Kothe's Hydrocarbon. 1,2-Bis(β-phenylethyl)benzene[1a]

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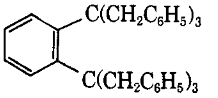
A hydrocarbon reported by Kothe in 1888 is shown, by several physical methods, to be 1,2-bis(β-phenylethyl)benzene. Several routes to prepare other similar hydrocarbons were attempted. It is suggested that the Kothe reaction may be a general one for obtaining various *o*-dialkylbenzenes.

In 1888 Kothe[2] reported obtaining a hydrocarbon, m.p. 72–73°, by the interaction of phthalic anhydride, benzyl chloride, and zinc dust, for which he proposed structure **1**.



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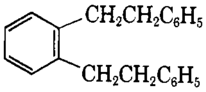
Since such a product presumably would form by the multiple addition of a benzylzinc reagent to phthalic anhydride followed by a reduction, we were greatly interested in repeating the synthesis to examine the product of this unprecedented series of transformations.

Initial attempts to obtain Kothe's hydrocarbon were unsuccessful when the reagents were allowed to interact only briefly. By carrying out the reaction in refluxing benzene for 24 hr., however, there was obtained a mixture of at least three products: a hydrocarbon, m.p. 83–85°, believed to be identical with that of Kothe, phthalide, and a higher melting solid, as yet unidentified. Kothe's hydrocarbon was finally separated from the other products by chromatography on alumina and fractional distillation of the ligroin eluate.

Molecular weight determinations by two methods indicated that Kothe's hydrocarbon contains two benzyl units, contrary to the structure originally proposed, which contains six benzyl units. Thus the problem of structure determination was reduced to distinguishing between two possibilities, **2** and **3**.



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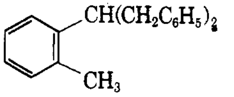

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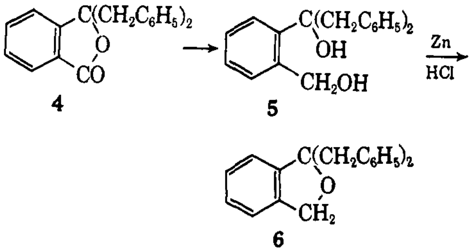
The ultraviolet spectrum is consistent with both **2** and **3**, since it resembles those of toluene and xylene. The infrared spectrum contains no band at 1380 cm.$^{-1}$ assignable to a C–CH$_3$ and thus is suggestive of structure **2**. Compelling evidence for **2** came from the n.m.r. spectrum, which exhibits only one peak assignable to aliphatic protons. Clearly the n.m.r. spectrum of **3** would be expected to contain several multiplet peaks as well as a singlet methyl peak. From the combined evidence of composition, molecular weight, and spectral properties, it is concluded that Kothe's hydrocarbon is 1,2-bis(β-phenylethyl)benzene (**2**). Although, to our knowledge, this compound has not been reported previously, three references have appeared to its *para* isomer, whose melting point has been variously reported as 89°,[3] 91°,[4] and 47–48.5°.[5] Since the first two melting points correspond closely to the hydrocarbon described here, it is possible their structure was incorrectly assigned. Alternatively the low melting compound,[5] believed to be the *para* isomer, may be bibenzyl (m.p. 52°). Certainly the identity of the *para* isomer remains in question.

Attempts to synthesize the alternative dibenzylated structure led to some significant failures although not to **3**. Reduction of 3,3-dibenzylphthalide (**4**) with lithium aluminum hydride gave diol **5**, which was subjected to treatment with zinc dust and hydrochloric acid. Instead of reduction product **3**, however, the product was 1,1-dibenzylphthalan (**6**) formed by dehydration.



In view of Pettit's recent observation[6] that benzyl–oxygen bonds are particularly susceptible to hydrogenolysis with mixed hydrides, we attempted the direct synthesis of **3** from 3,3-dibenzylphthalide (**4**) by using a lithium aluminum hydride–aluminum chloride reagent described by Nystrom.[7] The result, however, was a mixture of **5** and **6**, which could be converted entirely to **6** by treatment with zinc dust and acid.

The formation of a hydrocarbon by Kothe's method seems most likely a sequence of additions by benzylzinc reagent and one or more reduction steps. The appearance of phthalide as a product indicates the reducing power of the medium. A likely intermediate would be 1,3-dibenzylidenephthalan (**7**), which, however, was not found among the products. It is difficult to obtain by synthesis,[8] but a closely related phthalan (**8**) can be prepared in satisfactory yield by treatment of 3,3-dibenzylphthalide with benzylmagnesium chloride. We subjected this phthalan (**8**) to the action of zinc dust in boiling benzene to determine whether it would undergo

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(2) R. Kothe, *Ann.*, **248**, 56 (1888).

(3) K. Shishido and O. Odajima, *J. Soc. Chem. Ind. Japan*, **45**, Suppl. binding 222 (1942); *Chem. Abstr.*, **45**, 588 (1951).

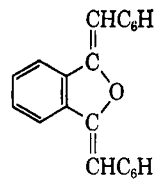
(4) Ng. Ph. Buu-Hoï, Ng. Hoan, and P. Jacquignon, *J. Chem. Soc.*, 1381 (1951).

(5) A. F. Dobryanskii and Y. I. Kornilova, *Sb. Statei Obshch. Khim. Akad. Nauk SSSR*, **1**, 315 (1953); *Chem. Abstr.*, **49**, 851 (1955).

(6) G. R. Pettit, B. Green, P. Hofer, D. C. Ayres, and P. J. S. Pauwels, *Proc. Chem. Soc.*, 357 (1962).

(7) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

(8) R. Weiss, K. Grobstein, and R. Sauermann, *Ber.*, **59B**, 301 (1926).



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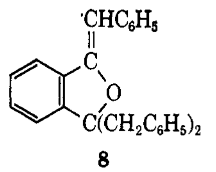

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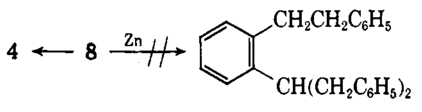
reduction to hydrocarbon 9. Instead lactone 4—a reverse aldol product—was the only compound isolated besides starting material. The phthalan is very susceptible to hydrolysis, as shown by its decomposition to 4 simply when heated in benzene, a property which had been observed before.[8]



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In view of current widespread interest in the synthesis and properties of *o*-dialkylbenzenes,[9,10] the reaction originally described by Kothe warrants further attention as a possible alternative to more classical synthetic methods for obtaining various dialkylbenzenes.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 21 double-beam spectrophotometer with sodium chloride optics. The ultraviolet spectra were determined in 95% ethanol on a Perkin-Elmer 4000 Spectracord. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected.

Preparation of Kothe's Hydrocarbon. Action of Benzyl Chloride and Zinc Dust on Phthalic Anhydride.[2]—A mixture of 37 g. of phthalic anhydride, 70 g. of zinc dust, and 100 ml. of benzene (previously dried over sodium) was heated to reflux temperature. Stirring was started, and a solution of 100 g. of benzyl chloride dissolved in 80 ml. of dry benzene was added over a period of 1 hr. while refluxing was maintained. During this time hydrogen chloride was evolved continually, and the reaction mixture became caked, so that stirring could not be continued. An additional 20 g. of benzyl chloride in 10 ml. of dry benzene was added in a few portions, and the mixture was heated under reflux without stirring for 15.5 hr. Then a solution of 10 g. of benzyl chloride in 10 ml. of dry benzene was added in three portions, and refluxing was continued for 8 hr. The flask was cooled in an ice bath and the mixture decomposed cautiously with 30 ml. of dilute hydrochloric acid. The yellow, supernatant organic layer was removed by decantation and combined with two ether washings and three benzene washings of the residue; the solution was steam distilled until the distillate was clear. When the residue was taken up in ether–benzene, and the solution allowed to stand for a day, diluted with ligroin (b.p. 60–90°), allowed to stand overnight, and then cooled in ice for 4 hr., a light yellow solid separated, m.p. 155–185° dec., yield 5.0 g. About 50 ml. of the filtrate was subjected to chromatography on a 2 cm. × 48 cm. column packed with basic alumina. Elution with 700 ml. of ligroin yielded oils. When the eluent was enriched with 1–5% benzene in ligroin, a crystalline substance was obtained, subsequently shown to be phthalide, m.p. 73–74.5°, mixture melting point with an authentic sample 72.5–75.0°. The remainder of the original filtrate, about 110 ml., was separated on a 3 cm. × 60 cm. chromatographic column of basic alumina by elution with 1.1 l. of ligroin. When the residue from the ligroin solutions was fractionally distilled at aspirator pressure, the portion of b.p. 240–250° solidified in the receiver. Additional amounts of slightly colored solid were obtained by repeated fractionation of the forerun and residue. The yield of colorless product, m.p. 73–83°, was 13.5 g. (19%). It was recrystallized several times from 95% ethanol to m.p. 83–85°; λ_{max} 262 mμ (log ε 2.34), 266 (2.31), 269 (2.29), 275 (1.96). The n.m.r. spectrum (carbon tetrachloride) contains one peak assignable to methylene protons (τ 6.16) and two peaks assignable to aromatic C–H (τ 3.03, 2.92).[11]

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74; mol. wt., 286. Found: C, 92.88; H, 7.36; mol. wt. (Rast, sealed, immersed tubes), 297, 288, 255; mol. wt. (osmometer), 292.

1,1-Dibenzyl-3-benzylidenephthalan (8).—To a solution of benzylmagnesium chloride, prepared in 100 ml. of ether from 9.3 ml. of benzyl chloride and 1.98 g. of magnesium, was added 6 g. of 3,3-dibenzylphthalide[12] in several portions during 5 min. The orange-brown solution was heated under reflux for 2 hr. and then decomposed with dilute hydrochloric acid. The ether layer was combined with ether washings of the aqueous layer and dried over anhydrous magnesium sulfate. By removal of the solvent a light orange, amorphous material was obtained, which was converted to solid by the addition of ethanol, m.p. 144–148°, yield 4.8 g. (65%). Three recrystallizations from ethanol–benzene changed the melting point to 143.5–146°, lit.[8] m.p. 139–149°; λ_{max} 232 mμ (log ε 4.01), 240 (3.99), 250 sh (3.81), 307 sh (4.27), 3.18 (4.40), 333 (4.44), 350 (4.20).

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.65; H, 6.23. Found: C, 90.03; H, 6.89.

Attempted Reduction of 1,1-Dibenzyl-3-benzylidenephthalan with Zinc Dust.—A mixture of 1.0 g. of the phthalan, 2 g. of zinc dust, and 20 ml. of dry benzene was stirred and heated under reflux for 24 hr., an additional 20 ml. of dry benzene being added after the first 23 hr. The hot mixture was filtered and the filtrate concentrated to about 10 ml. and set aside. The first crop of crystalline material consisted of 3,3-dibenzylphthalide, m.p. 203–207°, yield 0.17 g. (21%). By dilution of the filtrate with ethanol, concentration, and cooling, there were recovered two fractions of the starting material: 0.24 g. (24%), of m.p. 145–148°, and 0.27 g. (27%) of m.p. 138–144°. Heated 28 hr. in benzene alone, the phthalan was converted to 3,3-dibenzylphthalide in 60% yield.

Dibenzyl(*o*-hydroxymethylphenyl)carbinol (5).—To a suspension of 0.3 g. of lithium aluminum hydride in dry ether was added 1.0 g. of 3,3-dibenzylphthalide in small portions with intermittent stirring. The mixture was stirred at room temperature for 1 hr., then at reflux temperature for 45 min., and decomposed slowly with ordinary ether. Cold, dilute sulfuric acid was added to the flask, surrounded by an ice–salt bath, so that the temperature of the mixture was maintained at 3–8°. When it was strongly acid, ether and benzene were added to dissolve the white solid at the interface; the organic layer was separated and combined with ether and benzene washings of the water layer. After the solution had been dried over anhydrous magnesium sulfate, filtered, concentrated to 5 ml., and let stand, the colorless, crystalline alcohol appeared, m.p. 132–133.5°, yield 0.50 g. Recrystallized three times from benzene–petroleum ether (b.p. 40–60°), the alcohol melted at 133.5–134.0°, lit.[13] m.p. 133–134.5°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 82.74; H, 6.72.

A second crop, m.p. 128–130°, weighed 0.14 g. (total yield 64%). The infrared spectrum (10% chloroform) contains alcohol bands at 3535 and 3375 cm.$^{-1}$.

1,1-Dibenzylphthalan (6).—To a mixture of 0.5 g. of the above alcohol, 1 g. of zinc dust, and 10 ml. of benzene was added 1 ml. of concentrated hydrochloric acid dropwise during a few minutes. Addition of each drop of acid caused a vigorous reaction to ensue. The mixture was heated under reflux for 6.5 hr., let stand overnight, heated to boiling, and filtered. The filtrate, which was combined with benzene washings of the residue, was washed successively with saturated sodium sulfate, 5% sodium carbonate, and saturated sodium sulfate, and then dried over anhydrous magnesium sulfate. The solution was filtered and concentrated, and a few drops of ligroin were added to the residue after 2 days. Large colorless prisms were deposited, m.p. 81.5–84.5°, yield 0.20 g. (42%). It was recrystallized repeatedly from ligroin, m.p. 88.0–88.7°, lit.[12] m.p. 88–89°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.87; H, 6.91.

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[9] C. Hoogzand and W. Hübel, *Tetrahedron Letters*, **No. 18**, 637 (1961).

[10] L. R. C. Barclay, C. E. Milligan, and N. D. Hall, *Can. J. Chem.*, **40**, 1664 (1962).

[11] We are very grateful to Dr. Glenn Berchtold, Massachusetts Institute of Technology, for determination of this n.m.r. spectrum.

[12] W. Baker, W. D. Ollis, and T. S. Zealley, *J. Chem. Soc.*, 1447 (1952).

[13] A. Ludwig, *Ber.*, **40**, 3060 (1907).

The infrared spectrum (chloroform) indicates the absence of alcohol bands. The n.m.r. spectrum (carbon tetrachloride) contains two sharp peaks at τ 6.81 and 5.56, and an unresolved multiplet centered at about τ 3.0. The relative integrated intensities are 1.9, 1.0 and 7.8, respectively.[14]

Reduction of 3,3-dibenzylphthalide with a 1:1 molar mixture of lithium aluminum hydride–aluminum chloride in ether[7] led to a mixture of 1,1-dibenzylphthalan (6) and dibenzyl-*o*-(hydroxymethylphenyl)carbinol (5). A 0.73-g. sample of this mixture was converted by treatment with zinc dust and hydrochloric acid to 0.20 g. of 6 (m.p. 87.5–89.0°) whose infrared spectrum (chloroform) was identical with that of the phthalan obtained above.

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(14) This spectrum was measured at the University of New Hampshire with a Varian Model A-60 instrument.

Mercaptan Oxidations. VII. Oxidative Desulfurization of Benzyl Mercaptan, Benzyl Disulfide, and Related Species

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The base-catalyzed oxidation of benzyl mercaptan and benzyl disulfide was studied in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) at 23.5° and 80° in the presence of potassium *t*-butoxide, sodium methoxide, and potassium hydroxide. Oxidative desulfurization of the mercaptan and disulfide to benzoic acid was the predominant reaction observed in the presence of the alkoxide bases. The reaction path proposed involves the formation of peroxide ions which can rearrange to alkoxide ions that are unstable and decompose to benzaldehyde and α-toluenethiosulfinate ions ($C_6H_5CH_2S(O)S^-$). Apparently, the aldehyde and acid salt are oxidized rapidly to benzoic acid. The latter is substantiated by the fact that potassium α-toluenesulfonate could be oxidized rapidly to benzoic acid in quantitative yields. In the presence of potassium hydroxide, the main oxidation product was potassium α-toluenesulfonate. This is due apparently to the decreased basicity and increased sulfur nucleophilicity of the hydroxide ion. The oxidation of α,α'-dimercapto-*p*-xylene also was investigated. This compound was oxidized to terephthalic acid in 30 to 84% yield depending on the particular reaction conditions employed.

Previous studies in these laboratories have established that dipolar solvents markedly accelerate the base-catalyzed oxidation of mercaptans (thiols) by molecular oxygen.[1] If these reactions are allowed to proceed to completion, both alkyl and aryl mercaptans can be oxidized to their corresponding sulfonic acid salts.[2,3] The latter finding represents a new base-catalyzed oxidation reaction since the predominant product from the base-catalyzed oxidation of a mercaptan is usually the disulfide.[4] The present investigation is an extension of our previous studies on solvent effects in the base-catalyzed oxidation of sulfur compounds and is concerned with the oxidation of benzyl mercaptan, benzyl disulfide, and some related species. These compounds contain benzylic hydrogens which should be fairly acidic in a polar medium. Thus, it seemed worthwhile to determine if oxidation to the sulfonic acid or oxidative desulfurization to carboxylic acids would be the predominant course of reaction in mercaptans and disulfides of this general type.

Results

The base-catalyzed oxidation of benzyl mercaptan, benzyl disulfide, potassium α-toluenesulfonate, and α,α'-dimercapto-*p*-xylene has been studied at a constant oxygen partial pressure of one atmosphere at 23.5° and 80°. Reactions were carried out in dimethyl sulfoxide (DMSO, 80%)-*t*-butyl alcohol (20%)[5] using potassium hydroxide, sodium methoxide (NaOMe), and potassium *t*-butoxide (KO-*t*-Bu) as the bases. The ratio of base to reactant varied from 3 to 6 depending on the particular benzyl compound oxidized. Specific reaction conditions employed and product yields obtained under these conditions are summarized in Table I. In the presence of KO-*t*-Bu at 80°, benzyl mercaptan, benzyl disulfide, and potassium α-toluenesulfonate were converted to benzoic acid in 74 to 100 mole % yields. The mercaptan also formed benzyl disulfide and stilbene, the disulfide apparently being oxidized as it was formed. Stilbene was also a by-product of the disulfide oxidation. The initial rates of oxidation are shown in Fig. 1 for the system KO-*t*-Bu–DMSO–*t*-C_4H_9OH at 80°. All rates of oxygen consumption were extremely rapid. The acid salt consumed 2 moles oxygen/mole acid in 25 min. The mercaptan and disulfide were less reactive than the acid, consuming 0.75 and 0.45 mole oxygen/mole reactant, respectively, in 25 min. All rates of oxidation decreased in the latter stages of reaction since water and alcohols are formed, and the base is consumed by the acid products that are formed.

Under less vigorous conditions of oxidation (NaOMe at 23.5°) benzyl mercaptan and benzyl disulfide were still oxidized readily to benzoic acid, but the yield of disulfide from the mercaptan was increased by a factor of 2.5. Both reactions yielded a small quantity of stilbene. When the weak base, potassium hydroxide, was used, the mercaptan and disulfide yielded potassium α-toluenesulfonate as the main oxidation product at 23.5°. In the protic solvent methanol, oxidation of the mercaptan beyond the disulfide stage did not occur

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(1) T. J. Wallace, A. Schriesheim, and W. Bartok, *J. Org. Chem.*, **28**, 1311 (1963), and references therein.

(2) T. J. Wallace and A. Schriesheim, *Tetrahedron Letters*, 1131 (1963).

(3) T. J. Wallace and A. Schriesheim, paper to be submitted for publication.

(4) For a recent review of this area, see A. A. Oswald and T. J. Wallace, "The Anionic Oxidation of Mercaptans and the Co-Oxidation of Mercaptans with Olefins," Organic Sulfur Compounds, Vol. II, N. Kharasch, Ed., Pergamon Press, New York, N. Y., in press.

(5) This mixture has been employed as a solvent medium for the anionic oxidation of acidic hydrocarbons by Russell and co-workers [see Preprints, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 25, 1961].