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

The Preparation of *cis*- and *trans*-1,4-Dinitroxy-2-butene[1]

BY LEON FISHBEIN AND JOHN A. GALLAGHAN

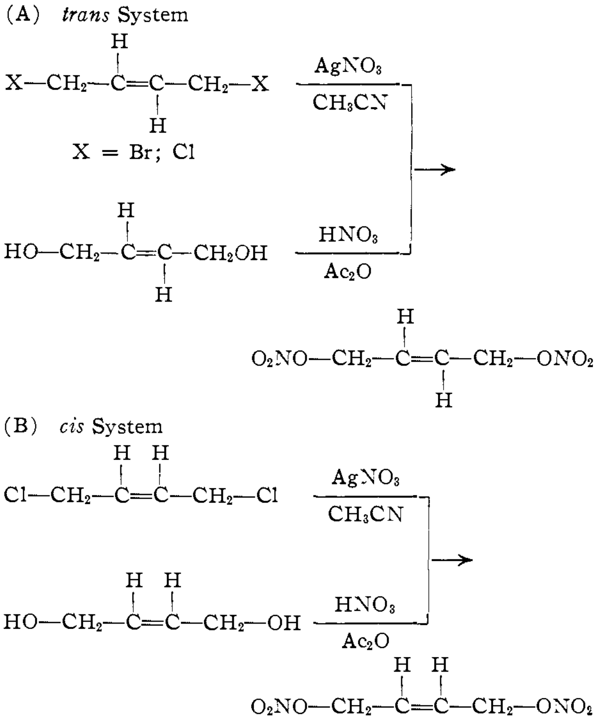
RECEIVED AUGUST 29, 1955

The *cis*- and *trans*-1,4-dinitroxy-2-butenes have been prepared and their configurations elucidated by chemical means. The nitration of *cis*- and *trans*-1,4-dihydroxy-2-butene to the corresponding dinitrate is shown to be stereospecific. Similarly, the conversion of the isomeric 1,4-dihalides to the corresponding dinitrates is stereospecific. No evidence could be found for the occurrence of an allylic rearrangement in this system.

Very little is known concerning the stereochemistry of unsaturated aliphatic nitrates and dinitrates. As part of a study on the preparation of unsaturated dinitrates, an investigation has been made of the isomeric 1,4-dinitroxy-2-butenes. The preparation and proof of the configuration of the isomeric dinitrates are summarized in Charts I and II.

CHART I

PREPARATION OF ISOMERIC 1,4-DINITROXY-2-BUTENES



Discussion

The *trans* System.—The reaction of *trans*-1,4-dibromo- or 1,4-dichloro-2-butene with silver nitrate in acetonitrile at 0° yielded a dinitroxybutene identical in physical properties with that obtained by the direct nitration of *trans*-1,4-dihydroxy-2-butene. The configuration of the dinitroxybutene thus prepared was established by bromination with either bromine in chloroform at −40°, or pyridinium bromide perbromide[2] in glacial acetic acid at room temperature. Bromination yielded a solid (m.p. 62–63°) dibromodinitrate derivative, which was identical with that obtained by the direct nitration of *meso*-1,4-dihydroxy-2,3-dibromobutane.

Since it is well established that the bromination of a double bond occurs by a *trans* addition,[3] it follows that the configuration of the parent dinitroxybutene was of the *trans* configuration.

The *cis* System—The reaction of *cis*-1,4-dichloro-2-butene with silver nitrate in acetonitrile produced a dinitroxybutene identical with that obtained by the nitration of *cis*-1,4-dihydroxy-2-butene. The configuration of the dinitroxybutene thus prepared was established by bromination. When the bromination procedures described for the *trans* isomer were employed, a liquid dibromodinitrate derivative was obtained which was identical with that obtained by the nitration of *dl*-1,4-dihydroxy-2,3-dibromobutane, as shown by their refractive indices and boiling points. It thus is apparent that the original dinitroxybutene was of the *cis* configuration.

The configurations of the isomeric 1,4-dinitroxy-2,3-dibromobutanes were subsequently confirmed by a resolution procedure.[4] Thus, when *dl*-1,4-dinitroxy-2,3-dibromobutane was treated with the alkaloid brucine, the dextrorotatory enantiomorph was obtained. Under identical conditions *meso*-1,4-dinitroxy-2,3-dibromobutane did not give an optically active product.

The physical properties of the isomeric 1,4-dinitroxy-2-butenes (see Experimental) are consistent with those usually ascribed to *cis* compounds, *i.e.*, the *cis* compound has the higher heat of combustion, (ΔH_c), boiling point, refractive index and density but a lower melting point than the *trans* isomer.

The formation of *cis*- or *trans*-1,4-dinitroxy-2-butene from the corresponding dihalo compound and silver nitrate in acetonitrile is apparently unattended by an allylic rearrangement, *i.e.*

$$XCH_2CH{=}CHCH_2X \longrightarrow [XCH_2CH{=}CH\overset{+}{C}H_2 \longleftrightarrow XCH_2\underset{+}{C}HCH{=}CH_2] \xrightarrow{NO_3^-} O_2NOCH_2CHONO_2CH{=}CH_2$$

The isomeric 1,4-dinitroxy-2-butenes are obtained in *ca.* 80% yield. In addition, the cooling curves show the presence of a single species in each case.

---

[1] Publication approved by the Bureau of Ordnance, Navy Department.

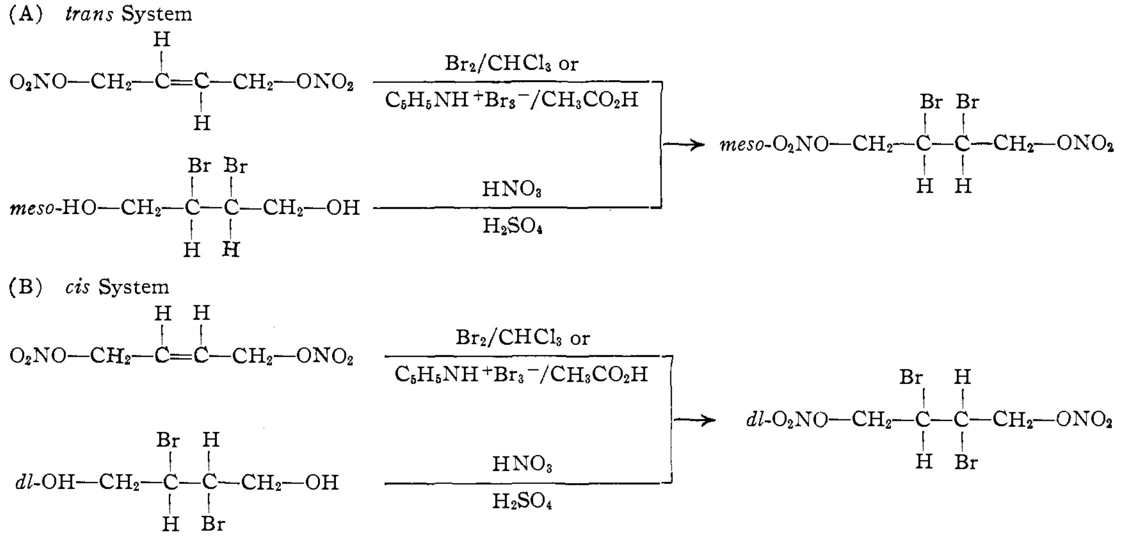
[2] L. F. Fieser [*J. Chem. Ed.*, **31**, 291 (1954)] has demonstrated that in the bromination of *cis*- and *trans*-stilbene, there is distinctly greater stereospecificity of the addition (*trans*) in bromination with pyridinium bromide perbromide than in bromination with free bromine.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 147–151.

[4] It is not necessary to resolve completely, but only to show that under identical conditions one isomer becomes optically active and the other does not. The development of optical activity on the part of the racemic form is due to the difference in the rates of reaction of the antipodes with brucine. This procedure is that of H. J. Lucas and C. W. Gould [THIS JOURNAL, **64**, 601 (1942)], which was employed to confirm the configurations of the diastereomeric 2,3-dibromobutanes, 3,4-dibromohexanes and the 4,5-dibromoöctanes.

CHART II

CHEMICAL PROOF OF CONFIGURATION



No evidence could be obtained for the formation of 1,2-dinitroxy-3-butene.[5] This observation is somewhat surprising in view of the fact that the conditions employed normally tend to promote a unimolecular ionization in an allylic system.

Experimental

Preparation of Intermediates.—*trans*-1,4-Dibromo-2-butene, m.p. 53–54°, prepared by the method of Shantz,[6] was readily converted to *trans*-1,4-dihydroxy-2-butene, b.p. 92–93° (1 mm.), $n^{20}_{\rm D}$ 1.4773, using the procedure of Prevost.[7] *trans*-1,4-Dichloro-2-butene, b.p. 70° (38 mm.), $n^{20}_{\rm D}$ 1.4897, $n^{25}_{\rm D}$ 1.4871, was prepared according to Mislow and Hellman.[8] *cis*-1,4-Dihydroxy-2-butene (General Aniline Corp.) was rectified *in vacuo* through a 20-inch fractionating column packed with 1/16-inch glass helices. The center cuts, boiling at 104° (3 mm.) and having $n^{20}_{\rm D}$ 1.4785 [reported[9] b.p. 100–102° (2 mm.), $n^{20}_{\rm D}$ 1.4782], were used in the procedure of Amundsen,[10] to prepare the corresponding *cis*-1,4-dichloro-2-butene, b.p. 58–59° (30 mm.), $n^{20}_{\rm D}$ 1.4902, $n^{25}_{\rm D}$ 1.4884. *meso*-1,4-Dihydroxy-2,3-dibromobutane, m.p. 133–134°, was prepared by the method of Prevost.[7] *dl*-1,4-Dihydroxy-2,3-dibromobutane, m.p. 87°, was prepared by the method of Valette.[11]

***meso*-1,4-Dinitroxy-2,3-dibromobutane.**—To a nitrating mixture consisting of 6.7 ml. of fuming nitric acid in 34 ml. of concentrated sulfuric acid at −20° was added portionwise and with vigorous stirring over a half-hour period, 5.0 g. (0.02 mole) of *meso*-1,4-dihydroxy-2,3-dibromobutane. After the addition of the *meso* compound was complete, the reaction mixture was kept at −20° for 10 minutes, then allowed to warm up to −10° over a 3-hour period. The reaction mixture was slowly poured onto 100 g. of crushed ice. The white precipitate which separated was filtered on a sintered-glass funnel, washed with a 5% aqueous sodium carbonate solution, water, then air-dried. The yield of crude product, m.p. 58–60°, was 4.5 g. (65%); recrystallization from petroleum ether (b.p. 35–55°) afforded colorless prisms, m.p. 62–63°, in yield of 4.1 g. (61%).

Anal. Calcd. for $C_4H_6O_6N_2Br_2$: C, 14.20; H, 1.77; N, 8.28. Found: C, 14.18; H, 1.98; N, 8.03.

***dl*-1,4-Dinitroxy-2,3-bromobutane.**—To a nitrating mixture consisting of 18 ml. of fuming nitric acid in 75 ml. of concentrated sulfuric acid at −20° was added portionwise and during vigorous stirring over a half-hour period 12.4 g. (0.05 mole) of *dl*-1,4-dihydroxy-2,3-dibromobutane. After the addition was complete, the reaction mixture was kept at −15° for 2 hours, then stored in a refrigerator overnight. The reaction mixture was allowed to warm up to room temperature over a 1-hour period, then poured onto *ca.* 150 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 evaporating the excess solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* at 1–2 mm. yielding 14.0 g. (83% yield) of product having b.p. 120° (1–2 mm.), $n^{20}_{\rm D}$ 1.5331; m.p. 12.8°.

Anal. Calcd. for $C_4H_6O_6N_2Br_2$: C, 14.20; H, 1.77; N, 8.28. Found: C, 14.44; H, 1.82; N, 8.02.

***trans*-1,4-Dinitroxy-2-butene. Method A. The Reaction of *trans*-1,4-Dibromo-2-butene with Silver Nitrate in Acetonitrile.**—To a solution of 51 g. (0.3 mole) of silver nitrate in 100 ml. of dry acetonitrile at 0° was added portionwise and with vigorous agitation over a 1-hour period, a solution of 21.4 g. (0.1 mole) of *trans*-1,4-dibromo-2-butene in 25 ml. of acetonitrile. A precipitate of silver bromide separated immediately upon addition of the dihalide. The reaction mixture was kept at 0° for 4 hours, then allowed to warm to room temperature overnight. The entire reaction was carried out in a minimum of light. The reaction mixture was filtered, producing a quantitative yield of silver bromide as a by-product. This residue was washed with fresh portions of acetonitrile. The filtrate and washings were combined, concentrated *in vacuo* to about one-third of the original volume, then poured into 200 ml. of distilled water. The oily phase which separated was taken up in methylene chloride. The aqueous phase was washed with two 50-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* at 2 mm. yielding 13.9 g. (78%) of colorless product having b.p. 82–83° (2 mm.), $n^{20}_{\rm D}$ 1.4698, $n^{25}_{\rm D}$ 1.4678, m.p. −26.2°, d^{25}_{4} 1.3658, $M_{\rm D}$ (calcd.) 36.47,[12] $M_{\rm D}$ (obsd.) 36.30, ΔH_c at 25° (in kcal./mole) −535.2.

---

(5) It is interesting to note that when 1,2-dichloro-3-butene is treated with silver nitrate in acetonitrile the reaction proceeds very slowly. At the end of a 7-day period the reaction had gone to only 56% completion, as determined by the quantity of silver chloride precipitated. The products obtained were a chloronitroxybutene and *trans*-1,4-dinitroxy-2-butene. The formation of this last compound can best be explained on the basis of an allylic rearrangement. This reaction is being investigated further.

(6) E. M. Shantz, THIS JOURNAL, **68**, 2557 (1946).

(7) C. Prevost, *Compt. rend.*, **183**, 1293 (1926).

(8) K. Mislow and H. M. Hellman, THIS JOURNAL, **73**, 244 (1951).

(9) C. S. Marvel and C. H. Young, *ibid.*, **73**, 1066 (1951).

(10) L. H. Amundsen, R. H. Mayer, L. S. Pitts and L. A. Malentacchi, *ibid.*, **73**, 2120 (1951).

(11) A. Valette, *Ann. chim.*, [12] **3**, 644 (1948).

(12) Values for the calculation of the molecular refractivity were taken from H. Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1751.

Anal. Calcd. for $C_4H_6N_2O_6$: C, 26.96; H, 3.37; N, 15.73. Found: C, 27.23; H, 3.19; N, 15.61.

Method B. **The Reaction of *trans*-1,4-Dichloro-2-butene with Silver Nitrate in Acetonitrile.**—This reaction, carried out in the same manner as that outlined in method A, gave an 80% yield of *trans*-1,4-dinitroxy-2-butene having b.p. 82° (2 mm.), $n^{20}{}_D$ 1.4698.

Method C. **The Reaction of *trans*-1,4-Dihydroxy-2-butene with a Nitrating Mixture of Fuming Nitric Acid in Acetic Anhydride.**—To a nitrating mixture consisting of 13.0 g. (0.20 mole) of 98% nitric acid in 50 ml. of acetic anhydride at −20° was cautiously added dropwise over a 45-minute period a solution of 4.4 g. (0.05 mole) of *trans*-1,4-dihydroxy-2-butene in 10 ml. of acetic anhydride. The reaction mixture was kept at −20° for 2 hours, allowed to warm up to +5° over a 1-hour period, then poured onto 50 g. of ice. The organic phase which separated was taken up in methylene chloride. The methylene chloride extract was successively washed with water, aqueous 5% sodium carbonate solution, water, then dried over anhydrous magnesium sulfate. The methylene chloride extract was concentrated by evaporating the excess solvent *in vacuo* at room temperature. The residue was then distilled *in vacuo* yielding 6.4 g. (72%) of product having b.p. 82–83° (2–3 mm.), $n^{20}{}_D$ 1.4692.

cis-1,4-Dinitroxy-2-butene. Method A. **The Reaction of *cis*-1,4-Dichloro-2-butene with Silver Nitrate in Acetonitrile.**—This reaction was carried out in the same manner as that of the *trans* isomer. There was obtained a 75% yield of dinitrate having b.p. 86–87° (2–3 mm.), $n^{20}{}_D$ 1.4721, $n^{25}{}_D$ 1.4700, $d^{25}{}_4$ 1.3736, m.p. −49.2°, M_D (calcd.) 36.47,[12] M_D (obsd.) 36.19, ΔH_c at 25° (in kcal./mole) −543.0.

Anal. Calcd. for $C_4H_6N_2O_6$: C, 26.96; H, 3.37; N, 15.73. Found: C, 26.87; H, 3.36; N, 15.84.

Method B. **The Reaction of *cis*-1,4-Dihydroxy-2-butene with a Nitrating Mixture of Nitric Acid in Acetic Anhydride.**—This reaction was carried out in the same manner as that of the *trans* isomer. There was obtained an 80% yield of *cis*-1,4-dinitroxy-2-butene having b.p. 69–70° (1 mm.), $n^{20}{}_D$ 1.4714.

The Bromination of *trans*-1,4-Dinitroxy-2-butene. Method A. **With Bromine in Chloroform.**—To a solution of 4.0 g. (0.0225 mole) of dinitrate, prepared from *trans*-1,4-dibromo-2-butene and silver nitrate, in 25 ml. of chloroform at −40° was added portionwise and with vigorous stirring a solution of 4.0 g. (0.025 mole) of bromine in 25 ml. of chloroform over a 1-hour period. The reaction mixture was kept at −45° for 1 hour, then at Dry Ice temperature overnight. The cream-colored precipitate which separated was filtered on a sintered-glass funnel, washed with fresh portions of chloroform and air-dried. The yield of crude product, m.p. 60–62°, was quantitative; recrystallization from petroleum ether (b.p. 35–55°) afforded colorless prisms, m.p. 62–63°, in yield of 7.5 g. (98.7%). The dibromodinitrate derivative thus obtained gave an undepressed melting point (62–63°) when mixed with an authentic sample of the *meso* derivative prepared by the direct nitration of *meso*-1,4-dihydroxy-2,3-dibromobutane. In a similar manner, the dinitrates prepared from the *trans*-dichloride or *trans*-diol gave complete duplication of results.

Method B. **With Pyridinium Bromide Perbromide in Glacial Acetic Acid.**—To a solution of 1.8 g. (0.01 mole) of the dinitrate in 50 ml. of glacial acetic acid was added portionwise 3.2 g. (0.01 mole) of pyridinium bromide perbromide.[2] The reaction mixture was heated on a steam-bath for 5 minutes during which time the reagent dissolved. The reaction mixture was cooled to room temperature then poured into 100 ml. of water. The aqueous solution was extracted successively with four 25-ml. portions of diethyl ether and of chloroform. The organic extracts were combined, dried over anhydrous sodium sulfate, then concentrated by taking off the solvents *in vacuo* at room temperature. There was obtained 3.20 g. (95%) of crude product, m.p. 60–62°; recrystallization from petroleum ether (b.p. 35–55°) afforded colorless prisms, m.p. 62–63°, in yield of 3.11 g. (92%). The dibromodinitrate derivative thus prepared gave an undepressed mixed melting point (62–63°) with an authentic sample of *meso*-1,4-dinitroxy-2,3-dibromobutane.

The Bromination of *cis*-1,4-Dinitroxy-2-butene. Method A. With Bromine in Chloroform.—To a solution of 3.2 g. (0.018 mole) of the dinitrate, prepared from *cis*-1,4-dichloro-2-butene and silver nitrate, in 25 ml. of chloroform at −40° was added portionwise and with vigorous stirring a solution of 4.0 g. (0.025 mole) of bromine in 25 ml. of chloroform. The reaction mixture was kept at −40° for 4 hours, then at 0° for 60 hours. The reaction mixture was concentrated by stripping off the excess chloroform *in vacuo* at room temperature. The residue was then distilled *in vacuo* at 1 mm. yielding 3.2 g. (53% yield) of dibromodinitrate derivative having b.p. 115–116° (1 mm.), $n^{20}{}_D$ 1.5333. The dibromodinitrate thus prepared was identical, as shown by the refractive index and boiling point, with the racemic derivative prepared by the direct nitration of *dl*-1,4-dihydroxy-2,3-dibromobutane.

In a similar manner, the dinitrate obtained by the nitration of *cis*-1,4-dihydroxy-2-butene yielded upon bromination *dl*-1,4-dinitroxy-2,3-dibromobutane, b.p. 116 (1 mm.), $n^{20}{}_D$ 1.5331.

Method B. **Bromination with Pyridinium Bromide Perbromide.**—To a solution of 5.34 g. (0.03 mole) of the dinitrate, prepared from *cis*-1,4-dichloro-2-butene and silver nitrate, in 50 ml. of glacial acetic acid was added portionwise and with vigorous agitation 9.6 g. (0.03 mole) of pyridinium bromide perbromide over a half-hour period. The reaction mixture was heated on a steam-bath for 5 minutes until complete solution was achieved, then kept in the absence of light at room temperature for 6 days. The reaction mixture was concentrated to *ca.* 15 ml. by removing most of the acetic acid *in vacuo* at room temperature. The residue was poured into 25 ml. of water and extracted successively with three 25-ml. portions of methylene chloride and of ether. The organic extracts were combined, dried over anhydrous sodium sulfate and concentrated by taking off the solvent *in vacuo* at room temperature. The residue was then distilled at 1 mm. to yield 9.3 g. (92%) of *dl*-1,4-dinitroxy-2,3-dibromobutane, b.p. 115° (1 mm.), $n^{20}{}_D$ 1.5332.

Partial Resolution of *dl*-1,4-Dinitroxy-2,3-dibromobutane.—To a solution of 7.5 g. (0.0222 mole) of *dl*-1,4-dinitroxy-2,3-dibromobutane, b.p. 120 (1–2 mm.), $n^{20}{}_D$ 1.5331, in 15 ml. of methylene chloride at −15° was added portionwise a cold solution of 3.45 g. (0.0074 mole) of brucine alkaloid in 15 ml. of methylene chloride. The reaction mixture was kept at −15° for 10 minutes, then placed in a refrigerator for 16 hours. To the methylene chloride solution was added petroleum ether (35–55°) until complete precipitation of the brucine salts was achieved. The precipitate was removed by suction filtration, washed with petroleum ether (30–50°) and then ether. The filtrate and washings were combined, dried over anhydrous sodium sulfate, then concentrated by taking off the excess solvents *in vacuo* at room temperature. The residue was then distilled at 1 mm. yielding 3.3 g. of dextrorotatory 1,4-dinitroxy-2,3-dibromobutane, b.p. 115–116° (1 mm.), $n^{20}{}_D$ 1.5328, $\alpha^{25}{}_D$ +6.26° (homogeneous; *l*, 1 dm.).

Anal. Calcd. for $C_4H_6N_2O_6Br_2$: C, 14.20; H, 1.77; N, 8.28. Found: C, 14.45; H, 1.89; N, 8.01.

Attempted Resolution of *meso*-1,4-Dinitroxy-2-butene.—Pure *meso*-1,4-dinitroxy-2-butene, m.p. 62–63°, was subjected to a resolution procedure in the same manner as the *dl* isomer. The product, recovered in 51% yield, melted at 62° and was devoid of optical activity, $\alpha^{24.5}{}_D$ 0.02° (*c* 1.00, methylene chloride; *l*, 1 dm.). Recrystallization from petroleum ether (35–55°) yielded colorless prisms, melting at 62–63° and devoid of optical activity.

Acknowledgments.—The authors wish to thank Mrs. P. Wheeler for the analyses; Mr. G. Carpenter for the determination of the heats of combustion and Mr. M. Kemp for the freezing point data.

INDIAN HEAD, MD.