Experimental

Vapor phase chromatographic (v.p.c.) analyses were performed using a stainless steel column 4 ft. long by 0.25 in. in diameter packed with 23% Dow Corning 200 silicone gum rubber on Chromosorb W. H^1 n.m.r. spectra were obtained on Varian Associates Model A-60 spectrometer at a radiofrequency of 60 Mc./sec. with carbon tetrachoride as a solvent and 1% of tetramethylsilane as an internal standard.

Preparation of Standards and Reagents.—Pentamethyldisiloxane was a Dow Corning Corporation product carefully redistilled having the properties: b.p. 85° at 750 mm., n^{25}_{D} 1.3715, d^{25}_{4} 0.7546, RD[3] 0.3008 (calcd. 0.3000).

Bistrimethylsiloxymethylsilane was prepared by the acid equilibration of hexamethyldisiloxane (2750 g., 16.9 moles) and 2,4,6,-8,10-pentamethylcyclopentasiloxane (359 g., 5.97 equiv.). The mixture was stirred and heated at 60° for 9 hr., filtered, and distilled to give bistrimethylsiloxymethylsilane: 735 g., 55.3% yield, b.p. 66° at 59 mm., n^{25}_{D} 1.3800, d^{25}_{4} 0.8136, RD 0.2847 (calcd., 0.2841). The literature[4a] reports b.p. 142° at 760 mm., n^{20}_{D} 1.3818, d^{20}_{4} 0.8194.

Anal. Calcd. for $(Me_3SiO)_2MeSiH$: Si, 37.85; SiH, 0.449. Found: Si, 37.95; SiH, 0.453.

Tristrimethylsiloxysilane was prepared by the hydrolysis of a mixture of trichlorosilane and trimethylchlorosilane in isopropyl alcohol, b.p. 85° at 30 mm., n^{25}_{D} 1.3846. The literature[4b] reports b.p. 67–68° at 11 mm., n^{20}_{D} 1.3860, d^{20}_{4} 0.854.

Anal. Calcd. for $(Me_3SiO)_3SiH$: Si, 37.9; SiH, 0.338. Found: Si, 37.8; SiH, 0.326.

The H^1 n.m.r. spectrum of this compound is two singlets with τ-values of 9.88 and 5.75 with integrated values of 27.3/1.0 (calcd. 27/1).

The hexenes were obtained from The Phillips Petroleum Co. and were at least 95% pure.

The Addition of Pentamethyldisiloxane to Hexene-1.—In a 300-ml. flask fitted with a condenser were placed pentamethyldisiloxane (14.8 g., 0.100 mole), hexene-1 (8.4 g., 0.10 mole), and 0.05 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. The reaction began at 45° and apparently was complete in less than 1 min. The temperature rose to 95° although the flask was cooled in a pan of cold water. Distillation yielded hexylpentamethyldisiloxane: 15.2 g., 66.1% yield, b.p. 198° at 750 mm., n^{25}_{D} 1.4087, d^{25}_{4} 0.7926, RD 0.3117 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

Anal. Calcd. for $C_{11}H_{28}OSi_2$: Si, 24.2. Found: Si, 24.46.

The Addition of Pentamethyldisiloxane to Hexene-2.—In a 200-ml. flask fitted with a condenser were placed pentamethyldisiloxane (14.8 g., 0.100 mole), hexene-2 (8.4 g., 0.10 mole), and 0.05 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. After heating for a total of 30 hr. the temperature had risen to 135°. Distillation yielded hexylpentamethyldisiloxane: 11.3 g., 48.7% yield, b.p. 200° at 750 mm., n^{25}_{D} 1.4075, d^{25}_{4} 0.7971, RD 0.3095 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

No products that might have formed by a methyl–trimethylsiloxy rearrangement were detected by v.p.c. in these experiments.

Anal. Calcd. for $C_{11}H_{28}OSi_2$: C, 56.8; H, 12.14; Si, 24.2. Found: C, 56.8; H, 12.4; Si, 24.24.

The adducts of hexene-1 and hexene-2 to pentamethyldisiloxane would be expected to have slightly different physical properties because different hexyl isomers or combinations of hexyl isomers may be present.[5]

The Addition of Bistrimethylsiloxymethylsilane to Hexene-2.—In a 2-l., one-necked flask vented *via* a condenser and calcium chloride tube were placed bistrimethylsiloxymethylsilane (222 g., 1.00 mole), hexene-2 (84.2 g., 1.00 mole), and 0.50 ml. of a 0.10 *M* chloroplatinic acid in isopropyl alcohol solution. The highest temperature reached while heating for a period of 10 hr. was 138°. Periodic v.p.c. analyses indicated the continuous formation of adduct and rearrangement products, and a 95% conversion after 10 hr. of heating. Distillation yielded these products.

A.—Bistrimethylsiloxymethylhexylsilane (137 g., 56.6% yield) had b.p. 70° at 5 mm., n^{25}_{D} 1.4071, and was partially separated into two components by v.p.c., indicating the presence of at least two isomers.[5] Bistrimethylsiloxymethylhexylsilane prepared in this manner has the following physical properties and analyses: b.p. 70° at 5 mm., n^{25}_{D} 1.4070, d^{25}_{4} 0.8320, RD 0.2959 (calcd. for $(Me_3SiO)_2SiMeHex$, 0.2961).

Anal. Calcd. for $C_{13}H_{34}O_2Si_3$: Si, 27.5. Found: Si, 27.44.

B.—Tristrimethylsiloxysilane (21.5 g., 0.0726 mole), 14.5% yield with a purity of 95%, had b.p. 69° at 14 mm., n^{25}_{D} 1.3850, d^{25}_{4} 0.8407, RD 0.2788 [calcd. for $(Me_3SiO)_3SiH$, 0.2818].

This product had identical H^1 n.m.r. and infrared spectra and v.p.c. retention times with the standard.

Anal. Calcd. for $(Me_3SiO)_3SiH$: Si, 37.9; SiH, 0.338. Found: Si, 36.9, 37.2; SiH, 0.322, 0.353.

C.—Hexylpentamethyldisiloxane (14.5 g., 0.0625 mole), 12.5% yield, with a purity of 96%, had b.p. 201° at 750 mm., n^{25}_{D} 1.4080, d^{25}_{4} 0.8026, RD 0.3074 (calcd. for $Me_3SiOSiMe_2Hex$, 0.3103).

Anal. Calcd. for $C_{11}H_{28}OSi_2$: C, 56.8; H, 12.14; Si, 24.15. Found: C, 55.96, 56.46; H, 12.58, 12.31; Si, 24.50.

The H^1 n.m.r. and infrared spectra as well as the v.p.c. retention time for this sample were indistinguishable from those of the product obtained from pentamethyldisiloxane and hexene-2.

D.—3,5-Bistrimethylsiloxyoctamethyltetrasiloxane (15.2 g., 6.4%) with a purity of 95% had b.p. 95° at 3 mm., n^{25}_{D} 1.3961, d^{25}_{4} 0.8838, RD 0.2719 [calcd. for $(Me_3SiO)_2MeSiOSiMe(OSiMe_3)_2$, 0.2697]. Literature[6] values given are b.p. 256°, n^{20}_{D} 1.3947, d^{20}_{4} 0.893.

Anal. Calcd. for $C_{14}H_{42}O_5Si_6$: C, 36.7; H, 8.79; Si, 36.75. Found: C, 39.02, 39.40; H, 9.21; Si, 34.94, 34.98.

The infrared spectrum was identical with that of a standard of $[(Me_3SiO)_2SiMe]_2O$. H^1 n.m.r. analysis revealed the presence of two types of methyl protons in the ratio of six to one, which is correct for the proposed structure.

The Attempted Addition of Tristrimethylsiloxysilane to Hexene-2.—A solution consisting of tristrimethylsiloxysilane (50.0 g., 0.169 mole), hexene-2 (14.2 g., 0.169 mole), and 0.17 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol was heated at reflux (108°) for 7 days. During the period of heating an additional 0.17 ml. of catalyst was added. Vapor phase chromatography indicated the amount of adduct formation (if any) to be less than 5%.

The Addition of Bistrimethylsiloxymethylsilane to Cyclohexene.—A solution of bistrimethylsiloxymethylsilane (22.2 g., 0.100 mole), cyclohexene (8.3 g., 0.10 mole), and 0.05 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol was heated at reflux for 4 days, at which time v.p.c. analysis showed a 90% conversion. The highest temperature attained was 150°. The products from the reaction were not isolated, but v.p.c. analysis of the solution showed a pattern that was almost identical with the curve of the addition of bistrimethylsiloxymethylsilane to hexene-2. Two of the products, however, were identified by their retention times as being $(Me_3SiO)_3SiH$ and $[(Me_3SiO)_2MeSi]_2O$.

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[3] Specific refractions calculated by means of the bond refractions of A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

[4] (a) R. O. Sauer, W. J. Schreiber, and S. D. Brewer, *J. Am. Chem. Soc.*, **68**, 962, 2753 (1946); (b) F. Feher and K. Lippert, *Chem. Ber.*, **94**, 2437 (1961).

[5] H. M. Bank, J. C. Saam, and J. L. Speier [*J. Org. Chem.*, **29**, 792 (1964)] have recently reported that *sym*-tetramethyldisiloxane and hexene-2 form a mixture of 1-, 2-, and 3-hexyl isomers.

[6] R. Muller, R. Kohne, and S. Sliwinski, *J. prakt. chem.*, [4] **9**, 63 (1959).

Preparation of *cis*-Cyclododecene, Cyclododecyne, and Cyclododecanone

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The *cis* isomer of cyclododecene (II) is now readily accessible by means of the diimide reduction of butadiene trimer, *trans,trans,cis*-1,5,9-cyclododecatriene (I), as recorded by Ohno and Okamoto very recently.[1] The same reaction has been observed independently in this laboratory and the details of our procedure will be given in the Experimental section. The present paper

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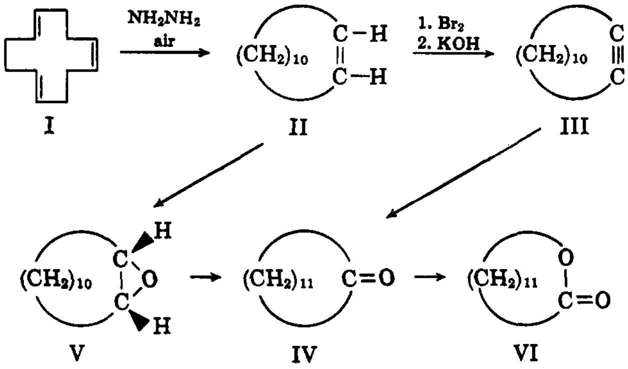
[1] M. Ohno and M. Okamoto, *Tetrahedron Letters*, 2423 (1964).

involves two novel routes to cyclododecanone (IV), starting from II, and related reactions.

Cyclododecyne (III) has been prepared from II by the addition of bromine and the following dehydrobromination by treating with potassium hydroxide in boiling isoamyl alcohol solution. The cyclic acetylene III thus produced in 50% total yield formed an oil, b.p. 136–137° (40 mm.), and gave a single peak on gas chromatography. This route would probably constitute the easiest way to the particular cycloalkyne.[2]



Hydration of III in the presence of mercuric sulfate dissolved in sulfuric acid–aqueous dioxane mixture gave an 86% yield of cyclododecanone (IV), m.p. and m.m.p. 60–61°. The infrared spectrum was superimposable on that of the authentic sample.[3]

Another route to cyclododecanone (IV) consists of the epoxidation of I and the following isomerization. The reaction with perbenzoic acid proceeded smoothly in chloroform solution to afford 78% yield of the novel *cis* epoxide V, b.p. 88–90° (1.5 mm.) Comparison of infrared spectra of V and the authentic *trans* isomer[3] showed considerable difference in the fingerprint region. A sample of V gave a single peak on gas chromatography. Treatment of V with magnesium iodide in ethereal solution[4] afforded cyclododecanone (IV) in nearly quantitative yield.

The Baeyer–Villiger oxidation of cyclododecanone with perbenzoic acid in chloroform solution has been recorded recently by Zapesochnaya, *et al.*,[5] to afford 1,12-dodecanolide (VI) in 66% yield. This reaction was found to be exceedingly slow upon iodometric following. The use of *p*-toluenesulfonic acid as a catalyst and an extendedperiod of reaction, *i.e.*, 2 weeks instead of the 12 hr. of the Russian workers, gave the dodecanolide (VI) in 84% yield.[6]

Experimental[7]

***cis*-Cyclododecene (II).**—A vigorous air stream was passed through a stirred solution of 16 g. (0.01 mole) of *trans,trans,cis*-1,5,9-cyclododecatriene (I),[8] 120 ml. of 100% hydrazine hydrate, and 0.5 g. of cupric acetate dissolved in 120 ml. of 99% ethanol. After 50 hr. of bubbling the exothermic reaction was brought to completion and the maximum reaction temperature was about 50°. The reaction mixture was extracted with *n*-hexane and the extract was washed (water, dilute HCl, $NaHCO_3$, and $Na_2S_2O_3$ solutions, and water), and dried ($CaCl_2$). Distillation *in vacuo* gave 13 g. of a colorless oil, b.p. 132–134° (35 mm.), n^{20}_{D} 1.4840 (lit.[9] n^{20}_{D} 1.4844). Gas chromatography (PEG–$AgNO_3$, He) indicated the contamination of *ca.* 5% of cyclododecane. No *trans*-cyclododecene was detected. The infrared spectrum of the product was in accord with the one previously recorded.[10] The silver nitrate adduct melted at 87–89° (lit.[11] m.p. 86–88°).

When the diimide reduction was carried out in aqueous dioxane solution, a considerable amount of higher boiling by-products resulted and the yield of II was less than 20%.

Cyclododecyne (III).—A solution of 6.0 g. (0.038 mole) of bromine in 60 ml. of carbon tetrachloride was added dropwise during 30 min. to a stirred solution of 5.0 g. (0.030 mole) of II in 20 ml. of the same solvent. The addition reaction was carried out at 0° and the crude 1,2-dibromocyclododecane (10 g.) obtained as the evaporation residue was dissolved in 60 ml. of isoamyl alcohol. To this solution 8 g. of potassium hydroxide was added and the mixture was refluxed for 10 hr. Distillation of the product *in vacuo* gave 2.5 g. (50% yield) of a colorless oil, b.p. 136–137° (40 mm.), which showd a single peak on gas chromatography (PEG–$AgNO_3$ or high-vacuum silicone), n^{20}_{D} 1.4977. The infrared spectrum was in accord with the one previously recorded.[10] The elemental analyses gave correct values.

When III was reduced with metallic sodium in liquid ammonia,[12] a mixture of both isomers of cyclododecene was produced. Gas chromatography (PEG–$AgNO_3$) indicated a *trans–cis* ratio of 87:13 (lit.[9] 78:22).

Cyclododecanone (IV) from III.—Several drops of concentrated sulfuric acid was added to a solution of 2.6 g. of III and 0.2 g. of mercuric sulfate dissolved in 20 ml. of 60% aqueous dioxane, and the mixture was heated at 80° for 1 hr. The reaction mixture was extracted with ether and the ethereal solution was washed ($NaHCO_3$ solution), dried (Na_2SO_4), and distilled to afford 2.3 g. (86% yield) of IV, b.p. 90–94° (1 mm.), which solidified immediately, m.p. and m.m.p.[3] 60–61°.

***cis*-Epoxycyclododecane (V).**—To 64 ml. (0.017 mole) of a 0.265 *M* chloroform solution of perbenzoic acid 2.0 g. (0.012 mole) of *cis*-cyclododecene (II) was added and the mixture was stirred at room temperature for 24 hr. The excess peracid was destroyed by shaking with sodium bisulfite solution and the chloroform layer was washed, dried, and concentrated. Distillation of the residue gave 1.8 g. (78% yield) of V as a colorless oil, b.p. 88–90° (1.5 mm.), n^{20}_{D} 1.4837. Infrared maxima (neat) showed 1265 and 750 cm.$^{-1}$. Gas chromatography (high-vacuum silicone) gave a single peak.

Anal. Calcd. for $C_{12}H_{24}O$: C, 79.06; H, 12.16. Found: C, 79.40; H, 12.23.

Cyclododecanone (IV) from V.—To 10 ml. of a 1 *M* ethereal solution of magnesium iodide 1.0 g. of *cis*-epoxycyclododecane (V) was added. When the solvent was nearly distilled off under stirring, a vigorous exothermic reaction occurred and the reaction temperature rose to about 100°. After an additional 2 hr. of heating at 80–85°, the cooled reaction mixture was extracted with ether and the ethereal solution was washed, dried, and evaporated *in vacuo*. The residue melted at 57–59° and weighed 1.0 g. (nearly quantitative yield). The infrared spectrum did not show any impurity peaks. Distillation *in vacuo* gave an analytical sample, m.p. and m.m.p. 60–61°.

1,12-Dodecanolide (VI).—In 85 ml. (0.023 mole) of a 0.265 *M* chloroform solution of perbenzoic acid, 3.0 g. (0.016 mole) of cyclododecanone (IV) and a trace of *p*-toluenesulfonic acid were dissolved and the solution was allowed to stand at room temperature in dark for 2 weeks, when the calculated amount of the peracid was consumed. The solution was washed ($Na_2S_2O_3$ and $NaHCO_3$ solutions and water), dried (Na_2SO_4), and distilled *in vacuo*. The oily lactone VI (2.7 g. or 84% yield), b.p. 88–91° (1

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(2) For the usual method of preparing cyclic acetylenes, see (a) G. Wittig, *Angew. Chem.*, **74**, 479 (1962), and references cited therein; (b) L. Ruzicka, M. Hürbin, and H. A. Boekenoogen, *Helv. Chim. Acta*, **16**, 498 (1933).

(3) G. Wilke, *Angew. Chem.*, **69**, 397 (1957).

(4) This procedure is analogous to the one described by Wilke and Wesslau [U. S. Patent 3,063,986 (Nov. 13, 1962); *Chem. Abstr.*, **58**, 10089 (1963)] for isomerization of other cyclo olefin epoxides.

(5) G. G. Zapesochnaya, I. A. Kovtun, I. K. Sarycheva, and N. A. Preobrazhenskii, *Zh. Obshch. Khim.*, **33**, 2133 (1963); *Chem. Abstr.*, **59**, 13812 (1963).

(6) The Baeyer–Villiger reaction of cycloalkanones of 4–8- and 13–16-membered rings has been described: see (a) S. L. Friess and P. E. Frankenburg, *J. Am. Chem. Soc.*, **74**, 2679 (1952); (b) S. L. Friess, *ibid.*, **71**, 2571 (1949); (c) L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

(7) Analyses were performed at the Elemental Analyses Center of Kyôto University. All temperatures are uncorrected.

(8) Supplied by Mr. H. Takahasi, Government Industrial Research Institute, Osaka, Japan. The sample contained 97.4% of the *trans,trans,cis* isomer, the rest being all *trans* isomer (2.4%) and impurities (0.2%).

(9) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

(10) V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955).

(11) M. Svoboda and J. Sicher, *Chem. Ind.* (London), 290 (1959).

(12) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).

mm.), n^{20}_{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.$^{-1}$.

Acknowledgment.—The authors are grateful to Professor K. Sisido for his interest in this work. They are also indebted to Mr. H. Takahasi for the supply of *trans,trans,cis*-1,5,9-cyclododecatriene. The cooperation of the people at Elemental Analyses Center of Kyôto University is gratefully acknowledged.

(13) H. Hunsdiecker and H. Erlbach, *Chem. Ber.*, **80**, 129 (1947).

(14) N. P. Solov'eva, E. K. Smol'yaninova, and V. N. Belov, *Zh. Obshch. Khim.*, **27**, 3015 (1957); *Chem. Abstr.*, **52**, 8126 (1958).

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

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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

$$\mathrm{RONO_2 + Na \longrightarrow RONa + NaNO_2} \qquad (1)$$

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).

$$\mathrm{RONO_2 + EtMgBr \longrightarrow ROH + Et_2NOH} \qquad (2)$$

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, α^{27}_{D} −3.28°, gave dextrorotatory α-phenylethyl chloride, α^{27}_{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}_{D} 1.4254, α^{26}_{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.