Tetrahedron. Vol. 24, pp. 4523 to 4533. Pergamon Press 1968. Printed in Great Britain

HYDROGENATION OF BENZENE TO PHENYLCYCLOHEXANE WITH SUPPORTED ALKALI METAL CATALYSTS

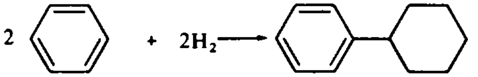
L. H. SLAUGH
Shell Development Company, Emeryville, California 94608

(*Received in USA* 22 *December* 1967; *accepted for publication* 23 *January* 1968)

Abstract—Several alkali metals supported on alumina or carbon catalyze the hydrogenation of benzene to phenylcyclohexane. By-products are cyclohexane, bicyclohexyl and trimeric (C_{18}) compounds. Yields of phenylcyclohexane of 84–87% have been obtained. The yield of phenylcyclohexane and the catalyst activity are dependent upon the alkali metal, the support, the temperature and the hydrogen pressure employed. The mechanism of the reaction is discussed.

INTRODUCTION

ALKALI metals have been shown to be catalysts for the hydrogenation of organic compounds.[1–4] Friedman *et al.* found these catalysts effective for the hydrogenation of a variety of polycyclic aromatic compounds to products containing isolated aromatic rings.[1] Benzene was employed as the solvent without it undergoing significant reaction at the conditions described (180–250°; 1400 psig). Metallic sodium has been claimed, however, to be a suitable catalyst for the hydrogenation of benzene to cyclohexane (200°; ~2200 psig).[5] We have found that the catalytic properties of alkali metals are dramatically altered by placing them on selected supports. In the presence of certain catalysts of the latter type, benzene can be hydrogenated to mainly phenylcyclohexane (Eq. 1). A description of this novel hydrodimerization reaction is presented below.



(1)

RESULTS AND DISCUSSION

Catalysts were prepared *in situ* and the reaction initiated simply by heating the alkali metal, support and benzene under hydrogen pressure to the desired temperature in a stirred autoclave. As the metal melts it flows onto the support. A further description of the catalysts is given below. The progress of the reaction was followed by monitoring the decrease in pressure. The product composition and catalyst activity were found to be dependent upon the alkali metal, the support, the temperature and the hydrogen pressure. Products formed in varying amounts are cyclohexane, bicyclohexyl, phenylcyclohexane, biphenyl and trimeric (C_{18}) compounds. Under optimum conditions (*vide infra*), the yield, based on converted benzene,* of phenylcyclohexane is 85–87%. Most of the experiments to be described were not at optimum conditions

---

* Throughout this article the yields are based on the converted benzene.

but the variables were controlled to permit an assessment of changes in the product brought about by variations in the reaction conditions.

Catalysts of potassium on several different supports were tested for activity at 200° and 600 psig of hydrogen (Table 1). Under these conditions, a support is vital to catalytic activity of the metal. Unsupported potassium was rapidly converted to white, powdery potassium hydride which was inactive. Also, it is essential that the support be pre-treated by drying it at elevated temperature (450–650° for alumina and ~120° for carbon). Potassium on non-dried alumina (Alcoa F-20) was totally ineffective. Although potassium on dried alumina is an effective catalyst (Expt 1),

TABLE 1. HYDROGENATION OF BENZENE OVER SUPPORTED POTASSIUM CATALYSTS[a]

Expt. No.	Support[b]	Conv of C_6H_6, %	Yields of Products[c,*]				
					Bicyclohexyl	Phenyl-cyclohexane	Trimer,[d] $C_{18}H_{26}$
1	Al_2O_3–C	78	52·8	0·1	6·7	33·9	6·4
2	SiO_2	0·5	52·6	31·6	0	15·8	~0
3	SiO_2–Al_2O_3	1·3	~0	0	0	54·2	45·8
4	Al_2O_3–D	34·2	24·9	0	0·5	69·1	5·5
5	Carbon	11·3	18·8	2·4	—	74·7	2·3
6	K_2CO_3	0	—	—	—	—	—
7	MgO[e]	0	—	—	—	—	—
8	Al_2O_3–B dried, 650°	65·7	59	0·4	3·4	33·8	3·5
9	Al_2O_3–B dried, 550°	35·5	48·4	0	2·8	47·3	1·5
10	Al_2O_3–F	82·0	48·6	0	8·2	34·9	8·2
11	Al_2O_3–G	60·7	51·4	0·2	3·2	40·3	4·9

[*] See footnote [*] on page 4525.

[a] Temp, 200°; press, vapor press of soln plus 600 psig of H_2 (800 psig total); reaction time, 1·0 hr; benzene, 35 g (448 mmoles); K, 2·9 g (74 mmoles); support, 7·1 g.

[b] See following Legend of catalysts for description.

[c] Material balances for product analyses (GLPC) were generally 100 ± 4%. The yields based on converted benzene are normalized to 100%.

[d] The main component of the trimeric product was $C_{18}H_{26}$ (two saturated rings and one aromatic ring present), although small amounts of $C_{18}H_{32}$ and $C_{18}H_{24}$ were also present.

[e] MgO, 10 g and K, 26 mmoles.

Legend of catalyst supports, Table 1

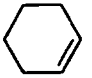
Al_2O_3–B	Alcoa activated F-20 alumina; not washed, dried 16 hr at 550° or 650°.
Al_2O_3–C	Alcoa activated F-20 alumina; washed with aqueous NH_4NO_3, then water; dried at 550° for 16 hr.
MgO	Dried at 550° for 16 hr.
SiO_2	Activated silica gel; not washed; dried 16 hr at 550°.
Al_2O_3–D	$AlCl_3$ was converted by aq NH_4OH to $Al_2(OH)_3$; dried to alumina at 550° (16 hr).
SiO_2–Al_2O_3	MSA-3 silica-alumina cracking catalyst (American Cyanamid Co); not washed; dried 16 hr at 550°.
Carbon	BKH activated charcoal; powdered; dried at 120–140° for several hr.
Al_2O_3–F	Alcoa activated F-20 alumina; washed with K_2CO_3 soln and then water to replace Na^+ with K^+.
Al_2O_3–G	$Al(NO_3)_3$ was converted by aqueous NH_4OH to $Al(OH)_3$ which was dried to Al_2O_3 at 550° (16 hr).

potassium on either dried silica (Expt 2), silica–alumina (Expt 3), potassium carbonate (Expt 6) or magnesium oxide (Expt 7) is inactive. Potassium on activated carbon promoted the hydrogenation of benzene to phenylcyclohexane in high yield, 75% (Expt 5). As indicated by the relatively low conversion of benzene, 11%, the rate of reaction was less with the K/carbon catalyst than it was with K/Al_2O_3 catalysts (compare Expts 1 and 5).

The activity (measured by the depth of conversion of benzene) and selectivity (measured by the yield of phenylcyclohexane) of K/Al_2O_3 catalysts depend upon the mode of preparation and treatment of the alumina. For example, potassium catalysts prepared with Alcoa F-20 alumina which had been washed with either ammonium nitrate or potassium carbonate solution to remove sodium ions were considerably more active than a similar catalyst prepared from unwashed alumina (Expts 1, 10 and 9, respectively). The most selective K/Al_2O_3 catalyst was one where the support had been prepared *via* hydrolysis of aluminum chloride and subsequent pyrolysis of the resultant aluminum hydroxide (Expt 4). The temperature at which the alumina is pre-treated also has an effect on the catalyst. Potassium on Alcoa F-20 alumina which had been dried at 650° (Expt 8) was a more active catalyst than one prepared from alumina dried at 550° (Expt 9).

Changing the metal/support ratio affects the extent of conversion of the benzene. An increase from 15 mmoles to 74 mmoles of potassium for 7 g of alumina increased the conversion of benzene from 23% to 62%: the yield of phenylcyclohexane was

TABLE 2. HYDROGENATION OF BENZENE OVER SUPPORTED POTASSIUM CATALYSTS[a]

Expt No.	Support[b]	Temp °C	Time, hr	H_2 Rxn Press, psig[c]	Conv of C_6H_6, %	Yield of Products[d, *]				
								Bicyclo hexyl	Phenyl-cyclo-hexane	Trimers, $C_{18}H_{26}$
12	Al_2O_3–C	100	19	400–900	10·8	95·2	1·2	0	3·6	0
13	Al_2O_3–C	100	20	600	22·6	97·8	0	0	2·2	0
14	Al_2O_3–C	200	1	800	62·6	41·5	0·4	2·9	44·2	11
15	Al_2O_3–C	228	1	900	26·6	45·8	0·9	0	50·3	3·0
16	Al_2O_3–C	250	1	1060	31·6	51·2	0	1·3	43·8	3·7
17	Al_2O_3–C	224	3	360	40·8	6·6	0	0	84·3	9·1
18	Al_2O_3–C	200	1	300	30·6	4·0	0·3	0	87·0	8·4
19	Al_2O_3–C	200	1	1640	96·8	88	0	8·9	2·7	0·4
20	Al_2O_3–C	200	0·2	1400	22·3	80·5	0	0	19·5	0
21	Carbon	225	1	900	30·4	11·4	0·4	0	81·0	7·2
22	Carbon	250	1	1020	5·8	33·6	0	0	66·4	0
23	Carbon	225	1	420	7·2	~0	0	0	63·5[e]	5·3

[*] See footnote * on page 4526.

[a] Amount of K on support, 74 mmoles except for Expt 12 and 17 where 51 mmoles were present. Amount of support, 7·1 g. Benzene, 450 mmoles.

[b] See Table 1 for Legend of catalysts.

[c] Includes vapor press of soln which was ~200 psi at 200° and ~400 psi at 250°.

[d] Material balances for product analyses (GLPC) were generally 100 ± 4%. The yields based on converted benzene are normalized to 100%.

[e] In addition to phenylcyclohexane, diphenyl was formed in 31·5% yield.

~46% (200°; 600 psig H_2; 1·0 hr). A further increase in the metal/support ratio did not significantly improve the catalyst.

The activity and selectivity of supported potassium catalysts are dependent upon the reaction conditions (Table 2). At 100°, potassium on alumina catalyzes the hydrogenation of benzene mainly to cyclohexane (Expts 12 and 13), whereas at 200–250°, substantial amounts of phenylcyclohexane are produced (Expts 14, 15 and 16). There exists an optimum reaction temperature above which catalyst activity declines. For example, a K/Al_2O_3 catalyst was more active at 200° (Expt 14) than at either 225° (Expt 15) or 250° (Expt 16). A similar temperature effect also occurred with K/carbon catalysts (Expts 21 and 22).

The hydrogen pressure markedly affects the product composition. The best yields of phenylcyclohexane have been obtained at low pressures. Several sets of experiments (17 and 15; 19 and 14; 21 and 23) demonstrate this; however, the effect is most unambiguously shown by Expts 18 and 20 where the conversions of benzene were not greatly different. With a reaction pressure of 1400 psig, the product was 80·5% cyclohexane and only 19·5% phenylcyclohexane, but at 300 psig the yield of phenylcyclohexane was 87%. In the latter case, significant amounts of trimers were formed. Excellent yields of phenylcyclohexane (84%) were also obtained in Expt 17 where the hydrogen pressure was low. Interestingly, with a K/carbon catalyst employed at low pressure, phenylcyclohexane and biphenyl were obtained in a combined yield of ~95% (Expt 23).

The other alkali metals were examined only briefly for catalytic activity. With rubidium or cesium on Al_2O_3–C (see Legend of supports, Table 1) at 100° (1200 psig), phenylcyclohexane was formed in 10–16% yield along with cyclohexane. These metals appear to promote the hydrodimerization reaction at a lower temperature than the corresponding potassium catalysts since under these conditions the latter produced almost entirely cyclohexane. Sodium on Al_2O_3–B has low activity at 150°, but will promote the formation of phenylcyclohexane in low yield. Sodium-potassium alloys (50% molar mixture) on Al_2O_3–C are less active at 200° and 800 psig than neat potassium on alumina and produce slightly lower yields of phenylcyclohexane (38% vs 44%, respectively). Lithium on Al_2O_3–C behaved quite differently from the other metal catalysts. At 200° and low pressures (100 psig of hydrogen plus 200 psig vapor pressure of the solution), the latter produced only cyclohexane.

It is surprising that unsupported potassium or potassium on silica, silica–alumina, magnesium oxide or potassium carbonate were poor catalysts whereas potassium on either alumina or activated carbon were effective. The appearances of these catalysts at the end of the reactions were all different. Unsupported potassium had been converted to white, powdery potassium hydride. The solids obtained with potassium on potassium carbonate and magnesium oxide were white and evolved hydrogen upon hydrolysis. Perhaps potassium hydride had been formed here also. Potassium on silica, silica–alumina and alumina were gray, lavender and black, respectively. Each evolved gas upon hydrolysis. The black appearance of the K/Al_2O_3 catalyst is more indicative of finely dispersed metal than of potassium hydride.

Phenylcyclohexane could be formed *via* the alkylation of benzene if cyclohexene were an intermediate. Two experiments indicate that this path is not the main one. When an equal molar mixture of benzene and cyclohexene was hydrogenated over a K/Al_2O_3 catalyst, the olefin was rapidly reduced to cyclohexane. A repeat of this experiment with C^{14}-labeled cyclohexene gave the results tabulated in Table 3. By comparing the C^{14}-activity of the reactant cyclohexene with that of the products, the following conclusions are indicated: (1) 96% of the cyclohexane product came from the C^{14}-cyclohexene; (2) a maximum of 5·9% of the phenylcyclohexane came from the reaction of C^{14}-cyclohexene and benzene; (3) less than 1% of the C^{14}-cyclohexene was converted to benzene. Although these experiments preclude a major participation of bulk cyclohexene in the formation of phenylcyclohexane, they do not preclude the possibility that cyclohexene is formed from benzene on the surface of the catalyst and that the former alkylates benzene before being desorbed. However, this seems very unlikely.

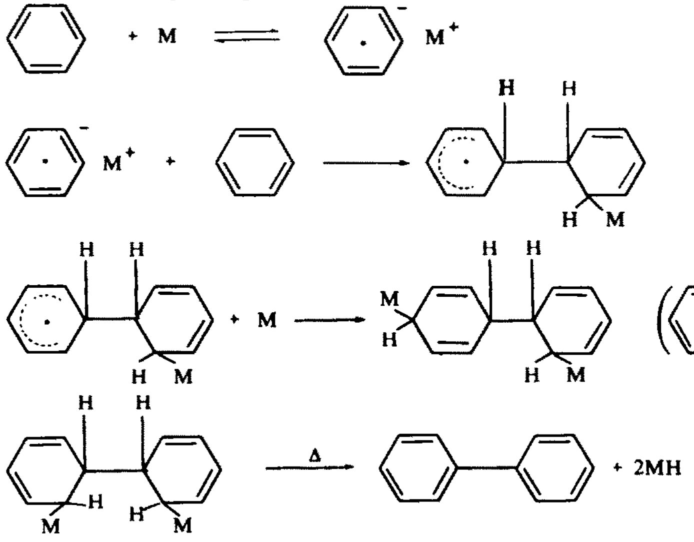
TABLE 3. HYDROGENATION OF A C^{14}-CYCLOHEXENE/BENZENE MIXTURE

Benzene = 205 mmoles
C^{14}-Cyclohexene = 195 mmoles (6·1 × 10^5 dpm/mmole)
K = 74 mmoles
Al_2O_3–C[a] = 7·1 g
H_2 = 100 psig (total pressure = 300 psig)
Time = 2 hr
Temperature 200°

Product composition	Product activity
Cyclohexane, 207 mmoles	5·87 × 10^5 dpm/mmole
Benzene, 110 mmoles	4·5 × 10^3 dpm/mmole
Phenylcyclohexane, 40·3 mmoles	3·6 × 10^4 dpm/mmole

[a] For a description of the catalyst support see the Legend to Table 1.

Benzene anion-radicals in tetrahydrofuran are sufficiently reactive to undergo displacement reactions on chlorosilanes[6] and butyl chlorides.[7] In the present case, phenylcyclohexane formation might be initiated by an attack of benzene anion-radicals on benzene to form dimeric intermediates which are subsequently hydrogenated. For example (Eqs 2–6):

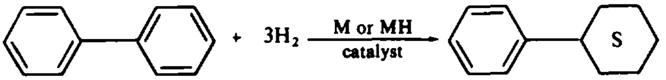


(2)

(3)

(4)

(5)



(6)

However, this mechanism seems less likely than the one presented below because higher temperatures favor the formation of phenylcyclohexane whereas the stability of anion-radicals dramatically decreases with increasing temperature.[8] It is doubtful that benzene anion-radicals would be present under the reaction conditions (~150–200°) unless the alumina or carbon supports stabilize them.

We prefer the following mechanism, illustrated with potassium, for the reactions which we envision as occurring on the surface of the support.

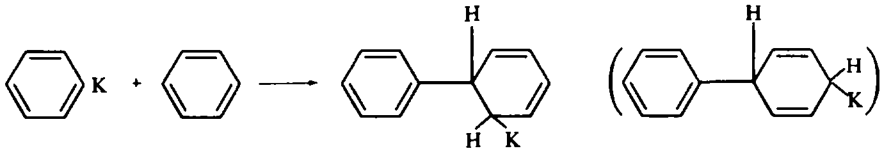
$$C_6H_6 + 2K \rightarrow C_6H_6K_2 \tag{7}$$

$$C_6H_6K_2 \rightarrow C_6H_5K + KH \tag{8}$$

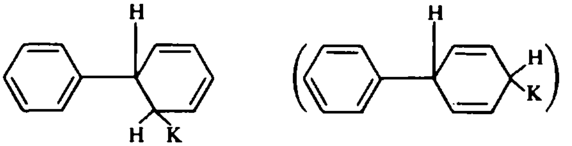
$$C_6H_6K_2 + 2H_2 \rightarrow \underset{\text{(1,4- or 1,3-cyclohexadiene)}}{C_6H_8} + 2KH \tag{9}$$

$$C_6H_8 + 2H_2 \xrightarrow[\text{catalyst}]{\text{K or KH}} \underset{\text{(cyclohexane)}}{C_6H_{12}} \tag{10}$$

$$C_6H_8 + 4KH \rightarrow C_6H_{12} + 4K \tag{11}$$



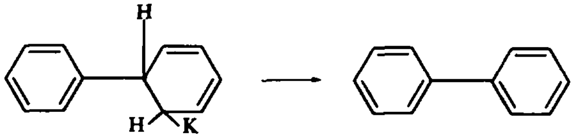
(12)



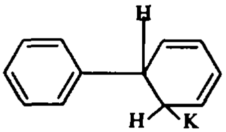
+ $C_6H_5K \longrightarrow C_6H_5^- \; C_6H_5K_2^+ C_6H_6$(13)

$$C_6H_5{-}C_6H_5K_2 + 2H_2 \rightarrow C_6H_5{-}C_6H_7 + 2KH \tag{14}$$

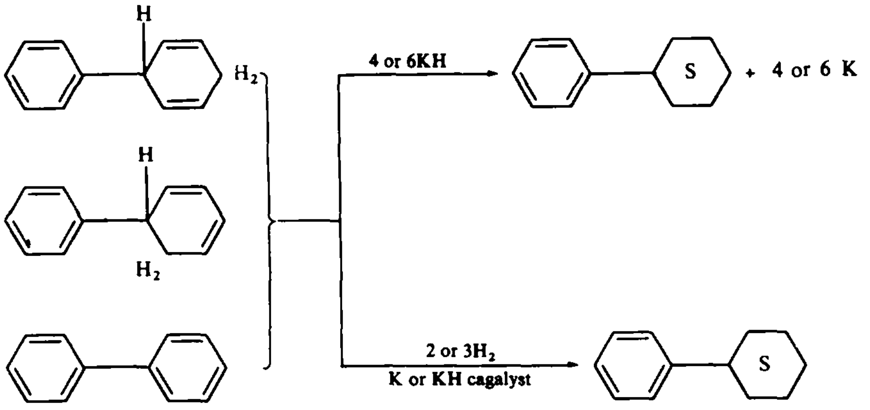
$$C_6H_5{-}C_6H_5K_2 \rightarrow C_6H_5{-}C_6H_5 + 2K \tag{15}$$



+ KH (16)



+ $H_2 \longrightarrow C_6H_5-C_6H_7$ (17)



(18)

(19)

An alternative to the formation of benzene anion-radicals is the formation of phenylpotassium. As proposed by Norton and Lanpher,[9] phenylpotassium could be formed by the addition of two equivalents of potassium to benzene followed by an elimination of potassium hydride (Eqs 7 and 8). Dimerized products probably arise from the attack of phenylpotassium on benzene (Eq 12). Morton and Lanpher[9] have presented evidence that phenylpotassium will add to benzene to give an adduct which reacts with a second phenylpotassium to form a dipotassio compound (Eqs 12 and 13). These dimeric metal adducts will decompose to give biphenyl (Eqs 15 and 16).[9] In the present study, with Na/Al_2O_3 and K/Carbon (Table 2, Expt 23) catalysts, biphenyl was a significant part of the product. Hydrogenation of one ring of the dimeric products to produce ultimately phenylcyclohexane can occur by either the reaction of hydrogen with dimeric potassio adducts (Eqs 14 and 17) or the reaction of hydrogen or potassium hydride with dimeric hydrocarbon intermediates (Eqs 18 and 19). Metal-carbon bonds of this type are known to undergo hydrogenolysis.[10, 11] Also, we demonstrated independently that supported potassium will readily catalyze the hydrogenation of biphenyl to phenylcyclohexane.* One stipulation of the above proposed mechanism is that metal be continuously regenerated on the surface of the support from KH. This could occur *via* reactions 11 and 18. Consistent with this, phenylcyclohexane, in addition to biphenyl, was produced by heating benzene with a K/Al_2O_3 catalyst at 200° in the *absence of added hydrogen.*

If the above mechanism is correct and the addition of phenylpotassium to benzene (Eq 12) is slow relative to the subsequent steps in the phenylcyclohexane forming sequence, increasing the hydrogen pressure should not facilitate dimer formation. On the other hand, increasing the hydrogen pressure would be expected to facilitate cyclohexane formation (Eqs 9 and 10). Indeed, this was found experimentally to be the case (*vide supra*); consequently, low pressures were employed to obtain high yields of phenylcyclohexane.

At 100° with a K/Al_2O_3 catalyst, the major product was cyclohexane, whereas at 200° phenylcyclohexane was the main product. This would indicate that either or both of the steps in phenylpotassium formation (Eqs 7 and 8) and the alkylation step

---

* Metal hydrides also have been shown to be hydrogenation catalysts. See Ref 11 and Refs cited therein.

(Eq 12) are favored relative to the steps (Eqs 9–11) for the hydrogenation of benzene by an increase in the reaction temperature. Possibly, at the lower temperatures, the reaction of benzene anion-radicals with hydrogen also may play a role in cyclohexane formation.

Qualitatively some metals were found to be better hydrodimerization catalysts than others (*vide supra*). This may be related to the abilities of their corresponding phenylmetals to add to benzene. Morton and Lanpher reported that phenylsodium added much less readily to benzene than did phenylpotassium.[9]

The two main by-products of the hydrodimerization reaction are bicyclohexyl and trimeric compounds containing one benzene nucleus. Bicyclohexyl likely results from a slow hydrogenation of phenylcyclohexane. The trimers are formed by hydrodimerization of benzene with phenylcyclohexane.

One can only speculate about the function of the necessary supports in promoting the formation of phenylcyclohexane. Perhaps the alumina and the activated carbon complex with the benzene and, thus, facilitate the addition of the phenylmetals to the aromatic ring (Eq 12).

EXPERIMENTAL

Reagents and supports. The alkali metals were purchased from Alfa Inorganics, Inc. Reagent grade benzene was used without further drying or purification.

Alcoa F-20 alumina was freed of Na ions by an NH_4OH wash (Al_2O_3–C). The presence of Na ions in the effluent wash was monitored by a flame test.

The preparation of Al_2O_3–D (Table 1) was as follows: $AlCl_3$ (1·13 kg) was dissolved in 4 l. water. To this was added, with stirring over 1·0 hr, 3·4 l. 5·64N NH_4OH. The resultant gel was placed on a filter and allowed to "age" overnight. The gel was washed on the filter with a large excess water (adjusted pH to ~9 with NH_4OH) over a period of 3 days until the eluent was free of chloride ions as determined by a $AgNO_3$ test. The gel was dried first at 120° and then at 550° for 16 hr. An analysis of the final material showed: Cl, 0·012%.

The preparation of Al_2O_3–G (Table 1) was about the same as Al_2O_3–D. That is, $Al(OH)_3$ was precipitated from $Al(NO_3)_3$aq by adding NH_4OH until the pH of the soln was 9·3. The ppt was "aged" overnight, filtered, washed, dried first at 120° and then at 550° for 16 hr. An analysis of the final alumina indicated: Na, 0·0008% and Si, 0·0069%.

General procedure of hydrogenating benzene. Inside a N_2-filled drybox, benzene, alkali metal and a selected support were placed in a stainless steel, 85-ml autoclave. The quantities of the reagents and the reaction conditions are listed in the text Tables. After the vessel was sealed and H_2 introduced, the system was heated to the desired temp. The autoclave was heated by placing it in a brass cup which was wrapped with a heating coil. Stirring was provided by a bar magnet (sheathed with stainless steel) placed inside the autoclave which was rotated by an external magnetic stirrer. The progress of the reaction was followed by the decrease in the press as measured by a suitable transducer and recorder. The cooled product could be analyzed directly by GLPC after the catalyst had been allowed to settle. Occasionally, the catalyst was destroyed by adding water portion-wise to the autoclave before the organic product was analyzed.

Product identification. The organic products were identified by the coincidence of the GLPC emergence times (polyphenyl ether/Carbowax and DC-710/firebrick columns) and mass spectrometric fragmentation patterns with those of authentic compounds. A Wilkins Autoprep GLPC was used for isolating the individual products obtained from the C^{14}-cyclohexene tracer experiment.

Benzene heated with K/Al_2O_3 *in the absence of hydrogen.* Benzene (451 mmoles), 7·1 g at Al_2O_3–C (see description of support in Table 1), and 74 mmoles K metal were placed in an 85-ml autoclave. The sealed autoclave was flushed with N_2 and heated and stirred at 200° for 4 hr. The product consisted of: cyclohexane, trace; benzene, 405 mmoles; phenylcyclohexane, 10·8 mmoles; biphenyl, 16·6 mmoles; trimers, 1·1 mmoles.

Hydrogenation of biphenyl. Cyclohexane (40 ml), biphenyl (46·8 mmoles), activated C (7 g) and K (74 mmoles) were placed in an 85-ml autoclave. The sealed autoclave was heated to 200°, H_2 introduced to 800 psig, and the contents stirred. After a 1 hr reaction period, H_2 absorption ceased. The product consisted of: bicyclohexyl, 3·1 mmoles; phenylcyclohexane, 37·0 mmoles. All of the biphenyl had been hydrogenated. A mass spectrometric analysis showed that C_{18} and C_{24} compounds were not formed.

Radioactivity measurements. The C_{14}-cyclohexene was purchased from Tracerlab. Inc. and further purified by distillative GLPC. The C^{14} activities of the compounds listed in Table 3 were determined by the liquid scintillation method. All net counting rates were converted to disintegrations per minute (dpm) by measurement of the exact counting efficiencies with calibrated C^{14}-containing solns.

Acknowledgements—Appreciation is expressed to G. W. Schoenthal for able technical assistance and to R. E. Thorpe for mass spectrometric analyses. Gratitude also is expressed to M. A. Muhs, B. E. Gordon and L. B. Skinner for assistance with purifying the C^{14}-cyclohexene and measuring the C^{14} activity of all the labeled products. Appreciation is expressed to H. A. Benesi and G. S. Levinson for samples of certain aluminas.

REFERENCES

[1] S. Friedman, M. L. Kaufman and I. Wender, *Abstracts, 148th ACS Meeting* L 27. Chicago, 30 August 4 September (1964).

[2] F. W. Bergstrom and J. F. Carbon, *J. Am. Chem. Soc.* **63**, 2934 (1941).

[3] Guyot, *Chim. et. Ind. Spec.* No. 410, April 1928; *Chem. Abstr.*, **22**, 4522 (1928).

[4] N. A. Orlov and N. D. Likhachev, *Ber. Dtsch. Chem. Ges.* **63B**, 2179 (1930).

[5] G. M. Whitman, U.S. Patent 2,443,016, 8 June (1948).

[6] D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.* **84**, 2843 (1962).

[7] E. P. Kaplan, Z. I. Kazakova and A. D. Petrov, *Acad. of Sci. (USSR) Bul. Div. of Chem. Sci.* (English Translation) No. 3, 513 (1965).

[8] A. Rembaum, A. Eisenberg and R. Haack, *J. Am. Chem. Soc.* **87**, 2291 (1965).

[9] A. A. Morton and E. J. Lanpher, *J. Org. Chem.* **23**, 1639 (1958).

[10] W. N. Ipatiew, G. A. Rasuwajew and I. F. Bogdanow, *Chem. Ber.* **63**, 335 (1930); W. N. Ipatiew and G. A. Rasuwajew, *Ibid.* **63**, 1110 (1930);
W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.* **54**, 3398 (1932);
H. Gilman, A. L. Jacoby and H. Lundeman, *Ibid.* **60**, 2336 (1938);
B. Sarry and W. Hanke, *Z. anorg. allg. Chem.* **296**, 229 (1958);
H. E. Podall, H. E. Petree and J. R. Zietz, *J. Org. Chem.* **24**, 1222 (1959);
K. Clauss and H. Bestian, *Liebigs Ann.* **654**, 8 (1962);
W. E. Becker and E. C. Ashby, *J. Org. Chem.* **29**, 954 (1964).

[11] L. H. Slaugh, *Tetrahedron* **22**, 1741 (1968); *J. Org. Chem.* **32**, 108 (1967).