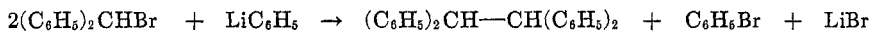


A SYNTHESIS OF 9,10-DIPHENYLPHENANTHRENE

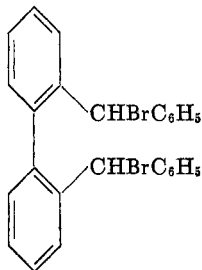
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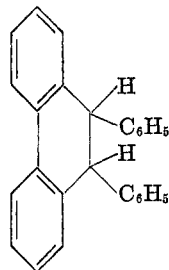
The observation of Wittig and Witt (1) that benzyl bromide reacts with phenyllithium to give dibenzyl has been applied recently to the synthesis of 9,10-dihydrophenanthrenes from "double" benzyl bromides of the 2,2'-bis-(bromomethyl)biphenyl type (2-7). As Wittig and Witt (1) have also shown that diphenylmethyl bromide and phenyllithium afford *sym*-tetraphenylethane:



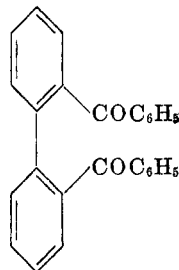
it seemed interesting to investigate whether the bis-secondary bromide (I) would react analogously but intramolecularly, yielding 9,10-dihydro-9,10-diphenylphenanthrene (II). This is, indeed, the case.



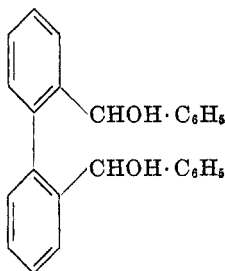
I



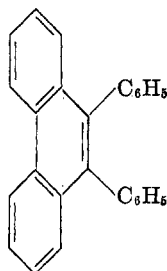
II



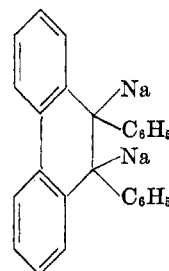
III



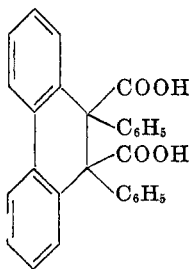
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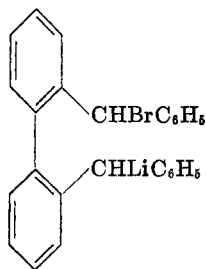
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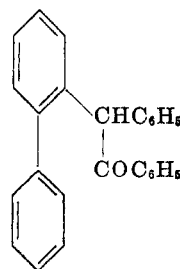
VI



VII



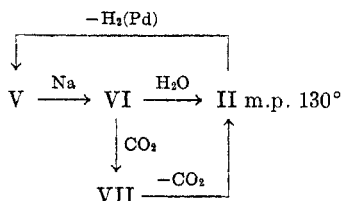
VIII



IX

2,2'-Dibenzoylbiphenyl (III) was reduced by lithium aluminum hydride in 65% yield to the corresponding disecundary alcohol (IV) and the latter was converted into I with phosphorus tribromide. The conversion of I into II by treatment with phenyllithium was effected with quantitative yield, and the structure (II) of the reaction product, m.p. 168–169°, was proven by dehydrogenation to 9,10-diphenylphenanthrene (V).

Schlenk and Bergmann (8) described a 9,10-dihydro-9,10-diphenylphenanthrene of m.p. 130°, which was formed by the addition of sodium metal to 9,10-diphenylphenanthrene (V) and hydrolysis of the disodium-addition product (VI). The carbonation of this addition product gives an acid (VII) which could be decarboxylated to the same 9,10-dihydro-compound of m.p. 130°.



It appears that the two compounds (II) of m.p. 168–169° and m.p. 130°, respectively, are *cis-trans*-isomers. As expected, their UV spectra (Fig. 1) are practically identical; also the infrared spectra show very small differences, *viz.* between 2800 and 2900 cm^{-1} , between 1360 and 1370 cm^{-1} and at about 1010 cm^{-1} . While it is impossible on the basis of the available evidence to assign definite configurations to the two isomers, the following conjecture seems likely: It can be assumed (9) that II is formed from I *via* an intermediary of type VIII. Due to the electrostatic attraction between the lithium and the bromine atoms, the two hydrogen atoms of II in the transition state will be near to each other, so that the compound of m.p. 168–169° would be the *cis*-form. On the other hand, the sodium atoms in VI are likely to be in the *trans*-configuration. Hydrolysis, thus, would give the *trans*-form of m.p. 130°—occurring either without inversion or with inversion at both carbon atoms. The dicarboxylic acid (VII) would be, by the same reasoning, the *trans*-form. (The model shows that the *trans*-form is capable of giving an anhydride. The *trans*-form of $\Delta^3,5$ -dihydrophthalic acid gives the *cis*-anhydride (10), but the acid (VII) cannot undergo an analogous isomerization as the enolizable hydrogen atoms are missing.)

9,10-Diphenylphenanthrene does not give a molecular compound with either of its dihydro-derivatives, as it has been observed for 9,10-diphenylanthracene and 9-phenylanthracene (11).

In view of the easy availability of 2,2'-diarylbiphenyls, the method described constitutes a new synthesis of 9,10-diarylphenanthrenes, which so far have been obtained by reduction of the 9,10-dihydroxy-9,10-diarylphenanthrenes (12) and by cyclodehydration of compounds of type (IX) (13).

EXPERIMENTAL

2,2'-Bis-(α -hydroxybenzyl)biphenyl (IV). To a solution of 3 g. of lithium aluminum hydride in 300 ml. of anhydrous ether, there was slowly added 10 g. of finely powdered 2,2'-

dibenzoylbiphenyl (12). The mixture was refluxed for 8 hours and cautiously was decomposed with ice and dilute sulfuric acid. The ethereal layer was washed with sodium bicarbonate solution and water, dried, and evaporated. The oily residue was triturated with a mixture of benzene and petroleum ether and the crystalline product (6.5 g.; 65%) was filtered and recrystallized from benzene. M.p. 193.5–194.5°.

Anal. Calc'd for $C_{26}H_{22}O_2$: C, 85.2; H, 6.0.

Found: C, 85.0; H, 5.9.

2,2'-Bis-(α -bromobenzyl)biphenyl (I). The dialcohol (IV) (7 g.) was dissolved in 250 ml. of warm benzene; at 50°, some drops of pyridine and then 20 g. of phosphorus tribromide, dissolved in an equal volume of benzene, were added. After two hours at 50°, the reaction was complete. The solution was washed with water until the washings were neutral, then with sodium bicarbonate solution, and again with water, dried, and concentrated. The solid residue weighed 8.4 g. (yield, 90%). Recrystallization from petroleum ether (b.p. 60–90°) gave two types of crystals: prismatic rods and rhombohedra. The former melted at 145–146° (slight sintering at 123°), the latter began to sinter at 123° and melted completely at 145°. It has not been decided whether the two products were dimorphous forms of the same compound or diastereoisomers which were easily interconvertible. Such interconversion has been observed for the α, β -dibromodibenzyls, $C_6H_5CHBr-CHBrC_6H_5$ (14).

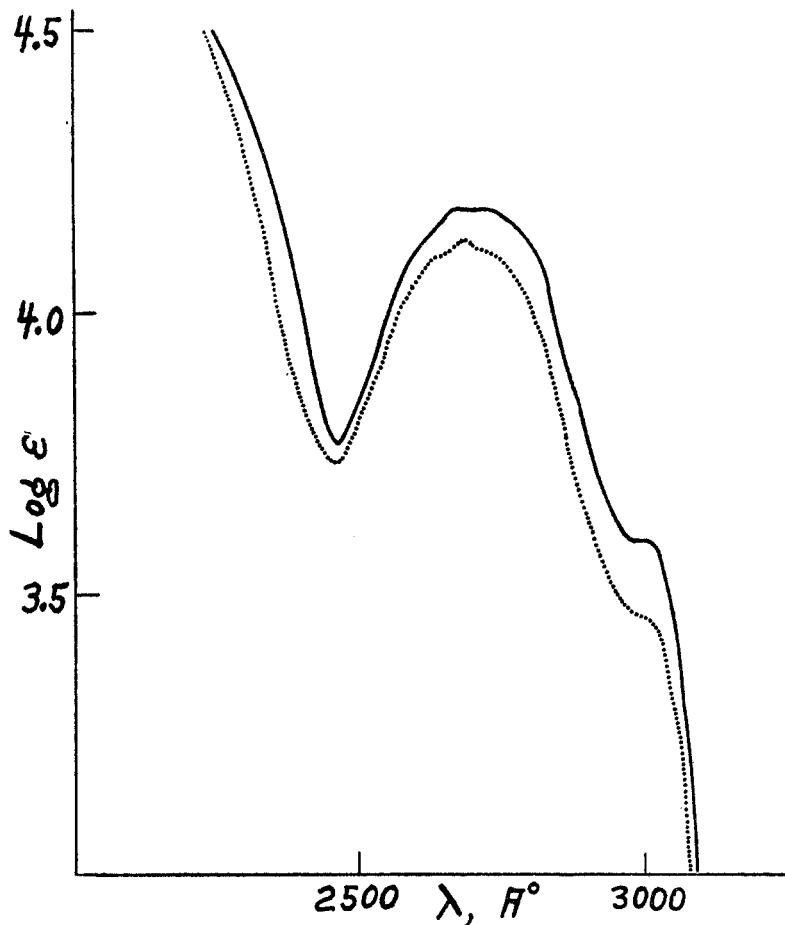


FIG. 1. ULTRAVIOLET SPECTRA OF 9,10-DIPHENYL-9,10-DIHYDROPHENANTHRENES (II), in alcoholic solution. —, Isomer, m.p. 130°; ·····, Isomer, m.p. 168–169°.

Anal. Calc'd for $C_{26}H_{20}Br_2$: Br, 32.5. Found: Br, 32.4.

9,10-Dihydro-9,10-diphenylphenanthrene, m.p. 168–169° (II). A solution of phenyllithium, prepared from 0.25 g. of lithium and 2.8 g. of bromobenzene in 25 ml. of ether, was added in a nitrogen atmosphere and with vigorous agitation, to a solution of 4.5 g. of the dibromide (I) in 120 cc. of benzene during 15 minutes. The slightly exothermic reaction was complete after a further half hour. The usual work-up gave colorless crystals which were triturated with petroleum ether and were recrystallized from a mixture of benzene and ethanol. Yield, 3 g. (100%); m.p. 168–169°.

Anal. Calc'd for $C_{26}H_{20}$: C, 94.0; H, 6.0.

Found: C, 93.8; H, 6.0.

Dehydrogenation of II, m.p. 168–169°. The foregoing substance (0.63 g.) was heated with 10% palladium-charcoal (0.20 g.) at 300° for four hours in the apparatus described by Fieser (15). Recrystallization of the solid product from benzene-ethanol gave 0.40 g. of 9,10-diphenylphenanthrene, m.p. 235° [literature (16), m.p. 235°], which was identified by a mixture melting point with an authentic specimen. From the mother liquor 0.28 g. of starting material was recovered, which was subjected to a renewed dehydrogenation. Total yield, 0.62 g. (quantitative).

Decarboxylation of 9,10-dihydro-9,10-diphenylphenanthrene-9,10-dicarboxylic acid (VII). The anhydride of the acid was prepared as described by Schlenk and Bergmann (8). The acid was heated in the presence of an equal amount of copper powder in boiling quinoline for five hours. The solution was cooled and poured into dilute sulfuric acid. The solid product which separated was dissolved in benzene and the solution was washed with bicarbonate solution and water, dried, and evaporated. Recrystallization of the solid residue gave a little 9,10-diphenylphenanthrene (V), m.p. 235°, obviously formed by simultaneous dehydrogenation, and the prisms of 9,10-dihydro-9,10-diphenylphenanthrene of m.p. 130°.

SUMMARY

2,2'-Bis-(α -bromobenzyl)biphenyl (I) reacts with phenyllithium to give 9,10-diphenyl-9,10-dihydrophenanthrene (II). The product is an isomer of the hydrocarbon prepared previously from 9,10-diphenylphenanthrene by the addition of sodium metal and the subsequent hydrolysis of the addition product. A tentative assignment of steric formulae to the two isomerides is proposed.

TEL-AVIV, ISRAEL

REFERENCES

- (1) WITTIG AND WITT, *Ber.*, **74**, 1474 (1941).
- (2) HALL AND TURNER, *Nature*, **163**, 537 (1949).
- (3) HALL, LESSLIE, AND TURNER, *J. Chem. Soc.*, 711 (1950).
- (4) HALL AND TURNER, *J. Chem. Soc.*, 3072 (1951).
- (5) BERGMANN AND SZMUSZKOVICZ, *J. Am. Chem. Soc.*, **73**, 5153 (1951).
- (6) BERGMANN AND PELCHOWICZ, *J. Am. Chem. Soc.*, **75**, 2663 (1953).
- (7) WITTIG AND ZIMMERMANN, *Ber.*, **86**, 629 (1953).
- (8) SCHLENK AND BERGMANN, *Ann.*, **463**, 1 (1928).
- (9) BERGMANN AND PELCHOWICZ, *J. Am. Chem. Soc.*, **75**, 4281 (1953).
- (10) NEVILLE, *J. Chem. Soc.*, **89**, 1744 (1906).
- (11) HAACK, *Ber.*, **62**, 1771 (1929).
- (12) WERNER AND GROB, *Ber.*, **37**, 2887 (1904).
- (13) See: BRADSCHER, *Chem. Revs.*, **38**, 447 (1946).
- (14) WISLICENUS AND SEELER, *Ber.*, **28**, 2694 (1895).
- (15) FIESER, *Experiments in Organic Chemistry*, 2nd Edition, p. 461–464, D. C. Heath and Co., Boston, Mass., 1941.
- (16) KLINGER AND LONNES, *Ber.*, **29**, 2152 (1896).