

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH & DEVELOPMENT, U. S. NAVAL POWDER FACTORY]

The Reaction of *dl*- and *meso*-2,3-Dibromobutane with Silver Nitrate in Acetonitrile. Failure of the Nitrate Ester Grouping to Exhibit the Neighboring Group Effect¹

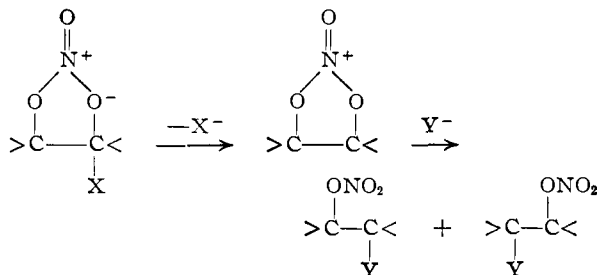
BY LEON FISHBEIN²

RECEIVED AUGUST 6, 1956

The reaction of *dl*-2,3-dibromobutane with silver nitrate in acetonitrile gives the mononitrate ester (of *threo*-2-bromo-3-butanol), and this in a somewhat slower reaction is then converted to the dinitrate of *meso*-2,3-butanediol. In other words, the first step occurs with retention of configuration, the second step with inversion. Precisely the same stereochemical results are obtained when *meso*-2,3-dibromobutane is treated with silver nitrate in acetonitrile; retention in the first step, inversion in the second. It is thus clear that while neighboring bromine participates, the neighboring nitrate ester group does not exhibit the neighboring group effect.

Winstein, Lucas and their co-workers have established the fact that an over-all retention of configuration results when an atom or a group of atoms participates in the displacement of a second functional group on an adjacent carbon atom.³ The neighboring group reaction has been demonstrated for a large number of atoms or groups of atoms and include the following: -I, -Br, -Cl, -CO₂⁻, -OCOCH₃, -OCH₃, -OH, O⁻, -NH₂, -NR₂, -SR, benzamido and aryl.

This paper concerns itself with a study, by stereochemical means, of the effectiveness of a β -nitrate ester group as a neighboring group in the reaction of alkyl bromides with silver nitrate. The nitrate ester group, in a formal way, closely resembles an acetoxy group and this suggested the possibility of an analogous cyclic intermediate



The 2,3-disubstituted butane system was selected for this investigation because of the known configurational relationships of the *dl*- and *meso*-dibromides,⁴ diols,⁵ *cis*- and *trans*-epoxides^{3a} and *erythro*- and *threo*-bromohydrins.^{3c}

Discussion

The reaction of *meso*-2,3-dibromobutane with silver nitrate in acetonitrile for 24 hr. at room temperature yielded as the only product a bromonitroxybutane⁶ which was identical with that ob-

(1) Publication approved by the Bureau of Ordnance, Navy Department.

(2) Charles Bruning Co., Inc., Teterboro, N. J.

(3) (a) S. Winstein and H. J. Lucas, *THIS JOURNAL*, **61**, 1576, 2845 (1939); (b) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941); (c) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780, 2787 (1942); (d) S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); (e) S. Winstein and R. B. Henderson, *ibid.*, **65**, 2196 (1943); (f) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948).

(4) R. T. Dillon, W. G. Young and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

(5) H. J. Lucas and C. E. Wilson, *ibid.*, **58**, 2396 (1936).

(6) The reaction of the diastereomeric 2,3-dibromobutanes with silver nitrate to prepare the bromonitroxybutanes is a rapid one (*ca.* 24 hr.) compared with that in which a dinitrate is obtained (*ca.* 45 days). This enables one to isolate the bromonitroxybutane uncontaminated with dinitrate.

tained by the direct nitration of *erythro*-2-bromo-3-butanol (see Chart 1) as shown by their refractive indices and infrared spectra.

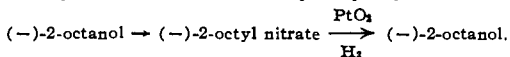
When either *meso*-2,3-dibromobutane or *erythro*-2-bromo-3-nitroxybutane was treated with silver nitrate in acetonitrile for *ca.* 45 days, there was formed a dinitrate ester of 2,3-butanediol which was identical with that obtained by the direct nitration of *dl*-2,3-butanediol (see Chart II)⁷ as shown by their refractive indices and infrared spectra.

Complete duplication of results was obtained employing *dl*-2,3-dibromobutane. Thus, the reaction with silver nitrate for *ca.* 24 hr. yielded *threo*-2-bromo-3-nitroxybutane. Upon treating the *dl*-dibromide or the *threo*-bromonitrate with silver nitrate for *ca.* 45 days, there was obtained the dinitrate ester of *meso*-2,3-butanediol.

The demonstration that either *dl*- or *meso*-2,3-dibromobutane could be recovered unchanged from a mixture consisting of dibromide, silver bromide and acetonitrile dismisses the possibility that these dibromides undergo isomerization prior to the reaction which produces bromonitroxybutane. Similarly, no isomerization could be demonstrated to occur for the diastereomeric-2-bromo-3-nitroxybutanes.

These facts can be rationalized in the following manner: The first step in the reaction of *dl*-2,3-dibromobutane with silver nitrate consists in the formation of *threo*-2-bromo-3-nitroxybutane by a neighboring group participation of a bromine atom. That the *threo* isomer is formed with retention of configuration and unmixed with its diastereomer³ strongly suggests a concerted process, in which the neighboring bromine atom participates in a back-

(7) That nitration occurs with a retention of configuration and no loss in optical purity was demonstrated by A. F. McKay, R. H. Meen and G. F. Wright [*THIS JOURNAL*, **70**, 430 (1948)]. Levorotatory 2,3-butanediol, $[\alpha]_D^{20} -12.89^\circ$ was nitrated with a mixture of fuming nitric acid and concentrated sulfuric acid to yield the levorotatory dinitrate ester, $[\alpha]_D^{20} -0.88^\circ$, which upon hydrogenolysis employing a palladium-on-charcoal catalyst produced levorotatory 2,3-butanediol, $[\alpha]_D^{20} -12.90^\circ$. Similarly, S. J. Cristol, [*THIS JOURNAL*, **77**, 2512 (1955)] has shown that no loss in optical purity occurs in the sequence



(8) The *threo* compound is formed with a stereospecificity > 95%. Infrared spectra were obtained for the pure *threo*- and *erythro*-2-bromo-3-nitroxybutanes as well as for synthetic mixtures of 95% *threo*-5% *erythro*, 90% *threo*-10% *erythro*, 95% *erythro*-5% *threo* and 90% *erythro*-10% *threo*. The infrared spectrum of the bromonitroxybutane, isolated from the reaction of *dl*-2,3-dibromobutane with silver nitrate over a 24-hr. period, was identical with that of pure *threo*-2-bromo-3-nitroxybutane. A similar high stereospecificity was observed for the reaction which produces the *erythro* isomer.

CHART I.—PREPARATION OF THE DIASTEREOMERIC 2-BROMO-3-NITROXYBUTANES

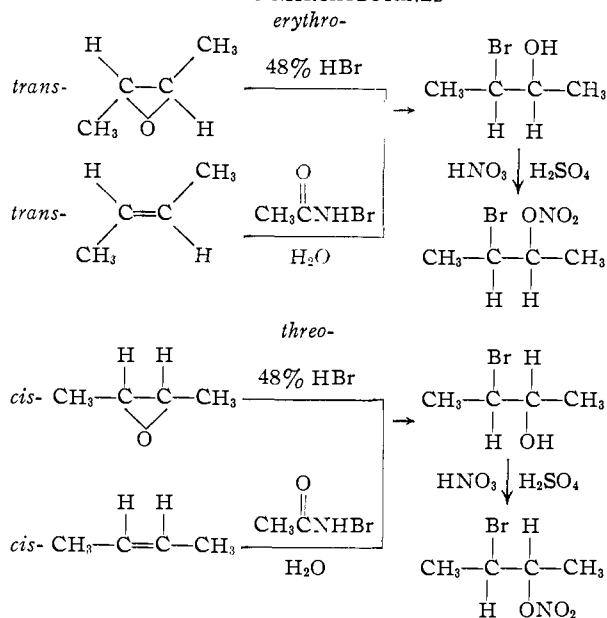
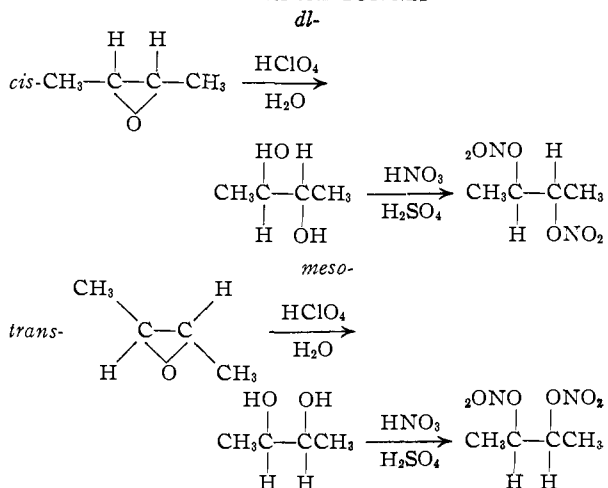
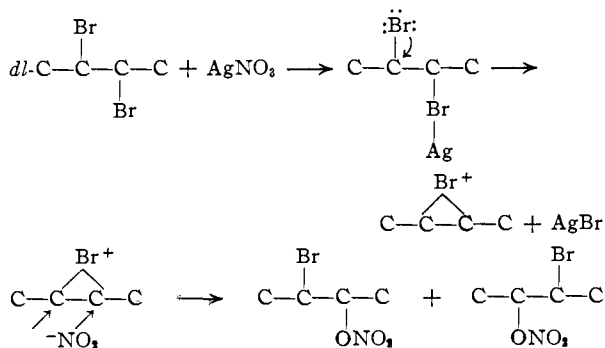


CHART II.—PREPARATION OF THE DIASTEREOMERIC 2,3-DINITROXYBUTANES



side internal displacing action while the C-Br bond of the carbon undergoing substitution is being weakened by an electrophilic attack on halogen by silver. This is followed by a back-side attack on the cyclic bromonium ion by nitrate ion yielding the *threo* isomer, *i.e.*, over-all retention of configuration



In the next step of the reaction sequence, the *threo*-2-bromo-3-nitroxybutane reacts with silver nitrate to yield the dinitrate ester of *meso*-2,3-butanediol, that is with inversion of configuration. Also noteworthy is the fact that the reaction occurs with complete stereospecificity: the *meso*-dinitrate contains less than 5% of the racemic stereoisomer.⁹

Kornblum, Smiley, Blackwood and Iffland¹⁰ have as a result of a careful examination of the reaction of silver nitrite with 2-octyl halides provided a demonstration that this reaction proceeds *via* a transition state possessing both S_N1 and S_N2 character. The results of the present investigation are fully consonant with their pull-push mechanism.

Of special interest is the observation that the *threo*-bromonitrate reacts with silver nitrate with clean inversion for it serves to emphasize, once again, the importance of the push exerted by the anion in the reactions of silver salts with strictly aliphatic halides.⁹

The reaction of the 2-bromo-3-nitroxybutanes with silver nitrate is exceedingly slow being *ca.* 90% complete after 45 days.¹¹ It is to be expected that in this reaction, as well as those involving α -halocarbonyl compounds, α -haloesters and 1,2-dichloride,¹² the S_N1 contribution to the transition state is minimized because of adjacent charge considerations.

Experimental

Preparation of Intermediates.—*dl*-2,3-Dibromobutane, b.p. 73° (47 mm.), n_D^{20} 1.5147, and *meso*-2,3-dibromobutane, b.p. 71.5–72° (50 mm.), n_D^{20} 1.5116, were prepared by the bromination of *cis*- and *trans*-2-butene (Phillips Petroleum Co., Research Grade), respectively [reported⁴ *dl*-2,3-dibromobutane, b.p. 75.6–75.8° (50 mm.), n_D^{20} 1.5147; *meso*-2,3-dibromobutane, b.p. 72.7–72.9° (50 mm.), n_D^{20} 1.5116]. *cis*-2,3-Epoxybutane, b.p. 60.5° (747 mm.), n_D^{20} 1.3826, and *trans*-2,3-epoxybutane, b.p. 55° (747 mm.), n_D^{20} 1.3736 (Carbide and Carbon Chemicals Co., Research Grade) [reported^{3a} *cis*-2,3-epoxybutane, b.p. 60° (742 mm.), n_D^{20} 1.3828; *trans*-epoxide, b.p. 54° (742 mm.), n_D^{20} 1.3736] were used in the procedure of Lucas and Wilson⁵ to prepare *dl*-2,3-butanediol, m.p. 6.5°, b.p. 54° (2 mm.), n_D^{19} 1.4320, and *meso*-2,3-butanediol, m.p. 33–34°, b.p. 60–61° (2 mm.) [reported⁵ *dl*-2,3-butanediol, m.p. 7.6°, b.p. 86° (16 mm.); *meso*-diol, m.p. 34.4°, b.p. 89° (16 mm.)]. *threo*-2-Bromo-3-butanol, b.p. 49–50° (13 mm.), n_D^{25} 1.4752, and *erythro*-2-bromo-3-butanol, b.p. 53–54° (13 mm.), n_D^{25} 1.4763, prepared by the reaction of *cis*- and *trans*-2,3-epoxybutane, respectively, with 48% HBr^{3a} were identical with the bromohydrins obtained from the reaction of the isomeric 2-butenes with N-bromoacetamide,^{3b} as shown by their boiling

(9) N. Kornblum, L. Fishbein and R. A. Smiley [THIS JOURNAL, **77**, 6261 (1955)] have shown that the reaction of optically active 2-octyl halides with silver nitrite (in diethyl ether) occurs with clean inversion. Also relevant is a recent report by N. Kornblum and D. Hardies [Abstracts of the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956, page 2-O] that in acetonitrile 2-octyl halides react with silver nitrite (and with silver nitrate) with inversion.

(10) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *ibid.*, **77**, 6269 (1955).

(11) It is interesting to note that 2-bromobutane reacts quantitatively with silver nitrate in acetonitrile within 5 minutes, 1-bromobutane in 20 hr. and 1,4-dibromobutane in 20 hr. (*cf.* Experimental).

(12) The extreme inertness of vicinal dichlorides is illustrated by experiments involving *dl*- and *meso*-2,3-dichlorobutane. When these dichlorides were treated with silver nitrate in acetonitrile under the identical conditions as described for the diastereomeric dibromides, the *meso*-dichloride was *ca.* 1% reacted in 5 months, the *dl*-isomer was completely unreacted in the same period. This is to be contrasted with the following reactivities: 1-chlorobutane, 55% reacted in 12 days; 2-chlorobutane, 86% in 10 days; 1,4-dichlorobutane, 80% in 33 days (*cf.* Experimental).

points, refractive indices and infrared spectra [reported^{3a} *threo*-2-bromo-3-butanol, b.p. 50.5° (13 mm.), n_D^{25} 1.4756; *erythro* isomer, b.p. 53.1° (13 mm.), n_D^{25} 1.4767].

***threo*-2-Bromo-3-nitroxybutane.**—To a nitrating mixture consisting of 4 ml. (0.09 mole) of fuming nitric acid and 3.2 ml. (0.06 mole) of concentrated sulfuric acid at -20° was added dropwise over a 45-minute period, 9.18 g. (0.06 mole) of *threo*-2-bromo-3-butanol (prepared by the reaction of *cis*-2,3-epoxybutane with 48% HBr). After the addition was complete, the reaction mixture was kept at -15° for 10-minutes, then at 0° for 45 minutes, after which it was poured onto ca. 50 g. of crushed ice. The oily phase which separated was taken up in methylene chloride. The methylene chloride extract was successively washed with ice-water, aqueous 5% sodium bicarbonate solution, water, then dried over anhydrous magnesium sulfate. The methylene chloride extract was concentrated by removing the solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 10.2 g. (86% yield) of product having b.p. 58° (8 mm.), n_D^{20} 1.4685.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.45; H, 4.05; N, 7.32.

In a similar manner the nitration of the *threo*-bromohydrin (prepared from *cis*-2-butene and N-bromoacetamide) gave a 73% yield of product having b.p. 60.5–61.5° (8–9 mm.), n_D^{20} 1.4686.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.51; H, 4.21; N, 6.80.

The infrared spectrum of *threo*-2-bromo-3-nitroxybutane displayed absorption bands at 1065 and 1135 cm^{-1} which were absent in that of the *erythro* isomer.

***erythro*-2-Bromo-3-nitroxybutane.**—When *erythro*-2-bromo-3-butanol (prepared by the reaction of *trans*-2,3-epoxybutane with 48% HBr) was nitrated in the same manner as that outlined for the *threo* isomer, there was obtained an 81% yield of product having b.p. 54° (6–7 mm.), n_D^{20} 1.4695.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.52; H, 4.26; N, 7.27.

The nitration of the *erythro*-bromohydrin (prepared from *trans*-2-butene and N-bromoacetamide) gave a 63% yield of product having b.p. 58° (8–9 mm.), n_D^{20} 1.4694.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.25; H, 4.17; N, 6.83.

The infrared spectrum of *erythro*-2-bromo-3-nitroxybutane exhibited bands at 1055, 1098 and 1155 cm^{-1} which were absent in that of the *threo* isomer.

***dl*-2,3-Dinitroxybutane.**—To a nitrating mixture consisting of 17 ml. (0.4 mole) of fuming nitric acid and 16.3 ml. (0.3 mole) of concentrated sulfuric acid at -10° was added portionwise over a 30-minute period, 8.7 g. (0.097 mole) of *dl*-2,3-butanediol. After the addition was complete, the reaction mixture was kept at 0° for 2 hr., then poured onto ca. 100 g. of crushed ice. The oily phase which separated was taken up in methylene chloride and successively washed with ice-water, aqueous 5% sodium bicarbonate solution, water, then dried over anhydrous magnesium sulfate. The methylene chloride extract was concentrated by removing the solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 13 g. (75%) of colorless product having b.p. 71° (3 mm.), n_D^{20} 1.4412.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.68; H, 4.32; N, 15.55.

The infrared spectrum of this material exhibited bands at 1015, 1025 and 1145 cm^{-1} which were absent in the *meso* isomer.

***meso*-2,3-Dinitroxybutane.**—The nitration of *meso*-2,3-butanediol by the procedure as outlined for the *dl*-isomer, yielded 75% of product having b.p. 65–66° (2 mm.), n_D^{20} 1.4414.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.94; H, 4.21; N, 15.56.

The infrared spectrum of this material displayed absorption bands at 1000, 1100 and 1175 cm^{-1} which were absent in the racemic isomer.

Reaction of *dl*-2,3-Dibromobutane with Silver Nitrate in Acetonitrile. Isolation of *threo*-2-Bromo-3-nitroxybutane.—To a solution of 10.8 g. (0.05 mole) of *dl*-2,3-dibromobutane in 25 ml. of acetonitrile at 25° was added in one portion a solution of 25.5 g. (0.15 mole) of silver nitrate in 10 ml. of

acetonitrile. The reaction mixture was kept at room temperature in the absence of light for 24 hr., then filtered, producing a 96% yield of silver bromide as a by-product. This residue was washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 100 ml. of distilled water. The oily phase which separated was taken up in methylene chloride. The aqueous solution was further extracted with two 20-ml. portions of methylene chloride. The methylene chloride extracts were combined, washed twice with 25-ml. portions of water, dried over anhydrous sodium sulfate and concentrated by removing the solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 7.3 g. (72%) of colorless product having b.p. 58° (8 mm.), n_D^{20} 1.4680, and possessing an infrared spectrum identical with that of *threo*-2-bromo-3-nitroxybutane prepared by the nitration of *threo*-2-bromo-3-butanol.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.52; H, 3.89; N, 6.92.

The Reaction of *meso*-2,3-Dibromobutane with Silver Nitrate in Acetonitrile. Isolation of *erythro*-2-Bromo-3-nitroxybutane.—This reaction was carried out in the same manner as that described for the *dl*-isomer. There was obtained a 73% yield of product having b.p. 58° (8–9 mm.), n_D^{20} 1.4698, and possessing an infrared spectrum identical with that of *erythro*-2-bromo-3-nitroxybutane prepared by the nitration of *erythro*-2-bromo-3-butanol.

Anal. Calcd. for $C_4H_8BrNO_3$: C, 24.24; H, 4.04; N, 7.07. Found: C, 24.50; H, 4.08; N, 7.07.

The Reaction of *dl*-2,3-Dibromobutane with Silver Nitrate in Acetonitrile. Isolation of *meso*-2,3-Dinitroxybutane.—To a solution of 26 g. (0.120 mole) of *dl*-2,3-dibromobutane in 20 ml. of acetonitrile at 25° was added in one portion a solution of 60 g. (0.353 mole) of silver nitrate in 60 ml. of acetonitrile. The reaction mixture was kept at room temperature in the absence of light for 45 days then filtered, producing a 92% yield of silver bromide as a by-product. This residue was washed with small portions of acetonitrile. The filtrate and washings were combined and poured into 150 ml. of distilled water. The oily phase which separated was taken up in methylene chloride. The aqueous phase was washed with fresh portions of methylene chloride. The methylene chloride extracts were combined, washed twice with 25-ml. portions of water, dried over anhydrous sodium sulfate and concentrated by removing the solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 16.7 g. (80%) of colorless product having b.p. 55–56° (1 mm.), n_D^{20} 1.4414, and identical with the dinitrate ester of *meso*-2,3-butanediol (prepared by the nitration of *meso*-2,3-butanediol) as shown by their infrared spectra.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.67; H, 4.56; N, 15.62.

The Reaction of *meso*-2,3-Dibromobutane with Silver Nitrate in Acetonitrile. Isolation of *dl*-2,3-Dinitroxybutane.—This reaction was carried out in the same manner as that outlined for the *dl*-isomer. There was obtained a 75% yield of product having b.p. 60° (2 mm.), n_D^{20} 1.4412. The infrared spectrum of this material was identical with that of the dinitrate ester of *dl*-2,3-butanediol (prepared by the nitration of *dl*-2,3-butanediol).

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.77; H, 4.51; N, 15.56.

The Reaction of *threo*-2-Bromo-3-nitroxybutane with Silver Nitrate in Acetonitrile.—To a solution of 6.58 g. (0.0346 mole) of *threo*-2-bromo-3-nitroxybutane (prepared by the nitration of the *threo*-bromohydrin) in 5 ml. of dry acetonitrile, was added in one portion a solution of 7.36 g. (0.0433 mole) of silver nitrate in 10 ml. of acetonitrile. The reaction mixture was kept at room temperature in the absence of light for 40 days, then filtered, producing a 90% yield of silver bromide as a by-product. This residue was washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 30 ml. of distilled water. The oily phase which separated was taken up in methylene chloride. The aqueous phase was washed with fresh portions of methylene chloride. The methylene chloride extracts were combined, washed with water, dried over anhydrous sodium sulfate and concentrated by removing the solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 4.2 g. (67%) of colorless prod-

uct having b.p. 58° (1–2 mm.), n_D^{20} 1.4417, and possessing an infrared spectrum identical with that of pure dinitrate ester of *meso*-2,3-butanediol.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.47; H, 4.23; N, 15.35.

The Reaction of *erythro*-2-Bromo-3-nitroxybutane with Silver Nitrate in Acetonitrile.—This reaction was carried out in the same manner as that described for the *threo*-isomer. There was obtained a 74% yield of product having b.p. 50° (1 mm.), n_D^{20} 1.4416, and possessing an infrared spectrum identical with that of pure dinitrate ester of *dl*-2,3-butanediol.

Anal. Calcd. for $C_4H_8N_2O_6$: C, 26.67; H, 4.44; N, 15.56. Found: C, 26.57; H, 4.67; N, 15.70.

The Attempted Isomerization of *meso*-2,3-Dibromobutane with Silver Bromide in Acetonitrile.—To a solution of 108.2 g. (0.5 mole) of *meso*-2,3-dibromobutane, b.p. 71° (50 mm.), n_D^{20} 1.5116, in 100 ml. of dry acetonitrile at 25° was added in one portion a solution of 42.4 g. (0.25 mole) of silver nitrate in 50 ml. of acetonitrile. The reaction mixture was stirred at room temperature in the absence of light for 24 hr. The reaction mixture was filtered and the silver bromide residue washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 250 ml. of distilled water. The oily phase which separated was taken up in diethyl ether. The aqueous phase was washed with fresh portions of ether. The ether extracts were combined, washed with water, dried over sodium sulfate and concentrated by removing the solvent at atmospheric pressure. The residue was then distilled *in vacuo* through a 18'' column packed with glass helices, a total of 10 fractions being collected.

Fractions 1–6 (48 g.) having b.p. 35–43° (8–9 mm.), n_D^{20} 1.5100–1.5040, were combined and rectified twice *in vacuo* yielding a 75% recovery of unreacted *meso*-dibromide, b.p. 61–62° (34 mm.), n_D^{20} 1.5112. The infrared spectrum of this material showed it to be 98% pure.

The infrared spectrum of pure *meso*-2,3-dibromobutane exhibits an absorption band at 1160 cm^{-1} which is absent in the racemic dibromide; the *dl*-2,3-dibromobutane displays an absorption band at 1100 cm^{-1} which is absent in the *meso*-dibromide. It was found that the isomeric dibromides could be detected to less than 2% in the presence of the other.

The Attempted Isomerization of *dl*-2,3-Dibromobutane with Silver Bromide in Acetonitrile.—Employing the procedure as described for the *meso* isomer led to an 80% recovery of the *dl*-dibromide. Infrared analysis showed this material to contain 3% of the isomeric impurity.

The Attempted Isomerization of *erythro*-2-Bromo-3-nitroxybutane with Silver Bromide in Acetonitrile.—A mixture of 15 g. (0.075 mole) of *erythro*-2-bromo-3-nitroxybutane, b.p. 54° (6–7 mm.), n_D^{20} 1.4695, and 18.8 g. (0.1 mole) of freshly precipitated silver bromide in 30 ml. of acetonitrile was allowed to stand at room temperature in the absence of light for 15 days. The reaction mixture was filtered and the

residue washed with fresh portions of acetonitrile. The filtrate and washings were combined and poured into 75 ml. of water. The organic layer was separated and taken up in methylene chloride. The aqueous solution was further extracted with small portions of methylene chloride. The methylene chloride extracts were combined, washed with three 20-ml. portions of water, dried over anhydrous sodium sulfate and concentrated by removing the solvent at atmospheric pressure. The residue was then rectified *in vacuo* yielding 12.2 g. (82%) of *erythro*-2-bromo-3-nitroxybutane, b.p. 55° (7 mm.), n_D^{20} 1.4698. Infrared analysis of this material showed it to contain less than 5% of the *threo* isomer.

A complete duplication of results was obtained when *threo*-2-bromo-3-nitroxybutane was treated with silver bromide in the same manner as that described for the *erythro* isomer.

Reaction of 1-Bromobutane, 2-Bromobutane, 1,4-Dibromobutane, 1-Chlorobutane, 2-Chlorobutane, 1,4-Dichlorobutane, *dl*- and *meso*-2,3-Dichlorobutane with Silver Nitrate in Acetonitrile at Room Temperature.—A solution consisting of 0.025 mole of alkyl halide, 25 ml. of acetonitrile and a 25% molar excess of silver nitrate was maintained at room temperature (24–28°) in the absence of light. The extent of the reaction was determined by isolating the silver halide formed. The silver halide was separated by filtration, washed twice with acetonitrile and dried. Table I records the results.

TABLE I

REACTION OF SILVER NITRATE WITH BROMO- AND CHLOROBUTANES IN ACETONITRILE AT ROOM TEMPERATURE

Halide	Extent of reactn., %	Hours
2-Bromo	Quant.	0.1
1-Bromo	Quant.	20
1,4-Dibromo	Quant.	20
1-Chloro	55	288
2-Chloro	86	244
1,4-Dichloro	80	792
<i>dl</i> -2,3-Dichloro	No reactn.	3720
<i>meso</i> -2,3-Dichloro	1	3720

Infrared absorption spectra were obtained with a Perkin-Elmer model 21 double beam spectrophotometer using homogeneous samples, NaCl prism and cell thickness of 0.025 mm.

Acknowledgment.—The author wishes to thank Mrs. P. P. Wheeler for the analyses; Dr. G. B. Wilmot and Mrs. N. F. Lyons for the infrared spectra. He also wishes to acknowledge the many helpful comments of Professor Nathan Kornblum of Purdue University.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Synthesis and Properties of an Allenic Nitrile

BY LEE IRVIN SMITH AND JACK S. SWENSON¹

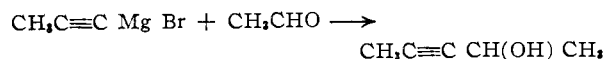
RECEIVED DECEMBER 5, 1956

Synthesis of the allenic nitrile, 2-cyano-2,3-pentadiene (I), has been achieved. The structure of the nitrile has been proved, and its behavior toward certain reagents has been studied. A combination of reduction and hydrolysis converted the allenic nitrile into 2-methylpentanamide, but reaction of the nitrile with Grignard reagents, phenyllithium or ethyl sodiomalonate all resulted in polymerization of the nitrile and no compounds formed by simple addition of these reagents could be isolated. The key to the synthesis of the allenic nitrile was the facile prototropic shift, occurring with 2-cyano-3-pentyne (IV) whereby the acetylenic nitrile rearranged into the allenic nitrile.

As a part of a program having as its object the synthesis of an allenic ketone, synthesis of the allenic nitrile I, 2-cyano-2,3-pentadiene, was under-

(1) Abstracted from a thesis by Jack S. Swenson, presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, August, 1956.

taken. The route to the allenic nitrile involved the sequence of steps



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