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SYNTHESIS OF MIXED POLYNITROORTHOCARBONATES AND RELATED DERIVATIVES

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ABSTRACT

Tris(polynitroalkoxy)chloromethanes (chloroorthoformates), a new class of compounds, are prepared by the chlorination of tris(polynitroalkoxy)methyl disulfides. The chloroorthoformates are reactive intermediates, which with alcohols give mixed 1:3 and 1:1:2 orthocarbonates. Additional derivatives are obtained with nucleophiles such as F^-, N_3^-, CN^-, and 2-imidazolidone.

INTRODUCTION

One of our research interests is the development of methods for the synthesis of polynitroaliphatic compounds that contain at least two different substituents.[1-4] There are several advantages for such methods: 1. a greater number of compounds can be prepared, 2. the physical and chemical properties of the compounds may be manupulated by the choice of substituents and

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3. they permit the preparation of a series of compounds which may be of value in the elucidation of property vs structure relationships.[5] There is, of course, one major disadvantage in that multi-step syntheses are generally required.

From this viewpoint, our attention was directed to the method of Hill and co-workers for the preparation of symmetrical polynitroaliphatic and polyfluoroaliphatic orthocarbonates.[6-9] Their method entails the reaction of a polynitro or polyfluoroalcohol with carbon tetrachloride in the presence of anhydrous ferric chloride. The mechanism of the reaction is purported to be the initial formation of the trichloromethyl ether as the rate determining step and then the increasingly faster formation of the dichloroformal, the chloroorthoformate and finally the symmetrical orthocarbonate.

$$ROH + CCl_4 \xrightarrow{FeCl_3} ROCCl_3 \xrightarrow{ROH} (RO)_2CCl_2 \xrightarrow{ROH}$$

$$(RO)_3CCl \xrightarrow{ROH} (RO)_4C$$

The reaction, in practice has been restricted to 2-fluoro-2,2-dinitroethanol, trinitroethanol and 2,2-dinitropropane-1,3-diol (and polyfluoroalcohols). With other nitroalcohols such as 2,2-dinitropropanol, side reactions predominate and the symmetrical carbonate has been the major product. However, it was reasoned that if the intermediates could be synthesized independently, they might then react with a second nitro or fluoroalcohol to

give a wide variety of mixed orthocarbonates.[10] This paper reports the synthesis of several polynitroaliphatic chloroorthoformates, a new class of compounds, and their reactions with alcohols and other nucleophiles.

RESULTS AND DISCUSSION

The chloroorthoformates 1, 2, 3 and 4 were prepared by the chlorination of the substituted tris(ethoxy)methyl trichloromethyl disulfides which have recently become available.[11] The chlorination proceeds readily in 1,2-dichloroethane solution at

$$(R'O)_3CSSCCl_3 \xrightarrow{Cl_2} (R'O)_3CCl + ClSCCl_3 + SCL_2$$

1, R' = $-CH_2C(NO_2)_2F$

$$(R'O)_2(R"O)CSSCCl_3 \xrightarrow{Cl_2} (R'O)_2(R"O)CCl + ClSCCl_3 + SCl_2$$

2, R' = $-CH_2C(NO_2)_2CH_3$
R" = $-CH_2C(NO_2)_2F$

3, R' = $-CH_2C(NO_2)_2F$
R" = $-CH_2CF_3$

4, R' = $-CH_2CF_3$
R" = $-CH_2C(NO_2)_2F$

ambient temperature, but for convenience, temperatures of 60-65° were generally used. The chloroorthoformates can be used *in situ*, or if necessary, isolated before being converted to other products. They are quite sensitive to moisture or humid air, whereupon they hydrolyze to an alcohol and carbonate, and therefore anhydrous conditions must be maintained during their formation and subsequent reactions. Treatment of the

chloroorthoformates with an alcohol at 60-80° in 1,2-dichloroethane solution produces mixed 1:2 and 1:1:2 orthocarbonates.

$$(R'O)_3CCl + R''OH \longrightarrow (R'O)_3COR''$$

$$(R'O)_2(R''O)CCl + ROH \longrightarrow (R'O)_2(R''O)COR$$

Alcohols which are resistant to chlorination and reaction with by-products can be added at the beginning; for more sensitive alcohols it is necessary to remove excess chlorine or even to isolate the chloroorthoformate before preparing the orthocarbonate. The alcohols that were used ranged from those containing strong electronegative substituents, eg., trinitroethanol, to ethanol. Diols were also employed and with 2,2-dinitropropane-1,3-diol the mono-product 11 could be easily prepared. The bis-product 12 required a much longer reaction time, which is consistent with the fact that molecular models indicate there is considerable steric resistance to the formation of the bis-derivative 12. Conversely, with 2,2,8,8-tetranitro-4,6-dioxane-1,9-diol where there is greater separation between the hydroxyls, the bis-product could be readily prepared while attempted preparation of the monoderivative led to mixtures.

Qualitatively, the rates of the reaction are, in general, inversely proportional to the cumulative effect of the electronegative substituents on both reactants, which is in keeping with the postulated intermediacy of carbenium ions.[6] Conversely, the stability of the orthocarbonates should be proportional to the additive effect of the electronegative

substituents if a decomposition mechanism proceeding via positive ions is assumed. Initially, there was some doubt that orthocarbonates incorporating non-substituted alcohols would be stable. However, tris(fluorodinitroethyl) ethyl orthocarbonate 9 was recovered unchanged upon prolonged standing in aqueous ethanol containing 10% trifluoroacetic acid. It would appear then that various functionalities can be easily introduced into orthocarbonates containing tris(polynitroalkyl) groups. Finally, it should be noted that, while no examples are given in this paper, mixed 2:2 orthocarbonates can be prepared from the chloro-orthoformates 2, 3, and 4 by a suitable choice of alcohol. The mixed orthocarbonates that have been prepared, and the reaction conditions and yields are presented in Table 1. Physical properties are shown in Table 2.

The chloroorthoformates also react with other nucleophiles. Tris(fluorodinitroethyl) chloroorthoformate 1 reacts with hydrogen fluoride-pyridine complex to yield tris(fluorodinitroethyl) fluoroorthoformate 20. With sodium azide and crown ether, the azido derivative 21 was formed and the cyano derivative 22 was prepared by the reaction of 1 with trimethylsilyl cyanide. With 2-imidazolidone, 1-tris(fluorodinitroethoxy)methyl-2-imidazolidone 23 was prepared. Compound 23 can be nitrated to the 3-nitramide 24 at 0^{o}, however at 25^{o} the tris(fluorodinitroethoxy)methyl group decomposes and the urethane, 1-(fluorodinitrocarbethoxy)-3-nitro-2-imidazolidone 25 is formed.

TABLE 1. Reaction Conditions for Mixed Orthocarbonates.

$[FC(NO_2)_2CH_2O]_3COR$

No.	R	mole ratio ROH/COF[a]	time (h)[b]	temp.	yield %
5	$-CH_2C(NO_2)_3$	2.0	74	65°	81
6	$-CH_2C(NO_2)_2CH_3$	2.8	23	65°	93
7	$-CH_2CF_3$ [c]	6.5	1	80°	98
8	$-CH_2CH_2NO_2$	1.2	7	65°	91
9	$-CH_2CH_3$	1.1	0.02	80°	88
10	$-CH_2-CH(O)-CH_2$ [d]	4.5	0.25	50°	81
11	$-CH_2C(NO_2)_2CH_2OH$	1.1	7	65°	89
12	$-CH_2(NO_2)_2CH_2O-C[FC(NO_2)_2CH_2O]_3$	0.5	96	65°	63
13	$-CH_2(NO_2)_2CH_2OCH_2O-C[FC(NO_2)_2CH_2O]_3COCH_2C(NO_2)_2CH_2$	0.45	30	65°	79

$[FC(NO_2)_2CH_2O][CH_3C(NO_2)_2CH_2O]_2COR$

14	$-CH_2C(NO_2)_2CH_3$	2.2	24	60°	89
15	$-CH_2CF_3$ [c]	15	1.5	80°	100
16	$-CH_2C(NO_2)_3$	2.0	45	65°	74

$[FC(NO_2)_2CH_2O]_2(F_3CCH_2O)COR$

17	$-CH_2C(NO_2)_3$	2.0	52	65°	82
18	$-CH_2C(NO_2)_2CH_3$	2.2	46	60°	83

$(F_3CCH_2O)_2[FC(NO_2)_2CH_2O]COR$

19	$-CH_2C(NO_2)_3$	2.0	48	60°	82

Footnotes to Table 1.

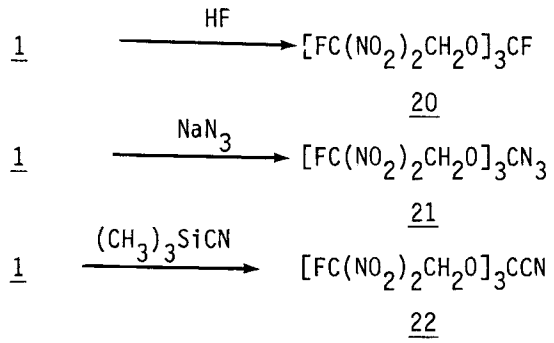
a) COF = Chloroformate. b) Time was measured from point at which the alcohol was added. c) For compounds 7 and 15, the alcohol was added after formation of the chloroorthoformate was complete. d) For compound 10, the chloroorthoformate was isolated and redissolved in dichloroethane before the addition of glycidol. A nitrogen purge was used to sweep hydrogen chloride from the reaction mixture.

TABLE 2. Physical Data for Mixed Orthocarbonates.

No.	mp, °C	^{1}H-NMR[a] δ	Molecular Formula	Elemental Analysis Calc'd/Found C	H	N	F
5	117-118	4.82 s, 4.69 d	$C_9H_8N_9F_3O_{22}$	16.60 16.78	1.24 1.16	19.36 19.25	8.75 8.93
6	116-118	4.66(d,6H), 4.38(s,2H)	$C_{10}H_{11}N_8F_3O_{20}$	19.36 19.41	1.79 1.82	18.07 18.03	9.19 9.39
7	57-59	4.75(d,6H), 3.99(q,2H)	$C_9H_8N_6F_6O_{16}$	18.96 19.05	1.41 1.51	14.74 14.50	19.99 19.66
8	89-91	4.74 d, 4.59 m, 4.15 m	$C_9H_{10}N_7F_3O_{18}$	19.26 19.35	1.80 1.83	17.47 17.20	10.16 9.98
9	oil	4.66(d,6H), 3.67(q,2H), 1.24(t,3H)	$C_9H_{11}N_6F_3O_{16}$	20.94 20.93	2.15 1.99	16.28 16.04	11.04 10.81
10	52-53	4.71 d, 4.00 m, 3.38 m, 3.14 m, 2.89 m, 2.63 m	$C_{10}H_{11}N_6F_3O_{17}$	22.07 22.06	2.04 2.05	15.44 15.27	10.47 10.52
11	79-82	4.74 d, 4.58 s, 4.52 s	$C_{10}H_{11}N_8F_3O_{21}$	18.88 18.84	1.74 1.73	17.61 17.36	8.96 9.20
12	133-135	5.17 d, 4.92 s	$C_{17}H_{16}N_{14}F_6O_{36}$	18.45 18.47	1.46 1.48	17.72 17.65	10.30 10.19
13	gum	5.20(d,12H), 4.98(s,2H) 4.81(s,4H), 4.67(s,4H)	$C_{20}H_{22}N_{16}F_6O_{42}$[b]				
14	129-131	5.15(d,2H), 4.71(s,6H), 2.35(s,9H)	$C_{12}H_{17}N_8FO_{20}$	23.54 23.59	2.80 2.82	18.30 18.16	3.10 3.07
15	oil	4.68(d,2H), 4.40(s,4H), 3.92(q,2H), 2.20(s,6H)	$C_{11}H_{14}N_6F_4O_{16}$	23.50 23.50	2.51 2.61	14.95 14.79	13.52 13.59
16	115-117	5.50(s,2H), 5.20(d,2H), 4.76(s,4H), 2.36(s,6H)	$C_{11}H_{14}N_9FO_{22}$	20.54 20.57	2.19 2.23	19.60 19.58	2.95 3.02
17	42-43	4.88(s,2H), 4.75(d,4H), 4.01(q,2H)	$C_9H_8N_7F_5O_{18}$	18.10 18.27	1.35 1.34	16.42 16.23	15.91 15.78
18	oil	4.67(d,4H), 4.40(s,2H), 3.92(q,2H), 2.18(s,3H)	$C_{10}H_{11}N_6F_5O_{16}$	21.21 21.28	1.96 1.97	14.84 14.61	16.78 16.54
19	oil	4.74(d,2H), 3.98(q,4H)	$C_9H_8N_5F_7O_{14}$	19.90 20.02	1.48 1.50	12.89 12.64	24.48 24.43

Footnotes to Table 2.

a) TMS was used as an internal standard. The NMR solvent was CD_2Cl_2 for compounds 8, 10 and 11. Acetone-d_6 was used for 12, 13, 14 and 16. For all others, $CDCl_3$ was used as the solvent. b) Compound 13 was very sensitive to shock, so elemental analysis was not attempted.



While a rather large number of examples of the preparative utility of chloroorthoformates have been presented, it is clear that the synthetic possibilities have not been exhausted. By the proper choice of reactants, many other similar derivatives may be prepared.

EXPERIMENTAL

Caution.

The compounds described herein are energetic explosives and should be handled with due care by experienced personnel. ^{1}H-NMR spectra were obtained with a Varian XL 200 spectrometer with TMS as the internal standard. IR spectra were obtained with a Beckmann model 167 spectometer. Elemental analysis were performed by Galbraith Laboratories Inc., Knoxville, Tenn. 37921. Melting points are uncorrected.

General Procedure for Chloroorthoformates 1, 2, 3, and 4.

A slow stream of gaseous chlorine was passed into a solution of 6.53g (0.10 mol) of tris(2-fluoro-2,2-dinitroethoxy)methyl trichloromethyl disulfide in 20 mL of dry 1,2-dichloroethane at

60-65° for 2h. The solution was then held at 60-65° for an additional 2h before the solvent was removed by a stream of dry nitrogen. The residue was washed with dry hexane to give 4.85g (95%) of a white solid, mp 69-72°.

Compounds 2, 3, and 4 were prepared in a similar manner from the respective disulfides.

The extreme moisture sensitivity of the trialkoxy chloromethanes prevented satisfactory elemental analyses. In general, lower chlorine content than the calculated value was obtained. However, the absence of sulfur was confirmed.

Representative Procedures for the Preparation of Mixed Orthocarbonates. A.) Tris(2-fluoro-2,2-dinitroethyl) (2,2-dinitropropyl) orthocarbonate 6.

A solution of 4.2g (0.028 mol) of 2,2-dinitropropanol and 6.35g (0.01) mol) of tris(2-fluoro-2,2-dinitroethoxy)methyl trichloromethyl disulfide in 20 mL of dry 1,2-dichloroethane was treated with gaseous chlorine for 2h. The solution was held at 60-65° for an additional 21h, at which time the solvent was removed and the residue washed consecutively with hexane and water. The solid residue, after drying, was recrystallized from $CHCl_3$ to give 5.80g (93%) of product, mp 116-117.5.

B.) Tris(2-fluoro-2,2-dinitroethyl)ethyl orthocarbonate 9.

Dry chlorine gas was passed into a solution of 6.53g (0.01 mol) of tris(fluorodinitroethoxy)methyl trichloromethyl disulfide

in 20 mL of dry 1,2-dichloroethane for 2h at 60°. After an additional 2h at 60°, excess chlorine and about 5 mL of solvent were removed with a stream of dry nitrogen. Then, 0.65 mL of anhydrous ethanol was added and the solution was refluxed for one minute. After cooling, the volatiles were removed and the oily residue was washed with hexane. The oil weighed 4.55g (88%) after it was dried in a vacuum desiccator. GLC analysis indicated the product was essentially pure.

For compound 10, the chloroorthoformate was isolated and redissolved in dichloroethane before the addition of glycidol. A nitrogen purge was then used to sweep hydrogen chloride from the reaction mixture. For compounds 7 and 15, the alcohol was added after formation of the chloroorthoformate was complete. See Tables 1. and 2. for reaction conditions and physical properties of the mixed orthocarbonates.

Tris(2-fluoro-2,2-dinitroethoxy)fluoromethane 20.

Tris(fluorodinitroethoxy)chloromethane 1, (0.01 mol) in 20 mL of dichloroethane was prepared as described above. Excess chlorine was removed with a stream of nitrogen after which the solution was transferred to a Teflon bottle containing 5 mL of HF/pyridine (70% HF). The mixture was stirred at ambient temperature for 20h and then it was poured onto ice and extracted with CH_2Cl_2. After drying and removal of the solvent, the residue was stirred with hexane and filtered to give 4.54g of solid, mp 90-95°. Recrystallization from $CHCl_3$ gave 3.88g (79%), mp

96-98°; ^{1}H NMR ($CDCl_3$/TMS) δ 4.85 d; mass spectrum (CI) m/e 519 ($M+C_2H_5^+$). Anal. Calc'd for $C_7H_6N_6F_4O_{15}$: C, 17.15; H, 1.23; N, 17.15; F, 15.50. Found: C, 17.33; H, 1.33; N, 16.98; F, 15.66.

Tris(2-fluoro-2,2-dinitroethoxy)azidomethane 21.

Compound 1 (3.36 mmol), isolated as described above, was dissolved in 10 mL of dry benzene containing 0.3g of 10-crown-6 ether. Sodium azide (0.45g, 6.9 mmol) was added and the mixture was stirred at ambient temperature for 20h. The reaction mixture was filtered and the filtrate was chromatographed on silica gel 60. Elution with CH_2Cl_2:hexane gave 1.09g (63%) of an oil; ^{1}H-NMR ($CDCl_3$/TMS) δ 4.75d; IR (film), 2155 cm^{-1} (N_3). Anal. Calc'd for $C_7H_6F_3N_9O_{15}$: C, 16.38; H, 1.18; F, 11.11; N, 24.57. Found: C, 16.52, H, 1.18; F, 10.91; N, 24.53.

Tris(2-fluoro-2,2-dinitroethoxy)acetonitrile 22.

Compound 1 (5 mmol) was isolated (vide supra) and dissolved in 10 mL of dry tetrahydrofuran. Trimethylsilyl cyanide (0.75g, 7.5 mmol) was added and the solution was refluxed for 24h. After removal of the solvent the residual oil was stirred with cold $CHCl_3$ to yield 1.20g (48%) of 22, mp 73-75°. Recrystallization from $CHCl_3$ raised the mp to 77-78°; ^{1}H-NMR (acetone-d_6/TMS) δ 5.45 d; IR (KBr disc) 2265 cm^{-1} (CN). Anal. Calc'd for $C_8H_6F_3N_7O_{15}$: C, 19.33; H, 1.22; F, 11.46; N, 19.72. Found: C, 19.35; H, 1.22; F, 11.37; N, 19.72.

1-Tris(2-fluoro-2,2-dinitroethoxy)methyl-2-imidazolidone 23.

Tris(fluorodinitroethoxy)chloromethane 1 (0.03 mol) was isolated (vide supra) and dissolved in 60 mL of dry 1,2-dichloroethane. 2-Imidazolidone (6.0g, 0.069 mol) was added and the mixture was stirred at ambient temperature for 24h. The solvent was them removed in vacuo and the residual solid was stirred with water, filtered and dried to give 12.75g of 23, mp 154-156°. Recrystallization from dichloroethane raised the mp to 155-156°; ^{1}H-NMR (C_6D_6/TMS) δ 4.46 (d, 6H), 4.00 (s, 1H), 2.66 (t, 2H); 2.20 (t, 2H); IR (KBr disc) 3480 (NH), 1725 (C=O), 1605 (NO_2) cm^{-1}. Anal. Calc'd for $C_{10}H_{11}F_3N_8O_{16}$: C, 21.59; H, 1.99; F, 10.25; N, 20.14. Found: C, 21.55; H, 2.00; F, 10.16; N, 19.96.

1-Tris(2-fluoro-2,2-dinitroethoxy)methyl-3-nitro-2-imidazolidone 24 and 1-(2-fluoro-2,2-dinitrocarbethoxy)-3-nitro-2-imidazolidone 25.

To an ice cold mixture of one mL of 90% HNO_3 and 3.5 mL of conc. H_2SO_4 was added 0.60g of 23 and the mixture was stirred vigorously at 0° for one h. It was then poured on ice and the precipitate was filtered and washed with water. After drying, the solid was recrystallized from dichloroethane to give 0.42g (65%) of 24, mp 202-203°; ^{1}H-NMR (acetone-d_6/TMS) δ 5.28 (d,6H), 4.27 (t, 2H), 3.64 (t, 2H); IR (KBr disc) 1765 (C=O), 1600 and 1575 shoulder (NO_2). Anal. Calc'd for $C_{10}H_{10}F_3N_9O_{18}$: C, 19.98; H, 1.68; F, 9.48; N, 20.97. Found: C, 20.01; H, 1.64; F, 9.45; N, 20.72.

A similar nitration of 23 at 24-27° for 3h produced a 76% yield of 25, mp 165-166°; ^{1}H-NMR (acetone-d_6/TMS) δ 5.64 (d, 2H), 4.28 (t, 2H), 3.91 (t, 2H); IR (KBr) 1820 and 1745 (C=O), 1607 and 1560 (NO_2) cm^{-1}; mass spectrum (CI) m/e 312 (M + 1).

Anal. Calc'd for $C_6H_6FN_5O_9$: C, 23.16; H, 1.94; F, 6.11; N, 22.51; Found: C, 23.15; H, 1.88; F, 6.17; N, 22.16.

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