TABLE I

DIMETALATION OF DIPHENYL ETHER

Organometallic Reagent	Solvent	Solvent Ratio	Reaction Conditions		Yield of Cyclic Derivative, %
			Temp.	Hr.	
n-Butyllithium	THF[a]-ether	1:1	Room temp.	14	32.0
n-Butyllithium	THF-ether	1:1.1	Mild reflux	4	45.5
n-Butyllithium	THF-ether	1:1.3	Mild reflux	5	50.5
n-Butyllithium	THF	—	-25 ± 5 + 0	5 + 12	16.6
Phenyllithium	THF-ether	1:1	Mild reflux	12	23.7
Methyllithium	THF	—	Mild reflux	12	0

[a] THF is tetrahydrofuran.

negative test. Color Test I[7] was strongly positive. The reaction mixture was poured jet-wise through a glass wool plug into a dried, nitrogen swept, addition funnel prior to derivatization.

Derivatization of the 2,2′-dilithiodiphenyl ether was carried out with 19.4 g. (0.015 mole) of dichlorodimethylsilane dissolved in 250 ml. of tetrahydrofuran in essential accordance with the published procedure.[1] The crude 10,10-dimethylphenoxasilin obtained weighed 17.8 g. (52.5%) and melted over the range 60–74°. Two recrystallizations from methanol raised the melting point to 74–79° (lit. m.p.,[1] 78.5–79.0°), 10.8 g. (32.0%). The material was not obtained in an optimum degree of purity, as the relative amounts obtained were of major importance. The melting point of a mixture with an authentic sample was undepressed, and the infrared spectra were superimposable.

The reaction was repeated under identical conditions but using larger quantities (2.5 times greater). The large bulk of the solutions proved difficult to handle and a lower yield of crude derivative was obtained (33.5%).

Dimetalation of diphenyl ether by n-butyllithium in tetrahydrofuran-ether mixed solvent at mild reflux. (A). 1:1.1 Tetrahydrofuran-ether ratio. A 440-ml. ether solution containing 0.575 mole of n-butyllithium was added rapidly to a solution of 42.5 g. (0.25 mole) of diphenyl ether and 350 ml. of tetrahydrofuran cooled to ice-bath temperature. The ice bath was removed, and the reaction mixture was warmed to a mild reflux temperature. Color Test II remained positive for 3 hr., but became negative after 4 hr. Color Test I was positive.

Derivatization was effected with 32.2 g. (0.25 mole) of dichlorodimethylsilane dissolved in 350 ml. of tetrahydrofuran as described in the previous experiment. Recrystallization of the crude solid from methanol gave 25.8 g. (45.5%) of 10,10-dimethylphenoxasilin, m.p. 75–79°.

(B). 1:1.3 Tetrahydrofuran-ether ratio. The above procedure was followed in the reaction of 46.8 g. (0.275 mole) of diphenyl ether dissolved in 400 ml. of tetrahydrofuran with 0.605 mole of n-butyllithium in 590 ml. of ether solution. A total of 5 hr. of mild reflux was necessary before Color Test II became negative. Derivatization with dichlorodimethylsilane gave 28.5 g. (50.5%) of 10,10-dimethylphenoxasilin, m.p. 74–79°.

Acknowledgment. This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Division, Wright-Patterson AFB, Ohio.

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY
AMES, IOWA

---

(7) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

---

gem-Dinitro Esters. III. Esters of 2,2-Dinitropropanol[1]

L. W. KISSINGER, M. SCHWARTZ, AND W. E. MCQUISTION

Received May 15, 1961

A number of esters of 2,2-dinitropropanol[2] were prepared and some of their physical properties measured during the screening of energy contributing compounds for plasticizing action in plastic bonded explosives (PBX). The use of energy contributing plastics and plasticizers would be expected to enhance the performance of the plastic bonded explosives described by James, Smith, and coworkers.[3]

Most of the esterifications were accomplished under mild conditions employing trifluoroacetic anhydride[4] or polyphosphoric acid[5] as condensing agent. In general, the purification of the esters was simpler when the former agent was used. In cases where both methods were used, the one giving the higher yield appears in the accompanying table. Table I also lists the physical properties measured. When tested, all the compounds in Table I appeared to be less sensitive than 2,4,6-trinitrotoluene to impact.

The carbonyl absorptions in the infrared[6] were shifted to shorter wave lengths compared to unsubstituted esters and occurred between 5.64 and 5.67 μ for all of the esters of the carboxylic acids except the formate and 2-methylacrylate (5.72 μ),

---

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) OSRD Report No. 2016, November 15, 1943.

(3) E. James, L. C. Smith, W. T. Barry, K. B. Fess, W. A. Lynch, C. L. Miller, J. B. Panowski, M. Schwartz, W. H. Stein, M. J. Urizar, D. W. Niemand, E. E. Shaw, and R. F. Warner, *U. S. At. Energy Comm.* LA-1448 (1952); *Chem. Abstr.*, 54, 21762 (1960).

(4) E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(5) The commercial product named "Polyphosphoric Acid" manufactured by the Victor Chemical Co. was used in this work.

(6) Infrared absorption spectra were determined with a Model 21 Perkin-Elmer instrument with matched 0.1-mm. sodium chloride cells and chloroform as solvent.

TABLE I

PROPERTIES OF 2,2-DINITROPROPYL ESTERS

2,2-Dinitropropyl Ester	Esterification Method (% Yield)	M.P.	B.P./Mm.	n_D^{25}	d_4^{25}	Formula	Calcd., %			Found, %[a]		
							C	H	N	C	H	N
Formate	PPA (45)		65/0.1	1.4505		$C_4H_6N_2O_6$	26.97	3.40	15.73	26.05	4.02	15.10
Acetate	TFAA (85)		75/0.5	1.4413		$C_5H_8N_2O_6$	31.25	4.20	14.58	31.48	4.37	14.17
Trifluoroacetate	TFAA (95)		46-8/0.07	1.3961		$C_5H_5F_3N_2O_6$	24.40	2.05	11.38	24.72	2.55	10.94
N Ethylcarbamate	See Experimental	21	80/0.02[b]	1.4611	1.40	$C_6H_{10}N_3O_6$	32.73	4.58	19.09	32.53	4.74	18.70
N-Ethyl-*N*-nitrocarbamate	See Experimental	34-36				$C_6H_9N_4O_8$	27.18	3.42	21.13	27.29	4.53	20.70
2-Methylacrylate	PPA (28)		71-72/0.03	1.4593		$C_7H_{10}N_2O_6$	38.53	4.62	12.84	38.48	4.58	12.57
2-Trifluoromethylacrylate	See Experimental	38-39				$C_7H_7F_3N_2O_6$	30.89	2.59	10.29	30.84	2.33	9.81
Malonate	PPA (44)	37-39			1.57	$C_9H_{12}N_4O_{12}$	29.35	3.29	15.22	28.43	3.11	14.91
Oxalate	PPA (12)	109-110				$C_8H_{10}N_4O_{12}$	27.13	2.85	15.82	26.97	3.63	15.07
Maleate	PPA[c] (53)	62-63			1.59	$C_{10}H_{12}N_4O_{12}$	31.59	3.18	14.74	31.58	3.20	14.64
Pentanedioate	PPA (81)	45-46			1.57	$C_{11}H_{16}N_4O_{12}$	33.34	4.07	14.14	33.58	4.28	13.58
Hexanedioate	PPA (79)	66-67			1.24	$C_{12}H_{18}N_4O_{12}$	35.13	4.42	13.66	35.37	4.80	13.55
4-Methyl-4-nitroheptanedioate[d]	PPA (45)	118-121				$C_{14}H_{21}N_5O_{14}$	34.79	4.38	14.49	34.56	4.93	13.90
of 4-(2-Carboxyethyl)-4-nitroheptanedioic acid[e]	PPA (10)	62-64			1.49	$C_{19}H_{27}N_7O_{20}$	33.88	4.04	14.56	33.11	4.19	14.69
α-Bromopropionate	PPA (53)		90/0.5	1.4793		$C_6H_9BrN_2O_6$	25.66	3.16	9.83	26.24	3.26	9.10
4-Nitro-4-azahexanoate	See Experimental		180/0.04[b]	1.4852	1.35	$C_8H_{14}N_4O_8$	32.65	4.77	19.04	32.98	5.16	18.64
Phosphate	See Experimental	146-147				$C_9H_{15}N_6O_{16}P$	21.86	3.04	17.00	21.76	3.45	16.46

[a] Microanalyses by M. J. Naranjo. [b] Pot temperature on distillation from a Hickman molecular still. [c] From the anhydride. [d] 4-Methyl-4-nitroheptanedioic acid, m.p. 110-111°, was obtained by hydrolysis of the dimethyl ester with 18% hydrochloric acid in 5 hr. under reflux. *Anal.* Calcd. for $C_8H_{13}NO_6$: C, 43.83; H, 5.98; N, 6.39. Found: C, 43.43; H, 6.13; N, 5.58. [e] N. J. Leonard and G. L. Shoemaker, *J. Am. Chem. Soc.*, **71**, 1762 (1949).

the trifluoroacetate (5.50 μ), the malonate (5.61 and 5.64 μ), and the oxalate (5.55 and 5.64 μ). The *gem*-dinitro absorptions occurred between 6.32–6.35 and 7.52–7.56 μ except for the malonate (6.30 and 7.51 μ), the trifluoroacetate (6.30 and 7.47 μ), and the 2-trifluoromethylacrylate (6.31, 7.45 μ, and 7.54 sh).

EXPERIMENTAL

Trifluoroacetic anhydride (TFAA) esterification method. One-fourth mole of the acid was slowly added to 55 g. (0.26 mole) of trifluoroacetic anhydride with stirring and cooling. To this stirred solution an equivalent amount of the alcohol was added at such a rate as to maintain gentle refluxing. After the addition was complete the solution was maintained at 60° for 4–5 hr., after which volatiles were stripped from the reaction mixture at 60°/40–50 mm. The residue was dissolved in ether, washed with ice water, washed free of acid with 5% sodium bicarbonate solution, and finally with water. After drying the solution with anhydrous magnesium sulfate, the ether was removed, and the product distilled through a 12-cm. vacuum-jacketed Vigreux column or a Hickman molecular still. Several of the crystalline esters were further purified by recrystallization from suitable solvents.

Polyphosphoric acid (PPA) esterification method. To a solution or suspension of 0.25 mole of the acid or anhydride in 150 g. of polyphosphoric acid at 50° an equivalent amount of the alcohol was added in portions with stirring. When the mildly exothermic reaction diminished, the reaction mixture was warmed to 75° for 3–4 hr., poured over ice while still warm, and the product extracted with ethyl acetate or ether. After washing free of acid with 5% sodium bicarbonate solution, the product was isolated and purified as described in the above method.

2,2-Dinitropropyl N-ethylcarbamate. A solution of 8.2 g. (0.114 mole) of ethyl isocyanate and 17 g. (0.113 mole) of 2,2-dinitropropanol in 200 ml. of chloroform was heated under reflux for 18 hr. Removal of the chloroform under reduced pressure and distillation of the residue from a Hickman still at 78–80°/0.02 mm. gave the theoretical yield of product with the properties given in Table I.

2,2-Dinitropropyl N-ethyl-N-nitrocarbamate. To a solution of 13.3 g. (0.06 mole) of 2,2-dinitropropyl *N*-ethylcarbamate in 125 ml. of acetic anhydride was added 100% nitric acid (125 ml.) while the temperature was kept below 10°. After 0.5 hr. the nitration mixture was poured over ice and the crude nitro compound was filtered, washed with water, and dried under vacuum giving 6 g. (37%) of product. After one crystallization from 95% ethanol, the 2,2-dinitropropyl *N*-ethyl-*N*-nitrocarbamate had the properties listed in Table I. The carbonyl absorption occurred at 5.59 μ and the nitro at 6.30, 7.50, and 7.72 μ in the infrared.[6]

Tris(2,2-dinitropropyl) phosphate. Phosphorus oxychloride (15 g.; 0.1 mole) was added to a solution containing 45 g. (0.3 mole) of 2,2-dinitropropanol and 0.2 g. of phosphorus trichloride in 100 ml. of toluene. After refluxing the mixture for 16 hr., the volatiles were removed under reduced pressure, 50 ml. of toluene was added, and the solution decolorized by percolating through a small activated charcoal column. Chilling the concentrated solution gave 13 g. (25%) of the ester having the properties listed in Table I.

2,2-Dinitropropyl 2-trifluoromethylacrylate. A solution of 15 g. (0.1 mole) of 2,2-dinitropropanol and 75 ml. of benzene was refluxed in a flask equipped with a water separator until no more water collected in the separator. 2-Trifluoromethylacrylic acid[7] (14 g., 0.1 mole) and 1 ml. of concd. sulfuric acid were added and the mixture refluxed for 16 hr. while 1.5 ml. of water (theory = 1.8 ml.) was collected in the separator. After washing the reaction mixture with 5% sodium bicarbonate solution, then with ice water, and drying over calcium sulfate the solvent was removed under reduced pressure giving 8.6 g. (32%) of crude white solid. Recrystallization from isopropyl ether gave an analytical sample with the properties given in Table I.

2,2-Dinitropropyl 4-nitro-4-azahexanoate. Addition of ethylnitramine to 2,2-dinitropropyl acrylate[8] by the method previously described[9] gave this ester with the properties listed in Table I in 63% yield. The carbonyl absorption occurred at 5.65 μ and the nitro at 6.32, 6.56, 7.55, and 7.74 μ in the infrared.[6]

Los Alamos Scientific Laboratory
University of California
Los Alamos, N. M.

---

[7] M. W. Buxton, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 366 (1954).

[8] T. M. Benziger, R. K. Rohwer, and W. H. Stein, *U. S. At. Energy Comm.* LAMS-1974 (1956), and references to the original work by Aerojet-General Corp. cited therein; *Chem. Abstr.*, **54**, 24363 (1960).

[9] L. W. Kissinger and M. Schwartz, *J. Org. Chem.*, **23**, 1342 (1958).

Tris(*n*-butyl)phosphine Sulfide

Ralph A. Zingaro and Raymond E. McGlothlin

Received May 15, 1961

Davies and Jones[1] reported that tris(*n*-butyl)phosphine reacts vigorously with sulfur, and more recently Chernick, Pedley, and Skinner[2] have measured the heat of reaction of tris(*n*-butyl)phosphine with sulfur. However, neither of these groups of investigators isolated or identified tris(*n*-butyl)phosphine sulfide. This compound is not reported by Kosolapoff,[3] and a careful search of the literature indicates that it has not been isolated or characterized. We have had need for this material, and its preparation and properties are herein reported.

Tris(*n*-butyl)phosphine reacts with bromine in hexane to form a heavy white precipitate of tris(*n*-butyl)phosphine dibromide. Addition of hydrogen sulfide to the latter results in the formation of tris(*n*-butyl)phosphine sulfide hydrobromide which separates out as a heavy oil and leaves any tris(*n*-butyl)phosphine oxide in solution, thus simplifying an otherwise difficult separation.

EXPERIMENTAL

The reaction must be carried out in a dry, nitrogen atmosphere. Into a 2-l., three-neck, oven-dried flask containing 101 g. (0.5 mole) of tris(*n*-butylphosphine in 1 l. of dry hexane, equipped with a stirrer, and gas inlet and outlet tubes was added dropwise, 80 g. (0.5 mole) of bromine. A voluminous white precipitate of tris(*n*-butyl)phosphine dibromide was formed. Hydrogen sulfide gas was then bubbled through

---

[1] W. C. Davies and W. J. Jones, *J. Chem. Soc.*, **33**, (1929).

[2] C. L. Chernick, J. B. Pedley, and H. A. Skinner, *J. Chem. Soc.*, **33**, 1851 (1957).

[3] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950.