Chlorination of the above products yielded a mixture of high boiling chlorides which were distinguishable from the dichloride of perfluoro-1-heptene but which had similar retention times. Analysis of aliquots of the combined aqueous extracts from the above reactions accounted for 85% of the fluoride utilized in the first reaction and 95% of that utilized in the second reaction. Small amounts of chloride ion were also detected.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Configurational Relationship of α-Phenylnitroethane and α-Phenylethylamine

BY NATHAN KORNBLUM, WILLIAM D. GUROWITZ,[1] HAROLD O. LARSON AND DONALD E. HARDIES

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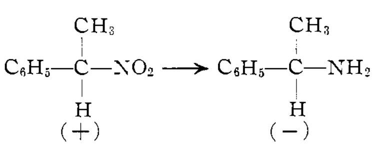
Contrary to an earlier report[3] by Kornblum and Fishbein, reduction of dextrorotatory α-phenylnitroethane gives levorotatory α-phenylethylamine. The earlier report[3] that dextrorotatory 2-nitroöctane gives dextrotatory 2-aminoöctane has been confirmed.

Recently,[2] the observation was made that dextrorotatory α-phenylnitroethane yields levorotatory α-phenylethylamine on reduction by iron and acetic acid. Inasmuch as Kornblum and Fishbein[3] had previously reported that (+)-α-phenylnitroethane gives (+)-α-phenylethylamine on hydrogenation over platinum oxide, this was a most unexpected result. The whole matter has, therefore, been reinvestigated.



$$\underset{(+)}{C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-NO_2} \longrightarrow \underset{(-)}{C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-NH_2}$$

Catalytic reduction of α-phenylnitroethane over platinum oxide in acetic acid had previously been carried out a total of four times.[3] Despite the use of a relatively large amount of catalyst—one gram of platinum oxide for six to eight grams of the nitro compound—no difficulty was reported in obtaining pure α-phenylethylamine (55–61% yields).[3] In the present study a total of thirteen experiments was carried out. When platinum oxide was used in amounts corresponding to that employed by Kornblum and Fishbein[3] no α-phenylethylamine could be isolated. In one run an amine whose $n^{20}D$ and b.p. corresponded to those of α-cyclohexylethylamine[4] was obtained. In another experiment almost twice the amount of hydrogen required for reducing the $-NO_2$ to $-NH_2$ was absorbed and a neutral product, which had the properties of ethylcyclohexane, was isolated.

Efforts to stop the reduction at the α-phenylethylamine stage by using less platinum oxide and operating at lower pressures gave erratic results. Usually the α-phenylethylamine was contaminated with another amine (probably α-cyclohexylethylamine[4]) and the yields of basic material varied all the way from 4 to 69%, the average being 23%.

In two early experiments racemic α-phenylnitroethane gave pure α-phenylethylamine. Attempts at repetition with the optically active nitro compound were, however, less than total successes. One experiment, however, is worth discussing. Here α-phenylnitroethane of $\alpha^{30}D$ − 9.58° gave dextrorotatory α-phenylethylamine ($\alpha^{26}D$ + 9.48°) rather than the levorotatory α-phenylethylamine previously reported.[3] This α-phenylethylamine of $\alpha^{26}D$ + 9.48° was contaminated with an amine and if, as is probable, the contaminant was α-cyclohexylethylamine, it was present to the extent of *ca.* 6%. Since α-cyclohexylethylamine and α-phenylethylamine of the same configuration have opposite signs of rotation, the possibility that the discrepancy between the present results and those of Kornblum and Fishbein derives from contamination by α-cyclohexylethylamine was considered. However, when a sample of α-phenylethylamine ($\alpha^{27}D$ + 32.37°) was hydrogenated over platinum oxide in acetic acid it gave α-cyclohexylethylamine of $\alpha^{25}D$ − 2.77°.[5] Clearly then contamination by 6% of α-cyclohexylethylamine would not reverse the sign of rotation of α-phenylethylamine.

TABLE I

REDUCTIONS OF OPTICALLY ACTIVE α-PHENYLNITROETHANE[a]

	α-Phenylnitroethane				α-Phenylethylamine	
Expt.	α^tD	t, °C.	Method of reduction	Yield, %	α^tD	t, °C.
1	+ 0.88°	26	Fe + gl. HOAc	54	− 0.92°	26
2	− 1.48	26	Fe + gl. HOAc	64	+ 1.64	27
3	− 9.58	30	Fe + gl. HOAc	81	+10.32	29.5
4	+10.85	26	$SnCl_2$ + HCl	36	−11.68	26
5	+11.11	24	$SnCl_2$ + HCl	42	−11.54	25
6	− 9.58	30	H_2 + PtO_2 in gl. HOAc	16	+ 9.48[b]	26

[a] All rotations taken on the pure liquid in a 1-dm. tube; α^tD represents observed rotation. [b] This sample of α-phenylethylamine probably contains 6% of α-cyclohexylethylamine.

α-Phenylethylamine and α-cyclohexylethylamine pick up carbon dioxide very rapidly and one could envision the possibility that carbonate (and/or carbamate) formation might be the source of the discrepancy.[6] Consequently, the rotations of samples of α-phenylethylamine and α-cyclohexylethylamine were determined before and after

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(1) Ethyl Corporation Fellow, 1956–1957.

(2) D. E. Hardies, Ph.D. Thesis, Purdue University, June, 1957.

(3) N. Kornblum and L. Fishbein, THIS JOURNAL, **77**, 6267 (1955); L. Fishbein, Ph.D. Thesis, Purdue University, 1954.

(4) The reduction of α-phenylethylamine to α-cyclohexylethylamine in 82% yield occurs under the conditions employed in these catalytic hydrogenations (*cf.* Experimental).

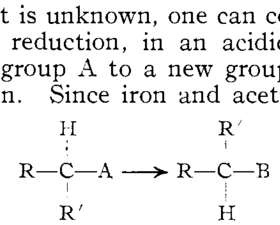
(5) This is in agreement with W. Leithe (*Ber.*, **65**, 660 (1932)) who reduced α-phenylethylamine of $[\alpha]^{15}D$ −40.3° to α-cyclohexylethylamine of $[\alpha]^{15}D$ +3.2° using platinum oxide and aqueous acetic acid.

(6) L. E. Young and C. W. Porter, THIS JOURNAL, **59**, 1438 (1937).

exposure to air. In both cases no significant difference was found.

In sharp contrast to catalytic hydrogenation, reduction by iron and acetic acid proceeds smoothly and reproducibly. As the data of Table I show, reduction by iron and acetic acid gives α-phenylethylamine having a rotation opposite in sign to that of the α-phenylnitroethane from which it is produced.

Although it is unknown, one can conceive of the *heterogeneous* reduction, in an acidic medium, of a functional group A to a new group B occurring with inversion. Since iron and acetic acid reductions, in common with catalytic hydrogenations, are heterogeneous processes, it seemed desirable to convert α-phenylnitroethane to the amine by means of a homogeneous reducing system. An acidic solution of stannous chloride proved suitable and using this reagent the configurational relationship obtained with iron and acetic acid was unambiguously confirmed; dextrorotatory α-phenylnitroethane is reduced to levoratatory α-phenylethylamine (Table I).



$$\mathrm{R}-\overset{\mathrm{H}}{\underset{\mathrm{R'}}{\mathrm{C}}}-\mathrm{A} \longrightarrow \mathrm{R}-\overset{\mathrm{R'}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{B}$$

While it is clear that the earlier report by Kornblum and Fishbein[3] is in error, the genesis of the error is not understood. Fishbein's original laboratory notes are in agreement with the values reported in the earlier paper.[3] The original notes also reveal that the routine practice of having all polarimetric readings taken independently by three observers was followed. Finally, the rotation of one of Fishbein's samples ($\alpha^{27}\text{D}$ + 6.50°) was redetermined; it had $\alpha^{26}\text{D}$ + 7.07°.

Because of the difficulties encountered in the catalytic hydrogenation of α-phenylnitroethane, the reduction of 2-nitroöctane[3] over platinum oxide in acetic acid was repeated. Here no difficulty was experienced in obtaining pure 2-aminoöctane and, as reported earlier,[3] the amine has the same sign of rotation as the 2-nitroöctane from which it is prepared.

Experimental[7,8]

Preparation of Optically Active α-Phenylnitroethane. (a) From α-Phenylethyl Bromide and Sodium Nitrite.—In a flask fitted with a drying tube was placed a solution of 26.6 g. of urea (dried at 110°) and 20 g. of sodium nitrite (0.30 mole) in 300 ml. of dimethylformamide (DMF) (dried over calcium hydride at room temp.). The solution was cooled to −18° and (−)α-phenylethyl bromide (36.72 g., 0.193 mole, $n^{20}\text{D}$ 1.5612, $\alpha^{29}\text{D}$ − 58.82°) was rapidly added to the stirred solution. The reaction mixture was maintained (with stirring) at −18 to −15° and protected from light. After 13 hours a negative test for organic halide was obtained: *ca.* 5 drops of the reaction solution are added to 2 ml. of water, the resulting mixture is extracted with petroleum ether (b.p. 35–37°), the petroleum ether phase is heated for several seconds under a jet of steam to expel the petroleum ether, and two drops of an acetonitrile solution saturated with silver nitrate are added; if a precipitate does not form within 1 minute the test is considered negative.

The DMF solution was worked up in a dimly lit room by pouring it into 800 ml. of ice-water layered with 100 ml. of benzene; the water layer was extracted three times more with 60 ml. of benzene, and then twice with 60 ml. of diethyl ether. The benzene and ether extracts were combined, washed with four 40-ml. portions of water and dried over anhydrous magnesium sulfate. This solution was filtered, concentrated *in vacuo* and the residue distilled. Twelve fractions were obtained; the first five which totaled 9.1 g. probably consisted mainly of α-phenylethyl nitrite and acetophenone, (b.p. 54–60° at 3 mm., $n^{20}\text{D}$ 1.5061 − 1.5341) and were discarded. Fractions 6–12 (b.p. 59–79 (1 mm.), $n^{20}\text{D}$ 1.5216 − 1.5375, 18.23 g.) were combined and washed twice with 100-ml. portions of 85% phosphoric acid. The organic layer was separated and treated at room temp. for 20 to 30 min. with 150 ml. of a reagent prepared by combining 100 ml. of a solution of 2,4-dinitrophenylhydrazine in 2 *N* aq. hydrochloric acid (saturated at 0°) with 50 ml. of 2 *N* aq. hydrochloric acid. The resulting precipitate and the aqueous phase were removed and the organic layer was dissolved in ethyl ether and dried over anhydrous magnesium sulfate. The solution was concentrated *in vacuo* and the residue rectified through a small packed column. After a small forerun, a total of 10.47 g. (36% yield) of (−)-α-phenylnitroethane was obtained, b.p. 61-62° (1 mm.), $n^{20}\text{D}$ 1.5212-1.5214, $\alpha^{30}\text{D}$ − 9.58°.

Anal. Calcd. for C_8H_9NO: C, 63.56; H, 6.00. Found: C, 63.63; H, 5.88.

(b) From α-Phenylethyl Chloride and Silver Nitrite.—Experiments 1 and 2 of Table I were carried out with α-phenylnitroethane prepared by the action of silver nitrite on α-phenylethyl chloride. These preparations are described in another paper.[9]

Reduction of (−)-α-Phenylnitroethane with Iron in Acetic Acid.—Iron filings (10 g., 60 mesh) were washed with 5% hydrochloric acid, the acid decanted off and the filings rinsed twice with glacial acetic acid. They were then transferred to a 200-ml. flask and 50 ml. of glacial acetic acid added. α-Phenylnitroethane (3.80 g., 0.0251 mole, $n^{20}\text{D}$ 1.5212, $\alpha^{30}\text{D}$ − 9.58°) dissolved in 15 ml. of glacial acetic acid was added to the stirred iron–acetic acid mixture over a period of half an hour. During this time no appreciable warming of the reaction mixture was noted. It was subsequently heated on a steam-bath for 3 minutes and then allowed to stir at room temperature for 30 minutes. This was followed by a 45-min. period on the steam-bath after which the reaction mixture was stirred for *ca.* 14 hours at room temperature. The gray mixture was cooled in an ice-bath and a 30% aqueous solution of sodium hydroxide was slowly added, with stirring, until the mixture was basic. The dark product was steam distilled, the distillate extracted with ethyl ether, and the ethereal solution dried over potassium hydroxide pellets. After concentrating the ethereal solution *in vacuo*, the residue was distilled. Without any forerun, a total of 2.46 g. (81% yield) of (+)-α-phenylethylamine was collected as six fractions which had $n^{20}\text{D}$ 1.5263–1.5264 and b.p. 67–68° (10 mm.) $\alpha^{29.5}\text{D}$ +10.32°. This colorless liquid is insoluble in water and dissolves readily in aqueous hydrochloric acid.

Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.45; H, 9.34; N, 11.35.

The benzamide was recrystallized from aqueous ethanol; m.p. 120–121°.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71. Found: C, 79.96; H, 6.92.

Reduction of (+)-α-Phenylnitroethane with Stannous Chloride.—A slight modification of the procedure of Southwick and Anderson[10] was used. To a well stirred solution of stannous chloride dihydrate (35.0 g., 0.156 mole, J. T. Baker C.P.) in 15 ml. of 37% hydrochloric acid plus 15 ml. of glacial acetic acid was added, all at once, a solution of α-phenylnitroethane (5.0 g., 0.033 mole, $n^{20}\text{D}$ 1.5213, $\alpha^{26}\text{D}$ +10.85°) in 15 ml. of 37% hydrochloric acid plus 35 ml. of glacial acetic acid. A nitrogen atmosphere was maintained at all times. The reaction was started at room temperature and during the addition of the nitro compound no appreciable warming was noted. The solution was then heated so as to maintain a temp. of 50-60° for 3 hours. The

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(7) All polarimetric determinations were made on the pure liquid in a 1 dm. tube and are denoted by $\alpha^t\text{D}$.

(8) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Dr. C. S. Yeh and Mrs. S. L. Margerum of this Department.

(9) N. Kornblum, W. J. Jones and D. E. Hardies, THIS JOURNAL, to be submitted.

(10) P. L. Southwick and J. E. Anderson, *ibid.*, **79**, 6227 (1957).

originally colorless solution went yellow-green, then green and, finally, became colorless. It was cooled in an ice-bath and *ca.* 40% aqueous sodium hydroxide was added until the white precipitate which first formed dissolved. The mixture was steam distilled, the distillate extracted with ethyl ether, and the ethereal solution shaken with 18% aqueous hydrochloric acid. The acidic aqueous solution was made basic, extracted with ethyl ether and the ethereal solution then dried over potassium hydroxide pellets. After concentrating, the residue was distilled. Without any forerun, a total of 1.43 g. (36% yield) of (−)-α-phenylethylamine was collected as four fractions, b.p. 68° (12 mm.), $n^{20}{\rm D}$ 1.5263, $\alpha^{26}{\rm D}$ − 11.68°.

Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.53; H, 9.03; N, 11.46.

The benzamide had m.p. 119–120°.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.84; H, 6.51; N, 6.17.

Repetition using 10.0 g. of α-phenylnitroethane ($n^{20}{\rm D}$ 1.5210, $\alpha^{24}{\rm D}$ + 11.11°) gave 3.36 g. (42% yield) of α-phenylethylamine ($\alpha^{25}{\rm D}$ 11.54°, $n^{20}{\rm D}$ 1.5261). *Anal.* Calcd. for $C_8H_{11}N$: N, 11.56. Found: N, 11.68.

Reduction of α-Phenylnitroethane over Platinum Oxide.—The following exemplify the results of thirteen experiments; (a) A solution of 5.0 g. (0.033 mole) of (−)-α-phenylnitroethane, b.p. 61° (1 mm.), $n^{20}{\rm D}$ 1.5212, $\alpha^{30}{\rm D}$ −9.58°, in 30 ml. of glacial acetic acid was shaken with hydrogen (3 atm. pressure) in the presence of 0.03 g. of platinum oxide, at room temperature. The theoretical amount (0.099 mole) of hydrogen was absorbed in 49 hours. The mixture was filtered, the catalyst washed with three 10-ml. portions of glacial acetic acid and the combined acetic acid solutions were made basic with aqueous sodium hydroxide. This was steam distilled, the distillate extracted with ethyl ether, and the ethereal solution shaken with 18% aqueous hydrochloric acid. The acidic aqueous solution was made basic with concentrated aqueous sodium hydroxide, extracted with ethyl ether, and the ethereal solution dried over potassium hydroxide pellets. After concentrating, the residue was distilled at 10 mm. Five fractions were obtained having, successively, $n^{20}{\rm D}$ 1.5157, 1.5173, 1.5190, 1.5211 and 1.5240. Fractions 1 and 2 totaled 0.19 g.; fractions 3, 4 and 5 were combined (0.70 g.) and redistilled, whereupon 0.63 g. (16% yield) of impure (+)-α-phenylethylamine, b.p. 64° (10 mm.), $n^{20}{\rm D}$ 1.5221, $\alpha^{26}{\rm D}$ +9.48°, was obtained. If, as is likely, the only basic impurity is α-cyclohexylethylamine ($n^{20}{\rm D}$ 1.4617) then an $n^{20}{\rm D}$ 1.5221 corresponds to *ca.* 6% contamination by α-cyclohexylethylamine.

Treatment of this amine sample ($n^{20}{\rm D}$ 1.5221) with benzoyl chloride gave the benzamide of (+)-α-phenylethylamine which, after recrystallization from aqueous ethanol, had m.p. 120–121°; mixed m.p. with the benzamide of (+)-α-phenylethylamine obtained by reduction of the nitro compound with iron and acetic acid (m.p. 120–121°) was undepressed.

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.98; H, 6.70; N, 6.21. Found: C, 79.93; H, 6.98; N, 6.31.

(b) A solution of 4.64 g. (0.038 mole) of α-phenylnitroethane ($n^{20}{\rm D}$ 1.5211) in 30 ml. of glacial acetic acid was hydrogenated over 1 g. of platinum oxide at an initial pressure of 45 p.s.i. After 20 min. no further pressure drop was noted, but the system was not disturbed for another 25 min. On working up the organic bases as in (a), five fractions (total wt. 0.71 g.) were obtained on distillation at 10 mm.; these boiled in the range 40–45° and had $n^{20}{\rm D}$ 1.4621, 1.4618, 1.4621, 1.4629 and 1.4639. α-Cyclohexylethylamine has $n^{20}{\rm D}$ 1.4618.

(c) A solution of 3.53 g. (0.023 mole) of α-phenylnitroethane ($n^{20}{\rm D}$ 1.5212) in 30 ml. of glacial acetic acid was hydrogenated over 0.9 g. of platinum oxide. In 45 min. the pressure dropped from 40 to 29 p.s.i.; the theoretical uptake for reducing the nitro group to an amino group is 6 p.s.i. The filtered acetic acid solution was made basic (*p*H 10–11) at ice temperature and then steam distilled into sodium hydroxide. The distillate was extracted with petroleum ether (b.p. 35–37°), the extracts dried over sodium hydroxide pellets, and the solvent then removed. The clear colorless liquid which remained (*ca.* 1 ml.) was vacuum distilled. The first three fractions, b.p. 40–41° (30 mm.), weighed 0.13, 0.16 and 0.10 g., respectively, were colorless and had $n^{20}{\rm D}$ 1.4331. By reducing the pressure to 2 mm. a fourth fraction (0.05 g., $n^{20}{\rm D}$ 1.4600) was obtained. Fractions 1–3 were insoluble in hydrochloric acid and in aqueous sodium hydroxide. Judging by the b.p. and $n^{20}{\rm D}$ the material was mainly ethylcyclohexane[11] (14% yield). A white solid formed in the fourth fraction on exposure to the air; this, coupled with the $n^{20}{\rm D}$ 1.4600, suggests that fraction 4 was mainly α-cyclohexylethylamine ($n^{20}{\rm D}$ 1.4617).

(d) A solution of 3.50 g. (0.023 mole) of α-phenylnitroethane ($n^{20}{\rm D}$ 1.5214) in 30 ml. of glacial acetic acid was hydrogenated over 0.1 g. of platinum oxide. Initially the pressure was 15 p.s.i., but in one hour there was no uptake of hydrogen. On raising the pressure to 40 p.s.i., 1 pound of hydrogen was absorbed out of the 5.6 pounds needed for conversion to α-phenylethylamine. At this point another 0.1 g. of platinum oxide was added and hydrogenation was resumed at 30 p.s.i. In 3 hours a 5-lb. pressure drop occurred; the product worked up as in (c) gave five colorless fractions having $n^{20}{\rm D}$, respectively, 1.4812, 1.4840, 1.4889, 1.4951 and 1.5009. All five fractions readily formed a white solid on exposure to air and they all dissolved in 10% hydrochloric acid; they apparently consist of mixtures of α-phenylethylamine ($n^{20}{\rm D}$ 1.5263) and α-cyclohexylethylamine ($n^{20}{\rm D}$ 1.4617). The 5 fractions weighed a total of 0.63 g. (*ca.* 22% yield).

(e) A reduction employing 4.0 g. of α-phenylnitroethane, 0.03 g. of platinum oxide, 30 ml. of glacial acetic acid and an initial pressure of 40 p.s.i. gave 0.98 g. (31% yield) of organic bases, $n^{20}{\rm D}$ 1.5000–1.5170. A Tollens test was negative indicating the absence of the hydroxylamine, $C_6H_5CHCH_3$-NHOH.

Hydrogenation of (+)-α-Phenylethylamine over Platinum Oxide.—A solution of 5.00 g. (0.0413 mole) of (+)-α-phenylethylamine b.p. 67° (10 mm.), $n^{20}{\rm D}$ 1.5263, $\alpha^{27}{\rm D}$ +32.37° (*Anal.* Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.31; H, 9.31; N, 11.76) in 30 ml. of glacial acetic acid containing 0.5 g. of platinum oxide was shaken with hydrogen (initial pressure 45 p.s.i.) at room temp. The theoretical quantity (0.12 mole) of hydrogen was absorbed in 5 hours. On working up the product as described in part (a) of the "Reduction of α-Phenylnitroethane over Platinum Oxide," an 82% yield of (−)-α-cyclohexylethylamine was obtained, $n^{20}{\rm D}$ 1.4617−1.4618, b.p. 58° (12 mm.). A sample was transferred to a polarimeter tube in a dry-box from which carbon dioxide and water had been removed: $\alpha^{25}{\rm D}$ −2.77°.

Anal. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.84; H, 13.70; N, 10.87.

The benzamide, recrystallized from aqueous ethanol, had m.p. 157–157.2°. The benzamide of (−)-α-cyclohexylethylamine is reported to have m.p. 162°[5] and the racemic benzamide a m.p. of 120.5°.[12]

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.71; H, 9.18; N, 5.93.

Effect of Carbon Dioxide on Optical Rotations. (a) **(+)α-Phenylethylamine.**—A sample of (+)-α-phenylethylamine prepared in the ordinary way, which had been stored for 3 years, was found to have $\alpha^{30}{\rm D}$ +31.39°. It was dissolved in ethyl ether and shaken with 20% aqueous sodium hydroxide. The ethereal solution was dried over potassium hydroxide, the solvent was removed under nitrogen, and the residue was distilled at 10 mm. using a nitrogen "bleed." Without exposure to carbon dioxide or moisture a polarimeter tube was filled; the amine had $\alpha^{27}{\rm D}$ + 32.37°.

(b). **(−)-α-Cyclohexylethylamine.**—A sample of this amine was purified, and its rotation, taken as in (a), was $\alpha^{29}{\rm D}$ −2.90°. Another portion of this same sample of amine was introduced into a polarimeter tube without any precautions against exposure to the air. Despite an exposure time of less than 1 minute, enough carbon dioxide was picked up to make the field in the polarimeter rather hazy. Despite this, the rotation can be stated with certainty to lie in the range $\alpha^{28}{\rm D}$ −2 to −5°.

Redetermination of Rotation of Fishbein's α-Phenylethylamine.—One of Fishbein's α-phenylethylamine samples ($\alpha^{27}{\rm D}$ + 6.50°) was available. In three years it had become brown and, hence, it was distilled from solid potassium

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(11) A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini (*J. Research Natl. Bur. Standards*, **36**, 134 (1946)) report $n^{20}{\rm D}$ 1.43304.

(12) M. Metayer, *Bull. soc. chim. France*, 276 (1952).

hydroxide at 12 mm. Five colorless fractions, boiling 67–68°, were obtained; the residue from the distillation consisted of a drop or so of a dark brown liquid. The $n^{20}D$ values for these fractions were 1.5256, 1.5261, 1.5262, 1.5262 and 1.5265. Fractions 2, 3 and 4 were combined and their rotation determined (polarimeter tube filled in the ordinary way, *i.e.*, no effort made vigorously to exclude CO_2 or H_2O): $\alpha^{26}D + 7.07°$.

Reduction of 2-Nitroöctane.—A solution of 8.5 g. of (−)-2-nitroöctane, b.p. 59° (1 mm.), $n^{20}D$ 1.4277, $\alpha^{28}D$ −8.25° (l 1 dm.), in 35 ml. of glacial acetic acid was shaken with hydrogen (3 atms. pressure) in the presence of 0.45 g. of platinum oxide at room temp. After 25 hours the theoretical quantity of hydrogen (12.8 lb.) was absorbed. On working up and distilling at 13 mm., there was obtained 2.89 g. of colorless amine, b.p. 64°, $n^{20}D$ 1.4234, $\alpha^{27}D$ − 1.95° (l 1 dm.).

Anal. Calcd. for $C_8H_{19}N$: C, 74.32; H, 14.85; N, 10.83. Found: C, 73.99; H, 15.05; N, 11.01, 10.96.

The benzamide, thrice recrystallized from cyclohexane, had m.p. 99.5–100.5°.

Lafayette, Ind.

[Contribution No. 2446 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, and the Department of Chemistry, Massachusetts Institute of Technology]

Small-Ring Compounds. XXVI. Nucleophilic Displacement Reactions of Some Halogen-substituted Phenylcyclobutenones[1]

By Marjorie C. Caserio, Howard E. Simmons, Jr., A. Earl Johnson and John D. Roberts

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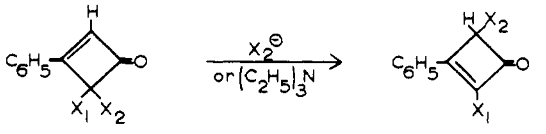
Displacement reactions between alkali halides and several cyclic allylic-type halides, namely, 2,2-dihalo-3-phenylcyclobutenones, have been found to proceed with rearrangement to give 2,4-dihalo-3-phenylcyclobutenones. The 2,2-dihalo-compounds also were found to rearrange to the corresponding allylic isomers on heating with triethylamine. The allylic iodides, 2-fluoro-4-iodo- and 2-chloro-4-iodo-3-phenyl-2-cyclobutenones, rearranged in reactions with halogens to form 2,2-dihalo-3-phenylcyclobutenones. Evidence is presented for the stereospecific nature of these reactions.

The interest which attends bimolecular nucleophilic displacements of allylic halides owing to the possibility of substitution with and/or without rearrangement,[2] SN2′ and SN2, respectively, prompted the investigation we now describe of the reactions of some halogen-substituted phenylcyclobutenones with various nucleophilic reagents.

Displacements with Halide Ions.—A series of 2,2-dihalo-3-phenylcyclobutenones (I) has been found to react with alkali halides in acetone solution to give exclusively the product of substitution with rearrangement. Thus 2,2-dichloro-, 2-chloro-2-bromo- and 2-fluoro-2-bromo-3-phenylcyclobutenones (Ia, Ib and Ic, respectively) rearranged to their 2,4-isomers IIa, IIb and IIc on treatment with the appropriate lithium halide.



Ia, $X_1 = X_2 = Cl$
b, $X_1 = Cl, X_2 = Br$
c, $X_1 = F, X_2 = Br$
d, $X_1 = F, X_2 = Cl$

IIa, $X_1 = X_2 = Cl$
b, $X_1 = Cl, X_2 = Br$
c, $X_1 = F, X_2 = Br$
d, . . .

The susceptibility of these allylic *gem*-dihalides to rearrange by what is very probably an SN2′ mechanism may be attributed largely to the presence of two α-halogen substituents on the allylic carbon system $-\overset{|}{C}_{\gamma}=\overset{|}{C}_{\beta}-\underset{|}{\overset{|}{C}}_{\alpha}-$. This has the effect of promoting SN2′ attack in competition with SN2 attack by a combination of polar and steric factors, as has been amply demonstrated by de la Mare and co-workers[3] for substitution reactions of α-substituted open-chain allylic compounds. The ease of rearrangement in the series of *gem*-dihalides here investigated appears to decrease with decreasing size and nucleophilicity of the halogen. Whereas bromide ion caused the 2-chloro-2-bromoketone Ib to rearrange rapidly at room temperature, the 2-fluoro-2-chloroketone Id was recovered unchanged after prolonged heating with lithium chloride in acetone. However, Id appears to be attacked by chloride ion with comparative ease since optically active Id, $[\alpha]^{25}D$ +12.0°, racemized with a half-life of approximately 19 hours at room temperature in acetone solution saturated with lithium chloride. It seems likely that racemization results from chloride exchange by an SN2 mechanism.

It was reported in earlier work[4] that triethylamine caused the rearrangement of 2,2-dichloro-3-phenylcyclobutenone (Ia). Under similar conditions, ketones Ib and Ic have also been found to rearrange to give IIb and IIc, respectively, but again the fluorochloroketone Id did not rearrange.

The resistance of Id to rearrangement by chloride was not matched by iodide ion. Thus, Id reacted readily with sodium iodide in acetone to give the product of rearrangement, 2-fluoro-4-iodo-3-phenyl-2-cyclobutenone (IIf). This result poses the question as to whether IIf is formed directly by SN2′ attack of iodide ion or by SN2 attack to form the *gem*-fluoroiodoketone as an intermediate followed by its rapid rearrangement. While the greater bulk of iodide relative to chloride ion would render attack by an SN2′ mechanism more favorable, the two-step mechanism is not unreasonable and no clear choice can now be made between the two alternatives.

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[2] For leading references on the abnormal mode of substitution (SN2′) see R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

[3] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3325, 3331, 3628 (1952); 3555 (1953); P. B. D. de la Mare, E. D. Hughes, P. C. Merriman, L. Pichat and C. A. Vernon, *ibid.*, 2563 (1958).

[4] J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., This Journal, **75**, 4765 (1953).