similar to those with indoöxine,[4] with the expected exception that aluminum was not precipitated.

### Experimental

**Preparation of Compounds.**—5,8-Quinolinequinone-5-(8-hydroxy-5-quinolylimide) was prepared from 5.0 g. of 8-quinolinol, 2.5 g. of hydroxylamine hydrochloride and 150 ml. of 2 *M* sodium carbonate in 150 ml. of methanol by passing air through the solution for six hours. The precipitated sodium salt was filtered, converted to the free base by suspension in acetic acid and finally recrystallized from ethanol, yield 2 g. (38%). Calcd. for $C_{18}H_{11}N_3O_2$: N, 13.95. Found: N, 14.08.

5,8-Quinaldinequinone-5-(8-hydroxyquinaldylimide) was obtained in 29% yield from 8-hydroxyquinaldine by the above procedure, m.p. 222°. Calcd. for $C_{20}H_{15}N_3O_2$: N, 12.77. Found: N, 12.73.

The corresponding indophenol from 3-methyl-8-quinolinol was obtained similarly in 39% yield, m.p. 235°. Calcd. for $C_{20}H_{15}N_3O_2$: N, 12.77. Found: N, 12.84.

Indophenols were also obtained from 2-phenyl-8-quinolinol and 2-styryl-8-quinolinol but were not purified because of their extreme insolubility in the common solvents. No reaction was obtained from 4-methyl-8-quinolinol or 8-quinolinol-5-sulfonic acid.

**Spectrophotometric Measurements.**—All spectra were determined with a Beckman DU spectrophotometer using 1.00-cm. cells at room temperature (25 ± 3°). Absorption spectra in 95% ethanol, chloroform and acetone were run on concentrations of 3–5 mg./l. The decomposition rate in hydrochloric acid was studied both in 50% acetone and 50% ethanol solutions with similar results in both solvents. The variation of extinction with *p*H was performed at 500, 550 and 600 mμ with 40% ethanol solution having an indooxine concentration of 0.00944 g./l. Hydrochloric acid and sodium hydroxide were used to adjust the *p*H which was measured with a Beckman H-2 Meter.

**Polarograms.**—A Sargent Model XXI Polarograph with a dropping mercury cathode having characteristics previously described[7] was used. The concentration of indooxine was 4.0 mg./l. in Britton and Robinson buffers in which ethanol had to be added to keep the substance in solution.

**Qualitative Tests.**—Spot tests were performed using a saturated alcoholic solution of 2-methylindoöxine and approximately 1% solutions of metal ions. In an acetate buffer of *p*H 5, blue precipitates were obtained from $Ag^+$, $Sn^{+++}$ and $Hg^{++}$. At *p*H 12 precipitates were obtained in addition from $Cd^{++}$, $Co^{++}$, $Cu^{++}$, $Fe^{++}$, $Mg^{++}$, $Mn^{++}$, $Ni^{++}$, $UO_2^{++}$, $Fe^{+++}$, $La^{+++}$ and $Th^{++++}$. No precipitates were observed with $Al^{+++}$, $Cr^{+++}$, $Na^+$ and $K^+$.

**Acknowledgment.**—This work was supported in part by a grant from the Research Corporation.

---

[7] Q. Fernando and J. P. Phillips, THIS JOURNAL, **74**, 3103 (1952).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KY.

---

## Isomerization of Saturated Hydrocarbons. X.[1] Catalytic Isomerization of Cycloheptane

BY HERMAN PINES, F. J. PAVLIK[2] AND V. N. IPATIEFF

RECEIVED JUNE 11, 1952

It has previously been shown that under certain controlled conditions aluminum bromide–hydrogen bromide does not cause isomerization of *n*-butane to isobutane[3] or alkylcyclopentanes[1,4] to cyclohexane and alkylcyclohexanes unless traces of olefins or alkyl halides were present. It was also shown that ultraviolet light[1,5] promotes the isomerization of these compounds in the presence of aluminum bromide–hydrogen bromide and that aluminum bromide in the presence of oxygen[1,6] and in the absence of hydrogen bromide causes a similar rearrangement. It was further shown that benzene inhibits isomerization.[1,7]

In order to explain the function of the various promoters an ionic mechanism was proposed[4,8] in which it was postulated that the alkyl halides added as such or formed *in situ*, acted as chain initiators.

These studies have now been extended to include cycloheptane and Table I summarizes the results obtained with this compound.

TABLE I

ISOMERIZATION OF CYCLOHEPTANE

From 3.5 to 4.8 grams of cycloheptane was used in each experiment. The reactions were made at 25°.

| Expt. | Reagents used: Moles per 100 moles of cycloheptane | | | | | Time, hours | Methyl-cyclohexane, % |
|---|---|---|---|---|---|---|---|
| | $AlBr_3$ | HBr | *s*-$C_4H_9Br$ | Benzene | Oxygen | | |
| 1 | 2 | 1 | | | | 9 | 0 |
| 2 | 3.0 | 1 | | | | 9 | 0 |
| 3 | 1.5 | 1 | 0.1 | | | 2 | 100 |
| 4 | 1.5 | 1 | 0.1 | 0.15 | | 2 | 7 |
| 5 | 1.5 | | | | 0.5 | 9 | 58 |
| 6 | 2 | 1 | | | | 2[a] | 2 |
| 7 | 2 | 1 | | | | 9[a] | 34 |

[a] Ultraviolet irradiation.

It was found that as in the case of butanes and alkylcyclopentanes, the isomerization of cycloheptane does not take place in the presence of a catalyst consisting of only aluminum bromide–hydrogen bromide (experiments 1 and 2).

If to these reactants is added 0.1 mole per cent. of *s*-butyl bromide, complete isomerization to methylcyclohexane occurs after two hours of contact (expt. 3) as compared to nine hours in the preceding two experiments. The addition of 0.15 mole per cent. of benzene greatly inhibits the isomerization reaction; only 7% of methylcyclohexane is formed (expt. 4).

The similarity of the isomerization of cycloheptane and alkylcyclopentanes was also shown by experiment 5 in which 0.5 mole per cent. of oxygen was introduced as a promoter and aluminum bromide in the absence of added hydrogen bromide was used as a catalyst; after a nine-hour contact time, 58% of methylcyclohexane was produced.

It was found that the isomerization of cycloheptane in the presence of an aluminum bromide–hydrogen bromide catalyst can also proceed in the absence of promoters, if the reactants are placed in a quartz tube and irradiated with ultraviolet light. After two hours of exposure about 2% and after nine hours 34% of cycloheptane undergoes isomerization. The mechanism of isomerization of cycloheptane is similar to that of alkylcyclopentanes and can be expressed as

$$RBr + AlBr_3 \rightleftharpoons [R^+][AlBr_4^-]$$

---

[1] For paper IX of this series see H. Pines, F. J. Pavlik and V. N. Ipatieff, THIS JOURNAL, **73**, 5738 (1951).

[2] Universal Oil Products Company Predoctorate Fellow 1949–1951.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595, 2518 (1946).

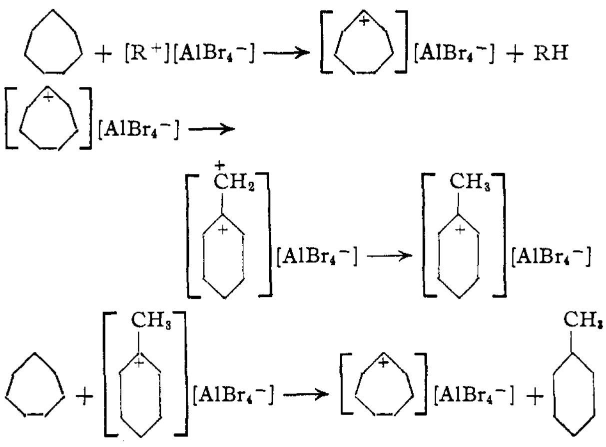
[4] H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

[5] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4055 (1950).

[6] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949).

[7] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4304 (1950).

[8] H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).



Oxygen and ultraviolet light cause the formation of a chain initiator, while benzene removes it and therefore causes the inhibition of the reaction.

It is important in the study of the isomerization of cycloheptane to keep the hydrocarbon in tightly covered bottles under an atmosphere of nitrogen or carbon dioxide. The presence of traces of peroxides or oxygenated hydrocarbons acts as a chain initiator; for that reason it is necessary that at frequent intervals a control experiment be made with aluminum bromide–hydrogen bromide as catalyst. If an isomerization occurs the cycloheptane should be passed over activated silica gel in order to remove any traces of oxygenated material that might have been formed.

### Experimental

A. **Apparatus and Procedure.**—A high vacuum apparatus described previously[4] was used for the purification of the reactants and for charging and discharging the reaction tube. The technique of adding the chain initiators, such as *s*-butyl bromide or oxygen was the same as described previously.[1] In the experiments in which ultraviolet irradiation was involved, a round bulb of clear fused quartz was affixed through a graded seal to the Pyrex reaction tube; this permits a more effective transmission of light to the reaction zone. A Cenco quartz cadmium–mercury vapor arc lamp was used at a distance of 20 cm. from the reaction tube.

B. **Materials.** 1. **Cycloheptane.**—It was prepared by adding to 0.17 mole of cyclohexanone dissolved in one liter of ether, 0.17 mole of diazomethane[9] in 500 ml. of ether and 200 ml. of anhydrous methanol. After three days standing at room temperature the product was distilled on a three-plate column. The ketones boiled at 154–180°, $n^{20}\text{D}$ 1.4570.

The mixture of ketones was reduced by the Wolff–Kishner reaction as modified by Huang-Minlon.[10] The hydrocarbons thus obtained, 16 g., were distilled on a forty-plate column. The following fractions were separated: (a) b.p. 79.2°, 4 ml., $n^{20}\text{D}$ 1.4242 corresponding to cyclohexane and (b) b.p. 117°, 12.1 ml., $n^{20}\text{D}$ 1.4448, corresponding to cycloheptane.

The cycloheptane was passed through 200-mesh size activated silica gel in order to remove any traces of oxygenated material present.

C. **Analysis.**—The composition of the hydrocarbons obtained from the isomerization was determined by means of infrared spectral analysis. The spectra of methylcyclohexane and of cycloheptane, used as standards, were identical with those reported by the American Petroleum Institute Project 44.

The wave lengths used for calculating the composition of the samples were: 9.24, 10.40, 11.06, 11.56 and 12.44 $\mu$.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

---

[9] E. Mosettig and A. Burger, THIS JOURNAL, **52**, 3456 (1930).

[10] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

---

# Lower Chlorides of Silicon

BY EUGENE G. ROCHOW AND ROSTISLAV DIDTSCHENKO

RECEIVED JUNE 24, 1952

The "inert pair" of *s* electrons in germanium, lead and tin, leads to well-defined monomeric bivalent compounds of these elements. However, compounds of bivalent silicon are represented only by the monoxide SiO (which sublimes only at red heat *in vacuo* and is polymeric) and a series of lower chlorides.[1–4] In the latter (and possible also in SiO) there are Si–Si bonds[4] and hence the silicon is not bivalent in the same sense as is tin in $SnCl_2$ or germanium in $GeCl_2$.

At the same time, the readiness with which $GeCl_2$ adds molecules like HCl[5] suggests that a dichloride of silicon would be very useful because it should absorb methyl chloride to form methylchlorosilanes. It was our intention to try to prepare $SiCl_2$ by methods similar to those used for the preparation of $GeCl_2$,[6] and then to investigate the addition of alkyl halides to such a dichloride.

### Experimental

The apparatus shown in Fig. 1 was constructed in order to attempt the reduction of silicon tetrachloride with silicon at temperatures higher than those permitted by the apparatus of Troost and Hautefeuille.[1] Silicon tetrachloride, purified by stirring with dry sodium carbonate and then by distillation, was frozen in bulb A and the apparatus was evacuated. The silicon tetrachloride was then allowed to vaporize through the fused silica tube I, which contained 15 g. of pure silicon (99.8%) and was heated to 1000°. After 15 minutes a yellow viscous oil began to collect in the small bulbs at the rate of about 1 cc. per hour. The silicon tetrachloride was condensed in bulb B, distilled back into A through the by-pass, and so recirculated repeatedly.

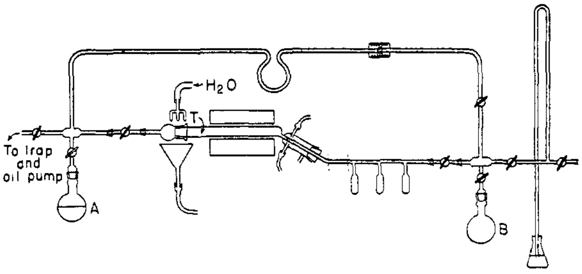


Fig. 1.

After 5 cc. of yellow oil had collected, it was transferred under dry nitrogen to a miniature still and distilled through a fractionating column 120 mm. long and 6 mm. in inside diameter, containing a nickel spiral wound around a coaxial glass rod. After some $SiCl_4$ and other volatile material had distilled up to 100° at atmospheric pressure, the pressure was reduced to 1 mm. and three fractions were collected at 70 to 120°, 120 to 170°, and 170 to 200°. Some decomposition in the distillation flask was evident, and a mirror of silicon formed on its walls. The products did not distil uniformly over the temperature ranges indicated, but appeared to be mixtures of relatively few components. However, the amounts were so small, and the heat capacity of the mercury-filled thermometer well so large, that more reliable boiling points could not be obtained. The fractions were sealed in the ampules in which they were collected.

---

[1] Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 459 (1871).

[2] R. Schwartz, *Ber.*, **80**, 444 (1947).

[3] R. Silvers and N. Gregor, *Z. anorg. allgem. Chem.*, **241**, 395 (1939).

[4] K. A. Hertwig and E. Wiberg, *Z. Naturforsch.*, **6b**, 336 (1951).

[5] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.*, **31**, 1526 (1927); L. M. Dennis and H. L. Hunter, THIS JOURNAL, **51**, 1151 (1929).

[6] L. M. Dennis and H. L. Hunter, *ibid.*, **51**, 1151 (1929).