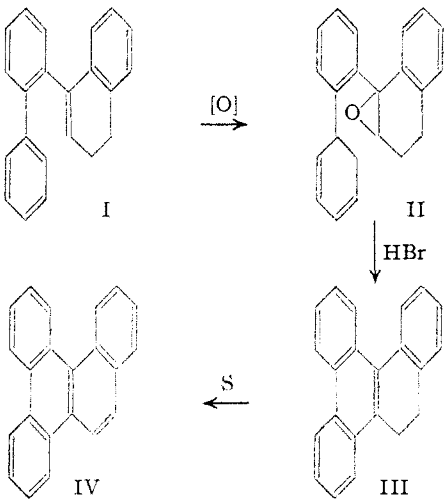
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XIII.[1] 1,2,3,4-Dibenzophenanthrene

BY CHARLES K. BRADSHER[2] AND LORENCE RAPOPORT

Seven methods, at least, have been applied in attempts to synthesize 1,2,3,4-dibenzophenanthrene (IV)[3,4,5] but only one of these successfully. This one,[4] Hewitt's brilliant application of the Pschorr synthesis, affords, at best, a long and arduous route to the hydrocarbon. Since this compound is one of the newest examples of a pentacyclic carcinogenic hydrocarbon,[6] it seemed desirable to devise a more convenient method for its preparation.

Using a modification of a method first applied to the synthesis of 9,10-cyclopenteno- and cyclohexenophenanthrenes,[7] we have now accomplished this end.



Our first attempts to prepare 1-(2-biphenyl)-3,4-dihydronaphthalene (I) were made using the Grignard reagent prepared from 2-iodobiphenyl. With α-tetralone, this Grignard reagent apparently reacted chiefly to produce enolization of the ketone and only a few drops of the product boiled within the expected range.

The known superiority of the aryllithium reagent over the Grignard reagent in its ability to add to sterically hindered carbonyl groups[8] led us to try the reaction of *o*-phenylphenyllithium with tetralone. The reaction product, upon distillation, gave the desired 1-(2-biphenyl)-3,4-dihydronaphthalene (I) in 47% yield. The dihydronaphthalene was next oxidized by the action of perphthalic acid[9] to give the oxide (II), which underwent cyclization in a boiling mixture of hydrobromic and acetic acids to give 1,2,3,4-dibenzo-9,10-dihydrophenanthrene (III). This hydrocarbon was easily dehydrogenated by the action of sulfur yielding 1,2,3,4-dibenzophenanthrene (IV). Our observations concerning the properties of this hydrocarbon are in almost complete agreement with those of Hewett.[4]

Work is in progress on the extension of the synthesis to the preparation of homologs of 1,2,3,4-dibenzophenanthrene.

Experimental

1-(2-Biphenyl)-3,4-dihydronaphthalene (I).—A solution of 70.3 g. of *o*-iodobiphenyl in 150 cc. of dry ether was added slowly to a suspension of 3.64 g. of finely cut lithium in 50 cc. of dry ether. The mixture was refluxed for one hour, then a solution of 29.2 g. of α-tetralone in 100 cc. of dry ether was added slowly. The solution was refluxed for ten hours, then decomposed by the action of ice and water. The ethereal solution was washed, dried, concentrated and the residue distilled under reduced pressure. After a fore-run of biphenyl (24 g.) and tetralone (7.5 g.), the desired product distilled as a viscous oil, b. p. 208–210° (8–9 mm.); yield 26.7 g. (47.5%). This material crystallized on standing to a solid, m. p. 70–73°. It was used in the following reaction without further purification. An analytical sample was obtained by recrystallization from alcohol, yielding white prisms, m. p. 75.5–76.5°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.32; H, 6.56.

Oxide of 1-(2-Biphenyl)-3,4-dihydronaphthalene (II).—The hydrocarbon (3.8 g.) was added to an excess of monoperphthalic acid in ether solution. After twelve hours, the acids were removed by extraction with sodium bicarbonate solution and the ethereal solution evaporated leaving the crude oxide in a condition suitable for the next step. The oxide crystallized on standing and a sample was purified for analysis by repeated recrystallization from ether–petroleum ether. This gave colorless prisms, m. p. 98–99°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.68; H, 5.96.

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[1] For the previous communication of this series see THIS JOURNAL, 65, 1643 (1943).

[2] National Research Fellow (participating basis), 1941–1942.

[3] Bergmann and Bergmann, THIS JOURNAL, 59, 1443 (1937).

[4] Hewett, *J. Chem. Soc.*, 193 (1938).

[5] Bergmann, THIS JOURNAL, 60, 1798 (1938).

[6] Hewett, *J. Chem. Soc.*, 1286 (1938).

[7] Bradsher, THIS JOURNAL, 61, 3131 (1939).

[8] *E. g.*, Wittig and Leo, *Ber.*, 64, 2395 (1931); Wittig and Petri, *ibid.*, 68, 924 (1935). For an excellent review on organolithium compounds, see Wittig, *Angew. Chem.*, 53, 241 (1940).

[9] When perbenzoic acid was used, the olefin showed a tendency to combine with more than one mole of the oxidant resulting in a greatly decreased yield of the final product. This phenomenon has been observed in the case of another related olefin, a report of which will be the subject of another communication.

1,2,3,4-Dibenzo-9,10-dihydrophenanthrene (III).—The crude oxide was dissolved in 45 cc. of acetic acid, 30 cc. of 34% hydrobromic acid added and the mixture refluxed for twenty-four hours. At the end of this period, the solution was diluted and the product taken up in benzene. The benzene solution was freed from acid and then evaporated. Upon vacuum distillation of the residue, a pale yellow resin was obtained. This material could not be crystallized and so was used directly in the dehydrogenation reaction. A sample of the dihydro compound was converted to the picrate in acetic acid solution giving dark red needles, m. p. 135–136°.

Anal. Calcd. for $C_{28}H_{19}N_3O_7$: N, 8.25. Found: N, 8.16.

1,2,3,4-Dibenzophenanthrene (IV).—The crude cyclization product was heated at 200–220° for thirty minutes with 0.4 g. of sulfur and then at 250° for an additional one and one-half hours. A pinch of zinc dust was added and the mixture heated for fifteen minutes longer. At the end of this heating, the product was vacuum-distilled directly from the reaction flask. The distillate, once recrystallized from acetic acid gave 1.93 g. (51% calculated from the dihydronaphthalene) of yellow crystals, m. p. 111.5–114°. Recrystallized, the product melted at 115–116° (Hewett[4] 114.5–115°).

Anal. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 95.26; H, 4.96.

The hydrocarbon formed a red picrate, m. p. 139.5–140.5° (Hewett[4] 140–140.5°).

Oxidation with sodium dichromate gave a red quinone, m. p. 238–240° (Hewett[4] 237–238°).

Summary

The olefin oxide type of cyclization has been found to afford a simple and convenient method for the preparation of 1,2,3,4-dibenzophenanthrene.

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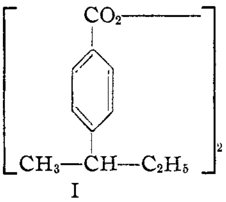
Optically Active Acyl Peroxides. Preparation, Decomposition, and Use as Catalysts for Vinyl Polymerization[1]

BY C. S. MARVEL, ROBERT L. FRANK[2] AND ERHARD PRILL[3]

This work on optically active acyl peroxides was undertaken in order, (1) to make use of their optical activity in following the kinetics of their thermal decomposition, and (2) to see if asymmetric polymerization of vinyl monomers could be accomplished to yield optically active polymers. Two optically active acyl peroxides, *l*-*p*-*s*-butylbenzoyl peroxide (I) and *l*-*o*-carbomenthoxbenzoyl peroxide (II), have been synthesized for these studies from the corresponding acid chlorides by treatment with aqueous sodium peroxide.



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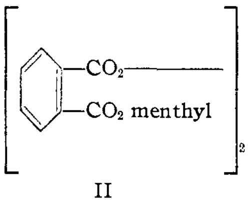

II

p-*s*-Butylbenzoic acid was prepared by two methods both starting with *p*-bromo-*s*-butylbenzene. It was obtained in 56% yield by reaction of the Grignard reagent with carbon dioxide and in 64.6% yield by the Rosenmund–von Braun method using cuprous cyanide,[4] with subsequent hydrolysis of the *p*-*s*-butylbenzonitrile.

The resolution of *p*-*s*-butylbenzoic acid was accomplished, after considerable experimentation, through the quinine salt. An acid with a specific rotation of −23.5° was recovered from the quinine salt after repeated recrystallization from methanol. Regeneration of the acid from the salt obtained by concentrating the mother liquors yielded an acid of specific rotation +18.2°. Attempted resolutions by means of the salts with brucine, cinchonidine and strychnine all gave poor results.

l-Menthyl acid phthalate was prepared according to the method of Pickard and Littlebury.[5]

The kinetics of the thermal decomposition of acyl peroxides in solution has been the object of a number of investigations.[6-10] In each instance the change in peroxide concentration was followed by iodometric determination of the remaining per-

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(1) This is the fifteenth communication on vinyl polymers. For the fourteenth see THIS JOURNAL, **64**, 2356 (1942).

(2) Du Pont Post-Doctorate Research Assistant, University of Illinois, 1940–1941.

(3) Du Pont Post-Doctorate Research Assistant, University of Illinois, 1941–1942.

(4) von Braun and Manz, *Ann.*, **488**, 111 (1931).

(5) Pickard and Littlebury, *J. Chem. Soc.*, **101**, 113 (1912).

(6) Walker and Wild, *ibid.*, 1132 (1937).

(7) Berezovskaya, Semikhatova and Ostrer, *Ber. Inst. physik. Chem. Akad. Wiss. Ukr. S. S. R.*, **9**, 3–16 (1938); *C. A.*, **34**, 2688 (1940).

(8) Berezovskaya and Semikhatova, *ibid.*, **11**, 51–9 (1938); *C. A.*, **34**, 3571 (1940).

(9) D. J. Brown, THIS JOURNAL, **62**, 2657 (1940).

(10) Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).