Table II. Ketenimines

Compound	M.P., °C.	Yield, %	Analysis, %					
			Calcd.			Found		
			C	H	N	C	H	N
Diphenylketen-(*N*-*p*-chlorophenyl)imine (2)	69.5–71	86.4	79.09	4.61	4.61	79.04	4.84	4.92
Di-*p*-chlorophenylketen-*N*-(*p*-tolyl)imine[a] (3)	82–84	57.4	71.60	4.26	3.98	71.22	4.56	4.19
Diphenylketen-*N*-(4-chloro-3-nitrophenyl)imine[b] (5)	72–73	71.4	68.86	3.73	8.03	68.66	4.06	8.08

[a] Prepared from the crude α-chloroimino chloride. [b] Toluene used instead of benzene as solvent.

of petroleum ether and sufficient ethyl ether to give a solution. It was filtered to remove traces of impurities, and the filtrate was allowed to stand, to give 19.1 grams of the product, m.p. 85–7° C.; (*1*) m.p. 74–5° C.; (*6*), m.p. 85–7° C. Another 7 grams of product, m.p. 82–4° C., was obtained from the filtrate after concentration and cooling. The combined yield was 26.1 grams (91.4%).

Diphenylketen-*N*-(*n*-butyl)imine (4). The compound was similarly prepared, 47.3% yield from the crude α-chloroimino chloride, n_D^{25} 1.6030; (*11*), b.p. 154–8° C. (0.15 mm.), n_D^{25} 1.6026, 1.6006.

N-(*p*-Tolyl)diphenylacetamide via diphenylketene. Into a flame-dried, one-liter three-necked flask carrying a mechanical stirrer and a reflux condenser carrying a calcium chloride drying tube were placed 13.25 grams (0.0500 mole) of α-chlorodiphenylacetyl chloride (*11*), 14 grams of copper powder and 300 ml. of anhydrous benzene. The mixture was refluxed with stirring for 2.5 hours, while an atmosphere of nitrogen was maintained over the mixture. The mixture was chilled, filtered, and the residue was washed with anhydrous benzene (2 x 50 ml.). To the combined filtrate and washings was added a solution of 5.37 grams (0.050 mole) of recrystallized *p*-toluidine in 100 ml. of benzene. After the reaction had subsided, the mixture was concentrated to dryness under reduced pressure, and the residual solid was recrystallized from aqueous acetone to give 11.8 grams (78.4%) of *N*-(*p*-tolyl)diphenylacetamide, m.p. 179–81° C. A mixture melting point with an authentic sample prepared by the reaction of diphenylacetyl chloride and *p*-toluidine was not depressed.

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Fluorodinitroethyl Esters of Dicarboxylic Acids

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The fluorodinitroethyl esters of fumaric, maleic, itaconic, and malonic acids were synthesized, using known procedures; the physical properties of the esters are given. Attempts to prepare bis(fluorodinitroethyl) methylenemalonate from bis(fluorodinitroethyl) malonate by two different procedures led to some unexpected products.

UNSATURATED dicarboxylic acid esters of fluoronitro alcohols have been of interest as comonomers in ester polymerization. Recently, the synthesis of esters of 2,2-difluoro-2-nitroethanol (*3*) was described. Completion of this work formed part of a series of unsaturated esters of negatively substituted alcohols consisting of 2,2,2-trifluoroethanol and 2,2,2-trinitroethanol. The authors now report the preparation of the analogous 2-fluoro-2,2-dinitroethyl esters of fumaric, maleic, itaconic, and malonic acids. Attempts to prepare bis(2-fluoro-2,2-dinitroethyl) methylenemalonate led to some unexpected derivatives of bis(2-fluoro-2,2-dinitroethyl) malonate.

Several standard methods of esterification were used for 2-fluoro-2,2-dinitroethanol, but no single method was useful for each ester, and the efficacy of each procedure depended upon the reactivity of the acid or acyl chloride. The esters and their properties are summarized in Table I.

Fumaric acid could not be esterified by the usual azeotropic distillation method. However, when fuming sulfuric acid was used as solvent (*1*), the half ester, 2-fluoro-2,2-dinitroethyl fumarate, I, formed preferentially at moderate temperatures; the bis ester, bis(2-fluoro-2,2-dinitroethyl) fumarate, II, could be obtained only after prolonged heating at 60° C. In contrast, II was prepared in 84%

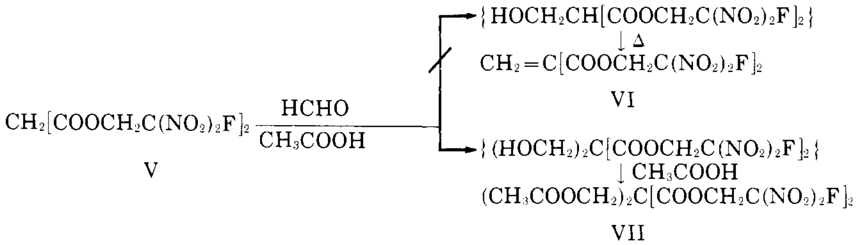
Table I. Physical Properties of Fluorodinitroethyl Esters

	Ester	Yield, %	M.P., °C.	Empirical Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
I	Acid fumarate	14[a]	126	$C_6H_5N_2O_8F$	28.57	28.78	2.00	2.12	11.12	11.01
II	Fumarate	27[a] 84[b]	76–77	$C_8H_6N_4O_{12}F_2$	24.75	24.73	1.55	1.52	14.44	14.34
III	Maleate	30	55–56	$C_8H_6N_4O_{12}F_2$	24.75	24.62	1.55	1.59	14.44	14.72
IV	Itaconate	65[b]	47–48	$C_9H_8N_4O_{12}F_2$	26.30	26.57	1.94	1.99	13.60	13.75
V	Malonate	61 5[b]	46–47	$C_7H_6N_4O_{12}F_2$	22.35	22.56	1.61	1.74	14.90	14.80
VII	Bis(acetoxymethyl)-malonate	13	88–90	$C_{13}H_{14}N_4O_{16}F_2$	30.01	30.20	2.72	2.87	10.77	11.12
VIII	Propane-tetra-carboxylate	47	94–95	$C_{15}H_{12}N_8O_{24}F_4$	23.57	23.38	1.58	1.84	14.66	14.23

[a] Method A. [b] Method B.

yield using fumaryl chloride with aluminum chloride catalyst at room temperature (2). Maleyl chloride differed in reactivity, since it could not be esterified using aluminum chloride catalyst; esterification of maleic acid by the azeotropic distillation method, or in sulfuric acid solvent, was also unsuccessful. However, a moderate yield of bis(2-fluoro-2,2-dinitroethyl) maleate, III, was obtained using maleic anhydride in polyphosphoric acid solvent (*4*), with little improvement in yield by varying the conditions of temperature and stoichiometry. Similar to fumaric acid, itaconic acid was esterified in best yield using itaconyl chloride with aluminum chloride catalyst in refluxing chloroform to give bis(2-fluoro-2,2-dinitroethyl) itaconate, IV.

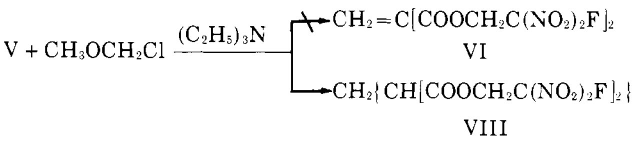
Bis(2-fluoro-2,2-dinitroethyl) malonate, V, was prepared from malonic acid by the azeotropic distillation method, using sulfuric acid catalyst. V was also prepared in low yield, using malonyl chloride with aluminum chloride catalyst. Attempts to prepare bis(2-fluoro-2,2-dinitroethyl) methylenemalonate, VI, from V gave some unexpected products. Two methods used for preparing diethyl methylenemalonate from diethyl malonate were applied to bis(fluorodinitroethyl) malonate in the attempted preparation of VI. The first method tried was the zinc chloride catalyzed condensation of formaldehyde with bis(fluorodinitroethyl) malonate in glacial acetic acid, Equation 1, followed by the attempted dehydration to the methylene group *in situ* by heating (*5*), Equation 2.



$$\underset{\text{V}}{CH_2[COOCH_2C(NO_2)_2F]_2} \xrightarrow[CH_3COOH]{HCHO} \begin{cases} \not\rightarrow \{HOCH_2CH[COOCH_2C(NO_2)_2F]_2\} & (1) \\ \qquad \downarrow \Delta & \\ \underset{\text{VI}}{CH_2{=}C[COOCH_2C(NO_2)_2F]_2} & (2) \\ \rightarrow \{(HOCH_2)_2C[COOCH_2C(NO_2)_2F]_2\} & (3) \\ \qquad \downarrow CH_3COOH & \\ \underset{\text{VII}}{(CH_3COOCH_2)_2C[COOCH_2C(NO_2)_2F]_2} & (4) \end{cases}$$

This reaction did not give the expected methylenemalonate, VI; instead, a compound identified as bis(2-fluoro-2,2-dinitroethyl) bis(acetoxymethyl)malonate, VII, was obtained. The formation of VII resulted from the condensation of two molecules of formaldehyde with one of V to produce bis(2-fluoro-2,2-dinitroethyl) bis(hydroxymethyl)malonate, Equation 3; this intermediate was then esterified with acetic acid to produce VII, Equation 4. The NMR, infrared, and elemental analyses of VII were consistent with the assigned structure. Also, the spectral data of VII compared well with the previously prepared 2,2-difluoro-2-dinitroethyl analog of VII (*3*).

The second method used for the attempted preparation of VI consisted of the reaction of methyl chloromethyl ether with bis(fluorodinitroethyl) malonate using triethylamine catalyst (*6*), Equation 5. The product of this reaction was not the desired VI, but tetrakis(2-fluoro-2,2-dinitroethyl) propane-1,1,3,3-tetracarboxylate, VIII, by elemental, infrared, and NMR analyses. The structure of VIII was further confirmed by comparison of its spectral data with those of the analogous product obtained from bis(2,2-difluoro-2-nitroethyl) malonate (*3*).



$$V + CH_3OCH_2Cl \xrightarrow{(C_2H_5)_3N} \begin{cases} \not\rightarrow \underset{\text{VI}}{CH_2{=}C[COOCH_2C(NO_2)_2F]_2} \\ \rightarrow \underset{\text{VIII}}{CH_2\{CH[COOCH_2C(NO_2)_2F]_2\}_2} \end{cases} \quad (5)$$

EXPERIMENTAL

All melting and boiling points are uncorrected. Elemental analyses were determined by Stanford University Microanalytical Laboratory, Stanford, Calif. Infrared spectra were run on a Perkin-Elmer 137 Infracord spectrophotometer, and NMR spectra were run on a Varian HR-100 spectrometer. The 2-fluoro-2,2-dinitroethanol used in this work was obtained from Aerojet-General Corp., Azusa, Calif. All other chemicals were obtained from the usual commercial sources. Fluorodinitroethyl ester preparations are summarized in Table I.

CAUTION. The fluorodinitro compounds described in this paper are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, or other means. Therefore, they should be handled with care. Since many fluorodinitro compounds are toxic to varying degrees, fluorodinitroethanol and its derivatives may cause painful burns when brought into contact with the skin.

2-Fluoro-2,2-dinitroethyl Fumarate, I. Method A. To a solution of 0.70 gram (0.006 mole) of fumaric acid in 10 ml. of 10% fuming sulfuric acid, there was added dropwise over 10 minutes 2.0 grams (0.013 mole) of fluorodinitroethanol. The mixture was heated to 43° C. for 15 hours, allowed to cool to ambient temperature, extracted once with 5 ml. of chloroform, and poured over 20 grams of ice. A light brown solid which separated was collected and dried to give 0.33 gram (14% yield), m.p. 105° to 110° C. The solid was recrystallized from benzene to give white crystals, I, m.p. 126° C.

Infrared spectrum (nujol): 5.72(m), acid C=O; 5.90(s), ester C=O; 6.12(s), 12.50(m), NO_2; 7.65(m), 8.24(m), 9.40(m), 10.02(w), 11.72μ(m).

Bis(2-fluoro-2,2-dinitroethyl) Fumarate, II. Method B. A solution of 50.0 grams (0.325 mole) of fluorodinitroethanol in 20 ml. of chloroform was added dropwise at ambient temperature over 20 minutes to a stirred mixture containing 20.0 grams (0.131 mole) of fumaryl chloride and 8.76 grams (0.066 mole) of aluminum chloride in 55 ml. of chloroform. The mixture was stirred until the hydrogen chloride evolution had almost ceased, and then was heated to reflux temperature for 1 hour. The mixture was cooled to ambient temperature and poured onto 300 grams of crushed ice containing 2 ml. of 12*N* hydrochloric acid. This acidic mixture was extracted with four 50-ml. portions of hot chloroform; the organic phases were combined and dried over magnesium sulfate, and the solvent was evaporated to a 100-ml. volume. Carbon tetrachloride (25 ml.) was added, and the solution was cooled to −20° C. The crystallized product, 42.5 grams (84% yield), was recrystallized from a solution of 20% carbon tetrachloride in chloroform to give 41.4 grams of colorless crystals, II, m.p. 76° to 77° C.

Infrared spectrum (nujol): 5.72(s), C=O; 6.20(s), 12.55(s), NO_2; 7.60(s), 8.30(s), 9.32(m), 11.78μ(m).

Method A. II was prepared in 27% yield using the same procedure described for I, except that the reaction mixture was heated to 60° C. for 15 hours.

Bis(2-fluoro-2,2-dinitroethyl) Maleate, III. At 60° to 70° C., 19.6 grams (0.20 mole) of maleic anhydride was dissolved in 300 grams of polyphosphoric acid. With stirring, 68.0 grams (0.44 mole) of fluorodinitroethanol was added portionwise to the acid mixture. After the alcohol addition, two phases were evident, but after 30 minutes at 80° to 85° C., the reaction mixture turned milky white; after 45 minutes, the mixture became one clear phase. Stirring was continued at 80° to 85° C. for an additional 3.5 hours. The mixture was cooled to 50° C. and poured with stirring onto 1 liter of crushed ice. The white flocculent precipitate which formed immediately was filtered, washed with water, and dried to give 23.5 grams (30% yield) of III. The ester was recrystallized as needles from a mixture of chloroform and carbon tetrachloride.

Infrared spectrum (nujol): 5.65(s), 5.71(m), C=O; 6.20(s), 12.55(w), 12.71(w), NO_2; 7.60(m), 8.32(m), 8.70μ(m).

Bis(2-fluoro-2,2-dinitroethyl) Itaconate, IV. Method B. IV was prepared in 65% yield, using the same procedure as described for II.

Infrared spectrum (nujol): 5.65(m) shoulder, 5.72(s), C=O; 6.22(s), 12.55(m), NO_2; 7.65(s), 8.72(s), 9.00(s), 11.72μ(m).

Bis(2-fluoro-2,2-dinitroethyl) Malonate, V. A mixture of 2.5 grams (0.024 mole) of malonic acid, 8.0 grams (0.052 mole) of fluorodinitroethanol, 0.1 ml. of concentrated sulfuric acid, and 15 ml. of benzene was refluxed until 0.048 mole of water was collected in a Dean-Stark trap. The solution was diluted to 65 ml. with benzene and washed with 50 ml. of saturated sodium bicarbonate solution. The organic phase was dried over magnesium sulfate, filtered, and evaporated at 40° C. (18 mm.), leaving a semisolid residue which crystallized on standing. The solid was recrystallized from 15 ml. of chloroform to give 5.5 grams (61% yield) of V, m.p. 46° to 47° C.

Infrared spectrum (nujol): 5.62(s), C=O; 6.21(s), 12.58(m), NO_2; 7.28(m), 7.60(m), 11.75μ(m).

Method B. V was obtained in 5% yield after 16 hours at ambient temperature. The procedure used was the same as that described for II.

Bis(2-fluoro-2,2-dinitroethyl) Bis(acetoxymethyl)malonate, VII. A mixture of 5.76 grams (0.015 mole) of bis(2-fluoro-2,2-dinitroethyl) malonate, 0.64 gram (0.021 mole) of paraformaldehyde, and 0.27 gram (0.002 mole) of zinc chloride in 40 ml. of glacial acetic acid was heated at 110° C. for 16 hours; the colorless mixture was then poured into 100 ml. of ice water with stirring. The semisolid product which precipitated was extracted into 150 ml. of methylene chloride and washed with two 50-ml. portions of a saturated aqueous sodium bicarbonate solution. The methylene chloride solution was dried over magnesium sulfate, filtered, and evaporated at 40° C. (18 mm.), leaving a semisolid residue weighing 4.0 grams. The product recrystallized slowly from benzene and gave 1.0 gram (13% yield) of VII, m.p. 88° to 90° C.

NMR spectrum in deuterochloroform with tetramethylsilane (TMS) reference: CH_3 protons at 7.8τ (singlet), $CH_3COOC\bar{H}_2$ protons at 5.5τ (singlet, $FC(NO_2)_2CH_2$ protons at 4.7τ (doublet, J = 13 cps.). The integral was consistent with the assignment of protons. Infrared spectrum (nujol): 5.75(s), C=O; 6.30(s), 12.50(m), NO_2; 7.30(s), 7.65(m), 8.20(m), 9.55(m), 11.75μ(m).

Tetrakis(2-fluoro-2,2-dinitroethyl) Propane-1,1,3,3-tetracarboxylate, VIII. To a stirred solution of 20 grams (0.053 mole) of bis(2-fluoro-2,2-dinitroethyl) malonate and 5.45 grams (0.054 mole) of triethylamine in 400 ml. of methylene chloride was added 5.2 grams (0.065 mole) of methyl chloromethyl ether at ambient temperature. The resulting mixture was then stirred for four hours at ambient temperature; the color of the mixture changed from deep yellow to colorless. The methylene chloride solution was washed with 100 ml. of 1*N* hydrochloric acid, dried over magnesium sulfate, and concentrated at 30° to 40° C. (18 mm.), leaving a white solid. Recrystallization of the solid from 200 ml. of chloroform gave 9.5 grams (47% yield) of VIII, m.p. 94° to 95° C.

NMR spectrum in deuterochloroform with TMS reference: $\bar{C}H_2(CH)_2$ protons at 7.5τ (triplet, J = 5.4 cps.), $CH_2(C\bar{H})_2$ protons at 6.3τ (triplet, J = 5.4 cps.), $FC(NO_2)_2CH_2$ protons at 4.7τ (doublet, J = 12.5 cps.). The integral was consistent with the assignment of protons. Infrared spectrum (nujol): 5.65(s), 5.70(s), C=O; 6.30(s), 12.80(s), NO_2; 7.30(m), 8.70(m), 11.75μ(m).

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