

(760 mm.), m. p.  $-13$  to  $-12^\circ$ ,  $n_D^{20}$  1.4760;  $d_4^{20}$  1.2078; and residue, 2.5 g. The catalyst was converted to 30 g. of red-brown viscous liquid; 14 g. of hydrogen chloride was recovered.

*Anal.* Calcd. for  $C_6H_{11}Cl$ : C, 38.00; H, 5.85; Cl, 56.15. Found: C, 38.10; H, 5.71; Cl, 56.42.

The presence of *t*-butyl chloride in the lower-boiling liquid (b. p.  $45-60^\circ$ ) was proved by adding about 0.1 g. of aluminum chloride to a solution of 1 cc. of the liquid in 1 cc. of benzene. Hydrogen chloride was evolved and the catalyst was converted to a clear yellow liquid. The upper layer was decanted and the excess benzene was permitted to evaporate spontaneously (overnight). Crystals of *p*-di-*t*-butylbenzene (m. p.  $76^\circ$ ) were deposited.

The trichlorohexane (m. p.  $-13$  to  $-12^\circ$ ) was shown to be substantially the same as the product (m. p.  $-14$  to  $-13^\circ$ ) obtained by the addition of *t*-butyl chloride to *cis*-dichloroethylene<sup>3</sup> in the presence of aluminum chloride. A mixture of the two products melted at  $-13.5$  to  $-13^\circ$ . Comparison of the infrared spectra<sup>14</sup> (see Fig. 1) confirmed their identity.

**Reaction of *trans*-Dichloroethylene with Isobutane.**—Comparatively little reaction occurred when a mixture of 30 g. of *trans*-dichloroethylene (purchased from Eimer and Amend), 55 g. of isobutane and 6 g. of aluminum chloride was rotated in the autoclave at room temperature. The liquid product consisted chiefly of unreacted dichloroethylene; about 6 g. of intermediate material and 2 g. of trichlorohexane fraction (b. p.  $190-200^\circ$ ) were obtained.

**Reaction of 1,1,2-Trichloro-3,3-dimethylbutane with Zinc.**—A solution of 30 g. of the trichlorohexane in 100 g. of *n*-propyl alcohol was refluxed over 10 g. of zinc dust for sixteen hours. The product was distilled until addition of water to the distillate no longer yielded an appreciable amount of water-insoluble material. There was obtained 15.5 g. of reaction product,  $n_D^{20}$  1.4272. Redistillation yielded 14 g. (75% yield) of chlorohexene

(b. p.  $102-103^\circ$ ;  $n_D^{20}$  1.4260;  $d_4^{20}$  0.8815; *MR* calcd., 34.26; *MR* obs. 34.42) and 1.5 g. of residue ( $n_D^{20}$  1.4320).

*Anal.* Calcd. for  $C_6H_{11}Cl$ : C, 60.74; H, 9.35; Cl, 29.91. Found: C, 60.54; H, 8.85; Cl, 30.34.

The infrared spectrum<sup>15</sup> of the chlorohexene was compared with that of product (b. p.  $102-104^\circ$ ,  $n_D^{20}$  1.4262) obtained by the dehydrochlorination of 1,1-dichloro-3,3-dimethylbutane<sup>5</sup> over calcium chloride at  $450^\circ$ . The materials were found to be substantially the same (see Fig. 2).

**Oxidation of 1-Chloro-3,3-dimethyl-1-butene.**—A mixture of 6.5 g. of the chlorohexene and a solution of 16 g. of potassium permanganate in 500 cc. of water was stirred at ice-bath temperature for eight hours and then at  $2-10^\circ$  for an additional eight hours. All of the permanganate reacted. The product was filtered and the filtrate was evaporated to 30 cc. and acidified with dilute sulfuric acid. Steam distillation of the acidified solution yielded 3 cc. of organic material which was taken up in ether. Removal of the ether yielded 2.5 g. of trimethylacetic acid, b. p.  $161-162^\circ$ , m. p.  $30-31^\circ$ , characterized as the *p*-bromophenacyl ester, m. p.  $76^\circ$ .

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### Summary

A trichloride, 1,1,2-trichloro-3,3-dimethylbutane, is the principal product of the reaction of isobutane with 1,2-dichloroethylene in the presence of aluminum chloride at room temperature. It is obtained in 35% yield when *cis*-dichloroethylene is used, and in less than 5% yield when *trans*-dichloroethylene is used.

The probable mechanism of the reaction is presented.

It is shown that the reaction serves as a means of evaluating recently proposed mechanisms for the alkylation of isoparaffins with olefins.

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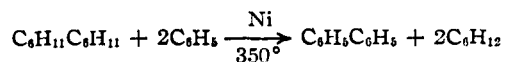
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## Sulfur as a Promoter for a Nickel Catalyst in Dehydrogenation

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The method of aromatizing a hydroaromatic compound by oxidizing it with benzene has given excellent results.<sup>4</sup> However, uniformly good yields were not obtained in attempting to duplicate results and extend the method. For example, in testing catalysts in the conversion of dicyclohexyl to diphenyl, *i.e.*



the yield of diphenyl after reaction for two hours varied from 1 to 90%.

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(2) Allied Chemical and Dye Corporation Fellow 1941-1942.

(3) Monsanto Chemical Company Fellow 1942-1943.

(4) Adkins, Richards and Davis, *THIS JOURNAL*, **63**, 1320 (1941).

The variability in yields was found to depend upon the quality of the benzene used. Fractionation of a sample of benzene which gave good results showed that the lower boiling fractions were better than the higher boiling ones. A number of false leads were followed which, however, led to the discovery that the addition of 25 mg. of tetramethyl tin or of carbon tetrachloride to 20 ml. of benzene and 2 g. of catalyst improved the yield of diphenyl so that the conversion was approximately 80%. The fruitful observation was made that the more thoroughly the benzene was purified from thiophene the poorer were the yields of diphenyl obtained. It was then found that the addition of a suitable amount of thiophene to pure benzene gave excellent yields of diphenyl. For example, the per cent. conversions of dicyclohexyl to diphenyl were with varying amounts of thiophene

as follows: 0 mg., 1%; 1 mg., 32%; 2 mg., 61%; 3 mg., 79%; 5 mg., 79%; 20 mg., 89% and 40 mg., 4%. These results were with 5 g. of dicyclohexyl in 20 ml. of thiophene-free benzene and 2 g. of reduced nickel chromite catalyst for two hours at 350° in a 270 ml. (void) steel reaction vessel. When the amount of catalyst was reduced to 1 g. the optimum amount of thiophene was 10 mg., the conversion being the same as with 20 mg. of thiophene and 2 g. of catalyst. The use of larger ratios than 10 mg. of thiophene per gram of catalyst gave lower conversions of dicyclohexyl. Thiophene-free benzene was obtained by boiling commercial benzene with Raney nickel and distilling.

Diphenyl sulfide was found to be even more satisfactory than thiophene as a promoter for the nickel catalyst. Some of the data are summarized in Table I. It may be noted that the ratio of diphenyl sulfide to catalyst for the optimum results is about twice as large as for thiophene, as might be expected from the sulfur content of the two compounds.

TABLE I

DEHYDROGENATION OF DICYCLOHEXYL (5 g.) WITH DIPHENYL SULFIDE AS A PROMOTER WITH A NICKEL CATALYST (2 g.) AT 350° FOR TWO HOURS

Diphenyl sulfide, mg.	Benzene, ml.	Diphenyl, % Conversion	% Solid
0	20	1	0
6	20	82	57
12	20	91	66
24	20	93	71
48	20	98	94
96	20	13	0
30	40	96	88
30	30	95	82
30	15	93	81
30	10	91	62

\* The "% solid" indicates the amount of diphenyl actually isolated. The "% conversion" given in this table and earlier is based upon refraction indices of the liquid product which may have also contained phenylcyclohexane as well as dicyclohexyl.

The effect of the addition of various amounts of thiophene, in promoting the formation of 4,5-benzohydrindene from 1-methyl-1,2-cyclopentano-decalin was also determined.<sup>5</sup> The reaction

(5) Experimental details on the preparation and properties of

was carried out at 350° for eight hours on 4 g. of the hydroaromatic compound in 20 ml. of pure benzene with 2 g. of catalyst. The optimum ratio of thiophene to catalyst was found to be approximately 10 mg. per gram of catalyst just as in the aromatization of dicyclohexyl. The yields of 4,5-benzohydrindene varied from 5 to 27 to 39 to 44 to 33 to 20 to 15 as the thiophene was increased from 0 to 5 to 10 to 20 to 30 to 40 to 50 mg. for 2 g. of catalyst.

The catalyst used in the dehydrogenations described above was prepared by the reduction of "nickel chromite" as previously described.<sup>4</sup> The amount of nickel in the catalyst before reduction is from 25 to 30%. The lower value corresponds to the analysis for NiCr<sub>2</sub>O<sub>4</sub>, *i.e.*, nickel chromite. After reduction all catalysts analyzed contained about 11% nickel in the metallic state.<sup>6</sup> Thus it may be calculated that the optimum ratio is of the order to 1 part of sulfur to about 30 parts of reduced nickel. It appears that the catalyst is deactivated if the ratio of sulfur to reduced nickel is as much as 1 to 20.

The addition of thiophene to a Raney nickel catalyst did not render it active for the dehydrogenation of dicyclohexyl in the process. Neither thiophene nor diphenyl sulfide had any effect either in promoting or poisoning the activity of platinum or palladium catalysts for the aromatization of dicyclohexyl. The addition of small amounts of sulfur or of nickel sulfide to the nickel catalyst increased the formation of diphenyl from dicyclohexyl in benzene solution, but the effect was not nearly so marked as with thiophene or diphenyl sulfide. Carbon bisulfide did not promote the activity of the nickel catalyst.

### Summary

Thiophene-free benzene is not effective with a nickel catalyst at 350° in the oxidation (dehydrogenation) of dicyclohexyl to diphenyl. However, benzene containing thiophene or diphenyl sulfide in a suitable proportion to the weight of catalyst present brings about an almost quantitative conversion of dicyclohexyl to diphenyl.

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these compounds will be given in a subsequent paper on the synthesis and dehydrogenation of polynuclear compounds.

(6) Covert, Connor and Adkins, *THIS JOURNAL*, **54**, 1652 (1932).