

method for the preparation of morpholine and obviates many steps necessary in other methods.

If instead of subjecting the mixture to dry distillation concentrated sodium hydroxide is added and the solution distilled with steam into hydrochloric acid, a yield of 65% of the hydrochloride of morpholine is obtained. This, when distilled over calcium oxide, gives about 45% of morpholine (based on diethanolamine).

If to the original reaction mass cold sodium hydroxide is added, and the resulting amine layer is extracted with ether, pure morpholine is obtained.

The picrate melts at 145–147°. Knorr gives the melting point of the picrate as 145–147°. N-(2-Chlorocinchoninyl)-morpholine was used for the analysis.

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: N, 10.13. Found: N, 10.07.

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Alkylation of Aromatics with Olefins in the Presence of Boron Fluoride¹

BY V. N. IPATIEFF AND A. V. GROSSE

In the course of our investigations on hydrocarbon reactions in the presence of metallic halides² the alkylation of aromatic hydrocarbons with olefins in the presence of boron fluoride was also accomplished. This fact is interesting in connection with recent similar work of Nieuwland³ in which the addition of acids, especially sulfuric acid, was considered to play an important part in these condensations.

As has been recently shown in our laboratories⁴ the sulfuric acid *per se* is an excellent alkylating catalyst under the conditions used by Nieuwland and the presence of boron fluoride is not necessary. On the other hand, boron fluoride *without acids* is also an alkylating catalyst.⁵

The alkylation of aromatic hydrocarbons with olefins, including ethylene,⁶ takes place in the

(1) Announced by V. N. Ipatieff before the Organic Section of the American Chemical Society at the Kansas Meeting on April 22, 1936.

(2) V. N. Ipatieff, A. V. Grosse and co-workers, *THIS JOURNAL*, **57**, 1616, 1722, 2415 (1935); **58**, 913, 915 (1936); *Ind. Eng. Chem.*, **28**, 461 (1936).

(3) S. J. Slanina, F. J. Sowa and J. A. Nieuwland, *THIS JOURNAL*, **57**, 1547 (1935).

(4) V. N. Ipatieff, B. B. Corson and H. Pines, *ibid.*, **58**, 919 (1936).

(5) For alkylations of paraffins, see Ref. 1, p. 1616.

(6) As contrasted to the actions of sulfuric acid, see Ref. 3.

presence of boron fluoride in a *nickel-lined*⁷ autoclave at room temperature and also at temperatures up to 250°.

In one particular experiment 250 cc. (219 g.) of benzene was treated in a rotating nickel-lined bomb with ethylene in the presence of 18.5 g. of boron fluoride and 2.0 g. of water for eight hours at 20–25°. The initial ethylene pressure was 20 atmospheres, which dropped readily to 10 atmospheres when fresh ethylene was pressed in. In all five refillings were made and 22 g. of ethylene was absorbed.

The reaction product, after washing and drying, was separated into the following fractions:

Fraction	Boiling points at 760 mm., °C	Volume in cc.	% of total product	$n^{20.0}_D$	Remarks: (All fractions water white and stable to $KMnO_4$ solution)
1	80 ± 1.5	180.0	72.0	1.5002	Pure benzene, solidifies in ice
2	81.5–135	1.0	0.4	1.4985	
3	136 ± 1	52.0	21.0	1.4960	Monoethyl benzene; $d^{20.0}_4$ 0.8674
4	137–182	3.5	1.5	1.4958	
5	183 ± 1	7.5	3.0	1.4974	Diethylbenzenes
Bottoms	>184	4.0	1.6	1.5032	
Losses		2.0	0.8		
Total		250.0	100		

As can be seen from these results over 25% of the benzene was alkylated to monoethyl-, diethyl and higher alkylbenzenes. The constants of our monoethylbenzene (see table) are in complete agreement with the values given in the literature (see "I. C. Tables," boil. point at 760 mm. 136°, n^{20}_D 1.4959, $d^{20.0}_4$ 0.8669). As a further check oxidation with boiling potassium permanganate solution gave only *benzoic acid*, melting at 122.0°, proving the absence of xylenes.

(7) For the role of nickel, see Ref. 1, pages 1617 and 1618.

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Thermal Type Silver-Silver Chloride Electrodes

BY C. K. RULE AND VICTOR K. LA MER

In connection with an investigation of the temperature coefficients of the e. m. f. of quinhydrone-

silver chloride cells in deuterium oxide, we have tested the reliability of silver-silver chloride electrodes made by a thermal method analogous to that recommended by Owen¹ and by Keston,² respectively, for the corresponding iodide and bromide electrodes. An electrode formed from a coil of platinum wire sealed into a tube of Jena normal glass was covered with a paste composed of seven parts of silver oxide and one part of silver chlorate and heated to decomposition in an electric furnace. No appreciable differences were observed when the percentage of silver chlorate was varied between 8 and 15.

Twelve electrodes immersed in 0.01 *M* hydrochloric acid solution exhibited ± 0.02 mv. as the average deviation from the mean. After standing for six weeks this value increased to not more than ± 0.04 mv. Freshly made electrodes agreed with the old within this limit.

A comparison of the "thermal" type electrodes with those made by decomposing a paste of silver oxide by heat and then electrolyzing for five hours in 0.2 *M* hydrochloric acid solution at 1.8 milliamperes per electrode showed that the electrolytic type tended to drift and were on the average about 0.04 mv. more positive.

CHANDLER LABORATORY RECEIVED OCTOBER 6, 1936
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(1) Owen, *THIS JOURNAL*, **57**, 1526 (1935).

(2) Keston, *ibid.*, **57**, 1671 (1935).

The Heat of Fusion of Stannic Iodide

BY SAMUEL S. TODD AND GEORGE S. PARKS

The changes in heat content of stannic iodide were measured by us in 1928 for the temperature intervals between 27 and 80, 120, 155 and 171°, respectively. A method of mixtures was used with a water calorimeter, the details of the apparatus and experimental procedure being given in a previous paper by Parks and Todd.¹ The sample of stannic iodide studied had been kindly prepared for us by Professor J. H. Hildebrand.

Although the error in the calorimetric measurements themselves was within 1%, considerable uncertainty as to the premelting effect in the crystalline material precluded at that time a reliable calculation of the heat of fusion of stannic iodide from our heat content data. Recently, however, Negishi² has obtained accurate information concerning the heat capacities of solid and liquid stannic iodide over a range of temperatures. Using his data and taking the melting point as 144°, we have now calculated the following fusion values from our four determinations pertaining to the 27–155° range: 7.23, 7.19, 7.24 and 7.25 cal. per gram. The mean heat of fusion is 7.23 (± 0.14) cal. per gram or 4530 cal. per mole.

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(1) G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).

(2) G. R. Negishi, *THIS JOURNAL*, **58**, 2293 (1936). Prof. J. H. Hildebrand kindly sent us these essential data prior to publication.

NEW BOOKS

Physical Aspects of Organic Chemistry. By WILLIAM A. WATERS, M.A., Ph.D. (Cantab.), University of Durham. Introduction by Professor T. Martin Lowry, George Routledge and Sons, Ltd., Broadway House, 68–74 Carter Lane, London E.C., England, 1935. xv + 501 pp. 14 × 22 cm. Price, 25s.

The title of this book does not indicate very clearly the nature of its contents. Actually it is largely concerned with current electronic ideas of valence and their application to organic chemistry, especially to details of reaction mechanism. The chapter headings are: Chemical Affinity, Physical Theories of Molecular Structure, Valency, Electrical Dipoles, Chemical Reactivity, Unsaturation, Free Radicals and Their Non-ionic Reactions, Ionization

and Ionic Reactions, Acidity, The Reactivity of Halogen Compounds, General Polarity, Hydrolysis and Esterification, Ionotropic Change, Molecular Rearrangement, Conjugation, Aromatic Compounds—I, Aromatic Compounds—II.

But this list does not furnish an adequate indication of the range of topics dealt with. Many of these subjects are exceedingly broad, have a lengthy and complicated history and even today have not reached any state of agreed opinion. One is therefore especially impressed with the skill of presentation. The author states in his preface: "The historical aspect of a rapidly developing subject has been kept continually in view, with the intention of giving a general outline of theoretical organic chemistry rather than