Dry Ice. The reaction mixture was worked up by conventional methods, but the yield of 2,4-diphenyl-3-butenoic acid, m.p. 123.5–124.5°, was only 9%. Recrystallization from ligroin (b.p. 90–95°) gave pure acid, m.p. 125–126°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92, neutral equivalent, 238.3. Found: C, 80.71; H, 6.06; neutral equivalent, 243. Ultraviolet spectrum (95% ethanol): λ_{max} 252 (log ϵ 4.352), 283.5 (log ϵ 3.318), 292.5 mμ (log ϵ 3.121).

This acid is relatively stable to a temperature of 150° for a short time, but after heating at 100–115° for 2 hr. in a capillary tube, the m.p. was 118–119°.

Methyl 2,4,-diphenyl-3-butenoate was prepared from the acid with diazomethane; after recrystallization from ethanol at low temperatures, the ester melted at 35–36°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.71; H, 6.37.

2,4-Diphenyl-3-buten-1-ol.[7] Methyl 2,4-diphenyl-3-butenoate was reduced with excess lithium aluminum hydride in ether, the reaction mixture worked up as usual and the product distilled, b.p. 175–185°/1.4 mm. The yield was 70%, but the distillate was a mixture containing about 82% of 2,4-diphenyl-3-buten-1-ol on the basis of combustion analysis. The infrared spectrum was that expected of such a mixture.

Attempts were made to remove the ester by saponification with aqueous methanolic potassium hydroxide or sodium ethylate, but neutral material recovered from the reaction still gave a low carbon analysis even though the ester group appeared to have disappeared on the basis of the infrared spectrum. The product was a viscous red oil which deposited a solid. The solid was purified by chromatography on neutral, activated alumina and recrystallization from alcohol, m.p. 137–138°. It was shown to be dimer I by analysis, ultraviolet absorption and a mixed melting point determination. The yield was about 10% based on 2,4-diphenyl-3-buten-1-ol in the reaction mixture used.

The residual red oil would not distill below 200° at 1 to 2 mm., and did not give a correct analysis for 2,4-diphenyl-3-buten-1-ol.

Crude 2,4-diphenyl-3-buten-1-ol from the lithium aluminum hydride reduction was treated with 3,5-dinitrobenzoyl chloride in pyridine and gave a 3,5-dinitrobenzoate in 27% yield, m.p. 125–126° after recrystallization from aqueous acetone.

Anal. Calcd. for $C_{23}H_{18}O_6N_2$: C, 66.02; H, 4.34. Found: C, 66.28; H, 4.23.

The small amount of the 3,5-dinitrobenzoate that was available was pyrolyzed under nitrogen, but neither 1,3-diphenyl-1,3-butadiene nor its dimer was obtained.

Crude 2,4-diphenyl-3-buten-1-ol was refluxed with 2.5*N* aqueous alcoholic sulfuric acid but no dimer was obtained.

Although the experiments described here are only preliminary, this method to 1,3-diphenyl-1,3-butadiene does not appear promising and further work in this direction is not planned.

LOS ANGELES, CALIF.

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

2-Phenyl-1,3-butadiene and Related Compounds[1]

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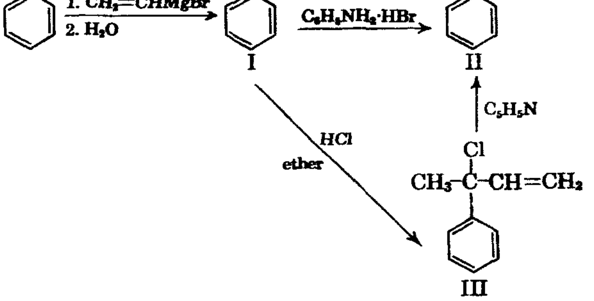
2-Phenyl-1,3-butadiene (II) has been prepared from acetophenone and vinylmagnesium bromide in a two-step synthesis. The synthesis and properties of several new and related compounds are given.

Recently, Normant discovered[2] that vinylmagnesium bromide could be prepared and used in reactions quite easily in tetrahydrofuran solvent. This work suggested a convenient route for the synthesis of 2-aryl-substituted dienes which are sometimes difficult to obtain in good yield by other methods. Thus, treatment of acetophenone with vinylmagnesium bromide gave methylphenylvinylcarbinol (I) in 75% yield. This carbinol (I) has been prepared previously by reaction[3] of acetophenone and the di-Grignard reagent of diacetylene, followed by hydrolysis and catalytic hydrogenation,[4] and by the action[5] of phenylmagnesium bromide on methyl vinyl ketone. However, the present method produced considerably better yields than previously reported. Dehydration of the carbinol (I) by slow distillation from aniline hydrobromide gave 2-phenyl-1,3-butadiene (II) in 61% yield. This represents an over-all yield of 46% from acetophenone for a two-step synthesis, and is possibly the best route presently available for preparing 2-phenyl-1,3-butadiene. All previous methods[6] involved numerous steps or poor yields or both. Treatment of methylphenylvinylcarbinol with an-



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[1] The work discussed herein was supported by a grant from the National Science Foundation for polymer research.

[2] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[3] Yu. S. Zal'kind and A. P. Ivanov, *Zhur. Obshchei Khim.*, **11**, 803 (1941); *Chem. Abstr.*, **36**, 3790 (1942).

[4] Kh. V. Bal'yan, *Zhur. Obshchei Khim.*, **24**, 501 (1954); *Chem. Abstr.*, **49**, 6174 (1955).

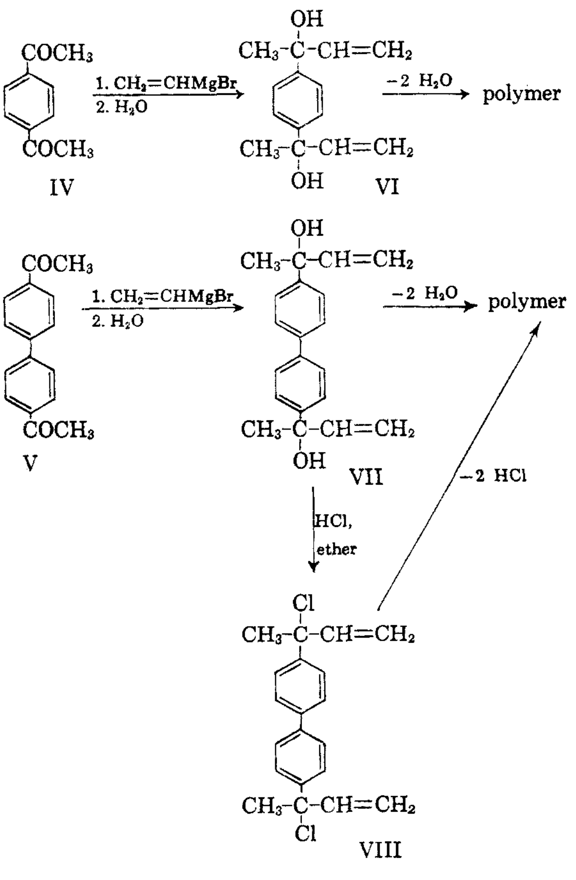
[5] A. I. Lebedeva and V. A. Shlyakova, *Zhur. Obshchei Khim.*, **19**, 1290 (1949); *Chem. Abstr.*, **44**, 1054 (1950).

[6] J. E. Faraday, *Faraday's Encyclopedia of Hydrocarbon Compounds*, Chemindex Ltd., Manchester, England, 1954, Volume 5.

hydrous hydrogen chloride in ether produced methylphenylvinylchloromethane (III) in 50.5% yield. Dehydrohalogenation of this chloro-compound (III) with pyridine produced 2-phenyl-1,3-butadiene (II) in only 36% yield, however.

In an effort to extend this apparently general method to the synthesis of difunctional dienes, reactions were run on *p*-diacetylbenzene (IV) and *p,p'*-diacetylbiphenyl (V). Reaction of vinylmagnesium bromide with *p*-diacetylbenzene (IV) produced *p*-phenylenebis(methylvinylcarbinol) (VI) in 67% yield. A similar reaction with *p,p'*-diacetylbiphenyl (V) gave *p,p'*-biphenylenebis(methylvinylcarbinol) (VII) in 68% yield. These products were presumed to be mixtures of the expected stereoisomers which were not separated. All attempts to dehydrate the dicarbinols resulted in the formation of insoluble glassy polymers. Oxidation of *p*-phenylenebis(methylvinylcarbinol) (VI) with alkaline potassium permanganate gave terephthalic acid.

Treatment of *p,p'*-biphenylenebis(methylvinylcarbinol) (VII) with anhydrous hydrogen chloride in ether produced *p,p'*-biphenylenebis(methylvinylchloromethane) (VIII) in 67% yield. Attempts to dehydrohalogenate this compound were also unsuccessful. These unsuccessful reactions appear to be due to the high reactivity of the difunctional dienes which would be expected to be produced and to their tendencies to form polymeric mixtures.



In an earlier attempt to prepare 2,2'-*p*-phenylenedibutadiene from *p*-phenylenebis(succinic acid), terephthalaldehyde was condensed with malonic ester to give tetraethyl *p*-phenylenebis(methylenemalonate) (IX) in 38% yield. Further reactions similar to those described for the preparation of phenylsuccinic acid[7] led to unidentifiable products so the reaction scheme was abandoned. Since this ester (IX) had not been made previously, its preparation is described in the experimental section.

EXPERIMENTAL[8]

Methylphenylvinylcarbinol (I). A solution of vinylmagnesium bromide in 1200 ml. of tetrahydrofuran was prepared from vinyl bromide (214 g., 2.0 moles) and magnesium (48.6 g., 2.0 g.-atoms) as described by Seyferth and Stone.[9] Acetophenone (200 g., 1.67 moles) dissolved in 500 ml. of tetrahydrofuran was added at a rate to maintain gentle reflux and stirring was continued an additional hour. After hydrolysis with 500 ml. of a saturated aqueous solution of ammonium chloride, the organic layer was distilled. The tetrahydrofuran was removed on a steam bath and the residue distilled through a 12-in. Vigreux column to yield 184 g. (75%) of methylphenylvinylcarbinol, a colorless liquid of b.p. 73–74° (1.0 mm.), n_D^{20} 1.5338 [reported[4] b.p. 62° (0.5 mm.), n_D^{20} 1.5338].

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.08; H, 8.41.

The infrared spectrum (10% solution in chloroform) shows bands at 3570, 3400 cm.$^{-1}$ (hydroxyl[10]) and 1642 cm.$^{-1}$ (vinyl) in addition to the expected methyl and benzene bands. No carbonyl absorption was present.

p-Phenylenebis(methylvinylcarbinol) (VI). This compound was prepared in a manner similar to that for methylphenylvinylcarbinol. The following reagents were used: vinyl bromide (48.2 g., 0.45 mole) and magnesium (11.0 g., 0.45 g.-atom) in tetrahydrofuran (300 ml.), *p*-diacetylbenzene[11] (24.0 g., 0.15 mole) in tetrahydrofuran (100 ml.). The yield of colorless crystals, recrystallized from cyclohexane, was 22.0 g. (67%), m.p. 99–100°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.05; H, 8.44.

The infrared spectrum (10% solution in chloroform) shows bands at 3635 and 3470 cm.$^{-1}$ (hydroxyl[10]) and 1642 cm.$^{-1}$ (vinyl) in addition to the expected methyl and benzene bands. No carbonyl absorption was noted.

p,p'-Biphenylenebis(methylvinylcarbinol) (VII). This compound was prepared in the usual manner from vinyl bromide (16.0 g., 0.15 mole) and magnesium (3.64 g., 0.15 g.-atom) in tetrahydrofuran (300 ml.) and *p,p'*-diacetylbiphenyl[12] (11.0 g., 0.046 mole) in tetrahydrofuran (300 ml.). It was necessary to warm the solution of the diketone to prevent

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[7] C. F. H. Allen and H. B. Johnson, *Org. Syntheses*, **30**, 83 (1950).

[8] The melting points are not corrected. We are indebted to Mr. Jozsef Nemeth of the Microanalytical Laboratory of the University of Illinois for the microanalyses of carbon and hydrogen, to Clark Microanalytical Laboratory, Urbana, Ill., for the microanalyses of chlorine, and to Mr. Paul McMahon of the University of Illinois for the infrared data.

[9] D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957).

[10] In each case, the second hydroxyl band (*ca.* 3400 cm.$^{-1}$) disappeared on dilution of the chloroform solution, indicating it was due to intermolecular hydrogen bonding.

[11] R. Riemschneider, *Gazz. chim. ital.*, **77**, 607 (1947).

[12] L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941).

crystallization and to add it while still warm. Recrystallization of the product from benzene–*n*-pentane (1:3) gave 9.2 g. of colorless crystals (68%), m.p. 117–118°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.66; H, 7.78.

The infrared spectrum (10% solution in chloroform) shows bands at 3562, 3400 cm.$^{-1}$ (hydroxyl[10]) and 1642 cm.$^{-1}$ (vinyl) in addition to the expected methyl and benzene bands. No carbonyl absorption was present.

Reaction of p-phenylenebis(methylvinylcarbinol) (VI) *with potassium permanganate.* A mixture of *p*-phenylenebis(methylvinylcarbinol) (1.00 g., 0.0046 mole), potassium permanganate (7.27 g., 0.046 mole), sodium hydroxide (1.00 g., 0.025 mole), and water (30 ml.) was heated under reflux for 24 hr. The mixture was cooled, and filtered from the manganese dioxide which was washed thoroughly with water. The filtrate was acidified with dilute sulfuric acid and the white precipitate obtained was filtered and washed with cold water. Recrystallization from glacial acetic acid yielded 0.46 g. of white crystals, m.p. above 300°.

An infrared spectrum (Nujol) of this acid was identical with a spectrum of authentic terephthalic acid.

A portion of this acid was converted to the ethyl ester, m.p. 42–44°. Mixed melting point with authentic diethyl terephthalate was 42–44°.

The 0.46 g. of product represents a 60% yield of terephthalic acid.

Methylphenylvinylchloromethane (III). A solution of methylphenylvinylcarbinol (10.0 g., 0.068 mole) in anhydrous ether (50 ml.) was cooled in an ice bath and anhydrous hydrogen chloride was bubbled through the solution for 3 hr. The ether and hydrogen chloride were removed at atmospheric pressure and the crude product dissolved in fresh ether (50 ml.). The ether solution was washed with dilute sodium carbonate and water and dried over anhydrous magnesium sulfate. Two distillations through a Vigreux column yielded methylphenylvinylchloromethane, a colorless liquid of b.p. 56–58° (0.5 mm.), n_D^{20} 1.5520. The yield was 5.7 g. (50.5%).

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.09; H, 6.66; Cl, 21.25. Found: C, 71.88; H, 6.65; Cl, 21.17.

The infrared spectrum shows bands at 1629 cm.$^{-1}$ (vinyl) and 720 cm.$^{-1}$ (C-Cl) in addition to the expected methyl and benzene bands. No absorption above 3040 cm.$^{-1}$ was present (no hydroxyl).

p,p'-Biphenylenebis(methylvinylchloromethane) (VIII). A solution of *p,p'*-biphenylenebis(methylvinylcarbinol) (3.00 g., 0.010 mole) in anhydrous ether (100 ml.) was cooled and treated with anhydrous hydrogen chloride for 1 hr. The product was isolated as in the previous example. Recrystallization from benzene–*n*-pentane yielded colorless needles (2.28 g., 67%), m.p. 144.5–145°.

Anal. Calcd. for $C_{20}H_{20}Cl_2$: C, 72.50; H, 6.09; Cl, 21.41. Found: C, 72.34; H, 6.08; Cl, 20.95.

The infrared spectrum (Nujol) shows a band at 1634 cm.$^{-1}$ (vinyl) in addition to the expected methyl and benzene bands. No absorption above 2910 cm.$^{-1}$ was noted (no hydroxyl).

2-Phenyl-1,3-butadiene (II). (*a*) *Dehydration of methylphenylvinylcarbinol.* Methylphenylvinylcarbinol (40.0 g., 0.27 mole), aniline hydrobromide (4 g.), and hydroquinone (0.5 g.) were mixed in a 100-ml., round-bottomed flask connected to a 6-in. Vigreux column with distillation take-off. The pressure was reduced to 13 mm. and the flask heated in an oil bath, initially at 100° so that a very slow distillation took place. The reaction took 4 hr. and the oil bath temperature was ultimately raised to 150°. In the receiver, which was cooled in an ice salt bath, was collected a colorless liquid of b.p. 57–63° (13 mm.), n_D^{20} 1.5475 [reported,[13] b.p. 55–64° (15 mm.), n_D^{20} 1.5489]. The product contained a few droplets of water, the bulk of which was physically removed using a separatory funnel and the sample was dried by adding a few pellets of anhydrous calcium chloride and letting it stand for a few hours at 0°. The drying agent was filtered off and a colorless liquid obtained[14] (21.5 g., 61%) which reacted instantaneously in the cold with maleic anhydride to form the expected Diels-Alder adduct, 4-phenyl-Δ^4-tetrahydrophthalic anhydride, in 85% yield; m.p. 104.5–105° (lit. m.p. 105°[13,15]).

2-Phenyl-1,3-butadiene and 1,4-naphthoquinone, heated at 100° for 2 hr., yielded the expected 1,4-dihydro-3-phenyl-9,10-anthroquinone, colorless crystals of m.p. 143.5–144° (recrystallized from ethanol) (reported,[15] m.p. 144°).

The infrared spectrum of 2-phenyl-1,3-butadiene shows bands at 1687, 1625, 1590 cm.$^{-1}$ (conjugated double bonds), and 1600, 1577, 1497 cm.$^{-1}$ (phenyl) in addition to the expected C—H bands.

(b) *Dehydrohalogenation of methylphenylvinylchloromethane.* A solution of methylphenylvinylchloromethane (8.0 g., 0.05 mole), pyridine (40 ml.), and hydroquinone (0.5 g.) was heated under reflux for 1 hr., cooled, and poured into cold 10% sulfuric acid. The oily layer was ether extracted, washed with water and dried over anhydrous magnesium sulfate. Distillation yielded 2-phenyl-1,3-butadiene (2.2 g., 36%), b.p. 57–66° (13 mm.), n_D^{20} 1.5470.

Tetraethyl-p-phenylenebis(methylenemalonate) (IX). Terephthalaldehyde[16] (10.0 g., 0.075 mole), malonic ester (32.0 g., 0.20 mole), piperidine (0.5 ml.), and dry benzene (80 ml.) were heated under reflux for 48 hr. A trap was used to remove water from the reaction as it was formed. The benzene was distilled off at atmospheric pressure and the excess malonic ester removed under vacuum [95–100° (15 mm.)]. The residue, on cooling, solidified to a yellow mass, which was recrystallized from methanol. Colorless crystals of m.p. 135–136° were obtained. The yield was 12.0 g. (38%).

Anal. Calcd. for $C_{22}H_{26}O_8$: C, 63.15; H, 6.26. Found: C, 63.34; H, 6.42.

The infrared spectrum (10% solution in chloroform) shows bands at 1725 cm.$^{-1}$ (unsaturated ester carbonyl) and 1634 cm.$^{-1}$ (conjugated double bond) in addition to the expected benzene bands. No aromatic aldehyde bands were present.

URBANA, ILL.

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[13] O. Grummitt and H. Leaver, *J. Am. Chem. Soc.*, **74**, 1595 (1952).

[14] This product can be redistilled carefully with an 80% recovery of material. However, the physical constants do not change and for most normal reactions involving this compound, the redistillation is not necessary.

[15] C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, 71, 2860 (1949).

[16] J. M. Snell and A. Weissberger, *Org. Syntheses*, Coll. Vol. III, 788 (1955).