mm.), $n^{20}\mathrm{D}$ 1.4738, solidified upon cooling in an ice–water bath (lit.[13] m.p. 2°) and gave correct elemental analyses. Infrared absorptions (neat) showed 1740 and 1255 cm.$^{-1}$. Hydrolysis with 5% sodium hydroxide solution gave a 93% yield of 12-hydroxydodecanoic acid, m.p. 84–85° (lit.[14] m.p. 84–85°) after recrystallizations from benzene. Infrared absorptions (Nujol) appeared at 3230 and 1678 cm.$^{-1}$.

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The Configurational Relationship of Optically Active α-Phenylethyl Nitrate to α-Phenylethyl Alcohol, α-Phenylethyl Chloride, and Methyl α-Phenylethyl Ether[1]

NATHAN KORNBLUM, WILLARD J. JONES, AND
DONALD E. HARDIES[2]

*Department of Chemistry, Purdue University,
Lafayette, Indiana*

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As part of a study of the stereochemistry and mechanism of the reactions of silver salts with alkyl halides,[3] a knowledge of the configuration of α-phenylethyl nitrate was required. Incidental to obtaining this information we have, in several new ways, confirmed the earlier configurational assignment for 2-octyl nitrate.[4]

The nitrate esters were converted to the corresponding alcohols under aprotic conditions; the use of aprotic solvents seemed desirable in order to avoid ambiguity, especially in the α-phenylethyl system. When (−)-2-octyl nitrate was treated with lithium aluminum hydride in ethyl ether, an 80% yield of (−)-2-octanol was obtained.[5] But application of this method to the reduction of α-phenylethyl nitrate did not give the alcohol. Instead, a mixture whose chief component appeared to be ethyl benzene was produced.[6]

Many years ago Chapman and Smith reported that sodium cleaves alkyl nitrates according to eq. 1,[7] a

$$\mathrm{RONO_2 + Na \longrightarrow RONa + NaNO_2} \tag{1}$$

process which would be expected to occur with retention of configuration. In accord with this expectation, the reaction of (−)-2-octyl nitrate with sodium in petroleum ether (b.p. 35–37°) gave (−)-2-octanol in 62% yield. However, with α-phenylethyl nitrate reaction did not occur to any significant extent, presumably because of the dark brown solid which soon covered the sodium. Eventually it was found that on treating levorotatory α-phenylethyl nitrate with potassium and sand a 25% yield of levoratory α-phenylethyl alcohol could be obtained.

That α-phenylethyl alcohol and α-phenylethyl nitrate having the same sign of rotation have the same configuration was confirmed by allowing (−)-α-phenylethyl nitrate to react with ethylmagnesium bromide[8]; this gave (−)-α-phenylethyl alcohol in 70% yield (eq. 2).

$$\mathrm{RONO_2 + EtMgBr \longrightarrow ROH + Et_2NOH} \tag{2}$$

Finally, it may be mentioned that early in this investigation the reduction of α-phenylethyl nitrate with aqueous–ethanolic ammonium polysulfide, a reagent used successfully in the 2-octyl series by Merrow and Van Dolah,[4] was examined. An 11% yield of α-phenylethyl alcohol having the same sign of rotation as the nitrate ester was isolated.

The configurational relationship of α-phenylethyl nitrate to α-phenylethyl chloride was established by treating the nitrate ester with lithium chloride in dry acetone. The nitrate ester, $\alpha^{27}\mathrm{D}$ −3.28°, gave dextrorotatory α-phenylethyl chloride, $\alpha^{27}\mathrm{D}$ +3.17°.[9] Since the reaction must have occurred with inversion, it follows that the nitrate ester and the chloride have the same sign of rotation when they have the same configuration, a result consonant with the fact that in the α-phenylethyl series the alcohol and the chloride have the same sign of rotation when they are of the same configuration.[10]

The stereochemical relationship of α-phenylethyl nitrate with methyl α-phenylethyl ether was achieved by treating a methanolic solution of the nitrate with sodium methoxide under kinetically second-order conditions. The ether produced (56% yield) had the opposite sign of rotation from the nitrate ester; hence, it is concluded that methyl α-phenylethyl ether and α-phenylethyl nitrate have the same sign of rotation when they have the same configuration. This is in accord with the fact that α-phenylethyl alcohol and its methyl ether have the same configuration when they have the same sign of rotation.[11]

Experimental[12]

The preparation of the optically active nitrate esters is described elsewhere.[3]

Cleavage of (−)-2-Octyl Nitrate by Sodium.—Levorotatory 2-octyl nitrate (8.75 g., 0.05 mole, b.p. 54° at 2 mm., $n^{20}\mathrm{D}$ 1.4254, $\alpha^{26}\mathrm{D}$ −14.29°) was dissolved in 50 ml. of petroleum ether[13] (b.p. 35–37°) and to this solution, cooled to 0°, was added

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[1] We wish to thank the Explosives Department of the Du Pont Co. for a grant which supported this work.

[2] From the doctoral dissertations of Willard J. Jones (1960) and Donald E. Hardies (1957).

[3] N. Kornblum, D. E. Hardies, and W. J. Jones, *J. Am. Chem. Soc.*, in press.

[4] S. J. Cristol, B. Franzus, and A. Shadan, *ibid.*, **77**, 2512 (1955); R. T. Merrow and R. W. Van Dolah, *ibid.*, **77**, 756 (1955).

[5] The reduction of racemic 2-octyl nitrate by lithium aluminum hydride has been described previously by L. M. Soffer, E. W. Parrotta and J. Di Domenico, *ibid.*, **74**, 5301 (1952).

[6] Catalytic hydrogenation of α-phenylethyl nitrate in butyrolactone over Adams platinum oxide catalyst also proceeded rapidly, but upon working up the reaction mixture none of the expected alcohol was detected. Again a mixture which seemed to contain much ethylbenzene was obtained.

[7] E. T. Chapman and M. H. Smith, *J. Chem. Soc.*, **20**, 576 (1867); *Z. Chem.*, 172 (1868).

[8] H. J. Hepworth, *J. Chem. Soc.*, **119**, 251 (1921).

[9] The corresponding reaction employing lithium bromide gave a good yield of pure, but racemic, α-phenylethyl bromide. The success achieved with lithium chloride is due to the rather slow rate at which α-phenylethyl chloride is racemized by lithium chloride in refluxing acetone; see Experimental.

[10] N. Kornblum, L. Fishbein, and R. A. Smiley, *J. Am. Chem. Soc.*, **77**, 6261 (1955).

[11] K. Mislow, *ibid.*, **73**, 4043 (1951).

[12] All rotations were determined using the pure liquid in a 1-dm. tube.

[13] The petroleum ether was shaken with 5% aqueous potassium permanganate for 15 min. and then distilled from solid potassium permanganate. It was then dried over sodium.

2.57 g. (0.11 g.-atom) of sodium. Stirring was then initiated. The system was swept with dry nitrogen throughout the experiment. Almost immediately after adding the sodium the solution began to boil and it became dark. After several minutes boiling stopped; at this point the sodium had a very shiny luster. The mixture was stirred for a total of 0.5 hr. at ice temperature and then about 50 ml. of water was carefully added. The petroleum ether was expelled by evacuation and the residual aqueous solution[14] was steam distilled. The distillate was extracted with ether; the extracts were dried over anhydrous potassium carbonate and distilled. There was obtained 4.00 g. (62% yield) of levorotatory 2-octanol, b.p. 45° (1 mm.), $n^{20}\mathrm{D}$ 1.4260, $\alpha^{25}\mathrm{D}$ −4.81°.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.92. Found: C, 73.90; H, 13.86.

Cleavage of (−)-α-Phenylethyl Nitrate by Potassium.—In a 300-ml. flask (oven dried and swept with dry nitrogen while cooling) was placed 50 ml. of petroleum ether[13] (b.p. 90–100°), 10 g. of sand (washed with hydrochloric acid and water and ignited just before using), potassium (8.75 g., 0.224 g.-atom), and levorotatory α-phenylethyl nitrate (12.5 g., 0.075 mole), b.p. 58° (1 mm.), $n^{20}\mathrm{D}$ 1.5089, $\alpha^{27}\mathrm{D}$ −1.80°. Stirring was begun and the system was flushed with nitrogen from time to time. About 5 min. after the addition of the nitrate ester the potassium was covered with a brown coating. Up to this point the reaction had been run at room temperature. The flask was now placed in ice for *ca.* 2 hr. and then it was maintained at room temperature for *ca.* 15 hr. The mixture was then cooled to 0°, cold methanol (*ca.* 50 ml.) was added slowly, and then the product was added to *ca.* 200 ml. of water and steam distilled. The distillate was saturated with sodium chloride and extracted with ethyl ether. After drying, the ether solution was distilled. There was obtained 2.30 g. (25% yield) of levorotatory α-phenylethyl alcohol, b.p. 53° (1 mm.), $n^{20}\mathrm{D}$ 1.5271, $\alpha^{26}\mathrm{D}$ −1.04°.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.75; H, 8.25.

Reaction of Ethylmagnesium Bromide with (−)-α-Phenylethyl Nitrate.—The Grignard reagent prepared from 70 g. (0.64 mole) of ethyl bromide and 15 g. (0.62 g.-atom) of magnesium was cooled to −5°. To it 20 g. (0.12 mole) of levorotatory α-phenylethyl nitrate ($\alpha^{27}\mathrm{D}$ −3.28°, $n^{20}\mathrm{D}$ 1.5091), diluted with 100 ml. of ethyl ether, was added dropwise while stirring and cooling at −5°. The reaction was immediate and vigorous. After addition of the nitrate was complete, the reaction mixture was allowed to warm to room temperature and agitated for 24 hr. It was then acidified with 5% sulfuric acid while keeping the temperature below 5°. The ether layer was washed with sodium bicarbonate and with water before drying over magnesium sulfate. Fractionation of the product through a short column gave 9.8 g. (68% yield) of pure levorotatory α-phenylethyl alcohol ($n^{20}\mathrm{D}$ 1.5274, $\alpha^{27}\mathrm{D}$ −2.90°).

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.46; H, 8.43.

The infrared spectrum of this material was superimposable on that of authentic α-phenylethyl alcohol.

Reduction of (−)-α-Phenylethyl Nitrate with Ammonium Polysulfide.—This reaction was carried out according to the procedure of Merrow and Van Dolah[4] except that it was only allowed to proceed for 1 day at room temperature. From 10.7 g. (0.064 mole) of levorotatory α-phenylethyl nitrate, b.p. 58° (1 mm.), $n^{20}\mathrm{D}$ 1.5089, $\alpha^{25}\mathrm{D}$ −6.05°, there was obtained 0.85 g. (11% yield) of levorotatory α-phenylethyl alcohol, b.p. 57° (1 mm.), $n^{20}\mathrm{D}$ 1.5268–1.5269, $\alpha^{27}\mathrm{D}$ −3.59°.

Reaction of (−)-α-Phenylethyl Nitrate with Lithium Chloride.—A mixture of 8 g. of levoratory α-phenylethyl nitrate ($\alpha^{27}\mathrm{D}$ −3.28°), 100 ml. of acetone which had been dried over Drierite and distilled directly into the reaction flask, and excess lithium chloride (10 g.), was refluxed for 60 hr. The reaction product was poured into a mixture of petroleum ether (b.p. 65–67°) and ice water, and the organic layer was then washed with water, dried, and fractionally distilled. The 3.65 g. of product had $\alpha^{27}\mathrm{D}$ +4.35°, $n^{20}\mathrm{D}$ 1.5265–1.5269. This α-phenylethyl chloride was, however, contaminated by a small amount of α-phenylethyl nitrate as shown by the infrared spectrum. Consequently, 2.55 g. of this chloride was treated with lithium chloride as before for an additional 72 hr. On working up the reaction mixture 2.35 g. of dextorotatory α-phenylethyl chloride ($\alpha^{27}\mathrm{D}$ +3.17°, $n^{20}\mathrm{D}$ 1.5267–1.5269) was isolated. This had an infrared spectrum superimposable on that of authentic α-phenylethyl chloride; no nitrate ester band was present.

Anal. Calcd. for C_8H_9Cl: C, 68.33; H, 6.46; Cl, 25.25. Found: C, 68.12; H, 6.21; Cl, 25.06.

Optical Stability of α-Phenylethyl Chloride in Presence of Chloride Ion.—α-Phenylethyl chloride (0.5 g., $\alpha^{25}\mathrm{D}$ +33.4°) was added to a slurry of excess lithium chloride in 5 ml. of acetone and refluxed for 20 hr. The recovered α-phenylethyl chloride had $\alpha^{27}\mathrm{D}$ +30.5°.

The Reaction of (+)-α-Phenylethyl Nitrate with Sodium Methoxide in Methanol.—At 20° a 0.4786 *M* solution of α-phenylethyl nitrate in methanol containing sodium methoxide (1.163 *M*) gave a second-order rate constant ($k = 1.86 \pm 0.02 \times 10^{-2}$ l. mole^{-1} hr.$^{-1}$) over the first 65% of the reaction.

Eight grams (0.047 mole) of dextrorotatory α-phenylethyl nitrate ($\alpha^{26}\mathrm{D}$ +1.63°, $n^{20}\mathrm{D}$ 1.5089) was added to solution of sodium (2.35 g., 0.102 g.-atom) in 50 ml. of methanol. The resulting clear solution was stirred at room temperature under dry nitrogen for 12 hr. after which stirring was discontinued. After a total of 132 hr. at room temperature, the white solid which had formed was isolated by filtration and washed with ether. This solid was insoluble in common organic solvents but dissolved in water; it decomposed upon heating in a Bunsen flame, but did not burn; it gave a brown ring test with ferrous sulfate and sulfuric acid. When a sample was added to aniline in cold hydrochloric acid and this solution in turn was added to a basic solution of β-naphthol, no red precipitate was formed. The solid weighed 3.08 g. (77% yield calcd. as $NaNO_3$). The methanolic filtrate was poured into water and extracted with ether, and the extracts were washed with water and dried over magnesium sulfate. Distillation through a small column gave 3.59 g. (56% yield) of levorotatory methyl α-phenylethyl ether, b.p. 76° (30 mm.), $n^{20}\mathrm{D}$ 1.4915–1.4917, $\alpha^{26}\mathrm{D}$ −3.79°.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.29; H, 9.04.

Reduction with Lithium Aluminum Hydride. A. 2-Octyl Nitrate.—Levoratory 2-octyl nitrate ($\alpha^{28}\mathrm{D}$ −2.71°, $n^{20}\mathrm{D}$ 1.4249) was reduced as described by Soffer, Parrotta, and Di Domenico[5] except that the reaction was first conducted at 0° for 57 hr. and then at 25° for 27 hr. An 80% yield of 2-octanol, $\alpha^{25}\mathrm{D}$ −1.10°, b.p. 55° (3 mm.), $n^{20}\mathrm{D}$ 1.4260, was obtained.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.76; H, 13.65.

B. α-Phenylethyl Nitrate.—This reduction was conducted at 0° for 200 hr. during which time relatively little gas was evolved. The product was a mixture from which no pure compound was isolated but which appeared to contain much ethyl benzene.

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[14] Prior to steam distillation a small portion of the aqueous solution was added to aniline in cold hydrochloric acid. The resulting solution gave a red precipitate with sodium β-napthoxide.

The Preparation of Diene Adducts of *o*-Quinones

F. J. Evans, H. S. Wilgus, III, and J. W. Gates, Jr.

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

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The reaction of dienes with *p*-quinones and the rearrangement of these adducts to hydroquinone deriva-