of steric strain everything said above would apply.

Isopropyl Group.—Most effective hyperconjugation might be expected from conformation A or B (2 = H, 1 = 3 = C) which allow mixed CH–CC hyperconjugation, whereas conformation A (1 = H, 2 = 3 = C), implying pure CC hyperconjugation, appears sterically most favorable. Hence, torsional rotation might again be expected to lead to a minor reduction in hyperconjugation energy from a value intermediate between the ones applicable to methyl and *t*-butyl to a value substantially the same as for *t*-butyl.

Cyclopropyl Group.—It is now well established that the cyclopropyl group can act as an electron donor through a hyperconjugative mechanism. The nodal plane of the GO involved in this resonance is the plane formed by the two extracyclic σ-bonds of the carbon atom at which the unsaturated radical is attached,[2] and no hyperconjugating GO's exist with nodal planes normal to this plane. Hence, a torsional rotation around the extracyclic σ-bond should be effective in inhibiting hyperconjugative resonance completely. Such steric inhibition of cyclopropyl resonance has been suggested previously and experimental evidence for its existence has been cited.[8] None of the other possible modes of relieving steric strain are likely to be important for the cyclopropyl radical.

It is thus seen that none of the distortions which are likely to be effective in relieving steric strain in molecules can *completely* inhibit hyperconjugative resonance except for the cyclopropyl group. The distortion which would most effectively reduce this resonance would be the out-of-plane bending of the alkyl group and, in unsymmetrical alkyl groups and particularly in cyclopropyl groups, the torsional rotation. Comparison of these predictions with the experimental evidence discussed by Illuminati[3] makes it unlikely that the phenomena cited by this author can be explained in terms of steric inhibition of resonance.

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[8] J. D. Robert, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

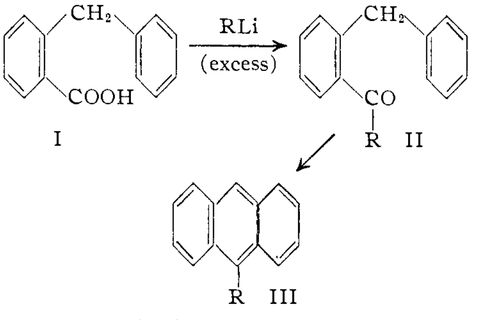
A New Base-catalyzed Cyclization Reaction

BY C. K. BRADSHER AND SIDNEY T. WEBSTER[1]

RECEIVED AUGUST 22, 1956

The reaction of *o*-benzylbenzoic acid (I) with an excess of methyllithium yields the readily cyclizable *o*-benzylacetophenone (II, R = CH_3). With phenyllithium, I affords a 70% yield of 9-phenylanthracene, by a new base-catalyzed cyclization. *p*- and *m*-tolyllithium afford smaller yields of the 9-arylanthracenes. With *o*-benzhydrylbenzoic acid and phenyllithium, no hydrocarbon is formed.

It has been shown earlier[2-5] that *o*-benzylphenones (II), in the presence of a boiling mixture of hydrobromic and acetic acids, cyclize, affording high yields of 9-substituted anthracene derivatives (III). The requisite ketones (II) were prepared in a four-step synthesis starting with *o*-chlorobenzaldehyde. A classical approach to the synthesis of *meso* alkyl anthracene derivatives of known structure involves the cyclization of an *o*-benzylbenzoic acid derivative (I), affording an anthrone, which is allowed to react with a Grignard reagent, and the resulting product dehydrated to yield the anthracene derivative III.



While some substituted anthrones afford good yields of the expected hydrocarbons, others have proved unstable[6-8] or were found to be largely converted to resins by the action of the Grignard reagent.[9,10] Other anthrones, particularly 1,2-benzanthrones, show considerable tendency to exist in the tautomeric anthranol form.[11] These difficulties made it appear desirable to examine an alternate route from the acid I to the hydrocarbon III. It was found that when *o*-benzylbenzoic acid is treated with an excess of methyllithium,[12-15] *o*-benzylacetophenone (II, R = CH_3) is obtained in 80% yield. Since it was shown that this ketone may be cyclized in 79% yield, the over-all yield of 9-methylanthracene (III, R = CH_3) from the acid I is quite satisfactory.

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[1] Taken in part from a thesis presented in partial fulfillment of the requirments for the M.A. degree, Duke University, 1956. This work was supported in part by a grant from the Duke University Research Council.

[2] C. K. Bradsher, THIS JOURNAL, **62**, 486 (1940).

[3] C. K. Bradsher, *ibid.*, **62**, 1077 (1940).

[4] C. K. Bradsher and F. A. Vingiello, *ibid.*, **71**, 1434 (1949).

[5] F. A. Vingiello, J. G. Van Oot and H. H. Hannabass, *ibid.*, **74**, 4546 (1952).

[6] L. F. Fieser and E. B. Hershberg, *ibid.*, **62**, 49 (1940).

[7] L. F. Fieser and A. K. Seligman, *ibid.*, **60**, 170 (1938).

[8] M. S. Newman, *ibid.*, **60**, 1141 (1938).

[9] E. de B. Barnett and F. C. Marrison, *Ber.*, **64**, 535 (1931).

[10] E. de B. Barnett and N. F. Goodway, *J. Chem. Soc.*, 1754 (1929).

[11] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **59**, 1028 (1937).

[12] H. Gilman and P. Van Ess, *ibid.*, **55**, 1258 (1933).

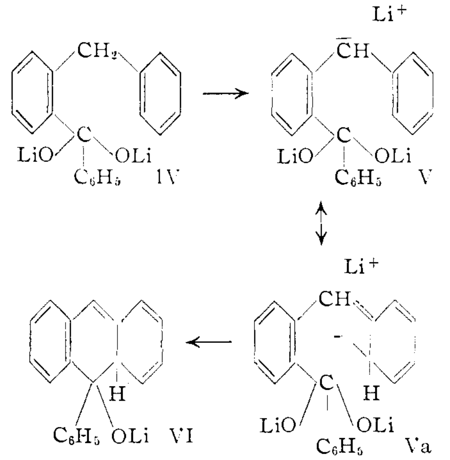
[13] P. Karrer and J. Benz, *Helv. Chim. Acta*, **31**, 1607 (1948).

[14] M. S. Newman and J. Mangham, THIS JOURNAL, **71**, 3342 (1949); M. S. Newman and T. S. Bye, *ibid.*, **74**, 905 (1952).

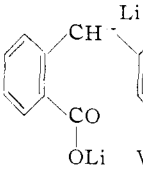
[15] C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952).

When phenyllithium was substituted for methyllithium, an entirely unexpected result was obtained. Only a trace of the expected *o*-benzylbenzophenone (II, R = C_6H_5) was isolated, accompanied by a 70% yield of 9-phenylanthracene (III, R = C_6H_5). It is clear that this is a new cyclization reaction and one that does not involve the ketone (II, R = C_6H_5), since under the conditions used (excess of phenyllithium), any ketone present, as such, in the reaction mixture would have reacted instantly yielding the salt of a tertiary alcohol.

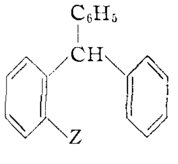
According to Gilman and Van Ess,[12] the isolation of ketones from the reaction of organolithium reagents with the lithium salts of organic acids depends upon the formation of a dilithium salt such as IV.



It may not be at once apparent why the salt IV should cyclize under the conditions of the experiment, but the presence of excess phenyllithium will probably bring about a conversion to carbanion V. One of the structures contributing to the resonance of the anion is Va which is geometrically arranged to permit a facile displacement of a LiO^- ion or, in effect, the loss of the elements of lithium oxide, accompanied by cyclization. It seems very probable that a molecule such as VI, in the presence of a strong base such as phenyllithium, would undergo what is, in effect, the elimination of the elements of lithium hydroxide, affording the hydrocarbon III (R = C_6H_5).[16] An alternate mechanism involving the cyclization of anion VII followed by displacement of a LiO group by phenyl seems less attractive since no anthrone was isolated from the hydrolysis product.



VII



VIII, Z = COOH
IX, Z = $C(OLi)_2C_6H_5$
X, Z = COC_6H_5
XI, Z = $COH(C_6H_5)_2$

With *m*-tolyllithium and *p*-tolyllithium, yields of the expected hydrocarbons (III) in the new base-catalyzed cyclization were only 30 and 17%, respectively. Although chromatography was used, the separation of pure products proved difficult. The amount of hydrocarbon actually formed is probably somewhat higher than the yields would indicate, but in any case the reaction does not appear of general use for the preparation of 9-arylanthracenes.

When *o*-benzhydrylbenzoic acid (VIII) was subjected to the action of phenyllithium under the same conditions used in the case of *o*-benzylbenzoic acid (I), no hydrocarbon was isolated, but instead a mixture containing 2-benzhydryltriphenylcarbinol (XI, 62%) and 2-benzhydrylbenzophenone (X, 29%) was obtained. The quantity of tertiary alcohol XI produced may possibly be due to the larger size of the benzhydryl group (relative to benzyl), which might result in the easy loss of the elements of Li_2O from the dilithio intermediate IX. Any ketone X formed in this way should react almost instantly to yield XI. The ketone actually recovered by addition of water to the reaction mixture had almost certainly existed as the dilithio derivative IX before hydrolysis. Failure of IX to yield 9,10-diphenylanthracene may be due either to unfavorable steric factors or to the fact that in this system any intermediate analogous to V has an additional ring within which the negative charge may be distributed.

Experimental[17]

***o*-Benzylacetophenone (II, R = CH_3).**—Methyllithium was prepared by reaction of 12.2 g. of lithium ribbon with 114 g. of methyl iodide in about 800 ml. of dry ether. To the organolithium reagent, 15 g. of *o*-benzylbenzoic acid[18] (m.p. 116–118°), dissolved in 500 ml. of dry ether, was added gradually with stirring. As soon as the addition of the organic acid was complete,[19] the mixture was treated with ice and the ethereal layer washed, dried and concentrated. The residue, a yellow oil, was distilled under reduced pressure, b.p. 149–150° (3 mm.), yield 12.04 g. (80%). The oil crystallized on seeding, and a sample recrystallized from petroleum ether melted at 48–49° (lit.[2] 49–50°) and did not depress the melting point of an authentic sample.

One gram of the recrystallized ketone was cyclized essentially as described previously.[2] The 9-methylanthracene was recrystallized from methanol as yellow needles, m.p. 80–81° (lit.[2] 80–81°), yield 0.72 g. (79%).

Reaction of *o*-Benzylbenzoic Acid with Phenyllithium.—Phenyllithium was prepared from 4.1 g. of lithium and 31.4 g. of bromobenzene in about 350 ml. of dry ether, and to this, 5 g. of *o*-benzylbenzoic acid was added gradually, with stirring. Stirring was continued for an additional 24 hr., and then ice-water was added and the ethereal layer washed, dried and concentrated. The residual oil solidified yielding 4.81 g. of crude yellow crystalline product, m.p. 135–145°. Recrystallization afforded a total of 3.81 g. (64%) of pale yellow 9-phenylanthracene, m.p. 151–153° (lit.[2] 154–155°), which was identified by a mixed melting point determination.

Another experiment was carried out as described above except the reaction was allowed to run for 5 days, and the

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(16) The possibility that 9-hydroxy-9-phenyl-9,10-dihydroanthracene is liberated by hydrolysis of this reaction mixture and is dehydrated during chromatography, and crystallization has not been excluded, although it appears to us less likely.

(17) All melting points were taken on the Fisher–Johns block and were corrected. Analysis by Galbraith Laboratories. The ultraviolet absorption spectra were measured in 95% ethanol solution using a Warren Spectracord recording spectrophotometer and 1-cm. quartz cells. The infrared absorption spectra were determined in carbon tetrachloride.

(18) E. De B. Barnett, J. W. Cook and I. G. Nixon, *J. Chem. Soc.*, 504 (1927).

(19) Essentially the same results were obtained when longer reaction times were used.

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° (2 mm.). 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.

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[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).

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

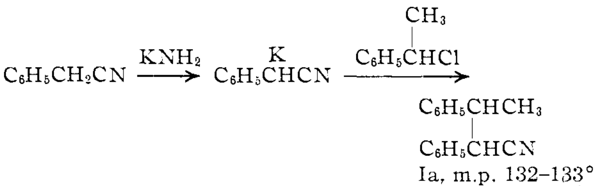
Configurations of Diastereoisomers of 2,3-Diphenylbutyronitrile Obtained in the α-Phenylethylation of Potassiophenylacetonitrile[1]

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]



$$C_6H_5CH_2CN \xrightarrow{KNH_2} C_6H_5\overset{K}{C}HCN \xrightarrow{C_6H_5\overset{CH_3}{\overset{|}{C}}HCl} \begin{array}{c} C_6H_5CHCH_3 \\ | \\ C_6H_5CHCN \end{array}$$

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 byproduct 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

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[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).