techniques were utilized throughout. Infrared spectral data were recorded for gaseous samples in a 75mm cell with KBr windows using a Beckman IR-20-A or a Perkin Elmer 599 spectrometer calibrated with a polystyrene film. ^{1}H, ^{19}F and ^{31}P nmr spectra were recorded using either a Varian XL-100 or a JEOL FX-90Q spectrometer. Chemical shifts are reported positive downfield from TMS, $CFCl_3$ and 85% H_3PO_4 respectively. External standards were used unless otherwise noted.

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Mass spectra were obtained for gas samples with a Hitachi-Perkin-Elmer RMU-6E spectrometer. GC/MS data were obtained with a LKB-2091 instrument. A Rayonet photochemical reactor (Southern New England Ultraviolet Co., Middleton, CT) containing reactor lamps RPR-3000A was used as the energy source. The photoreaction tube used consisted of a 200-mL quartz tube attached to a vacuum stopcock and a 10/30 joint to allow entry to the vacuum line. A modification of this device having a second tube (50 mL) connected via a bridging stopcock was used in some instances to assure mixing of the two reactants in the gas phase.

Materials

P_2F_4 was prepared by the method of Centofanti and Rudolph [8]. Ethyne (Matheson), diphenylethyne, 2-butyne (Pfalz and Bauer), and propyne (Columbia Organic Chemical Co.) were distilled before use. 1,1,1-Trifluoropropyne, 1,1,1-trifluoro-2-butyne and perfluoro-2-butyne were prepared by literature methods [9]. 1,1,1,4,4,4-Hexafluoro-2-butyne was prepared via the reaction of 2-butynedioic acid (Aldrich) with sulfur tetrafluoride (PCR). A 26.7 mmol sample of HO_2CCCCO_2H, 180 mmol SF_4 and 11 mmol BF_3 were condensed in a stainless steel bomb and heated for 8 h at 170-180 °C. Upon cooling and fractionation, 6.1 mmol of CF_3CCCF_3 was obtained.

Reaction of P_2F_4 with C_2H_2

In a typical reaction 1.3 mmol of C_2H_2 and 1.3 mmol of P_2F_4 were frozen into the quartz tube. The contents were allowed to warm to room temperature with no evidence of reaction. After 2-4 hours of irradiation there was an orange-gold colored film on the walls of the reactor, typical of photolysis of P_2F_4. The reaction mixture was fractionated to recover only PF_3,a small quantity of PF_2H and unreacted C_2H_2, though about half that charged was not recovered in the volatile products. The same reaction was carried out in 5 ml of dry toluene with essentially the same result. The orange solid remaining in the reaction vessel in this case showed only broad bands between 800-1300 cm^{-1} in the infrared spectrum.

Reaction with PhCCPh

Diphenylethyne, 1.57 mmol, and 0.85 mmol of P_2F_4 were condensed with 10 mL toluene in the quartz reactor and photolyzed for 2.5 h. A yellow-orange solution and solid precipitate formed. Fractionation gave PF_3 as the only volatile product (in addition to solvent). The precipitate, apparently polymeric, was not further characterized.

Reaction with other alkynes

Succeeding experiments were carried out by condensing the two reactants in the quartz reactor, allowing them to warm to room temperature and photolyzing the gaseous mixtures for periods of 2-4 h. In some instances, as noted below, reaction to give nonvolatile products was observed as the two reagents mixed in the liquid phase. In these instances, the two reagents were either frozen at different levels in the reactor so they did not mix before vaporizing or were condensed separately in the two-armed reactor, described earlier, where they again vaporized prior to mixing. Typical quantities used were 0.75-1.25 mmol. Reaction mixtures were fractionated (usually -45°, -95°, -126°, -196 °C) on the vacuum line and the fractions containing P_2F_4 and the alkyne returned to the reaction vessel. Irradiation and fractionation were repeated a total of three times in general. By that time any remaining P_2F_4 was essentially completely converted to PF_3. Reactant ratios used and volatile products obtained with product yield and trap temperature are summarized in Table I. In general

TABLE I
Photoreactions of P_2F_4 with alkynes

Alkyne	P_2F_4/alkyne ratio	Principle volatile products (Yield)
$CH_3C\ CH$	1:1	$CH_3C(PF_2)=C(PF_2)H$ (5%)
		$CH_3C(PF_2)_2C(PF_2)_2H$ (5%)
	2:1	$CH_3C(PF_2)_2C(PF_2)_2H$ (20%)
$CH_3C\ CCH_3$	1:1	$CH_3C(PF_2)=C(PF_2)CH_3$ (10%)
$CF_3C\ CH$	1:1	$CF_3C(PF_2)=C(PF_2)H$ (25%)
$CF_3C\ CCH_3$	1:1	$CF_3C(PF_2)=C(PF_2)CH_3$ (60%)
$CF_3C\ CCF_3$	1:1	$CF_3C(PF_2)=C(PF_2)CF_3$ (65%)
HC CH	1:1	
PhC CPh	1:1	

the quartz reaction vessel was coated with an orange 'metallic' appearing film characteristic of the photolysis of P_2F_4 as well as varying quantities of additional solid materials which are assumed to be polymeric but have not yet been characterized.

Physical data

NMR and IR parameters measured for volatile products are listed in Tables II and III, respectively. (P-H coupling was not resolved in the nmr spectra.) Vapor pressure and mass spectral data are given below. Assignments and relative intensities are given for the principal peaks essential to identification of the compound.

$CH_3(PF_2)CCH(PF_2)$, $C_3H_4P_2F_4$. Vapor pressure at 0.0 °C, 17.0 mmHg. 178 ($C_3H_4P_2F_4^+$, 50); 159 ($C_3H_4P_2F_3^+$, 11); 109 ($C_3H_4PF_2^+$, 99); 89 ($C_3H_3PF^+$, PF_3H^+, 18); 76 ($C_2H_2PF^+$, 10); 72 ($C_3H_5P^+$, 23); 69 (PF_2^+, $C_3H_2P^+$, 100); 68 (C_3HP^+, 9); 58 ($C_2H_3P^+$, 11); 50 (PF^+, 12); 43 (CP^+, 47); 41 ($C_3H_5^+$, 15); 39 ($C_3H_3^+$, 48); 38 ($C_3H_2^+$, 15).

$CH_3C(PF_2)_2CH(PF_2)_2$, $C_3H_4P_4F_8$. No vapor pressure data recorded. 316 ($C_3H_4P_4F_8^+$, 6); 247 ($C_3H_4P_3F_6^+$, 9); 178 ($C_3H_4P_2F_4^+$, 7); 159 ($C_3H_4P_2F_3^+$, 25); 109 ($C_3H_4PF_2^+$, 28); 89 ($C_3H_3PF^+$, PF_3H^+, 19); 71 ($C_3H_4P^+$, 73); 69 (PF_2^+, $C_3H_2P^+$, 100); 65 (CH_3PF^+, 12); 50 (PF^+, 12); 41 ($C_3H_5^+$, 10); 39 ($C_3H_3^+$, 28); 38 ($C_3H_2^+$, 8).

$CH_3C(PF_2)C(PF_2)CH_3$, $C_4H_6P_2F_4$. V.p. 9.5 mmHg at 22 °C. 192 ($C_4H_6P_2F_4^+$, 18); 173 ($C_4H_6P_2F_3^+$, 1); 123 ($C_4H_6PF_2^+$, 100); 103 ($C_4H_5PF^+$, 5); 96 ($C_4H_6P_2F_4^+$, 1); 89 ($C_3H_3PF^+$, PF_3H^+, 2); 77 ($C_4H_5P_2F_2^{2+}$?, 6); 69 (PF_2^+, $C_3H_2P^+$, 71); 54 ($C_4H_6^+$, 28); 53 ($C_4H_5^+$, 96). Second isomer gave essentially the same pattern except m/e54 peak had intensity 1; see text.

$CF_3C(PF_2)C(PF_2)CH_3$, $C_4H_3P_2F_7$. V.p. 23.0 °C, 23 mmHg; 0.0 °C, 4.5 mmHg; -23 °C, 1 mmHg. 247 ($C_4H_4P_2F_7^+$, 3); 178 ($C_4H_4PF_5^+$, $C_3H_4P_2F_4^+$, 7); 140 ($C_4H_4PF_3^+$, $C_3H_4P_2F_2^+$, 4); 138 ($P_2F_4^+$, $CF_3PF_2^+$, 2); 116 ($C_6H_6F_2^+$?, 19); 109 ($C_4H_4F_3^+$, $C_3H_4PF_2^+$, 1); 107 ($C_4H_2F_3^+$, 1); 105 ($C_4F_3^+$, 1); 93 ($C_3F_3^+$, 2); 90 ($C_4H_4F_2^+$, 5); 89 ($C_4H_3F_2^+$, PF_3H^+, 100); 88 ($C_4H_2F_2^+$, PF_3^+, 11); 70 (PF_2H^+, CF_3H^+, $C_4H_3F^+$, 11); 69 (PF_2^+, CF_3^+, $C_4H_2F^+$, 92); plus peaks due to benzene (see text).

$CF_3C(PF_2)C(PF_2)H$, $C_3HP_2F_7$. V.p. 0.0 °C, 42 mmHg. 232 ($C_3HP2F_7^+$, 7); 213 ($C_3HP_2F_6^+$, 7); 163 ($C_3HPF_5^+$, $C_2HP_2F_4^+$, 21); 143 ($C_3F_4P^+$, $C_2P_2F_3^+$, 11); 138 ($CF_3PF_2^+$, $P_2F_4^+$, 16); 125 ($C_3HPF_3^+$, $C_2HP_2F_2^+$, 36); 106 ($C_3HPF_2^+$, $C_2HP_2F^+$, 13); 93 ($C_2PF_2^+$, $C_3F_3^+$, 6); 88 (PF_3^+, CF_4^+, 9); 81 ($C_2F_3^+$, CPF_2^+,

TABLE II.

Infrared Spectra of Volatile Products: P_2F_4 + Alkynes

$CH_3(PF_2)C{=}C(PF_2)H$	$CH_3(PF_2)_2CC(PF_2)_2H$	$CH_3C(PF_2)C(PF_2)CH_3$	$CF_3C(PF_2)C(PF_2)H$	$CF_3C(PF_2)C(PF_2)CH_3$	$CF_3C(PF_2)C(PF_2)CF_3$
2970 m	2972 m	2940 (m)		2990 (w)	
2925 w	2941 w	2880 (w)		2930 (w)	
2860 (vw)	2895 w				
1650 (w)					1675 (w)
1605 (m)		1615 (w)		1585 (m)	
1568 (w)		1585 (vw)		1440 (w)	
1480 (m)	1460 (w)	1435 (m)			1370 (w)
1390 (m)	1390 (w)		1380 (w)	1375 (w)	
1370 (sh)	1375 (sh)	1385 (m)	1322 (m)	1260 (s)	1230 (s)
			1280 (m)	1205 (s)	
		1190 (m)	1235 (m)		
1105 (m)	1075 (w)		1170 (s)	1190 (sh)	1180 (s)
1030 (m)	1025 (m)	1055 (s)	1099 (w)	1145 (s)	1155 (vs)
				1130 (sh)	1010 (w)
1000 (m)				1000 (m)	
			968 (m)	960 (w)	
972 (m)			917 (m)	940 (w)	860 (sh)
				890 (w)	
945 (m)		950 (m)	880 (sh)	825 (vs)	830 (s)
930 (m)		925 (sh)	827 (s)	760 (m)	810 (sh)
		890 (s)			
		865 (sh)			
892 (m)		850 (sh)			
820 (vs)	830 (s)	815 (vs)			
680 (s)	730 (m)	740 (m)	730 (m)	725 (m)	745 (m)
610 (m)		660 (s)	605 (m)	677 (m)	695 (m)
					660 (s)
					625 (w)

TABLE III.

Nmr Spectra of Volatile Products: P_2F_4 + Alkynes

Compound	^1H	^{31}P	^{19}F
$CH_3(PF_2)CC(PF_2)H$ (C_6D_6)	δ = 1.8 (area 1, CH) broad, unresolved multiplet	δ = 198.9; J_{PF} = 1185 Hz (t) unresolved fine structure; broader of two triplet signals	δ = -96.2; J_{PF} = 1167 Hz (d) broader of two doublets
	δ = 1.2 (area 3, CH_3) broad unresolved multiplet	δ = 205.6; J_{PF} = 1173 Hz (t) unresolved fine structure	δ = -94.7; J_{PF}; = 1172 Hz (d)
$CH_3(PF_2)_2CC(PF_2)_2H$	δ = 2.1 (area 1) unresolved multiplet	δ = 220.9; J_{PF} = 1213 Hz (t) at least 9 peaks/multiplet	δ = -98.4; J_{PF} = 1191 Hz (d) each a triplet, J ≈ 28 Hz
	δ = 1.3 (Area 3) J_{PH} = 12 H_z, (t)	δ = 233.1; J_{PF} = 1222 Hz (t) less well resolved	δ = -89.5, J_{PF} = 1196 Hz (d)
$CH_3(PF_2)CC(PF_2)CH_3$	δ = 1.75, broad multiplet	δ = 199.5; J_{PF} = 1173 Hz (t)	δ = -99.8; J_{PF} = 1110 Hz (area 1) (d) δ = -103.9, J_{PF} = 1165 Hz (area 2) (d)
$CF_3(PF_2)CC(PF_2)H$	δ = 6.9 complex multiplet, J = 4, 14 Hz (quartet of doublets?)	δ = 191; J_{PF} = 1200 Hz (t) complex multiplet δ = 187; J_{PF} = 1221 Hz (t)	δ = -57.1; $^3J_{PF}$ = 62 Hz (d) δ = -92.5; $^1J_{PF}$ = 1220 Hz (d) } area 1 δ = -93.5; $^1J_{PF}$ = 1195 Hz (d) } δ = -94.9, $^1J_{PF}$ = 1175 Hz (d) } area 0.1 δ = -93; $^1J_{PF}$ <1200 Hz (d) } (lower peak obscured)
$CF_3(PF_2)CC(PF_2)CH_3$	δ = 1.97; J = 2 Hz δ = 1.81	δ = 191.0; J_{PP} = 14.6 Hz{^{19}F} (d) δ = 189.2; J_{PP} = 7.5 Hz {^{19}F} (d) J_{PF} = 1200 Hz (second order)	δ = -50.9; $^3J_{PF}$ = 95 Hz (d) δ = -99; $^1J_{PF}$ = 1220 Hz Second order, not right to left symmetric
$CF_3(PF_2)CC(PF_2)CF_3$*		δ = 179 Hz; $^1J_{PF}$ = 1238 Hz (t) $^3J_{PF}$ = 87 Hz (q)	δ = -50.9; $^3J_{PF}$ = 94 Hz (d) ^4J = 10 Hz (t?) δ = -92.1; J_{PF} = 1243 Hz (d)

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*no suggestion of second isomer in either spectrum.

9); 75 ($C_3HF_2^+$, 94); 69 (CF_3^+, PF_2^+, 100); 57 ($C_3H_2F^+$, 20); 56 (C_3HF^+, 11); 55 (C_3F^+, 7); 50 (CF_2^+, PF_2+, 22).

$CF_3C(PF_2)C(PF_2)CF_3$, $C_4P_2F_{10}$. V.p. 19 °C, 45 mmHg; 0.0 °C, 13.5 mmHg; -23 °C, 0.5 mmHg. 300 ($C_4P_2F_{10}^+$, 4); 281 ($C_4P_2F_9^+$, 4); 231 ($C_4PF_8^+$, $C_3P_2F_7^+$, 16); 212 ($C_4PF_7^+$, $C_3P_2F_6^+$, 4); 193 ($C_4PF_6^+$, $C_3P_2F_5^+$, 16); 155 ($C_4PF_4^+$, $C_3P_2F_3^+$, 6); 143 ($C_3PF_4^+$, $C_2P_2F_3^+$, 46); 124 ($C_3PF_3^+$, $C_2P_2F_2^+$, 56); 105 ($C_3PF_2^+$, $C_2P_2F^+$, $C_4F_3^+$, 25); 93 ($C_2PF_2^+$, $C_3F_3^+$, 30); 81 ($C_2F_3^+$, CPF_2^+, 10); 69 (PF_2^+, CF_3^+, 100); 50 (PF^+, CF_2^+, 6).

RESULTS AND DISCUSSION

Products of the reactions described were characterized by means of their gas phase infrared spectra, by mass spectroscopy, and by NMR spectroscopy. The infrared spectra, Table II, show the peaks expected in the CH, C=C, and PF stretching regions. The mass spectral fragmentations are consistent with the presence of the expected structural components. NMR spectra show the expected resonances, Table III, and provide further evidence for specific isomers, as discussed below.

The isolation of useful yields of bifunctional fluorophosphines by means of the photoreaction of P_2F_4 to alkynes is highly dependent on the alkyne involved. As can be seen in Table I, increasing the extent of fluorination of the alkyne is the dominant factor among the alkynes used in these experiments. Neither acetylene itself nor diphenylacetylene gave any isolable volatile product. This appears to contrast directly with the results obtained with alkenes where the higher the extent of fluorination, the poorer the yields [3]. We believe there are two reasons for this. It is expected that the phosphorus centered radical is quite electrophilic. In the alkenes, fluorine attached to the carbon in the double bond should reduce electron density in the bond, limiting its susceptibility to electrophilic attack, while in the alkynes the fluorine is necessarily one carbon atom removed and therefore less effectively electron withdrawing. The second factor involves the competing formation of polymeric materials. With acetylene and with diphenylacetylene, in particular, the failure to isolate volatile addition products appeared due largely to this factor. With the alkenes, the extent of substitution adjacent to the double bond also is a negative factor in product formation [2]. This is certainly a result of steric interference with the incoming PF_2 moiety. No such interference is of consequence in the present instance.

As expected, cis/trans isomerism is apparent in these addition reactions and the distribution is essentially random in the two cases where we were able to make that determination. Separation and quantification of the isomers is the ideal procedure, but this is hampered by the small quantities of materials prepared in this study and by their high sensitivity to oxidation. GC/MS was successful in the case of $CH_3C(PF_2)C=C(PF_2)CH_3$ in demonstrating the presence of two isomers in similar abundance. A sample of the product mixture in benzene solution was injected into an OV101 column with the GC oven at ambient temperature. Among the six peaks resulting (in addition to solvent) were four which were clearly identifiable from the MS data. Two with relatively short retention times corresponded to $C_4H_6P_2F_4$ while two with somewhat longer retention times gave peaks at m/e=P+16 and P+32, corresponding to the oxidized compound. The multiple GC peaks obtained suggested substantial reaction in the experimental system so that no quantitative conclusion can be drawn regarding relative abundance of the two isomers, except that they appear similar. Experiments with other compounds were even less conclusive.

NMR data indicate that approximately equal quantities of two isomers are present in $CF_3C(PF_2)C=C(PF_2)CH_3$. As shown in Table III, two signals of essentially equal intensity were obtained in the ^1H spectrum. The difference in coupling in the two signals indicates two different methyl groups, appropriate to two different isomers. Similarly, the ^{19}F decoupled ^{31}P spectrum shows two signals, each apparently a doublet but with different peak separations. The two ^{31}P signals expected of one isomer of this compound could give a doublet of doublets due to splitting of each phosphorus signal by the other, but the coupling constants should be the same. Again, the two signals are of similar intensity suggesting similar amounts of two isomers.

The potential to add two moles of P_2F_4 was demonstrated only with CH_3CCH. In that case, two mole addition was sufficiently facile that both products were obtained in comparable yield even when a 1:1 reaction ratio was used. In other instances two mole addition products were either nonvolatile and inseparable from the inevitable polymeric products produced in these reactions or were not formed. In either event, they were not identified.

In summary the photoreaction of P_2F_4 with alkynes gives sufficiently high yields of product when fluorinated alkynes are used that subsequent chemistry, e.g. coordination with metals, of the products can be explored.

The probable presence of both cis and trans isomers of the potential ligands in the product mixtures will certainly complicate their study, however, and effectively reduces the product yield for a given isomer to about half of the bulk yield. Nonetheless, the potential electronic characteristics of a chelate ring containing e.g $CF_3C(PF_2)C{=}C(PF_2)CF_3$ may warrant the attempt.

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