Anal. Calcd. for $C_{22}H_{27}NO \cdot HCl$: C, 73.82; H, 7.89; Cl, 9.91. Found: C, 74.18; H, 7.65; Cl, 9.98.

1-Benzyl-4-phenyl-4-valeroylpiperidine hydrochloride was prepared in 48% yield; m.p., 200.0–203.0°.

Anal. Calcd. for $C_{23}H_{30}NO \cdot HCl$: Cl, 9.54. Found: Cl, 9.90.

4-Phenyl-4-acetylpiperidine. 1-Benzyl-4-phenyl-4-acetylpiperidine (86.1 g., 0.294 mole) was dissolved in 200 ml. of glacial acetic acid and 500 ml. of ethanol. Ten grams of 10% palladium-charcoal was added and the mixture hydrogenated at 560 lb. and 55°. The theoretical amount of hydrogen was taken up in 4 hr. The catalyst was removed by filtration, the filtrate concentrated to an oil and the oil made basic with 10% sodium hydroxide. The resulting oil was extracted with benzene, washed with water, concentrated to an oil, and distilled; b.p., 90–96°; 0.1 mm.; 4.43 g. of colorless oil (74.4%). A small portion of the base was converted to the hydrochloride and crystallized from methanol–ethyl acetate, m.p. 241–242°.

Anal. Calcd. for $C_{13}H_{17}NO$: N, 6.91. Found: N, 6.93.

The propionyl, butyryl, and valeroyl analogs were similarly prepared.

4-Phenyl-4-propionylpiperidine was prepared in 38.8% yield; hydrochloride, m.p. 206–207°.

Anal. Calcd. for $C_{14}H_{19}NO \cdot HCl$: C, 66.24; H, 7.94; Cl, 13.97. Found: C, 65.96; H, 7.79; Cl, 13.72.

4-Phenyl-4-butyrylpiperidine was prepared in 70.6% yield; b.p. 90–100°, 0.1 mm., hydrochloride, m.p. 165.6°.

Anal. Calcd. for $C_{15}H_{21}NO$: N, 6.06. Found: N, 6.13.

4-Phenyl-4-valeroylpiperidine was prepared in 73.2% yield; hydrochloride, m.p. 113–115°.

Anal. Calcd. for $C_{15}H_{23}NO \cdot HCl$: Cl, 12.58. Found: Cl, 12.80.

1-(2-Chloroethyl)-4-phenyl-4-propionylpiperidine. 1-(2-Hydroxyethyl) - 4 - phenyl- 4 - propionylpiperidine (32.5 g., 0.109 mole) was suspended in 400 ml. of benzene and 2 drops of pyridine. The solution was heated to reflux and a solution of thionyl chloride (13.1 g., 0.11 mole) in 50 ml. of benzene was added over 15 min. Reflux was continued for 1.5 hr. After standing for 2 days, the white solid was filtered and recrystallized from ethanol; m.p., 220–223° dec.; 31.7 g., yield 91.9%.

2-Phenylaminoethylbromide hydrobromide. This compound was prepared by Pearlman's method,[9] as were 3-phenylaminopropylbromide hydrobromide and 2-(4-methylphenylamino)ethyl bromide hydrobromide.

3-Phenylaminopropylbromide hydrobromide was prepared from *N*-3-hydroxypropyl aniline;[10] m.p., 128.5–129.5° (from ethanol), yield 63.5%.

Anal. Calcd. for $C_9H_{12}BrN \cdot HBr$: Br, 54.19. Found: Br, 53.95.

2-(4-Methylphenylamino)ethylbromide hydrobromide was prepared from 2-(4-methylanilino)ethanol; m.p., 178.9° (from acetone–ether), yield 54.2%.

Anal. Calcd. for $C_9H_{12}BrN \cdot HBr$: C, 36.64; H, 4.44. Found: C, 36.34; H, 4.26.

2-(4-Methylphenylamino)ethanol. This compound was prepared by the general method of Adams and Segur,[11] b.p., 95–97°/0.1 mm.; n_D^{25} 1.5616; yield, 76.4%.

Anal. Calcd. for $C_9H_{13}NO$: N, 9.26. Found: N, 9.23.

1-(2-Hydroxyethyl)-4-phenyl-4-propionylpiperidine hydrochloride. Method A. A mixture of 4-phenyl-4-propionylpiperidine, (36 g., 0.166 mole), ethylene chlorohydrin (22 g., 0.25 mole), sodium carbonate (32 g., 0.3 mole), and 150 ml. of *n*-butyl alcohol was refluxed for 24 hr. with stirring. The mixture was cooled, inorganic salts filtered and the filtrate concentrated to an oil. The oil was taken up in ether and a few small pieces of solid carbon dioxide added to precipitate any unchanged secondary amine. The ether solution was filtered and ethereal hydrogen chloride was added. The resulting white gum solidified on standing. Recrystallization from ethanol–ethyl acetate gave 35.5 g. of product (71.7%), m.p., 184–185°.

1-[2-(4-Chlorophenylamino)ethyl]-4-phenyl-4-propionylpiperidine hydrochloride. Method B. A mixture of 1-(2-chloroethyl)-4-phenyl-4-propionylpiperidine hydrochloride (6.32 g., 0.02 mole), 4-chloroaniline (10.2 g., 0.08 mole), and 50 ml. of Methyl Cellosolve (R) solvent was refluxed for 16 hr. The solution was chilled for several hours and the resulting solid recrystallized from ethanol; m.p., 216–218°, 5.8 g., yield, 71.3%.

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(9) W. M. Pearlman, *J. Am. Chem. Soc.*, **70**, 871 (1948).

(10) R. E. Rindfusz and V. L. Harnack, *J. Am. Chem. Soc.*, **42**, 1720 (1920).

(11) R. Adams and J. B. Segur, *J. Am. Chem. Soc.*, **45**, 785 (1923).

gem-Dinitroalkyl Acrylates

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The preparation of a number of nitroalkyl acrylates, crotonates, and methacrylates has been reported.[1] The synthesis of a series of *gem*-dinitroalkyl acrylates is described in this paper. The acrylates were prepared in 47–75% yield by refluxing a benzene solution of acrylic acid or methacrylic acid with the appropriate *gem*-dinitro alcohol in the presence of sulfuric acid catalyst, until the theoretical amount of water was evolved. The properties of the compounds which were prepared are summarized in Table I.

The majority of the *gem*-dinitro alcohols were prepared by the Henry reaction of the *gem*-dinitroalkane and formaldehyde.[2] The only exceptions were 3,3-dinitro-1-butanol, which was prepared from 3,3-dinitro-1-butylamine,[3] and *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine (IV), which was synthesized as shown in Chart I.

The Mannich condensation of 2,2-dinitropropanol and ethanolamine[4] gave *N*-(2,2-dinitropropyl)-ethanolamine, (I), which was nitrated directly to give *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine nitrate (II). Using a procedure similar to that de-

(1) N. S. Morans and R. P. Zelinski, *J. Am. Chem. Soc.*, 72, 2125 (1950).

(2) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, 79, 2953 (1957).

(3) L. Herzog, K. Klager, and M. H. Gold, *J. Org. Chem.*, *in press*.

(4) The condensation of 2,2-dinitroethanol and ethanolamine has been reported, H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, 76, 5124 (1954).

TABLE I

gem-DINITROALKYL ACRYLATES

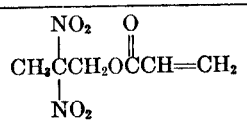
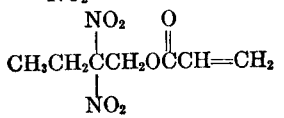
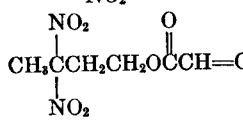
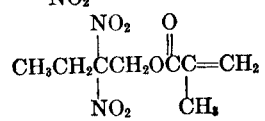
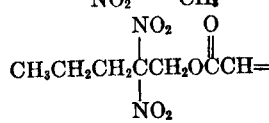
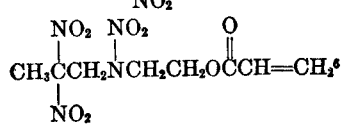
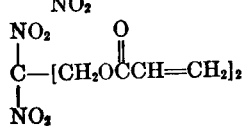
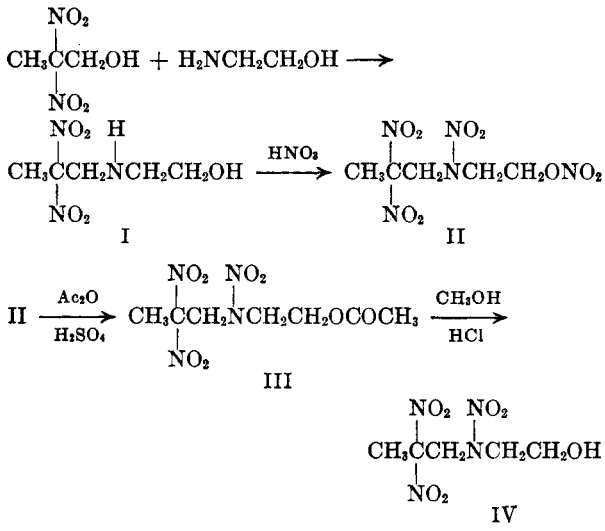
Acrylate	Yield, %	B.P.	n_D^{25}	d_4^{25}	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
	72.0	83/1 mm.	1.4600 (23)	1.303	$C_6H_8N_2O_6$	35.30	3.95	13.73	35.64	3.99	14.21
	67.8	74/2 μ	1.4579	1.257	$C_7H_{10}N_2O_6$	38.54	4.52	12.85	38.44	4.58	13.05
	75.2	78–80/2 μ	1.4660	—	$C_7H_{10}N_2O_6$	38.54	4.52	12.85	38.00	4.77	12.62
	71.4	124/2 mm.	1.4588	1.225	$C_8H_{12}N_2O_6$	41.38	5.22	12.07	40.80	5.45	11.48
	47.4	73–74/8 μ	1.4571	—	$C_8H_{12}N_2O_6$	41.38	5.22	12.07	40.89	5.19	12.63
	62.0	56–57 (m.p.)	—	—	$C_8H_{12}N_4O_8$	32.88	4.14	19.17	33.10	4.19	19.19
	52.0	91–93/3 μ	1.4727 (24)	—	$C_9H_{10}N_2O_8$	39.42	3.68	10.22	39.41	3.65	9.92

CHART I



scribed by Wolfrom *et al.*,[5] the nitrate ester was readily converted with acetic anhydride and sulfuric acid to the corresponding acetate (III), which was hydrolyzed to *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine (IV).

EXPERIMENTAL[7,8]

N-(2,2-Dinitropropyl)-N-nitroethanolamine nitrate (II). A mixture of 30.0 g. (0.5 mole) of ethanolamine, 80 ml. of methanol, 31.0 g. (0.5 mole) of glacial acetic acid, and 75.0 g. (0.45 mole) of 90% 2,2-dinitropropanol was refluxed for 3 hr. The methanol was removed by concentration *in vacuo* and the residual brown oil was diluted with water. The aqueous solution was extracted twice with methylene chloride. The combined extracts were washed with water and saturated sodium chloride solution, dried, and concentrated, leaving 46.0 g. of brown oil.

A mixture of 220 ml. of absolute nitric acid and 195 ml. of concd. sulfuric acid was heated to 40–45° and the above oil was added in 10 min. The yellow solution was heated at 54–57° for 35 min., cooled, and poured onto ice. The beige colored solid was collected, washed well with water, and recrystallized from methanol to give 27.0 g. (21.2%) of almost colorless plates, m.p. 108–111°.

Anal. Calcd. for $C_5H_9N_5O_9$: C, 21.21; H, 3.20. Found: C, 21.89; H, 3.33.

N-(2,2-Dinitropropyl)-N-nitroethanolamine acetate (III). A solution of 1.0 g. (0.0035 mole) of *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine nitrate in 8 ml. of acetic anhydride was cooled in an ice bath and 1 ml. of concd. sulfuric acid was added. On warming, an exothermic reaction with gas evolution took place. After 5–10 min. at 80°, the solution was cooled and poured onto ice. The solid was collected and recrystallized from methanol to give 0.54 g. (54.2%) of colorless plates, m.p. 56–57°.

Anal. Calcd. for $C_7H_{12}N_4O_8$: C, 30.00; H, 4.32; N, 20.00. Found: C, 30.44; H, 4.55; N, 20.01.

N-(2,2-Dinitropropyl)-N-nitroethanolamine (IV). A solution of 0.4 g. of *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine acetate, 12 ml. of methanol, and 1 ml. of concd. hydrochloric acid was refluxed for 3.5 hr. and concentrated, leaving a solid, m.p. 53–55°. Recrystallization of the product from chloroform yielded colorless needles, m.p. 59–60°.

Anal. Calcd. for $C_5H_{10}N_4O_7$: C, 25.21; H, 4.23; N, 23.53. Found: C, 25.48; H, 4.06; N, 23.78.

2,2-Dinitrobutyl acrylate. This preparation is typical of the synthesis of the *gem*-dinitroalkyl acrylates. A mixture of 164 g. (1.0 mole) of 2,2-dinitrobutanol, 108 g. (1.5 moles) of glacial acrylic acid stabilized with methylene blue, 500 ml. of benzene, and 2 ml. of concd. sulfuric acid was refluxed under a Dean-Stark trap until the theoretical amount of water was collected. The solution was diluted with 250 ml. of benzene and washed with five 250-ml. portions of water, three 250-ml. portions of 5% sodium bicarbonate, and two 250-ml. portions of water. The solution was dried over sodium sulfate, concentrated, and the residue distilled to give 148 g. (67.8%) of 2,2-dinitrobutyl acrylate, b.p. 74/2 μ, n_D^{25} 1.4579.

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(5) M. I. Wolfrom, R. S. Bower, and G. G. Maher, *J. Am. Chem. Soc.*, **73**, 874 (1951).

(6) In this preparation acrylic acid and trifluoroacetic anhydride were used according to the procedure of A. H. Ahlbrech and D. W. Codding, *J. Am. Chem. Soc.*, **75**, 984 (1953).

(7) All melting points and boiling points are uncorrected.

(8) Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

Di- and Tetracarboxydiphenylmethanes and Derivatives

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The condensation of aromatic compounds with carbonyl compounds to form diphenylmethanes has been known for many years. There are many references to the condensation of "activated" aromatics such as phenols, anilines, toluene, and naphthalene with acetone, formaldehyde, etc. However, there are few references to the condensation of negatively substituted benzenes such as benzoic acid, nitrobenzene and x-chloronitrobenzenes with formaldehyde. Prior to this publication, the condensation of the phthalic acids (*o*, *m*, or *p*) with formaldehyde to form diphenylmethanes had not been reported.

In 1894, Schopff[2] and Weil[3] in separate communications reported the condensation of benzoic acid with formaldehyde to give a product which they stated was the *meta*-substituted diphenylmethane. It was reasoned that since the product had a lower melting point than the known *para* isomer and did not form anthrone-1-carboxylic acid on heating with sulfuric acid, it must have been the *meta* isomer.

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(2) M. Schopff, *Ber.*, **27**, 2321, 2324 (1894).

(3) H. Weil, *Ber.*, **27**, 3315 (1894).