

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization Accompanying Alkylation. III. The Alkylation of Benzene with Neopentyl Chloride and Neopentyl Alcohol*

BY HERMAN PINES, LOUIS SCHMERLING AND V. N. IPATIEFF

Previous papers^{1a} from these Laboratories on the alkylation of aromatic compounds covered the conditions and catalysts which cause isomerization of the alkyl group by hydrogen migration. None of the reactions cited involved a change in the carbon skeleton structure of the alkyl group.

The present paper deals with the alkylation of benzene with neopentyl alcohol using sulfuric acid and aluminum chloride as catalysts and with neopentyl chloride using the latter catalyst. With sulfuric acid the expected² product, *t*-amylbenzene, was isolated in about 30% yield. This, then, is the first example of an isomerization accompanying alkylation of benzene in which a methyl group and not a hydrogen atom migrates.

Surprisingly, the only product which could be isolated from the action of neopentyl alcohol and benzene in the presence of aluminum chloride was the unrearranged product, neopentylbenzene, which was obtained in about 9% yield. Still more surprisingly, the only product isolated from the reaction of neopentyl chloride with benzene and aluminum chloride was 2-methyl-3-phenylbutane (about 24% yield) suggesting the intermediate formation of isopropylethylene since it has been shown^{1b} that isopropylethylene reacts with benzene in the presence of aluminum chloride to yield 2-methyl-3-phenylbutane.

Experimental

Neopentyl alcohol was prepared by the reaction of *t*-butylmagnesium chloride and formaldehyde.³ It boiled at 110–111°; m. p. 50–52°. Neopentyl chloride was prepared by essentially the same method as that described by Whitmore and Fleming,⁴ b. p. 83.3–84.5°.

The alkylations were carried out in the usual manner. The products were washed, distilled and the monoalkylbenzenes were identified by means of their mono- and diacetamino and monobenzamino derivatives.⁵

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(1) (a) Ipatieff, Pines and Schmerling, *THIS JOURNAL*, **60**, 353 (1938); (b) Ipatieff, Pines and Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

(2) Whitmore ("Organic Chemistry," p. 128) has stated that "all reactions which result in the removal of a hydroxyl group from neopentyl alcohol result in *t*-amyl products."

(3) Conant, Webb and Mendum, *THIS JOURNAL*, **51**, 1246 (1929).

(4) Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

(5) Ipatieff and Schmerling, *ibid.*, **60**, 1876 (1938).

Neopentyl Alcohol-Benzene-Sulfuric Acid.—Neopentyl alcohol 22.8 g. (0.25 mole), benzene 20 g. (0.25 mole) and 80% sulfuric acid (250 cc.) were heated at 65° for six hours. Two layers were formed. The dark upper layer (46.5 g.) was made alkaline with sodium hydroxide and steam distilled. The hydrocarbon distillate was dried and fractionally distilled. The hydrocarbon layer consisted of unreacted benzene and the following fractions of alkylbenzenes: Cuts 1–2, 175–183°, 3.7 g., n_D^{20} 1.4905; 3, 183–188°, 2.3, 1.4919; 4, 188–194°, 1.8, 1.4922; 5, 194–200°, 1.9, 1.4921; 6, 200–204°, 1.8, 1.4913; 7–8, 204–230°, 2.2, 1.4900–1.4878; 9, above 230°, 2.0.

Cut 3, Diacetamino derivative: m. p. 178–181°; mixed m. p. with an authentic specimen showed that the compound was *t*-amylbenzene.

Cut 5, Diacetamino derivative, m. p. 174–175°; the monoacetamino and monobenzamino derivatives melted at 139–141° and 107–108°, respectively. The compound was chiefly *t*-amylbenzene.

Neopentyl Alcohol-Benzene-Aluminum Chloride.—The apparatus used consisted of a three-necked flask, provided with a mercury-sealed stirrer, dropping funnel, and reflux condenser. Fifty-nine grams of benzene and 44.4 g. of re-sublimed aluminum chloride was placed in the flask, which was surrounded by ice water, and a solution of 22 g. of neopentyl alcohol in 19 g. of benzene was added during two hours. At the beginning the benzene was frozen but it soon melted as the alcohol was added. The aluminum chloride gradually dissolved in the mixture, which was brown, when all the alcohol had been added. The reaction mixture was refluxed for eight hours. Two layers were formed: the upper-hydrocarbon layer (62 g.) was yellow-orange; the lower-catalyst layer (70 g.) was dark brown. The hydrocarbon layer consisted mostly of unreacted benzene. The alkylated benzene had the following properties: Cut 1, 78–165°, 0.6 g., n_D^{20} 1.4906; 2, 165–177°, 1.5, 1.4890; 3, 177–182°, 1.0, 1.4895; 4, 182–186°, 0.8, 1.4902.

The diacetamino derivatives of Cut 2 and Cut 4 melted at 231–233.5° and 239–240°, respectively. The latter, when mixed with an authentic specimen of diacetaminoneopentylbenzene (m. p. 240–241°), melted at 239–240°.

The monoacetamino derivative of Cut 2 melted at 141–143°. Mixed melting point determinations with the corresponding derivative of *t*-amylbenzene and 2-methyl-3-phenylpentane showed that Cut 2 was neither of these, the mixtures melting at 120–122 and 126–130°, respectively. The mixed melting point with authentic acetaminoneopentylbenzene (m. p. 164°) was 147–153°, indicating that Cut 2 was impure neopentylbenzene.

Neopentyl Chloride-Benzene-Aluminum Chloride.—Neopentyl chloride (18.7 g.) was added slowly at 0° under stirring to a mixture consisting of 18.7 g. of benzene and 5 g. of aluminum chloride. Two layers were formed: the upper hydrocarbon layer weighed 16 g., while the lower catalyst

layer weighed 18 g. Besides unreacted benzene, the upper layer contained alkylbenzenes, which distilled as follows: Cut 1, 184–188°, 2.0 g., n_D^{20} 1.4901; 2, 188–193°, 2.4, 1.4911; 3, 193–195°, 1.9, 1.4915.

Cut 1 consisted of 2-methyl-3-phenylbutane. Diacetamino derivative, m. p. 187–189°, no depression in m. p. with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 189°).

Cut 3, Monoacetamino derivative, m. p. 142–143°. The mixed m. p. with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 147°) was 143–145°; with that of *t*-amylbenzene (m. p. 140°) was 130–133°.

Mono benzamino derivative, m. p. 137–138°. The mixed melting point with the same derivative of authentic 2-methyl-3-phenylbutane (m. p. 141°) was 138–139°.

Diacetamino derivative, m. p. 183–184°. A more soluble fraction, m. p. 175–178°, was also obtained, indicating a mixture.

Summary

The alkylation of benzene with neopentyl alcohol gives *t*-amylbenzene (30% yield) when sulfuric acid is used as catalyst and neopentylbenzene (9% yield) when aluminum chloride is used.

Neopentyl chloride and benzene react in the presence of aluminum chloride to form 2-methyl-3-phenylbutane (24% yield).

RIVERSIDE, ILLINOIS

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMICAL LABORATORY, LEHIGH UNIVERSITY]

The Reaction of Fluorenone and Diazomethane—A New Route to 9-Phenanthrol Derivatives

BY RAYMOND F. SCHULTZ, EMMA DIETZ SCHULTZ AND JOHN COCHRAN¹

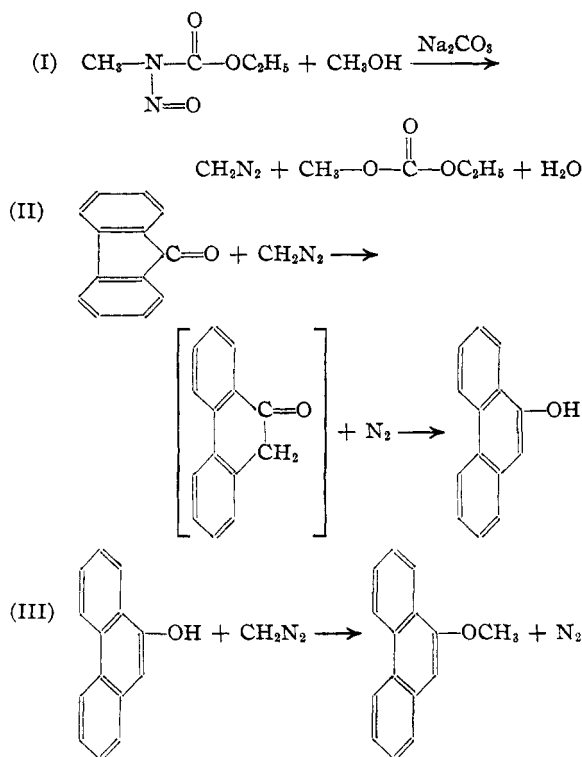
Cyclic aliphatic ketones react with diazomethane in methanol to form ketones with larger rings.² We have carried out an analogous reaction between fluorenone, an aromatic cyclic ketone, and diazomethane, and obtained a 50% yield of 9-methoxyphenanthrene. This provides a new route to 9-phenanthrol derivatives which are difficult to prepare in good yields. The best reported method is that of Fieser, Jacobsen and Price³ involving the reaction of phenanthrene and methyl alcoholic bromine in which was obtained a 28–30% yield of 9-phenanthrol, based on phenanthrene consumed.

Our procedure is essentially that employed by Kohler, Tishler, Potter and Thompson,^{2c} except that we use a solvent mixture of diethyl ether and methanol instead of methanol alone, in which fluorenone is not too soluble. As products we isolated the following: 5% of 9-phenanthrol, 30% of 9-methoxyphenanthrene, 1.5% di-9-phenanthryl ether, 0.5 g. of an unknown substance, m. p. 279–281°, and 30% unchanged fluorenone. This corresponds to a 51% yield of 9-phenanthrol derivatives based on fluorenone consumed. The main reactions concerned probably are:

(1) Part of this work was carried out by John Cochran in part fulfillment of the requirements for the degree of B. S. in Chemical Engineering, Lehigh University.

(2) (a) Mosettig and Burger, *THIS JOURNAL*, **52**, 3456 (1930); (b) Meerwein, *Chem. Zentr.*, **104**, I, 1758 (1933), German Patent 579,309; (c) Robinson and Smith, *J. Chem. Soc.*, 371 (1937); (d) Giraitis and Bullock, *THIS JOURNAL*, **59**, 951 (1937); (e) Kohler, Tishler, Potter and Thompson, *ibid.*, **61**, 1057 (1939).

(3) Fieser, Jacobsen and Price, *ibid.*, **58**, 2163 (1936).



Two equivalents of diazomethane, introduced as ethyl-N-methyl-N-nitrosocarbamate, were always added since the 9-phenanthrol first formed competed with fluorenone for the diazomethane.

9-Phenanthrol was isolated by extraction of an ether solution of the product with 10% sodium hydroxide³ and subsequent acidification of the