separated. Filtration and recrystallization from water yielded 5.2 g. (68%) of colorless plates, m. p. 204–205°. A mixed melting point with an authentic sample of *dl*-cineolic acid, m. p. 204–205°, prepared by the method of Wallach and Gildemeister,[7] gave no depression. (Wallach and Gildemeister report m. p. 196–197°, while m. p. 204–206° is reported by Rupe and Ronus[8] for this compound. Wallach and Gildemeister undoubtedly had impure material, as can readily be seen from their reported values for carbon and hydrogen.)

Anal. Calcd. for $C_{10}H_{16}O_5$: mol. wt., 216.2. Found (titration): mol. wt., 216.6.

Solution of the acid in boiling acetic anhydride, followed by removal of the solvent and recrystallization of the residue from ligroin, gave a quantitative yield of cineolic anhydride, m. p. 77–78°.[9]

---

(7) O. Wallach and E. Gildemeister, *Ann.*, **246**, 268 (1888).

(8) H. Rupe and M. Ronus, *Ber.*, **33**, 3544 (1900).

(9) O. Wallach, *Ann.*, **258**, 320 (1890).

Bureau of Entomology and Plant Quarantine
Agricultural Research Administration
U. S. Department of Agriculture
Beltsville, Maryland
Received October 22, 1946

The Catalytic Formation of Toluene from Benzene and Benzene–Methane at High Pressures

By V. N. Ipatieff and G. S. Monroe

Berthelot[1] observed the formation of toluene, along with other products, when a mixture of benzene and methane was passed through a porcelain tube at red heat. When benzene alone was subjected to the same treatment no toluene was obtained.

In high pressure experiments (232 atm., 600°) over alumina–silica cracking catalyst (15 wt. % aluminum oxide), we obtained toluene in low yields (1.1%) from benzene alone and in somewhat higher yields (4.6%, based on the weight of benzene charged) from benzene–methane, with the mole ratio of methane:benzene at 9:1. The biphenyl yield in the two cases was 9.6 and 3.0%, respectively.

The results obtained over a nickel–silica hydrogenation catalyst[2] are given below:

Table I

Conversion of Benzene and Benzene–Methane into Toluene over Nickel–Silica Catalyst at 372°

H. L. S. V.,[a] C_6H_6 1.0 ± 0.1
Mole ratio, CH_4/C_6H_6 1.8 ± 0.2

Charge	Press., atm.	Yields[b] as wt. % benzene charge Toluene	Carbon	% Recovered Benzene	Methane
C_6H_6	1	0.0	2.1	92.7	
C_6H_6	410	12.3	2.4	79.3	
C_6H_6	545	14.9	3.1	76.7	
$C_6H_6 + CH_4$	1	0.0	0.7	95.5	100.8
$C_6H_6 + CH_4$	410	15.3	1.0	83.0	98.0
$C_6H_6 + CH_4$	545	20.5	1.2	74.8	100.2

[a] Hourly liquid space velocity, volume of liquid charged per unit volume of catalyst per hour. [b] Naphthalene was found in the residues obtained from the fractionation of the liquid product.

Experimental

All experiments were made in continuous flow apparatus.[3] The total amount of benzene charged, either alone or when methane was present, varied from 1 to 1.5 moles, depending on the length of the experiment. The yields are reported on a once-through basis. A fresh charge of catalyst was used for each run. The composition of the liquid product was determined by fractionation, the toluene in the fraction between the benzene and the toluene plateaux of the distillation curve being evaluated by the refractive index. The presence of toluene was confirmed by the preparation of the 2,4-dinitro derivative. The biphenyl and naphthalene remaining behind in the fractionation residues were identified by mixed melting point.

---

(1) Berthelot, "Les Carbures d'Hydrogene," Gauthier-Villers, Paris, 1901.

(2) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

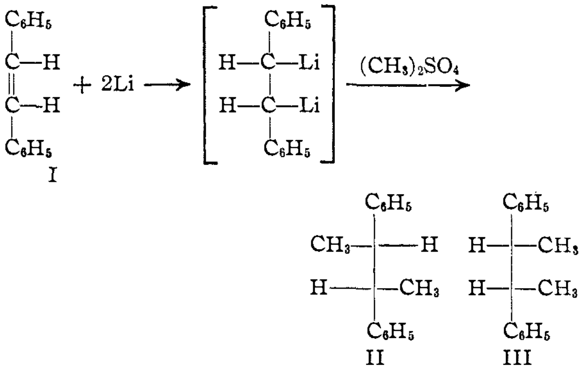
(3) Ipatieff and Monroe, This Journal, **67**, 2168 (1945).

Universal Oil Products Company
Research and Development Laboratories
Riverside, Illinois
Received June 14, 1946

The Bonding in Dimetalated Diphenylethane

By G. S. Myers, H. H. Richmond and George F Wright

In elaboration of previous work[1] it has been found that the same ratio (3:1) of *dd,ll*-2,3-diphenylbutane, II, to the *dl,ld*-diastereomer is formed with dimethyl sulfate whether the intermediate dimetalated diphenylethane, I, is formed from the reaction of either lithium or sodium with stilbene.



This ineffectiveness of the metal toward configuration of the reaction product II + III might suggest an ionic structure for I. Certainly the metal atoms are loosely bound. The list of reagents, like oxygen and methyl iodide, which will remove the metal entirely (stilbene being regenerated) has been extended in the present study by inclusion of sulfur and arsenic trichloride.

In spite of this evident loose bonding, no evidence of ion transport can be obtained after long electrolysis of disodiumdiphenylethane in glycol dimethyl ether solution between a mercury cathode and platinum anode. Although the conductance is quite low, the cathode contained no sodium after passage of fourteen coulombs. There was no observable migration of the color of the solution from either electrode. The solution reacted normally upon subsequent treatment with benzaldehyde.

---

(1) G. F. Wright, This Journal, **61**, 2106 (1939).

Experimental[2]

Dimetalated Diphenylethane.—The glycol dimethyl ether used as reaction medium was purified by refluxing over sodium under nitrogen until the blue sodium ketyl was formed when benzophenone was added. The dimethyl sulfate was purified by shaking with half-saturated aqueous sodium carbonate, drying with sodium sulfate and distilling to retain the fraction, b. p. 71.5° (10 mm.).

A solution of 27.0 g. (0.15 mole) of *trans*-stilbene in 300 cc. glycol dimethyl ether added over two to five hours to a stirred three-necked flask containing rigorously pure nitrogen and 13.8 g. (0.60 atom) of sodium wire or 4.16 g. (0.60 atom) of lithium wire suspended in 125 cc. of glycol dimethyl ether. Reaction was then completed by thirty minutes of subsequent stirring. The heat of reaction was small.

Reaction with Sulfur.—When 5 cc. (0.0021 mole) of the blue-green disodiumdiphenylethane solution was added to 2 g. of sulfur under nitrogen, the color changed to cherry red and the solution became warm. Subsequent processing yielded 0.3 g. of stilbene, m. p. 122°. Regeneration of stilbene was 75% of the theoretical amount.

Reaction with Arsenic Trichloride.—To 28 cc. (0.034 mole) of arsenic trichloride under nitrogen was added 5 cc. of the blue-green disodiumdiphenylethane solution. The solution turned black and became very warm. Hydrolysis with water and subsequent steam distillation yielded 0.18 g. (45%) of regenerated stilbene, m. p. 122°.

Electrolysis of Disodiumdiphenylethane Solution.—Forty ml. of the disodiumdiphenylethane solution was transferred under oxygen-free conditions to a 100-ml. test-tube equipped with a mercury cathode at the bottom (area 4 sq. cm.) and a 50-mesh platinum gauze anode (16 sq. cm.) 7 cm. above the cathode. A current of 3 milliamp. at 3 volts was passed for two hours. The solution was then drained off, the mercury washed with dry glycol dimethyl ether and filtered through a pin hole into water. Titration of the water solution with 0.2 *N* sulfuric acid showed no alkalinity present.

Reaction with Dimethyl Sulfate.—The reaction of disodium- or dilithiumdiphenylethane with methyl sulfate was very slow at −40°, but faster when the reaction mixture was held at 15–20° by a water-bath. To the stirred blue-green solution from 27 g. of stilbene was added 27.4 cc. (0.29 mole) of dimethyl sulfate in 150 cc. of glycol dimethyl ether over one hour. This bleached the solution to a pale lilac color. The reaction mixture was then filtered to remove excess metal as well as the metal sulfate. The filtrate was distilled under 10 mm. to remove excess glycol dimethyl ether. The dry residue was treated with water and ether; evaporation of the ether left 32.5 g. of crude product which was dissolved in benzene. Bromine was then added until a permanent brown color resulted. After vacuum evaporation of the benzene, the residue was steam distilled to remove the diphenylbutanes from non-volatile stilbene dibromide. Collection in ether of the diphenylbutanes in the distillate gave a solution which on vacuum evaporation yielded 29.6 g. of diphenylbutanes or 93%.

Separation of the diphenylbutanes was effected by ethanol crystallization. Solution of the 29.6 g. of product in 25 cc. of boiling ethanol yielded 6 g. of *meso*-2,3-diphenylbutane, m. p. 124° on cooling. A further 0.5 g. was obtained by concentration of the mother liquors. The remaining liquid isomer weighed 20.2 g. and distilled at 130–140° (10 mm.). The ratio of the *meso* isomer yield (6.5 g.) to that of the impure *dd,ll* isomer (19.5 g.) is 1:3 whether the metal is lithium or sodium.

Summary.—The yield of *dd,ll* and *dl,ld*-2,3-diphenylbutane is the same when either disodium or dilithiumdiphenylethane is treated with dimethyl sulfate. No transport can be detected when disodiumdiphenylethane is electrolyzed in glycol dimethyl ether.

Chemical Laboratory
University of Toronto
Toronto, Canada

Received November 2, 1946

---

[2] All melting points corrected against known standards.

Studies in the Quinoline Series. VII. 2-Dihydroxystyrylquinolines

By Alice G. Renfrew

Trypanocidal action has characterized certain 2-styrylquinolines especially when tested as quaternary salts.[1] Because the methylenedioxy group is frequently found in alkaloids and because both methylenedioxyphenyl[2] and catechol[3] structures influence physiological action in some cases, these modifications of the styryl group were utilized in the present study.

Experimental

2-(3,4-Dihydroxystyryl)-4-chloro-6-methoxyquinoline.—The condensation of 2-methyl-4-hydroxy-6-methoxyquinoline with piperonaldehyde was carried out by refluxing for twenty-four hours in acetic anhydride.[4] The condensation product was a tan powder, initially obtained as an oil because of the presence of piperonaldehyde. Extraction with ether and with aqueous alkali removed residual reactants, yield, 50%. A small sample, crystallized from pyridine, melted at 306°. This base, suspended in concentrated hydrochloric acid, forms an orange salt.

The preparation of the 4-chloro derivative was carried out by gently refluxing the above piperonal–quinoline condensation product with five volumes of phosphorus oxychloride; at the same time two chlorine atoms are introduced in the methylene group of the 3,4-methylenedioxystyryl nucleus.[5] For complete reaction it was found advantageous to use enough phosphorus oxychloride to permit rapid solution of the 4-carbostyril at refluxing temperature.

When the excess phosphorus oxychloride was decomposed in ice-water, and partially neutralized with alkali, a bright orange hydrochloride separated.

Anal. Calcd. for $C_{19}H_{12}NO_3Cl_3 \cdot HCl$: Cl, 31.91. Found: Cl, 32.0.

After prolonged treatment with aqueous carbonate, the above chloro-compound was converted to 2-(3,4-dihydroxystyryl)-4-chloro-6-methoxyquinoline; m. p. 173°, on recrystallization from 100 volumes of alcohol.

Anal. Calcd. for $C_{18}H_{14}NO_3Cl$: N, 4.28; Cl, 10.85. Found: N, 4.38; Cl, 11.09.

2-(3,4-Dihydroxystyryl)-4-amino-6-methoxyquinoline.—Replacement of the 4-chloro substituent by an amino group was carried out in the usual manner with ammonia in phenol. The 4-amino derivative, liberated from the hydrochloride, was not very soluble in ether or chloroform, but was crystallized from thirty volumes of hot absolute alcohol. The product was a tan solid; m. p. 205°, yield, 54%.

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: N, 9.1. Found: N, 8.8.

2-(3,4-Dihydroxystyryl)-4-thiocresyl-6-methoxyquinoline, CC975.[6]—The condensation of thiocresol with 2-(3,4-dihydroxystyryl)-4-chloro-6-methoxyquinoline was carried out in refluxing chloroform.[7] The reaction product

---

[1] Browning, Cohen, Ellingworth and Gulbranson, *Proc. Roy. Soc.* (London), **100B**, 293 (1926). Findlay, "Recent Advances in Chemotherapy," The Blakiston Company, Philadelphia, Pa., 1939.

[2] Bruckner and Fodor, *Ber.*, **71**, 541 (1938).

[3] Barger and Dale, *J. Physiol.*, **41**, 19 (1910); Hartung, *Chem. Rev.*, **9**, 389 (1931).

[4] Shaw and Wagstaff, *J. Chem. Soc.*, **77** (1933).

[5] Fittig and Remsen, *Ann.*, **159**, 129 (1871); "Ortho-, Meta-, and Para-hydroxybenzalrhodanines and 3,4-Dihydroxybenzalrhodanine as Possible Reagents for Inorganic Analysis," T. E. Robbins, Thesis, University of Georgia, 1939; "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 549.

[6] CC indicates the identification number assigned to the compound, for test purposes, by the Chemotherapy Center for Tropical Diseases under the National Research Council.

[7] Renfrew, This Journal, **68**, 1433 (1946).