neutral fraction dissolved in dry benzene and chromatographed on alumina. A 1:1 mixture of benzene and absolute ethanol was used as the eluting solvent. Two fractions were taken, a fluorescent fraction (ultraviolet lamp) and a yellow fraction which moved down the column only when the eluting solvent was added. Crystallization of the residue from the fluorescent fraction from ethanol yielded 3.5 g. (58%) of 9-phenylanthracene, m.p. 150–152°. The mother liquor was concentrated and distilled, yielding 1.7 g., b.p. 210–245°(2mm.). Recrystallization from ethanol afforded 0.7 g. of 9-phenylanthracene, m.p. 149–151°. The total yield of 9-phenylanthracene, m.p. 149–151°, was 4.2 g. (70%). The second chromatographic fraction afforded 0.4 g. of a yellow solid, m.p. about 50°. This was probably *o*-benzylbenzophenone (II, R = C_6H_5), for 0.25 g., cyclized in the usual way,[2] yielded 0.2 g. of 9-phenylanthracene, m.p. 152–155°.

In another run, worked up by fractional distillation, a fraction boiling at 215–230° (3 mm.) afforded a 4% yield of *o*-benzyltriphenylcarbinol, m.p. 133° (lit.[20] 133–134°). This showed the typical infrared absorption spectrum of a triphenylcarbinol[21] (including the characteristic absorption at 2.79 μ due to the OH group) and was further identified by cyclization to 9,9-diphenyl-9,10-dihydroanthracene, m.p. 194–195° (lit.[20] 195–196°).

Reaction of *o*-Benzylbenzoic Acid with *m*-Tolyllithium.—The lithium reagent was prepared from 34.2 g. of *m*-bromotoluene and allowed to react with 5 g. of *o*-benzylbenzoic acid as in the case of the phenyl analog. After 21 hr., the reaction mixture was decomposed and the product isolated by chromatography. From the fluorescent fraction, 1.9 g. (30%) of 9-(*m*-tolyl)-anthracene was obtained by crystallization, m.p. 94–96° (lit.[5] 97–98.5°). This hydrocarbon gave maxima in ultraviolet absorption at 258, 316, 332, 347 and 366 mμ.

Reaction of *o*-Benzylbenzoic Acid with *p*-Tolyllithium.—When an excess of *p*-tolyllithium was allowed to react with 5 g. of *o*-benzylbenzoic acid and the product worked up as above, 1.1 g. (17%) of 9-(*p*-tolyl)-anthracene was obtained from ethanol, m.p. 142–145° (lit.[4] 145–145.5°). The identity of our product was established by a mixed melting point determination. Ultraviolet absorption maxima were the same as those observed for the 9-(*m*-tolyl)-anthracene.

Reaction of Phenyllithium with *o*-Benzhydrylbenzoic Acid (VIII).—The reaction of 6.8 g. of *o*-benzhydrylbenzoic acid[22] with an excess of phenyllithium was carried out as with *o*-benzylbenzoic acid and the mixture of products separated by fractional crystallization from benzene and benzene–ethanol. A total of 6.2 g. (62%) of *o*-benzhydryltriphenylcarbinol (XI) was obtained, m.p. 219.5–222.5° with previous sintering at 216.5–218.5° (lit.[23] 216.5–217°). The melting point was higher than reported, but the compound had approximately the expected composition and showed an infrared absorption spectrum resembling very closely that of *o*-benzyltriphenylcarbinol including the characteristic absorption at 2.80 μ due to the hydroxyl group.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 89.49; H, 6.24.

From the mother liquors, by crystallization from ethanol, 2.1 g. (29%) of *o*-benzhydrylbenzophenone (X) was isolated, m.p. 84–86° (lit.[24] 84–86°). The identity of the product was shown by a mixed melting point determination.

(20) F. F. Blicke and R. A. Patelski, THIS JOURNAL, **58**, 559 (1936).
(21) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A162**, 419 (1937).
(22) A. Baeyer, *Ann.*, **202**, 36 (1880).
(23) G. Wittig and M. Leo, *Ber.*, **64**, 2395 (1931).
(24) C. F. Koelsch, *J. Org. Chem.*, **3**, 456 (1938–1939).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

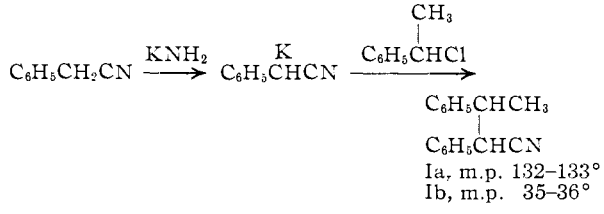
Configurations of Diastereoisomers of 2,3-Diphenylbutyronitrile Obtained in the α-Phenylethylation of Potassiophenylacetonitrile[1]

BY WALLACE R. BRASEN AND CHARLES R. HAUSER

RECEIVED AUGUST 6, 1956

The higher melting isomer of 2,3-diphenylbutyronitrile, obtained in the α-phenylethylation of potassiophenylacetonitrile with α-phenylethyl chloride in liquid ammonia, was shown to have the *erythro* configuration by relating it to *meso*-α,α′-dimethylbibenzyl. The lower melting nitrile must then have the *threo* configuration. The *threo*-nitrile was found to be converted to the *erythro* isomer by a catalytic amount of potassiophenylacetonitrile in liquid ammonia.

Recently[2] the two diastereoisomers of 2,3-diphenylbutyronitrile, Ia and Ib, were prepared in approximately equal yields (29–30%) from the α-phenylethylation of potassiophenylacetonitrile with α-phenylethyl chloride in ether. Isomer Ia was obtained exclusively (99% yield) when the α-phenylethylation was carried out in liquid ammonia containing a little ether.[2]



Ia, m.p. 132–133°
Ib, m.p. 35–36°

The two isomers of this nitrile had been prepared previously[3] in unreported yield through the conjugate addition of methylmagnesium iodide to α,β-diphenylacrylonitrile, although the lower melting one was obtained only as a liquid. The higher melting isomer also has been produced as a by-product in the α-phenylethylation of the sodio derivative of α-carbethoxyphenylacetonitrile.[4]

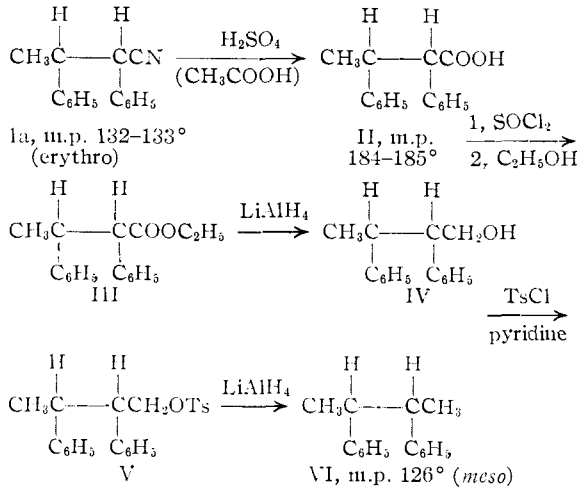
In the present investigation the higher melting isomer of 2,3-diphenylbutyronitrile (Ia) was shown to have the *erythro* configuration. The lower melting one Ib must then have the *threo* configuration. Thus the former isomer, which was obtained in 99% yield by the α-phenylethylation of potassiophenylacetonitrile in liquid ammonia,[2] was found to produce *meso*-α,α′-dimethyldibenzyl (VI) on replacing the nitrile group by a methyl group as represented in transformation A. Each step in the transformation was realized in 90% yield, the overall yield being 75%.

Since base-catalyzed hydrolyses of certain optically active nitriles having α-hydrogen have been

(1) Supported by the National Science Foundation.
(2) C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).
(3) Ramart-Lucas, *Ann. chim. phys.*, [8] **30**, 424 (1913).
(4) A. A. Plentl and M. T. Bogert, THIS JOURNAL, **63**, 989 (1941).

observed to be accompanied by racemization,[5] nitrile Ia was hydrolyzed in acidic medium employing a mixture of sulfuric and acetic acids (first step in transformation A). No isomerization was ob-

Transformation A



served under these conditions. Thus, not only was the single racemic acid II obtained in 90% yield,[6] but this acid was also reconverted to the original nitrile Ia in 42% yield. The latter reaction was accomplished through the acid chloride and corresponding amide.

Presumably the other steps in transformation A were likewise unaccompanied by isomerization. Somewhat related lithium aluminum hydride reductions of optically active acids having α-hydrogen activated by a phenyl group at the asymmetric center have been accomplished without racemization,[7] and similar results have been obtained with certain optically active esters.[8] The preparation of *p*-toluenesulfonic esters of optically active alcohols and their hydride ion displacements, which would be analogous to the conversion of alcohol IV to hydrocarbon VI, are known to be unaccompanied by racemization.[9]

In connection with this work, it was observed that the threonitrile (Ib), which was obtained along with the *erythro* isomer in the α-phenylethylation of potassiophenylacetonitrile in ether, is converted (isomerized) rapidly and completely to the *erythro*-nitrile by a catalytic amount of potassiophenylacetonitrile in liquid ammonia. Thus, the former isomer was converted to the latter within ten minutes by ten mole per cent. of the base. A further study is being made of this and related conversions.

(5) See R. L. Shriner, R. Adams and C. S. Marvel in Gilman, "Organic Chemistry, an Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 243. We observed slight isomerization on hydrolyzing nitrile Ia in basic medium.

(6) Ramart-Lucas (ref. 3) reported that the acid-catalyzed hydrolysis of nitrile Ia at 180–200° produced not only acid II but also a lower melting acid (m.p. 135°). A preliminary experiment has indicated that under our conditions the *threo*-nitrile (Ib) likewise undergoes hydrolysis without epimerization.

(7) R. H. Baker and S. H. Jenkins, Jr., THIS JOURNAL, **71**, 3968 (1949).

(8) A. Stoll, A. Hoffmann and W. Schlientz, *Helv. Chim. Acta*, **32**, 1947 (1949).

(9) D. J. Cram, THIS JOURNAL, **74**, 2129 (1952).

Experimental[10]

Hydrolysis of Nitrile Ia to Acid II.—A solution of 110 g. (0.5 mole) of 2,3-diphenylbutyronitrile (Ia, m.p. 132–133°)[2] in a mixture of 100 ml. of 50% sulfuric acid and 300 ml. of glacial acetic acid was refluxed for 4 days. The reaction mixture was then diluted with an equal volume of water and cooled. The resulting precipitate was collected on a funnel and taken up in a solution of 122 g. (1 mole) of potassium carbonate in 500 ml. of water. After filtration, the solution was acidified with hydrochloric acid to precipitate 2,3-diphenylbutyric acid (II) which was collected on a funnel, washed with water and recrystallized from acetone and water. The yield was 108 g. (90%), m.p. 184–185°, reported[4] m.p. 186°.

Conversion of Acid II to Ester III.—A suspension of 108 g. (0.45 mole) of 2,3-diphenylbutyric acid (II, m.p. 184–185°) in 200 ml. of benzene and 98 g. (0.9 mole) of thionyl chloride was heated until the solid had dissolved. About 100 ml. of the benzene and the excess thionyl chloride were distilled from the solution, and 200 ml. of 60–90° ligroin added. The solution was cooled, and the deposited 2,3-diphenylbutyryl chloride was washed with 30–60° petroleum ether. This acid chloride was heated with 500 ml. of absolute ethanol until all of the solid had dissolved. The solution was cooled, and the fluffy precipitate collected and washed with absolute ethanol to give 120.6 g. (90%) of ethyl 2,3-diphenylbutyrate (III), m.p. 91–92°. The melting point was not changed by recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.56; H, 7.57.

Reduction of Ester III to Alcohol IV.—A solution of 93.8 g. (0.35 mole) of ethyl 2,3-diphenylbutyrate (III) in 400 ml. of anhydrous ether was added during 25 minutes to a slurry of 9.5 g. (0.25 mole, 40% excess) of lithium aluminum hydride in 200 ml. of anhydrous ether, and the mixture stirred for and refluxed for 3 hours. The excess hydride was decomposed by the addition of ethyl acetate, followed by enough 10% sulfuric acid to dissolve the aluminum salts. The ether layer was separated, washed with 10% potassium carbonate, and dried over potassium carbonate. The solvent was removed, and the solid residue taken up in hot 60–90° ligroin. The solution was cooled to precipitate 78.5 g. (99%) of 2,3-diphenylbutanol (IV), m.p. 111–112° (large colorless crystals).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.25; H, 7.90.

This alcohol (m.p. 110–111°) was obtained in 98% yield by the reduction of 2,3-diphenylbutyryl chloride with lithium aluminum hydride essentially as described for the ester.

Conversion of Alcohol IV to Tosylate V.—A solution of 33.9 g. (0.15 mole) of 2,3-diphenylbutanol (IV) and 31.6 g. (0.165 mole) of *p*-toluenesulfonyl chloride in 50 ml. of pyridine was allowed to stand for 12 hours. The product V was isolated essentially as described by Cram[11] for a similar tosylate. The oily product was taken up in benzene and 60–90° ligroin. Upon cooling there was deposited 52 g. (93%) of the *p*-toluenesulfonic ester of 2,3-diphenylbutanol (V), m.p. 90.5–91°.

Anal. Calcd. for $C_{23}H_{24}O_3S$: C, 72.62; H, 6.36. Found: C, 72.66; H, 6.52.

Displacement of Tosylate V to Form Hydrocarbon VI.—A solution of 21.36 g. (0.056 mole) of the *p*-toluenesulfonate V in 125 ml. of anhydrous ether was added to a slurry of 20 g. (0.502 mole) of lithium aluminum hydride in 300 ml. of anhydrous ether, and the mixture stirred for 24 hours at room temperature. The product was isolated essentially as described by Cram[9] for a similar hydrocarbon. There was obtained 11.4 g. (97%) of *meso* α,α'-dimethylbibenzyl (VI), m.p. 124.5–125.5°, reported m.p. 126°.[12] The melting point was not depressed on admixture with an authentic sample of VI (*meso*).[13] The *dl*-form of α,α'-dimethylbibenzyl is a liquid (m.p. 8°).[13]

(10) Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Co., Urbana, Ill.

(11) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949).

(12) A. Liepins, *Univ. Lat. Kim. Fak.*, **1**, 228 (1930) (*C. A.*, **25**, 3328).

(13) This sample was prepared in 84% yield by the reduction of *trans*-α,α'-dimethylstilbene with sodium in ether.

Reconversion of Acid II to Nitrile Ia.—2,3-Diphenylbutyryl chloride (9 g., 0.035 mole), prepared as described above, was stirred with 100 ml. of concentrated aqueous ammonia for one hour. The suspended solid was removed by filtration, dried and crystallized from benzene to give 5 g. (60%) of 2,3-diphenylbutyramide, m.p. 193–193.5°, reported[4] m.p. 193°.

The amide (4 g., 0.017 mole) was heated with 20 ml. of thionyl chloride, and the solution poured on crushed ice. The resulting solid was crystallized from acetone and water to give 2.6 g. (70%) of 2,3-diphenylbutyronitrile (Ia), m.p. 132–133°. The melting point was not depressed on admixture with a sample of the nitrile obtained by the α-phenylethylation of potassiophenylacetonitrile in liquid ammonia.[2]

Isomerization of *threo*-Nitrile (Ib) to *erythro*-Nitrile (Ia).—*threo*-2,3-Diphenylbutyronitrile (Ib) (5.9 g., 0.025 mole), prepared by the α-phenylethylation of potassiophenylacetonitrile in ether,[2] was dissolved in 50 ml. of anhydrous ether, and the solution added within one minute to a stirred solution of 0.0025 mole of potassiophenylacetonitrile in 100 ml. of liquid ammonia (prepared from potassium amide and phenylacetonitrile).[2] After stirring 10 minutes, 1 g. of solid ammonium chloride was added, and the reaction mixture worked up to give 5.7 g. (97%) of *erythro*-2,3-diphenylbutyronitrile (Ia), m.p. 131–133°. One recrystallization from acetone and water gave 5.4 g. (92%) of this product melting at 132–133°, showing no depression when mixed with an authentic sample.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Self-alkylation of α-Phenylethyl Chloride to Form Isomeric Dimeric Halides and Dimeric Olefins by Amide Ion. Isomerization of *cis*-α,α'-Dimethylstilbene to *trans* Isomer[1]

BY WALLACE R. BRASEN, SIMON W. KANTOR, PHILIP S. SKELL AND CHARLES R. HAUSER

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The self-alkylation of α-phenylethyl chloride was effected by means of the amide ion in liquid ammonia to form the diastereoisomers of the dimeric halide, 2-chloro-2,3-diphenylbutane, which on dehydrohalogenation produced *cis*- and *trans*-α,α'-dimethylstilbenes and an unidentified product. The self-alkylation of optically active α-phenylethyl chloride gave an optically active dimeric halide. The over-all conversion of α-phenylethyl chloride to *cis*- and *trans*-α,α'-dimethylstilbenes and the isomerization of the *cis* olefin to the *trans* isomer were effected by the amide ion.

The self-alkylation of benzyl and benzhydryl chlorides was effected recently[2] by means of the amide ion in liquid ammonia to form the corresponding dimeric halides, which, on further treatment with this base, underwent dehydrohalogenation to give stilbene and tetraphenylethylene, respectively. The self-alkylation may be illustrated with benzhydryl chloride with which a transient red-orange color is produced indicative of the intermediate formation of a carbanion (equation 1).

$$(C_6H_5)_2CHCl \xrightarrow{\bar{N}H_2} (C_6H_5)_2\bar{C}—Cl \xrightarrow{(C_6H_5)_2CHCl} (C_6H_5)_2CH—\underset{Cl}{\underset{|}{C}}(C_6H_5)_2 \quad (1)$$

The analogous self-alkylation of α-phenylethyl chloride promised to be particularly interesting since the resulting dimeric halide should exist in diastereoisomeric forms which on dehydrohalogenation might produce isomeric olefins. This was studied in the present investigation.

As anticipated the addition of one mole of sodium amide to two moles of α-phenylethyl chloride in liquid ammonia and ether produced the two diastereoisomers of 2-chloro-2,3-diphenylbutane which were obtained as a solid (I) and a liquid (II) in yields of 48 and 37%, respectively. This inverse addition procedure appears to be necessary for satisfactory results with sodium amide since this reagent, when present in excess, effects the dehydrohalogenation of the dimeric halide. On the other hand, lithium amide does not bring about the dehydrohalogenation under ordinary conditions, and the addition of α-phenylethyl chloride to an excess of this reagent gave isomers I and II in yields of 47 and 43%, respectively. Lithium amide is probably the reagent of choice for the preparation of the dimeric halides (equation 2).

$$C_6H_5\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}—Cl \xrightarrow{\bar{N}H_2} C_6H_5\underset{CH_3}{\underset{|}{\bar{C}}}—Cl \xrightarrow{C_6H_5\overset{CH_3}{\overset{|}{C}}HCl} C_6H_5\overset{CH_3}{\overset{|}{C}}H—\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}C_6H_5 \quad (2)$$

I, m.p. 67–68°
II, liquid

The solid isomer I was isolated by crystallization and the liquid isomer II, by molecular distillation (at 55–60°). Since both isomers decompose readily at about 75°, ordinary distillation was not practical.[3] The solid isomer gave acceptable analytical values for chlorine, hydrogen and carbon and the liquid isomer, for chlorine and hydrogen. The liquid isomer gave a slightly high value for carbon, but, in view of its instability, the result may be considered satisfactory.

The mechanism for the self-alkylation of α-phenylethyl chloride is considered to involve the common S_N2 type of displacement (equation 2). In agreement with this, optically active α-phenylethyl chloride ($\alpha^{25}D$ +84.32°)[4] produced with

(1) Supported in part by the National Science Foundation.

(2) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956).

(3) In a preliminary experiment, distillation at 150° at 15 mm. was accompanied by the loss of hydrogen chloride, and only an impure liquid product was obtained. A similar observation has been reported by M. S. Kharasch and M. Kleiman, THIS JOURNAL, **65**, 14 (1943). These workers obtained material boiling at 147–148° at 11 mm. which contained halogen, but they gave no analytical values.

(4) See W. J. Chambers, W. R. Brasen and C. R. Hauser, *ibid.*, in press.