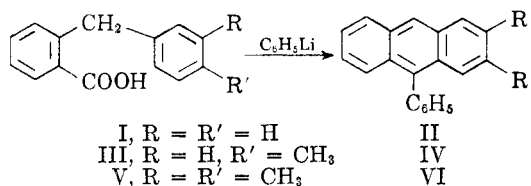


Further Extension of the Base-Catalyzed Cyclization

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Received August 12, 1957

In an earlier communication² it was shown that *o*-benzylbenzoic acid (I) will react with an excess of phenyllithium to afford a 70% yield of 9-phenylantracene (II). In the interest of learning more about the limits of this novel cyclization, the

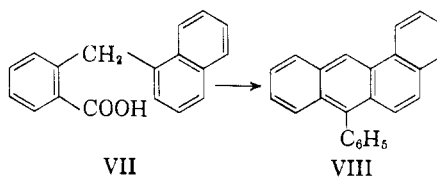


action of phenyllithium on some substituted benzylbenzoic acids has been investigated.

With *o*-(4-methylbenzyl)benzoic acid (III) a 42% yield of the known³⁻⁵ 2-methyl-9-phenylantracene (IV) was obtained. In one experiment in which an excess of a lithium metal was present, none of the 2-methyl-9-phenylantracene (IV) was isolated as such, and the principal product was a new, well-defined molecular compound, containing 2-methyl-9-phenyl-9,10-dihydroanthracene in combination with the fully aromatic analog (IV).⁶

The reaction of *o*-(3,4-dimethylbenzyl)benzoic acid (V) with an excess of phenyllithium gave a 41% yield of what is believed to be 2,3-dimethyl-9-phenylantracene (VI).⁷

With *o*-(1-naphthylmethyl)benzoic acid (VII) cyclization takes place into the 2-position producing the known⁸ 10-phenyl-1,2-benzanthracene (VIII) in 58% yield. These observations eliminate the somewhat remote possibility that the entering



phenyl group is introduced at the methylene bridge, and is further confirmation for the reaction mechanism proposed earlier.²

EXPERIMENTAL

Spectroscopic data. All ultraviolet absorption spectra were obtained in 95% ethanol solution using a Warren Spectracord spectrophotometer and 1-cm. quartz cells. All infrared spectra were determined in carbon tetrachloride solution a Perkin-Elmer Model 21 double beam spectrophotometer with 1.0-mm. sodium chloride cells.

Phenyllithium. Except as noted phenyllithium was prepared by the action of 31.4 g. of bromobenzene on 2.78 g. lithium in 350 ml. of dry ether, the procedure being carried out under a nitrogen atmosphere. An additional 3-4 ml. of bromobenzene was added to react with any remaining lithium and stirring continued for one hour.

2-Methyl-9-phenylantracene (IV). To an ether solution of phenyllithium a solution containing 5 g. of *o*-(4-methylbenzyl)benzoic acid⁹ in 150 ml. of dry ether was added gradually with stirring over a period of 30 min. The dark reaction mixture was stirred for 15 hr. at room temperature and then about 200 ml. of ice water was added dropwise with cooling and stirring. The ether layer was separated, washed with water until neutral and finally dried over sodium sulfate. The ether was removed on the steam bath and the residue dissolved in 50 ml. of dry benzene and chromatographed by passing it through a 2.5 × 35 cm. column carefully packed with 125 g. of alumina (Merk and Co.). Benzene was used for elution of the hydrocarbon fraction. Since no crystalline product was obtained, the chromatographic process was repeated, the benzene solution was concentrated and the fluorescent residue crystallized from ethanol. The granular light yellow crystals were collected, 2.48 g. (42%), m.p. 120°¹⁰ (lit.^{3,4} 119°). A mixed melting point with an authentic sample¹¹ of 2-methyl-9-phenylantracene gave no depression. Ultraviolet absorption maxima were observed at 227, 257, (316), 333, 348, and 366 mμ. These maxima correspond closely to those reported for a 9-phenylantracene system.¹²

Products obtained with excess lithium metal. When the above reaction was carried out as described but using 4.1 g. instead of 2.78 g. of lithium metal, and only a total of 31.4 g. of bromobenzene, the hydrocarbon fraction amounted to 2.13 g. (48%) of white crystals of what is believed to be a molecular compound between 2-methyl-9-phenyl-9,10-dihydroanthracene and 2-methyl-9-phenylantracene (IV). The analytical sample, crystallized from ethanol, melted at 87-88°; ultraviolet absorption maxima occurred at 257, (271), 316, 333, 348, and 366 mμ.

Anal. Calcd. for C₂₁H₁₆C₂₁H₁₈:¹³ C, 93.64; H, 6.36. Found: C, 93.92; H, 6.01.

(9) L. Gresley, *Ann.*, **234**, 234 (1886).

(10) All melting points were determined on the Fisher-Johns block and are corrected.

(11) We are indebted to Dr. Frank A. Vingiello of the Virginia Polytechnic Institute for this sample.

(12) E. de B. Barnett, J. W. Cook, and T. E. Ellison, *J. Chem. Soc.*, 855 (1928).

(13) This calculation is based upon the assumption that the molecular compound is a 1:1 combination of the two hydrocarbons. The carbon and hydrogen analysis seems to indicate a possibility that there is a larger proportion of the fully aromatic compound (IV).

(1) Monsanto Chemical Co. Fellow, 1956-1957.

(2) C. K. Bradsher and S. T. Webster, *J. Am. Chem. Soc.*, **79**, 393 (1957).

(3) R. Scholl, H. Dehnert, and L. Wanka, *Ann.*, **493**, 56, 82 (1932).

(4) H. Hemilian, *Ber.*, **16**, 2360 (1883).

(5) F. A. Vingiello and J. G. Van Oot, *J. Am. Chem. Soc.*, **73**, 5070 (1951).

(6) It is well known that the alkali metals reduce the anthracene nucleus at the 9,10 positions, e.g., W. Schlenk, J. Appentodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914); W. Schlenk and E. Bergmann, *Ann.*, **463**, 158, 276 (1928).

The formation of a well-defined molecular compound containing one mole of 9-phenylantracene to one mole of 9-phenyl-9,10-dihydroanthracene has been observed earlier, E. Haack, *Ber.*, **62**, 1771 (1929).

(7) The possibility that cyclization has occurred *ortho* rather than *para* to a methyl group has not been excluded, but it has already been shown that in the aromatic cyclodehydration of 2-(3'-methylbenzyl)benzophenone only the *para* cyclization product is isolated (76% yield; ref. 5).

(8) F. A. Vingiello, A. Borkovec, and J. Shulman, *J. Am. Chem. Soc.*, **77**, 2320 (1955).

A sample of the molecular compound was dehydrogenated in the presence of 10% palladium-charcoal catalyst at a temperature of 220–310°, affording a 70% yield of 2-methyl-9-phenylanthracene (IV), m.p. 120.5–122°. This material gave no depression of melting point when mixed with an authentic sample.⁵

*Oxidation of the molecular compound: 3-methyl-10-phenyl-10-hydroxyanthrone.*¹⁴ One gram of the molecular compound was dissolved in 3.5 ml. of acetic acid and oxidized by dropwise addition of a water solution containing 1.87 g. of chromic anhydride. After the mixture had been heated on the steam bath for 1.5 hr., it was poured into water and the product which separated was crystallized from ethanol, yield 0.85 g. (75%) of granular crystals, m.p. 192–199°. The analytical sample was obtained as colorless granular crystals, m.p. 197.5–199.5° (lit.¹⁵ 198°).

Anal. Calcd. for C₂₁H₁₆O₂: C, 83.98; H, 5.37. Found: C, 83.70; H, 5.35.

The infrared absorption spectrum showed the characteristic absorptions for hydroxyl and carboxyl at 2.79 and 5.98 μ , respectively.¹⁶

2-Methyl-9-phenyl-9,10-dihydroanthracene. From the mother liquor from which the molecular compound had separated, 0.12 g. of long white needles were obtained, m.p. 87–88°. Once recrystallized from ethanol the fine white needles melted at 89.5–90.5°.

Anal. Calcd. for C₁₂H₁₈: C, 93.29; H, 6.71. Found: C, 93.45; H, 6.72.

Ultraviolet absorption maxima were observed at 250, (262), 267, 271, and 276 m μ .

2,3-Dimethyl-9-phenylanthracene (VI). A solution containing 5 g. of *o*-(3,4-dimethylbenzyl)benzoic acid¹⁷ (V) in dry ether was treated with phenyllithium and worked up as in the preparation of 2-methyl-9-phenylanthracene (IV). Recrystallization of the crude product from ethanol afforded 2.42 g. (41%), m.p. 164–166°. The analytical sample crystallized from ethanol as shiny yellow crystals, m.p. 171.5–172.5°.

Anal. Calcd. for C₂₂H₁₈: C, 93.57; H, 6.43. Found: C, 93.36; H, 6.51.

The ultraviolet absorption spectrum had maxima at 228, 259, (316), 332, 348, and 366 m μ .

10-Phenyl-1,2-benzanthracene (VIII). Starting with 5 g. of *o*-(1-naphthylmethyl)benzoic acid (VII),¹⁸ and following the procedure used in the case of the preparation of the analogs (IV and VI), the benzene solution containing the hydrocarbon fraction from the chromatographic separation was concentrated and the product crystallized by addition of ethanol as light yellow plates, m.p. 182–185°, yield 4.06 g. (58%). A sample recrystallized from benzene-ethanol melted at 184–186° (lit.³ 183–184°) and did not depress the melting point of an authentic sample.¹⁹

The ultraviolet absorption spectrum showed maxima at 222, 259, 271, 281, 291, (300), 320, 335, 351, and 366 m μ . This is in good agreement with the reported values.⁸

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(14) L. F. Fieser, *Experiments in Organic Chemistry*, Second Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 233.

(15) A. Guyot and C. Staehling, *Bull. soc. chim. France*, [3] **33**, 1104 (1905).

(16) It was shown that 10-phenyl-10-hydroxyanthrone [E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2638 (1923)] gave absorptions at 2.79 and 5.98 μ .

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

(18) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 1028 (1937).

(19) We are indebted to Frances Montgomery for preparing this sample, using the method of Vingiello, Borkovec, and Shulman (ref. 8).

A Quantitative Study of the Decomposition of *N*-Bromoacetamide in Chloroform and Ethyl Alcohol

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Received August 14, 1957

Reports^{2–4} on the synthesis of *N*-bromoacetamide (NBA) mention its decomposition to form bromine. Also bisacetamide hydrobromide has been reported as a decomposition product⁵ or as a by-product from slow addition reactions of NBA.⁶ The present investigation involves quantitative iodometric analysis and quantitative measurements of hydrogen bromide formation during the decomposition of NBA in chloroform-ethyl alcohol mixtures.

Both the NBA and any bromine formed during decomposition would be expected to react with excess potassium iodide to give triiodide ion. In aqueous acetic acid one mole of NBA has been reported to react with iodide ion to give two equivalents of iodine.⁷ This reaction has now been investigated in water with and without acid present as shown in Table I. With acid present these analytical results show that two equivalents of iodine were formed per mole of NBA while in the absence of acid one equivalent of iodine was formed per mole of NBA. The interaction of the acid with the NBA before the potassium iodide was added caused some loss of oxidizing capacity so that the results were low and relatively unreliable as shown in the second entry of Table I. The best analyses in an acid medium were obtained when the acid was added with the potassium iodide or after the potassium iodide. The average value for the determinations with delayed acid addition was 1.996 ± 0.011 where the precision sets the 95% confidence limits of the average.

These analytical results on NBA are consistent with Equation 1 for the reaction in the absence of acid. When acid was added after this reaction took place further iodine was released according to Equation 2 (see the last two entries of Table I). When acid was added with the potassium iodide the reaction given in Equation 3, which is the sum of Equations 1 and 2, took place. No other equations are consistent with the analytical results in the presence of excess iodide ion. No reaction producing hydrogen ion and iodate ion in the absence of added acid can be considered because the reaction

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(2) A. W. Hofmann, *Ber.*, **15**, 407 (1882).

(3) C. Mauguin, *Ann. chim.*, [8], **22**, 302 (1911).

(4) A. Wohl, *Ber.*, **52**, 51 (1919).

(5) A. Hantzsch and F. E. Dollfus, *Ber.*, **35**, 249 (1902).

(6) R. E. Buckles, *J. Am. Chem. Soc.*, **71**, 1157 (1949).

(7) T. Seliwanow, *Ber.*, **26**, 423 (1893).