4-Chloro-3-(trifluoromethyl)-styrene.—A suspension of 8.5 g. of phosphorus(V) oxide in 150 ml. of dry benzene was added to 35.0 g. of 4-chloro-3-(trifluoromethyl)-α-methylbenzyl alcohol and 1 g. of hydroquinone. The mixture was shaken vigorously at about 25°. When there was no increase in temperature upon further shaking, usually after about fifteen minutes, the benzene layer was decanted from the partially hydrated phosphorus(V) oxide and rectified through a 2-foot column packed with glass helices. An additional gram of hydroquinone was added before rectification. The distillate contained 24.5 g. of 4-chloro-3-(trifluoromethyl)-styrene, b. p. 68–69° (6 mm.).

All of the styrenes listed in Table III were prepared by the same method.

Emulsion Polymerization of Trifluoromethyl- and Chloro-(trifluoromethyl)-substituted Styrenes.—Samples of the styrenes were polymerized under comparable conditions. The polymerizations were performed at 50° under atmospheric pressure in a 3-necked flask (300 ml.) fitted with an efficient stirrer and a thermometer. Five grams of the styrene was added to 150 ml. of distilled water, 0.3 g. of potassium persulfate and 2 ml. of Tergitol No. 4. After a reaction period of twelve hours, the polymer was precipitated by pouring the emulsion into 300 ml. of 10% sodium chloride solution. The polymer was filtered and washed with water. After reprecipitating the polymer from an acetone solution by dilution with methanol, the solid polymer was dried for twenty-four hours at 70°.

Molecular Weights of Polymers.—The average molecular weights of the polymers were determined by the viscosity method.[9] A mixed solvent (100 ml. of benzene with 150 ml. of acetone) was used and the equation constants ($K = 3.57 \times 10^{-4}$, $a = 0.67$) were determined using samples of polystyrene of known average molecular weight.

Summary

1. The preparation of nine new trifluoromethyl- and chloro-(trifluoromethyl)-substituted styrenes is described.

2. Polymers of these styrenes were prepared and their average molecular weights determined.

3. It was found that substituted bromobenzenes in which a chlorine is ortho to a bromine do not react with magnesium in ether while those in which the chlorine is in a position other than ortho readily form a Grignard reagent.

LAFAYETTE, IND. RECEIVED[10] MARCH 30, 1950

---

[9] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, pp. 144–146.

[10] Original manuscript received October 24, 1949.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. VII.[1] The Effect of Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide–Hydrogen Bromide

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF

It has been shown previously[3,4] that under certain controlled conditions aluminum bromide–hydrogen bromide did not cause the isomerization of *n*-butane to isobutane or methylcyclopentane to cyclohexane unless traces of olefins or alkyl halides were present. In order to explain the function of the traces of olefins a chain mechanism has been proposed[5] in which it was suggested that the olefins reacted with the hydrogen halide to form the corresponding alkyl- or cycloalkyl halide which in the presence of aluminum bromide reacted with the saturated hydrocarbon such as methylcyclopentane to form cyclohexane.

This study has been extended in order to determine whether the isomerization of methylcyclopentane can proceed without the addition of the above mentioned types of chain initiator. The reaction was conducted in the presence of ultraviolet light; it was assumed that under these conditions the hydrogen bromide will undergo a partial dissociation into a hydrogen and a bromine atom and the latter then will react with methylcyclopentane to form the corresponding bromide. It was found that isomerization proceeded when a reaction tube containing methylcyclopentane, aluminum bromide and hydrogen bromide in a molal ratio of approximately 100:2:1, was exposed for nine hours to a quartz cadmium–mercury vapor arc lamp. The degree of isomerization of methylcyclopentane to cyclohexane was increased from 18 to 24% when quartz instead of a Pyrex reaction tube was used. In the absence of hydrogen bromide, even after eighteen hours of irradiation, isomerization did not occur (Table I). The appearance of the reaction mixture before and after exposure to ultraviolet did not change; the solution was homogeneous and colorless. In two experiments (5 and 7) the small amounts of non-condensable gases produced during the reaction were collected and analyzed by a mass spectrometer[6]; the gases contained over 97% of hydrogen.

The results obtained are in accordance with the proposed chain mechanism of isomerization,[5] which can be presented as

---

[1] For paper VI of this series see H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **71**, 749 (1949).

[2] Universal Oil Products Company Predoctorate Research Fellow 1947–1949.

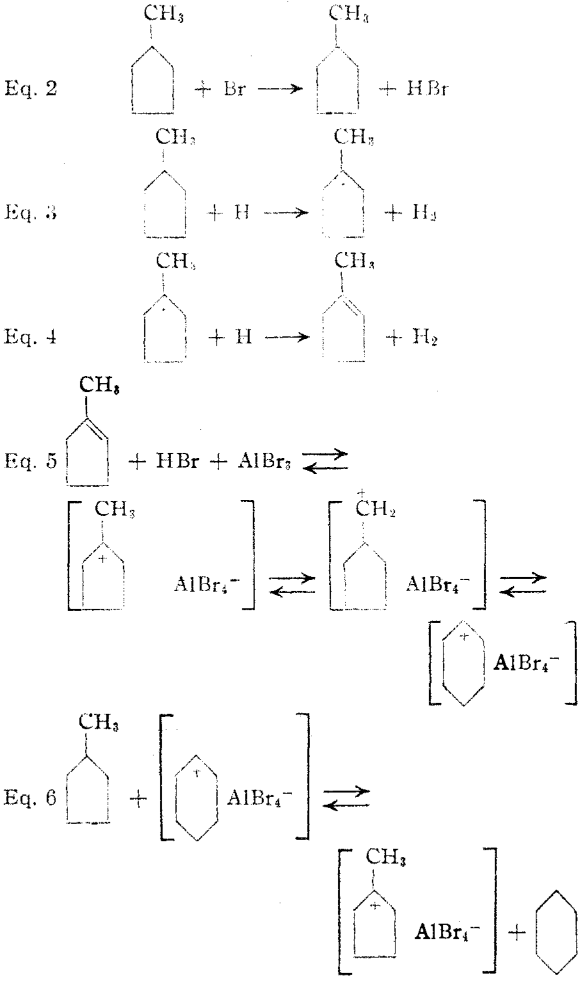
[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 585, 2518 (1946).

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

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

[6] The analysis of the gases on a mass spectrograph was made by Mr. Joseph Grutka at the Laboratory of the Universal Oil Products.

Eq. 1 $$HBr \xrightarrow{h\nu} H + Br$$



The irradiation apparently causes the dissociation of the hydrogen bromide into atoms of hydrogen and bromine which in turn may react with the methylcyclopentane; this would eventually result in the formation of traces of cycloölefins or cycloalkyl bromide which are necessary for the initiation of an ionic chain reaction for the isomerization of methylcyclopentane. Equations 1–4 represent the various steps by which an initiator for the isomerization reaction may be formed; in addition to the above indicated equations one could also formulate other somewhat similar steps involving atoms and free radicals, which would also result in the formation of cycloalkyl bromide. Equations 5 and 6 have been discussed previously.[4]

Inasmuch as the mechanism proposed above involves a chain reaction in which it is assumed that a cycloalkene or a cycloalkyl bromide is formed, it would then be expected that the addition of compounds which can readily react with the chain initiators, would result in the inhibition of the isomerization. It was actually found that the addition of 0.03 mole per cent. of benzene decreases the yield of cyclohexane produced from 24 to 6%. The results obtained are in agreement with those reported previously.[1] The experimental data are given in Table I.

TABLE I

ISOMERIZATION OF METHYLCYCLOPENTANE

The approximate molal ratio of reagents used in each experiment was: C_6H_{12}:$AlBr_3$:HBr = 100:2.00 (±0.04): 1.00 (±0.03); P for Pyrex reaction tube; Q for quartz reaction tube.

Expt.	Reaction tube	Moles of methylcyclopentane used × 10²	Time of irradiation hours	Mole % of benzene[a]	% of cyclohexane in methylcyclopentane
1	P	1.96	18[b]	0.00	0
2	P	1.36	18[c]	.00	0
3	P	1.93	18	.00	18
4	Q	1.04	9	.00	24
5	Q	2.60	30	.00	29[d]
6	Q	2.44	9	.03	6
7	Q	4.38	9	.71	1[e]

[a] Mole per cent. based on methylcyclopentane charged. [b] The experiment was carried out in diffused light. [c] Hydrogen bromide was not present in this experiment. [d] Non-condensable gas, 0.206 cc. at S. T. P., was produced; this represents 0.035 mole per cent. of gas based on methylcyclopentane charged. The gas consisted of 98.9% of hydrogen. [e] 0.060 cc. at S. T. P. of gas was obtained, which represents 0.006 mole per cent. of gas based on methylcyclopentane charged. The gas was composed of 97.7 mole % of hydrogen.

Experimental

The high vacuum apparatus and technique used was essentially that described previously.[4] Purification of the methylcyclopentane with sodium–potassium alloy, however, was found unnecessary. For experiments requiring benzene, a standard solution of purified benzene in pure methylcyclopentane was prepared. Portions of this solution were diluted with more methylcyclopentane until the desired concentration of benzene was obtained; this concentration was determined by means of ultraviolet spectrum analysis.

To get more effective transmission of light to the reaction zone, a round bulb of clear fused quartz was affixed through a graded seal to the Pyrex reaction tube. After all the components had been distilled into the reaction tube, the latter was sealed off, then fixed in a vertical position at a distance of 20 cm. from the source of radiation—a Cenco quartz cadmium–mercury vapor arc lamp. The exposure took place at room temperature (about 27°); no heating of the reaction tube by the arc lamp was observed.

Summary

The isomerization of methylcyclopentane to cyclohexane in the presence of aluminum bromide–hydrogen bromide proceeds in the absence of added chain initiators, when the reactants are exposed to ultraviolet light. Small amounts of benzene inhibit the isomerization.

A mechanism of the isomerization is discussed.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 11, 1950