## **Path of Partial Hydrogenation of** *0-, m-,* **and p-Terphenyll**

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The partial hydrogenation of  $o$ -,  $m$ -, and  $p$ -terphenyl at high temperatures (200-275°) and pressures (1500-2500 p.s.i.g.) was studied to determine the initial path of the hydrogenation. Two catalysts, copper chromite and nickel, were used in this work. Initial hydrogenation of *0-* and m-terphenyl in the presence of copper chromite gives as primary intermediates 1,2-diphenylcyclohexane and **1,3-diphenylcyclohexane,** respectively, indicating that the center ring is attacked in preference to the outer ring. p-Terphenyl, however, gave a mixture that indicated that the initial reduction proceeds primarily by a random attack with a slight preference for the outer ring. The nickel catalyst showed marked differences in selectivity compared with copper chromite. o-Terphenyl was hydrogenated primarily to **1,2-diphenylcyclohexane,** while m- and p-terphenyl gave the primary intermediates, 3-cyclohexylbiphenyl and 4-cyclohexylbiphenyl, respectively. The possible hydrogenation path of the one ring reduced intermediates, as well as the relative ease of reduction of various intermediates, is suggested.

Studies<sup>2</sup> of the partial hydrogenation of biphenyl, diand triphenylmethane, and other aromatic substituted compounds3 indicate that the mechanism of the hydrogenation of compounds containing two or more aromatic nuclei is stepwise. These workers found that aromatic rings are saturated one at a time. In addition, the rate<sup>2</sup> of hydrogenation of the partially hydrogenated species was found to be equal to the rate of hydrogenation of their aromatic precursors. Their work was done in acetic acid at **25'** and 75-p.s.i.g. hydrogen pressure using platinum oxide catalyst.

Using the same conditions, partial hydrogenation studies of *0-,* m-, and p-terphenyl have also been made by Smith and Crompton.<sup>4</sup> These workers showed that



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**(2) H. A.** Smith, D. M. Alderman, C. D. Schacklett, and C. M. Welch, *J. Am. Chem. Soc.. TI,* **3772 (1949).** 

**(3) K.** Meischer and K. Hoffman, *Helu. Chim. Acto,* **24, 548 (1941).** 

**(4) H.** A. Smith and C. E. Crompton, "Catalytic Hydrogenation of the Polyphenyl Systems, **o-,** *m-,* and p-Terphenyl." Scientific Report **N70NR-390,** Task Order **I (PB110778),** Oct. **4, 1949.** 

the primary intermediates in the case of *0-* and m-terphenyl were 1,2-diphenylcyclohexane (I) and 1,3-diphenylcyclohexane (VI), respectively. p-Terphenyl, however, yielded 4-cyclohexylbiphenyl (XII) as the principal intermediate.

It was of interest to make a similar study of the path of partial hydrogenation of the terphenyl isomers under more extreme conditions. Accordingly, in this investigation, the isomers were partially hydrogenated in the presence of copper chromite and nickel catalysts at high temperatures and high pressures.<sup>5</sup>

## Results and Discussion

Copper Chromite Catalyzed Reductions.-Table I summarizes the vapor phase chromatographic data on partially reduced o-terphenyl. In the sample reduced in the presence of copper chromite the ratio of center ring reduced product I to end ring reduced product I1 was 10:1. Since II was produced in very small





<sup>a</sup> Girdler G-13 copper chromite was used in all runs using copper catalyst. <sup>b</sup> Girdler G-49 nickel catalyst was used in this run and in run 13 (Table III). All other nickel reductions were made with Harshaw 0500P nickel catalyst (ref. 6).

(5) Except for run 2, the reductions were carried out at  $275 \pm 15^{\circ}$ . At these temperatures, it is believed that the temperature differential only affects the rate of the hydrogenation and not the path of the hydrogenation (product distribution). The reductions in the presence of copper chromite catalyst were normally carried out at **2000** to **2500** p.8.i.g. while those with nickel were carried out at about **1500** p.8.i.g. The use of high preasures with copper chromite catalyst was necessary in order to obtain reasonable rates of hydrogenation. Again, at these elevated pressures, it is believed that pressure differentials at the early stages have no effect on the product distribution but only on the rate of the hydrogenation.

(6) In runs 2 and 13, Girdler G-49 nickel catalyst was used. in this laboratory has shown that, although Harshaw **0500P** nickel and Girdler G-49 nickel differ in their activity, no difference in product composition resulting from their use was notsd. Therefore, with the exception of run **2** and **3,** Harshaw **0500P** nickel catalyst was used.



amounts, it seems reasonable to assume that 111 was derived predominantly from I.

If it is assumed that 2-phenylbicyclohexyl (111) was derived from 2-cyclohexylbiphenyl (II), the ratio then becomes 3 : 1. Since the statistical product distribution for outer ring reduced **I1** to inner ring reduced product I is 2:1, it is apparent that the middle ring of  $\varrho$ -terphenyl is reduced in preference to the outer ring.

The vapor phase chromatographic results of the *m*terphenyl reductions are shown in Table **11.** In samples 3 and 4 reduced to levels of  $22$  and  $28\%$ , the ratio of middle ring reduced product **VI** to outer ring reduced product **VI1** is 1.6:l and 2.2:1, respectively. In addition, each mixture contained no compound IX with both terminal rings saturated.

**TABLE I1 PEAK AREA** (%) **OF THE COMPONENTS OF PARTIALLY HYDROGENATED m-TERPHENYL** 

	---Sample no.---------					
	3	4	5	6	7	8
	-% hydrogenation-					
	22	28	50	14	24	36
Components	$CuCrO4$ catalyst $---Ni$ catalyst $---$					
$m$ -Tercyclohexyl $(X)$	0	0	0	0.7	1.6	7.0
1.3-Dicyclohexylbenzene						
(IX)	0	0	35	2.8	5.6	0
3-Cyclohexylbiphenyl (VII)	21	24	0	21	29	47
1.3-Diphenylcyclohexane						
(VI)	34	.54	.57	6.3	8.0	30
3-Phenylbicyclohexyl (VIII)	0	0	8.3	4.7	8.4	0
$m$ -Terphenyl	43	21	0	63	46	13

Since 1,3-dicyclohexylbenzene  $(IX)$  in sample 5  $(50\%$ saturated) must arise from single end ring reduced prod-



uct **VII,** the ratio of inner ring reduced product **VI** to outer ring reduced product **VI1** becomes 1.6: **1** for initial saturation of one ring. This is strong evidence that initial saturation of m-terphenyl in the presence of copper chromite at levels ranging from 22 to  $50\%$  proceeds selectively toward the middle ring and produces VI as the primary product.

It is interesting to note that the concentration of 1,3 diphenylcyclohexane (VI) in sample *5* was nearly equivalent to that found in sample **4,** indicating that, as hydrogenation proceeds, this species is not readily attacked. In addition, the component with one outer saturated ring, **VII,** is absent, having been reduced to dicyclohexylbenzene (IX). Therefore, it appears that under these hydrogenation conditions, the catalyst preferentially adsorbs m-terphenyl and selectively reduces the middle ring. Then, as the concentration of *na*terphenyl approaches zero, reduction of the biphenyl derivative **VI1** occurs in preference to reduction of 1,3 diphenylcyclohexane (VI). **VI1** yields a much greater concentration of the more sterically favored product, l13-dicyclohexylbenzene **(IX)** , than 3-phenylbicyclohexyl (VIII). On this basis, the relative ease of reduction (and possibly adsorption of the aromatic species on the catalyst surface) appears to follow the order: *m*terphenyl > 3-cyclohexylbiphenyl > 1,3-diphenylcyclohexane.

The results of the partial hydrogenation of  $p$ -terphenyl (Table 111) differ considerably from those of o-









<sup>a</sup> The elemental analyses were performed by Dr. Carol K. Fitz, 115 Lexington Avenue, Needham Heights 94, Mass. <sup>b</sup> Calculated from carbon-hydrogen analyses. <sup>c</sup> Girdler G-13 copper chromite catalyst. <sup>d</sup> Girdler G-49 nickel catalyst. <sup>e</sup> Harshaw 0500P nickel catalyst.  $\prime$  No C, H analysis performed. The  $\%$  hydrogenation for this run was calculated from the area  $\%$  of each component on the **gas chromatogram.** 

and m-terphenyl. Hydrogen uptake equivalent to onering saturation (33%) gave a product mixture containing outer ring reduced product XI1 and inner ring reduced species XI in a 2:1 ratio. This is the ratio expected for a statistical product distribution. An increase in the level of reduction to  $43\%$  gave results which could lead to two possible conclusions. If it is assumed that all of the 4-phenylbicyclohexyl (XIII) arises from  $1,4$ -diphenylcyclohexane  $(XI)$ , then the ratio of the outer ring reduced product XI1 to middle ring reduced product XI becomes *statistical* (about **2** : 1). On the other hand, if it is assumed that 4-phenylbicyclohexyl (XIII) arises from hydrogenation of 4-cyclohexylbiphenyl (XII), then the initial reduction must have proceeded selectively toward the *outer* ring and the ratio of outer ring reduced product to inner ring reduced product becomes about **20** : 1.



Fisher-Taylor-Hirschfelder models show that the phenyl groups in 1,4-diphenylcyclohexane (XI) are more sterically hindered by the cyclohexylene hydrogens than the phenyl groups by the cyclohexyl hydrogens in 4-cyclohexylbiphenyl (XII), XI1 would be expected to be reduced more readily than XI. In view of the p-terphenyl data and the predicted behavior of the intermediate species, it is suggested that the relative ease of hydrogenation (and possibly relative adsorption) of the various species in the early stages appears to follow the order:  $p$ -terphenyl  $> 4$ -cyclohexylbiphenyl *2* **1,4-diphenylcyclohexane.** 

The greater ease of reduction of the terphenyls and cyclohexylbiphenyls VI1 and XI1 compared with the benzene species VI and XI may be explained by steric factors.<sup>†</sup> The terphenyl molecule contains no group that can sterically prevent its adsorption on the catalyst surface and also prevent the approach of hydrogen to one of the rings. Undoubtedly, each terphenyl isomer

exhibits a preferred conformation that ultimately determines the initial path of the hydrogenation. This point is discussed in the last paragraph. However, saturation of an aromatic ring to a bulky cyclohexyl or cyclohexylene group yields a species that sterically is less favored for hydrogenation than terphenyl itself. The bulky group can hinder the approach of an adjacent aromatic ring to the catalyst surface as well as hinder the approach of hydrogen to an adjacent aromatic ring. Smith and co-workers? have shown that monoalkyl-substituted benzene derivatives such as methyl-, ethyl-, n-propyl-, n-butylbenzene, and others have relative hydrogenation rates that vary from **62** to 38 compared to 100 for benzene. In addition,? highly branched monoalkyl-substituted benzenes, like isobutylbenzene and t-butylbenzene, have relative hydrogenation rates of about **25** compared to 100 for benzene. It has also been shown<sup>3</sup> that in the hydrogenation of compounds with two benzene rings, such as diphenylacetic acid, the hydrogenated mixture contained mainly a compound with one ring saturated. This indicated<sup>3</sup> that the original material is reduced in preference to partially saturated material, even though the rate of hydrogenation of both species was found to be equivalent. Thus, the hydrogenation of the biphenyl derivatives VI1 and XI1 would be expected to proceed with greater ease than the hydrogenation of the benzene intermediates, 1,3-diphenylcyclohexane (VI) and 1,4 diphenylcyclohexane (XI). In these compounds the bulky cyclohexylene group affects both aromatic rings as indicated by Fisher-Taylor-Hirschfelder models.

Nickel-Catalyzed Reductions-Hydrogenation of the terphenyl isomers in the presence of nickel catalyst gave products with marked differences in composition compared with the copper chromite work.

Qualitatively, the rate of hydrogenation with the two catalyst systems, copper chromite and nickel, can be compared (Table IV). At about the same temperature and pressure, the terphenyls are reduced about 10 to **20**  times faster with nickel than with copper chromite catalyst. In addition, the intermediates also underwent hydrogenation at a faster rate. This resulted in product mixtures containing a greater concentration of two ring and three ring reduced species. Since in most cases a high concentration of the major component was obtained, this presented no complication to the determination of the reduction path.

Only in the o-terphenyl hydrogenated product does the middle ring reduced component predominate (Table I). The ratio of the inner ring reduced product I to

**<sup>(7)</sup> H. A. Smith and E. F. H. Pennekamp,** *J.* **Am.** *Chem.* **Soc., VI, 276 (1945).** 



outer ring reduced product I1 is **3** : 1, indicating that oterphenyl is preferentially attacked at the middle ring in the presence of nickel catalyst. Hydrogenation of m-terphenyl to  $14-24\%$  (less than one ring saturated) gave a product containing a ratio of VI to VI1 of about 1 :4 (Table 11). With this isomer, a change in the reduction path compared to o-terphenyl takes place and outer ring saturated product predominates; the ratio is twice that required for statistical product distribution.

The data for the reduction levels equivalent to onering saturation (run **8)** would lead one to conclude that hydrogenation of m-terphenyl is random. This readily shows that the initial path of reduction of m-terphenyl with nickel catalysts is therefore more accurately determined at the very early stages of saturation.

Hydrogenation of p-terphenyl in the presence of a nickel catalyst unquestionably proceeds by an outerring path (Table III). At 17 and  $32\%$  saturation, the only species produced was 4-cyclohexylbiphenyl (XII) .



The selectivity for outer-ring reduction manifests itself even at a high reduction level **(58%).** At this level 4 cy clohexylbiphenyl (XII) and 1,4-dicyclohexylbenzene  $(XIV)$  comprise 74% of the sample.

Compared with copper chromite results, it is evident that in the presence of nickel catalyst the meta and para isomers show no tendency to be reduced at a center ring. These isomers show a definite preference for outer-ring reduction with the para isomer showing a greater selectivity for outer-ring attack than the meta isomer.

Table V sums up the results of these studies in terms of the relative tendencies of each terphenyl isomer to undergo outer-, center-, or random-ring reduction with copper chromite and nickel catalysts under the conditions described. The results with platinum oxide catalyst reported by Smith and Crompton<sup>4</sup> are shown for comparison. It is interesting to note that copper





chromite and platinum oxide catalysts gave similar results under grossly different conditions.

The reaction path for the initial saturation of one ring of each terphenyl isomer may be explained by steric and electronic factors. The exceptionally strong tendency for the center ring of o-terphenyl to be reduced first may be explained by the restriction of rotational freedom at the carbon-carbon bonds between phenyl groups. This may cause the center ring to be selectively adsorbed on the catalyst. With the meta isomer, rotational restriction decreases, so that the selective reduction of the center ring is less pronounced than with o-terphenyl. The rings of the p-terphenyl isomer have essentially complete rotational freedom, and selectivity for center ring attack disappears. In addition, a stronger contribution of polar excited states (resonance) is expected with p-terphenyl than with *0-* or m-terphenyl. The para isomer can more readily achieve three-ring resonance, resulting in charge centers on the terminal rings. The meta isomer can only achieve tworing resonance, resulting in charge centers on the inner and outer ring. The *ortho* isomer could achieve threering resonance, but the steric requirements for this may not be satisfied and therefore two-ring resonance would be most probable. Ultraviolet absorption studies<sup>3</sup> of polyphenyl isomers show that *ortho* isomers exhibit an absorption shift that is attributed to a hindered biphenyl absorption. No absorption due to three-ring resonance was found. The present results show that there is a definite stepwise attack on a single ring probably followed by desorption and readsorption for further hydrogenation.

## **Experimental**

Hydrogenation.-Eastman reagent grade *0-, m-,* and p-terphenyl, Girdler **G-13** copper chromite, and two nickel catalysts, Girdler **G-49** nickel, and Harshaw 0500P nickel, were used. All hydrogenations were performed in a 300-ml. Aminco rocking

**<sup>(8)</sup>** G. F. **Woods,** "Preparation and Properties of Some Polyphenyls," **WATR 59-496,** Sept. **1959,** pp. **79-85.** 

autoclave. No solvent was employed. In each experiment, 25 g. of terphenyl and 2.5 g. of powdered catalyst were used.

The charged autoclave was pressurized with hydrogen to 300 p.8.i.g. below the desired reduction pressure and heated to the desired temperature without shaking. Shaking was then started, and the approximate degree of hydrogenation was obtained by following the pressure drop in the system. The partially hydrogenated terphenyl mixture was dissolved in benzene, and the benzene solution was filtered to remove catalyst and then concentrated to an oil or solid using a Buchler flash evaporator.

Table IV summarizes the partial hydrogenation experiments carried out on the three terphenyl isomers. The per cent reduction achieved in each caae was calculated from the carbon-hydrogen analytical data. The difference in the number of hydrogen atoms in partially reduced product and terphenyl, divided by 18, the number of hydrogen atoms needed for 100% hydrogenation, times 100, gives the per cent hydrogenation of the sample.

Product Analyses.<sup>9</sup>-The products were separated by vapor phase chromatography using an Aerograph Model A-350B vapor fractometer. Ten microliters of a tetrahydrofuran solution of the sample was used. The helium flow rate was about 75 ml./ min. The following column packings  $(0.25 \text{ in.} \times 6 \text{ ft.})$  and temperatures were used: 15% Craig polyester succinate, 30-60 mesh Chromosorb P at  $210^{\circ}$ ;  $15\%$  Apiezon L<sup>®</sup> on 30-60-mesh Chromosorb W at  $260^\circ$ ; and  $15\%$  polyphenyl ether OS-138 on 30-60-mesh Chromosorb P at 250".

Area per cent of each peak on the chromatogram was determined by the triangulation method. In most cases the component waa collected in a capillary as it eluted from the chromatographic column.

Identification of the eluted components was based on ultraviolet (in cyclohexane) and infrared (KBr or liquid film) absorptions and, in some cases, on carbon-hydrogen analysis. 1,3-Diphenylcyclohexane and 1,4-dicyclohexylbenzene were compared with authentic samples. The order of elution from the chromatographic column also aided in the identification of some components.

1,2-Diphenylcyclohexane had infrared bands at 13.1 and 14.4 *p,* characteristic of monosubstituted benzene, and ultraviolet  $\lambda_{\text{max}}$  at 253, 259, and 265 m $\mu$ , characteristic of monoalkyl-substituted benzene.

Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>: C, 91.5; H, 8.5. Found: C, 91.4; H, 8.6.

2-Cyclohexylbiphenyl had infrared bands at  $13.3$  and  $14.4 \mu$ ; ultraviolet  $\lambda_{\text{max}}$  at 233 m<sub> $\mu$ </sub> due to biphenyl absorption, shifted probably owing to steric effects.

2-Phenylbicyclohexyl had infrared bands at 13.2 and 14.4 *p,*  characteristic of monosubstituted benzene; ultraviolet **Amax** at 254, 260 and 266 m $\mu$ , characteristic of monoalkyl-substituted benzene.

Anal. Calcd. for C<sub>18</sub>H<sub>26</sub>: C, 89.3; H, 10.7. Found: C, 89.2; H, 10.5.

1,2-Dicyclohexylbenzene was a minor component. It was found that 1,4-dicyclohexylbenzene eluted from the V.P.C.

(9) **The authors gratefully acknowledge the analytical work of** J. **L. Driscoll. A.** E. **Bekebrede, and** W. **R. Smith** of **these laboratories.** 

column between p-tercyclohexyl and 4-phenylbicyclohexyl. Therefore, the component eluting between o-tercyclohexyl and 2phenylbicyclohexyl was considered to be **1,2-dicyclohexylbenzene.** 

 $o$ -Tercyclohexyl showed infrared absorption at 3.4  $\mu$  and no absorption in the ultraviolet. This component was the first to elute from the chromatographic column as would be expected.

The retention time and infrared and ultraviolet spectra of the unreduced sample were identical with those of startingo-terphenyl.

1,3-Diphenylcyclohexane had infrared bands at 13.3 and 14.4  $\mu$ , characteristic of monosubstituted benzene; ultraviolet  $\lambda_{\text{max}}$ at 254, 259, and 268 m $\mu$ , characteristic of monoalkyl-substituted benzene. It waa also identified by comparison with an authentic sample of 1,3-diphenylcyclohexane<sup>10</sup> (prepared by hydrogenation of 1,3-diphenylcyclohexane<sup>11</sup> at room temperature at 150-p.s.i.g. hydrogen pressure).

3-Cyclohexylbiphenyl showed infrared absorption at 12.6, characteristic of meta-disubstituted benzene, and  $13.2$  and  $14.3^{\circ} \mu$ , characteristic of monosubstitution; ultraviolet  $\lambda_{\text{max}}$  at 248 m $\mu$ , characteristic of biphenyl absorption.

3-Phenylbicyclohexyl was assumed to elute between 1,3-dicyclohexylbenzene and 1,3-diphenylcyclohexane since in the pterphenyl work, 4-phenylbicyclohexyl eluted between 1,4-dicyclohexylbenzene and **1,4-diphenylcyclohexane.** The area per cent of this component did not exceed  $8.3\%$ .

1,3-Dicyclohexylbenzene had infrared absorption, 12.6, characteristic of meta-disubstituted benzene, and  $13.3$  and  $14.3$   $\mu$ , Characteristic of monosubstitution.

m-Tercyclohexyl (infrared, 3.4  $\mu$ ; no ultraviolet absorption) was the first to elute from the column. The retention time and infrared and ultraviolet spectra of the unreduced compound were identical with those of starting m-terphenyl.

1,4-Diphenylcyclohexane had infrared bands at 13.3 and 14.4  $\mu$ , characteristic of monosubstituted benzene; ultraviolet  $\lambda_{\max}$  at 254, 260, and 268 m $\mu$ , characteristic of monoalkyl-substituted benzene.

4-Cyclohexylbiphenyl had infrared bands at 12.0, characteristic of para disubstitution, and 13.2 and 14.4 *p,* characteristic of biphenyl absorption.

4-Phenylbicyclohexyl had infrared bands at 13.3 and 14.4  $\mu$ , characteristic of monosubstitution; ultraviolet **Amsx** 250, 254- 260, and 268 m $\mu$ , characteristic of monoalkyl-substituted ben, zene .

1,4-Dicyclohexylbenzene showed infrared absorption at 12.2, characteristic of para-disubstitution, and at 13.3 and 14.4  $\mu$ , of monosubstitution; ultraviolet  $\lambda_{\text{max}}$  258, 263, and 272 m $\mu$ , benzenoid fine structure, identical with an authentic sample of 1,4-dicyclohexylbenzene purchased from Distillation Products Industries.

p-Tercyclohexyl had infrared absorption at 3.4 *p,* and no absorption in the ultraviolet, **As** with the ortho and meta isomers, this component waa the first to elute from the column.

The retention time and the infrared and ultraviolet spectra of the unreduced compound were identical with those of starting *p*terphenyl .

**(10) C. D. Nenitzaesen and D. Curcaneanu,** *Eer.,* **70B, 3468 (1937).** 

**(11)** *G.* **F. Woods and I.** W. **Tucker,** *J.* **Am.** *Chem.* **Soc.,** *TO,* **2174 (1948)**