THE ACTION OF ACETYLENE ON ARYL HYDROCARBONS IN THE PRESENCE OF A MERCURY CATALYST. II

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The preparation of unsymmetrical diphenylethane and other hydrocarbons of the type $CH_3CH(C_6H_4R)_2$ from acetylene and the appropriate aryl hydrocarbons has already been described by Reichert and Nieuwland.[1] The same compounds had been obtained by Fischer[2] by the action of paraldehyde and concentrated sulfuric acid. Toluene, so treated, formed the ditolyl derivative where the methyl is supposed to be para to the ethylidene group. These were made in other ways by Anschütz[3] and Haiss.[4] The place of the entering ethylidene group with respect to the alkyl of the nucleus has never been definitely proved by any of the authors mentioned, although it has been assumed that it is in the para position. Condensation is brought about by passing acetylene into the hydrocarbon in the presence of sulfuric acid and mercuric oxide or mercuric sulfate when a reaction represented by the following equation takes place

$$CH\equiv CH + 2C_6H_5R \longrightarrow CH_3CH(C_6H_4R)_2$$

In the present paper this series of compounds has been extended by application of the above reaction to several benzene homologs and to other aryl hydrocarbons. Acetylene gives ethylidene hydrocarbons of the above type with normal and *iso*propylbenzenes, normal and tertiary butylbenzenes, methyl and ethylphenylmethane, methyl*iso*propylphenylmethane, and tetrahydronaphthalene.

Ethylidene-*bis-tert.*-butylbenzene is a white, crystalline solid. The other ethylidene compounds have the general properties of unsymmetrical diphenylethane. They are viscous, amber colored liquids of high boiling points and are better distilled under reduced pressure. They are non-volatile in steam.

Several multinuclear hydrocarbons were subjected to the action of acetylene but no reaction occurred with triphenylmethane, diphenyl, diphenylmethane or dibenzyl. There seemed to be some connection between the character of the substituents in the benzene ring and the facility with which acetylene reacts. Toluene gave a yield of over 40%; benzene somewhat less of the ethylidene compounds.[1] The xylenes, with practically the same molecular weight as ethylbenzene, gave very much higher yields than the latter, while mesitylene with three substitutions in the ring gave 18 to 20% yields and the propylbenzenes were

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[1] Reichert and Nieuwland, This Journal, **45**, 3090 (1923).

[2] Fischer, *Ber.*, **7**, 119 (1874).

[3] Anschütz, *Ann.*, **235**, 215 (1886).

[4] Haiss, *Ber.*, **15**, 1476 (1882).

found to give less than 10% yields. Of hydrocarbons having about the same molecular weight, the di- and trisubstituted ones reacted with greater ease, probably because of the greater compactness and symmetry of the resulting ethylidene compounds. The formation of ring diethylidene compounds was found to occur to a small extent with diphenylethane and ditolylethane giving dimethylanthracene hydride and tetramethylanthracene hydride. None of the hydrocarbons described here, which were all distilled under reduced pressure, was accompanied by such a product except tetrahydronaphthalene.

Naphthalene resembled most benzene derivatives with unsaturation in the side chain in that it did not react with acetylene. But if one of the rings is saturated as it is in tetrahydronaphthalene, condensation readily occurs, with the formation of ethylidene-*bis*-tetrahydronaphthalene. The tetrahydronaphthalene then showed the same behavior as would have been expected of a dialkyl benzene.

Experimental Part

Ethylidene-*bis*-*n*-propylbenzene was prepared from *n*-propylbenzene obtained by the Fittig reaction from propyl bromide and bromobenzene. Acetylene was passed into a mixture of 130 g. of *n*-propylbenzene, 25 g. of concentrated sulfuric acid and 5 g. of mercuric oxide, the mixture being kept below 10°. When three-fourths of the theoretical quantity of acetylene had been absorbed the contents of the flask was neutralized with sodium hydroxide solution and was steam distilled until all the unchanged propylbenzene had come off. The ethylidene compound was extracted with ether from the residue, a plastic, grayish brown solid. The ether was evaporated and the residue distilled under reduced pressure; b. p. 192–194° at 42 mm. *Anal.* Calcd.: C, 89.7; H, 10.27. Found: C, 89.9; H, 9.8.

The solid referred to above was isolated and dried. It is amorphous and insoluble in water and the common organic solvents. When heated

TABLE I

BOILING POINTS OF HYDROCARBONS

Hydrocarbon	B. p., °C.	Pressure, mm.
$CH_3CH(C_6H_4CH_2CH_2CH_3)_2$	192–194	42
$CH_3CH[C_6H_4CH(CH_3)_2]_2$	240–245	15
$CH_3CH(C_6H_4CH_2CH_2CH_3)_2$	244–248	37
$CH_3CH[C_6H_4CH(CH_3)CH_2CH_3]_2$	250–252	11
$CH_3CH[C_6H_4C(CH_3)_3]_2$	212–214[a]	16
$CH_3CH[C_6H_4CH(C_2H_5)_2]_2$	234–236	29
$CH_3CH[C_6H_4CH(CH_3)CH(CH_3)_2]_2$[b]	225–228	13
$CH_3CH(C_{10}H_{12})_2$	261–263[c]	16

[a] M. p. 94°.

[b] *Anal.* Calcd.: C, 88.6; H, 11.42. Found: C, 87.7; H, 10.55.

[c] B. p. 384, atm. pressure by pyrometer and thermometer.

it decomposed without melting. It seemed, therefore, useless to examine it further for the present.

The other ethylidene compounds were prepared in a similar manner. Ethylidene-*bis-tert.*-butylbenzene was separated from the small amount of an oily impurity accompanying it in the distillate by solution with alcohol in which it was less soluble than the oil. It was recrystallized from 95% alcohol.

The boiling points of the new hydrocarbons prepared are given in the accompanying table.

Summary

1. Ethylidene hydrocarbons of the general formula $CH_3CH(C_6H_4R)_2$ have been prepared from acetylene in the presence of concentrated H_2SO_4 and HgO from the following benzene derivatives: propyl- and *iso*propylbenzenes, *n*-butylbenzene, *tert.*-butylbenzene, methylethylphenylmethane, methyl*iso*propylphenylmethane, diethylphenylmethane. These are all viscous, amber colored liquids of high boiling points, excepting ethylidene-*bis-tert.*-butylbenzene which is a white crystalline solid.

2. Tetrahydronaphthalene gives with acetylene ethylidene-*bis*-tetrahydronaphthalene and also a six-ringed compound in small quantities.

3. Polynuclear hydrocarbons such, for example, as diphenyl, diphenylmethane, dibenzyl, triphenylmethane and naphthalene do not react with acetylene.

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THE CATALYTIC CONDENSATION OF ACETYLENE WITH PHENOLS. II. RESORCINOL

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Introduction

In 1923 Wenzke and Nieuwland[1] reported the condensation of acetylene with resorcinol in the presence of sulfuric acid and mercury salts. The product was not separated from the alcoholic reaction mixture until it had undergone a dehydration. This second reaction was induced by diluting with water, whereupon a fine yellow precipitate slowly formed. On oxidation with stannic chloride this precipitate yielded hydroxymethylfluorone (II), indicating that the yellow compound was dihydroxymethylxanthene (IV). It was thought desirable, however, to make a more complete study of the reaction in an attempt to secure the primary product in the pure state, and to discover if this reaction resembled other acetylene reactions in giving the same products as acetaldehyde.

[1] Wenzke and Nieuwland, THIS JOURNAL, **46**, 179 (1924).