hydrogen gave conversions of 39–43%, with as much as 15 and 41% of the carbon monoxide charge reacting to give methane and dimethyl ether, respectively. When carbon dioxide was added to the carbon monoxide (mole ratio, CO: CO_2 = 3.1:1.0) the methanol conversion was raised to 64% and the formation of dimethyl ether reduced to about 1%.

Results obtained with aqueous formaldehyde solutions indicate that the formation of methanol from carbon dioxide and hydrogen under pressure may proceed along two paths. After reduction of the carbon dioxide to the formaldehyde stage, part of the methanol is formed by direct hydrogenation of the formaldehyde and part by the Cannizzaro reaction.

RIVERSIDE, ILL. RECEIVED[3] OCTOBER 13, 1945

[3] Original manuscript received May 19, 1943.

[CONTRIBUTION FROM THE LABORATORIES OF SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Direct Catalytic Conversion of Methylcyclopentane to Benzene

BY B. S. GREENSFELDER AND D. L. FULLER[1]

Methylcyclopentane can be converted to benzene by means of the two well-known reactions

$$MeCyC_5H_9 \longrightarrow CyC_6H_{12};\ \Delta F^\circ = -3600 + 10T \quad (1)$$

$$CyC_6H_{12} \longrightarrow C_6H_6 + 3H_2;\ \Delta F^\circ = 53{,}700 - 96.6T \quad (2)$$

The free energy values[1a] correspond to the gas phase equilibria. The first reaction is promoted by catalysts such as aluminum chloride plus hydrochloric acid,[2] and molybdenum sulfide,[3] and the second by catalysts[4] such as nickel, chromic oxide and the platinum metals.

From the free energies given and the simple gas laws, it is evident that the extent of reaction (1) is independent of the pressure and decreases slowly with increasing temperature, being about 10% at 350°. Reaction (2) is hindered by pressure but favored by higher temperatures, and above 475° can go nearly to completion even with high hydrogen dilution at 25 atmospheres.

Adding (1) and (2), gives

$$MeCyC_5H_9 \longrightarrow C_6H_6 + 3H_2;\ \Delta F^\circ = 50{,}100 - 86.6T \quad (3)$$

and it is evident that the thermodynamic relationships for this reaction are very much like those for the simple dehydrogenation of cyclohexane to benzene, given above as reaction (2). It is therefore of interest to study the behavior of methylcyclopentane in the presence of a catalyst capable of converting it to benzene in a single step according to reaction (3).

Experimental Results

All experiments were performed in a continuous flow reaction system. The apparatus comprised a stainless steel catalyst tube (32 in. long × $^5/_8$ in. i. d.) supported in a vertical electrical furnace with preheat and main heat windings, the axial catalyst temperature profile being ±3°. Automatic temperature and pressure controllers and recorders were used. The hydrocarbon was fed into the top by a Hills–McCanna proportioning pump and the confluent diluent gas was measured by rotameters. The reaction product was condensed with ice water at the reaction pressure and the total liquid product was sampled hourly for analysis.

A representative summary of the data obtained in the experiments with methylcyclopentane at 490° and MoO_2/Al_2O_3 catalyst (*ca.* 14% molybdenum on "Alorco" Grade A activated alumina) is given in Table I.

In order to determine the nature of the aromatics found by specific dispersion and acid absorption, several samples were distilled. An example is given in Fig. 1 corresponding to Run 111, hours 1–2, in which about 75% wt. aromatics was found by analysis. From the curve and $n^{20}{}_D$ values for various cuts, it will be seen that about 68% of the reported aromatics is benzene, the remainder boiling above 80° with $n^{20}{}_D$ 1.5664. In other runs, the bottoms had $n^{20}{}_D$ values varying from 1.51 to 1.59, and in some cases a larger fraction of the aromatics produced was benzene.

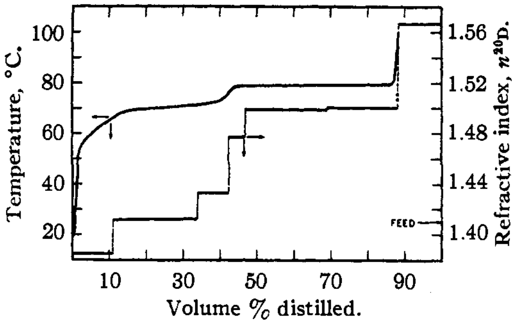

Fig. 1.—Distillation, run 111, hours 1–2.

When a suitable amount of this high boiling aromatic material was collected, it was analytically distilled under reduced pressure. The distillation curve was steep at first and then less so, but no significant plateaus were found. The distillation was stopped at 260° (corrected to 760 mm.) at which point about half the material had passed overhead. Apparently a large number of hydrocarbons was present; the high refractive index suggests that they were mainly polycyclic aromatics.

It is seen that high conversions of methylcyclopentane to benzene and other aromatics can be obtained over molybdena–alumina catalyst. The percentage conversion diminishes rapidly with the length of the process period and a beneficial effect of added hydrogen is observed.

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[1] Present address: General Aniline and Film Corporation, Easton, Penna.

[1a] A. W. Francis, "Science of Petroleum," Vol. III, Oxford University Press, London, 1938, p. 2094, and approximations based on Moore and Parks, THIS JOURNAL, **61**, 2561 (1939); Glasebrook and Lovell, *ibid.*, **61**, 1717 (1939); and Schmitt, *Compt. rend.*, **199**, 1299 (1934).

[2] Nenitzescu and Cantuniari, *Ber.*, **66B**, 1097 (1933).

[3] Puchkov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1677 (1938).

[4] E. C. Williams and M. de Simo, "Twelfth Report of the Committee on Catalysis," National Research Council, John Wiley and Sons, Inc., New York, 1940, Chap. IX.

Table I

Direct Aromatization of Methylcyclopentane with Molybdena-Alumina Catalyst at 490°

Run (series J)	Diluent	Molal ratio, diluent to methylcyclopentane	Contact time,[a] sec.	Pressure, atm.	Yield,[b] % vol.	Liquid product analysis		
						Elapsed time, hours	Aromatics,[c] % wt.	Olefins,[f] % wt.
78	H_2	5	100	20	79	1, 4, 6, 10	39 25 22 17	2
111	H_2	3	100	10	76	1-2, 3-6, 7-10	76 44 33[d]	4
79	H_2	3	100	10	73	1, 4, 6, 10	79 51 41 35	1
73	H_2	3	100	10	79	1-2, 5-6, 9-10	63 42 32	4
80	H_2	3	50	10	83	1, 5, 8, 10	48 34 23 28	3
110	H_2	3	30	10	80	1, 3, 5, 8	52 29 20 15[e]	5
81	H_2	10	50	10	68	1, 3, 7, 12	64 45 33 30	2
89	N_2	10	50	10	53	1-3, 4-7, 8-9	74 20 2	1
87	H_2	3	30	1	21	1-5, 6-12	85 9	10
88	N_2	3	30	1	0	1-4	No liq. product	..

[a] Based on vaporized liquid plus gaseous feed entering the reactor at the specified temperature and pressure, taken as ideal gases, and on the total catalyst volume. No corrections made for change in the total number of molecules during reaction. [b] Yield expressed as liquid product condensed at 0 to 5° at the operating pressure. Theoretical yield for 100% conversion of methylcyclopentane to benzene is 79% vol. Cracking is seen to be high in some cases. [c] Aromatics determined on liquid product by specific dispersion. See also refs. *d* and *e* and the distillations described in text. [d] Aromatics determined by sulfuric acid absorption for hours 1-2 and 7-10 are 75 and 32% wt., respectively. [e] Aromatics determined by sulfuric acid absorption for hours 1, 5 and 8 are 52, 22 and 18% wt., respectively. [f] Olefins determined by Rosenmund bromine absorption method are given as an approximate average for each run.

Discussion

The direct production of benzene from methylcyclopentane is an example of simultaneous alkylcyclopentane ring isomerization (expansion) and dehydrogenation to an aromatic. So far as we are aware, there is no previous mention in the literature of this reaction. Kazanskii and Plate[5] have converted alkylcyclopentanes to aromatics (over platinized charcoal at 300 to 350°) but by an entirely different mechanism. They found that methyl-, ethyl- and propylcyclopentane yield only paraffins[6] (with added hydrogen), while *n*-butyl- and higher cyclopentanes can give aromatics. Furthermore, under their conditions, *n*-hexane and higher paraffins can be dehydrocyclized to aromatics,[5,7] so their results on substituted cyclopentanes parallel typical paraffin dehydrocyclizations, which they too assert to be the case. Thus, the structures of the aromatics they found may be accounted for by a simple dehydrocyclization mechanism: namely, ring closure of the butyl or higher alkyl groups onto adjacent carbon atoms of the parent cyclopentane ring with simultaneous dehydrogenation of the new ring, followed by fission of the parent ring, thereby producing ortho-substituted aromatics.

Detailed consideration indicates that in view of the results on certain paraffins reported in ref. 7 any similar paraffins resulting from simple ring fission (with added hydrogen) of some of the lower alkylcyclopentanes studied in ref. 6 should be capable of cyclization to aromatics as a subsequent step in the same operation. In the case of *n*-butyl- and higher alkylcyclopentanes, we then have an alternative path for aromatic formation, namely, ring fission to paraffins followed by dehydrocyclization to aromatics. The results given in refs. 5 and 7 suggest that but minor quantities of aromatics usually arise in this fashion. With complex structures this alternative path may assume importance, as discussed in ref. 5.[7a]

The present work portrays the simultaneous (a) isomerization of the five-carbon-atom alicyclic ring to a ring of six carbon atoms, and (b) dehydrogenation of the six-carbon-atom alicyclic structure to an aromatic. References 2, 3 and 4 have shown reactions (a) and (b) to occur separately but we find no prior study of the simultaneous occurrence of the two steps.

Reference should be made to the work of Nenitzescu and Cioranescu[8] on the conversion of methylindane and methylhydrindane to naphthalene over platinized charcoal at 310 and 350°, under which conditions methylcyclopentane remained unchanged. Similar results on substituted indanes over palladinized charcoal or selenium, but at 450° minimum temperature in sealed tubes, were published by Ruzicka and Peyer.[9] Finally, it is of interest to mention that the direct conversion of cycloheptane and cycloöctane rings to aromatics with selenium as catalyst at 390 to 440° has been reported by Ruzicka and Seidel.[10]

In the present work it has been noted that side reactions occur, including formation of polycyclic aromatics, cracking, and production of olefins. The beneficial influence of hydrogen is probably connected with the suppression of these reactions, which tend to form tarry and carbonaceous deposits on the catalyst.

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(5) Kazanskii and Plate, *Ber.*, **69B**, 1862 (1936).

(6) Zelinskii, Kazanskii and Plate, *ibid.*, **68B**, 1869 (1935).

(7) Kazanskii and Plate, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 496 (1939).

(7a) This paragraph contains supplementary material received August 30, 1945.

(8) Nenitzescu and Cioranescu, *Ber.*, **69B**, 1040 (1936).

(9) Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935).

(10) Ruzicka and Seidel, *ibid.*, **19**, 424 (1936).

Summary

Methylcyclopentane has been converted directly to benzene (and other aromatics) by simultaneous isomerization and dehydrogenation over molybdena-alumina catalyst in the presence of hydrogen. The extent of reaction is dependent on both thermodynamic conditions and length of process period.

EMERYVILLE, CALIFORNIA RECEIVED[11] MARCH 30, 1942

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[11] This manuscript was originally received on March 30, 1942, and after examination by the Editorial Board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee, and at their request was withheld from publication, in a confidential file, until clearance was granted on August 30, 1945.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Hydrolysis of Diphenyldichlorosilane

BY CHARLES A. BURKHARD

The hydrolysis of diphenyldichlorosilane[1] to diphenylsilanediol has been reported by several authors.[2] Depending upon the conditions under which the hydrolysis is carried out it is possible to obtain crystalline, amorphous, or oily products. The hydrolysis of diphenyldichlorosilane to polyphenylsiloxane-α,ω-diols has also been reported.[3]

The purpose of the present paper is to give a report of a study of the hydrolysis of diphenyldichlorosilane in which the direct synthesis of α,ω-diols, $HO[Si(C_6H_5)_2O]_nH$, and α,ω-dichlorides, $Cl[Si(C_6H_5)_2O]_{n-1}Si(C_6H_5)_2Cl$, in which $n \geqslant 2$, was attempted. A similar investigation has been made with dimethyldichlorosilane by Patnode,[4] in which he was able to isolate polymethyl-α,ω-dichloropolysiloxanes, $Cl[Si(CH_3)_2O]_nSi(CH_3)_2Cl$, in which $n = 1$ to 5.

Experimental

Diphenylsilanediol.[2c]—To a heterogeneous mixture of 77 ml. of toluene, 161 ml. of *t*-amyl alcohol and 666 ml. of water is added dropwise with stirring 200 g. of diphenyldichlorosilane[5] dissolved in 77 ml. of toluene. The solution is maintained at 25° with a cooling coil. About one-half hour is required for addition of the chloride, after which the solution is stirred for another ten minutes. The solution is then filtered by suction and the crystals are washed with water until free of acid and air dried. These crystals are practically free of polymeric materials. Further purification may be effected by crystallization from warm methyl ethyl ketone and chloroform; yield 156 g., 93%, m. p. 148° dec.

Anal. Calcd. for $C_{12}H_{12}SiO_2$: C, 66.62; H, 5.59; Si, 12.96; OH/molecule, 2.00. Found: C, 66.2; H, 5.34; Si, 13.1; OH/molecule, 1.95.

Hexaphenylcyclotrisiloxane.[6]—Ten grams of diphenylsilanediol is dissolved in 150 ml. of ether and 5 ml. of concd. hydrochloric acid is added. After heating under reflux for three hours, the ether is removed and the crystals are collected. Flat plates are obtained from benzene and ethanol, or glacial acetic acid; m. p. 190°, b. p. 290-300° (1 mm.).

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: C, 72.68; H, 5.09, Si, 14.16; mol. wt., 595. Found: C, 73.4; H, 5.18; Si, 14.0; mol. wt. (benzene), 567, (ethylene dibromide), 540.

Octaphenylcyclotetrasiloxane,[6]—A drop or two of aqueous caustic is added to a boiling solution of diphenylsilanediol in 95% ethanol. On cooling, the tetramer precipitates. When recrystallized from benzene and ethanol, or glacial acetic acid, needles are obtained; m. p. 201-202°, b. p. 330-340° (1 mm.).

Anal. Calcd. for $C_{48}H_{40}Si_4O_4$: C, 72.68; H, 5.09; Si, 14.16; mol. wt., 793. Found: C, 73.2; H, 5.29; Si, 14.2; mol. wt. (benzene), 810, (ethylene dibromide), 802.

Partial Hydrolysis of Diphenyldichlorosilane

Part A. Ratio of 2:1 and 1.5:1,—Four moles (1012 g.) of diphenyldichlorosilane was dissolved in 1000 ml. of ether. To this was added dropwise with vigorous stirring two moles (36 g.) of water in 400 ml. of dioxane. After complete addition of the water-dioxane solution, hydrogen chloride was blown off with dry nitrogen. The ether and dioxane were removed by distillation and the residue distilled under vacuum using dry nitrogen as an inert atmosphere. The fractions obtained in the vacuum distillation are tabulated in Table I.

TABLE I

Cut	Press., mm.	T, °C.	Wt., g.	% Cl	Remarks
1	44-45	175-210	285	22.9	Fluid
2	1	120-190	18	19.4	Fluid
3	1	220-256	202	13.3	Fluid
4	1	256-290	70	8.2	Crystallized
5	1	280-305	63	6.3	Crystallized
6	1	300-340	66	6.8	Viscous liquid
Residue	...	.....	...	5.8	Glassy

Cuts 1 and 2 were impure diphenyldichlorosilane. Cut 3 was combined with cuts of the same boiling range from other hydrolyses and redistilled. The majority boiled at 238-241° (1 mm.). The tetraphenyl-1,3-dichlorodisiloxane which was thus isolated was purified by crystallization from hexane to give waxy hexagonal rods; m. p. 38°, b. p. 238-241° (1 mm.).

Anal. Calcd. for $C_{24}H_{20}Si_2OCl_2$: Cl, 15.72. Found: Cl, 15.3.

Hexaphenyl-1,5-dichlorotrisiloxane was isolated from cut 5 boiling at 290-303° (1 mm.). Considerable hexaphenylcyclotrisiloxane was also found in this boiling range but, by extracting with *n*-heptane, separation of the dichloride from the cyclic polymer was effected. Attempts

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[1] A discussion of the nomenclature used in this paper is given by Sauer (*J. Chem. Ed.*, **21**, 303 (1944)).

[2] (a) Dilthey and Eduardoff, *Ber.*, **37**, 1139 (1904); (b) Martin, *ibid.*, **45**, 403 (1912); (c) Kipping, *J. Chem. Soc.*, **101**, 2108 (1912); (d) Kipping and Robinson, *ibid.*, **105**, 487 (1914); (e) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).

[3] (a) Kipping, *J. Chem. Soc.*, **101**, 2125 (1912); (b) Kipping and Robinson, *ibid.*, **105**, 484 (1914).

[4] Patnode, THIS JOURNAL, unpublished.

[5] The diphenyldichlorosilane (27.68% Cl) was furnished by Dr. Gilliam [THIS JOURNAL, **67**, 1772 (1945)].

[6] The identities of the cyclic diphenylsilanediol condensation products, which have beeen described by Kipping,[2a] have been questioned in a recent publication.[2e] A discussion of this point is given in a later paper [Burkhard, Decker and Harker, THIS JOURNAL, **67**, 2174 (1945)].