

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 Ronus⁸ 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 C₁₀H₁₆O₆: 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).

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

BY V. N. IPATIEFF AND G. S. MONROE

Berthelot¹ 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 catalyst² are given below:

TABLE I

CONVERSION OF BENZENE AND BENZENE-METHANE INTO
TOLUENE OVER NICKEL-SILICA CATALYST AT 372°

Charge	Press., atm.	Yields ^b as wt. % benzene charge		% Recovered	
		Toluene	Carbon	Benzene	Methane
C ₆ H ₆	1	0.0	2.1	92.7	
C ₆ H ₆	410	12.3	2.4	79.3	
C ₆ H ₆	545	14.9	3.1	76.7	
C ₆ H ₆ + CH ₄	1	0.0	0.7	95.5	100.8
C ₆ H ₆ + CH ₄	410	15.3	1.0	83.0	98.0
C ₆ H 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.

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

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

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.

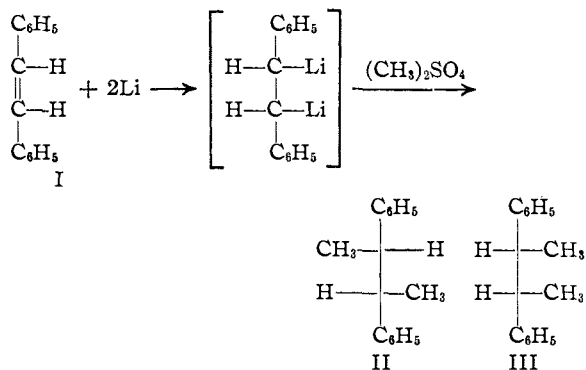
(3) Ipatieff and Monroe, *THIS JOURNAL*, **67**, 2168 (1945).

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The Bonding in Dimetalated Diphenylethane

BY G. S. MYERS, H. H. RICHMOND AND GEORGE F. WRIGHT

In elaboration of previous work¹ it has been found that the same ratio (3:1) of *dd, ll*-2,3-diphenylbutane, II, to the *dl, dl*-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).