# THE REACTION OF LITHIUM ALUMINUM HYDRIDE WITH DIBIPHENYLENEETHYLENE, DIBIPHENYLENEBUTADIENE, AND DIBIPHENYLENEBUTATRIENE. FULVENES AND THERMOCHROMIC ETHYLENES. PART 27[1]

D. LAVIE AND E. D. BERGMANN

Amongst the fulvenes which exhibit the unusual feature of a polar character of their semicyclic double bond (1–4), dibiphenyleneethylene (I) represents a still more puzzling type of hydrocarbon. Its symmetry overcompensates the polarity which its fulvene character demands. Nevertheless, dibiphenyleneethylene adds lithium-organic compounds (5) and even certain Grignard reagents, such as benzylmagnesium chloride (6), and is capable of serving as acceptor in the Michael reaction (7, 8).

This reactivity is probably due to the very high polarizability of I. It has been found that its electronic polarization (molecular refraction) is 32% higher than the sum of the atomic (or bond) equivalents and that this effect persists into the infrared, *i.e.*, into a region far removed from the absorption bands (9, 10). *I is not highly polar, as the fulvenes, but highly polarizable* (11, 12). To the reactions of I which are due to this high polarizability has recently been added that with lithium aluminum hydride (12). The two reactants form a colored metal-organic product which upon hydrolysis gives dibiphenyleneethane (II, R = H). Assuming that—at least formally—the reacting species is Li^+H^- (12, 13), the colored intermediate should be 9-lithiodibiphenyleneethane (II, R = Li). This has now been proven by the observation that the colored intermediate reacts with benzyl chloride to give the known (6) 9-benzyldibiphenyleneethane (II, R = $CH_2C_6H_5$).
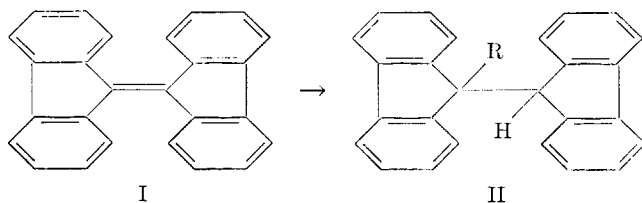
It seemed interesting to extend this study to higher analogs of dibiphenyleneethylene (I), *viz.*, 1,4-dibiphenylenebutadiene (III) and 1,4-dibiphenylenebutatriene (V), representing a diene and a cumulene (14) system, respectively. Their investigation was expected to show whether the behavior of I may not be due to its peculiar geometric structure, in which the *ortho*-hydrogen atoms interfere with the planarity of the molecule (15).

Dibiphenylenebutadiene (III) adds *two moles* of lithium aluminum hydride; hydrolysis of the alkali-organic intermediate gives 1,4-dibiphenylenebutane

---

[1] Part 26: Bull. Soc. chim. France, **20,** in press (1953).

(IV, R = H), which is available by an unambiguous synthesis, *viz.* the reduction
of III with sodium metal and amyl alcohol (16, 17). The presence of two lithium
atoms in the intermediate, which may be formulated as IV, R = Li, is proven
by its reaction with benzyl or *p*-chlorobenzyl chloride, leading to 1,4-dibenzyl-
and 1,4-di-(*p*-chlorobenzyl)-1,4-dibiphenylenebutane, respectively (IV, R =
$CH_2C_6H_5$; R = $CH_2C_6H_4Cl$). The infrared spectrum of (IV, R = $CH_2C_6H_4Cl$)
shows the absence of aliphatic double bonds (in the 950–1000 cm^{-1} region);
its ultraviolet spectrum (Fig. 1, Table I) is practically identical with that of
fluorene (18). In order to prove the formulae, 1,4-dibenzyl-1,4-dibiphenylene-
butane (IV, R = $CH_2C_6H_5$) and the corresponding 1,4-di-*p*-chlorobenzyl com-
pound were prepared by the successive action of butyllithium and benzyl chloride
(or *p*-chlorobenzyl chloride) on IV, R = H. The chloro compounds obtained by
the two methods did not show any mutual depression of their melting points;
moreover, they gave the same X-ray powder diagrams (Fig. 2, No. 1 and 2).
Similarly, Wittig, Davis, and Koenig (19) had prepared IV, R = $CH_2C_6H_5$, from

TABLE I
ULTRAVIOLET SPECTRA [maxima in Å (log E_m)]

Fluorene	2650 (4.28)	2890 (3.79)	3000 (3.92)
1,4-Di-(*p*-chlorobenzyl)-1,4-dibiphenylene-butane (IV, R = $CH_2C_6H_4Cl$)	2670 (4.54)	2925 (4.09)	3040 (4.24)
1,4-Di-(*p*-chlorobenzyl)-1,4-dibiphenylene-2-butene (VI, R = $CH_2C_6H_4Cl$)	2690 (4.58)	2920 (4.10)	3040 (4.22)

IV, R = H, with phenyllithium and benzyl chloride, and also by dehalogenation
of 9-benzyl-9-bromomethylfluorene.

III   IV
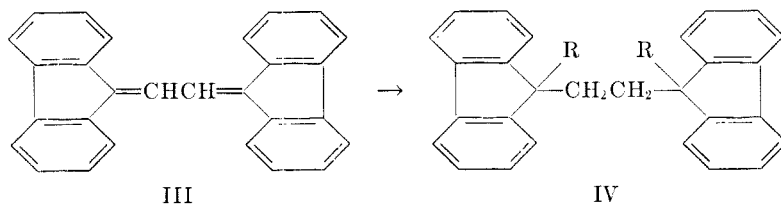
Also 1,4-dibiphenylenebutatriene (V) adds *2 moles* of lithium aluminum
hydride. The expected formula (VI, R = Li) for the colored addition product
has been proven by its reaction with benzyl or *p*-chlorobenzyl chloride. According
to analysis and molecular weight, the reaction products (VI, R = $CH_2C_6H_5$;
$CH_2C_6H_4Cl$) contained *two* benzyl (*p*-chlorobenzyl) groups; in their infrared
spectrum the double bond absorbed distinctly at 957 cm^{-1}, indicating *trans*-
configuration. No absorption was observed at 1650 cm^{-1}, probably because of the
symmetry of the molecules [See McMurry and Thornton (20)]. The ultraviolet
spectrum of (VI, R = $CH_2C_6H_4Cl$) (Fig. 1; Table I) is—expectedly—practically
identical with that of IV, R = $CH_2C_6H_4Cl$, and that of fluorene.

In accordance with these deductions, hydrolysis of the adduct from V gave
1,4-dibiphenylene-2-butene (VI, R = H), which had been prepared before by
Wislicenus (16).

It is noteworthy, but may well be taken as proof for the constitutional similarity of IV and VI (R = $CH_2C_6H_5$; $CH_2C_6H_4Cl$), that the corresponding pairs—
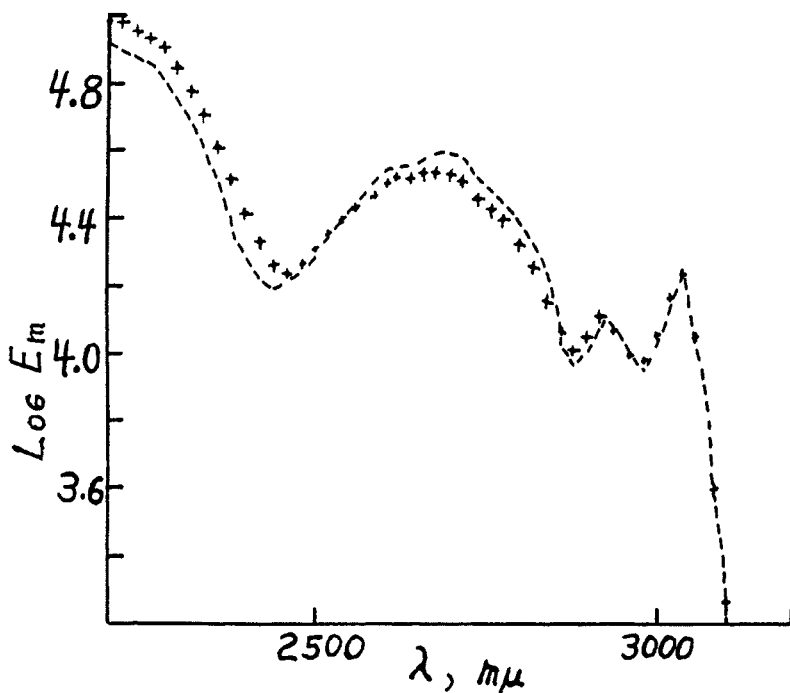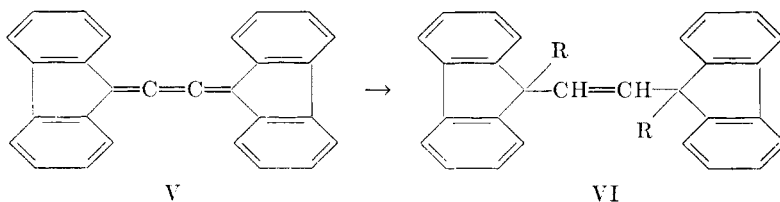

FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA IN DIOXANE. $(++++)$1,4-Di-(p-chlorobenzyl)-1,4-dibiphenylene-2-butene; (- - - - - -)1,4-di-(p-chlorobenzyl)-1,4-dibiphenylenebutane.

although definitely differentiated by the presence or absence of the central double bond—do not show the phenomenon of mutual melting point depression.

Finally, the structure of VI, R = $CH_2C_6H_4Cl$, was proven by its synthesis from 1,4-dibiphenylene-2-butene (VI, R = H) with butyllithium and p-chlorobenzyl chloride. The products obtained by the two methods not only had identical melting points and gave no depression of the melting point on mixing, but they proved identical under the polarizing microscope and gave the same X-ray powder diagram (Fig. 2, No. 3 and No. 4). As by-product in the synthesis, invariably small amounts of dibiphenylenebutadiene (III) were obtained which was identified by mixture m.p. and the absorption spectrum [Fig. 3; see E. Bergmann and Hirshberg, (21)]. It is assumed that the addition product (VI,
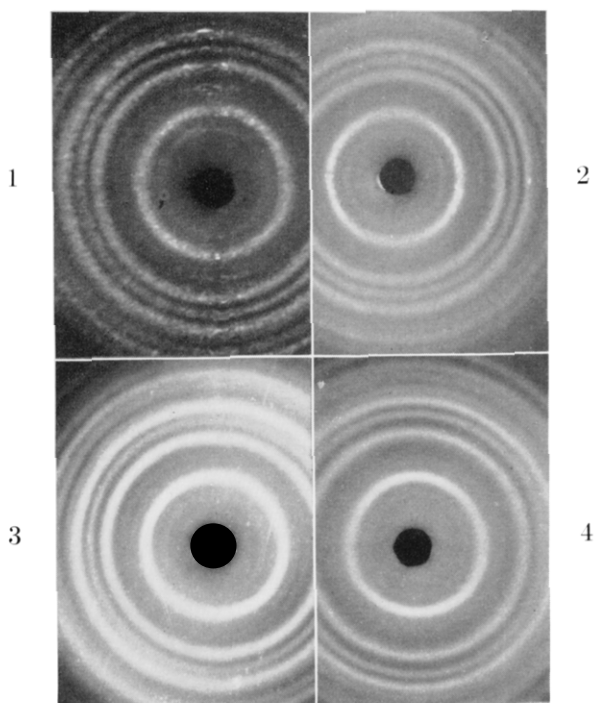
FIG. 2. X-RAY POWDER DIAGRAMS

No. 1: Reaction product from 1,4-dibiphenylenebutadiene (III), lithium aluminum hydride, and *p*-chlorobenzyl chloride.

No. 2: 1,4-Di-(*p*-chlorobenzyl)-1,4-dibiphenylenebutane (IV), R = $CH_2C_6H_4Cl$), from 1,4-dibiphenylenebutane (IV, R = H), butyllithium, and *p*-chlorobenzyl chloride.

No. 3: Reaction product from 1,4-dibiphenylenebutatriene (V), lithium aluminum hydride, and *p*-chlorobenzyl chloride.

No. 4: 1,4-Di-(*p*-chlorobenzyl)-1,4-dibiphenylene-2-butene (VI, R = $CH_2C_6H_4Cl$), from 1,4-dibiphenylene-2-butene (VI, R = H), butyllithium, and *p*-chlorobenzyl chloride.
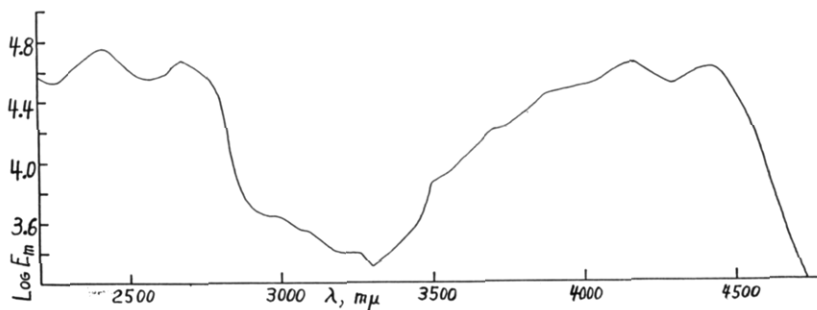

FIG. 3. ULTRAVIOLET ABSORPTION SPECTRUM OF 1,4-DIBIPHENYLENEBUTADIENE IN DIOXANE SOLUTION

R = Li) is partly oxidized by traces of oxygen (see 12 and experimental). In addition, a very small quantity of a hydrocarbon was isolated from the above

reaction; it contained only one benzyl group per molecule of (V) and is, therefore, tentatively assumed to be 1-benzyl-1,4-dibiphenylene-2-butene (VIa).
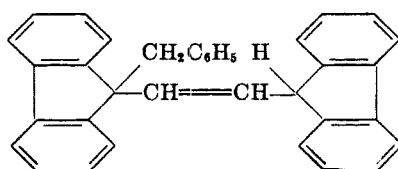

VIa

Both III and V show, therefore, the same high polarizability of the double bonds emanating from the five-membered ring, which is so characteristic for dibiphenyleneethylene (I). The two double bonds of this description, furthermore, react, both in III and V, *independently of each other*. This fact represents an interesting confirmation of the results of Simpson's (22) recent study of internal dispersion forces in polyenes. This author attributed the observed shortening of the 2,3-bond in butadiene to the existence of an internal dispersion force; its prerequisite is the *polarizability of the individual double bonds*.

Fuson, de Wald, and Gaertner (23) have recently published an analogous study of the reaction of metal-organic compounds with III and with 1,6-dibiphenylenehexatriene. Some of their results are of importance in connection with the observations reported in the present paper. With phenyllithium, III gives a bis-adduct (VII); its structure follows from the fact that the hydrolysis gives the same hydrocarbon (VIII; m.p. 302°) (together with the diastereomeride) which can also be obtained from benzylidenefluorene (IX) by addition of sodium metal (to X) and subsequent hydrolysis (24, 25):
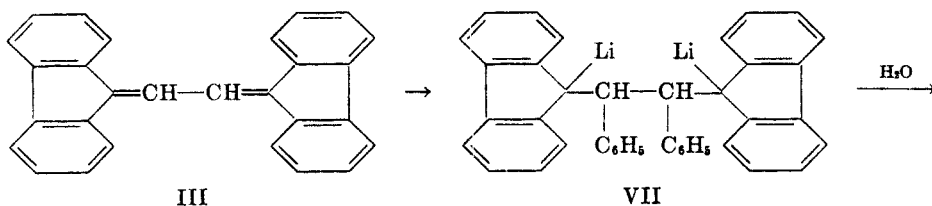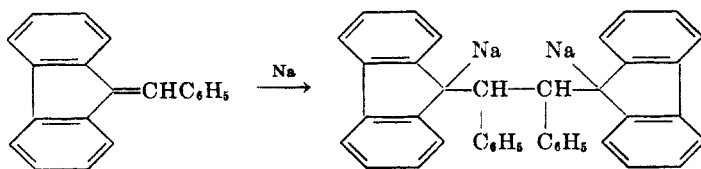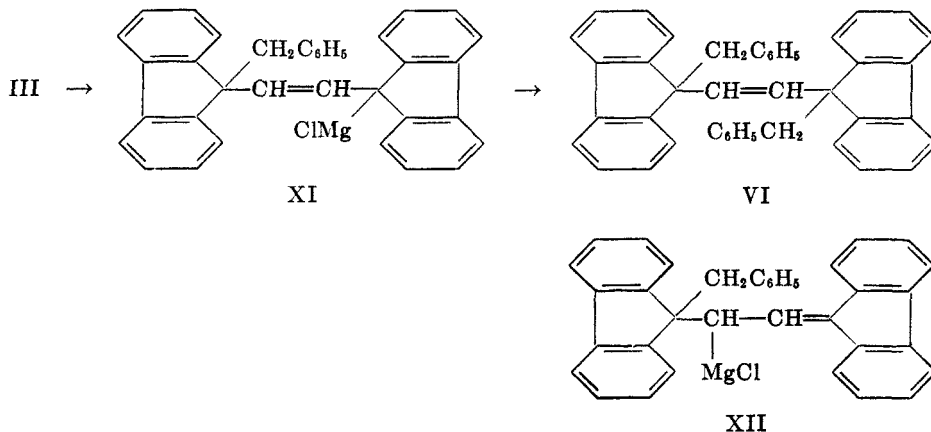

III   VII
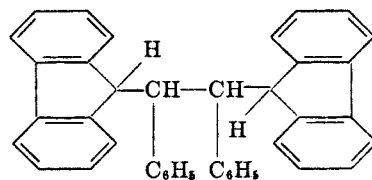

VIII

IX   X

Benzylmagnesium chloride and III, however, reacted in the ratio 1:1. The product was formulated as XI, as its reaction with benzyl chloride led to VI, R = $CH_2C_6H_5$. This hydrocarbon was identical with that obtained from dibi-

III →

$$-CH=CH-$$ with $CH_2C_6H_5$ and $ClMg$ substituents

XI

→

$$-CH=CH-$$ with $CH_2C_6H_5$ and $C_6H_5CH_2$ substituents

VI

$$-CH-CH=$$ with $CH_2C_6H_5$ and $MgCl$ substituents

XII

phenylenebutatriene (V), according to the mixture m.p., and especially the infrared spectrum. In the reaction with benzylmagnesium chloride, III reacts as one single polar system; however, it may be argued that the primary reaction is (as is probable also in the case of phenyllithium or lithium aluminum hydride) half-sided, leading to XII, which then undergoes an allylic shift to XI. Allylic shifts of a similar type have been reported in the reaction of alkylmagnesium *chlorides* with ethylene oxides (26–28).

Fuson and co-workers (23) have also carried out a synthesis of 1,4-dibenzyl-1,4-dibiphenylenebutane (IV, R = $CH_2C_6H_5$) and have obtained a hydrocarbon (m.p. 301–302°) which is different from the one described in the present communication; they treated successively 9-methoxy-9-benzylfluorene with sodium metal and ethylene bromide. A scrutiny of their method revealed, however, that a much more complex reaction takes place than the one expected and that the product obtained is VIII, not IV, R = $CH_2C_6H_5$. It is likely that 9-methoxy-9-benzylfluorene is first converted into benzylidenefluorene:

fluorene with OCH_3 and $CH_2C_6H_5$ substituents $\xrightarrow{-CH_3OH}$ fluorene with $=CHC_6H_5$ substituent
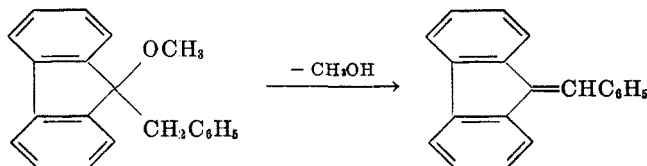
which then undergoes the normal reaction with metallic sodium.

EXPERIMENTAL

9-Benzyldibiphenyleneethane (II, R = $CH_2C_6H_5$). To a solution of 0.38 g. (0.01 mole) of lithium aluminum hydride in 50 cc. of anhydrous dioxane (prepared by refluxing the components for 10 minutes), 1.64 g. (0.005 mole) of dibiphenyleneethylene (I) (29) was added in portions and the mass which had turned orange-colored was refluxed for two hours. When 0.7 g. (0.005 mole) of benzyl chloride was added, the color of the solution disappeared immediately. After decomposition with ice and dilute hydrochloric acid, the reaction product crystallized spontaneously (1.7 g.); it was recrystallized from a mixture of benzene and alcohol, m.p. 234–235°. The product did not depress the melting point of an authentic (6) specimen of 9-benzyldibiphenyleneethane (II, R = $CH_2C_6H_5$).

1,4-Dibiphenylenebutadiene (III). For the preparation of this hydrocarbon, a number of methods have been suggested. Wislicenus (16) obtained it by autoxidation of an alcoholic-alkaline solution of fluorene [see Kuhn and Winterstein (30)] in the course of one week (yield, 20%), and Wieland and co-workers (31, 32) described a method which consists of the following steps: dehydration of 9-methylfluorenol to biphenyleneethylene, bromination and treatment of the dibromide with hot dimethylaniline. However, due to the instability of the biphenyleneethylene, this gave only an over-all yield of 10.5%. Later on, this method was considerably improved, when it was discovered that 9-methyl-9-chlorofluorene (which is easily obtained from 9-methylfluorenol) reacts with bromine to give the desired dibromide in quantitative yield. The procedure can be simplified still further; it was now found that methylfluorenol in acetic anhydride gives with bromine directly the dibromide in quantitative yield. This is the more surprising as the alcohol remains unchanged when treated with acetic anhydride alone under the same conditions, or when it is treated with bromine in carbon tetrachloride as solvent. As in the case of the chloro compound, *direct* halogenation has to be assumed. Wieland and Krause (32), incidentally, report that methylfluorenol and liquid bromine give the dibromide "in low yield".

To a solution of 19.6 g. of 9-methylfluorenol (33) in 350 cc. of acetic anhydride, there was added at 60–70° and with vigorous agitation, a solution of 16 g. of bromine in 20 cc. of the same solvent. The reaction mixture was poured onto ice and the crystalline product filtered, washed with water, and dried. The crude *dibromide* (33 g.; 90% yield) of m.p. 131–132° (dec.) was sufficiently pure for the next step; recrystallization from alcohol raised the m.p. to 143° (dec.), as indicated in the literature (31).

A mixture of 10 g. of the dibromide and 25 cc. of freshly distilled dimethylaniline was heated for 90 minutes at 150°. Upon cooling, 1.2 g. (23%) of pure dibiphenylenebutadiene (III) crystallized out; after washing with methanol, it melted at 355°.

1,4-Dibiphenylenebutane (IV, R = H). (*a*) To a suspension of 0.25 g. of $LiAlH_4$ in 30 cc. of anhydrous dioxane, there was added 0.7 g. of dibiphenylenebutadiene (0.002 mole). After refluxing for 2 hours, the dark green reaction mixture was decomposed with ice and dilute hydrochloric acid and the crystalline material which separated was filtered, washed with water, dried, and triturated with ether. The insoluble material (0.4 g.) was recrystallized repeatedly from acetic acid or butyl alcohol, yielding white crystals, m.p. 223–224°, of dibiphenylenebutane (IV, R = H).

(*b*) To a boiling solution of 0.5 g. of dibiphenylenebutadiene in 30 cc. of amyl alcohol, 3 g. of sodium was added in portions; the refluxing was continued until complete decolorization had been effected. The hot solution was filtered and, after addition of some acetic acid, cooled. The dibiphenylenebutane which separated was filtered and washed with alcohol. M.p. and mixture m.p. 220–221°.

The hydrocarbon had been prepared before (16, 17) by reduction of III; VI, R = H; or V.

1,4-Dibenzyl-1,4-dibiphenylenebutane (IV, R = $CH_2C_6H_5$). To the reaction mixture obtained as in the previous experiment, 0.055 g. of benzyl chloride (0.0044 mole) in 10 cc. of dry dioxane was added. After refluxing for one hour and decomposition with ice and acid, the crystalline material was filtered and washed with water. Repeated crystallizations from

acetic acid or a butyl alcohol-toluene mixture gave colorless, small needles, of m.p. 236–237°. The infrared spectrum showed the absence of a double bond.

Anal. Calc'd for $C_{42}H_{34}$: C, 93.7; H, 6.3.

Found: C, 93.6; H, 6.4.

A sample of the hydrocarbon was also prepared according to Wittig, Davis, and Koenig (19) from 1,4-dibiphenylenebutane (IV, R = H) with phenyllithium and benzyl chloride. The melting point of the product was only 213–214° (Wittig and co-workers give 209–210°), but no depression with the above substance was observed. The lower melting point is perhaps due to the presence of an impurity which is not removed even by repeated crystallization.

1,4-Di-(p-chlorobenzyl)-1,4-dibiphenylene-butane (IV, R = $CH_2C_6H_4Cl$). (a) The same reaction was carried out, using 0.7 g. of p-chlorobenzyl chloride. The crude product was triturated with hot alcohol and recrystallized a few times from a butyl alcohol-toluene mixture (Norit). Fine, colorless needles of m.p. 237–239°, which are very difficultly soluble in carbon disulfide.

Anal. Calc'd for $C_{42}H_{32}Cl_2$: C, 83.0; H, 5.3.

Found: C, 83.5; H, 5.2.

The saturated solution of the compound in carbon disulfide ($\sim 5\%$) does not show any absorption in the 1600–1700 and in the 950–1000 cm^{-1} region.

(b) To a butyllithium solution prepared from 0.2 g. of lithium wire in 20 cc. of dry ether and 1.5 g. of butyl bromide, there was added a solution of 0.5 g. of 1,4-dibiphenylenebutane (IV, R = H) in 30 cc. of dry toluene. The whole operation was carried out in an atmosphere of nitrogen. The orange-colored solution was heated for one hour in a water-bath and a toluene solution of 1.5 g. of p-chlorobenzyl chloride was added, which caused the color to disappear. After refluxing for one hour, the mixture was decomposed with cold dilute hydrochloric acid and the organic layer was washed, separated, and dried. Distillation *in vacuo* left an oily mass which solidified partly overnight; the crystalline material was filtered, washed with methanol, and recrystallized from butanol (Norit); white needles of m.p. 242–243°; which was not depressed by admixture of the preceding product.

Anal. Calc'd for $C_{42}H_{32}Cl_2$: C, 83.0; H, 5.3.

Found: C, 83.1; H, 5.4.

1,4-Dibiphenylenebutatriene (V). The following is an improvement of the original procedure (17). A mixture of 6 g. of 1,4-dibiphenylene-2-butyne-1,4-diol, 36 cc. of hydriodic acid (*d.* 1.7), 36 cc. of acetic acid, and 3.6 g. of iodine is heated, with stirring, in the water-bath for three hours. The mixture is poured into water and the red product is filtered, washed with water, and triturated with boiling ethanol. The yield is quantitative and the product pure enough for further use. The crystallization from nitrobenzene (heating as short as possible) gives bright red leaflets, m.p. 300–302°.

1,4-Dibiphenylene-2-butene (VI, R = H). To a suspension of 0.40 g. of LiAlH₄ in 20 cc. of dry dioxane, there was added 0.10 g. of dibiphenylenebutatriene (V); the mass, which turned dark-green, was refluxed for one hour and decomposed as usual. The product was filtered and recrystallized from a mixture of butyl alcohol with toluene or xylene to give white platelets of m.p. 267–268° (orange melt); the m.p. was not depressed by admixture of an authentic sample of 1,4-dibiphenylene-2-butene (16). In recrystallizing the crude product, a very small amount of golden-red crystals, m.p. 346–348°, remained undissolved. They were identified (by mixture m.p.) as dibiphenylenebutadiene (III). Dibiphenylenebutene (VI, R = H) or its dilithio-derivative are, evidently, very prone to autoxidation. This is also evidenced by the color of the melt of VI, R = H, which points to dehydrogenation to III.

1,4-Dibenzyl-1,4-dibiphenylenebutene (VI, R = $CH_2C_6H_5$). To the reaction mixture prepared from 0.2 g. of LiAlH₄ in 30 cc. of dry dioxane and 0.5 g. of dibiphenylenebutatriene, there was added an excess of benzyl chloride (0.5 g.) in dioxane solution. The dark green color of the reaction mixture disappeared; after refluxing for one hour, ice and acid was added, and the reaction product was filtered. From butyl alcohol or a benzene-alcohol mixture there formed white needles of m.p. 239–240°.

Anal. Calc'd for $C_{42}H_{32}$: C, 94.0; H, 6.0.

Found: C, 93.7; H, 6.2.

A mixture melting point with a sample prepared according to Fuson, *et al.* (23) showed no depression. Both samples showed the same infrared absorption band at 957 cm⁻¹.

1,4-Di-(p-chlorobenzyl)-1,4-dibiphenylene-2-butene ($R = CH_2C_6H_4Cl$). (a) When *p*-chlorobenzyl chloride (1 g.) was added to the reaction mixture prepared as above, a semi-solid product was obtained which was filtered and triturated with ether. Precipitation of the benzene solution with alcohol and recrystallization from a butyl alcohol-toluene mixture (Norit) afforded white needles of m.p. 237°, easily soluble in carbon disulfide.

Anal. Calc'd for $C_{42}H_{30}Cl_2$: C, 83.3; H, 5.0.

Found: C, 83.6; H, 5.3.

Infrared spectrum. A solution of the compound (0.07 g.) in carbon tetrachloride (1 cc.) showed a strong band at 975 cm⁻¹ (cell thickness: 0.1 mm.) and none in the range 1600–1700 cm⁻¹.

(b) A solution of butyllithium, prepared as above, was added in an atmosphere of nitrogen to a suspension of 1 g. of 1,4-dibiphenylene-2-butene (VI, R = H) in 50 cc. of toluene. The brown reaction mixture was stirred at room temperature for one-half hour; then a toluene solution of *p*-chlorobenzyl chloride was added. After decomposition, about 100 mg. of a yellow, insoluble product separated, which was filtered from the organic layer and washed with ether; m.p. 355–360°. It was identified as dibiphenylenebutadiene (III) by its ultraviolet spectrum (Fig. 3), analysis, and mixture m.p.

Anal. Calc'd for $C_{28}H_{18}$: C, 94.9; H, 5.1.

Found: C, 94.8; H, 5.1.

Distillation of the solvents left a yellow oil which crystallized partially. Filtration and recrystallization from butanol yielded 50 mg. of white needles, m.p. 227—229°. No depression occurred, when the substance was mixed with the product from the previous experiment.

Anal. Calc'd for $C_{42}H_{30}Cl_2$: C, 83.3; H, 5.0.

Found: C, 83.5; H, 5.2.

From the mother-liquors, two types of crystals precipitated slowly, which could be separated mechanically. One was identical with the above product, the second formed yellow prisms, from propyl alcohol, m.p. 222–223°. According to the analysis, the substance is probably 1-benzyl-1,4-dibiphenylene-2-butene (VIIa).

Anal. Calc'd for $C_{35}H_{25}Cl$: C, 87.5; H, 5.2.

Found: C, 87.6; H, 5.5.

9-Ethynylfluorenol. In an attempt to improve the preparation of 1,4-dibiphenylene-2-butyne-1,4-diol, the starting material for the synthesis of (V) (17), the condensation of fluorenone and acetylene was carried out in the system potassium hydroxide-butyraldehyde dibutylacetal (34, 35). However, only 9-ethynylfluorenol could be isolated from the reaction mixture.

A suspension of 11.2 g. (0.2 mole) of potassium hydroxide in 50 g. of butyraldehyde dibutylacetal (36) was heated, with vigorous agitation, at 150° for a half-hour, and subsequently cooled to 0°. Through this suspension, a current of dry acetylene was passed until 1.5 g. was absorbed. Then, 9 g. of fluorenone was added and the mixture was agitated for two hours and decomposed with ice. The organic layer was washed with water, dried, and concentrated, and the oily residue was triturated with petroleum ether.

Anal. Calc'd for $C_{15}H_{10}O$: C, 87.4; H, 4.9.

Found: C, 87.0; H, 4.7.

The carbinol gave a precipitate with ammoniacal silver nitrate solution.

Reaction of 9-methoxy-9-benzylfluorene with sodium. A solution of 4 g. of 9-methoxy-9-benzylfluorene in 150 cc. of anhydrous ether was converted into the red sodium-organic compound by treatment with 3.2 g. of sodium wire (Schlenk tube). The product was decanted from excess sodium wire and divided in two approximately equal parts, one being heated with 6.5 g. of freshly distilled ethylene bromide and refluxed until the color disappeared (about 1 hour), the other being decomposed with a few drops of cold water. In both

cases, the reaction product was insoluble in ether; m.p. 310–315°. Two crystallizations from xylene brought the melting point up to 320°; also the mixture m.p. was 320°.

The product was also identical (mixture m.p.) with the hydrocarbon (2,3-diphenyl-1,4-dibiphenylenebutane), prepared according to Schlenk and E. Bergmann, by the action of sodium on benzylidenefluorene and hydrolysis of the alkali-organic product formed (24, 25).

SUMMARY

1. Dibiphenyleneethene (I) gives by reaction with lithium aluminum hydride a monolithio-derivative of dibiphenyleneethane.

2. 1,4-Dibiphenylenebutadiene (III) adds two moles of lithium aluminum hydride and gives a dilithio-derivative of 1,4-dibiphenylenebutane (IV, R = Li).

3. 1,4-Dibiphenylenebutatriene (V), too, adds two moles of the mixed hydride and forms a dilithio-derivative of 1,4-dibiphenylene-2-butene (VI, R = Li).

4. The theoretical significance of these results is discussed.

5. 9-Methoxy-9-benzylfluorene is converted into benzylidenefluorene by treatment with metallic sodium.

REHOVOTH, ISRAEL
TEL-AVIV, ISRAEL

REFERENCES

(1) A. PULLMAN, B. PULLMAN, AND RUMPF, *Bull. soc. chim. France*, **15**, 757 (1948); BERTHIER AND B. PULLMAN, *Bull. soc. chim. France*, **16**, D 461 (1949).
(2) WHELAND AND MANN, *J. Chem. Phys.*, **17**, 264 (1949).
(3) LUMBROSO, PACAULT, AND B. PULLMAN, *Bull. soc. chim. France*, **17**, 34 (1950).
(4) E. BERGMANN AND FISCHER, *Bull. soc. chim. France*, **17**, 1084 (1950).
(5) ZIEGLER AND SCHAEFER, *Ann.*, **511**, 101 (1943).
(6) FUSON AND PORTER, *J. Amer. Chem. Soc.*, **70**, 895 (1948).
(7) PINCK AND HILBERT, *J. Amer. Chem. Soc.*, **68**, 2014, 2739 (1946).
(8) E. BERGMANN AND LAVIE, *J. Amer. Chem. Soc.*, **74**, 3173 (1952).
(9) E. BERGMANN AND FISCHER, *Bull. Research Council Israel*, **1**, No. 4, 83 (1951).
(10) E. BERGMANN, FISCHER, AND JAFFE, *J. Am. Chem. Soc.*, **75**, in press (1953).
(11) E. BERGMANN AND FISCHER, *Bull. soc. chim. France*, **19**, 712 (1952).
(12) LAVIE AND E. BERGMANN, *Bull. soc. chim. France*, **18**, 250 (1951).
(13) TREVOY AND BROWN, *J. Amer. Chem. Soc.*, **71**, 1675 (1949).
(14) Nomenclature: KUHN AND WALLENFELS, *Ber.*, **71**, 783 (1938).
(15) E. BERGMANN, BERTHIER, A. PULLMAN, AND B. PULLMAN, *Bull. soc. chim. France*, **17**, 1079 (1950).
(16) WISLICENUS, *Ber.*, **48**, 617 (1915).
(17) E. BERGMANN, HOFFMANN, AND WINTER, *Ber.*, **66**, 46 (1933).
(18) MAYNEORD AND ROE, *Proc. Roy. Soc. (London)*, A **158**, 634 (1937).
(19) WITTIG, DAVIS, AND KOENIG, *Ber.*, **84**, 627 (1951).
(20) McMURRY AND THORNTON, *Anal. Chem.*, **24**, 318 (1952).
(21) E. BERGMANN AND HIRSHBERG, *Bull. soc. chim. France*, **17**, 1091 (1950).
(22) SIMPSON, *J. Amer. Chem. Soc.*, **73**, 5363 (1951).
(23) FUSON, DE WALD, AND GAERTNER, *J. Org. Chem.*, **16**, 21 (1951).
(24) SCHLENK AND E. BERGMANN, *Ann.*, **463**, 63 (1928).
(25) SCHLENK AND E. BERGMANN, *Ann.*, **479**, 42 (1930).
(26) GOLUMBIC AND COTTLE, *J. Amer. Chem. Soc.*, **61**, 996 (1939).
(27) COTTLE AND POWELL, *J. Amer. Chem. Soc.*, **58**, 2267 (1936).
(28) HUSTON AND BRAULT, *J. Org. Chem.*, **15**, 1211 (1950).
(29) SCHMIDT AND WAGNER, *Ber.*, **43**, 1796 (1910).

(30) KUHN AND WINTERSTEIN, *Helv. Chim. Acta*, **11,** 128 (1928).

(31) WIELAND, REINDEL, AND FERRER, *Ber.*, **55,** 3313 (1922).

(32) WIELAND AND KRAUSE, *Ann.*, **443,** 129 (1925).

(33) ULLMANN AND VON WURSTEMBERGER, *Ber.*, **38,** 4105 (1905).

(34) CH. WEIZMANN, British Patent 580,921 [*Chem. Abstr.*, **41,** 2429 (1947)]; U. S. Patent 2,435,524 [*Chem. Abstr.*, **42,** 3772 (1948)].

(35) E. BERGMANN AND CO-WORKERS, *J. Appl. Chem.* (London), **3,** in press (1953).

(36) CH. WEIZMANN, E. BERGMANN, AND SULZBACHER, *J. Org. Chem.*, **15,** 918 (1950).