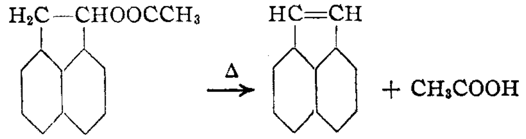
[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

Acenaphthylene and its Polymerization Products

BY RALPH G. FLOWERS AND HARRY F. MILLER

In the course of a program of high polymer research, a study of the polymerization products of acenaphthylene was deemed advisable. Acenaphthylene has been prepared from its dihydro derivative, acenaphthene, by earlier workers, using several different methods.[1] Two improved processes were developed for the production of acenaphthylene (II) during this work. One of these methods was a catalytic vapor phase dehydrogenation of acenaphthene (I) and the other method, according to the scheme[2]



III II

1-Acetoxyacenaphthene (III) was obtained in 88% yield from acenaphthene, glacial acetic acid and Pb_3O_4 according to the procedure of Fieser and Cason.[3]

The polymerization of acenaphthylene by various workers,[4,1b] prior to this investigation, had been carried out by the action of heat alone and by strong acids. The products described by these earlier workers were of relatively low molecular weight, consisting of polymers of from six to twenty-two units per molecule. Acenaphthylene was polymerized in the present work by the action of boron trifluoride gas at low temperatures, and benzoyl peroxide at 80°. The polyacenaphthylene obtained by these methods was of high molecular weight. Several copolymers of acenaphthylene with other polymerizable compounds were also formed.[5]

Experimental

Acenaphthylene (II) by the Dehydrogenation of Acenaphthene (I).—The most efficient vapor phase dehydrogenation of (I) was carried out by passing the acenaphthene vapors, mixed with air, up through a stainless steel column 1.125″ diameter and 30″ high, packed with a catalyst in pellet form,[6] consisting of 10% manganese dioxide and 90% aluminum oxide. A pressure of about 100 mm. was maintained in the system by means of a rotary pump. A condenser of stainless steel was connected to the top of the column and heated with low pressure steam to prevent solidification of the acenaphthylene in the condenser. The product was collected in a water-cooled receiver, having a large surface. Five hundred grams (3.25 mole) of (I) was distilled up through the column, heated to 450–485°. The product was collected and distilled at 93–96° (2 mm.). The solidified distillate, 341 g. (2.25 mole), 70% yield of acenaphthylene, crystallized from alcohol as large yellow plates.

Acenaphthylene (II) from 1-Acetoxyacenaphthene (III).—In the first method used, 208 g. of (III) was passed down through an inclined, heated, quartz tube at the rate of 3 cc. per minute, the tube being maintained at a temperature of 520°. The vapors were diluted with carbon dioxide to reduce side reactions. The product was collected in a receiver, cooled with Dry Ice. This solid material was then pulverized and thoroughly washed with water to remove the acetic acid formed during the reaction.

After drying, the product was distilled under diminished pressure, using hydroquinone as a polymerization inhibitor. The main fraction, 122 g. (82% yield), boiled at 103–105° (3 mm.). The distillate, when recrystallized from ethyl alcohol, crystallizes out as large yellow plates, melting at 92–93°.

A later adaptation of the above method consisted of dropping (III) at the rate of 3 to 5 cc. per minute, down through a vertical stainless steel column, heated to 520° and packed with $^1/_8$″ pellets[5] of 10% copper borate and 90% alumina. A pressure of 2 mm. was maintained in the system. The product was collected in a water-cooled receiver. The exhaust gases from the receiver were passed through a trap containing a solvent, such as diethylene glycol monobutyl ether, to dissolve the particles of sublimation. Seventy-two grams of (III) was converted to 45 g. (87% yield) of acenaphthylene by this method.

Polyacenaphthylene.—Polyacenaphthylene was obtained when 180 g. of (II), dissolved in 500 cc. of chlorobenzene and cooled to 0°, was treated intermittently with boron trifluoride gas over a period of two hours.

Methyl alcohol was added to the dark purple chlorobenzene solution. The polymer, 180 g. (100% yield), precipitated out as a white powder and was filtered with suction from the then colorless filtrate. Molecular weights of over 150,000 were obtained on this material, using the method of Mead and Fuoss[7] for the determination of high molecular weights.

Polymerization of Acenaphthylene (II) with Other Monomers.—Twenty-nine g. of vinylcarbazole, 9 g. of (II) and 0.2 g. of benzoyl peroxide, dissolved in 100 cc. of benzene, were heated for forty-eight hours in an oil-bath. The product, twice precipitated from a benzene solution with methyl alcohol, was a white powder, which did not soften below 200°. A nitrogen content of 5.85% was found, which corresponds to a product containing 19% acenaphthylene polymer. An infrared absorption spectrum taken of this material, as well as of samples of polyvinyl carbazole and polyacenaphthylene, showed that the product was a true copolymer and not merely a mixture of the two separate polymers.

Ten grams of styrene and 5 g. of (II) in 25 cc. of benzene, cooled to 0°, were treated with boron trifluoride gas for fifteen minutes. A white powder, 13.5 g., was obtained by precipitation of the benzene solution with methyl alcohol. This product had a softening point of about 150°.

Nine grams of methyl methacrylate, 1 g. of (II) and 0.05 g. of benzoyl peroxide in 15 cc. of benzene were heated in

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[1] (a) Dziewonski and Rapalski, *Ber.*, **45**, 2491 (1912); (b) Campbell, *J. Chem. Soc.*, **107**, 918 (1915); (c) Lewis, U. S. Patent 1,649,833; *C. A.*, **22**, 433^4 (1928); (d) Jaeger, British Patents 318,617 and 318,618; *C. A.*, **24**, 2145^7 (1930); (e) Wulff, Nicodemus and Treppenhauer, U. S. Patent 2,004,884; *C. A.*, **29**, 5129^4 (1935); (f) Kalle and Co., German Patent 248,994; *C. A.*, **6**, 2850^7 (1912); (g) Monti, *Gazz. chim. ital.*, **68**, 608 (1938); (h) Braun and Bayer, *Ber.*, **59B**, 920 (1926).

[2] Flowers, U. S. Patent 2,390,363; *C. A.*, **40**, 1543^8 (1946).

[3] Fieser and Cason, THIS JOURNAL, **62**, 432 (1940).

[4] (a) Dziewonski and Leyko, *Ber.*, **47**, 1679 (1914); (b) Dolinski and Dziewonski, *ibid.*, **48**, 1930 (1915); (c) Dziewonski and Stolyhwo *ibid.*, **57**, 1531 (1924); (d) Dziewonski and Olesiowna, *I szy Zjazd Chemikow. Polikich*, 58 (1923); *C. A.*, **18**, 982 (1924); (e) Campbell, Cromwell and Hager, THIS JOURNAL, **58**, 1051 (1936).

[5] Miller and Flowers, British Patent Application No. 24441/45.

[6] Catalysts in pellet form were obtained from Harshaw Chemical Company, Cleveland, Ohio.

[7] Mead and Fuoss, *J. Phys. Chem.*, **47**, 59 (1943).

100° oil-bath for seventy-two hours. The product, obtained by precipitation with methyl alcohol, was a white powder. No unreacted acenaphthylene was found. A softening point of approximately 160° was found for this material.

A similar experiment, using vinyl acetate in place of methyl methacrylate, was also carried out. This copolymerization product of (II) with vinyl acetate had a softening point of about 180°.

All of the polymerization and copolymerization products of (II) were found to be soluble in benzene and trichloroethylene, and insoluble in methyl alcohol, acetone and ether.

Acknowledgment.—The authors wish to thank Dr. Kenneth Goldblum of the General Electric Plastics Laboratory, for the molecular weight measurements.

Summary

Two improved methods for the preparation of acenaphthylene have been described. A high molecular weight polymer of acenaphthylene and polymerization products of acenaphthylene with vinylcarbazole, styrene, methyl methacrylate and vinyl acetate, were prepared.

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[Contribution from the Radiation Laboratory and Chemistry Department of the University of California]

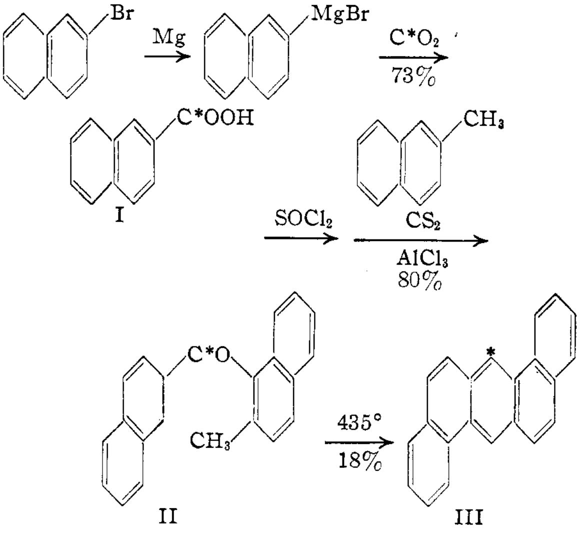
The Synthesis of 1,2,5,6-Dibenzanthracene Labeled in the 9-Position with Carbon-14[1]

By Charles Heidelberger, Phyllis Brewer and William G. Dauben

Ever since the discovery of the carcinogenic power of certain pure polynuclear aromatic hydrocarbons by Kennaway and Hieger[2] in 1930, these substances have been the subject of a considerable number of investigations of the relationship of structure and carcinogenic power. This work was carried on chiefly by Cook and his co-workers in England and by Fieser and his group in America and has resulted in the assay of over a thousand compounds for their ability to produce tumors in mice. The three highly active compounds that have been most widely studied are 20-methylcholanthrene, 3,4-benzpyrene, and 1,2,5,6-dibenzanthracene. Recent studies of the metabolism of dibenzanthracene by R. N. Jones,[3] utilizing ultraviolet absorption as his analytical technique, have given considerable insight into the distribution of this compound in the animal organism. There still remains the question of studying the degradation and other chemical transformations of the carcinogenic hydrocarbons, and long-lived radioactive carbon appeared to offer a method by which these and similar problems may be investigated. Therefore, we have synthesized 1,2,5,6-dibenzanthracene labeled in the 9-position.

The preparation of this compound was carried out according to the procedure of Fieser and Cason.[4] The acid chloride, prepared from β-naphthoic acid, was allowed to react with β-methylnaphthalene and aluminum chloride. The resulting ketone was pyrolyzed at 435°, and dibenzanthracene was obtained. The β-naphthoic acid was prepared by carbonation of the Grignard reagent from β-bromonaphthalene with radioactive carbon dioxide according to the method of Dauben, Reid and Yankwich.[5]

The following is a summary of the reactions employed and the yields obtained[6]



The over-all yield of dibenzanthracene based on carbon dioxide was 11%.

A number of trial runs using non-isotopic carbon dioxide were carried out on the scale employed in the final synthesis, and the over-all yields based on carbon dioxide ranged from 6–12%. The yield in the carbonation reaction was lower than those reported by Dauben, Reid and Yankwich[5] for several other acids, owing to the formation of a considerable neutral fraction from which some dinaphthyl ketone could be isolated. The Friedel and Crafts reaction ran smoothly on a small scale,

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[1] This paper is based on work performed under Contract W-7405-Eng-48 with the Manhattan Project in connection with the Radiation Laboratory and the Department of Chemistry of the University of California.

[2] Kennaway and Hieger, *British Med. J.*, **1**, 1044 (1930).

[3] Jones, Dunlap and Gogek, *Cancer Research*, **4**, 209 (1944), and earlier papers.

[4] Fieser, "Organic Reactions," Vol. I, John Wiley and Sons, N. Y., 1942, p. 151.

[5] Dauben, Reid and Yankwich, in preparation.

[6] The radioactive carbon atom is indicated by an asterisk. It must be remembered that although only one carbon is labeled, owing to the symmetry of the molecule the compound will react as though both of the *meso* positions are marked.