[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

# Catalysis by Metal Halides. IV. Relative Efficiencies of Friedel–Crafts Catalysts in Cyclohexane–Methylcyclopentane Isomerization, Alkylation of Benzene and Polymerization of Styrene

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Friedel–Crafts catalysts have been separated into three categories. In the presence of a co-catalyst only the most acidic of the metal halides will bring about the isomerization of methylcyclopentane to cyclohexane, *e.g.*, gallium chloride–isopropyl chloride. Less reactive systems which will not isomerize methylcyclopentane at 80° can still catalyze alkylation of benzene at 25°, *e.g.*, ferric chloride–isopropyl chloride. Still less active systems which can neither catalyze the isomerization of methylcyclopentane or the alkylation of benzene can catalyze the polymerization of styrene, *e.g.*, boron fluoride–isopropyl chloride.

## Introduction

In connection with the aluminum halide-catalyzed disproportionation of trimethylsilanes,[2] a measure of the relative effectiveness of Lewis acids in catalyzing organic reactions was needed. Comparable data from which the relative effectiveness of Friedel–Crafts catalysts can be judged are widely scattered. One of the earliest comprehensive studies concerned the racemization of optically active $\alpha$-phenethyl chloride.[3] Although the results were complicated by concentration and solvent effects the following activity sequence was indicated in the presence of benzene: $SbCl_5 > SnCl_4 > BF_3 > HgCl_2 > TiCl_4$. Calloway summarized the available data in 1935 in regard to the acylation of benzene and concluded that the relative effectiveness of metal halides was $Al_2Cl_6 > Fe_2Cl_6 > ZnCl_2 > SnCl_4 > TiCl_4, ZrCl_4$.[4]

A more extensive reactivity series of catalytic ability in the acylation of benzene was later presented by Dermer, *et al.*, $Al_2Cl_6 > SbCl_5 > Fe_2Cl_6$ $TeCl_4 > SnCl_4 > TiCl_4 > TeCl_4 > BiCl_3 > ZnCl_2$.[5] Grosse and Ipatieff have considered the catalytic ability of various metal halides in the reaction between benzene and ethylene in the presence of hydrogen chloride.[6] They found catalytic ability to decrease in the order: $Al_2Cl_6 > TaCl_5, ZrCl_4 > CbCl_4 > BeCl_2 > TiCl_4$. Burk, in a compilation of data, suggests the following series of reactivities: $Al_2Br_6 > Al_2Cl_6 > Fe_2Cl_6 > ZrCl_4 > BF_3 > TiCl_3 > TiCl_4 > SbCl_5$.[7]

In the present work aluminum bromide, gallium chloride, gallium bromide, boron trifluoride, boron trichloride, ferric chloride, stannic chloride, antimony trichloride, antimony pentachloride and zirconium tetrachloride have been tested as catalysts in the three reactions

$$RX + C_6H_6 \longrightarrow RC_6H_5 + HX$$

$$C_6H_5CH{=}CH_2 \longrightarrow (C_6H_5CHCH_2)_n\text{-}$$

The results indicate a catalytic sequence of $Al_2Br_6 > Ga_2Br_6, Ga_2Cl_6 > Fe_2Cl_6, SbCl_5 > ZrCl_4, BF_3, BCl_3, SnCl_4, SbCl_3$.

## Results

**Methylcyclopentane–Cyclohexane Isomerization.**—Methylcyclopentane was treated with a variety of Friedel–Crafts catalysts in the presence and absence of promoters or co-catalysts such as alkyl chlorides or water. After the desired reaction period the products were analyzed by gas–liquid chromatography (g.l.c.). The results of these experiments are summarized in Table I.

TABLE I

ISOMERIZATION OF METHYLCYCLOPENTANE

| | | Reaction Conditions | | Cyclohexane/ Methyl-cyclopentane |
|---|---|---|---|---|
| Catalyst[a] | Promoter[b] | °C. | Hr. | |
| $Ga_2Cl_6$ | None | 25 | 18 | 0.001 |
| $Al_2Br_6$ | None | 25 | 18 | .001 |
| $BF_3$ | None | 80 | 18 | .001 |
| $Fe_2Cl_6$[c] | None | 80[c] | 18 | .001 |
| $Ga_2Cl_6$ | $CH_3Cl$ | 25 | 18 | .0085 |
| $Ga_2Cl_6$ | $i$-$C_3H_7Cl$ | 25 | 18 | .330 |
| $Ga_2Cl_6$ | $H_2O$ | 25 | 18 | .039 |
| $Ga_2Cl_6$ | $O_2$ | 25 | 18 | .004 |
| $Al_2Br_6$ | $CH_3Br$ | 25 | 18 | .004 |
| $Al_2Br_6$ | $i$-$C_3H_7Br$ | 25 | 18 | .640 |
| $Al_2Br_6$ | $H_2O$ | 25 | 18 | .395 |
| $Al_2Br_6$ | $O_2$ | 25 | 18 | $<$ .001 |
| $Al_2Br_6$ | $(CH_3)_3SiBr$ | 25 | 18 | $<$ .001 |
| $Al_2Br_6$ | $CH_3COBr$ | 25 | 18 | 2.60 |
| $Ga_2Br_6$ | $i$-$C_3H_7Br$ | 25 | 18 | 0.187 |
| Catalysis by moist aluminum bromide[d] | | | | |
| | | 25 | 48 | 8.77 |
| | | 25 | 144 | 8.77 |
| | | 50 | 24 | 4.60 |
| | | 50 | 48 | 4.76 |
| | | 50 | 72 | 4.78 |
| | | 80 | 6 | 1.91 |
| | | 80 | 12 | 2.60 |
| | | 80 | 18 | 2.60 |

[a] 5.0 ml. of methylcyclopentane at 25° used in each experiment; 1.87 moles of catalyst as $MX_3$. [b] 0.29 mole. [c] Heterogeneous. [d] Approximately 0.50 g. of anhydrous aluminum bromide handled without special precautions.

In addition to the experiments listed in Table I the following catalyst systems were found to produce less than 1 part in 1000 of rearrangement of methylcyclopentane in 18 hours at 80°: antimony(V) chloride–isopropyl chloride; antimony(III) chloride–isopropyl chloride; ferric chloride–

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[1] Iowa State University, Ames, Iowa.

[2] G. A. Russell, THIS JOURNAL, **81**, 4815, 4825, 4831 (1959).

[3] K. Bodendorf and H. Bohme, *Ann.*, **516**, 1 (1935); H. Bohme and O. Siering, *Ber.*, **71**, 2372 (1938).

[4] N. D. Calloway, *Chem. Revs.*, **17**, 327 (1935).

[5] O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, THIS JOURNAL, **63**, 2881 (1941).

[6] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **1**, 559 (1936).

[7] R. E. Burk, "12th Report of the Committee on Catalysis, National Research Council," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 251.

isopropyl chloride; boron chloride–isopropyl chloride; boron chloride–water; boron fluoride–isopropyl chloride, boron fluoride–water; boron fluoride–isopropyl alcohol; stannic chloride–isopropyl chloride, zirconium tetrachloride–isopropyl chloride.

The aluminum bromide-catalyzed isomerization of methylcyclopentane has been considered previously by Pines, Abraham, Aristoff and Ipatieff.[8] The results given in Table I are in complete agreement with the conclusions reached by this group. The results summarized in Table I indicate that aluminum bromide, gallium bromide and gallium chloride are superior catalysts for the isomerization of methylcyclopentane. Even for aluminum and gallium halides a co-catalyst is necessary. sec.-Alkyl halides are satisfactory promoters, whereas methyl halides are ineffective. Water is a much more effective co-catalyst for aluminum bromide than for gallium chloride. In the absence of illumination oxygen has no effect as a promoter for either gallium chloride or aluminum bromide catalysis.

Some qualitative statements can be made about the fate of the co-catalyst in the experiments summarized in Table I. Methyl halides in the presence of gallium chloride or aluminum bromide were only partially consumed whereas isopropyl halides in the presence of these catalysts as well as gallium bromide were consumed completely with the concurrent formation of a $C_3$-hydrocarbon. Isopropyl halides were not consumed and little $C_3$-hydrocarbon was found at 80° in the presence of stannic chloride, boron trichloride, boron trifluoride, zirconium tetrachloride, ferric chloride or antimony trichloride. Antimony pentachloride resulted in the partial decomposition of isopropyl chloride at 80° with the formation of some $C_3$-hydrocarbon. Isopropyl alcohol in the presence of boron trifluoride at 80° yielded substantial amounts of a $C_3$-hydrocarbon, presumably propylene from dehydration.

From the data of Table I, it is possible to obtain $\Delta F$ and $\Delta H$ for the isomerization of methylcyclopentane to cyclohexane. Values calculated for $\Delta F$ are $-1.29$ kcal. mole$^{-1}$ at 25°, $-1.01$ at 50° and $-0.67$ at 80°. Over the temperature range 25–80° $\Delta H$ is $-4.70$ kcal. mole.$^{-1}$. These values can be compared with data obtained from heats of combustion and heat capacities. Thus, the difference in free energy between methylcyclopentane and cyclohexane obtained in this manner is $\Delta F° = -1.16$ at 25° in the liquid phase while $\Delta H°$ for the liquid phase isomerization of methylcyclopentane to cyclohexane at 25° is $-4.27$ kcal. mole$^{-1}$.[9] Stevenson and Morgan, using a different analytical technique, have reported equilibrium constants for the isomerization of methylcyclopentane to cyclohexane of 7.59 at 27°, 4.12 at 59° and 1.99 at 100° indicating $\Delta H$ to be $-4.1$.[10] The present data, the data of Stevenson and Morgan, and earlier data,[11] yield the following equation over the temperature range 25–140°.

$$\ln K = -4.93 + \frac{2.098}{RT}$$

$$(\Delta H = -4.20,\ \Delta F_{298.1} = 1.25 \text{ kcal. mole}^{-1})$$

**Alkylation of Benzene.**—A series of experiments were performed wherein benzene, alkyl chloride and metal halide were allowed to react in the presence of methylcyclopentane. The degree of reaction between the alkyl chloride and benzene was followed qualitatively by g.l.c. by observation of the decrease in alkyl halide concentration and detection of the alkylation product. Results are summarized in Table II.

TABLE II

ALKYLATION OF BENZENE IN PRESENCE OF METHYLCYCLOPENTANE[a]

| Catalyst[b] | Alkylating[c] agent | $\frac{C_6H_{12}}{C_5H_9CH_3}$ | Alkylation products |
|---|---|---|---|
| $Al_2Br_6$ | $CH_3Br$ | 0.002 | Toluene, $CH_3Br$ all consumed |
| $Al_2Br_6$ | $i$-$C_3H_7Br$ | .230 | Cumene, $i$-$C_3H_7Br$ all consumed |
| $Ga_2Cl_6$ | $CH_3Cl$ | .007 | Toluene, $CH_3Cl$ all consumed |
| $Ga_2Cl_6$ | $i$-$C_3H_7Cl$ | .117 | Cumene, $i$-$C_3H_7Cl$ all consumed |
| $Fe_2Cl_6$[d] | $i$-$C_3H_7Cl$ | $<$ .0001 | Cumene, $i$-$C_3H_7Cl$ all consumed |
| $BF_3$ | $i$-$C_3H_7OH$ | $<$ .0001 | Cumene, $i$-$C_3H_7OH$ all consumed |
| $BF_3$ | $i$-$C_3H_7Cl$ | $<$ .0001 | $i$-$C_3H_7Cl$ not consumed, cumene not detected |
| $SnCl_4$ | $i$-$C_3H_7Cl$ | $<$ .0001 | $i$-$C_3H_7Cl$ not consumed, cumene not detected |
| $SbCl_3$[d] | $i$-$C_3H_7Cl$ | $<$ .0001 | $i$-$C_3H_7Cl$ not consumed, cumene not detected |
| $SbCl_5$[d] | $i$-$C_3H_7Cl$ | $<$ .0001 | Cumene, $i$-$C_3H_7Cl$ nearly all consumed |
| $ZrCl_4$[d] | $i$-$C_6H_7Cl$ | $<$ .0001 | $i$-$C_3H_7Cl$ not consumed, cumene not detected |

[a] Reaction mixture contained 4.0 ml. of methylcyclopentane and 1.0 ml. of benzene at 25°; reaction conditions were 18 hours at 25.0°. [b] 1.87 mmoles as $MX_3$, $MX_4$ or $MX_5$. [c] 0.29 mmole. [d] Heterogeneous.

The results summarized in Table II demonstrate that the presence of an aromatic hydrocarbon retards the isomerization of methylcyclopentane. This is in agreement with the results of Pines, *et al.*,[8] and undoubtedly arises from the fact that benzene removes carbonium ions or incipient carbonium ions from the reaction mixture.

$$R^+MX_4^- + C_6H_6 \longrightarrow RC_6H_5 + HX + MX_3$$

All of the catalyst systems which bring about a rapid isomerization of methylcyclopentane also alkylate benzene. Moreover, the systems gallium chloride–methyl chloride, alumiunm bromide–methyl bromide, ferric chloride–isopropyl chloride, boron fluoride–2-propanol and antimony pentachloride–isopropyl chloride, which are ineffective catalysts for the isomerization of methylcyclopentane, will alkylate benzene. Catalyst systems which are inefficient in the alkylation of benzene are boron fluoride–isopropyl chloride, stannic chloride–isopropyl chloride, antimony trichloride–isopropyl chloride and zirconium chloride–isopropyl chloride. The inability of boron fluoride to cata-

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[8] H. Pines, B. M. Abraham and V. N. Ipatieff, THIS JOURNAL, **70**, 1742 (1948); H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949); **72**, 4055, 4304 (1950); **75**, 4775 (1953).

[9] F. D. Rossini, *et al.*, "Selected Properties and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 471–472.

[10] D. P. Stevenson and J. H. Morgan, THIS JOURNAL, **70**, 2773 (1948).

[11] (a) A. L. Glasebrook and W. G. Lovell, *ibid.*, **61**, 1717 (1939); (b) G. C. S. Schuit, H. Hoog and J. Verheus, *Rec. trav. chim.*, **59**, 793 (1940); (c) S. Mizushima, Y. Morino and R. Huzisiro, *J. Chem. Soc., Japan*, **62**, 587 (1941).

lyze the alkylation of benzene by an alkyl chloride is well known.[12]

**Polymerization of Styrene.**—A series of experiments was performed wherein styrene, metal halide and alkyl chloride were allowed to react in the presence of methylcyclopentane. The products were analyzed for cyclohexane by g.l.c. and for polystyrene by precipitation in methanol. The results are summarized in Table III.

TABLE III

POLYMERIZATION OF STYRENE IN PRESENCE OF METHYLCYCLOPENTANE[a]

| Catalyst[b] | Alkyl halide[c] | $\frac{C_6H_{12}}{C_5H_9CH_3}$ | Polymerization products |
|---|---|---|---|
| $Al_2Br_6$ | $CH_3Br$ | 0.0027 | $CH_3Br$ all consumed, 0.35 g. polystyrene |
| $Al_2Br_6$ | $i$-$C_3H_7Br$ | .0077 | $i$-$C_3H_7Br$ all consumed, 0.8 g. polystyrene |
| $Ga_2Cl_6$ | $CH_3Cl$ | .0050 | $CH_3Cl$ all consumed, 0.6 g. polystyrene |
| $BF_3$ | $i$-$C_3H_7Cl$ | < .0001 | $i$-$C_3H_7Cl$ not completely consumed, 0.8 g. polystyrene |
| $Fe_2Cl_6$[d] | $i$-$C_3H_7Cl$ | < .0001 | $i$-$C_3H_7Cl$ all consumed, 1.0 g. polystyrene |
| $SnCl_4$ | $i$-$C_3H_7Cl$ | < .0001 | $i$-$C_3H_7Cl$ not completely consumed, 0.60 g. polystyrene |
| $SbCl_3$ | $i$-$C_3H_7Cl$ | < .0001 | $C_3H_7Cl$ not completely consumed, 0.20 g. polystyrene |

[a] Reaction mixtures contained 4.0 ml. of methylcyclopentane and 1.0 ml. of styrene at 25°; reaction conditions were 18 hr. at 25°. [b] 1.87 mmoles as $MX_3$ or $MX_4$. [c] 0.29 mmole. [d] Heterogeneous.

All catalysts which alkylated benzene also polymerized styrene. In addition, the systems boron fluoride–isopropyl chloride, stannic chloride–isopropyl chloride and antimony trichloride–isopropyl chloride also brought about the polymerization of styrene. Styrene inhibited the isomerization of methylcyclopentane, presumably by acting as a trap for carbonium ions. In the cases of catalysts which could not alkylate benzene (boron fluoride, stannic chloride and antimony trichloride) the co-catalyst (isopropyl chloride) was only partially consumed. For catalysts capable of alkylating benzene the co-catalyst (either methyl or isopropyl halide) was completely consumed.

## Discussion

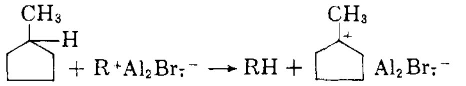
The results summarized in Tables I–III indicate this sequence of catalytic ability for Friedel–Crafts catalysts, $Al_2Br_6 > Ga_2Br_6, Ga_2Cl_6 > Fe_2Cl_6, SbCl_5 > ZrCl_4, SnCl_4, BCl_3, BF_3, SbCl_3$. Aluminum bromide is a more effective isomerization catalyst than gallium bromide when isopropyl bromide is used as a co-catalyst while in the presence of water aluminum bromide is a more effective catalyst than gallium chloride. These results are consistent with the observation that the reaction of methyl bromide with toluene at 0° is more selective when catalyzed by gallium bromide[13a] than when catalyzed by aluminum bromide.[13b] Moreover, the rate of the alkylation reaction is much faster when catalyzed by aluminum bromide than when catalyzed by gallium bromide.[13c] In the disproportionation of ethyltrimethylsilane and other substituted silanes the catalyst sequence observed was $Al_2Br_6 > Al_2Cl_6 > Al_2I_6 > Ga_2Br_6 > BCl_3, Ga_2Cl_6, ZrCl_4, SnCl_4, SbCl_3$.[2] The agreement between these catalyst series suggests that they are both a measure of the acidity of the metal halide. Although an acidity series is not necessarily independent of the reference base, it is suggested that the most general series of Lewis acidity is $Al_2Br_6 > Al_2Cl_6 > Al_2I_6 > Ga_2Br_6 > Ga_2Cl_6 > Fe_2Cl_6 > SbCl_5 > ZrCl_4, SnCl_4 > BCl_3, BF_3, SbCl_3$.

Catalysts or catalyst systems can be grouped into three classes. The more active will readily isomerize methylcyclopentane to cyclohexane at 25°, alkylate benzene at 25° and polymerize styrene at 25°. Typical examples of these systems are aluminum bromide–isopropyl bromide, gallium chloride–isopropyl chloride and aluminum bromide–water.[14]

Less reactive catalysts which are extremely inefficient in the isomerization of methylcyclopentane at 25° nevertheless readily alkylate benzene and polymerize styrene. In this group are gallium chloride–methyl chloride, aluminum bromide–methyl bromide, boron fluoride–isopropyl alcohol, ferric chloride–isopropyl chloride and antimony pentachloride–isopropyl chloride.

Finally, a third group of catalysts can be recognized which are ineffective in the isomerization of methylcyclopentane at 80° or in the alkylation of benzene at 25° but which will still polymerize styrene. This group contains the catalyst systems stannic chloride–isopropyl chloride, boron fluoride–isopropyl chloride and antimony trichloride–isopropyl chloride.

These results are in agreement with the conclusion of Professor H. C. Brown that the catalytic ability of metal halides does not necessarily invoke complete ionization of a carbon–halogen bond.[13,15] Instead, the complex between a metal halide and alkyl halide can react with a nucleophile without the intervention of actually free carbonium ions. This consequently results in a considerable gradation of catalytic ability. Thus, to bring about the isomerization of methylcyclopentane we conclude that a relatively free carbonium ion is necessary.



On the other hand, catalyst systems which are ineffective in the isomerization of methylcyclopentane still can alkylate benzene readily. Here a free carbonium ion is not a requirement and alkylation need involve only an incipient carbonium ion, for example, as in complex I.[13,15] In the case of the polymerization of styrene catalytic ability requires still less polarization of the carbon–halogen bond than in the alkylation of benzene. Thus, the polymerization of styrene can be catalyzed by various

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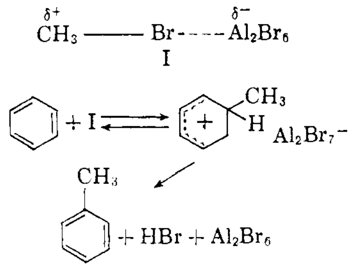
(12) (a) A. Wohl and E. Wertyporoch, *Ber.*, **64**, 1357 (1931); (b) R. L. Burwell and S. Arc er, THIS JOURNAL, **6'**, 032 (1942); (c) G. F. Hennion and R. A. Kurz, *ibid.*, **65**, 1001 (1943).

(13) (a) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956); (b) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955); (c) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6245, 6249 (1956); S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

(14) Although the last system cannot alkylate an aromatic ring it does readily exchange deuterium atoms for aromatic hydrogen atoms [J. Kenner, M. Polanyi and P. Szego, *Nature*, **135**, 267 (1935)].

(15) H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).



systems which are ineffective in the alkylation of benzene. We conclude that styrene is a better nucleophile than benzene, presumably because of the stability of II.

$$C_6H_5CH{=}CH_2 + (CH_3)_2\overset{\delta+}{C}H{-}Cl{-}{-}{-}\overset{\delta-}{B}F_3 \longrightarrow$$

$$C_6H_5\overset{+}{C}HCH_2CH(CH_3)_2\ BF_3Cl^- \quad \text{II}$$

$$\text{II} + C_6H_5CH{=}CH_2 \longrightarrow \longrightarrow (C_6H_5CH{-}CH_2)_n{-}$$

The catalytic ability of these systems is of course determined by both the acidity of the metal halide and the ease of ionization of the alkyl chloride. Thus, gallium chloride–isopropyl chloride readily isomerizes methylcyclopentane whereas gallium chloride–methyl chloride is an ineffective catalyst. Here the difference in catalytic ability results from different stabilities of the incipient cations [$(CH_3)_2CH^+$ more stable than $CH_3^+$]. Differences in catalytic ability can also result from different stabilities of the incipient anions. For example, the system boron fluoride–isopropyl alcohol readily alkylates benzene whereas boron fluoride–isopropyl chloride does not. This difference between the alkylation ability of alcohols and chlorides is well known and has been explained as being due to the greater stability of $BF_3OH^-$ relative to $BF_3Cl^-$.[12c] Interestingly, sec.-alkyl fluorides, or even prim.-alkyl fluorides, readily alkylate benzene in the presence of boron fluoride.[12b,16] Here the added resistance to ionization of a carbon–fluorine bond is offset by the stability of $BF_4^-$ relative to $BF_3Cl^-$.[12b,16]

## Experimental

**Preparation of Reaction Mixtures.**—Samples were prepared in a Stock-type high vacuum apparatus.[17] The vacuum line contained no greased stopcocks or picein seals and was thoroughly flamed before the preparation of each reaction mixture. Methylcyclopentane (Phillips research grade, 99.9% pure) was stored first over calcium hydride and then over a sodium mirror. The benzene used was a C.P. grade stored over a sodium mirror in the vacuum line. Freshly distilled styrene was introduced into the vacuum line when needed.

Aluminum bromide and gallium chloride were prepared by the reaction of an excess of the anhydrous hydrogen halide with the desired weight of aluminum or gallium. The metallic halides were prepared in bulbs with break-off tips which were sealed to the vacuum line, opened, and the metallic halide sublimed into an ampoule which was an integral part of the reaction vessel for the preparation of the metallic halide. The co-catalyst, methylcyclopentane, benzene and/or styrene were transferred into the ampoule, the ampoule sealed and placed in a thermostated water-bath for the desired reaction period. Distilled antimony pentachloride and stannic chloride were vacuum transferred into the vacuum line as were the boron halides. Sublimed ferric chloride was vacuum resublimed, directly into an ampoule attached to the vacuum line. Zirconium tetrachloride and antimony trichloride were added to ampoules in a nitrogen dry-box. The ampoules were attached to a vacuum line by a greased joint and the volatile reactants introduced. Heterogeneous samples were shaken in a thermostated bath at 25°. At 80° the heterogeneous samples were not shaken.

**Analysis of Reaction Products.**—The methylcyclopentane–cyclohexane ratio in the reaction products was determined by g.l.c. The reaction ampoules were opened at liquid nitrogen temperatures and connected to a simple apparatus whereby the contents of the ampoule could be distilled under vacuum. At the end of the distillation the reaction ampoule was warmed to 50° for a few minutes at 0.3 mm. pressure. The reaction products were collected at liquid nitrogen temperature in a trap containing 2 ml. of frozen 10% aqueous sodium hydroxide. Air then was allowed to enter the trap, the trap removed from the vacuum apparatus and warmed to room temperature. The stoppered tube was shaken to ensure destruction of any hydrogen halide or metallic halide that might have been transferred or entrained in the distillation. Samples of 10 μl. were analyzed by g.l.c. for methylcyclopentane and cyclohexane. No other hydrocarbons were found in significant amounts. When an alkyl halide was used as a co-catalyst its concentration in the products was noted qualitatively by g.l.c. Samples which could possibly have contained methyl halides were never allowed to warm above 5°. Calibration of the analytical technique with prepared samples of methylcyclopentane and cyclohexane in an A-column[18] of a Perkin-Elmer model 154B Vapor Fractometer using helium as a carrier gas indicated

$$\frac{\text{mole cyclohexane}}{\text{mole methylcyclopentane}} = 1.05\,\frac{\text{area cyclohexane peak}}{\text{area methylcyclopentane peak}}$$

Experiments in which the methylcyclopentane–cyclohexane isomerization had gone to completion left an oily residue after the vacuum distillation. The other experiments in Table I involving aluminum and gallium halides left a solid, colorless catalyst. From these experiments involving slightly moist aluminum bromide at 25° a total of 0.73 g. of catalyst-free oil was obtained by treatment of the residues with pentane and water. This represented 7% by weight of the methylcyclopentane used. Distillation gave 0.33 g. of material boiling at 83–90° at 9.2 mm. This material most likely is a mixture of compounds containing twelve carbon atoms derived from the addition of a carbonium ion containing six carbon atoms to a molecule of a cyclohexene or methylcyclopentene.[19]

TABLE IV

DISPROPORTIONATION OF SUBSTITUTED SILANES IN CYCLOHEXANE SOLUTION[a]

| Silane | Silane concn., *M* | Temp., °C. | Time, hr. | Silane, % disproportionated | Cyclohexane isomerized, % |
|---|---|---|---|---|---|
| $(CH_3)_3SiC_2H_5$ | 0.23 | 80 | 89 | 7.1 | <0.01 |
| $(CH_3)_3SiBr$ | 0.73 | 80 | 20 | 2.0 | .05 |
| $(CH_3)_3SiH$ | 1.06 | 40 | 10 | 4.6 | < .01 |
| $(CH_3)_3SiC_6H_5$ | 1.04 | 40 | 1 | 0.07 | < .01 |

[a] 0.15 *M* aluminum bromide.

For experiments involving the alkylation of benzene the vacuum transfer of the reaction product was continued for about 15 minutes at 50°. The reaction products were analyzed for alkyl halide, cyclohexane and methylcyclopentane by g.l.c. at 25°. Toluene or cumene were detected by g.l.c. at higher temperatures, 80–100°.

For experiments involving the polymerization of styrene the vacuum distillation of reaction products was completed at a temperature not above 25°. Catalyzed depolymerization of the polystyrene, even under these conditions, may

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(16) G. Oláh, S. Kuhn and S. Olah, *J. Chem. Soc.*, 2174 (1957).

(17) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(18) Perkin-Elmer Corp., Norwalk, Conn.

(19) Bicyclohexyl and dimethylbicyclopentyl previously have been identified in the aluminum halide-catalyzed isomerization of cyclohexane [V. N. Ipatieff and V. I. Komarewsky, THIS JOURNAL, **56**, 1926 (1934)].

account for the low yields of polystyrene found in several of the experiments (Table III). The residual polystyrene and residual catalyst were dissolved in benzene and precipitated by methanol. This process was repeated twice more and the polystyrene finally obtained as a brittle porous mass by the vacuum sublimation of benzene from a frozen benzene solution of the polymer.

**Silanes as Co-catalysts.**—In the preceding papers the rate of disproportionation of ethyltrimethylsilane, bromotrimethylsilane, trimethylsilane and phenyltrimethylsilane in cyclohexane solution and in the presence of aluminum bromide were reported.[2] The solvent also was examined by g.l.c. for isomerization during these disproportions. In no case was any appreciable isomerization of the cyclohexane to methylcyclopentane observed (see Table IV).

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

# Mechanism of Isocyanate Reactions with Ethanol[1]

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The rates of reaction with ethanol of a group of phenyl-substituted isocyanates (phenyl isocyanate, *m*-tolylene diisocyanate and *p,p'*-diisocyanatodiphenylmethane) and a group of benzyl-substituted isocyanates (benzyl isocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate and 5-*t*-butyl-1,3-xylylene diisocyanate) were measured and compared. The energies of activation were calculated using the Arrhenius equation. The benzyl type reacts more slowly than the phenyl type, but their rates converge at higher temperatures because the former have significantly higher energies of activation. The reaction mechanism, which is the same for both classes, is first order in isocyanate and in alcohol concentration. The observation that electron-withdrawing substituents accelerate the rate of reaction is discussed with respect to the fine mechanism of the reaction.

In recent years, a new type of polyester rubber[2] has been developed which requires the use of diisocyanates. In this synthesis, the reaction of hydroxyl groups with isocyanate groups is quite important. We chose this reaction for study in order to compare several new diisocyanates with previously available diisocyanates.

There are several publications in the literature on the rate of reaction of phenyl isocyanates with alcohols.[3–9] There are also papers on the rate of reaction of substituted-phenyl isocyanates with alcohol[10,11] in the presence of amine catalysts. However, there have been no papers published comparing the reactivity of phenyl and benzyl isocyanates.

## Experimental

**Synthesis.**—The isocyanates which could not be obtained commercially were synthesized by the method of Siefken[12]

$$RNH_2 \cdot HCl + COCl_2 \longrightarrow RNCO + 3HCl$$

The apparatus consisted of a 500-ml. baffled cylindrical flask provided with vigorous stirring, a gas inlet tube, a thermocouple well, and an air condenser which was attached to a gas scrubber containing 25% alkali to remove hydrogen chloride and phosgene from the off-gases. The flask was wrapped with a tape heating element. Facilities for switching from phosgene to nitrogen were provided at the inlet tube so that the system could be freed of phosgene before it was opened.

The solid amine hydrochloride was stirred and heated in *o*-dichlorobenzene, under nitrogen, until the solvent reached its boiling point. Phosgene then was passed in until all the hydrochloride reacted as noted by the change from an inhomogeneous to a homogeneous solution. The reaction mixture was freed of solvent at 115° (100 mm.) and the residue was distilled through a two-plate column. The reaction data and yields are given in Table I.

**Rate Studies.**—The reactions were run in a stoppered, 100-ml. graduated cylinder under a nitrogen atmosphere, using freshly distilled isocyanates, absolute ethanol and reagent grade toluene. An example follows (typical data are plotted in Fig. 1).

Eighty-five milliliters (72.4 g.) of toluene was measured into the graduated cylinder. The cylinder was stoppered and placed in the thermostat at 30.00° (±0.05°) or 40.00° and allowed to come to temperature equilibrium for one-half hour. Similarly, 15 ml. (12.2 g.) of absolute ethanol was measured into a tared, stoppered, 25-ml. graduate and allowed to come to temperature equilibrium. Sufficient isocyanate was added to the toluene to yield approximately 0.1 *N* isocyanate in the final solution. The ethanol was poured into the toluene solution at zero time. The exact weight of ethanol added was determined by the difference in the initial and final weights of the 25-ml. graduate. Two-milliliter samples, which were withdrawn while maintaining a stream of nitrogen over the open cylinder, were taken at intervals varying from 30 seconds to 30 minutes. The samples were drained into 10-ml. aliquots of approximately 0.04 *N* dibutylamine in toluene. The isocyanate sample was permitted to stand with the dibutylamine for five minutes, then 150 ml. of methanol and 1 ml. of brom phenol blue indicator solution were added. The excess dibutylamine was titrated with 0.01 *N* hydrochloric acid. This titer was subtracted from the titer of a 10-ml. aliquot of dibutylamine solution, the difference being the isocyanate normality. The analytical procedure was checked with known amounts of each isocyanate used and was shown to be reproducible within the overall experimental error. It also was demonstrated that the dibutylamine reacted with the isocyanate quantitatively in less than one minute. Thus, the amine solution was an effective shortstop.

## Discussion and Results

The study by Baker and Gaunt[4] indicates that the probable mechanism of reaction of phenyl isocyanate and alcohols follows the path

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