An Improved Procedure for the Synthesis of Fluorodinitroethyl and Trinitroethyl Esters of Carboxylic Acids

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Recent investigations in this laboratory concerning structure–physical property relationships of nitroaliphatic and fluoronitroaliphatic compounds generated a need for the bistrinitroethyl and bisfluorodinitroethyl esters of a homologous series of dibasic acids. Furthermore, we desired to obtain certain of these esters in rather large quantities for testing of explosive properties.

A study of the literature available to us revealed several approaches which have been used to effect esterifications with 2,2,2-trinitroethanol (**1**) and 2-fluoro-2,2-dinitroethanol (**2**). The low basicity of these alcohols requires the use of a strong condensing agent or a reactive carboxylic acid derivative to effect esterification. The esterification methods generally used are: (1) transesterification of the methyl ester of the desired acid and the alcohol in fuming sulfuric acid,[1] (2) the acid and alcohol in fuming sulfuric acid solvent,[2] (3) the acid and alcohol in polyphosphoric acid solvent,[3] (4) the aluminum chloride catalyzed reaction of the acid chloride and the alcohol in an inert solvent,[4] and (5) the neat acid chloride and the alcohol.[5] The first two of these methods have been found to work well only in specific cases and the yields of ester have been found to vary widely depending on the carboxylic acid used. Esterification of malonic acid and trinitroethanol in polyphosphoric acid failed to give us the desired ester. Esterification *via* the aluminum chloride catalyzed reaction of the acid chloride appeared to us to be the most generally applicable procedure giving good yields.

Although the acid chloride–aluminum chloride procedure gave excellent yields of the bistrinitroethyl glutarate and bistrinitroethyl pimelate, we obtained a colored product in the preparation of bistrinitroethyl sebacate. Column chromatography and repeated recrystallization from a variety of solvent systems failed to give us the pure ester. This problem, as well as the difficulty in obtaining the requisite acid chlorides of the desired carboxylic acids, prompted us to seek another esterification procedure using the cheaper and more readily available carboxylic acids.

Trifluoroacetic anhydride has been used successfully as a condensing agent in esterification reactions for some time.[6,7] The acetate and trifluoroacetate of 2,2-dinitropropanol have been prepared using trifluoroacetic anydride as condensing agent.[8] It also has been shown to be an exceptionally powerful reagent for the esterification of sterically hindered acids and/or alcohols.[9] The reported procedures generally involve dissolving the carboxylic acid and alcohol in trifluoroacetic anhydride solvent. Esterification generally proceeds in high yield by merely stirring the solution a short time at ambient temperatures.

We have found that this general procedure gives, in most cases, quantitative yields of 2,2,2-trinitroethyl and 2-fluoro-2,2-dinitroethyl esters with a variety of mono- and dicarboxylic acids (Table I). A reaction time of 1.5 hr at ambient temperature was found sufficient for the esterification of all the acids in Table I with the exception of malonic and ethylmalonic acids.[10] In all cases, the product is isolated by merely pouring the trifluoroacetic anhydride solution into cold aqueous 1 *M* potassium hydrogen phosphate solution and filtering the crude solid ester. Since trifluoroacetic anhydride is, by far, the lowest boiling constituent (bp 40°) of the crude reaction mixture before work-up, it should be possible, on a larger scale, to recover part of it by distillation before work-up.

Succinic acid failed to yield any ester with **1** under the reaction conditions employed. This result is due presumably to intramolecular anhydride formation competing with esterification.[6] Likewise, glutaric acid gave lower yields of esterified products than might be expected. Oxalic acid was fragmented by trifluoroacetic anhydride and yielded no ester.

Experimental Section

Caution! Both 2,2,2-trinitroethanol (**1**) and 2-fluoro-2,2-dinitroethanol (**2**) are moderately shock sensitive explosives and should be handled with care. Compound **2** may cause painful burns upon contact with the skin.

All carboxylic acids were obtained from commercial sources and used without further purification. Fluorodinitroethanol[11,12] was obtained from the Naval Ordnance Laboratory, White Oak, Md., and was distilled [bp 55–56° (0.5 mm)] prior to use. Trinitroethanol was prepared from tetranitromethane, dried by azeotropic distillation, and crystallized (mp 70°) from carbon tetrachloride–methylene chloride solution, all by known procedures.[13] The crystalline trinitroethanol was stored under carbon tetrachloride in the refrigerator. Trifluoroacetic anhydride was obtained from Eastman Organics and was used as received.

All melting points were obtained on a Mel-Temp apparatus using sealed tubes and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument using deuteriochloroform as solvent and tetramethylsilane as internal reference. Infrared spectra were obtained in chloroform solution on a Beckman IR-20 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Esterification Procedure.—A 50-ml, single-necked, round-bottomed flask containing a Teflon-coated magnetic

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[1] M. H. Gold and K. Klager, *Tetrahedron, Suppl. 1*, **19**, 81 (1963).

[2] (a) M. B. Frankel, *J. Org. Chem.*, **27**, 331 (1962); (b) J. C. Colby (to U. S. Rubber Co.), U. S. Patent, 3,160,654 (Dec 8, 1964); *Chem. Abstr.*, **62**, 7644 (1965).

[3] (a) Reference 1; (b) L. A. Kaplan in "The Chemistry of the Nitro and Nitroso Groups," Part 2, H. Feuer, Ed., Interscience, New York, N. Y., 1970, p 305.

[4] Reference 2a.

[5] (a) N. S. Marans and R. P. Zelinski, *J. Amer. Chem. Soc.*, **72**, 5329 (1950); (b) H. Feuer, H. B. Hass, and R. D. Lowrey, *J. Org. Chem.*, **25**, 2070 (1960).

[6] J. M. Tedder, *Chem. Rev.*, **55**, 787 (1955).

[7] P. F. E. Cook and A. J. Showler, *J. Chem. Soc.*, 4594 (1965).

[8] L. W. Kissinger, M. Schwartz, and W. E. McQuistion, *J. Org. Chem.*, **26**, 5203 (1961).

[9] R. C. Parish and L. M. Stock, *ibid.*, **30**, 927 (1965).

[10] Presumably for steric reasons, optimum yields of esters of malonic and ethylmalonic acids were obtained after 18 hr at ambient temperature.

[11] M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

[12] V. Grakauskas and K. Baum, *ibid.*, **33**, 3080 (1968).

[13] NAVORD Report (Naval Ordnance Laboratory, White Oak, Md.) 6752, K. E. Shipp and M. E. Hill, "An Improved Process for the Preparation of 2,2,2-Trinitroethanol," Jan 5, 1960, pp 14–17.

TABLE I

TRINITROETHYL AND FLUORODINITROETHYL ESTERS[a]

Acid	Alcohol	Crude yield, % (recrystallized yield, %)[b]	Registry no.	Mp, °C	Nmr data, δ	Ir data, cm^{-1}
Malonic	**1**	100 (94)	35027-56-6	56.0–57.0	5.49 (s, 4), 3.65 (s, 2)	1785, 1600, 1290
Glutaric	**1**	80 (77)	35027-57-7	61.0–62.0	5.45 (s, 4), 2.52 (t, 4), 2.05 (q, 2)	1765, 1600, 1295
Adipic	**1**	99 (96)	35027-58-8	88.5–90.0	5.41 (s, 4), 2.45 (t, 4), 1.70 (m, 4)	1770, 1605, 1295
Pimelic	**1**	99 (94)	35027-59-9	55.0–56.2	5.40 (s, 4), 2.45 (t, 4), 2.0–1.1 (m, 6)	1770, 1600, 1295
Suberic	**1**	100 (96)	35027-60-2	58.0–59.0	5.40 (s, 4), 2.40 (t, 4), 1.90–1.15 (m, 8)	1770, 1600, 1295
Sebacic	**1**	100 (94)	20721-00-0	46.0–47.0	5.40 (s, 4), 2.40 (t, 4), 1.90–1.15 (m, 12)	1770, 1600, 1295
Dodecanedioic	**1**	98 (93)	35027-62-4	33.0–33.7	5.40 (s, 4), 2.40 (t, 4), 1.90–1.15 (m, 16)	1770, 1600, 1295
Ethylmalonic	**1**	63 (40)	35027-63-5	47.2–48.5	5.45 (s, 4), 3.50 (t, 1), 1.98 (quint, 2), 1.00 (t, 3)	1770, 1600, 1290
Malonic	**2**	68 (55)	25595-91-9	47.2–49.5 (lit.[c] 46–47°)	5.30 (d, 4, *J* = 16 Hz), 3.60 (s, 2)	1780, 1605, 1305 [lit.[c] ir (Nujol) 1780, 1610, 1315]
Glutaric	**2**	47 (44)	35027-65-7	53.5–55.0	5.22 (d, 4, *J* = 17 Hz), 2.50 (t, 4), 2.05 (q, 2)	1770, 1605, 1310
Adipic	**2**	100 (97)	35027-66-8	77.0–78.0	5.22 (d, 4, *J* = 17 Hz), 2.45 (t, 4), 1.68 (m, 4)	1770, 1605, 1310
Pimelic	**2**	89 (80)	35027-67-9	34.0–35.0	5.22 (d, 4, *J* = 17 Hz), 2.44 (t, 4), 1.95–1.15 (m, 6)	1765, 1605, 1310
Suberic	**2**	100 (89)	35027-68-0	46.0–47.5	5.21 (d, 4, *J* = 17 Hz), 2.45 (t, 4), 1.95–1.15 (m, 8)	1765, 1605, 1310
Sebacic	**2**	99 (88)	35027-69-1	31.5–32.0	5.20 (d, 4, *J* = 17 Hz), 2.40 (t, 4), 1.95–1.15 (m, 12)	1765, 1605, 1310
Dodecanedioic	**2**	99 (95)	35027-70-4	40.0–42.2	5.21 (d, 4, *J* = 17 Hz), 2.40 (t, 4), 1.90–1.20 (m, 16)	1765, 1605, 1310
Ethylmalonic	**2**	100 (95)	35027-71-5	49.0–50.0	5.30 (d, 4, *J* = 16 Hz), 3.50 (t, 1), 1.97 (quint, 2), 1.00 (t, 3)	1765, 1605, 1305
Benzoic	**2**	92 (74)	35027-72-6	47.0–48.5	8.15–7.25 (m, 5), 5.43 (d, 2, *J* = 17 Hz)	1745, 1605, 1310
Cinnamic	**2**	100 (96)	35027-73-7	63.0–64.0	7.78 (d, 1, *J* = 16 Hz), 7.45 (m, 5), 6.38 (d, 1, *J* = 16 Hz), 5.30 (d, 2, *J* = 17 Hz)	1735, 1630, 1600, 1305

[a] All compounds in this table gave satisfactory (±0.3%) analyses for C, H, N, and F. The analytical data were made available to the referees and to the Editor. [b] Recrystallized yields represent first and second crops of ester from methanol–water. [c] Bis(2-fluoro-2,2-dinitroethyl) malonate has been reported: M. E. Hill, D. L. Ross, C. L. Coon, and L. O. Ross, *J. Chem. Eng. Data*, **14**, 410 (1969).

stirring bar was charged with 11 mmol of a dicarboxylic acid or 22 mmol of a monocarboxylic acid, 25 mmol of **1** or **2** (4.60 g of **1** or 3.85 g of **2**), and 10 ml of trifluoroacetic anhydride. The reaction flask was then fitted with a drying tube and the reaction mixture was stirred at ambient temperature for 1.5 hr.[10] The reaction mixture was then poured into 75 ml of a cold (ice temperature) solution of 1 *M* aqueous dipotassium hydrogen phosphate. The reaction flask was rinsed twice with methanol and the rinsings were added to the phosphate solution. The phosphate solution containing the oily ester was stirred at 5° until the ester solidified. The solidified crude ester was filtered, washed with water, and vacuum dried to give the crude yield in Table I.

The crude esters were all recrystallized from methanol–water solution. The recrystallized yield in Table I is based only on the first and second crops from methanol–water.