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 Fluoride[1]

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

In the course of our investigations on hydrocarbon reactions in the presence of metallic halides[2] 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 Nieuwland[3] 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 laboratories[4] 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 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:

Charge, 250.0 cc.

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.

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(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.

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

UNIVERSAL OIL PRODUCTS CO.
RIVERSIDE, ILL.
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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-