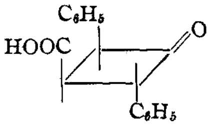

which is racemized too in the course of esterification by diazomethane.

Furthermore, the observation reported by Schlenk and Bergmann[3] may be recalled, that fluorene-9-carboxylic acid behaves—at least to a certain extent—abnormally toward diazomethane, giving dimethyl dibiphenylenesuccinate.

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(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 Clarke[1] 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 $C_{18}H_{14}$: 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 $C_{18}H_{12}$: 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 phenylsodium[3] or in the interaction between the latter compound and a second bromobenzene molecule or in both processes. Horn and Polanyi[4] 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 $(C_6H_4)_3$ too, indicating formation of phenyl radicals and their disproportionation into benzene and phenylene radicals C_6H_4.[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 recystallization from the same solvent, m. p. 194–195.5°.

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(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.

(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

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

quite definitely that in all cases studied the reaction is faster for the heavy compound.

TIMES OF ONE-HALF REACTION (IN MIN.)

Catalyst	Temp., °C.	$C_2H_2D_2$	C_2H_4
Nickel	+64	13	28
Platinum	−21	12	18
Cobalt	0	2.8	3.5

The columns give the nature of the catalyst, the temperature of the experiment, the time of half reaction for the heavy and light compound.

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 21, 1938

Some Phenacyl and *p*-Substituted Phenacyl Esters

BY R. V. LUNDQUIST

Some phenacyl and *p*-substituted phenacyl esters of organic acids have been prepared for the identification of those acids. They were prepared by the method of Judefind and Reid.[1]

Heptylic Acid.—The phenacyl ester was a liquid.

Dichloroacetic Acid.—The phenacyl ester was a liquid; the *p*-bromophenacyl ester, observed m. p. 98.2 to 99.3°; the *p*-chlorophenacyl ester, observed m. p. 93.0 to 93.8°.

α-Bromo-*n*-butyric Acid.—The phenacyl ester was a liquid; the *p*-phenylphenacyl ester, observed m. p. 103.5 to 104.0°.

Acetylsalicylic Acid.—The phenacyl ester, observed m. p. 105.0 to 105.5°.

The esters were obtained in excellent yield and the solid esters were purified easily to a constant melting point.

[1] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

CONTRIBUTION FROM THE
CHEMISTRY LABORATORY
UNIVERSITY OF IDAHO
MOSCOW, IDAHO

RECEIVED MAY 25, 1938

Acid Dissociation Constants in Dioxane–Water Mixtures. A Correction of the Dissociation Constant of Benzoic Acid

BY CECIL C. LYNCH AND VICTOR K. LA MER

Professor Martin Kilpatrick and Dr. L. John Minnick of the University of Pennsylvania kindly called our attention to the fact that the dissociation constants of benzoic acid as given in the "International Critical Tables," Vol. VI, p. 279, are in error by a factor of ten and that this had led to an unnecessary restriction of statement in our paper of the above title.[1] When the most recent value for 25°[2] is plotted in our Fig. 8 instead of the erroneous "I. C. T." value (6.15×10^{-4}), the anomalous behavior of benzoic acid as compared with acetic, propionic and butyric acids disappears. Log K_{benzoic} becomes a linear function of the reciprocal of the dielectric constant between $D = 78$ and 21, and now conforms closely to the behavior of the three aliphatic acids. In Table III, p. 1257, K_{acetic} ($D = 34.3$) should read 5.62×10^{-7} instead of 5.01×10^{-7} and the second datum for propionic acid ($D = 21.0$) should read 5.33×10^{-9} instead of 5.30×10^{-9}.

[1] Lynch and La Mer, THIS JOURNAL, **60**, 1252 (1938).

[2] 6.31×10^{-5}, Brockman and Kilpatrick, *ibid.*, **56**, 1483 (1934).

DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 23, 1938

The Hydrolysis of Methyl Iodide

BY RICHARD A. OGG, JR.

The hydrolysis of methyl iodide in pure water[1] has been shown to be kinetically first order with respect to methyl iodide, and unretarded in rate by the resulting hydriodic acid. Essentially similar results have been found by the author in a brief study of methyl iodide hydrolysis in a mixture of equal volumes of anhydrous methanol and water. The solutions (some 0.02–0.08 molar in methyl iodide) were heated in sealed nitrogen-filled tubes. Reaction was followed by titration of the resulting hydriodic acid. The last stages of the reaction were complicated by formation of considerable iodine (Moelwyn-Hughes found only traces)—undoubtedly as a result of the side reaction $CH_3I + H_3O^+ + I^- \longrightarrow CH_4 + I_2 + H_2O$. (The solutions containing most iodine gave off inflammable gas on opening the tubes.) Displacement of the equilibrium

$$CH_3OH + H_3O^+ + I^- \rightleftarrows CH_3I + 2H_2O$$

to the right by the large concentration of methanol in the solvent explains the importance of the side reaction—as contrasted to the results in pure aqueous solution.

Very good first order rate constants were obtained up to some 60% completion of the reaction (iodine formation then became troublesome). At 100 and 55° the rate constants were found to be, respectively, some 3×10^{-4} (average from

[1] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A164**, 295 (1938).