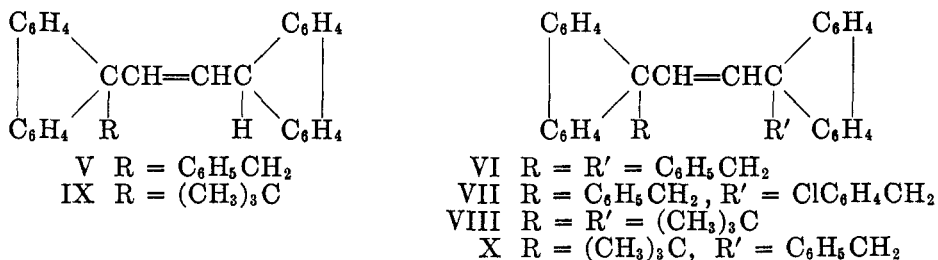


chloride does undergo benzylation in the presence of benzyl chloride. When the adduct and the alkyl chloride were brought together, the dibenzyl compound was produced in very good yields.



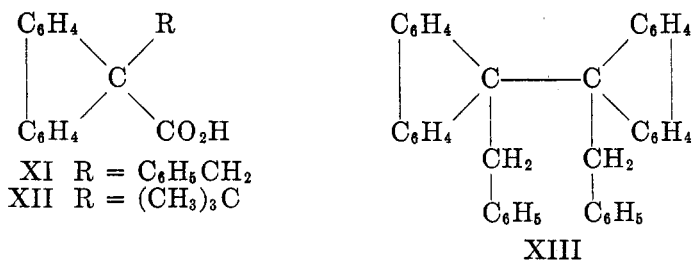
When *p*-chlorobenzyl chloride was employed as the alkylating agent, the chloro derivative (VII) of the diphenyl compound was formed. The same compound (VII) was produced by benzylation of the adduct obtained from the diene and *p*-chlorobenzylmagnesium chloride. The fact that these two products are identical shows that the dibenzylbutene is symmetrical and leaves little doubt as to the correctness of the structures that have been assigned.

The series of reactions leading to the preparation of the dibenzylbutene (VI) and its chloro derivative (VII) was carried out with other halide pairs: *tert*-butyl chloride and benzyl chloride, *sec*-butyl bromide and *tert*-butyl chloride, phenethyl bromide and *tert*-butyl chloride. The unsymmetrical products possessed lower melting points and were appreciably more soluble than the symmetrical dibenzyl derivative.

When *tert*-butyl chloride was the alkylating agent in the above reactions, a high-melting product was obtained which proved to be 1,4-di-*tert*-butyl-1,4-dibiphenylene-2-butene (VIII). It is postulated that halogen-metal or radical interchange³ took place between *tert*-butyl chloride and the Grignard reagent employed. The *tert*-butylmagnesium chloride so formed could then condense with the diene to form an adduct, which by reaction with more *tert*-butyl chloride would yield the di-*tert*-butylbutene (VIII). The postulated radical interchange was substantiated further when a 10% conversion to the di-*tert*-butylbutene was effected by the addition of *tert*-butyl chloride to a reaction mixture containing only the diene and a Grignard reagent such as phenylmagnesium bromide which does not add to the diene.

Further evidence about the dibenzylbutene (VI) was obtained by treating it with ozone. The mixture resulting from the ozone treatment was decomposed by glacial acetic acid in the presence of hydrogen peroxide. The product, however, was not the expected 9-benzyl-9-fluorene-carboxylic acid (XI) which is known (6), but a hydrocarbon which proved to be identical with the dibenylation product of dibiphenyleneethylene (XIII) (1) and the product of Vanscheidt and Moldavski (7) prepared by the bimolecular reduction of 9-benzylfluorene.

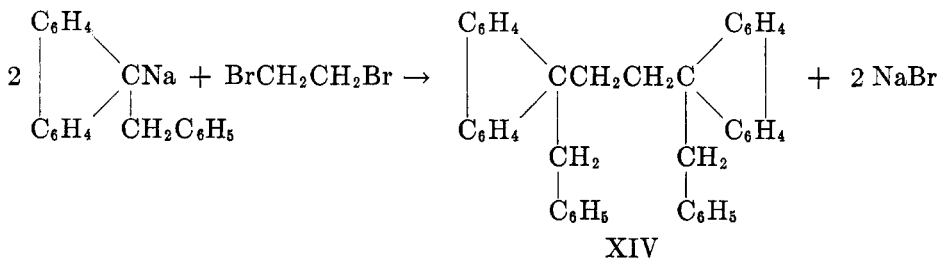
³ Only four other examples have been recorded in the literature of such radical interchange without catalytic influence (4, 5).



The transformation of the butene (VI) to the dibenzylethane (XIII) by ozone is apparently without precedent; it is consistent, however, with the structure assigned to the butene.

Attempts to degrade the butene by other oxidizing agents were unsuccessful. The butene yielded an epoxy derivative with perbenzoic or performic acid. An attempt to open the oxide ring by treating the oxide with glacial acetic acid in the presence of *p*-toluenesulfonic acid reconverted the oxide to a hydrocarbon which appeared to be isomeric with the original butene.

A satisfactory proof of structure of the butene (VI) would be realized if 1,4-dibenzyl-1,4-dibiphenylenebutane (XIV) could be prepared from the butene and compared with an authentic sample. It was found possible to synthesize the butane by treating the sodium derivative of 9-benzylfluorene with ethylene bromide. The sodium derivative was made according to the general method of Schlenk and Bergmann (8).

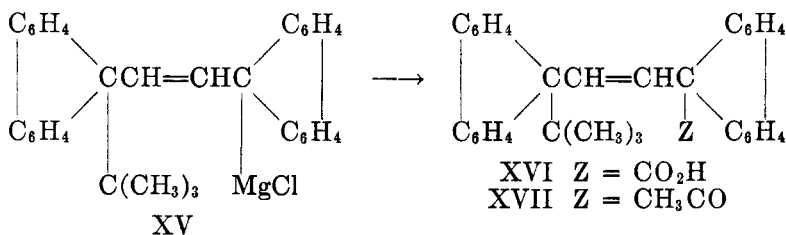


This line of attack failed, most unexpectedly, because preparation of the butane from the butene could not be effected by catalytic hydrogenation. Possibly one factor was the failure to find a proper solvent. Of the common organic solvents, only benzene and chloroform dissolve the butene in appreciable amounts at room temperature. Its solubility in ether, methylcyclohexane, ethanol, and glacial acetic acid is negligible. No change in melting point occurred when the butene was dissolved in thiophene-free benzene and subjected to a pressure of thirty pounds of hydrogen over platinum oxide in the usual low-pressure hydrogenation apparatus. When the olefin was dissolved in hot methylcyclohexane, it precipitated rapidly from solution as the temperature of the solvent fell, and was recovered unchanged. A change in melting point was observed when the reduction was attempted in hot glacial acetic acid at low pressures, or in benzene over Raney nickel at 75° and high pressures, but no pure substance was isolated.

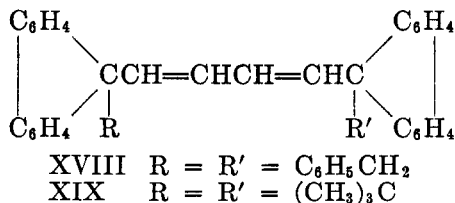
The addition of *tert*-butylmagnesium chloride to the orange diene took place with extraordinary facility to give 1-*tert*-butyl-1,4-dibiphenylene-2-butene (IX) in essentially quantitative yield. This compound has one active hydrogen atom at the 4 position. When it was treated with a Grignard reagent and the resulting complex was allowed to react with *tert*-butyl chloride, an 80% transformation of the mono-*tert*-butylbutene (IX) to 1,4-di-*tert*-butyl-1,4-dibiphenylene-2-butene (VIII) was accomplished. The same compound was obtained more directly by *tert*-butylation of the Grignard complex formed by the reaction of *tert*-butylmagnesium chloride with the diene under the experimental conditions employed in the preparation of the dibenzylbutene.

Cleavage of this di-*tert*-butylbutene (VIII) by ozone was unsuccessful. However treatment of 1-*tert*-butyl-4-benzyl-1,4-dibiphenylene-2-butene (X) with ozone, followed by decomposition of the ozonide with glacial acetic acid and hydrogen peroxide, gave the expected 9-*tert*-butyl-9-fluorene-carboxylic acid (XII). An authentic sample of this acid, a new compound, was prepared by carbonation of the Grignard reagent from 9-*tert*-butyl-9-chlorofluorene.

The adduct (XV) obtained by the reaction of *tert*-butylmagnesium chloride with the diene was shown to be a Grignard reagent by the fact that it underwent carbonation and acylation to yield the corresponding acid (XVI) and ketone (XVII), respectively.



Experiments with the hexatriene (IV) gave results very similar to those with the ethylene (I) and the butadiene (III). The red hexatriene was prepared according to the directions of Schmitt (9) in an over-all yield of 14%, based on fluorenone. The reaction of this hexatriene with benzylmagnesium chloride, and then with benzyl chloride yielded a product which is believed to be the dibenzylhexadiene (XVIII).



Several attempts to bring about the reaction of this compound with maleic anhydride or *p*-benzoquinone in benzene or xylene yielded only unchanged starting material. When nitrobenzene was employed as solvent for the reaction,

When a sample of the monobenzylbutene, mono- or di-*tert*-butylbutene, or 1-*tert*-butyl-1,4-dibiphenylene-2-butene-4-carboxylic acid (XVI), was heated above its melting point in a small Erlenmeyer flask, long fine needles of the orange dibiphenylenebutadiene (III) formed on the bottom and sides of the flask. When distillation of 0.1 g. of 1-*tert*-butyl-1,4-dibiphenylene-2-butene was attempted at 180–200° (1 mm.), a few hundredths of a gram of low melting (65°) hydrocarbon collected on the cold finger. This product was not investigated further. From the pot itself, 0.06 g. of dibiphenylenebutadiene was obtained. Pyrolysis of the dibenzylbutene and the dibenzylhexadiene resulted in tar formation.

EXPERIMENTAL⁴

1-Benzyl-1,4-dibiphenylene-2-butene. A solution of benzylmagnesium chloride, prepared from 4.2 g. of benzyl chloride, 1.0 g. of magnesium, and 80 ml. of dry ether was heated under reflux for 2 hours. The solution was decanted quickly from the excess magnesium into a second flask containing 1.5 g. of 1,4-dibiphenylene-1,3-butadiene. The mixture was stirred under reflux for 9 to 12 hours and poured into an ice-hydrochloric acid mixture. The organic layer was washed with water and filtered to permit recovery of 40–80% of unchanged diene. When the ethereal filtrate was concentrated, a product deposited by crystallization of the residue from glacial acetic acid. The product, which corresponded to about 40% conversion, was yellow and melted over a very long range, 155–170°. Several batches of this product were subjected to fractional crystallization in glacial acetic acid. Two compounds were isolated. 1-Benzyl-1,4-dibiphenylene-2-butene formed wafer-thin, white plates; m.p. 179–180°.

Anal. Calc'd for C₁₅H₂₆: C, 94.13; H, 5.87.

Found: C, 93.90; H, 6.05.

The second compound was isolated in little more than trace amounts. It formed yellow, spherical clusters when allowed to crystallize slowly from glacial acetic acid; m.p. 184–185°. Its constitution has not been determined.

1,4-Dibenzyl-1,4-dibiphenylene-2-butene. The adduct from benzylmagnesium chloride and the orange diene was prepared as in the preceding experiment. As the reaction proceeded, the very insoluble butadiene gradually dissolved, giving an intense purple reaction mixture. At the end of the reflux period considerable amounts of the orange hydrocarbon were still present; 2.0 g. of benzyl chloride was added and the mixture stirred under reflux overnight. The reaction complex was decolorized by the addition of the benzyl chloride, and precipitation of magnesium salts and possibly some of the organic product occurred. The reaction mixture was decomposed with dilute hydrochloric acid, ice, and water. The ether layer was separated and washed well with water. It was necessary to collect all ether- and water-insoluble material which formed at the interface during this washing, since this insoluble material represents the major part of the product. After washing with a small portion of ether, 1.6–1.8 g. (71–80%) was obtained as a slightly yellow product which melted at 229–233°. Recrystallization from glacial acetic acid gave a pure white compound; m.p. 237–239° (corr.); it formed long, thick needles and was very slightly soluble in ether, acetone, alcohol, or glacial acetic acid, but readily soluble in chloroform and benzene.

Anal. Calc'd for C₁₂H₁₂: C, 93.99; H, 6.01.

Found: C, 93.81; H, 6.00.

Other 1,4-dialkyl-1,4-dibiphenylene-2-butenes. The experimental procedure for the condensation of other Grignard reagents with the diene, followed by alkylation, was similar to that described for the dibenzyl compound, differing only in the manner of isolation. A magnesium-free Grignard reagent, in ten-molar excess, was added to the solid olefin. After

⁴All analyses are microanalyses by Miss Rachel Kopel and Miss Emily Davis.

the mixture had been heated for 4-8 hours, under reflux, the appropriate halide was added, and the mixture was stirred under reflux overnight. It was decomposed, and the organic layer filtered, if necessary, to remove unchanged diene; the ether was dried over sodium sulfate and treated with charcoal in a filter cell. The clarified solution was concentrated and the product crystallized from glacial acetic acid by evaporating the remainder of the lower boiling solvent.

1-p-Chlorobenzyl-4-benzyl-1,4-dibiphenylene-2-butene. The reaction of *p*-chlorobenzylmagnesium chloride with the diene afforded a low yield, and benzylation of the intermediate adduct gave only a 10% conversion to the butene with 69% recovery of starting material. The same product was obtained by *p*-chlorobenylation of the adduct from benzylmagnesium chloride and the diene. The product became tacky after several recrystallizations from glacial acetic acid and proved to be troublesome to purify; it formed broad white needles; m.p. 216-218° (corr.).

Anal. Calc'd for $C_{42}H_{31}Cl$: C, 88.32; H, 5.47.

Found: C, 88.07; H, 5.77.

1-tert-Butyl-4-benzyl-1,4-dibiphenylene-2-butene. Alkylation of the Grignard reagent, prepared by the condensation of dibiphenylenebutadiene and *tert*-butylmagnesium chloride, with benzyl chloride gave the desired white hydrocarbon in a yield of 60%; m.p. 166-167° (corr.).

Anal. Calc'd for $C_{39}H_{34}$: C, 93.18; H, 6.82.

Found: C, 93.34; H, 7.12.

When the condensation product of benzylmagnesium chloride and the diene was treated with *tert*-butyl chloride, a mixture was obtained. The major product was identical with the compound just described, *1-tert-butyl-4-benzyl-1,4-dibiphenylene-2-butene*; m.p. 165-166°. The remainder of the product was *1,4-di-tert-butyl-1,4-dibiphenylene-2-butene*; m.p. 248-250°.

1-sec-Butyl-4-tert-butyl-1,4-dibiphenylene-2-butene. This hydrocarbon was obtained in an 80% yield when the reaction mixture from *tert*-butylmagnesium chloride and the diene was treated with *sec*-butyl bromide. The product formed large, white, clumped crystals from a 1:5 chloroform-alcohol mixture; m.p. 191-192° (corr.).

Anal. Calc'd for $C_{36}H_{36}$: C, 92.26; H, 7.74.

Found: C, 92.07; H, 7.96.

When the alternate series of reactions was attempted, *i.e.*, addition of *sec*-butylmagnesium bromide to the diene and alkylation with *tert*-butyl chloride, the expected compound could not be isolated. A reaction occurred, very little unchanged diene could be recovered, but the only product that could be identified from the mixture was *1,4-di-tert-butyl-1,4-dibiphenylene-2-butene*.

1,4-Di-tert-butyl-1,4-dibiphenylene-2-butene. The procedure was similar to that described for the preparation of the dibenzylbutene. The product was rather insoluble in ether, most of it (65%) being collected directly by filtration of the separated and washed organic layer. An additional 25% can be obtained by working up the ethereal filtrate as described in the case of the unsymmetrical butenes. The hydrocarbon formed very large hexagonal crystals by slow crystallization from benzene; m.p. 248-250° (corr.).

Anal. Calc'd for $C_{36}H_{36}$: C, 92.26; H, 7.74.

Found: C, 92.21; H, 7.89.

1-tert-Butyl-1,4-dibiphenylene-2-butene. The Grignard reagent, prepared from 4.0 g. of *tert*-butyl chloride and 1.0 g. of magnesium in 75 ml. of dry ether, was stirred under reflux for 2 hours and then decanted quickly from the excess magnesium into a flask containing 1.5 g. of the solid diene. A characteristic deep wine-red color developed quickly and the mixture was maintained under reflux for 6 hours. The reaction mixture underwent decomposition to give a clear ether layer with no unchanged diene present. The ether layer was washed well, dried, and allowed to evaporate to dryness at room temperature. The slightly yellow crystalline residue was powdered, slurried with a little methanol, and filtered. The crude product weighed 1.7 g. (98%); m.p. 138-143°. It crystallized slowly from

glacial acetic acid as thick white rods, or from alcohol as very slender needles, 147–148° (corr.).

Anal. Calc'd for $C_{32}H_{28}$: C, 93.16; H, 6.84.

Found: C, 92.99; H, 6.81.

Conversion of 1-tert-butyl-1,4-dibiphenylene-2-butene to 1,4-di-tert-butyl-1,4-dibiphenylene-2-butene. The mono-*tert*-butylbutene (0.8 g.) was added in the form of a fine powder to a filtered Grignard solution that had been prepared from 1.0 g. of magnesium and 4.2 g. of *tert*-butyl chloride in 100 ml. of dry ether. The mixture assumed a light pink color. After the mixture had been stirred for 6 hours under reflux, 3.0 g. of *tert*-butyl chloride was added. The color disappeared immediately, but the mixture was maintained for an additional 5 hours at the reflux temperature. It was poured on an ice-hydrochloric acid mixture and the organic layer together with insoluble material was washed with water. The organic layer was allowed to evaporate to dryness. The yellow crystalline residue was slurried with a small portion of ether and a single recrystallization from toluene gave 0.75 g. (83%) of a pure compound, which formed thick rods, m.p. 245–247°. There was no depression of melting point when this compound was mixed with an authentic sample of 1,4-di-*tert*-butyl-1,4-dibiphenylene-2-butene.

Demonstration of Grignard radical interchange. A clear, filtered Grignard solution prepared from 2.0 g. of magnesium and 7.0 g. of bromobenzene in 100 ml. of dry ether was added to 1.0 g. of dibiphenylenebutadiene. The mixture quickly developed a very deep purple color; however, after a 6-hour period of stirring under reflux, 90% of the butadiene was recovered when the reaction mixture was decomposed. No other product was isolated.

To an identical reaction mixture, after the 6-hour reflux period, 2.5 g. of *tert*-butyl chloride was added and the mixture stirred under reflux overnight. Decomposition of the reaction mixture in the usual manner led to the recovery of 0.6 g. (60%) of the diene. The ether-soluble fraction was concentrated by evaporating the ether from a volume of 30 ml. of glacial acetic acid to the final total volume of 15 ml. There was a slow deposition of 0.1 g. (7.5%) of slightly yellow crystals which were purified readily by crystallization from glacial acetic acid or a small volume of toluene; m.p., 244–246° (uncorr.). The compound was identical with an authentic sample of 1,4-di-*tert*-butyl-1,4-dibiphenylene-2-butene as shown by infrared spectra and a mixed melting point determination.

1-tert-Butyl-1,4-dibiphenylene-2-butene-4-carboxylic acid. The Grignard complex of *tert*-butylmagnesium chloride and the diene was prepared as described above. After a reflux period of 8 hours, heating was discontinued and a slow stream of carbon dioxide was passed over the surface of the stirred solution. All color had disappeared completely at the end of 2 hours. The reaction mixture was decomposed, and the ether layer separated, washed well with water, and dried. The ether solution was concentrated and the product crystallized from glacial acetic acid after the ether had been evaporated; yield, 1.25 g. (65%). An analytical sample formed large colorless prisms; dec. 233°, with the evolution of gas, preliminary softening and color change to orange-yellow at 200°.

Anal. Calc'd for $C_{33}H_{28}O_2$: C, 86.81; H, 6.18.

Found: C, 86.59; H, 6.44.

1-tert-Butyl-4-acetyl-1,4-dibiphenylene-2-butene. A reaction mixture of 1-*tert*-butyl-1,4-dibiphenylene-2-butene-4-magnesium chloride was poured with rapid stirring into a solution of 4.0 g. of acetyl chloride in 75 ml. of dry ether. The mixture was protected under a atmosphere of nitrogen and the flask cooled externally by a salt-ice water bath. The mixture was held at this temperature for one-half hour, then allowed to come to room temperature, and finally heated under gentle reflux for 3 hours. The solution was poured on an ice-hydrochloric acid mixture and processed as in the preceding experiment. Yield, 0.75 g. (40%) of colorless cubes, m.p. 178–181°. The sample for analysis was recrystallized several times from glacial acetic acid, then ethanol; m.p. 181–182° (corr.).

Anal. Calc'd for $C_{24}H_{20}O$: C, 89.83; H, 6.65.

Found: C, 89.74; H, 6.95.

Ozonization of 1,4-dibenzyl-1,4-dibiphenylene-2-butene. A solution of 0.7 g. of the butene in 50 ml. of chloroform was subjected for 25 minutes to a fine stream of oxygen containing

2-4% ozone. Removal of the chloroform *in vacuo* at room temperature left a yellow viscous residue, which was dissolved completely by 10 ml. of glacial acetic acid. The addition of 3 ml. of 30% hydrogen peroxide caused the precipitation of a white, flocculent product; however, complete solution was obtained once again by warming the mixture on a steam-bath. With continued application of heat, a product precipitated a second time from the solution. After 15 to 20 minutes, the flask was removed from the steam-bath and allowed to stand for complete crystallization. This product amounted to 0.15 g. An analytical sample, prepared by crystallization from alcohol, consisted of white, silky needles; m.p. 202-203° (corr.).

Anal. Calc'd for $C_{40}H_{30}$: C, 94.07; H, 5.93.

Found: C, 94.16; H, 6.20.

Infrared spectra comparisons, a carbon-hydrogen analysis, and a mixed melting point determination, proved the product to be 1,2-dibenzyl-1,2-dibiphenyleneethane.

1,4-Dibenzyl-1,4-dibiphenylenebutene-2,3-oxide. A solution of 1.5 g. of 1,4-dibenzyl-1,4-dibiphenylene-2-butene and approximately 1.2 g. of perbenzoic acid in 50 ml. of chloroform was allowed to stand in the dark for 2 days at 5°, then an additional day at room temperature. At the end of this time, titration of the excess perbenzoic acid with thiosulfate showed an apparent consumption of 89% of the peracid required. The chloroform solution was washed with 10% sodium hydroxide, then water, and dried. The solvent was removed by evaporation and the residue recrystallized from chloroform-ethanol mixtures to yield 1.0 g. (65%) of a light tan product; m.p. 219-222° (uncorr.). An analytical sample, recrystallized many times from ethyl acetate, then acetone, was white and melted at 225-226° (corr.).

Anal. Calc'd for $C_{42}H_{32}O$: C, 91.11; H, 6.00.

Found: C, 90.83; H, 6.18.

Hydrolysis of 1,4-dibenzyl-1,4-dibiphenylenebutene-2,3-oxide. One gram of the oxide was suspended in 15 ml. of glacial acetic acid, a few crystals of *p*-toluenesulfonic acid were added, and the mixture was heated under reflux for 7 hours. The solution was concentrated and allowed to stand for complete crystallization. The product, after two recrystallizations, weighed 0.6 g.; m.p. 153-156°. A sample, prepared for analysis from glacial acetic acid, melted at 157-158.5°. The compound had the composition of a hydrocarbon with an empirical formula very similar to that of the original butene. It decolorized bromine-carbon tetrachloride and acetone-permanganate solutions.

Anal. Calc'd for $C_{44}H_{32}$: C, 93.99; H, 6.01.

Found: C, 94.34; H, 6.22.

9-Benzyl-9-chlorofluorene. A solution of 4.0 g. of 9-benzylfluorene, prepared in 70% yield by the procedure of Ullmann and Wurstenberger (12), in 75 ml. of dry ether was saturated with anhydrous hydrogen chloride at ice-bath temperatures. The yellow solution was allowed to stand at room temperature for one hour and then poured into ice and water. The ether layer was separated, washed well, and dried over sodium sulfate. Removal of the ether *in vacuo* at room temperature left a residue, which was crystallized from ether-ligroin mixtures; yield 2.8 g. (65%) of colorless product. An analytical sample consisted of silky needles melting, with decomposition, at 97-98° (corr.). The product is not stable for long periods.

Anal. Calc'd for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20.

Found: C, 82.88; H, 5.40.

9-Benzyl-9-methoxyfluorene. The remainder of the chloride was heated under reflux in methanol for 2 hours; the solution was concentrated to a volume of 15 ml. and cooled strongly; 1.1 g. (55%) of crude product separated. A sample, recrystallized five times from methanol, melted at 78-79° (corr.).

Ana. Calc'd for $C_{21}H_{18}O$: C, 88.08; H, 6.35.

Found: C, 88.16; H, 6.43.

1,4-Dibenzyl-1,4-dibiphenylenebutane. Approximately 0.8 g. of sodium wire was added to a solution of 1.0 g. of 9-benzyl-9-methoxyfluorene in 40 ml. of dry ether. The flask was stoppered and shaken at room temperature for 3 days. A finely divided orange-red product appeared at the end of the first day. After 3 days, the suspension of the organo-sodium compound was decanted quickly from the excess sodium wire into a flask containing 3.2 g.

of freshly distilled ethylene bromide. The flask was warmed gently until the red color of the sodio-derivative had disappeared. The ether was removed by evaporation and the residue washed with water to yield 0.46 g. (49%) of slightly yellow product that softened at 270° and melted completely at 290°. This rather insoluble hydrocarbon was recrystallized from benzene and chloroform to a constant melting point of 301–303°.

Anal. Calc'd for $C_{42}H_{34}$: C, 93.64; H, 6.36.

Found: C, 94.04; H, 6.01.

1,6-Dimethoxy-1,6-dibiphenylenehexane. A suspension of 4.0 g. of crude 1,6-dibiphenylenehexane-1,6-diol (9) in 75 ml. of ether was saturated with dry hydrogen chloride. The major portion of the solvent was removed by evaporation and the solid washed with small portions of ether to remove excess hydrogen chloride. This crude dichloride was not purified further, but suspended in methanol and heated under reflux with this reagent for 4 hours. After being allowed to stand overnight, a considerable fraction of the product was found to be unchanged diol. A crude separation of the alcohol from the methyl ether was effected at this stage by extraction of the solid with benzene; the insoluble fraction was discarded. Further purification of the benzene-soluble fraction yielded 0.95 g., m.p. 183–185°. The analytical sample from benzene, m.p. 187–188° (corr.).

Anal. Calc'd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77.

Found: C, 86.02; H, 6.99.

1,6-Dibenzyl-1,6-dibiphenylenehexane. A solution of 0.9 g. of 1,6-dimethoxy-1,6-dibiphenylenehexane in 75 ml. of dry ether was shaken over 0.6 g. of sodium wire for 3 days. The ethereal suspension of the red sodium derivative was decanted from the excess sodium wire into a flask containing 1.1 g. of benzyl chloride. With the disappearance of the color, the ether solution was washed with water, dried over magnesium sulfate, and evaporated to dryness. The residue was slurried with a small portion of methanol, filtered, and dried to yield 0.6 g., m.p. 185–192° (uncorr.). Repeated recrystallization of the solid from glacial acetic acid gave lustrous white plates; m.p. 208–209° (corr.).

Anal. Calc'd for $C_{44}H_{38}$: C, 93.24; H, 6.76.

Found: C, 93.40; H, 6.89.

1,6-Dibenzyl-1,6-dibiphenylene-2,4-hexadiene. This compound was prepared in yields of 24–32% from 1,6-dibiphenylene-1,3,5-hexatriene, benzylmagnesium chloride, and benzyl chloride by a procedure similar to that described for the preparation of 1,4-dibenzyl-1,4-dibiphenylene-2-butene. An analytical sample recrystallized from glacial acetic acid or chloroform-alcohol mixtures appeared as glistening white plates; m.p. 219–220° (corr.).

Anal. Calc'd for $C_{44}H_{34}$: C, 93.91; H, 6.09.

Found: C, 94.18; H, 6.32.

1-tert-Butyl-1,6-dibiphenylene-2,4-hexadiene. The procedure described for the preparation of 1-tert-butyl-1,4-dibiphenylene-2-butene was followed. From 2.0 g. of the scarlet hexatriene, 1.8 g. of the crude mono-tert-butylhexadiene was isolated; m.p. 140–148°; yield 78%. An analytical sample formed colorless, short needles; m.p. 164–165° (corr.).

Anal. Calc'd for $C_{34}H_{30}$: C, 93.10; H, 6.90.

Found: C, 92.91; H, 6.85.

1,6-Di-tert-butyl-1,6-dibiphenylene-2,4-hexadiene. The procedure described for the preparation of 1,4-di-tert-butyl-1,4-dibiphenylene-2-butene was followed. Yield, 45% of an ether-insoluble product. The silvery white plates were recrystallized from benzene to the constant melting point 265–267° (corr.).

Anal. Calc'd for $C_{38}H_{38}$: C, 92.26; H, 7.74.

Found: C, 92.13; H, 7.86.

Ozonolysis of 1,6-di-tert-butyl-1,6-dibiphenylene-2,4-hexadiene. A solution of 2.3 g. of the diene in 50 ml. of methylene chloride, cooled externally by an ice-salt water mixture, was treated for 2 hours with a slow stream of ozone. The solvent was then removed *in vacuo* and the semi-crystalline residue was dissolved in 20 ml. of glacial acetic acid. The mixture was warmed on a steam-bath for 2 hours while 6 ml. of 30% hydrogen peroxide was added in portions. The mixture was diluted with ether and extracted with several portions of

dilute, warm sodium hydroxide solution. The combined alkaline extracts were acidified to precipitate 0.7 g. of tan product. This acid was recrystallized from glacial acetic acid, then benzene; it formed white needles, m.p. 224–226°, with preliminary softening. A mixed melting point determination with an authentic sample of 9-*tert*-butyl-9-fluorene-carboxylic acid gave no depression.

Anal. Calc'd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81.

Found: C, 80.91; H, 6.88.

When 1-*tert*-butyl-4-benzyl-1,4-dibiphenylene-2-butene was treated in this manner, the same acid, 9-*tert*-butyl-9-fluorene-carboxylic acid, was isolated.

sym-Diphenyldifluorenylethane. Phenyllithium was prepared by the dropwise addition of 4.7 g. of bromobenzene to a stirred mixture of 0.4 g. of lithium chips in 100 ml. of dry ether. The reaction mixture was stirred under reflux for one hour, and the reagent was filtered quickly through a glass-wool plug into a flask containing 1.5 g. of dibiphenylene-butadiene. The mixture slowly turned red as it was stirred under reflux for 18 hours. It was decomposed by adding water slowly to the cooled reaction flask. The organic layer with its insoluble product was separated, washed, and filtered. The white product was washed with ether and dried to give 1.5 g. (69%) of white powder. This crude product sintered and softened below 300° but did not liquefy completely up to 320°. Several recrystallizations of the compound from benzene raised the melting point to 335°. An analytical sample from the same solvent, as slender white rods or needles, melted very sharply at 345–346° (uncorr.).

Anal. Calc'd for $C_{40}H_{30}$: C, 94.07; H, 5.93.

Found: C, 93.84; H, 6.11.

An authentic sample of this compound was prepared for comparison according to the method of Schlenk and Bergmann (10). The crude product had a long melting range and two different crystalline forms were observed to be present after recrystallization from benzene. These were separated as well as possible by hand, and the fractions subjected to fractional crystallization. A high-melting product, 346–347° (uncorr.), formed small white needles and was identical to the compound derived from the addition of phenyllithium to 1,4-dibiphenylene-1,3-butadiene. The second fraction formed colorless cubes from benzene, m.p. 320°. It seems to be the product which was isolated and described by Schlenk and Bergmann (10).

Anal. Calc'd for $C_{40}H_{30}$: C, 94.07; H, 5.93.

Found: C, 94.35; H, 6.09.

The same lower-melting product was isolated from the crude reaction product of dibiphenylenebutadiene with phenyllithium, when it was reexamined.

9-*tert*-Butyl-9-chlorofluorene. A solution of 5.0 g. of fluorenone in 50 ml. of dry ether was added to a Grignard reagent which had been prepared from 4.0 g. of *tert*-butyl chloride, 80 ml. of dry ether, and 1.0 g. of magnesium. The addition of the fluorenone caused a color change of yellow to orange-red to dark green in the reaction mixture. The mixture was stirred under reflux for 3 hours, then was decomposed and processed in the usual manner. The organic layer was concentrated to yield a reddish oil, which did not crystallize. The chloride was obtained most expeditiously by omitting the isolation of the alcohol. The ether solution of the crude alcohol from the preceding Grignard reaction was dried and saturated with dry hydrogen chloride. The ether mixture was poured on ice and the excess hydrogen chloride was removed by washing the organic layer with water. The ether fraction was dried over sodium sulfate and allowed to evaporate to dryness. The residue was recrystallized from ligroin-benzene mixtures. A yield of 2.2 g. (31%) of crude, yellow product was obtained; m.p. 92–97°. A sample was recrystallized to constant m.p. 104–105° from high-boiling petroleum ether; it formed large white prisms.

Anal. Calc'd for $C_{17}H_{17}Cl$: C, 79.51; H, 6.68.

Found: C, 79.39; H, 6.61.

9-*tert*-Butyl-9-fluorene-carboxylic acid. A solution of 1.0 g. of 9-*tert*-butyl-9-chlorofluorene in 20 ml. of dry ether was added dropwise to a stirred ether solution containing excess magnesium turnings. The reaction was initiated with a little methyl iodide. The reaction

mixture turned an orange-yellow and after the mixture had been stirred under reflux for 2 hours, a slow stream of carbon dioxide was introduced into the reaction vessel. A pink color developed, but disappeared after a short time. The mixture was treated with dilute hydrochloric acid; the organic layer was separated, washed, and dried. The ether solution was concentrated and the residue recrystallized from benzene. Large colorless prisms were deposited; yield, 0.8 g. of an acid, soluble in warm sodium bicarbonate. An analytical sample from benzene or acetonitrile melted at 224–226°, with preliminary softening. Mixed melting point determinations with the acids obtained by ozonization of 1,6-di-*tert*-butyl-1,6-dibiphenylene-2,4-hexadiene and 1-*tert*-butyl-4-benzyl-1,4-dibiphenylene-2-butene showed no depression.

Anal. Calc'd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81.

Found: C, 81.02; H, 7.00.

SUMMARY

The Grignard reagents, *tert*-butylmagnesium chloride, benzylmagnesium chloride, and *p*-chlorobenzylmagnesium chloride, have been found to add in a 1,4-manner to 1,4-dibiphenylene-1,3-butadiene. *sec*-Butylmagnesium bromide, phenethylmagnesium bromide, and phenylmagnesium bromide failed to react with this olefin.

The Grignard reagents, *tert*-butyl-, and benzyl-magnesium chloride, condensed additively with 1,6-dibiphenylene-1,3,5-hexatriene in a 1,6-manner.

In contrast to this terminal addition of Grignard reagents, phenyllithium has been found to add twice to dibiphenylenebutadiene. The product of the reaction is a mixture of the stereoisomeric *sym*-diphenyldifluorenylethanes.

Radical interchange between Grignard reagents and alkyl halides was observed when various Grignard reagents were allowed to react with *tert*-butyl chloride in the presence of a third reactant, dibiphenylenebutadiene.

An anomalous ozonization of an olefin has been described.

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REFERENCES

- (1) FUSON AND PORTER, *J. Am. Chem. Soc.*, **70**, 895 (1948).
- (2) INGOLD, *J. Chem. Soc.*, 1268 (1928).
- (3) WIELAND AND KRAUSE, *Ann.*, **443**, 129 (1925).
- (4) KHARASCH AND FUCHS, *J. Org. Chem.*, **10**, 292 (1945).
- (5) KHARASCH, LAMBERT, AND URRY, *J. Org. Chem.*, **10**, 298 (1945).
- (6) WISLICENUS AND MOCHER, *Ber.*, **46**, 2785 (1913).
- (7) VANSCHIEDT AND MOLDAVSKI, *Ber.*, **64**, 917 (1931).
- (8) SCHLENK AND BERGMANN, *Ann.*, **463**, 202 (1928).
- (9) SCHMITT, *Ann.*, **547**, 103 (1941).
- (10) SCHLENK AND BERGMANN, *Ann.*, **463**, 1 (1928).
- (11) ZIEGLER AND SCHÄFFER, *Ann.*, **411**, 101 (1934).
- (12) ULLMANN AND WURSTEMBERGER, *Ber.*, **38**, 4108 (1905).