stoichiometric pathway:

$$2RCOOH{\cdot}R'_3N + N_3P_3Cl_6 = (RCO)_2O + R'_3N{\cdot}HCl + 2$$

On the basis of IR evidence, we could establish that this reaction proceeds to completion within a few minutes in the temperature range −10–0 °C and can be carried out in a large variety of organic solvents. All the carboxylic acids tested (acetic, propionic, benzoic, *p*-toluic, succinic, ethylenediaminetetraacetic, phthalic, pyromellitic, and polyacrylic) were successfully converted into the corresponding anhydrides. Compound **2** has been isolated as the triethylammonium salt. It was found unable to promote further conversion of carboxlyic acid salts into anhydrides, although an unidentified and slow reaction could be observed.

The structure of **2** has been established on the basis of elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopy. In fact, the IR spectrum shows two strong bands at 1215 and 1170 cm^{-1}, attributed to the P=N and P—O^- bonds, two strong bands at 590 and 520 cm^{-1} related to the P–Cl bonds and the characteristic bands of Et_3N^+H ion. The ^1H NMR spectrum is consistent with that expected for triethylammonium ion, and the ^{31}P NMR spectrum shows a triplet centered at 1.93 ppm, attributed to the P atom in position 2, and a doublet centered at −21.09 ppm, attributed to P atoms in positions 4 and 6.

The reaction has been applied to the preparation of linear polyacrylic anhydride using a polyacrylic acid with M_r 150 000 as the starting material. In this case, the reaction was not quantitative, possibly because of steric hindrance, but the conversion of the carboxylic acid into anhydride was sufficiently large, ranging between 75 and 90%.

Experimental Section

Materials. $N_3P_3Cl_6$ was purchased from EGA-Chemie, West Germany, and was recrystallized from *n*-heptane, mp 113–114 °C. Polyacrylic acid, M_r 150 000, was supplied as an aqueous solution by Polyscience Inc. It was purified by dialysis, recovered by lyophilization, and dried at 50 °C under vacuum. Carboxylic acids were pure grade products; triethylamine, tri-*n*-butylamine, and pure grade solvents were purified and dried by standard methods. Isolated chemicals (Et_3NHCl and ArCOOCOAr) were identified by comparison of their IR spectra and melting points with those of authentic samples.

Physical Measurements. Melting points were taken in open capillary tubes and are uncorrected. The IR spectra were recorded by using a 577 Perkin-Elmer spectrophotometer. ^1H NMR and ^{31}P NMR spectra were recorded with a WP-80DS Bruker NMR spectrometer.

Procedure for Detection of Anhydride Formation. Carboxylic acid (2 mequiv) was dissolved in CH_2Cl_2 (6–10 mL) with the addition of Et_3N or $(n\text{-}Bu)_3N$ (2 mmol). With stirring $N_3P_3Cl_6$ (1 mmol) was added as a solid to the carboxlyate solution kept in a cold bath (−10–0 °C). Immediately after dissolution (about 1 min), the reaction mixture was put into an IR cell (path length 0.1 mm), and the spectrum was recorded. The total operation time was ~8 min. The IR spectra were identical with those obtained at longer reaction times.[9]

Preparation of Benzoic Anhydride. Benzoic acid (4.88 g, 0.04 mol) was dissolved in dry Et_2O (100 mL) and was neutralized by addition of 4.04 g (0.04 mol) of Et_3N. The solution was cooled to −10 °C, and then 6.94 g (0.02 mol) of $N_3P_3Cl_6$ was added with stirring. Immediately an exothermic reaction took place, with consequent formation of a white precipitate. The mixture was kept for 20 min at −10 °C and then filtered. The insoluble product (yield 2.60 g, 0.019 mol) was identified as pure $Et_3N{\cdot}HCl$. The clear solution was passed through a silica gel chromatographic column and eluted by dry Et_2O. Pure benzoic anhydride (0.42 g, 0.018 mol) was recovered from the eluate, while the triethylammonium salt of the halocyclophosphazene derivative was completely retained by the column.

Preparation of Polyacrylic Anhydride. Polyacrylic acid (4.2 g) and 10.9 g of $n\text{-}Bu_3N$ were dissolved at room temperature in 100 mL of CH_2Cl_2. $N_3P_3Cl_6$ (10.15 g) was added with stirring to the salt solution. After 30 min, 200 mL of Et_2O was added to the clear reaction mixture. A gelatinous precipitate of crude polymeric product was obtained. It was recovered by filtering under dry nitrogen and by washing extensively with CH_2Cl_2.[10] Finally, the product was dried at 50 °C under vacuum (yield 3.9 g). The polyacrylic anhydride was linear, as proved by its easy solubility in *N,N*-dimethylformamide.[11] The conversion of its carboxylic groups into anhydride, measured according to ref 12, amounted to 85 ± 5%. IR (KBr) 1805 (s, sharp), 1760 (s, sharp), 1700 (m, sh), 1620 (w), 1030 cm^{-1} (s, br).

Preparation of $(N_3P_3Cl_5O^-)(C_2H_5)_3N^+H$. $N_3P_3Cl_6$ (13.92 g, 0.040 mol) was added with stirring to 5.08 g (0.020 mol) of pyromellitic acid neutralized by 8.08 g (0.080 mol) of Et_3N in 100 mL of CH_2Cl_2 at 0 °C. After 10 min the mixture was evaporated to dryness under vacuum. The solid was extracted with 100 mL of cold benzene, from which 18.2 g of crude product was recovered. Crystallization from Et_2O–*n*-hexane yielded 16.4 g (0.038 mol): mp 85–87 °C; IR (KBr) 2910 (s), 2835 (m), 2700 (m), 2500 (w), 1460 (m), 1400 (w), 1375 (m), 1218 (vs, br), 1170 (vs, br), 590 (vs, sharp), 545 (m, sh), 520 cm^{-1} (vs. sharp). ^1H NMR (CD_2Cl_2–$(CH_3)_4Si$) δ 1.37 (9 H, t, J = 7 Hz, $3CH_3$), 3.12 (6 H, m, J = 7 Hz, $3CH_2$); 10.71 (1 H, br, ^+NH]; ^{31}P NMR (CD_2Cl_2–H_3PO_4, 85%) δ 1.93 (1 P, t, J = 44 Hz, $P(O^-)Cl$), −21.09 (2 P, d, J 44 Hz, $2PCl_2$).

Anal. Calcd for $(N_3P_3Cl_5O^-)(C_2H_5)_3N^+H$: C, 16.72; H, 3.72; Cl, 41.23; N, 13.01; P, 21.60. Found: C, 17.02; H, 3.79; Cl, 40.20; N, 13.19; P, 21.92.

Acknowledgment. We thank Dr. L. Settembri and Mr. M. Barbini for the NMR investigations.

Registry No. 2 (R′ = Et), 78685-93-5; acetic acid, 64-19-7; propionic acid, 79-09-4; *p*-toluic acid, 99-94-5; succinic acid, 110-15-6; ethylenediamine tetraacetic acid, 60-00-4; phthalic acid, 88-99-3; pyromellitic acid, 89-05-4; benzoic acid, 65-85-0; polyacrylic acid, 9003-01-4; acetic anhydride, 108-24-7; propionic anhydride, 123-62-6; *p*-toluic anhydride, 13222-85-0; succinic anhydride, 108-30-5; ethylenediamine tetraacetic anhydride, 23911-25-3; phthalic anhydride, 85-44-9; pyromellitic anhydride, 89-32-7; benzoic anhydride, 93-97-0; polyacrylic anhydride, 25301-00-2; $N_3P_3Cl_6$, 940-71-6.

(9) Only in the case of polyacrylic acid was the final IR spectrum obtained in about 25 min at room temperature.

(10) The polymeric anhydride remains soluble in CH_2Cl_2 solution but becomes insoluble in the same solvent precipitated once by Et_2O.

(11) J. C. H. Hwa, W. A. Fleming, and L. Miller, *J. Polym. Sci., Part A*, 2, 2385 (1964).

(12) Y. Levin, M. Pacht, L. Goldstein, and E. Katchalski, *Biochemistry* 3, 1905 (1964).

Reactivity of an (Arylthio)thiocarbonyl Radical. Intramolecular Addition to the Azido Group

Luisa Benati and P. Carlo Montevecchi *

Istituto di Chimica Organica dell'Università, 40136 Bologna, Italy

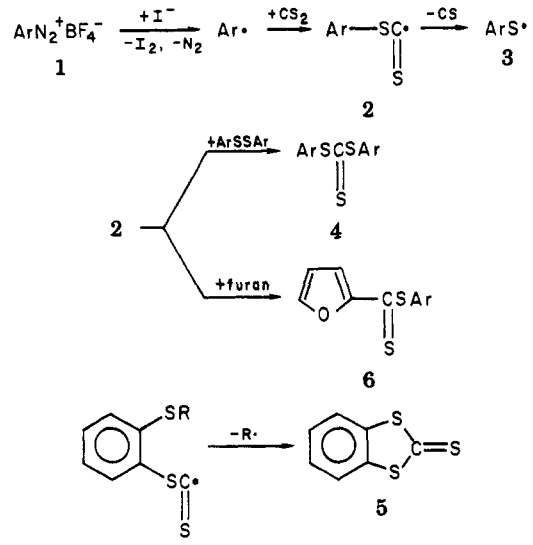
Received March 12, 1981

In a previous paper we reported that the reduction of aryldiazonium tetrafluoroborates (**1**) with iodide ions in the presence of carbon disulfide led to (arylthio)thiocarbonyl radicals (**2**) by addition of the corresponding aryl radicals to the sulfur atom of carbon disulfide.[1] Radical

(1) L. Benati and P. C. Montevecchi, *J. Org. Chem.*, 41, 2639 (1976).

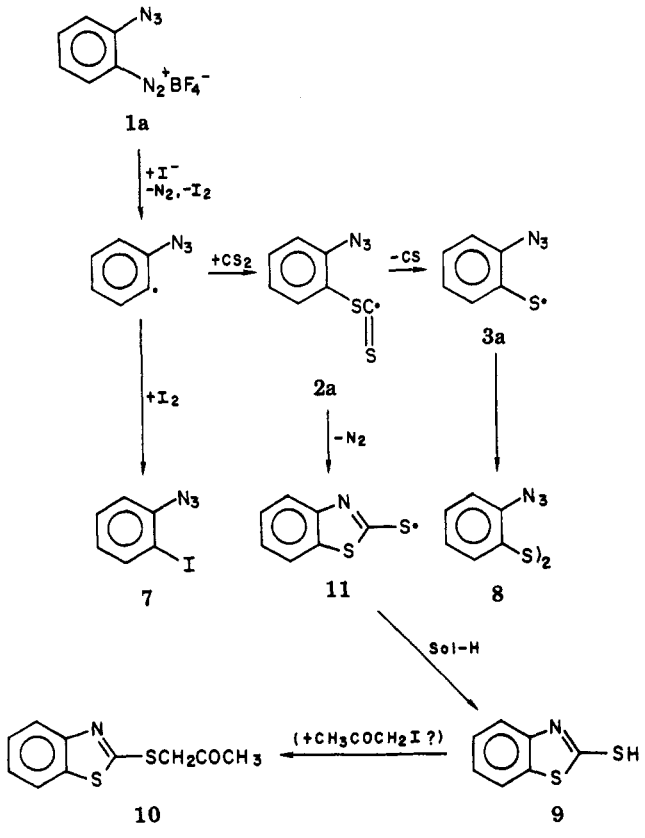
0022-3263/81/1946-4570$01.25/0

Scheme I[a]



[a] R = alkyl.

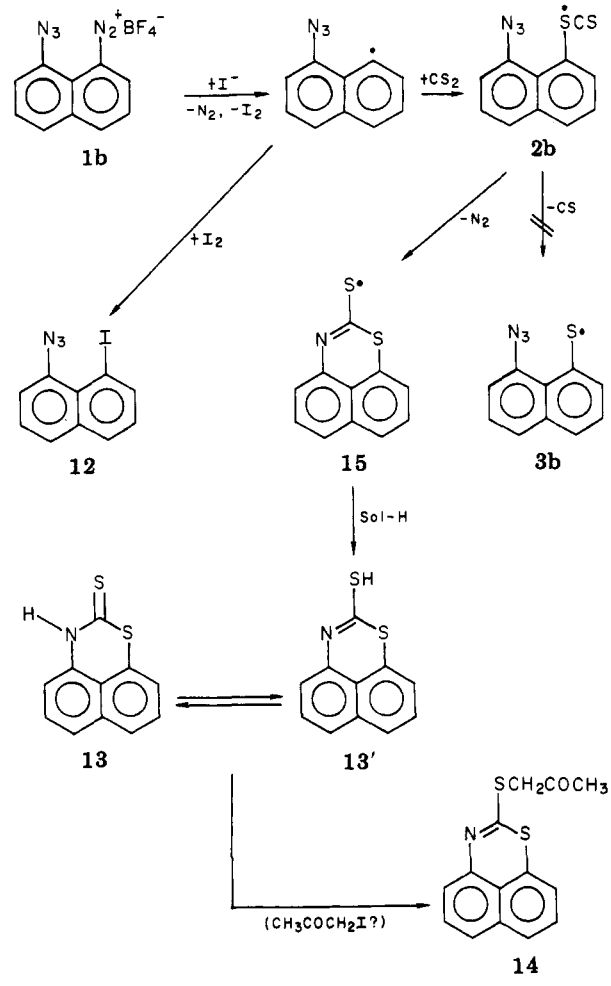
Scheme II



2 shows an unusual reactivity, undergoing loss of carbon monosulfide as a major reaction to afford arylthio radical 3. On the other hand, 2 is capable of giving substitution on the sulfur atom of disulfides and intramolecular substitution on the sulfur atom of *o*-alkylthio substituents but not of *o*-arylthio substituents.[2] In fact, reaction of 2 with diaryl disulfides generated by dimerization of radicals 3 gives diaryl trithiocarbonate (4), and 1,3-benzodithiole-2-thione (5) is formed from *o*-alkylthio-substituted (arylthio)thiocarbonyl radicals; the same product 5 is not observed with *o*-arylthio substituents.[2] Moreover, radical 2

(2) L. Benati and P. C. Montevecchi, *J. Org. Chem.*, 42, 2025 (1977).

Scheme III



gives rise to aromatic substitution of the furan ring, affording aryl, 2-furancarbodithioate (6), but it does not react with benzene (Scheme I).

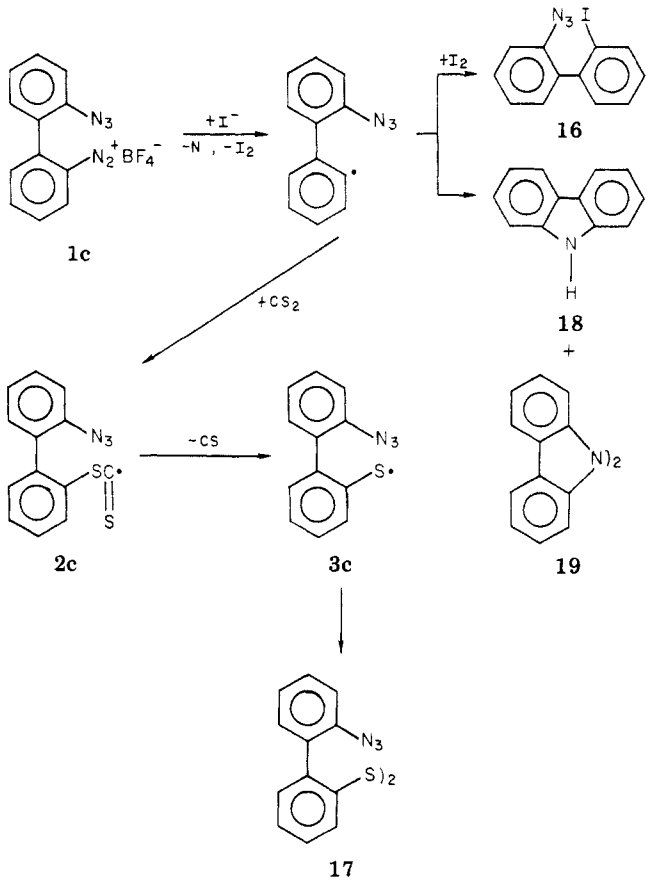
We now report results obtained from a study of some azido-substituted (arylthio)thiocarbonyl radicals, which was undertaken in order to gain more information on the reactivity of radical 2 and provide possible further examples of addition of carbon radical on the azido group,[3] which might offer a synthetic approach to new heterocyclic compounds.

The first radical investigated was the [(*o*-azidophenyl)thio]thiocarbonyl radical (2a). Column chromatography on silica gel of the reaction mixture obtained from reduction of (*o*-azidophenyl)diazonium tetrafluoroborate (1a) in an acetone/carbon disulfide mixture gave *o*-iodophenyl azide (7, 4.5%), bis(2′-azidophenyl) disulfide (8, 30%), 2-mercapto-1,3-benzothiazole (9, 13%), and 2-(acetonylthio)-1,3-benzothiazole (10, 6%) (Scheme II)

Compound 7 is produced by reaction of the intermediate *o*-azidophenyl radical with iodine. Disulfide 8 clearly arises by dimerization of (*o*-azidophenyl)thio radical 3a, formed by loss of carbon monosulfide from the corresponding thiocarbonyl radical 2a, in turn generated by addition of *o*-azidophenyl radical to carbon disulfide. More interesting is the formation of compound 9, which can be accounted for by intramolecular addition of thiocarbonyl radical to

(3) The reactivity of azido group toward free radicals has not been much explored; recently, we have reported the first, definite evidence of addition of a carbon radical to the azido group. [L. Benati, P. C. Montevecchi, and P. Spagnolo, *Tetrahedron Lett.*, 815 (1978), and references cited therein].

Scheme IV



the α-nitrogen atom of *o*-azido group followed by nitrogen loss to give radical **11** and then **9** by a hydrogen abstraction reaction from the solvent. The formation of derivative **10** might be explained by reaction of **9** with iodoacetone formed by trapping of acetonyl radical with iodine. However, no evidence of any iodoacetone was observed in the reaction mixture. Analogous results were obtained from reduction of (8-azido-1-naphthyl)diazonium tetrafluoroborate (**1b**), which led to isolation of the expected 1-iodo-8-azidonaphthalene (**12**, 4%) together with two green products, identified as 1,3-naphtho[*d*,*e*]thiazine-2-thiol (**13**, 45%) and 2-(acetonylthio)-1,3-naphtho[*d*,*e*]-thiazine (**14**, 16%) (Scheme III). Compound **13** appears to be formed from intermediate radical **15**, arising from intramolecular addition of thiocarbonyl radical **2b** to the α-nitrogen atom of the *peri*-azido group. Hydrogen abstraction of radical **15** from the solvent would eventually lead to the product **13**, possibly through its tautomeric form **13′**. Reaction of **13** (or **13′**) with iodoacetone would afford thiazine **14**. In such a case formation of the expected dimerization product of radical **3b** was not observed, thus providing evidence that for radical **2b** intramolecular addition to the *peri*-azido group is most favored over loss of carbon monosulfide. This trend is in line with the expectation that cyclization leading to a six-membered ring would be more feasible than that leading to a five-membered ring. Attempts to obtain cyclization to a seven-membered ring failed. In fact, reduction of (2-azido-2′-biphenylyl)diazonium tetrafluoroborate (**1c**) furnished iodo derivative **16** (3%), bis(2-azido-2′-biphenylyl) disulfide (**17**, 57%), carbazole (**18**, 8%) and traces of *N*,*N*′-bicarbazolyl (**19**) as the only identifiable products (Scheme IV). Compound **17** is the dimerization product of radical **3c** formed from thiocarbonyl radical **2c** by loss of carbon monosulfide; **18** and **19** are expected from intramolecular addition to the azido group of 2-azido-2′-biphenylyl radicals.[3]

Experimental Section

o-Azidoaniline,[4] 8-azido-1-naphthylamine,[5] and 2-azido-2′-biphenylylamine[6] were prepared according to literature. *o*-Iodophenyl azide (**7**),[7] 2-mercapto-1,3-benzothiazole (**9**), carbazole (**18**), and *N*,*N*-bicarbazolyl (**19**)[8] were identified by spectral comparison with authentic specimens. 2-(Acetonylthio)-1,3-benzothiazole (**10**)[9] was identified by melting point and spectral data.

Aryldiazonium Fluoroborates. Tetrafluoroborates **1a–c** were prepared from the corresponding arylamines by the standard procedure.[10] The amine (0.02 mol) was suspended in hydrochloric acid (6 mL) and water (6 mL) and diazotized at 0 °C with sodium nitrite (1.6 g) in water (5 mL). After the mixture was stirred at 0 °C for 30 min, the diazonium salt was precipitated by adding dropwise 50% fluoboric acid (4 mL). The fluoroborate was filtered and washed with a little cold water, EtOH (3 mL), and Et_2O (10 mL). Dry fluoroborates have to be handled very carefully; fluoborate **1c** may explode on being shaken or rubbed with a nickel spatula. Crude fluoroborates were used without further purification.

Reduction of Aryldiazonium Fluoroborate (1). General Procedure. The salt (0.01 mol) was dissolved in acetone (150 mL). To the solution was first added CS_2 (30 mL) and than NaI (2.0 gr) in small quantities under stirring. The mixture was stirred at room temperature for 1–2 h, and then the solvent evaporated. The crude was dissolved in chloroform, washed with water and dried and the solvent removed under vacuum. The mixture was chromatographed on a silica gel column.

Elution was as follows: pentane eluted iodoarenes (**7**, **12**, and **16**), disulfides (**8** and **17**) and traces of *N*,*N*-bicarbazolyl (**19**); 5% ether-pentane eluted benzothiazoles (**9** and **10**); 20% ether–pentane eluted 1,3-naphtho[*d*,*e*]thiazines (**13** and **14**) and carbazole (**18**). Continued elution with higher polarity solvent mixtures afforded untractable tarry materials.

From (*o*-azidophenyl)diazonium fluoroborate (**1a**) were separated the following. *o*-Iodophenyl azide (**7**): 4.5%; oil. Bis(2-azidophenyl) disulfide (**8**) 30%; mp 137 °C; mass spectrum, *m*/*e* 300 ($M^{+\cdot}$), 243, 154, 122; IR ν_{max} 2110 cm^{-1}. Calcd for $C_{12}H_8N_6S_2$: C, 48.0; H, 2.68; N, 28.0; S, 21.35. Found: C, 47.8; H, 2.64; N, 27.8; S, 21.2. 2-Mercapto-1,3-benzothiazole (**9**): 13%; mp 177–179 °C. 2-(Acetonylthio)-1,3-benzothiazole (**10**): 6%; mp 70–71 °C; mass spectrum *m*/*e* 223 ($M^{+\cdot}$), 181, 148, 136, 122; IR ν_{max} 1720 cm^{-1}.

From (8-azido-1-naphthyl)diazonium fluoroborate (**1b**) were obtained the following. 1-Iodo-8-azidonaphthalene (**12**): 4%; mp 70–71 °C; mass spectrum, *m*/*e* 295 ($M^{+\cdot}$), 267, 140; IR ν_{max} 2100 cm^{-1}. Calcd for $C_{10}H_6IN_3$: C, 40.7; H, 2.05; I, 43.0; N, 14.24. Found: C, 41.0; H, 2.02; I, 42.8; N, 14.3. 2-(Acetonylthio)-1,3-naphtho[*d*,*e*]thiazine (**14**): 16%; green needles; mp 66–68 °C; mass spectrum *m*/*e* 273 ($M^{+\cdot}$), 230, 216, 184, 172, 140; IR ν_{max} 1450, 1710 cm^{-1}. Calcd for $C_{14}H_{11}NOS_2$: C, 61.5; H, 4.06; N, 5.13; S, 23.45. Found: C, 62.0; H, 4.10; N, 5.18; S, 23.39. 1,3-Naphtho-[*d*,*e*]thiazine-2-thione (**13**) 45%; green needles; mp 196–198 °C; mass spectrtum, *m*/*e* 217 ($M^{+\cdot}$), 173; IR ν_{max} 3340, 1570 cm^{-1}. Calcd for $C_{11}H_7NS_2$: C, 60.8; H, 3.25; N, 6.45; S, 29.5. Found: C, 61.0; H, 3.21; N, 6.48; S, 29.1.

From (2-azido-2′-biphenylyl)diazonium fluoroborate (**1c**) were separated the following. 2-Azido-2′-iodobiphenyl (**16**): 3%; mp 55–56 °C; mass spectrum, *m*/*e* 321 ($M^{+\cdot}$), 293; IR ν_{max} 2070 cm^{-1}. Calcd for $C_{12}H_8IN_3$: C, 44.9; H, 2.51; I, 39.5; N, 13.09. Found: C, 45.3; H, 2.48; I, 39.1; N, 14.2. *N*,*N*-Bicarbazolyl (**19**): traces; mp 220–221 °C. Bis(2-azido-2′-biphenylyl) disulfide (**17**): 57%;

(4) J. H. Hall and E. Patterson, *J. Am. Chem. Soc.*, **89**, 5856 (1967).
(5) C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 756 (1969).
(6) S. F. Gait, M. E. Peek, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Perkin Trans. 1*, 1248 (1974).
(7) A. V. Oleinik, N. L. Gusarskaya, V. M. Treoshnikov, and N. N. Vyshinskii, *Zh. Prikl. Spektrosk.*, **20**, 1045 (1974); *Chem. Abstr.* **82**, 49527 (1975).
(8) W. A. Waters and J. E. White, *J. Chem. Soc. C*, 740 (1968).
(9) V. F. Kuckerov, *J. Gen. Chem. USSR (Engl. Transl.)*, **19**, 752 (1949); *Chem. Abstr.*, **44**, 3489*b* (1950).
(10) D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc. C*, 1518 (1967).

mp 124–125 °C; mass spectrum, m/e 452 (M^+·), 200, 199; IR ν_{max} 2030 cm^{-1}. Calcd for $C_{24}H_{16}N_6S_2$: C, 63.7; H, 3.56; N, 18.57; S, 14.17. Found: C, 63.2; H, 3.50; N, 18.6; S, 14.2. Carbazole (18): 8%; mp 246–247 °C.

Acknowledgment. We acknowledge support from the Consiglio Nazionale Ricerche, Rome.

Registry No. 1a, 59328-04-0; 1b, 59327-96-7; 1c, 62284-29-1; 7, 54467-95-7; 8, 78715-74-9; 9, 149-30-4; 10, 23385-34-4; 12, 67173-64-2; 13, 78715-75-0; 14, 78715-76-1; 16, 67173-62-0; 17, 67173-63-1; 18, 86-74-8; 19, 1914-12-1; CS_2, 75-15-0; NaI, 7681-82-5.

Fluorination of Methanediphosphonate Esters by Perchloryl Fluoride. Synthesis of Fluoromethanediphosphonic Acid and Difluoromethanediphosphonic Acid[1]

Charles E. McKenna* and Pei-de Shen[2]

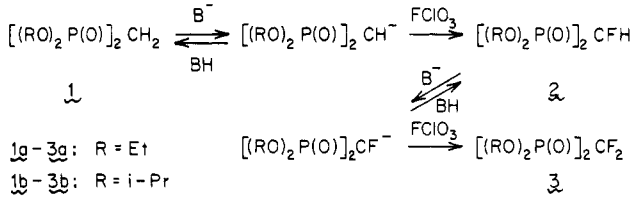
Department of Chemistry, University of Southern California, Los Angeles, California 90007

Received June 3, 1981

Although α-halogenated chloro, bromo, and iodo derivatives of tetraalkyl methanediphosphonates **1** have been known for some time,[3] the corresponding fluoro derivatives (**2, 3**) have not been available. Very recently, tetraethyl difluoromethanediphosphonate (**3a**) was prepared in 12% overall yield from dibromodifluoromethane and sodium diethyl phosphonate via diethyl bromodifluoromethanephosphonate.[4] Our interest in devising a *direct* route to both mono- and difluoromethanediphosphonates has led us to investigate the reaction of alkyl methanediphosphonates with perchloryl fluoride.[5,6] This reagent has been shown to α-fluorinate diethyl sodiomalonate,[7] giving a mixture of the mono- (29%) and difluoromalonate (42%) esters in toluene;[8] in ethanol, alkylation of the carbanion also occurs,[8] resulting in unwanted side product. The same method has been used to prepare other α-fluoro carboxylate derivatives, e.g., a series of 2-fluoro fatty acids with antifungal activity[9] and 2-alkyl 2-fluorocyanoacetates.[10]

In general, analogy between the methanedicarboxylate and methanediphosphonate groups in terms of methylene reactivity must be applied with caution. However, we find that perchloryl fluoride reacts smoothly with tetraisopropyl or tetraethyl methanediphosphonate carbanion in dry toluene to form both the corresponding fluorophosphonate and difluorophosphonate esters (**2a,b, 3a,b**) in total yields of up to 85%, if potassium *tert*-butoxide rather than Na or NaOEt is used as base (see Scheme I). The fluorination

Scheme I



Scheme II

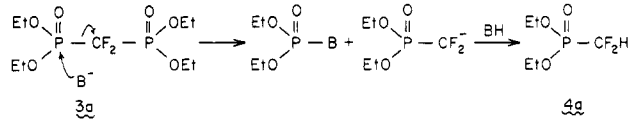


Table I. Fluorination of Methanediphosphonate Esters[a]

base	ester	base/ester ratio	% yield[b] 2	3	4
Na	1a	1.25:1	24[d]	17[d]	
t-BuOK	1a	2:1	34	21	7
t-BuOK	1a	1:1	47	16	trace
t-BuOK	1a	1:1[c]	22	45	18
Na	1b	1.30:1	28[d]	18[d]	
t-BuOK	1b	2:1	42	43	trace
t-BuOK	1b	3:1	32	33	trace
t-Bu-OK	1b	1:1	48	13	trace
t-BuOK	1b	0.60:1[c]	8	73	11

[a] As described in the Experimental Section. [b] By ^{19}F NMR analysis. [c] Retreatment of preceding reaction mixture. [d] Isolated yields.

reaction proceeds virtually as a titration of base with perchloryl fluoride and shows a readily recognizable end point marked by a characteristic color change from dark to pale yellow. Termination of the reaction is also indicated by the end of a temperature rise accompanying the reaction and cessation of perchloryl fluoride uptake.

Results illustrating the effects of some of the reaction parameters are summarized in Table I. By suitable adjustment of the proportion of starting materials, either product can be made to predominate; for example, with 1 equiv of potassium *tert*-butoxide as base, the monofluoromethane derivative of tetraisopropyl methanediphosphonate (**2b**) was prepared in 48% yield. With 2 equiv of this base, the difluoro (**3b**) derivative could be prepared directly in 43% yield, with an increase to 73% being possible on further reaction of the monofluoro product. The choice of base is important in this respect, since only a single equivalent of Na could be used, while NaOEt would be expected to give some alkylation side product, as discussed above. In addition to being a stronger base (the α-proton of **1** is less acidic than the α-proton in ethyl malonate), potassium *tert*-butoxide offers the advantages of allowing addition of more than 1 equiv of base if desired while avoiding unwanted alkylation of the carbanion and, in fact, gives the best yields. Exposure of the sodium salt[11] of tetraethyl methanediphosphonate (**1a**) in toluene solution to a stream of perchloryl fluoride results in the formation of resinous material, with reduced amounts of the desired mono- (**2a**) and difluorinated (**3a**) products. The yields are also lower when Na/toluene is used in place of potassium *tert*-butoxide with the isopropyl ester **1b**. With potassium *tert*-butoxide as the base, yields appear to be somewhat higher with the isopropyl ester than with the ethyl ester **1a**; addition of more than 1 equiv of base to the latter is accompanied by formation of a monophosphoryl side product, identified as **4a**. This com-

(1) Presented as part of a paper given at the International Conference on Phosphorous Chemistry, Duke University, Durham, N.C., June 1-6, 1981.
(2) Chinese Visiting Scholar, on leave from the Shenyang Research Institute of Chemical Industry, Shenyang, Liaoning, China.
(3) O. T. Quimby, J. D. Curry, D. A. Nicholson, J. B. Prentice, and C. H. Roy, *J. Organomet. Chem.*, **13**, 199 (1968).
(4) D. J. Burton and R. M. Flynn, *J. Fluorine Chem.*, **15**, 263 (1980).
(5) J. F. Gall in "Kirk-Othmer Encyclopedia of Chemical Technology", Vol 9, 2nd ed., Interscience, New York, 1966, pp 598–610.
(6) For handling and safe use of this reagent see also: Bulletins DC-1819 and ds I-1819, Pennsalt Chemicals Corp., Philadelphia, PA. The company is now Pennwalt and distributes perchloryl fluoride through its subsidiary, Ozark-Mahoning Co.
(7) C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 6533 (1958).
(8) H. Gershon, J. A. A. Renwick, W. K. Wynn, and R. D'Ascoli, *J. Org. Chem.*, **31**, 916 (1966).
(9) H. Gershon and R. Parmegiani, *J. Med. Chem.*, **10**, 186 (1967).
(10) H. Gershon, S. G. Schulman and A. D. Spevack, *J. Med. Chem.*, **10**, 536 (1967).
(11) J. D. Baldeschwieler, F. A. Cotton, B. D. N. Rao, and R. A. Schunn, *J. Am. Chem. Soc.*, **84**, 4454 (1962).

0022-3263/81/1946-4573$01.25/0