an excess of paraformaldehyde.[2] The experimental procedure involved distillation of I and the authors reported that explosions were encountered during this operation. In addition, compound I made by this method was very low melting (30°) and unstable.

An investigation of this reaction in this laboratory by G. Leston[3] showed that compound I could be obtained with a much higher melting point (65–66°), but that it was still hygroscopic and decomposed in the presence of moisture.

We now wish to report a more efficient preparation of I which eliminates the explosion hazard and affords in 80% yield pure I, m.p. 72°, directly from the reaction solution.

Pure I was found to be nonhygroscopic and stable. The presence of small amounts of water and formaldehyde was found to decrease the melting point and to cause I to react with the absorbed atmospheric moisture. The ready dissociation of I to trinitromethane and formaldehyde in water has recently been studied.[4]

EXPERIMENTAL

2,2,2-Trinitroethanol. In a three-necked flask which was provided with a stirrer, reflux condenser, and thermometer were placed 100 ml. of carbon tetrachloride, 2.12 g. (1.4 mmoles) of trinitromethane and 0.45 g. of paraformaldehyde (14.3 mmoles of formaldehyde assuming 95% formaldehyde). The turbid solution was heated with stirring for 3 hr. at 60–65° and then at reflux for 30 min. Concentrating the solution to 30 ml. and cooling in the refrigerator gave trinitroethanol in the form of long needles. Further concentration of the filtrate gave additional crops of crystals, m.p. 72°. The overall yield was 80%.

Anal. Calcd. for $C_2H_3O_7N_3$: C, 13.26; H, 1.66; N, 23.20. Found: C, 13.22; H, 1.62; N, 23.02.

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(2) N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

(3) Unpublished results from the M.S. dissertation of G. Leston, Purdue, 1949.

(4) J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.*, **77**, 496 (1955).

Polymerizable Esters of Trinitroethanol[1]

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The preparation of polymerizable mononitroalcohol esters of acrylic acid was described by D'Alelio.[2] Marans and Zelinski[3] showed that trinitroethanol (I) reacts readily with acetyl chloride and propionyl chloride to give the expected esters of I in high yields. We now wish to report the preparation of esters of I with unsaturated acids which are enumerated in Table I. In all cases the acid chlorides were employed and with the monobasic acids the highest yields were obtained in the absence of a solvent. This was also the case with fumaryl chloride, but the reaction temperature had to be raised to 130°. In the preparation of ditrinitroethyl itaconate the reaction was performed in petroleum ether. On heating, trinitroethyl acrylate and trinitroethyl methacrylate (II) were converted to high melting translucent solids of high softening range. Ester II was also copolymerized with ditrinitroethyl fumarate.

Attempts to prepare a monomer from isopropenyl isocyanate and compound I were unsuccessful. Reactions which were carried out in the presence of a polymerization inhibitor such as trinitrobenzene led to a viscous oil which turned to a solid during distillation at low pressure. It had the correct analysis for a polymer of trinitroethyl *N*-isopropenylcarbamate.

EXPERIMENTAL

Trinitroethyl methacrylate (II). Three grams (0.019 mole) of trinitroethanol and 10 ml. of methacrylyl chloride were agitated with a stream of dry nitrogen while the temperature was raised to 80° and kept there for 3 hr. The excess acid chloride was removed *in vacuo*, the residue dissolved in ether, washed successively with water, 1.5*N* potassium carbonate, and again with water, and the ether solution was dried with calcium sulfate. Distillation at 95° and 5 mm. caused the ester to crystallize in the condenser. Recrystallization from petroleum ether (b.p. 60–70°) at −60° gave *trinitroethyl methacrylate*, m.p. 26°.

Trinitroethyl acrylate. The procedure was the same as described above, except that the reaction was carried out at 28° for 2 hr.

Ditrinitroethyl fumarate. The reaction was conducted at 100° for 4 hr. and then at 130° for 3 more hr. After work-up as described above, a solid, m.p. 119°, remained. It was recrystallized from dibutyl ether to give *ditrinitroethyl fumarate*, m.p. 150°.

Ditrinitroethyl itaconate. The procedure was the same as described for the preparation of ester II except that petroleum ether (b.p. 60–70°) was employed as a solvent and the reaction mixture was refluxed for 16 hr. Removal of the solvent gave an oil which solidified on adding ethanol. Recrystallization from ethanol gave *ditrinitroethyl itaconate*, m.p. 97°.

Polymerization experiments. Heating ester II at 70° in an airtight flask for 6 days gave a yellow translucent solid which softened at 250–280°.

Similar treatment of trinitroethyl acrylate gave a solid of softening range 170–210°.

Heating an equimolar mixture consisting of ester II and ditrinitroethyl fumarate in a sealed flask at 70° for 6 days gave a translucent solid softening at 150–190°.

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(1) From the Ph.D. Thesis of Robert D. Lowrey, Purdue University, February 1950.

(2) G. F. D'Alelio, U. S. Patent 2,499,804 (Sept. 21, 1948).

(3) N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

TABLE I

UNSATURATED ESTERS OF TRINITROETHANOL

Compound	B.P.	M.P.	Yield, %	Formula	Calcd.			Found		
					C	H	N	C	H	N
Trinitroethyl acrylate	80/2 mm.	...	41	$C_5H_5N_3O_8$	25.53	2.21	17.87	25.25	2.18	17.90
Trinitroethyl methacrylate	95/5 mm.	26	54	$C_6H_7N_3O_8$	28.92	2.83	16.87	28.60	2.76	16.78
Trinitroethyl crotonate	97/5 mm.	...	60	$C_6H_7N_3O_8$	28.92	2.83	16.85	29.90	2.88	16.32
Ditrinitroethyl fumarate	...	150	18	$C_8H_6N_6O_{16}$	21.71	1.35	19.00	22.05	...	18.45
Ditrinitroethyl itaconate	...	97	9	$C_9H_8N_6O_{16}$	23.68	1.75	18.42	...	...	18.00

Polytrinitroethyl N-isopropenylcarbamate. Three grams (0.019 mole) of trinitroethanol, 0.85 g. (0.01 mole) of isopropenyl isocyanate[4] and 0.005 g. of trinitrobenzene were allowed to stand 1 week at 24°, and the mixture was then diluted with ether. A small amount of material which did not dissolve was discarded. Washing the solution with water until the water layer was colorless, drying with anhydrous calcium sulfate, and distilling *in vacuo*, left a dark semisolid which did not distill at 100° and 2 mm. It was purified by washing with hot petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_6H_8N_4O_8$: C, 27.28; H, 3.05, N, 21.21. Found: C, 27.35; H, 3.38; N, 21.18.

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[4] D. D. Coffmann, U. S. Patent, **2,334,476** (Nov. 16, 1943).

Polymerization of Perfluorobutyne-2[1]

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High molecular weight polymers of perfluorobutyne-2 have not been previously reported although recent publications[2–4] have described the thermal and catalytic preparation of trimers and tetramers of this bis(perfluoroalkyl)acetylene.

It has now been found that perfluorobutyne-2 forms a new, thermally stable, high molecular weight polymer under the influence of γ-radiation. Exposure of perfluorobutyne-2 to a Co^{60} source for sixty-seven hours at a rate of 3.6×10^5 r./hr. produced, in quantitative yield, a white, inert, solid polymer that is not attacked or wetted by boiling concentrated sulfuric acid, concentrated nitric acid or 50% sodium hydroxide solution. The polymer is insoluble in ether, carbon tetrachloride, methyl alcohol, benzene, and all other common laboratory solvents.

Preliminary data indicate that the thermal behavior of this polymer, polyperfluorobutyne, is quite different from that of polytetrafluoroethylene. The decomposition curve obtained from a thermogravimetric analysis in nitrogen showed an initiation point at 425°, approximately the same temperature as was found for polytetrafluoroethylene; at the 50% decomposition point, however, the curve for polyperfluorobutyne was about 75° above that of polytetrafluoroethylene.

Pyrolysis of polyperfluorobutyne and polytetrafluoroethylene in an evacuated system showed a more marked difference in behavior. Production of gaseous products from polytetrafluoroethylene began at 430°; the temperature was raised to 550°, and after six hours, one-half of the polytetrafluoroethylene had formed gaseous products; three hours at 630° completed the decomposition of this polymer sample. In contrast, with the same heating schedule, polyperfluorobutyne did not form gaseous products until a temperature of 550° had been reached, and after four hours at 630° only about 40% of the weight of the sample was converted to gaseous products. This pyrolysis does not necessarily indicate greater thermal stability in polyperfluorobutyne but does show a type of decomposition different from that of polytetrafluoroethylene.

The infrared spectrum of polyperfluorobutyne resembled that of polytetrafluoroethylene in the position of its major absorption peaks; there was a shift, however, to somewhat higher frequencies than those found for polytetrafluoroethylene.

Elemental analysis confirmed the assumption that this new product is a polymer of perfluorobutyne and that neither carbon nor fluorine was lost by fragmentation in the irradiation process. An empirical formula of C_4F_6 was obtained from the analysis.

Assumptions of the structure of this new polymer are at the present only speculative. As perfluorobutadiene is known to polymerize rather easily,[5] the possibility that perfluorobutyne-2

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[1] This work was supported in part by the Office of Naval Research, Chemistry Branch, under Contract N-onr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[4] J. F. Harris, Jr., U. S. Patent **2,923,746**, February 2, 1960.

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