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.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

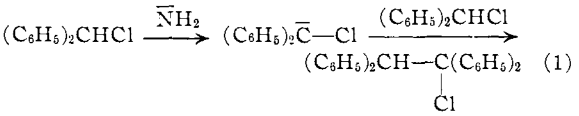
Self-alkylation of α-Phenylethyl Chloride to Form Isomeric Dimeric Halides and Dimeric Olefins by Amide Ion. Isomerization of *cis*-α,α'-Dimethylstilbene to *trans* Isomer[1]

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

RECEIVED AUGUST 6, 1956

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.

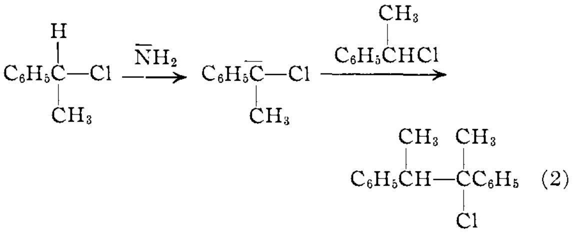
The self-alkylation of benzyl and benzhydryl chlorides was effected recently[2] by means of the amide ion in liquid ammonia to form the corresponding dimeric halides, which, on further treatment with this base, underwent dehydrohalogenation to give stilbene and tetraphenylethylene, respectively. The 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).



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

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).



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

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

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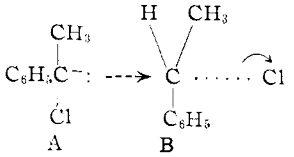
(1) Supported in part by the National Science Foundation.

(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.

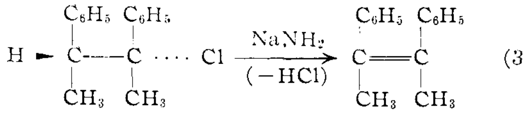
(4) See W. J. Chambers, W. R. Brasen and C. R. Hauser, *ibid.*, in press.

lithium amide optically active 2-chloro-2,3-diphenylbutane ($\alpha^{26}\text{D}$ −20.25°, solid isomer I). Although the portion of the α-phenylethyl chloride converted to the carbanion (component A) may have racemized, the portion undergoing the displacement (component B) presumably underwent inversion as indicated below.



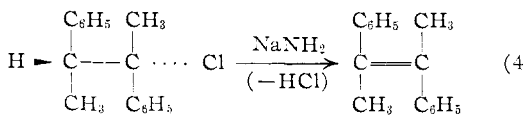
It should be mentioned that, in contrast to the self-alkylation of benzhydryl chloride (equation 1) but similar to that of benzyl chloride,[2] the self-alkylation of α-phenylethyl chloride may be effected without being accompanied by the production of color. Therefore the intermediate carbanions from α-phenylethyl and benzyl chlorides appear to be colorless. The fact that color is produced on adding α-phenylethyl chloride to excess sodium amide in liquid ammonia may be ascribed to the ionization of the *cis*- or *trans*-α,α′-dimethylstilbene some of which is formed under these conditions (see below).

The dehydrochlorination of the solid racemic diastereoisomer I was effected with a molecular equivalent of sodium amide in liquid ammonia to form pure *cis*-α,α′-dimethylstilbene (III) in 85% yield. Similar treatment of the liquid racemic diastereoisomer II with sodium amide produced *trans* α,α′-dimethylstilbene IV in 51% yield and an unidentified oil. On the assumption that these dehydrohalogenations involve the common *trans* β-elimination, the solid isomer I would be assigned the *threo* configuration and the liquid isomer II, the *erythro* configuration (equations 3 and 4). Of course if the less common *cis* β-elimination should operate, these assignments of configurations would be reversed.[5]



$$\mathrm{H}\blacktriangleright\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}\cdots\mathrm{Cl}\xrightarrow[(-\mathrm{HCl})]{\mathrm{NaNH_2}}\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}=\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}\qquad(3)$$

I (*threo*), m.p. 67–68° III (*cis*), m.p. 66°

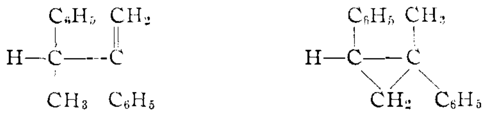


$$\mathrm{H}\blacktriangleright\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdots\mathrm{Cl}\xrightarrow[(-\mathrm{HCl})]{\mathrm{NaNH_2}}\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5}}{\mathrm{C}}}=\underset{\mathrm{C_6H_5}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\qquad(4)$$

II (*erythro*), liquid IV (*trans*), m.p. 106°

Preliminary attempts to establish definitely the configurations of diastereoisomers I and II have been unsuccessful. Thus, on reduction of these dimeric halides with sodium in liquid ammonia, each isomer gave mainly (70–73%) *meso*-α,α′-dimethylbibenzyl.[6] On treatment of the halides with moist silver oxide in acetone, each isomer produced a mixture of alcohols from which the higher melting 2,3-diphenyl-2-butanol was isolated in 40% yield.[7] An attempt to reconvert this alcohol or its isomer to the solid halide II failed.

The unidentified oil that was obtained as by-product along with *trans*-α,α′-dimethylstilbene from the dehydrohalogenation of liquid diastereoisomer II might have contained dimer V or VI. The formation of these products would have involved a methyl hydrogen instead of the hydrogen activated by the phenyl group. Similar structures have been proposed by Kharasch and Kleiman[8] for certain products obtained from the reaction of anethole hydrobromide with sodium amide.



V VI

From the foregoing results it might be expected that treatment of α-phenylethyl chloride with a molecular equivalent or more of sodium amide in liquid ammonia would yield largely a mixture of *cis*- and *trans*-α,α′-dimethylstilbenes. Actually it has been reported by Kharasch and Kleiman[8] and confirmed by us that the addition of the halide to an excess of the reagent produces about a 40% yield of the *cis* olefin and higher boiling oil. However, we further found that the rapid addition of the halide to a molecular equivalent of the reagent produces much more material boiling within the range expected for dimeric hydrocarbons and correspondingly less of the higher boiling oil. Crystallization of a portion of this mixture gave a 40% yield of the *cis* olefin and an 18% yield of the *trans* olefin. More significantly, treatment of another portion of the mixture with potassium amide, followed by crystallization, produced a 73% yield of the *trans* olefin, and an unidentified solid which calculated for a dimeric hydrocarbon amounted to a 9% yield. The treatment with potassium amide converted the *cis* olefin to the *trans* isomer as discussed below. These results show that α-phenylethyl chloride is indeed converted mainly to a mixture of *cis*- and *trans*-α,α′-dimethylstilbenes by a molecular equivalent of sodium amide but that at least one other hydrocarbon, perhaps V or VI, is also produced.

The high boiling polymeric material that is produced when α-phenylethyl chloride is added to excess sodium amide appears to arise through the alkylation of the dimeric olefins, particularly the *trans* isomer by some of the halide. Thus, not only do the dimeric olefins produce red colors in the presence of sodium amide (indicating the formation of the required carbanions) but none of the polymeric material is obtained when the self-alkylation of α-phenylethyl chloride is carried out under conditions that do not form dimeric olefins. In an experiment with potassium amide, a solid that appeared to be a trimer was isolated. This product was obtained in 24% yield along with a 29% yield of the *trans* dimeric olefin IV and high boiling

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(5) In view of the complexity of the molecules, *cis* elimination cannot be rigidly excluded.

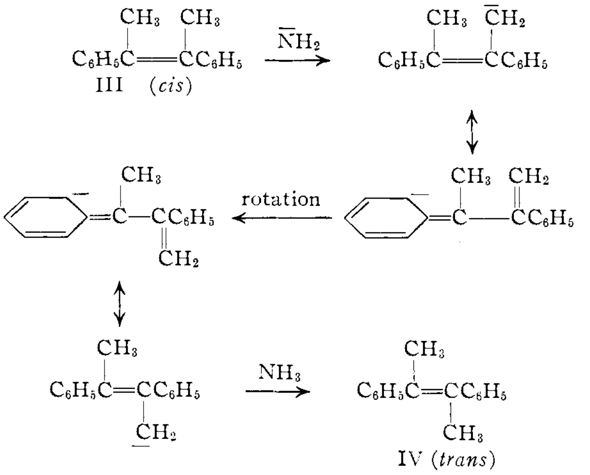
(6) This might be accounted for on the basis that the reduction of the halide involved the intermediate formation of a free radical or carbanion, the *dl*-form of which underwent isomerization to give the more stable *meso* form resulting in the production of the more stable *meso* hydrocarbon.

(7) This might be accounted for on the basis that an intermediate carbonium ion was formed (S$_\text{N}$1) resulting in the production of both alcohols from each halide.

(8) M. S. Kharasch and M. Kleiman, This Journal, **65**, 11 (1943).

material when α-phenylethyl chloride was added to excess potassium amide in liquid ammonia. The fact that the *trans* dimeric olefin was isolated in this experiment, whereas the *cis* isomer is generally obtained with sodium amide, is not surprising since potassium amide effects the isomerization of the *cis* olefin to the *trans* isomer more readily than sodium amide. In another experiment with potassium amide, both the *cis* and *trans* olefins (III and IV) were isolated. Also, small amounts (1–2%) of styrene and acetophenone imine were obtained. The origin of the latter type of product was considered recently.[2]

In connection with the present work it was observed that *cis*-α,α'-dimethylstilbene (III) is isomerized readily by potassium amide in liquid ammonia, and more slowly by sodium amide in this medium, to form the *trans* olefin IV. Thus, the former isomer was converted to the latter in 91% yield by 25 mole % of potassium amide within 1 hr. and in 30% yield by sodium amide under similar conditions. Since both isomers produce persistent red colors with the amide ion, the mechanism for this isomerization appears to involve the intermediate formation of carbanions, several resonance forms of which should allow free rotation around the central carbon–carbon bond (Scheme A).


SCHEME A

It is of interest that three consecutive reactions have now been realized with α-phenylethyl chloride and the amide ion. These are the self-alkylation of this halide, the dehydrohalogenation of the dimeric halide and the isomerization of *cis*-α,α'-dimethylstilbene (formed from dimeric halide I) to the *trans* isomer. Evidently the relative rates of these reactions decrease in this order.

Finally it should be pointed out that a relatively strong base such as sodium amide appears to be required for the self-alkylation of α-phenylethyl chloride, which is initiated by the ionization of the α-hydrogen (see equation 2), leading to the formation of dimeric olefins. Thus, Hughes, Ingold and co-workers[9] have shown that the weaker base sodium ethoxide converts α-phenylethyl bromide to the monomeric olefin styrene (from β-elimination) along with the substitution product. We have observed that this base similarly converts α-phenylethyl chloride to styrene (24%) and ethyl α-phenylethyl ether (59%). None of the dimeric olefin (or halide) was found. However, certain halides having a more reactive α-hydrogen and no β-hydrogen such as *o*- and *p*-nitrobenzyl chlorides[10] and 9-bromofluorene[11] produce dimeric olefins with methoxide or hydroxide ion or even with weaker bases.

Experimental[12]

Self-alkylation of α-Phenylethyl Chloride to Form Dimeric Halide (Isomers I and II). (A) With Sodium Amide.—Employing the apparatus described previously[2] for inverse addition, a suspension of 1.0 mole of sodium amide[13] in 500 ml. of liquid ammonia was added during 15 minutes to a stirred solution of 280 g. (2.0 mole) of α-phenylethyl chloride in 500 ml. of liquid ammonia and 100 ml. of dry ether. No color was produced. The grayish suspension was stirred until the ammonia had evaporated. The oily product was taken up in ether and the ethereal solution was washed with 2 *M* hydrochloric acid, followed by 10% sodium bicarbonate solution. After drying over calcium chloride the solvent was removed at the water aspirator keeping the temperature below 60°. The oil residue was diluted with an equal volume of 30–60° petroleum ether and refrigerated to deposit a dense, white, crystalline solid. The mother liquor from the crystallization was cooled to −70°, and two more crops of crystals were collected. The combined solids were recrystallized from 30–60° petroleum ether to give 116.3 g. (48%) of I, m.p. 67–68°.

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.49. Found: C, 78.55; H, 7.19; Cl, 14.54.

The mother liquors from the above crystallizations were freed of petroleum ether at the aspirator (below 60°) and the residue subjected to molecular distillation at 55–60° employing a Hickmann still at 10^{-4} to 10^{-5} mm. The distillation was stopped when about half of the material had distilled. Both the distillate and the residual liquid in the pot gave essentially the same refractive index, $n^{25}D$ 1.5748, and only slightly different values when analyzed for the dimeric halide. The total yield of the liquid isomer II was 90 g. (37%).

Anal. Calcd. for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.49. Found (for distillate): C, 79.25; H, 6.92; Cl, 14.41 (for pot residue): C, 79.38; H, 6.87; Cl, 14.35.

When 0.5 mole of α-phenylethyl chloride was added during 2 minutes to 1.0 mole of sodium amide in liquid ammonia (slight red color) and 0.6 mole of ammonium chloride then added, there was isolated after extensive fractional crystallization from petroleum ether only a 26% yield of I, m.p. 67–68°, and a 7% yield of *cis*-α,α'-dimethylstilbene, m.p. 65–66°; reported m.p. 66°.[14] A mixed melting point of these two products was depressed to 43–53°. Mixed melting points of each of the products with authentic samples were not depressed. No attempt was made to isolate isomer II of the dimeric halide.

(B) With Lithium Amide.—The self-alkylation of α-phenylethyl chloride was carried out several times with lithium amide[15] in liquid ammonia by adding the halide to 10–100% excess of the reagent. In one experiment in which a 100% excess of lithium amide was used, the reaction mixture was stirred for 5 hours after the halide had been added. No color was produced at any time. The gray suspension was worked up essentially as described above for the reaction with sodium amide to give a 47% yield of isomer I, m.p. 67–68°, and a 43% yield of liquid isomer II. Admix-

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[9] E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

[10] C. A. Bischoff, *Ber.*, **21**, 2072 (1888); P. Walden and A. Kernbaum, *ibid.*, **23**, 1958 (1890); G. Romeo, *Gazz. chim. ital.*, **35**, [I] 111 (1905).

[11] J. Thiele and A. Wanscheidt, *Ann.*, **376**, 278 (1910).

[12] Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

[13] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., p. 122.

[14] E. Ott and v. R. Schröter, *Ber.*, **61**, 2135 (1928).

[15] See C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **75**, 1068 (1953).

ture of a sample of the former product with a sample of the solid isomer prepared by means of sodium amide did not depress the melting point.

Self-alkylation of Optically Active α-Phenylethyl Chloride.—To a stirred suspension of 0.13 mole of lithium amide[15] in 700 ml. of liquid ammonia was added during 2 minutes 16.9 g. (0.12 mole) of α-phenylethyl chloride, $\alpha^{25}\text{D}$ +84.32°,[4] in 100 ml. of anhydrous ether. After 1 hr., ether was added and the liquid ammonia removed. The ethereal solution was washed with water and dried over calcium chloride. The solvent was removed *in vacuo* keeping the temperature below 60°. An equal volume of pentane was added and the solution refrigerated to give 14 g. (95%) of crude 2-chloro-2,3-diphenylbutane from which there was isolated 6 g. (41%) of isomer I, m.p. 66–67°, $\alpha^{26}\text{D}$ −20.25° (*c* 2, in pure benzene). The liquid isomer II was not isolated.

Dehydrohalogenation of Isomers I and II of Dimeric Halide.—A solution of 6.12 g. (0.025 mole) of solid isomer I in 25 ml. of dry ether was added in one minute to a stirred suspension of 0.025 mole of sodium amide in 125 ml. of liquid ammonia. After 1 hr., 100 ml. of ether was added and the ammonia removed on the steam-bath. Water was added and the two layers separated. The ethereal layer was washed with water, dried over calcium chloride and the solvent removed. The oily residue was taken up in methanol and the solution cooled to precipitate 4.4 g. (85%) of *cis*-α,α'-dimethylstilbene (III) melting at 65–66° without recrystallization. The reported melting point for pure III is 66°.[14]

On similarly adding 67 g. (0.28 mole) of liquid isomer II to 0.28 mole of sodium amide there was obtained, after two recrystallizations of the product from methanol, 29 g. (51%) of *trans*-α,α'-dimethylstilbene (IV), m.p. 105–106°, reported m.p. 107°.[14] Evaporation of the mother liquor left a considerable amount of oil. This oil might have contained the solid, m.p. 74–75°, that was isolated in the over-all formation of dimeric olefins from α-phenylethyl chloride as described below. None of the *cis* olefin III was found.

Attempts to Determine Configurations of Isomers I and II. (A) By Reduction with Sodium.—To a solution of 3.06 g. (0.0125 mole) of isomer I in 200 ml. of liquid ammonia and 50 ml. of dry ether was added in small pieces 2 g. of sodium. The blue color of the sodium disappeared rapidly at first but then persisted during the following 2 hr. of stirring. Ammonium chloride was added, the ammonia removed, and water and ether were added. The ethereal layer was washed with 2 *M* hydrochloric acid, followed by 10% sodium bicarbonate solution and dried over calcium chloride. The solvent was removed and the semi-solid, white, residue was taken up in methanol. The solution was cooled to precipitate 1.9 g. (73%) of *meso*-α,α'-dimethylbibenzyl, m.p. 124.5–125.5°, reported m.p. 126–127°,[14] and 128°.[16]

When isomer II of the dimeric halide was treated similarly with sodium in liquid ammonia, the *meso* hydrocarbon was again obtained, the yield being 70%.

(B) By Treatment with Silver Oxide.—A sample of isomer I of the dimeric halide was treated with a 10% excess of moist silver oxide in acetone for 2 hr. The mixture was filtered and the acetone evaporated from the filtrate. Four recrystallizations of the oily residue from 30–60° petroleum ether gave a 40% yield of the higher melting isomer of 2,3-diphenyl-2-butanol, m.p. 83.5–84.5°. A mixed melting point with an authentic sample of this alcohol[17] was not depressed.

Similar treatment of isomer II of the dimeric halide gave essentially the same result.

Dimeric Olefins from α-Phenylethyl Chloride and Alkali Amides.—To a stirred suspension of 1.05 moles of sodium amide in one liter of liquid ammonia was added during 10 minutes a solution of 140.5 g. (1.0 mole) of α-phenylethyl chloride in 300 ml. of dry ether. The mixture (which soon became slightly red) was stirred for about 1.5 hr. while the ammonia was allowed to evaporate. Ether and 2 *M* hydrochloric acid were added and the layers separated. The ethereal solution was washed with hydrochloric acid, followed by water and dried over calcium chloride.

One-half of the dried ethereal solution was freed of solvent, and the residue fractionally crystallized from methanol to give first, 7.8 g. (15%) of *trans*-α,α'-dimethylstilbene, m.p. 105–106°, and second, 22.4 g. (43%) of solid, m.p. 57–59°, which apparently consisted of 92.5% of *cis*-α,α'-dimethylstilbene and 7.5% of the *trans* isomer.[18] The estimated yields of the *trans* and *cis* olefins are 18 and 40%, respectively.

The other half of the dried ethereal solution of the reaction products was treated with 0.0625 mole (an estimated 25 mole %) of potassium amide in liquid ammonia as described below for the isomerization of the *cis* to *trans* olefin. The solvents were removed and the residue crystallized twice from methanol to give 38 g. (73%) of *trans*-α,α'-dimethylstilbene, m.p. 105–106°. The mother liquor from the crystallizations was reduced in volume and refrigerated for 2 days to give 4.6 g. (9%) of a solid which melted at 74–75° after two recrystallizations from methanol. This substance was assumed to be a dimeric hydrocarbon.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.34; H, 7.71. Found: C, 92.26; H, 7.74.

In a similar experiment employing molecular equivalents of α-phenylethyl chloride and sodium amide, the solvent was removed from the dried ethereal solution of the reaction products and the residue distilled to give an 81% yield of material that boiled within the range that might be expected for the dimeric hydrocarbons.

In another experiment 0.10 mole of α-phenylethyl chloride was added to 0.2 mole of sodium amide in only 25 ml. of liquid ammonia (no red color) to give an 88% yield of such material.

In an early experiment α-phenylethyl chloride in ether was added to an excess of potassium amide in liquid ammonia in the usual manner. There were obtained a 41% yield of *cis*-α,α'-dimethylstilbene, a 6% yield of the *trans* olefin and 1–2% yields of styrene (isolated as the dibromide) and acetophenone imine (isolated as the semicarbazone). The *cis* olefin (m.p. 64–66°) was identified by ozonization to form acetophenone and by hydrogenation to give *meso*-α,α'-dimethylbibenzyl, m.p. 125–126°; reported m.p. 126–127°[14] and 128°.[16] The *trans* olefin (m.p. 105.5–106.5°) was analyzed.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.25, 92.36; H, 7.52, 7.64.

Dimeric and Trimeric Olefins from α-Phenylethyl Chloride and Potassium Amide.—To a stirred solution of 0.615 mole of potassium amide[19] in 700 ml. of liquid ammonia was added during 45 minutes a solution of 70 g. (0.5 mole) of α-phenylethyl chloride in 250 ml. of dry ether. The deep red mixture was stirred for 15 minutes longer and solid ammonium chloride added, followed by ether. The ammonia was removed and water added. The ethereal layer was washed with hydrochloric acid, followed by sodium bicarbonate solution and dried. The solvent was removed and the residue distilled *in vacuo* to give two fractions boiling at 90–125° at 1 mm. and at 145–165° at 1 mm. The first fraction (18.7 g.) partially solidified and on crystallization from methanol gave 15 g. (29%) of *trans*-α,α'-dimethylstilbene, m.p. 105–106°. The second fraction (23 g.) was taken up in methanol and cooled to give, after several recrystallizations from methanol, 12.6 g. (24%) of solid, m.p. 98–99°, which judging from its boiling point appeared to be a trimeric hydrocarbon.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.73; H, 7.65.

Like *trans*-α,α'-dimethylstilbene, this hydrocarbon gave a very slow positive test for unsaturation with potassium permanganate.

Isomerization of *cis*-α,α'-Dimethylstilbene to *trans* Isomer.—These experiments were carried out with samples of the *cis* olefin III melting at 54–56° which, on the basis of the curve reported by Ott,[18] was contaminated with approximately 13% of the *trans* isomer IV.

To a stirred solution of 0.078 mole of potassium amide in 500 ml. of liquid ammonia was added a solution of 63.5 g. (0.305 mole) of the 87% *cis* olefin in 150 ml. of dry ether. A deep red color developed immediately and persisted until excess ammonium chloride was added 1 hr. later. The ammonia was removed from the gray suspension. Water and ether were added and the layers separated. The ethe-

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[16] F. v. Wessely and H. Welleba, *Ber.*, **74**, 777 (1941).

[17] This sample was prepared by Dr. A. J. Weinheimer by the epoxidation of *cis*-α,α'-dimethylstilbene followed by catalytic hydrogenation.

[18] See E. Ott, *Ber.*, **61B**, 2124 (1928).

[19] See R. S. Yost and C. R. Hauser, This Journal, **69**, 2325 (1947).

real solution was washed with hydrochloric acid, followed by bicarbonate solution and dried over calcium chloride. The solvent was removed and the solid residue recrystallized from ethanol to give 57.5 g. (91%) of *trans*-α,α'-dimethylstilbene (IV), m.p. 105–105.5°.

In a similar manner, a solution of 20.8 g. (0.1 mole) of the 87% *cis* olefin in 125 ml. of dry ether was added to a stirred suspension of 0.025 mole of sodium amide in 500 ml. of liquid ammonia to produce a persistent red color. After adding ammonium chloride, the mixture was worked up essentially as described above to give, on recrystallization of the product from methanol, 6.5 g. (31%) of the *trans* olefin IV, m.p. 104–105°, and on further recrystallization, 12.1 g. (58%) of recovered impure *cis* olefin III, m.p. 54–56° (having the composition of the original mixture).

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Cyclopropyl Ketones. I. Synthesis and Spectra of 1-Aroyl-2-arylcyclopropanes[1]

BY RICHARD J. MOHRBACHER[2a] AND NORMAN H. CROMWELL[2b]

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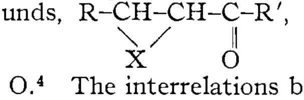
To extend our studies of three-ring carbonyl compounds we have synthesized members of a heretofore unknown class of cyclopropyl ketones. Reaction of α-diazo-4-phenylacetophenone with styrene gave *cis*- and *trans*-1-(4'-phenylbenzoyl)-2-phenylcyclopropanes. The *trans* isomer was also prepared by (a) reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride, (b) reaction of the new ketone 4-phenylacrylophenone with phenyldiazomethane, and (c) reaction of 4-biphenylylmetallic compounds with the new nitrile 2-phenylcyclopropanecarbonitrile. Four more new cyclopropane carbonyl compounds, 1-benzoyl-2-phenylcyclopropane, 4-phenylbenzoylcyclopropane and the *p*-nitrobenzyl esters of *cis* and *trans* 2-phenylcyclopropanecarboxylic acids, were synthesized. The ultraviolet and infrared spectra of all pertinent compounds were determined and structural assignments, based on spectral results, were made. The results of spectral studies of ethylenimine, ethylene oxide and cyclopropane ketones were compared.

Previous publications from this Laboratory have dealt with studies of the chemistry of *cis* and *trans* forms of analogous series of three-ring carbonyl compounds,

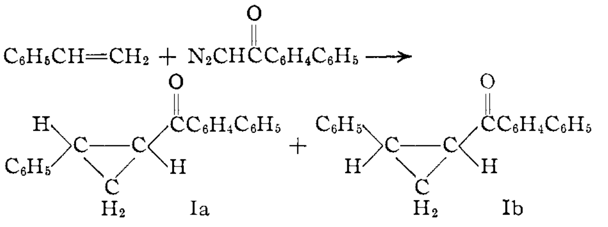


$\mathrm{R{-}\underset{X}{\underbrace{CH{-}CH}}{-}\underset{\underset{O}{\|}}{C}{-}R'}$, where X was N–R″[3] or O.[4] The interrelations between the stereochemistry and absorption spectra of such pairs of isomers have been discussed, and it has been concluded that the geometrical isomer which has its characteristic carbonyl associated absorption band at the lower frequency in both the ultraviolet and infrared ranges of the spectrum possesses the *trans* structure.[3c–e,4] Speculation has been put forth that isomeric pairs of simple arylaroylcyclopropanes might exhibit physical properties analogous to the ethylenimine and ethylene oxide ketones.[3d]

The purpose of the present study was to investigate methods of preparing stereoisomeric pairs of simple 1-carbonyl-2-arylcyclopropanes, particularly stereoisomers in the unknown class of compounds, 1-aroyl-2-arylcyclopropanes, and to study the absorption spectra of such simple cyclopropane carbonyl compounds, free from the effect of other three-ring substituents.

1-(4'-Phenylbenzoyl)-2-phenylcyclopropane (I) was selected as the arylaroylcyclopropane of choice because it would be one of the simplest examples which might exhibit strong carbonyl associated light absorptions (free from the effect of other three-ring substituents) and which might be expected to give rise to solid isomers. Four different methods were employed to prepare 1-(4'-phenylbenzoyl)-2-phenylcyclopropane in yields ranging from poor to fair: (1) reaction of α-diazo-4-phenylacetophenone with styrene, (2) reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride, (3) reaction of 4-phenylacrylophenone (II) with phenyldiazomethane and (4) reaction of 4-biphenylyl organometallic compounds with 2-phenylcyclopropanecarbonitrile (IV).

α-Diazo-4-phenylacetophenone reacted with a large excess of styrene at 140° to yield a sirupy product from which, after considerable manipulation, a 23% yield of a mixture of *cis*- and *trans*-1-(4'-phenylbenzoyl)-2-phenylcyclopropane was isolated.



$$\mathrm{C_6H_5CH{=}CH_2 + N_2CH\overset{\overset{O}{\|}}{C}C_6H_4C_6H_5 \longrightarrow}$$

A more successful procedure, suggested by D'yakonov's[5] extensive study of the reaction of diazo compounds and olefins, employed copper powder as a catalyst and a lower reaction temperature to give yields of 40% of theoretical of the *trans* isomer Ia. No trace of the *cis* isomer Ib was found. Several runs of the reaction between α-diazo-4-phenylacetophenone and *o*-nitrostyrene (a less easily polymerizable styrene derivative[6]) yielded unreacted *o*-nitrostyrene and intractable polymeric solids.

The reaction of di-(4-biphenylyl)-cadmium with 2-phenylcyclopropanecarbonyl chloride produced satisfactory yields of *trans*-1-(4'-phenylbenzoyl)-2-phenylcyclopropane (Ia), considering the difficulties

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[3] (a) N. H. Cromwell, *et al.*, THIS JOURNAL, **65**, 312 (1943); (b) **71**, 708 (1949); (c) **73**, 1044, 5929 (1951); (d) *J. Org. Chem.*, **17**, 414 (1952); (e) THIS JOURNAL, **75**, 6252 (1953); **77**, 6723 (1955).

[4] N. H. Cromwell and R. A. Setterquist, *ibid.*, **76**, 5752 (1954).

[5] I. A. D'yakonov, *et al.*, *J. Gen. Chem.*, *U.S.S.R.*, **23**, 66 (1953).

[6] R. H. Wiley and N. R. Smith, THIS JOURNAL, **72**, 5198 (1950).