

dilute hydrochloric acid the product was taken up in ether. The ethereal solution was washed with dilute acid and with water and extracted with 2.5% sodium hydroxide, and on acidifying the alkaline extract there was obtained 4 g. of grayish material. On two crystallizations from benzene this afforded nearly pure 4-methoxy-4'-benzoyldiphenyl, m. p. 193–195°, yield 1.1 g. (22%). A small amount of a highly colored impurity was removed on reprecipitation from an alkaline solution, and further crystallization from benzene gave round, faintly yellow crystal-clusters, m. p. 194–195°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.14. Found: C, 83.42; H, 5.14.

No pure products were isolated from the mother liquor. On conducting the rearrangement according to Blicke and Weinkauff³ the alkali-soluble product amounted to only about 2% of the ester used and it consisted largely of 4-hydroxydiphenyl.

The acetate formed colorless plates, m. p. 127–128°, from methyl alcohol.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.09. Found: C, 80.00; H, 5.39.

The methyl ether, prepared with the use of dimethyl sulfate and alkali, crystallized from benzene as colorless needles, m. p. 165–166°. It was identified by comparison with the samples described below.

Friedel and Crafts Reaction.—A solution of 10 g. of 4-methoxydiphenyl and 6.9 cc. of benzoyl chloride in 130 cc. of tetrachloroethane was cooled to -10° and 8 g. of aluminum chloride was added all at once. The mixture was stirred mechanically and allowed to come to room temperature. After eighteen hours ice and acid were added, the solvent was removed with steam, and the moist product was taken up in benzene. On concentrating the solution to a volume of 50 cc. and cooling, 5.8 g. of nearly pure 4-methoxy-4'-benzoyldiphenyl, m. p. 165–167°, crystallized. The mother liquor was concentrated to a volume of 25 cc. and treated with petroleum ether. The material which separated on one crystallization from methyl alcohol gave 6.1 g. of a product melting at 91–92° (flat needles). This substance is insoluble in alkali and depresses the melting point of 4-methoxydiphenyl; it is undoubtedly 4-methoxy-3-benzoyldiphenyl, which Hey and Jackson² prepared by a synthesis establishing the structure and for which they report the melting point 93°.

Synthesis of 4-Methoxy-4'-benzoyldiphenyl.—A solution of 0.5 g. of 4-methoxy-4'-carboxydiphenyl¹ in 10 cc. of thionyl chloride was refluxed gently for one hour and the excess reagent was removed at reduced pressure. The residue was dissolved in 25 cc. of thiophene-free benzene, 0.3 g. of aluminum chloride was added and the mixture was refluxed for one hour. The reaction product, recovered in the usual way, crystallized from alcohol or benzene as colorless needles, m. p. 165–166°. Mixed melting point determinations of this 4-methoxy-4'-benzoyldiphenyl with both of the samples obtained above indicated the identity of all three preparations.

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A New Synthesis of Morpholine

BY BURT L. HAMPTON AND C. B. POLLARD

Morpholine was first prepared by L. Knorr¹ by heating diethanolamine and an excess of concentrated hydrochloric acid in a sealed tube and then refluxing the reaction mass with potassium hydroxide. Because of low yields Knorr abandoned this method for the sulfuric acid method.² In both cases he failed to state his yields. However, Jones and Burns³ have shown that morpholine is formed in about a 10% yield by the action of sulfuric acid on diethanolamine following the directions of Knorr. Therefore the yield using hydrochloric acid and potassium hydroxide must have been considerably lower. The only other methods for the preparation of morpholine are indirect ones and need not be reviewed here.

In his first preparation Knorr assumed the chlorohydrin of diethanolamine to be formed. Ring closure with loss of hydrogen chloride was then effected by refluxing in potassium hydroxide solution. He based this assumption on the fact that he was able to isolate the chlorohydrin of N-phenyldiethanolamine in a similar reaction; however, he was unable to isolate the chlorohydrin of diethanolamine because of its similarity in properties to the parent substance.

We have shown in this investigation that the chlorohydrin does not necessarily have to be formed and that no dehydrating agent other than that of heat on the hydrochloride is necessary for the formation of morpholine from diethanolamine. This was surprising in view of the work of Knorr.

Preparation.—Diethanolamine (2 moles) is placed in a round-bottomed flask fitted with a thermometer and an air-cooled condenser. Concentrated hydrochloric acid is added slowly until the solution is acid to litmus. The solution is then heated rapidly until the water is driven off, and the temperature of the solution is kept at 200–210° for fifteen hours. The reaction mass is now allowed to cool, an excess of calcium oxide is added, and the mixture subjected to dry distillation. The resulting liquid is dried over solid sodium hydroxide and refluxed over metallic sodium for thirty minutes; it is then subjected to fractionation. The entire product boils at from 126–129° and is practically anhydrous. The yield is around 48%. This procedure offers a rapid

(1) Knorr, *Ber.*, **22**, 2081 (1889).

(2) Knorr, *Ann.*, **301**, 1 (1898).

(3) Jones and Burns, *This Journal*, **47**, 2966 (1925).

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

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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RECEIVED JULY 22, 1936

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-

(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.