Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.56; H, 4.6; N, 9.15. Found: C, 70.48; H, 4.5; N, 9.44.

4-(*m*-Nitrostyryl)-quinoline.—After repeated recrystallization, the styryl compound was finally obtained in pure form from a mixture with the corresponding dilepidine derivative.

Lepidine (5 g.), *m*-nitrobenzaldehyde (5.3 g.), and 3 cc. of concentrated hydrochloric acid were heated in a two-necked flask at 120° (inside temperature) during three hours. After cooling to room temperature, chloroform (50 cc.) was added and the mixture kept in an ice-bath for two hours. The solid was then filtered off, washed with 50 cc. of chloroform, the yellow-brown crystals suspended in water, and made alkaline to litmus with 8 *N* sodium hydroxide solution. The yellow solid was dissolved in chloroform, the solution washed with water, dried over anhydrous sodium sulfate, filtered, and the filtrate evaporated to dryness, giving 6.2 g. of yellow solid.

The crude product was dissolved in 15 volumes of boiling absolute ethanol plus 8 volumes of chloroform, filtered, and the filtrate kept in the refrigerator overnight. A small crop of cream-colored crystals which separated was filtered off and dried (0.7 g.); m. p. 220–230°. Microchemical analysis indicated that it was slightly impure dilepidine derivative. The mother liquor was kept in the refrigerator for a week, giving a second crop of cream-colored solid (0.5 g.); m. p. 217–231°.

The mother liquor of the second crop was evaporated to dryness (4.9 g.); m. p. 130–134°. It was recrystallized from 8 volumes of boiling absolute ethanol. The pure *m*-styryl compound separated on cooling, and was filtered off and dried (3.7 g.).

4-(*p*-Nitrostyryl)-quinoline.—When prepared as described for the *m*-styryl compound, in the presence of hydrochloric acid, the *p*-styryl derivative could not be separated from its impurity (probably the dilepidine compound) by repeated recrystallization. The most satisfactory method for obtaining the pure *p*-styryl compound when the impurity was the dilepidine derivative (*not* the carbinol compound) was by treatment with hydrochloric acid, as follows:

Impure *p*-styryl derivative (4 g.) was treated with 240 cc. of chloroform and a trace (0.1 g.) of insoluble material (which seemed to consist mainly of the more insoluble dilepidine derivative) filtered off. To the filtrate was added 100 cc. of 5% hydrochloric acid and the mixture swirled. The hydrochlorides which separated were filtered off, suspended in 150 cc. of 1% hydrochloric acid, the suspension boiled for a few minutes, filtered while hot, and the yellow solid washed with about 50 cc. of hot 1% hydrochloric acid. The solid hydrochloride was then suspended in dilute sodium hydroxide solution, the base extracted with chloroform, the chloroform solution washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness (2.5 g.). This material was now recrystallized by dissolving in 15 volumes of boiling absolute ethanol plus 25 volumes of chloroform. The solution was kept in the refrigerator overnight, and the crystals filtered off and dried (2.2 g.).

Summary

The three mononitrophenyllepidylcarbinols and their acetates and monohydrochlorides have been prepared and some of their properties are described. The corresponding styryl derivatives were isolated in pure form.

A method has been developed for the preparation of the *m*- and *p*-nitrobenzylidene dilepidines in good yield, and some of their properties are recorded.

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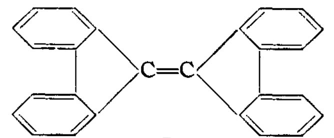
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Addition of Grignard Reagents to the Olefin, Bidiphenyleneethylene

BY REYNOLD C. FUSON AND HERSCHEL D. PORTER[1]

Attempts to add Grignard reagents to olefins, involving a large number of hydrocarbons and a wide range of experimental conditions, have yielded only negative results.[2,3,4] Apparently successful attempts reported in some instances,[5,6] were subsequently found to have been misleading.[7]

The demonstration by Pinck and Hilbert[8] that bidiphenylethylene (I) as well as its tetrabromo derivative was capable of reacting additively with various carbonyl reagents suggested that this highly conjugated olefin might also combine with Grignard reagents. This idea was favored by the discovery of Ziegler and Schäfer[9] that phenyllithium condensed with bidiphenyleneethylene to give 1-phenyl-1,2-bidiphenyleneethane (II, R = C_6H_5).



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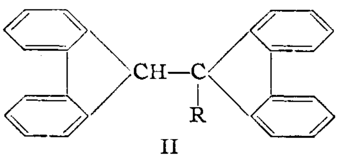

II

In the present work it has been found that certain Grignard reagents will react with bidiphenyleneethylene to produce the corresponding substituted ethanes (II). It appeared that the best chance of success was to employ *t*-butyl or benzyl Grignard reagents, shown by Kharasch and Weinhouse[10] to be the most reactive.

When *t*-butylmagnesium chloride was allowed to react with bidiphenyleneethylene, 1-*t*-butylbidiphenyleneethane (II, R = C_4H_9) was produced in good yield. Similarly, benzylmagnesium chlo-

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[1] Rohm and Hass Research Assistant, 1946–1947.

[2] Gilman and Crawford, THIS JOURNAL, **45**, 554 (1923).

[3] Kinney and Larsen, *ibid.*, **57**, 1054 (1935).

[4] Gilman and Peterson, *ibid.*, **48**, 423 (1926).

[5] Rupe and Bürgin, *Ber.*, **43**, 172 (1910).

[6] Rupe, *Ann.*, **402**, 149 (1913).

[7] Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).

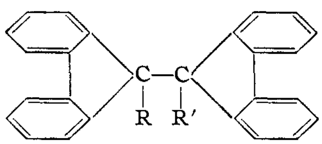
[8] Pinck and Hilbert, THIS JOURNAL, **57**, 2398 (1935); **68**, 2014 (1946).

[9] Ziegler and Schäfer, *Ann.*, **511**, 101 (1934).

[10] Kharasch and Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

ride gave 1-benzylbidiphenyleneethane (II, R = $C_6H_5CH_2$). In one experiment with the benzyl reagent the chief product was 1,2-dibenzylbidiphenyleneethane (III, R = R′ = $C_6H_5CH_2$). It seemed likely that this product formed through benzylation of the primary adduct by excess benzyl chloride present in the solution of the Grignard reagent. In confirmation of this surmise, it was found that the dibenzyl derivative could be made in good yield by treating the olefin with benzylmagnesium chloride and then adding benzyl chloride to the resulting reaction mixture.

p-Chlorobenzylmagnesium chloride reacted in much the same way as the benzyl Grignard reagent. The structures assigned to the alkylated ethanes are indicated by analogy with the products obtained in other addition reactions of the olefin. They are given additional support by the following observations.



III

Treatment of the addition product from the olefin and benzylmagnesium chloride with *p*-chlorobenzyl chloride yielded 1-benzyl-2-*p*-chlorobenzylbidiphenyleneethane (III, R = $C_6H_5CH_2$, R′ = $ClC_6H_4CH_2$). The same derivative was formed by benzylation of the adduct from *p*-chlorobenzylmagnesium chloride and the olefin.

The bidiphenyleneethylene was prepared by the action of methanolic potassium hydroxide on 9-bromofluorene according to the directions of Thiele and Wanscheidt.[11] The bromofluorene was synthesized by a new method—treatment of fluorene with N-bromosuccinimide by the procedure of Ziegler, Späth, Schaaf, Schumann and Winkelmann.[12] The bromofluorene was made also by photochemical bromination of fluorene by the procedure of Sampey and Reid.[13] This method has the advantage of extreme simplicity and affords higher yields.

Attempts to condense less reactive Grignard reagents with bidiphenyleneethylene failed. Neither phenylmagnesium bromide nor methylmagnesium iodide proved to be capable of undergoing addition.

Inasmuch as Ziegler, Späth, Schaaf, Schumann and Winkelmann[12] have been able to add phenyllithium to benzalfluorene, it seemed possible that the Grignard reagent might react in a similar manner. Efforts to bring about condensation of this olefin with *t*-butylmagnesium chloride were, however, unsuccessful.

Experimental

9-Bromofluorene.—A solution of 99.6 g. of commercial fluorene (m. p. 108–111°) in 500 ml. of dry thiophene-free benzene was heated for four hours under reflux with an equimolar amount (106.8 g.) of N-bromosuccinimide, prepared (in 71% yield) by the directions of Ziegler, Späth, Schaaf, Schumann and Winkelmann.[12] The precipitate of succinimide which formed during this process was removed by filtration, the solvent distilled from the filtrate, and the residue taken up in 500 ml. of hot, high-boiling petroleum ether. Cooling caused long needle-like crystals of 9-bromofluorene to precipitate; yield 69 g., 47%; m. p. 103–104°.

The bromofluorene was also prepared, in approximately the yields reported, by the photochemical bromination of fluorene according to the directions of Sampey and Reid.[13]

Bidiphenyleneethylene.—The general directions of Thiele and Wanscheidt[11] were followed. A solution of 20 g. of 9-bromofluorene in 150 ml. of acetone was caused to react at room temperature with a solution of 10 g. of potassium hydroxide in 30 ml. of methanol. After one hour, 100 ml. of water was added, with vigorous stirring. The precipitate of bidiphenyleneethylene was collected by filtration and allowed to dry in the air overnight. The products of two such preparations were taken up in 50 ml. of boiling benzene, and precipitation was induced by the addition of 50 ml. of boiling alcohol; yield 64%; m. p. 188–190° (uncor.).

1-*t*-Butyl-1,2-bidiphenyleneethane.—A solution of *t*-butylmagnesium chloride, prepared from 9.25 g. of *t*-butyl chloride, 2.43 g. of magnesium and 130 ml. of absolute ether, was freed of magnesium by forcing it through a glass wool plug by means of nitrogen pressure. The *t*-butylmagnesium chloride was added to a solution of 3.28 g. of bidiphenyleneethylene in 100 ml. of a mixture of equal parts of dry benzene and absolute ether. After the material had been heated for eighteen hours under reflux in an atmosphere of nitrogen, with constant stirring, it was poured on an ice–hydrochloric acid mixture. The organic layer was separated and washed with very dilute hydrochloric acid. After the solvent had been removed by distillation, the residue was taken up in 15 ml. of boiling chloroform; precipitation was induced by the addition of 30 ml. of 95% ethanol; yield 2.63 g., or 68%. After the above purification procedure had been repeated ten times, the material was found to be analytically pure; m. p. 221–223° (cor.).

Anal. Calcd. for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.24; H, 6.90.

1-Benzyl-1,2-bidiphenyleneethane.—A solution of benzylmagnesium chloride, prepared from 5.06 g. of benzyl chloride, 0.97 g. of magnesium and 100 ml. of absolute ether, was heated under reflux for one hour. Bidiphenyleneethylene (3.28 g.) was added in the form of small crystals. The solution was stirred overnight under gentle reflux, poured on an ice–hydrochloric acid mixture and processed as in the preceding experiment. A precipitate of 2.42 g. of light yellow needles melting at 223–231° (uncor.) was obtained; yield 57.6%. The sample for analysis did not reach a constant melting point until it had been subjected to twelve purifications in the manner described for the purification of 1-*t*-butyl-1,2-bidiphenyleneethane; m. p. 240–241° (cor.).

Anal. Calcd. for $C_{33}H_{24}$: C, 94.24; H, 5.75. Found: C, 94.25; H, 5.92.

1-*p*-Chlorobenzyl-1,2-bidiphenyleneethane.—A solution of *p*-chlorobenzylmagnesium chloride was prepared by the dropwise addition of 3.22 g. of *p*-chlorobenzyl chloride to 0.49 g. of magnesium in 50 ml. of absolute ether. After the solution was stirred under reflux for one hour, 3.28 g. of bidiphenyleneethylene was added in the form of small crystals. The solution was heated under reflux in an atmosphere of dry nitrogen for sixteen hours and worked up in the usual manner. Removal of the solvent produced a red oil which deposited yellow crystals when triturated with 100 ml. of low-boiling petroleum

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(11) Thiele and Wanscheidt, *Ann.*, **376**, 269 (1910); Wittig and Lange, *ibid.*, **536**, 266 (1938).

(12) Ziegler, Späth, Schaaf, Schumann and Winkelmann, *ibid.*, **551**, 80 (1942).

(13) Sampey and Reid, THIS JOURNAL, **69**, 235 (1947).

ether. The compound was purified in the manner described for 1-*t*-butyl-1,2-bidiphenyleneethane; m. p. 234–235° (cor.); yield 12.5%.

Anal. Calcd. for $C_{33}H_{23}Cl$: C, 87.11; H, 5.10. Found: C, 86.97; H, 5.38.

1,2-Dibenzyl-1,2-bidiphenyleneethane.—A solution of benzylmagnesium chloride was formed by the addition of 0.67 g. of benzyl chloride to 0.14 g. of magnesium in 16 ml. of absolute ether. One gram of bidiphenyleneethylene was added immediately after the addition of the benzyl chloride was complete. The reaction mixture was diluted with 50 ml. of absolute ether, heated under reflux overnight and processed in the usual manner. The analytical sample was prepared by repeated recrystallization from a solvent composed of six parts of benzene and one part of toluene; m. p. 204–205° (cor.); yield 36%.

Anal. Calcd. for $C_{40}H_{30}$: C, 94.07; H, 5.93. Found: C, 93.80; H, 6.27.

A solution of benzylmagnesium chloride, prepared from 2.53 g. (0.02 mole) of benzyl chloride, 0.48 g. of magnesium and 50 ml. of absolute ether, was protected from the air by a stream of dry nitrogen and stirred for one hour to ensure completion of the reaction. A solution of 3.28 g. (0.01 mole) of bidiphenyleneethylene in 50 ml. of dry benzene and 30 ml. of absolute ether was then added. After the solution had been heated under reflux for four hours, 3 g. of benzyl chloride was added. The mixture was heated under reflux for fifteen hours and processed in the usual manner. The product was purified by dissolving in hot chloroform and reprecipitating by the addition of boiling alcohol. After two such operations the melting point was 196–198° (uncor.); a mixed melting point with the 1,2-dibenzyl-1,2-bidiphenyleneethane obtained previously was not depressed (196–198°).

1-Benzyl-2-*p*-chlorobenzyl-1,2-bidiphenyleneethane.—The benzylmagnesium chloride was prepared as in the preceding experiment and allowed to react with 3.28 g. of bidiphenyleneethylene dissolved in 100 ml. of a solvent composed of equal parts of dry benzene and absolute ether. After the solution had been heated under reflux for eighteen hours, 3.50 g. of *p*-chlorobenzyl chloride was added, and the reaction mixture was heated overnight under reflux, with mechanical stirring. The reaction mixture was poured on an ice–hydrochloric acid mixture, and the organic layer was washed with water. The reddish oil that remained, after removal of the solvent and trituration with low-boiling petroleum ether, deposited 1.69 g. of yellow, sandy crystals. Purification was accomplished by dissolving the compound in hot chloroform, and reprecipitating it by the addition of boiling alcohol. The analytical sample consisted of white needles and possessed a melting point of 203–205° (uncor.).

Anal. Calcd. for $C_{40}H_{29}Cl$: C, 88.13; H, 5.36. Found: C, 87.87; H, 5.66.

The addition product of *p*-chlorobenzylmagnesium chloride and bidiphenyleneethylene was prepared as in the preparation of 1-*p*-chlorobenzyl-1,2-bidiphenyleneethane. After the reaction mixture had been heated under reflux for eight hours, 2.78 g. of benzyl chloride was added, and the solution was heated under reflux overnight. The reaction mixture was poured on an ice–hydrochloric acid mixture; the organic layer was separated, washed with water and evaporated to dryness. The residual, red oil was triturated with a mixture of 8 ml. of benzene and 4 ml. of carbon tetrachloride in a bath of solid carbon dioxide; a precipitate of 0.37 g. (7%) was deposited. The material was purified as in the above experiment. Softening occurred at 195–199° and melting took place at 199–202°. A mixture with the product obtained in the preceding experiment softened at 196–199° and melted at 199–203°.

Attempted Reaction with Phenylmagnesium Bromide.—A solution of phenylmagnesium bromide, prepared from 3.14 g. of bromobenzene, was protected at all times from the air by an atmosphere of nitrogen. Bidiphenyleneethylene (3.2 g.) was added, and the solution was heated under reflux for twenty-five hours. It was then poured on an ice–hydrochloric acid mixture and worked up in the usual manner. A total of 2.84 g. (89%) of the original hydrocarbon was recovered.

Attempted Reaction with Methylmagnesium Iodide.—An ether solution, containing 0.02 mole of methylmagnesium iodide, was heated overnight under reflux with 3.28 g. (0.01 mole) of bidiphenyleneethylene. In addition to 2.53 g. (77%) of bidiphenyleneethylene recovered, a small amount of bidiphenyleneethane was obtained; m. p. 247–248° (cor.).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.50; H, 5.49. Found: C, 94.45; H, 5.75.

Attempted Reaction of Grignard Reagents with Benzalfluorene.—The Grignard solution was prepared as described in the preparation of 1-*t*-butyl-1,2-bidiphenyleneethane. A solution of 2.55 g. of benzalfluorene, prepared in 70% yield according to the directions of Henle,[14] in 50 ml. of absolute ether was added, and the solution heated overnight under reflux in an atmosphere of nitrogen. A total of 2.11 g. (83%) of unchanged benzalfluorene was obtained.

In a similar experiment 5.10 g. (0.02 mole) of benzalfluorene was added to a solution of 0.04 mole of benzylmagnesium chloride, and the solution was heated under reflux for twenty-four hours. A total of 4.33 g. (84%) of unchanged benzalfluorene was recovered.

Summary

Grignard reagents have been found to react additively with the olefin, bidiphenyleneethylene. Reaction with *t*-butyl-, benzyl- or *p*-chlorobenzylmagnesium chlorides converts the olefin to the corresponding 1-alkylbidiphenyleneethane.

When the adduct obtained with benzylmagnesium chloride was treated with *p*-chlorobenzyl chloride, the product was 1-benzyl-2-chlorobenzylbidiphenyleneethane. The same compound was produced by the action of benzyl chloride on the adduct formed by *p*-chlorobenzylmagnesium chloride and the olefin. These facts show that the two points of attachment of the Grignard reagent are symmetrically situated.

URBANA, ILLINOIS RECEIVED SEPTEMBER 15, 1947

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[14] Henle, *Ann.*, **347**, 290 (1906).