



which is racemized too in the course of esterification by diazomethane.

Furthermore, the observation reported by Schlenk and Bergmann³ may be recalled, that fluorene-9-carboxylic acid behaves—at least to a certain extent—abnormally toward diazomethane, giving dimethyl dibiphenylenesuccinate.

(3) Schlenk and Bergmann, *Ann.*, **463**, 194 (1928).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE

RECEIVED MARCH 4, 1938

Remark on the Mechanism of the Fittig Reaction

BY O. BLUM-BERGMANN

(1) Bachmann and Clarke¹ have shown, some years ago, that the by-products formed in the biphenyl synthesis from boiling chlorobenzene and sodium metal indicate the intermediary formation of free phenyl radicals. Analogous results are obtained at room temperature, working in benzene solution.

To bromobenzene (50 g.), dissolved in benzene (50 g.) in a Schlenk tube,² sodium slices (10 g.) were added in nitrogen atmosphere, reaction starting quickly and causing a marked rise in temperature. When this first reaction ceased, the mass was shaken for two days, diluted with benzene (100 cc.) and separated by decantation from the excess sodium metal. Water was added, the benzene solution washed several times with water, dried and evaporated *in vacuo* and the residue fractionated at 13–15 mm. (a) B. p. 123–129°. This fraction crystallized completely; it consisted of pure biphenyl; m. p. 69–71°; yield 6.8 g. (b) B. p. 165–200°. The yellowish oil solidified almost quantitatively, on trituration with methyl alcohol; yield 2.1 g. From methyl alcohol, stout prisms, m. p. 56–57°, which according to their physical properties and the analysis proved to be *o*-phenyl-biphenyl, described before by Bachmann and Clarke.¹ (Calcd. for C₁₈H₁₄: C, 93.9; H, 6.1; mol. wt., 230. Found: C, 93.5; H, 6.0; mol. wt. (camphor), 241, 236.) (c) B. p. 200–250°, yellowish oil, which crystallized on trituration with light petroleum (b. p. 80–100°) (yield 0.26 g.) and was purified from the same solvent. Long needles of triphenylene; m. p. and mixed m. p. with an authentic sample, 195° (Calcd. for C₁₈H₁₂: C, 94.7; H, 5.3; mol. wt., 228. Found: C, 94.6; H, 5.3; mol. wt. (camphor), 257, 255).

(2) Theoretically free phenyl radicals may occur either in the formation from sodium and bromobenzene of

phenylsodium³ or in the interaction between the latter compound and a second bromobenzene molecule or in both processes. Horn and Polanyi⁴ showed that, on interaction with dilute sodium vapor, bromobenzene forms biphenyl, undoubtedly via phenyl radicals. On the surface of metallic sodium, on the other hand, it will be expected that a second sodium atom will always be near enough for phenylsodium formation when the first metal atom has removed the halogen from the C-Hal bond,⁵ although, obviously, temporary radical formation cannot be excluded. Therefore it is more likely that the reaction of the alkylsodium compound with bromobenzene involves the intermediary production of the radicals. In favor of this, the observation may be reported that phenylsodium, on interaction with bromobenzene, gives triphenylene (C₁₈H₁₄),⁶ too, indicating formation of phenyl radicals and their disproportionation into benzene and phenylene radicals C₆H₄.⁶

Diphenylmercury (6 g.) was shaken in benzene solution with sodium slices (10 g.) for two days;⁷ the phenylsodium containing mass was then separated by decantation from the excess metal, and bromobenzene (7 cc.) (twice the theoretical amount) added. The mixture was kept at 70° for forty-eight hours and poured out into water. Treatment as above gave (besides some bromobenzene) (a) biphenyl, b. p. 120–160° (22 mm.), m. p. 65°, yield 1.45 g.; (b) triphenylene, b. p. 200–220° (13 mm.) after trituration of the crude product (1 g.) with light petroleum and recrystallization from the same solvent, m. p. 194–195.5°.

(3) Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

(4) Horn and Polanyi, *Z. physik. Chem.*, **25B**, 151 (1934).

(5) Ziegler and Schaefer, *Ann.*, **479**, 150 (1930).

(6) In the famous experiments of Wieland, Popper and Seefried [*Ber.*, **55**, 1816 (1922)] on the dissociation of benzene-azotriphenylmethane, the occurrence of benzene instead of free phenyl may also be due to incidental formation of triphenylene which so far has not been isolated from the reaction mixture.

(7) Compare Schlenk and Holtz, *ibid.*, **50**, 268 (1917).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE

RECEIVED MARCH 4, 1938

Hydrogenation of Ethylene and Partially Deuterized Ethylene on Catalytic Metal Surfaces

BY G. G. JORIS AND J. C. JUNGERS

The hydrogenation on catalytic copper of ethylene, ethylene-*d*₄ and partially deuterized ethylene (50%*D*) has been measured and found to be faster for the heavy compound.¹ To gain further information on this reaction and establish that this was not due to accidental circumstances, the hydrogenation of ethylene and partially deuterized ethylene was carried out on nickel, cobalt and platinum surfaces. The rates measured for mixtures of 5 cm. of ethylene and 7.5 cm. of hydrogen are given in the table and show

(1) G. G. Joris, H. S. Taylor and J. C. Jungers, *THIS JOURNAL* **1982** (1938).

(1) Bachmann and Clarke, *THIS JOURNAL*, **49**, 2089 (1927). Cf. J. v. Braun and Kurtz, *Ber.*, **70**, 1224 (1937); Oldham and Ubbelohde, *J. Chem. Soc.*, 201 (1938).

(2) Compare Houben-Weyl, "Die Methoden der organischen Chemie," Vol. IV, Georg Thieme Leipzig, 1924, p. 959.