

optical purity of the α -phenylethyl chloride having α^{25}_D -43.65° is 40%.

Dextrorotatory α -phenylethyl alcohol yields dextrorotatory α -phenylethyl nitrite (nitrosyl chloride in pyridine). Furthermore, thermal decomposition of dextrorotatory α -phenylethyl nitrite yields dextrorotatory α -phenylethyl alcohol. This is the basis for the configurational relationship for these two compounds given in Chart I.³³ Conversion of α -phenylethyl alcohol to the nitrite by nitrosyl chloride not only retains configuration but occurs with complete retention of optical purity. This was demonstrated as follows:

(-) α -Phenylethyl alcohol (86 g., 0.7 mole), n^{20}_D 1.5265, α^{25}_D -32.2° , was treated with nitrosyl chloride.¹⁹ The (-) α -phenylethyl nitrite obtained (46 g., 44% yield) had n^{20}_D 1.4926, α^{25}_D -42.5° , b.p., 52° (2 mm.). *Anal.* Calcd. for $C_8H_9NO_2$: C, 63.57; H, 5.96; N, 9.26. Found: C, 63.22; H, 5.99; N, 8.91. When a sample of this nitrite (α^{25}_D -42.5°) was methanolized at room temperature according to the procedure employed with (+)2-octyl nitrite (*vide supra*), (-) α -phenylethyl alcohol, n^{20}_D 1.5261, α^{25}_D -32.2° , was obtained.¹¹

In run 2 of Table III, (-) α -phenylethyl chloride of 40% optical purity yield (-) α -phenylethyl nitrite of α^{25}_D -8.45° . Thus this nitrite is $8.45/59.6 \times 100 = 14\%$ optically pure and the step $RCl \rightarrow RONO$ took place with $14/40 \times 100 = 36\%$ retention of optical purity.

The (+) α -phenylnitroethane produced in run 2 has α^{27}_D $+2.80^\circ$ and, by catalytic reduction with Adams catalyst in glacial acetic acid,⁶ there was obtained (+) α -phenylethylamine having α^{27}_D $+6.50^\circ$; this amine is $6.50/37.95 \times 100 = 17\%$ optically pure. Thus the sequence $RCl \rightarrow$

(33) We are indebted to Dr. S. A. Herbert for these experiments (ref. o, Table I).

$RNO_2 \rightarrow RNH_2$ occurred with $17/40 \times 100 = 43\%$ retention of optical purity.

Reaction of (+) α -Phenylethyl Chloride with One-half of the Stoichiometrical Amount of Silver Nitrite (Run 3), Table III.—This was carried out using 51 g. (0.36 mole) of (+) α -phenylethyl chloride (b.p. $48-49^\circ$ (1-2 mm.), n^{20}_D 1.5271, α^{27}_D $+10.86^\circ$, l 2 dm.) and 27.7 g. (0.18 mole) of silver nitrite in 300 ml. of anhydrous ether. The addition of the chloride was made over a three-hour period with continuous stirring (absence of light). The mixture then was stirred for 19 hours at 0° . The silver salts were filtered off, washed thoroughly with ether and the filtrate and washings were combined. After removal of the solvent *in vacuo* at room temperature, the residue was distilled and 16 fractions were obtained.

(a) Attempted Isolation of α -Phenylethyl Nitrite.—Fractions 1-9 having n^{20}_D 1.5110-1.5225 were combined (36.7 g.) and rectified repeatedly but it proved impossible to isolate α -phenylethyl nitrite free of the chloride.

(b) Isolation of "Unreacted" (+) α -Phenylethyl Chloride.—Fractions 10-12, n^{20}_D 1.5245-1.5228 (3.0 g.), were combined with 19.0 g. of high boiling material (n^{20}_D 1.5195-1.5278) from the attempted isolation of the nitrite ester, and the mixture was rectified.¹⁸ There was obtained 7.5 g. (30% recovery) of "unreacted" (+) α -phenylethyl chloride, b.p. $46-47^\circ$ (1-2 mm.), n^{20}_D 1.5271, α^{25}_D $+0.90^\circ$ (l 2 dm.). *Anal.* Calcd. for C_8H_9Cl : C, 68.33; H, 6.41. Found: C, 68.70, 68.66; H, 6.61, 6.60.

The "unreacted" α -phenylethyl chloride thus retained $0.90/10.86 \times 100 = 8\%$ of its optical activity.

(c) Attempted Isolation of α -Phenyl Nitroethane.—Fractions 13-15 having n^{20}_D 1.5215-1.5248 were combined (7.7 g.) and twice rectified¹⁸ *in vacuo*. The nitro compound free of halogen could not be isolated.

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The Reduction of Optically Active 2-Nitroöctane and α -Phenylnitroethane^{1,2}

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Conditions are described for reducing optically active nitro compounds to active amines. In this way the configurational relationship of 2-nitroöctane and of α -phenylnitroethane to other compounds of the 2-octyl- and α -phenylethyl series is established. Not all reducing agents give optically active amines; the implications of this fact are discussed briefly.

In order to determine the stereochemistry of the reaction of silver nitrite with 2-octyl and α -phenylethyl halides, a method of establishing the configurations of 2-nitroöctane and α -phenylnitroethane was needed.³ Reduction to the amines seemed an attractive way of relating these nitro compounds to the halides. It transpired that the nitro compounds could be reduced to optically active amines with little, if any, loss in optical purity—but not by all reducing agents.

Thus, reduction of optically active 2-nitroöctane by lithium aluminum hydride gives 2-aminoöctane in 73% yield, but the amine is completely racemic. In contrast, reduction by iron powder and acetic acid produces optically active 2-aminoöctane (expt. 1 and 2, Table I). The amount of racemization for the entire sequence $ROH \rightarrow RBr \rightarrow RNO_2 \rightarrow RNH_2$ is 18%. Hence, even if all of the racemization for this sequence occurs in the step $RNO_2 \rightarrow$

RNH_2 , the iron and acetic acid reduction is 82% stereospecific. However, there are cogent reasons for believing that a good part (and perhaps all) of the 18% racemization takes place prior to the step $RNO_2 \rightarrow RNH_2$,⁸ so that the iron and acetic acid reduction must occur with considerably better than 82% retention of optical purity.

The 2-aminoöctane produced on hydrogenating (-)2-nitroöctane, α^{27}_D -12.77° , over Adams catalyst is 96% racemized when absolute ethanol is the solvent (expt. 7). Repetition, except that reduction was interrupted after 55% of the theoretical amount of hydrogen had been absorbed, gave (-)2-aminoöctane of α^{27}_D -0.48° , *i.e.*, 89% racemized. Of especial interest was the observation that the recovered (-)2-nitroöctane had α^{27}_D -0.15° ; the "unreacted" 2-nitroöctane had suffered a 99% loss of optical activity (expt. 8).

Since optically active 2-nitroöctane is racemized on forming salts,⁴ this loss of activity is readily intelligible. Not only does the solution become basic because of the 2-aminoöctane produced but, in addition, a small amount of alkali is liberated on

(1) Paper VIII in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(2) This research was supported by the United States Air Force under Contract No. AF18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(3) N. Kornblum, L. Fishbein and R. Smiley, *THIS JOURNAL*, **77**, 6261 (1955).

(4) N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffand, *ibid.*, **69**, 309 (1947).

TABLE I
 SUMMARY OF THE REDUCTIONS OF OPTICALLY ACTIVE 2-NITROOCTANE^a

Expt.	2-Octanol ^b		Opt. purity, %	2-Bromoöctane		2-Nitroöctane		Method of reduction	Yield, %	2-Aminoöctane ^b		% Retention of optical purity for ROH \rightarrow RNH ₂ ^c
	$[\alpha]_D^{20}$	<i>t</i> , °C.		$[\alpha]_D^{20}$	<i>t</i> , °C.	$[\alpha]_D^{20}$	<i>t</i> , °C.			$[\alpha]_D^{20}$	<i>t</i> , °C.	
1	-9.28°	30	90	+31.5°	32	-14.19°	28	Fe + gl. HAc	68	-3.81°	27	82
2	-9.28	30	90	+31.5	32	-13.44	28	Fe + gl. HAc	61	-3.66	29	80
3	+9.58	27	94	^d		+12.29	28	Fe + aq. HAc	52	+3.82	28	79
4	+9.4	27	91	-31.41	27	+14.77	27	H ₂ + PtO ₂ in gl. HAc	81	+3.38	14	72
5	-9.32	26	90	+31.6	27	-14.28	29	gl. HAc	78	-3.12	16	67
6	+8.96	28	87	-29.08	29	+16.4 ^f	29	H ₂ + PtO ₂ in gl. HAc	48	+3.09	24	69
7	-8.8	27	85	+30.4	26	-12.77	27	H ₂ + PtO ₂ in abs. EtOH	68	-0.17	27	4
8	-8.8	27	85	+30.4	26	-12.77 ^e	27	abs. EtOH	72	-0.48	27	11
9	+8.96	28		-29.08	29	+16.4 ^f	30	LiAlH ₄	73	-0.02	27	0

^a Unless otherwise noted, all rotations were taken on the pure liquid in a 1-dm. tube; α^d_D represents observed rotation, $[\alpha]_D^{20}$ represents specific rotation. ^b Cf. Table I (preceding paper) for rotations of the optically pure compounds. ^c Cf. preceding paper for discussion of this calculation. ^d The (+)2-nitroöctane used was prepared from (-)2-iodoöctane, $\alpha^{27}_D -40.75^\circ$. This experiment was conducted by R. A. Smiley to whom our thanks are due. ^e The reduction was terminated after 55% of the theoretical quantity of hydrogen was absorbed. The "unreacted" nitro compound had $\alpha^{26}_D -0.15^\circ$ (99% racemization). ^f Specific rotation, $C = 5.0$, abs. alcohol.

reduction of platinum oxide to platinum.⁵ In order to learn whether or not 2-aminoöctane is sufficiently basic to racemize 2-nitroöctane an ethanol solution of optically active 2-nitroöctane was treated with a few drops of the amine; racemization occurred readily.

It is then, perhaps, not so surprising that when 2-nitroöctane ($\alpha^{27}_D +14.77^\circ$) is hydrogenated over Adams catalyst in glacial acetic acid, the (+)2-aminoöctane has $\alpha^{14}_D +3.38^\circ$ (expt. 4, also see expt. 5 and 6 of Table I), which corresponds to an over-all stereospecificity of 72% for the entire sequence ROH \rightarrow RNH₂ and therefore, in all probability, a greater than 72% retention of optical purity in the reduction step.⁶

However, reductions employing platinum oxide, even in acetic acid, are not free of some racemization. That this is so is apparent from the rotations of 2-nitroöctane and 2-aminoöctane recorded in Table I. For example, in expt. 1 (iron and acetic acid), 2-aminoöctane of $\alpha^{27}_D -3.81^\circ$ is obtained from 2-nitroöctane of $\alpha^{28}_D -14.19^\circ$. The amine produced in expt. 4 (platinum oxide in acetic acid) would, then be expected to have a rotation of at least 3.97° , *i.e.*, $14.77 \times 3.81/14.19$; instead it has $\alpha^{14}_D 3.38^\circ$, which is only 85% of the rotation it would have had if the reduction had been carried out with iron and acetic acid. Similarly, the 2-aminoöctane of expt. 5 has but 81% of the rotation it would have had if iron and acetic acid had been employed.⁷

Two reductions using platinum oxide in acetic acid were carried out with active α -phenylnitroethane. In one, nitro compound of $\alpha^{32}_D +1.28^\circ$ was converted to α -phenylethylamine of $\alpha^{32}_D +3.20^\circ$, and in the other α -phenylnitroethane

having $\alpha^{27}_D +2.80^\circ$ gave α -phenylethylamine of $\alpha^{27}_D +6.50^\circ$. This corresponds to 44% retention of optical purity for the entire sequence RCl \rightarrow RNO₂ \rightarrow RNH₂ and, hence, reduction occurs with at least 44% retention of optical purity. However, for reasons discussed in the preceding paper,⁸ while it is certain that some of the 56% racemization of the entire sequence occurs in the step RCl \rightarrow RNO₂, the fact that platinum oxide in acetic acid reductions of 2-nitroöctane proceed with at least 15-19% racemization makes it a virtual certainty that these two catalytic reductions of α -phenylnitroethane are attended by a minimum of 20% racemization.

Aside from their value in connection with the stereochemical studies of the preceding paper⁸ these findings have interesting implications of their own. Thus, it is clear that the mechanism of reduction by iron and acetic acid does not involve any symmetrical intermediate. This must also be true for that part of the catalytic hydrogenation by platinum in acetic acid which produces optically active amine.⁸

Configurational assignments for a number of bicyclic terpene derivatives have been made which involve catalytic reduction of secondary nitro compounds over platinum oxide.⁹ In view of the foregoing this seems not to be a good practice, especially when ethanol is used as the solvent and the product is a liquid.

The generalization that reduction by lithium aluminum hydride does not affect racemizable asymmetric centers is based on the clean-cut demonstration¹⁰ that (-)2-methylbutanoic acid and *l*-menthone are reduced to the corresponding optically pure alcohols. However, since reduction of

(5) K. Miescher and C. Sholz, *Helv. Chim. Acta*, **20**, 263 (1937); H. Smith, C. W. Keenan and B. W. Gieseemann, *THIS JOURNAL*, **76**, 229 (1954).

(6) Throughout this discussion the small differences in rotation resulting from measurements at different temperatures are ignored.

(7) The disparity between reductions employing iron and acetic acid on the one hand and platinum oxide and acetic acid on the other is even greater if expt. 2 or 3 is employed as the reference point.

(8) Conceivably, all the racemization observed in these catalytic hydrogenations takes place prior to reduction. Recovery of the unreacted nitro compound from a hydrogenation which has only been permitted to go half way would settle this point.

(9) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938); D. S. Noyce, *THIS JOURNAL*, **73**, 20 (1951); E. E. van Tamelen and R. J. Thiede, *ibid.*, **74**, 2616 (1952).

(10) D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950).

active 2-nitroöctane by lithium aluminum hydride gives completely racemic 2-aminoöctane, it is apparent that this generalization needs to be qualified.

It seems likely that lithium aluminum hydride racemizes the 2-nitroöctane by salt formation prior to reduction; this raises the interesting possibility that lithium aluminum hydride reductions actually involve the anion of the nitroparaffin and that the characteristic difference (formation of azo compounds) when aromatic nitro compounds are reduced by this reagent¹¹ derives from the fact that aromatic nitro compounds are incapable of forming salts.

Experimental¹²

The synthesis of the optically active nitro compounds employed here is described in the preceding paper.³

Reduction of (-)-2-Nitroöctane with Iron and Glacial Acetic Acid (Expt. Table I).—A mixture of 10.5 g. (0.19 mole) of iron powder and 50 g. of glacial acetic acid was placed in a 500-ml. three-necked flask fitted with a Tru-Bore precision stirrer, an addition funnel, and a reflux condenser. Stirring was initiated and 6.7 g. (0.042 mole) of (-)-2-nitroöctane, n_{20}^D 1.4880, $\alpha_{25}^{20} -14.19^\circ$, in 15 ml. of glacial acetic acid was cautiously added dropwise. The mixture became quite hot during the addition of the nitro compound and it occasionally was necessary to immerse the flask in ice. It also was necessary periodically to add small portions of acetic acid in order to keep the mixture fluid. After addition of the nitro compound was completed (1.5 hours) the mixture was stirred at room temperature for an additional three-quarters of an hour.

The reaction mixture was rendered alkaline and the amine steam distilled out. The amine was taken up in diethyl ether and dried over potassium hydroxide. The ether was removed by distillation, and the residue distilled to give 3.7 g. (68% yield) of (-)-2-aminoöctane, b.p. 60–61° (11 mm.), n_{20}^D 1.4240, $\alpha_{27}^{20} -3.81^\circ$; lit. values¹³: $\alpha_{15}^{15} -5.14^\circ$, b.p. 65° (21 mm.), n_{20}^D 1.4232.

Anal. Calcd. for $C_8H_{19}N$: C, 74.42; H, 14.73; N, 10.85. Found: C, 74.69; H, 14.59; N, 10.60.

(-)-2-Aminoöctane was characterized further by preparing the benzamide which was recrystallized twice from cyclohexane; m.p. 101–102°; lit. values¹⁴: *d*- or *l*-benzamide of 2-aminoöctane melts 101–102°, while the benzamide of the racemic amine has m.p. 74–75°.

Anal. Calcd. for $C_{10}H_{23}NO$: C, 77.25; H, 9.87; N, 6.00. Found: C, 77.10, 77.15; H, 9.88, 9.85; N, 6.30, 6.25.

Reduction of (+)-2-Nitroöctane Using Platinum Oxide in Glacial Acetic Acid (Expt. 4, Table I).—A solution of 8.0 g. (0.05 mole) of (+)-2-nitroöctane, b.p. 73–74° (2 mm.), n_{20}^D 1.4280, $\alpha_{27}^{20} +14.77^\circ$, in 30 ml. of glacial acetic acid was shaken with hydrogen (four atmospheres pressure) in the presence of 1.0 g. of platinum oxide, at room temperature. The theoretical quantity of hydrogen was absorbed in two hours.

The mixture was filtered, the catalyst washed with two 15-ml. portions of glacial acetic acid and the acidic extracts combined and neutralized with aqueous sodium hydroxide. The free amine was taken up in diethyl ether and the aqueous phase was extracted further with diethyl ether by means of a continuous extraction apparatus. The extracts were combined, dried over potassium hydroxide, then concentrated by distillation. The residue was distilled yielding 5.2 g. (81% yield) of (+)-2-aminoöctane, b.p. 55–56° (9 mm.), n_{20}^D 1.4240, $\alpha_{14}^{15} +3.38^\circ$. The benzamide, recrystallized twice from cyclohexane, had m.p. 101–102°.

Reduction of (-)-2-Nitroöctane with Platinum Oxide in Absolute Ethanol (Expt. 7, Table I).—At room temperature

(11) W. G. Brown and R. F. Nystrom, *THIS JOURNAL*, **70**, 3738 (1948).

(12) Unless otherwise noted, rotations were determined using the pure liquid compound in a 1-dm. tube.

(13) F. G. Mann and J. Reid, *J. Chem. Soc.*, 3384 (1950).

(14) F. G. Mann and J. W. G. Porter, *ibid.*, 456 (1944).

using 1.0 g. of platinum oxide, a solution of 7.0 g. (0.044 mole) of (-)-2-nitroöctane, n_{20}^D 1.4282, $\alpha_{27}^{20} -12.77^\circ$, in 25 ml. of absolute ethanol was shaken with hydrogen (four atmospheres pressure) until the theoretical quantity was absorbed (two hours). The reduction mixture was filtered, the catalyst was washed with four 5-ml. portions of absolute ethanol, and then the filtrate and washings were combined and concentrated. Rectification gave 3.87 g. (68% yield) of (-)-2-aminoöctane, b.p. 53–54° (8 mm.), n_{20}^D 1.4240, $\alpha_{27}^{20} -0.17^\circ$. This sample of 2-aminoöctane gave a benzamide, m.p. 74–75° after two recrystallizations from cyclohexane, which showed no depression in a mixed m.p. with authentic racemic benzamide (m.p. 74–75°). Another portion of this sample of 2-aminoöctane was converted to the Schiff base with 9-anthraldehyde and this, after two recrystallizations from 70% aqueous ethanol, had m.p. 61–62°, $\alpha_{27}^{20} -0.07^\circ$ (l 2 dm., c 1.00, abs. ethanol) and gave an undepressed m.p. when mixed with authentic racemic Schiff base having m.p. 61–62° (see below).

The Partial Reduction of (-)-2-Nitroöctane with Platinum Oxide in Absolute Ethanol (Expt. 8, Table I).—A solution of 9.7 g. (0.061 mole) of (-)-2-nitroöctane, n_{20}^D 1.4282, $\alpha_{27}^{20} -12.77^\circ$, in 25 ml. of absolute ethanol was shaken with hydrogen (four atmospheres pressure) in the presence of 1.0 g. of platinum oxide at room temperature. Reduction was discontinued when 55% of the theoretical amount of hydrogen was absorbed. The mixture was filtered, the catalyst washed with three 5-ml. portions of absolute ethanol and the filtrate and washings combined and concentrated *in vacuo* at room temperature.

Isolation of "Unreacted" 2-Nitroöctane.—The residue was taken up in 15 ml. of petroleum ether (30–37°); the extract was cooled to 0° and then extracted first with ice-cold 20% aqueous acetic acid containing urea and then with water. (The yellow-orange ethereal extract immediately turned pale green upon treatment with the acetic acid.) The petroleum ether phase was dried over anhydrous sodium sulfate, then concentrated *in vacuo* at room temperature. The residue was distilled yielding 3.9 g. (89% recovery) of (-)-2-nitroöctane, b.p. 77–78° (3 mm.), n_{20}^D 1.4280, $\alpha_{27}^{20} -0.15^\circ$, a 98.9% loss in optical purity.

Isolation of 2-Aminoöctane.—The aqueous acetic acid phase was rendered alkaline with potassium hydroxide; the amine which separated was taken up in petroleum ether (30–37°), dried over potassium hydroxide, then concentrated *in vacuo* at room temperature. The residue was distilled yielding 3.1 g. (72% yield) of (-)-2-aminoöctane, b.p. 55–56° (9 mm.), n_{20}^D 1.4241, $\alpha_{27}^{20} -0.48^\circ$. The benzamide, after one recrystallization from petroleum ether (b.p. 60–70°) melted at 76–77° and had $\alpha_{27}^{20} -0.15^\circ$ (c 1.95, absolute ethanol, l 2 dm.) whence $[\alpha]_{27}^{20} -3.85^\circ$. This benzamide gave a depressed m.p. (62–76°) when mixed with the racemic benzamide of m.p. 74–75°. The Schiff base with 9-anthraldehyde had m.p. 62–63° after two recrystallizations from aqueous ethanol and had $\alpha_{27}^{20} -0.22^\circ$ (c 1, absolute ethanol, l 2 dm.), $[\alpha]_{27}^{20} -11.0^\circ$. It gave a depressed m.p. of 54–62° when mixed with authentic racemic Schiff base (m.p. 61–62°).

Reduction of (+)-2-Nitroöctane with Lithium Aluminum Hydride.—In a one-liter three-necked flask fitted with a Tru-Bore tantalum stirrer, reflux condenser, and an addition funnel were placed 4.7 g. (0.123 mole) of lithium aluminum hydride and 200 ml. of anhydrous ether. The system was swept out with dry nitrogen and 6.6 g. (0.041 mole) of (+)-2-nitroöctane, n_{20}^D 1.4280, $\alpha_{27}^{20} +0.82^\circ$ (c 5.0 absolute ethanol), $[\alpha]_{30}^{20} +16.4^\circ$, in 50 ml. of anhydrous ether was introduced at such a rate as to produce gentle reflux. After addition, stirring was continued at room temperature for one-half hour.

The flask was immersed in ice, and the excess lithium aluminum hydride was decomposed by addition of water. The organolithium complex was then decomposed by 250 ml. of 20% sodium potassium tartrate solution. The reaction mixture was exhaustively extracted with ether, the ethereal extracts were dried over potassium hydroxide, then concentrated on a water-bath. The residue was rectified. There was obtained 3.8 g. (73% yield) of 2-aminoöctane, b.p. 43–44° (5 mm.), n_{20}^D 1.4241, $\alpha_{23}^{20} 0.02^\circ$. The amine was characterized by its benzamide, m.p. and mixed m.p. with racemic benzamide of 2-aminoöctane 74–75°. The 9-anthraldehyde Schiff base melted at 61–62° and gave no depression with authentic racemic Schiff base (m.p. 61–62°).

Preparation of the Schiff Base of 9-Anthraldehyde and Racemic 2-Aminoöctane.—One gram (0.008 mole) of racemic 2-aminoöctane, 10 ml. of abs. ethanol and 1.65 g. (0.008 mole) of 9-anthraldehyde refluxed for ten minutes, allowed to come to room temperature and then placed in a refrigerator gave 2.3 g. of product, m.p. 60–62°. When recrystallized from 70% aqueous ethanol it yielded 2.1 g. (83% yield) of yellow crystals, m.p. 61–62°.

Anal. Calcd. for $C_{23}H_{27}N$: C, 87.0; H, 4.41; N, 8.51. Found: C, 87.0; H, 4.37; N, 8.51.

Catalytic Reduction of (+)- α -Phenylnitroethane.—A solution of 6.0 g. (0.40 mole) of (+)- α -phenylnitroethane (b.p. 92° (2 mm.), n_D^{20} 1.5215, α_D^{25} +2.80°) in 30 ml. of glacial acetic acid was reduced at 4 atm. (1.0 g. of Adams

platinum oxide). The theoretical amount of hydrogen was absorbed in 18 minutes and there was obtained 2.8 g. (58% yield) of (+)- α -phenylethylamine, b.p. 71–72° (10 mm.), n_D^{20} 1.5269, α_D^{25} +6.50°. This gave the benzamide; recrystallized from absolute ethanol (m.p. 124–125°) and then from petroleum ether (b.p. 60–70°); m.p. 124–125°; lit. values: (–)benzamide deriv., m.p. 124.5–125.5¹⁶; racemic benzamide of α -phenylethylamine has m.p. 120°.¹⁶

Anal. Calcd. for $C_{15}H_{16}NO$: C, 80.0; H, 6.67; N, 6.22. Found: C, 79.81, 79.82; H, 6.81, 6.89; N, 6.57, 6.48.

(15) W. Marckwald and R. Meth, *Ber.*, **38**, 808 (1905).

(16) M. Kann and J. Tafel, *ibid.*, **27**, 2308 (1894).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Mechanism of the Reaction of Silver Nitrite with Alkyl Halides. The Contrasting Reactions of Silver and Alkali Metal Salts with Alkyl Halides. The Alkylation of Ambident Anions^{1,2}

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The reaction of silver nitrite with alkyl halides proceeds *via* a transition state which has both S_N1 and S_N2 character in proportions that vary gradually with the structure of the halide. The products of the reaction reflect this variation in character: The greater the carbonium contribution to the transition state the greater is the yield of nitrite ester and the smaller is the yield of nitroparaffin. This preference of an anion (NO_2^-) for covalency formation at the atom of higher electronegativity (oxygen) is general and forms the basis of the contrasting reactions of silver salts and alkali metal salts (*e.g.*, $AgCN$ and $NaCN$) with alkyl halides. Electrophilic attack by silver on the halogen of the alkyl halide greatly enhances the carbonium contribution to the transition state and this results in a preference for covalency formation to the most electronegative atom of the anion. Silver ions, while very effective for this purpose, are not unique. Changes in the reaction medium and in the structure of the alkylating agent also may have a profound effect on the nature of the transition state and, when this happens, the nature of the products changes. The following generalization about the alkylation of anions possessing two different reactive positions (*i.e.*, ambident anions), which is fully applicable even when silver is absent, provides a simple rationale for the hitherto unsolved problem of carbon *vs.* oxygen alkylation, oxygen *vs.* nitrogen alkylation, etc., in anions derived from acetoacetic ester, phenols, nitroparaffins, α -pyridone, acid amides, thioamides, etc.: The greater the S_N1 character of the transition state the greater is the preference for covalency formation with the atom of higher electronegativity and, conversely, the greater the S_N2 contribution to the transition state the greater the preference for bond formation to the atom of lower electronegativity. Specific examples of the application of this principle are given. The demonstration that the reaction of silver nitrite with alkyl halides has a transition state possessing S_N1 and S_N2 character rather than being the sum of two simultaneously occurring processes, the S_N1 and the S_N2 , has an important bearing on the question of border-line mechanisms in substitution reactions at a saturated carbon atom.

The studies described in the present paper when taken in conjunction with the results of the preceding papers of this group⁴ provide a secure basis for describing the mechanism of the reaction of silver nitrite with alkyl halides. This is a reaction which at one and the same time exhibits carbonium ion character and bimolecular nucleophilic displacement character. Precise allocation of the proportions of S_N1 and of S_N2 contribution to the transition state is, of course, not possible and, indeed, as will be seen, the relative importance of the pull exerted by silver and the push due to nitrite ion varies with the structure of the halide and with the solvent.

It will be recalled⁴ that the yield of nitro compound falls progressively as silver nitrite is treated

(1) Paper IX in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

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(3) In part from the doctoral dissertation of Robert A. Smiley, Purdue University, June, 1954.

(4) (a) N. Kornblum, B. Taub and H. E. Ungnade, *THIS JOURNAL*, **76**, 3209 (1954); (b) N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub and S. A. Herbert, *ibid.*, **77**, 5528 (1955); (c) N. Kornblum, L. Fishbein and R. A. Smiley, *ibid.*, **77**, 6261 (1955); (d) N. Kornblum and L. Fishbein, *ibid.*, **77**, 6266 (1955).

with primary, secondary and tertiary halides. In contrast, the yield of nitrite ester rises in going from primary, to secondary to tertiary halides.

Two explanations suggest themselves for this progressive change in the character of the reaction. The effect may be a steric one, for models reveal that NO_2^- has a greater steric requirement when it comes in to form a C–N bond than when it comes in to form a C–O bond. Consequently, it is conceivable that formation of nitro compounds is retarded more strongly than formation of nitrite esters when it becomes increasingly difficult to approach the carbon atom on the side rearward to the carbon-halogen bond.

A second possibility is that a carbonium ion would react more rapidly with the oxygen of a nitrite ion than with the nitrogen (perhaps because of simple electrostatic considerations inasmuch as the nitrogen is essentially neutral while the oxygen atoms share the negative charge between them). In any event, if we make this assumption, the increasing proportion of nitrite ester becomes intelligible since on going from primary to secondary to tertiary halides the ease of carbonium ion formation is increased.

Kinetic studies argue against the first and sup-