from alcohol. One and six-tenths grams of tribenzyl thiophosphoric amide, melting point 121–123°, was obtained. It was identified by a mixed melting point.

Thermal Decomposition of Thiophosphoric Triamides to Dimeric Thiophosphoric Acid Imide Amides.—Thiophosphoric trianilide and thiophosphoric tribenzylamide were converted to the imide amide. Twenty-three grams of thiophosphoric trianilide was heated at 215–225° for two hours under a vacuum of 30 mm. mercury. Six grams of aniline distilled over. The residual solid was recrystallized from alcohol and gave 10 g. of thiophosphoric anil anilide, m. p. 233–235°. This product did not depress the melting point of a sample of the material prepared by the method of Michaelis and Karstens.[6] The anil anilide was readily converted back to the triamide by heating with an excess of aniline at the boiling point for four hours.

Tribenzylthiophosphoric amide was converted to the imide amide by the same method, yield 70%, m. p. 197–199°. *Anal.* Calcd. for $C_{28}H_{30}N_4P_2S_2$: N, 10.22; P, 11.31; S, 11.68; mol. wt., 548 Found: N, 10.34; P, 11.01; S, 11.68; mol. wt., 560.

The Reaction of 2-Naphthylamine and Phosphorus Pentasulfide.—A mixture of 9.2 g. of phosphorus pentasulfide, 45 g. of 2-naphthylamine and 70 g. of diethylbenzene was heated for two hours at 185° with stirring. The diethylbenzene was removed by steam distillation and the excess amine by extraction with cold alcohol. The residue was recrystallized from alcohol and gave 7 g. of phosphoric tri-2-naphthalide, m. p. 168–170°. A mixed melting point with a sample of the material prepared from 2-naphthylamine and phosphorus oxychloride by the method of Rudert[2] gave no depression.

Summary

The reaction of six moles of a primary aliphatic or aromatic amine with one mole of phosphorus pentasulfide at 130–180° gave crystalline thiophosphoric triamides. Secondary amines usually gave oily products, piperidine and tetrahydroquinoline being exceptions.

The reaction of four moles of aniline with one mole of phosphorus pentasulfide at room temperature gave thiophosphoric dianilide. This dianilide appears to be an intermediate in the formation of the trianilide. The thiophosphoric triamides are very stable toward hydrolysis; the phosphorus sulfur linkage of thiophosphoric tri-2-naphthalide is an exception. The triamides of primary amines are hydrolyzed on prolonged heating with 85% phosphoric acid or glacial acetic acid.

Thiophosphoric diamides are very sensitive to hydrolysis.

The primary amine triamides upon heating to 225°, *in vacuo*, lose amine to form a dimeric imide amide. This reaction is easily reversible.

The preparation of thiophosphoric monoanilide from aniline and phosphorus pentasulfide was unsuccessful.

CLEVELAND, OHIO RECEIVED SEPTEMBER 8, 1947

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[6] Michaelis and Karstens, *Ber.*, **28**, 1237, 1895.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

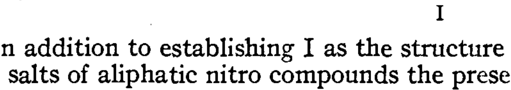
The Basis for the Reported Optical Activity of the Salts of Aliphatic Nitro Compounds: 2-Nitrobutane[1]

BY NATHAN KORNBLUM, JOHN T. PATTON[2] AND JOSEPH B. NORDMANN

The experimental basis for the report that 2-nitrobutane gives an active sodium salt[3] has been reëxamined in view of the recent finding that the optical activity attributed to the salts of 2-nitrooctane is really due to the presence of 2-octyl nitrate.[4] It has now been found that the 2-nitrobutane previously employed was contaminated with 2-butyl nitrate and that the activity ascribed to the sodium salt of 2-nitrobutane is due to this impurity.

Dextrorotatory-2-nitrobutane prepared according to the earlier workers[3] is only partially soluble in aqueous sodium hydroxide. The resulting aqueous alkaline solution, which contains the sodium salt of 2-nitrobutane, is devoid of activity whereas the insoluble portion is still *dextro*rotatory. Examination of the alkali insoluble material reveals that it is *d*-2-butyl nitrate $[\alpha]^{24}\mathrm{D}$ $+7.0°$.

The "*d*-2-nitrobutane" was freed of *d*-2-butyl nitrate, and any other contaminants, by treatment with cold 96% sulfuric acid. Thus purified, *d*-2-nitrobutane has $[\alpha]^{20}\mathrm{D}$ $+7.2°$, gives a negative test for nitrate esters, and is completely soluble in aqueous sodium hydroxide; the resulting solution is inactive. When sodium methoxide is used as the base the sodium salt is again devoid of activity and the 2-bromo-2-nitrobutane produced by brominating this salt is also inactive. These results, as well as the various other properties of the salts of aliphatic nitro compounds, lead to the conclusion that they possess the hybrid structure I.[5]



I

In addition to establishing I as the structure of the salts of aliphatic nitro compounds the present investigation corroborates the recent observation[4] that, contrary to the accepted view, the reaction of an alkyl halide with silver nitrite (The Victor

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[1] Presented at the Atlantic City meeting of the American Chemical Society, April. 1947.

[2] Allied Chemical and Dye Fellow 1945–1947.

[3] Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927).

[4] Kornblum, Lichtin, Patton and Iffland, THIS JOURNAL, **69**, 307 (1947).

[5] L. P. Hammett, "Physical Organic Chemistry." McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 67.

Meyer reaction) yields not only the anticipated nitroparaffin and alkyl nitrite but also a number of other products. As detailed in the experimental portion of this paper, the reaction of 2-iodobutane with silver nitrite gives 2-nitrobutane, 2-butyl nitrite, 2-butyl nitrate, 2-butanol and butanone.[6] Just as with 2-nitroöctane, the yield of pure 2-nitrobutane is very low, *ca.* 15%.

Experimental

Racemic 2-Iodobutane.—This compound was prepared according to Clarke.[7] It was rectified through a 12-inch modified Widmer column[8] fitted with a variable take-off head[8a]; yield 80–87%, b. p. 118°, n^{20}_{D} 1.4959, d^{20}_{4} 1.5962; literature values, b. p. 117–118°[9]; b. p. 118–119°; d^{20}_{4} 1.5952[10]; b. p. 121°, d^{20}_{4} 1.585, n^{19}_{D} 1.4945.[11]

Racemic "2-Nitrobutane."—Using 120 g. of racemic 2-iodobutane and following as closely as possible the directions of the previous investigators[3] 4 g. of "2-nitrobutane" was obtained; b. p. 30–31° (36 mm.); n^{20}_{D} 1.4042; lit. values,[3] b. p. 35–36° (17 mm.), n^{21}_{D} 1.4057. An authentic sample obtained from the Commercial Solvents Corporation had n^{20}_{D} 1.4040.

That the "2-nitrobutane" thus prepared is a mixture was demonstrated by shaking it with 10% aqueous sodium hydroxide; about 33% of the "2-nitrobutane" failed to dissolve even after prolonged shaking. This insoluble material was taken up in low boiling petroleum ether and dried over magnesium sulfate. The solvent was removed at atmospheric pressure leaving a colorless liquid, b. p. 121°, n^{20}_{D} 1.4016. Synthetic 2-butyl nitrate (see below) has b. p. 124°, n^{20}_{D} 1.4015. In contrast, 2-butyl nitrite (see below) has b. p. 68°, n^{20}_{D} 1.3710.

The aqueous alkali insoluble material gave a positive test for nitrates esters[12] and a negative test for nitrite esters.[13]

***d*-2-Butanol.**—Eastman Kodak Co. White Label 2-butanol was resolved according to Ingersoll.[14] The *d*-2-butanol distilled at 99°, n^{20}_{D} 1.3954, d^{20}_{4} 0.809, $[\alpha]^{25}_{\mathrm{D}}$ +10.9° (no solvent); lit. values[15]: b. p. 99°, n^{20}_{D} 1.3954, d^{20}_{4} 0.808, $[\alpha]^{20}_{\mathrm{D}}$ +13.87°.

***l*-2-Iodobutane.**—Following the procedure of Clarke,[7] 89 g. of *d*-2-butanol ($[\alpha]^{22}_{\mathrm{D}}$ +10.9°) was treated with 138 g. of iodine and 24 g. of red phosphorus. The product was rectified[8a]; yield 199 g. (90%), b. p. 117.5–118°, n^{20}_{D} 1.4948, d^{20}_{4} 1.5959, M_{D} (calcd.) 33.47, M_{D} (found) 33.61; $[\alpha]^{24}_{\mathrm{D}}$ −15.9° (no solvent); lit. values,[15] b. p. 117–118°, d^{17}_{4} 1.5970, $[\alpha]^{17}_{\mathrm{D}}$ −31.98°.

Pure *d*-2-Nitrobutane.—One hundred and forty grams of *l*-2-iodobutane ($[\alpha]^{24}_{\mathrm{D}}$ −15.9°) was treated with 175 g. of recrystallized silver nitrite[16] and 60 g. of freshly ignited quartz sand following, as closely as possible, the directions of the previous investigators.[3]

The silver nitrite and sand were placed in a 500 ml. round-bottom flask fitted with a condenser (the outlet of which led to a dry ice–acetone cooled trap), a tantalum Hershberg stirrer and a dropping funnel. The flask was submerged in an ice–salt mixture and the *l*-2-iodobutane was added dropwise over the course of one and one-half hours. Upon the addition of the first few ml. of iodide copious evolution of brown fumes was observed. When addition of the 2-iodobutane was complete the reaction mixture was allowed to come to room temperature and to stand overnight (*ca.* twelve hours). The flask was then heated at 90° for one hour and at the end of this period was fitted with a condenser set for downward distillation. Twenty-four grams of material distilled at atmospheric pressure when the reaction product was heated on a steam-bath (Fraction A). Further heating on the steam-bath under reduced pressure (60 mm.) gave an additional 38 g. of distillate (Fraction B). The Dry Ice trap contained 9 g. of a blue liquid, the color of which was discharged upon standing overnight at Dry Ice temperature.

Thirty-six grams of Fraction B, upon rectification[8a] at 188 mm., gave several fractions (Table I).

TABLE I

Fract.	B. p., °C.	Wt., g.	n^{20}_{D}
1	29	4.0	1.3762
2	30–51	1.0	1.3780
3	52–58	4.0	1.3891
4	60–61	5.0	1.3960
5	62–78	1.5	1.3970
6	79–80	6.0	1.4015
7	81–85	1.2	1.4029
8	86–87	10.5	1.4043
Dry Ice trap		1.4	1.3743

To 8 g. of Fraction 8 (Table I) was added 30 ml. of 96% sulfuric acid (precooled to 0°) at such a rate that the temperature did not rise above 3°. The solution was shaken for five minutes at 0° and then poured onto 50 g. of ice which was covered with 50 ml. of 30–60° petroleum ether. The aqueous layer was separated and extracted with fresh portions of petroleum ether. The extracts were combined, washed with water and dried over "Drierite." The solvent was removed at atmospheric pressure and the residue distilled under reduced pressure. The yield of pure 2-nitrobutane was 4.2 g., b. p. 60° at 70 mm., 137° at 760 mm. (Emich); n^{20}_{D} 1.4040, d^{20}_{4} 0.9627, M_{D} (calcd.) 26.21, M_{D} (found) 26.21, $[\alpha]^{20}_{\mathrm{D}}$ +7.20° (no solvent); lit. values,[3] b. p. 35–36° at 17 mm., n^{21}_{D} 1.4057, d^{17}_{4} 0.9854, $[\alpha]^{22}_{\mathrm{D}}$ +8.83°. An authentic sample of 2-nitrobutane obtained from Commercial Solvents Corporation was rectified and a middle cut taken; b. p. 140° (Emich), n^{20}_{D} 1.4040, d^{20}_{4} 0.9633.

Anal.[17] Calcd. for $C_4H_9NO_2$: C, 46.53; H, 8.79; N, 13.58. Found: C, 46.78, 46.87; H, 8.74, 8.69; N, 13.85, 13.90.

In contrast to "2-nitrobutane" prepared according to the earlier workers,[3] 2-nitrobutane thus purified is readily and completely soluble in aqueous alkali, gives a negative nitrate test,[12] and also gives a negative test for nitrite esters.[13]

Experiments with Pure *d*-2-Nitrobutane

(a) Racemization of *d*-2-Nitrobutane by the Action of Sodium Methoxide.—To a solution of 2 g. of *d*-2-nitrobutane ($[\alpha]^{20}_{\mathrm{D}}$ +7.20°) in 5 ml. of absolute methanol was

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(6) It should be pointed out that both instances in which products other than the nitro compound and alkyl nitrite were isolated involved secondary halides. It seems likely that the same result will be obtained with primary and tertiary halides; this point is being investigated.

(7) Clarke, THIS JOURNAL, **30**, 1149 (1908).

(8) Smith and Adkins, *ibid.*, **60**, 657 (1937).

(8a) Subsequent use of this column will be indicated by the superscript 8a.

(9) DeLuynes, *Ann.*, **132**, 276 (1864).

(10) Lieben, *ibid.*, **150**, 96 (1869).

(11) Kenyon, Phillips and Pittman, *J. Chem. Soc.*, 1080 (1935).

(12) S. P. Mulliken, "A Method of the Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1916, Vol. II, p. 27. We have found that with Mulliken's diphenylamine–sulfuric acid reagent 2-butyl nitrate gives a purple color, 2-nitrobutane a blue color and 2-butyl nitrite a slight yellow color. Mulliken, it should be noted, reports that alkyl nitrites, alkyl nitrates and nitroparaffins all give an intense blue color.

(13) Bose, *Analyst*, **56**, 504 (1931).

(14) A. W. Ingersoll, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 403.

(15) Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

(16) Mallinckrodt silver nitrite was purified as described previously[4] except that 60 g. of impure silver nitrite was used instead of 84 g. per four liters of water. From 300 g. of crude silver nitrite 250 g. of purified product was obtained.

(17) All analyses are microanalyses by Miss Theta Spoor of the University of Illinois unless otherwise stated.

added 15 ml. of 1.56 *N* methanolic sodium methoxide. The resulting solution was optically inactive $[\alpha]^{23}_{\mathrm{D}}$ 0.00 ($C = 10$).

(b) **Racemic 2-Bromo-2-nitrobutane from the Sodium Salt of *d*-2-Nitrobutane.**—The optically inactive methoxide solution obtained from *d*-2-nitrobutane (see preceding paragraph) was treated with an excess of bromine–water, care being taken to prevent the reaction mixture from becoming acidic. The alcoholic solution was then poured into water whereupon the brominated product separated as an oil. The mixture was then extracted with diethyl ether and the ether solution dried over "Drierite"; the resulting solution of crude 2-bromo-2-nitrobutane showed no optical activity, $[\alpha]^{24}_{\mathrm{D}}$ 0.00°; $l = 1$ dm. The ether was then removed by warming in an air stream, following which the residual oil was chromatographed on an aluminum oxide–Celite column using low boiling petroleum ether to develop the chromatogram. The solvent was removed and the residue chromatographed once again, this time on Darco; low boiling petroleum ether was used to develop the chromatogram. Most of the solvent was removed by blowing a stream of dry air over the solution at room temperature and the remainder by shaking at 30° in a vessel evacuated to 15 mm. The 3 g. (85% yield), of colorless product was still optically inactive, $[\alpha]^{24}_{\mathrm{D}}$ 0.00 (no solvent) $l = 1$ dm., n^{20}_{D} 1.4678, d^{20}_4 1.4927, M_{D} (calcd.) 34.05, M_{D} (found) 33.95.

Anal. Calcd. for $C_4H_8NO_2Br$: C, 26.37; H, 4.39; N, 7.69; Br, 43.90. Found: C, 26.25, 26.39; H, 4.41, 4.52; N, 7.69, 7.39; Br, 43.89, 43.67.

(c) **Racemization of *d*-2-Nitrobutane by the Action of Aqueous Sodium Hydroxide.**—Two-tenths gram of *d*-2-nitrobutane, ($[\alpha]^{20}_{\mathrm{D}}$ +7.20°) was shaken for ten minutes with 1 ml. of 20% aqueous sodium hydroxide. The mixture was then diluted with 1 ml. of water and shaken for an additional ten minutes. The *d*-2-nitrobutane had now dissolved completely and the resulting solution was devoid of optical activity ($C = 10$, $l = 1$ dm.).

(d) **Preparation of a Solid Derivative of 2-Nitrobutane. [2-(4-carboxyphenylazo)-2-nitrobutane].**—Immediately after neutralization, the aqueous alkaline solution of *d*-2-nitrobutane from the preceding section was coupled with diazotized *p*-aminobenzoic acid. The product was recrystallized from 85% ethanol, m. p. 128–128.7°; mixed m. p. undepressed; lit. values,[18] m. p. 128–129°.

Similar experiments were carried out with pure *l*-2-nitrobutane of $[\alpha]^{23}_{\mathrm{D}}$ −1.95°. In all instances the results agree with those obtained above but since the initial specific rotation is relatively low, the results are not as conclusive as those reported for the *dextro*rotatory isomer.

By-products of the Reaction between 2-Iodobutane and Silver Nitrite.—The reaction between 2-iodobutane and silver nitrite gives not only 2-nitrobutane and 2-butyl nitrite but also 2-butyl nitrate, 2-butanol and butanone. Their isolation from fractions A and B (see earlier section entitled "Pure-*d*-2-Nitrobutane") is described below.

(a) ***d*-2-Butyl Nitrate.**—Fraction 6 (Table I) was shaken by hand with 10 ml. of 20% aqueous sodium hydroxide for twenty minutes following which 10 ml. of water was added and the shaking continued for an additional twenty minutes; the organic phase was isolated and the treatment repeated. The organic layer was then washed with water and finally shaken with 10 ml. of 85% phosphoric acid for thirty minutes after which the mixture was allowed to stand until separation of the two layers was complete (*ca.* twelve hours.). The acid was drawn off and the organic layer was washed with water and dried over "Drierite." There was obtained 4 g. of colorless liquid, n^{20}_{D} 1.4016. Upon distillation at atmospheric pressure there was collected 3.7 g. of a colorless product, b. p. 124°, d^{20}_4 1.026, n^{20}_{D} 1.4016, M_{D} (calcd.) 28.80, M_{D} (found) 28.90, $[\alpha]^{24}_{\mathrm{D}}$ +7.02°, $l = 1$ dm. (no solvent); lit. values,[19] b. p. 124°, d^0 1.0382. Synthetic 2-butyl nitrate (see below) has b. p. 124°, d^{20}_4 1.029, n^{20}_{D} 1.4015.

The *d*-2-butyl nitrate thus isolated from the Victor Meyer reaction gave a positive nitrate ester test[12] and a negative nitrite test.[13]

Anal. Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.77. Found: C, 40.46, 40.57; H, 7.64, 7.72; N, 11.72, 11.63.

(b) ***d*-2-Butyl Nitrite.**—Fraction A (24 g.) was dried over sodium sulfate and rectified at 200 mm. pressure using ice-water in the condenser.[8a] There was obtained 6.3 g. of *d*-2-butyl nitrite boiling at 30°. At atmospheric pressure the b. p. is 68° (Emich), d^{20}_4 0.8720, n^{20}_{D} 1.3710, M_{D} (calcd.) 27.01, M_{D} (found) 27.04, $[\alpha]^{24}_{\mathrm{D}}$ +0.44° (no solvent); lit. values[20] b. p. 68°, d^0 0.8981. Synthetic 2-butyl nitrite (see below) has b. p. 68° (Emich), d^{20}_4 0.8728, n^{20}_{D} 1.3710. The *d*-2-butyl nitrite thus isolated from the Victor Meyer reaction gives a positive test for nitrite esters.[13] The fact that this compound was a nitrite was further demonstrated by diazotizing *p*-toluidine with it and then coupling the diazonium salt with alkaline beta-naphthol according the procedure described for 2-octyl nitrite.[4] The crude azo compound after three recrystallizations from glacial acetic acid melted 132–132.7° and a mixed m. p. with an authentic sample showed no depression. The yield of pure azo compound was 40%. Under the same conditions 2-nitrobutane and 2-butyl nitrate did not diazotize *p*-toluidine.

(c) **2-Butanol.**—Two grams of Fraction 4, Table I (n^{20}_{D} 1.3960) was passed through a short column of aluminum oxide–Celite without the use of any solvent. The 1.1 g. of liquid thus obtained gave only a faint nitrite ester test[13] and had n^{20}_{D} 1.3967. This material was heated at reflux for five hours with 2.7 g. of phthalic anhydride and 3 g. of dry pyridine. No brown deposit was formed in the condenser nor was there any evolution of oxides of nitrogen as in the case when 2-butyl nitrite is subjected to the same treatment. At the end of this time the resulting solution was cooled to room temperature and poured into an excess of 37% hydrochloric acid. The oil which separated was taken up in benzene and the solution filtered. The solvent was removed and the remaining solid recrystallized from 60–90° petroleum ether. There was obtained 2.4 g. (67% yield) of 2-butyl hydrogen phthalate, m. p. 56–57°, $[\alpha]^{23}_{\mathrm{D}}$ 0.00, $l = 1$ dm. ($C = 20$); lit. values,[15] m. p. 56–57° (racemic), 46–47° (active). A mixed m. p. with racemic 2-butyl hydrogen phthalate showed no depression. The mother liquor was checked for optical activity, $[\alpha]^{23}_{\mathrm{D}}$ 0.00. It is interesting to note that whereas the 2-octanol produced in the Victor Meyer reaction between 2-bromoöctane and silver nitrite is optically active[4] the 2-butanol obtained here is completely racemic.

When 2-butyl nitrite is subjected to the phthalic anhydride–pyridine treatment 2-butyl hydrogen phthalate is formed; on the other hand 2-butyl nitrate does not give any phthalate ester.

(d) **Butanone.**—Fraction 1, Table I (n^{20}_{D} 1.3762) was passed through a silicic acid–Celite column. There was obtained, without the aid of a solvent, 1.8 g. of product, n^{20}_{D} 1.3785. This was treated with 1.5 g. of 2,4-dinitrophenylhydrazine.[21] A yellow, amorphous precipitate formed at once. It was filtered off while the solution was still hot. Upon cooling the filtrate, yellow needles of the 2,4-dinitrophenylhydrazone of butanone were deposited. After recrystallization from ethanol the derivative melted at 110–111° and showed no depression in a mixed m. p.; lit. value,[22] m. p. 111°. The yellow, amorphous material which came out of the hot solution does not melt below 200°. When 2-butyl nitrite was subjected to the same treatment only the amorphous material was obtained. With 2-butyl nitrate there was no evidence of any reaction.

Racemic 2-Butyl Nitrate.—A 500-ml. three-neck flask was fitted with a stirrer, condenser and dropping funnel and then immersed in a salt–ice mixture. In the flask was placed 190 g. of finely powdered silver nitrate and 137

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[18] Degering and Feasley, *J. Org. Chem.*, **8**, 12 (1943).

[19] Bertoni, *Gazz. chim. ital.*, **20**, 374 (1890).

[20] Bertoni, *Gazz. chim. ital.*, **18**, 434 (1888).

[21] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

[22] Ref. 21, p. 221.

g. of 2-bromobutane was added dropwise over a period of two hours. At the end of this time the reaction mixture was allowed to come to room temperature and then to stand for twelve hours. It was then heated at 60° until the organic layer gave a negative test for halogen. The flask was then fitted with a condenser set for downward distillation and heated to 80° at 60 mm. pressure; there was obtained 61 g. of distillate. This was shaken for one hour with 75 ml. of 85% phosphoric acid, and then allowed to stand in contact with the acid overnight. The acid layer was withdrawn, the organic layer was washed with water, dried over magnesium sulfate and then rectified.[8a] There was obtained 58 g. (49% yield) of 2-butyl nitrate boiling at 59° (80 mm.). At atmospheric pressure the nitrate boils at 124° (Emich), n^{20}_D 1.4015, d^{20}_4 1.029, M_D (calcd.) 28.80, M_D (found) 28.81, lit. value,[19] b. p. 124°, d^0 1.0382.

Anal.[23] Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62. Found: C, 40.68, 40.34; H, 7.62, 7.79.

Racemic 2-Butyl Nitrite.—(a) Thirty-nine grams of racemic 2-butanol was treated with 38 g. of sodium nitrite and 15.5 ml. of 96% sulfuric acid according to the method of Noyes.[24] Upon rectification[8a] there was obtained 49 g. (83% yield) of a pale yellow liquid; b. p. 28° at 180 mm. At atmospheric pressure the nitrite ester boils at 68° (Emich), n^{20}_D 1.3710, d^{20}_4 0.8726, M_D (calcd.) 27.01, M_D (found) 27.02; lit. values,[20] b. p. 68°, d^0 0.8981.

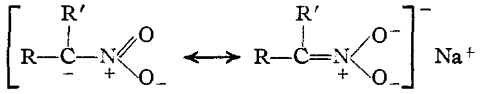
(b) Following the procedure described by Kornblum and Oliveto[25] 30 g. of racemic 2-butanol was treated with 40 g. of nitrosyl chloride. One modification was made, namely, the omission of the use of petroleum ether in working up the product; yield 21 g. (50%) boiling at 27° under 180 mm. pressure. At atmospheric pressure the nitrite boils at 68° (Emich); n^{20}_D 1.3710, d^{20}_4 0.8728.

Anal.[26] Calcd. for $C_4H_9NO_2$: N, 13.58. Found: N, 13.67, 13.70.

Summary

Contrary to an earlier report, optically active 2-nitrobutane does not give an active sodium salt upon treatment with sodium methoxide. Furthermore, 2-bromo-2-nitrobutane prepared from this salt is optically inactive.

It is concluded that the correct structure for the salts of aliphatic nitro compounds is



The action of silver nitrite on 2-iodobutane has been shown to form 2-nitrobutane, 2-butyl nitrate, 2-butyl nitrite, 2-butanol and butanone.

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(23) Microanalyses by Dr. Carl Tiedcke, New York, N. Y.

(24) Noyes, THIS JOURNAL, **55**, 3888 (1933).

(25) Kornblum and Oliveto, *ibid.*, **69**, 465 (1947).

(26) "The Pharmacopaeia of the United States of America," Mack Printing Co., Easton, Pa., 1942, 12 revision, p. 597.

LAFAYETTE, INDIANA RECEIVED AUGUST 1, 1947

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. VIII. Configurations of Some Compounds as Revealed by Rotatory Dispersion Curves[1]

BY THOMAS D. O'BRIEN,[2] JAMES P. MCREYNOLDS[3] AND JOHN C. BAILAR, JR.

The determination of configuration of ions of the type $[M(AA)_2b_2]$ and $[M(AA)_2bc]$[4] by chemical means presents several difficult problems and no general method has yet been suggested. It is often stated that the *cis* compounds are more highly colored and more soluble than the *trans*, but there are so many exceptions to these rules that no reliance can be placed in them. Differences in reactivity of *cis* and *trans* isomers have been observed in several cases, but they are so scattered that generalization cannot be drawn from them. Finally, the fact that a compound is prepared from another of known structure is of no value in determining configuration because molecular rearrangements are common in such reactions.

Unless one or more of the coördinating groups is optically active, *trans* complexes are not resolvable, while those of the *cis* configuration are. Thus, it is definite that the optically active (violet) form of $[Co\ en_2\ Cl_2]^+$ (Ib) must have the *cis* configuration, while the inactive (green) form must be *trans* (Ia). If, on the other hand, the coördinating groups are optically active, both isomers of the complex will rotate the plane of polarized light, so that the presence of optical activity does not serve to distinguish one isomer from the other. As will be shown in this paper, however, the rotatory dispersion curves often give the desired information.

It has previously been pointed out[5] that the rotatory dispersion curves of resolved *cis*-dichloro-bis-ethylenediamine cobaltic chloride, $[Co\ en_2Cl_2]Cl$ (Ib) and the corresponding compound of *levo*-propylenediamine, $[Co(l\text{-}pn)_2Cl_2]Cl$, (IIb) are strikingly alike in general shape and in the positions of maxima, minima and points of zero rotation. The same is true of the carbonato complexes. Several investigators have shown that *cis* cobaltic complexes containing optically active diamines do not exist in all the possible stereo-

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(1) Constructed from portions of the doctorate theses of James P. McReynolds (1938) and Thomas D. O'Brien (1941).

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(3) Died, June 19, 1943.

(4) The following abbreviations are used: AA = a group occupying two coördination positions; en = ethylenediamine; pn = propylenediamine; a, b and c = groups occupying one coördination position; Y = group occupying two coördination positions. The various compounds referred to are designated for convenience by Roman numerals, those of the ethylenediamine series being assigned odd numbers and those of the propylenediamine series, even numbers. For *trans* isomers, the Roman numeral is followed by the letter "a," for *cis* isomers, by "b."

(5) Bailar and McReynolds, THIS JOURNAL, **61**, 3199 (1939).