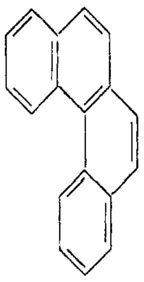
[FROM THE SCIENTIFIC DEPARTMENT, ISRAELI MINISTRY OF DEFENCE]

A NEW SYNTHESIS OF 3,4-BENZOPHENANTHRENE

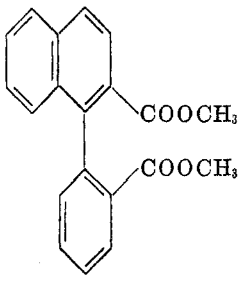
ERNST D. BERGMANN AND ZVI PELCHOWICZ

Received September 21, 1953

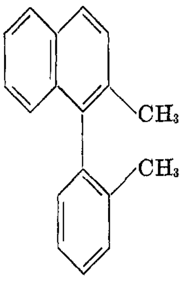
The present investigation adds to the known methods of the synthesis of the system of 3,4-benzophenanthrene (1–9a) a new one which appears especially suitable for the preparation of derivatives of I. Its starting point is the dicarbomethoxy derivative (II) of 1-phenylnaphthalene; the corresponding di-(bromomethyl) compound is transformed into the 9,10-dihydro-derivative of I with phenyllithium, a method (10–13) which has been employed successfully for the synthesis of 3,4,5,6-dibenzophenanthrene (14).



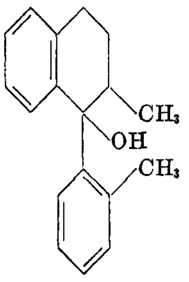
I



II



III



IV

By a mixed Ullmann condensation of methyl 1-bromonaphthalene-2-carboxylate and methyl 2-iodobenzoate, II was obtained in 25% yield. Reduction of II with lithium aluminum hydride, followed by reaction with phosphorus tribromide and phenyllithium, gave 9,10-dihydro-3,4-benzophenanthrene in 51% yield. The palladium dehydrogenation of the latter gave a 95% yield of I.

In a variation of this route, 1-(*o*-tolyl)-2-methylnaphthalene (III) was prepared by reaction between 2-methyl-1-tetralone and *o*-tolyllithium, followed by dehydration of the carbinol (IV) and dehydrogenation with sulfur. When III was treated with N-bromosuccinimide and the crude reaction product was subjected to the reaction with phenyllithium, a bromine-containing material was obtained, from which, after dehydrogenation, 3,4-benzophenanthrene was isolated only in poor yield. Evidently, III also undergoes nuclear bromination which is not altogether without parallel (15, 16).

The spectrum of 9,10-dihydro-3,4-benzophenanthrene (Fig. 2) is characteristically different from that of III. In addition to the band at 2300 Å, it shows strong absorption *and fine structure* in the region between 3000 and 3400 Å. This is most likely due to the fact that the ethane bridge brings the naphthalene and the benzene rings into one plane, and, therefore, into a state of conjugation. It is also interesting to compare this spectrum with that of 4,5-dimethyl-9,10-dihydrophenanthrene (13) which has its main absorption band at 2600 Å and only a very weak band (log ϵ 1.9) at 3100 Å. As this compound is distorted by the

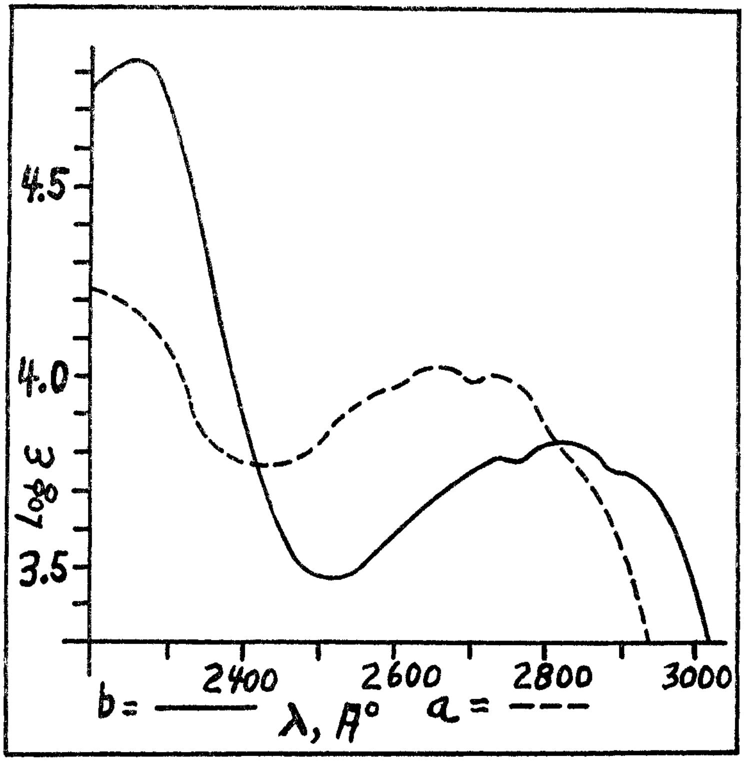


FIG. 1. ULTRAVIOLET SPECTRA OF 1-(*o*-tolyl)-2-methyl-3,4-dihydronaphthalene (Curve a) and 1-(*o*-tolyl)-2-methylnaphthalene (III) (Curve b), both in alcohol.

mutual interference of the two methyl groups, it is concluded that in the dihydroderivative of I no such interference exists.

EXPERIMENTAL

1-(o-Tolyl)-2-methyl-3,4-dihydronaphthalene. An ethereal solution of 15 g. of 2-methyl-1-tetralone (17) was slowly added to a solution of *o*-tolyllithium, prepared from 1.6 g. of

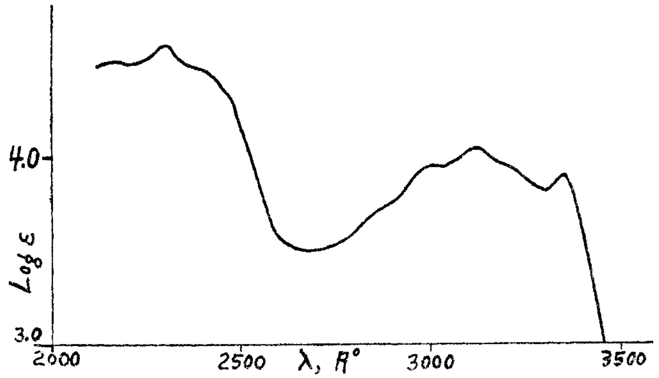


FIG. 2. ULTRAVIOLET SPECTRUM OF 9,10-DIHYDRO-3,4-BENZOPHENANTHRENE, IN ALCOHOL.

lithium and 18 g. of *o*-bromotoluene in 100 ml. of ether. The exothermic reaction was completed by heating the mixture for 1 hour under reflux. The product (IX) was decomposed with ice-cold dilute sulfuric acid and the oil obtained upon evaporation of the solvent was heated at 100° for 30 minutes with a crystal of iodine. Distillation in a vacuum (1.3 mm.) gave 5.5 g. (37%) of unchanged 1-methyl-2-tetralone and 13.5 g. of 1-(*o*-tolyl)-2-methyl-3,4-dihydronaphthalene (at 139–142°). Calculated on the ketone entered into reaction, the yield is quantitative.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.3; H, 7.7.
Found: C, 92.1; H, 7.8.

The absorption spectrum of the hydrocarbon (Fig. 1, a) shows a double maximum at about 2700 Å; it resembles the spectrum of 1,1-diphenylethylene (18).

1-(o-Tolyl)-2-methylnaphthalene (III). The foregoing hydrocarbon (11 g.) was heated with sulfur (1.67 g.) at 190° until the evolution of hydrogen sulfide ceased, and the product was distilled directly under 0.75 mm. pressure. The hydrocarbon (III) boiled at 133–136° as a slightly yellowish, viscous oil. Yield, 9.5 g. (86%).

Anal. Calc'd for $C_{18}H_{16}$: C, 93.0; H, 7.0.
Found: C, 92.8; H, 7.1.

The absorption spectrum of III (Fig. 1, b) shows a slight shift of the maximum towards the visible. It is similar to the spectrum of 1-phenylnaphthalene (19) and 1-(*o*-tolyl)naphthalene (19), but shows a still greater departure from the conjugation between the two ring systems.

Methyl 1-(o-carbomethoxyphenyl)naphthalene-2-carboxylate (II). The mixture of 30 g. of methyl 1-bromo-2-naphthoate and 100 g. of methyl *o*-iodobenzoate with 40 g. of copper powder was heated at 190–200° for three hours and was extracted with benzene. The benzene residue was fractionated and the part distilling at 200–205°/0.75 mm. was collected. Yield, 9 g. (25%).

Anal. Calc'd for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0.
Found: C, 74.8; H, 5.1.

9,10-Dihydro-3,4-benzophenanthrene. The solution of 6.8 g. of II in 50 cc. of anhydrous ether was added slowly to 1.5 g. of lithium aluminum hydride in 150 cc. of the same solvent. The mixture was refluxed for one hour and worked up as usual. The colorless diprimary alcohol so obtained did not crystallize; to its solution in 200 ml. of benzene there were added a few drops of pyridine and 4.5 ml. of phosphorus tribromide. After heating for 2 hours at 60°, the solution was washed thoroughly with water, sodium bicarbonate solution, and again water and concentrated. The 1-(*o*-bromomethylphenyl)-2-bromomethylnaphthalene so obtained (8.3 g.) was a brownish viscous oil which was treated further as follows:

To its solution in 150 ml. of anhydrous ether, a solution of phenyllithium, prepared from 0.36 g. of lithium and 4.0 g. of bromobenzene in 40 cc. of ether, was added within 30 minutes. The reaction was completed by refluxing for one hour and the mixture worked up as usual. The product was distilled and gave a fraction boiling at 200–205°/1.7 mm., which remained liquid, but which gave a well-defined *picrate* in quantitative yield, as fine red-brown needles from alcohol, m.p. 93–94°. The yield of the hydrocarbon was 2.5 g. (51%).

Anal. Calc'd for $C_{18}H_{14}$: C, 93.9; H, 6.1.
Found: C, 93.8; H, 6.3.

3,4-Benzophenanthrene (I). The mixture of 0.7 g. of the foregoing hydrocarbon and 0.2 g. of palladium-charcoal (10%) was heated at 300° for 4 hours. The product was extracted with benzene and the solution was concentrated. The residue crystallized upon addition of a few drops of alcohol. Yield, 0.67 g. (95%). M.p. 68°; m.p. of the *picrate* 126–127°, as indicated in the literature (10).

SUMMARY

A new synthesis of 3,4-benzophenanthrene (I) is described, starting from methyl 1-(*o*-carbomethoxyphenyl)naphthalene-2-carboxylate (II) and using

the reaction of the corresponding bis-bromomethyl compound with *phenyllithium* for the construction of the fourth ring.

TEL-AVIV, ISRAEL

REFERENCES

(1) COOK, *J. Chem. Soc.*, 2524 (1931).
(2) HEWETT, *J. Chem. Soc.*, 1286 (1938).
(3) I. G. FARBEN, British Patent 459,108 [*Chem. Abstr.*, **31**, 4136 (1937)].
(4) GANGULY, *Science and Culture*, **7**, 320 (1941) [*Chem. Abstr.*, **36**, 3172 (1942)].
(5) HEWETT, *J. Chem. Soc.*, 596 (1936).
(6) NEWMAN AND JOSHEL, *J. Am. Chem. Soc.*, **60**, 485 (1938); NEWMAN AND WOLF, *J. Am. Chem. Soc.*, **74**, 3225 (1952).
(7) BACHMANN AND EDGERTON, *J. Am. Chem. Soc.*, **62**, 2970 (1940).
(8) F. BERGMANN AND SZMUSZKOWICZ, *J. Am. Chem. Soc.*, **69**, 1367 (1947).
(9) SZMUSZKOWICZ AND MODEST, *J. Am. Chem. Soc.*, **70**, 2542 (1948).
(9a) TATEVORYAN AND ZABAYAN, *Chem. Abstr.*, **47**, 4869 (1953).
(10) HALL AND TURNER, *Nature*, **163**, 537 (1949).
(11) HALL, LESSLIE, AND TURNER, *J. Chem. Soc.*, 711 (1950).
(12) HALL AND TURNER, *J. Chem. Soc.*, 3072 (1951).
(13) E. BERGMANN AND PELCHOWICZ, *J. Am. Chem. Soc.*, **75**, 2663 (1953).
(14) E. BERGMANN AND SZMUSZKOWICZ, *J. Am. Chem. Soc.*, **73**, 5153 (1951).
(15) BUU-HOÏ, *Ann.*, **556**, 1 (1944); BUU-HOÏ AND LECOCQ, *Compt. rend.*, **226**, 87 (1948).
(16) BARNES, *J. Am. Chem. Soc.*, **70**, 145 (1948).
(17) SCHROETER, *Ber.*, **51**, 1600 (1918).
(18) SHOEPFLE AND RYAN, *J. Am. Chem. Soc.*, **54**, 3687 (1932); JONES, *J. Am. Chem. Soc.*, **65**, 1818 (1943).
(19) FRIEDEL AND ORCHIN, *Ultraviolet Spectra of Aromatic Compounds*, No. 290, 291; John Wiley and Sons, New York, 1951.