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Reductive Coupling of Aromatic Compounds*

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Benzene mixed with hydrogen fluoride and a platinum or rhodium catalyst is hydrogenated at room temperature and 1–5 atm pressure to yield cyclohexane and a reductive coupling product, phenylcyclohexane, the latter amounting to as much as 25% by weight of the hydrogenation products. Similarly, reductive coupling products are obtained from phenol or chlorobenzene, the former giving cyclohexylidine diphenol and the latter a mixture of monochlorinated phenylcyclohexanes. Results are consistent with the assumption that these reactions proceed by way of cycloalkene intermediates which react with unchanged aromatic compound to form the reductively coupled products. Readily available equipment for such hydrogenations is described.

INTRODUCTION

There have been several recent reports of the detection of cyclohexane intermediates in the hydrogenation products of benzene and its homologs. Thus Siegel, Ku, and Halpern (*1*) detected about 0.002 mole % of dimethylcyclohexenes in liquid-phase hydrogenation products from *m*- and *p*-xylenes, which supported their conclusion that cycloalkenes, desorbed from the surface of the catalyst, are intermediates in the reduction process. Similarly, Hartog and Zwietering (*2*) found that olefins were easily observed with ruthenium or rhodium as catalysts, maximum concentrations of 0.18% and 3.4% being reached in hydrogenation of benzene and *o*-xylene, respectively, over ruthenium. Madden and Kemball (*3*) noted the presence of traces of cyclohexene during the early stages of vapor-phase hydrogenation of benzene over nickel and likewise Weitkamp (*4*) obtained octahydro (olefinic) compounds from the hydrogenation products of methylnaphthalene.

Thirty years ago Truffault (*5*) observed formation of phenylcyclohexane in the hydrogenation of benzene over nickel in the presence of phosphorus pentoxide. He supposed that cyclohexene was formed as an intermediate and he suggested, but did not demonstrate, that it then reacted with benzene under the influence of phosphorus pentoxide to form phenylcyclohexane. Truffault's observations have apparently remained unconfirmed to date.

Very recently Slaugh (*6*) reported the hydrogenation of benzene to phenylcyclohexane with supported alkali metal catalysts. He obtained yields of 84–87% on the basis of converted benzene, and presented data which indicated that the product probably was not formed through the alkylation of benzene by cyclohexene.

In the present paper we report results of hydrogenating benzenoid compounds in hydrogen fluoride, a study originally undertaken to determine reactions possible at a platinum cathode during the interfacial anodic polymerization (*7*) of benzene in hydrogen fluoride.

EXPERIMENTAL

Reductive Coupling of Benzene

Initial experiments, conducted by bubbling hydrogen through a mixture of ben-

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zene, hydrogen fluoride, and platinum-on-carbon catalyst until practically all the benzene had evaporated, showed the formation of a liquid b.p. 230–240°. This liquid consisted of about 75% phenylcyclohexane and 25% dicyclohexyl as shown by combustion analysis, infrared spectral examination, and quantitative gas chromatography.

Further work was conducted at superatmospheric pressures in a 500-ml Monel flask (Scientific Glass Apparatus Company Catalog JF 6310) containing a Teflon-coated, magnetically activated, stirring bar. Connection was made to a calibrated hydrogen reservoir through a copper tube fitted snugly in a 24/40 S/T Teflon stirring gland (Will Scientific, Inc. Catalog 25530). The Teflon gland was used as a closure for the Monel flask and was held in place by means of a removable clamp.

Operation was essentially similar to that used with the conventional Adams (*8*) hydrogenator. The flask was cooled, charged with hydrogen fluoride, organic material and catalyst, and then flushed out with hydrogen. After warming to room temperature it was connected to a calibrated hydrogen reservoir, pressurized with hydrogen, and the stirrer started. A water bath located between the flask and the magnetic stirrer drive was used to regulate reaction temperature. A reaction time of 18–20 hr was allowed in all cases.

Upon completion of the run, the flask was cooled to —80°, the pressure released, and the flask opened. Sufficient 10% aqueous potassium hydroxide was then slowly added to neutralize the hydrogen fluoride, the flask contents being kept chilled during the addition. After neutralization the readily volatile organic products were recovered by steam distillation, and the less volatile materials by benzene extraction of the catalyst and aqueous phases.

Both product fractions were analyzed for benzene, cyclohexane, phenylcyclohexane and cyclohexylcyclohexane by quantitative gas chromatography.

Table 1 summarizes results.

Reaction of cyclohexene and benzene. A mixture of 5 g of cyclohexene and 10 g of benzene was slowly added to a mitxure of 10 g of benzene and 25 g of hydrogen fluoride. After evaporation of the hydrogen fluoride, distillation of the product gave 4 g of a liquid which, by gas chromatographic analysis, containing 98% phenylcyclohexane.

Reductive Coupling of Phenol

A mixture of 35 g of phenol, 5 g of 5% platinum on carbon, and 160 g of hydrogen fluoride was reacted with hydrogen at about 3 atm pressure for 18 hr at room temperature. After evaporation of hydrogen fluoride, the product was neutralized with potassium hydroxide and extracted with benzene. Distillation of the benzene extract yielded 3.3 g of solid which sublimed at 100–140° at 0.25 mm. On recrystallization from hexane it melted at 128–129.5° and was identified a *p*-cyclohexyl phenol by combustion analysis, molecular weight determination, nonaqueous titration, and IR spectrum.

Extraction of the catalyst with boiling benzene yielded 4.3 g of crude *p,p′*-cyclohexylidine diphenol m.p. 148–185° which, on crystallization from acetone melted at 187–188° [Dianin, Schmidlin, and Lang (*9*) give 186° corr]. Its identity was also confirmed by combustion analysis, molecular weight determination, nonaqueous titration, and IR spectrum.

Reductive Coupling of Chlorobenzene

A mixture of 168 g of hydrogen fluoride, 40 g of chlorobenzene, and 5 g of 5% platinum on carbon was treated with hydrogen under about 3 atm pressure for 18 hr at room temperature. On evaporation of hydrogen fluoride and distillation of the organic material there was obtained 1 g of an oil, b.p. 255–260°. The oil contained 17.5% chlorine (calculated for monochlorinated phenylcyclohexane, 18.2% Cl) and its infrared spectrum indicated the probable presence of both chlorophenylcyclohexane and chlorocyclohexylbenzene.

RESULTS AND DISCUSSION

Catalytic hydrogenation of several types of aromatic compounds in hydrogen fluoride results in reductive coupling. The observed

TABLE 1
Benzene Hydrogenation in HF—Effect of Reaction Variables

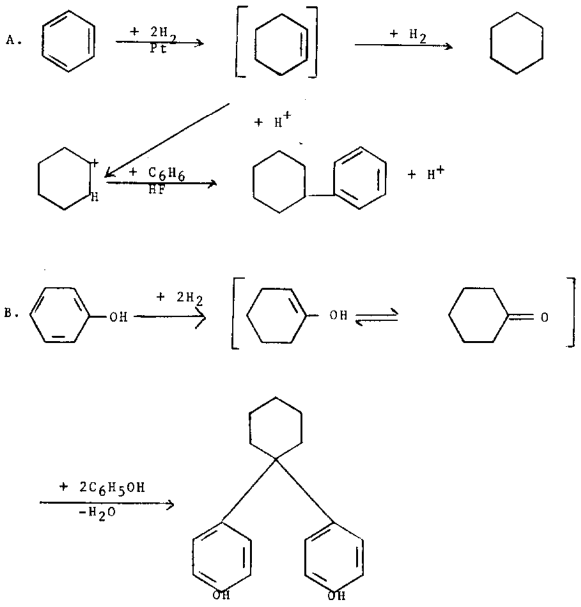
Catalyst[a] (g)	HF (g)	C_6H_6 (g)	Temp. (°C)	Initial press. (atm)	C_6H_6 (g)	C_6H_{12} (g)	$C_6H_5 \cdot C_6H_{11}$ (g)	$(C_6H_{11})_2$ (g)	C_6H_6 converted (%)	Organic material recovery (g)	H_2 used (moles)	H_2 accounted for in product (%)
0.5	5	8.8	20	3.4	8.1	0.4	0.2	0.001	8	8.6	0.024	75
0.5	40	44	20	1.7	38.6	2.7	0.8	—	12	42.1	0.137	77
5.0	5	8.8	40	1.7	0.8	6.7	1.1	—	91	8.6	0.280	90
5.0	5	44	20	1.7	29.0	13.0	0.9	—	34	42.9	0.538	88
5.0	40	44	40	3.4	16.9	18.0	7.5	0.16	62	42.4	0.746	99
2.75	22.5	26.4	32	2.6	10.2	12.3	4.1	—	61	26.6	0.545	90
2.75	22.5	26.4	32	2.6	10.0	10.8	4.2	0.08	62	24.2	0.545	81

[a] 10% platinum on carbon (Englehard, Inc.).

[b] *Under conditions* similar to those used in the fifth run above substitution of an equivalent weight of platinum as platinum oxide, or rhodium as 5% rhodium of carbon (Englehard, Inc.), for the platinum on carbon catalyst gave similar products in somewhat different proportions. No phenylcyclohexane was obtained with Raney nickel *(10)* catalyst under otherwise similar conditions.

coupling reactions are consistent with the assumption that cyclohexene or its derivatives are involved as intermediates, and offer indirect confirmation of Truffault's observation that phenylcyclohexane can be produced during liquid-phase catalytic hydrogenation.

In the instances reported here, reductive coupling occurs to a substantial degree, yielding the products shown in the reaction scheme, presumably by way of the indicated intermediates.



C. $2\ C_6H_5Cl \xrightarrow[-\ HCl]{+\ 3H_2} C_{12}H_{15}Cl$

Reaction A illustrates possible steps in the hydrogenation of benzene in hydrogen fluoride with a noble metal catalyst. The first step or steps, leading to cyclohexene, probably takes place with both benzene and hydrogen adsorbed on the catalyst. There is no evidence of products which could be attributed to the presence of free cyclohexadiene. (In separate experiments, 1,3- and 1,4-cyclohexadienes were shown to react violently with a benzene–hydrogen fluoride mixture to yield complex polymeric products.) Part of the cyclohexene intermediate, either remaining adsorbed on the catalyst, or being desorbed and then readsorbed, is further reduced to cyclohexane. The remainder of the cyclohexene intermediate may be protonated and may then proceed by the normal alkylation reaction to yield phenylcyclohexane. Under conditions using a large ratio of hydrogen fluoride to benzene, nearly half of the reacted benzene proceeds to this product. We believe that the protonation step is most likely to occur with desorbed cyclohexene.

Effects of some operating variables in reaction A have been studied as shown in Table 1. It is clear that the reductive coupling product, phenylcyclohexane, is formed in substantial amount over a considerable range of operating conditions, with the presence of large proportions of hydrogen fluoride appearing favorable to its formation.

Interaction of cyclohexane with benzene is probably not the source of phenylcyclohexane since the former substances show little tendency to form phenylcyclohexane in the presence of hydrogen fluoride and platinum at the pressures and temperatures used. Cyclohexene, however, reacts readily with benzene in hydrogen fluoride to form phenylcyclohexane.

In the reductive coupling of benzene to form phenylcyclohexane various precious metal catalysts such as platinum oxide, platinum on carbon, or rhodium on carbon are effective, while no coupling has been observed with Raney nickel (*10*).

Reaction B appears to follow a course analogous to Reaction A. Thus cyclohexenol or its corresponding ketone may form as an intermediate and subsequently interact with phenol to form the cyclohexylidine bis-(phenol). The by-products *p*-cyclohexylphenyl and resin can form by an acid-promoted degradation of the diphenol, a type of degradation originally observed by Dianin *et al.* (*9*) and further indicated by our own observation that the diphenol is converted to *p*-cyclohexylphenol and resin by contact with hydrogen fluorine.

Reaction C is considered similar to Reaction A except that some of the chlorine is eliminated as hydrogen fluoride.

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