and were then titrated with 0.1 N arsenite using a polarized platinum-platinum electrode as indicator. The results are shown in Table I.

It will be seen that both methods yielded quantitative iodine consumption values and that in the presence of pyridine, the iodine uptake was five times that in the presence of acetate.

A repetition of the above experiment using monochlorohydroquinone, dichlorohydroquinone, and tetrachlorohydroquinone gave 8, 6, and 2 milliequivalents of iodine consumed per millimole of substance. This result indicates that the excess iodine consumption in the presence of pyridine is due to the oxidation of the ring hydrogen atoms of hydroquinone.

By titrating iodide with silver nitrate solution it was shown that all the iodine consumed was reduced to iodide. This reaction has been incorporated into a scheme of analysis for phenol, catechol and hydroquinone soon to be published.

Summary

1. The reaction between hydroquinone, iodine and pyridine has been extended to the preparation of a dipyridinium and a tripyridinium betaine.

2. The reaction products have been isolated as reineckeate, picrate, and cadmium iodide salt.

3. The analytical features of the reaction have been shown.

BETHESDA, MD. RECEIVED MAY 28, 1945

[CONTRIBUTION FROM THE UNIVERSAL OIL PRODUCTS COMPANY]

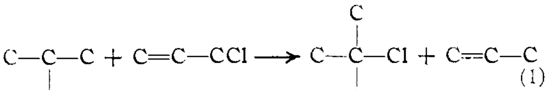
Condensation of Saturated Hydrocarbons with Haloölefins. I. The Reaction of Isobutane with Vinyl Chloride and Allyl Chloride[1]

BY LOUIS SCHMERLING

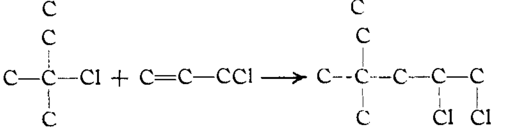
Investigation of the condensation of saturated hydrocarbons with haloölefins has led to a new method for the preparation of saturated halohydrocarbons as well as to an insight into the mechanism of the reactions. The present communication describes the results obtained by the interaction of isobutane with vinyl and allyl chlorides in the presence of aluminum chloride.

A 35–40% yield of 1-chloro-3,4-dimethylpentane and a 13–15% yield of 1,2-dichloro-4,4-dimethylpentane were obtained by the reaction of isobutane with allyl chloride at about −10°. The structure of the chloroheptane was determined by converting it to the corresponding alcohol, which yielded derivatives identical with those prepared from synthetic 3,4-dimethylpentanol. The structure of the dichloroheptane was established by conversion to 4,4-dimethyl-1-pentene by reaction with zinc and alcohol.

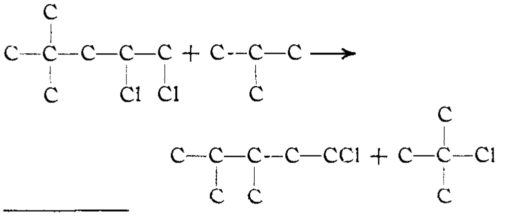
The following hypothesis is presented as the probable mechanism of the reaction. It is analogous to that recently proposed for the alkylation of isoparaffins with olefins.[2]



$$C{-}\underset{\substack{|\\ C}}{C}{-}C + C{=}C{-}CCl \longrightarrow C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl + C{=}C{-}C \qquad (1)$$



$$C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl + C{=}C{-}CCl \longrightarrow C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C{-}\underset{\substack{|\\ Cl}}{C}{-}\underset{\substack{|\\ Cl}}{C} \qquad (2)$$



$$C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}C{-}\underset{\substack{|\\ Cl}}{C}{-}\underset{\substack{|\\ Cl}}{C} + C{-}\underset{\substack{|\\ C}}{C}{-}C \longrightarrow C{-}\underset{\substack{|\\ C}}{C}{-}\underset{\substack{|\\ C}}{C}{-}C{-}CCl + C{-}\overset{\substack{C\\ |}}{\underset{\substack{|\\ C}}{C}}{-}Cl \qquad (3)$$

The t-butyl chloride formed by eq. 3 starts a new cycle by reacting with allyl chloride as in eq. 2. The reaction indicated in eq. 1 is assumed to occur only as the initiating step. Although it is assumed that propene is formed in negligible amounts, it was not isolated under the reaction conditions used. The propene apparently reacts either with isobutane (*via* t-butyl chloride) to yield heptane[2] or with the catalyst to form the so-called lower layer complex.

That the reaction of eq. 2 can occur is shown by the fact that 1,2-dichloro-4,4-dimethylpentane may be prepared in 48% yield by the condensation of t-butyl chloride with allyl chloride at −20 to −10° in the presence of aluminum chloride.[3]

Evidence in support of eq. 3 was obtained by showing that 1-chloro-3,4-dimethylpentane and t-butyl chloride are produced by the reaction of the dichloroheptane with isobutane in the presence of aluminum chloride. The rearrangement of the carbon skeleton which occurs is readily explained by Whitmore's[4] "common basis of intramolecular rearrangements." It differs somewhat from the previously described rearrangements in that migration of the methyl group is preceded by migration of one of the methylene hydrogens of the neopentyl group.

Increasing the temperature at which the reaction of isobutane with allyl chloride was carried out resulted in a decrease in the yield of chlorinated products, the decrease being due to the conversion of the chlorides to paraffins. Thus, for example

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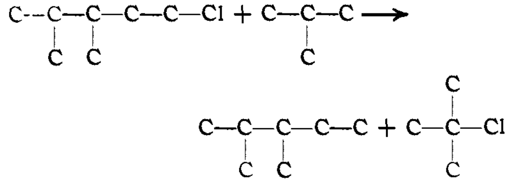
(1) Presented before the Organic Division of the American Chemical Society at the New York meeting, September, 1944.

(2) L. Schmerling, THIS JOURNAL, **66**, 1422 (1944).

(3) To be described in a forthcoming publication.

(4) F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).



$$C{-}\underset{C}{C}{-}\underset{C}{C}{-}C{-}C{-}Cl + C{-}\underset{C}{C}{-}C \longrightarrow C{-}\underset{C}{C}{-}\underset{C}{C}{-}C{-}C + C{-}\overset{C}{\underset{C}{C}}{-}Cl \quad (4)$$

The *t*-butyl chloride may react with the catalyst to form lower layer or may be converted into octene or octyl chloride which is then converted to octanes. In an experiment (expt. 3, Table I) in which conditions were such as to permit complete conversion of the primary products to paraffins, liquid paraffins were formed to the extent of 320% by weight of the propene available from the allyl chloride. This represents the reaction of 1.6 moles of isobutane per mole of allyl chloride. Hydrogen chloride was obtained in at least 80% of the theoretical yield.

The yield of paraffinic product is also increased by an increase in the ratio of catalyst to allyl chloride. This is shown quite clearly by comparison of expts. 3, 4 and 5, Table I. It will be noted that the use of a lower reaction temperature offsets the effect of the higher catalyst to allyl chloride ratio.

Extension of the reaction to vinyl chloride gave as the principal product 1,1-dichloro-3,3-dimethylbutane, which was obtained in 40% yield at −10° and in 20% yield at 25°. *t*-Butyl chloride (about 10% yield) was a by-product of the reaction together with liquid isoparaffins. The structure of the dichloride was proved by converting it to *t*-butylacetaldehyde and was confirmed by showing that it was identical with the product obtained by the addition of *t*-butyl chloride to vinyl chloride.

TABLE I

CONDENSATION OF ISOBUTANE WITH ALLYL CHLORIDE

Experiment	1	2	3	4	5	6
Reactants, g.						
Isobutane	380	350	365	355	160	384
Allyl chloride	94	92	164	188	90	82
Aluminum chloride	15	80	80	80	15	20
Temperature, °C.	−10[a]	−5[a]	+5[a]	−25	+5[a]	−25
Products, g.						
Condensable gas	325	277	120	192	74	325
Liquid product	135	151	284	260	137	113
Hydrogen chloride[b]	4	8	63	6	17	2
Catalyst layer	21	88	128	116	33	46
Loss	4	0	14[c]	47[c]	4	0
Yields, weight % of allyl chloride charge						
Liquid paraffins	9	50	175	85	85	12
Chloroheptane	60	68	0	35	30	48
Dichloroheptane[d]	33	28	0	14	15	26
Higher-boiling	25	9	0	15	25	19
Catalyst increase	6	9	29	19	20	32
Yields, % of theory[e]						
Chloroheptane	35	40	0	20	17	28
Dichloroheptane	15	13	0	6	7	12

[a] Approximate temperature of the liquid product at the end of the experiment. [b] As determined by increase in weight of soda-lime tower in exit line. More was present in solution in the liquid and catalyst. [c] Chiefly isobutane because of mechanical difficulties. [d] The values given are probably somewhat high owing to presence of chloroheptane. [e] Based on the allyl chloride.

The formation of the dichlorohexane instead of monochlorohexane is easily explained on the basis of the mechanism proposed above. Isobutane is converted to *t*-butyl chloride, which then condenses with vinyl chloride to form 1,1-dichloro-3,3-dimethylbutane. The primary chlorine atoms are relatively unreactive and only a very small amount of the dichloride is reduced to monochlorohexane by the reaction illustrated by eq. 3. In the case of the allyl chloride condensation, the dichloroheptane contains a secondary chlorine atom and reacts readily with isobutane, yielding monochloroheptane and *t*-butyl chloride. Under conditions which are such as to bring about the reduction of a chlorine atom of the dichlorohexane, both chlorine atoms are replaced, and the product consists of isoparaffins and only a very small amount of monochlorohexane.

Experimental[5]

Condensation of Isobutane with Allyl Chloride

Procedure.—The experiments were carried out in a three-necked flask equipped with a dropping funnel, a mercury-sealed stirrer, and a condenser cooled by Dry Ice. Uncondensed gases passed through a soda lime tower into a trap cooled to −78°. Aluminum chloride and isobutane were placed in the flask, the mixture was stirred, and the dropwise addition of redistilled allyl chloride was begun. In all the experiments except those carried out at −25°, the reaction temperature was that of the refluxing mixture, no cooling bath being used; the temperatures recorded in Table I are those prevailing at the end of the experiment. The temperature of −25° was maintained by means of an acetone-bath to which pieces of Dry Ice were added as required. After all of the allyl chlorine had been added, stirring was continued, usually for ten minutes, and the contents of the flask were allowed to settle. The upper layer was decanted into a receiver cooled to −78° which contained 10 g. of ice, in order that any dissolved catalyst would be hydrolyzed when the temperature reached 0°. The product was allowed to come to room temperature and was finally warmed to 40°, the overhead gases passing through a soda lime tower into a trap cooled by Dry Ice mixture. The stabilized liquid was washed with water, dried, and distilled through a 14-inch total reflux fractionating column.[6]

Results.—The results of six typical experiments are summarized in Table I and Fig. 1. Experiment 3 is discussed briefly for purposes of illustration. It was found that little hydrogen chloride was evolved until about 90 g. of allyl chloride had been added (during two hours) to the mixture of 355 g. of isobutane and 80 g. of aluminum chloride. At this point (which corresponds approximately to the end of experiment 2) the catalyst was an orange-brown semisolid, most of which was coagulated on the wall of the flask. As more allyl chloride was added, a copious evolution of hydrogen chloride took place and the catalyst became more fluid and darker (red-brown) in color. The temperature of the reaction mixture rose to about 0–5° during the latter part of the experiment, because of the predominance of higher boiling liquid over isobutane. Stirring was continued for ten minutes after all of the allyl chloride had been added, and the product was worked up as outlined.

1-Chloro-3,4-dimethylpentane.—The chloroheptane boils with practically no decomposition at 150–151° at

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[5] Microanalyses by Dr. T. S. Ma, University of Chicago.

[6] C. L. Thomas, H. L. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

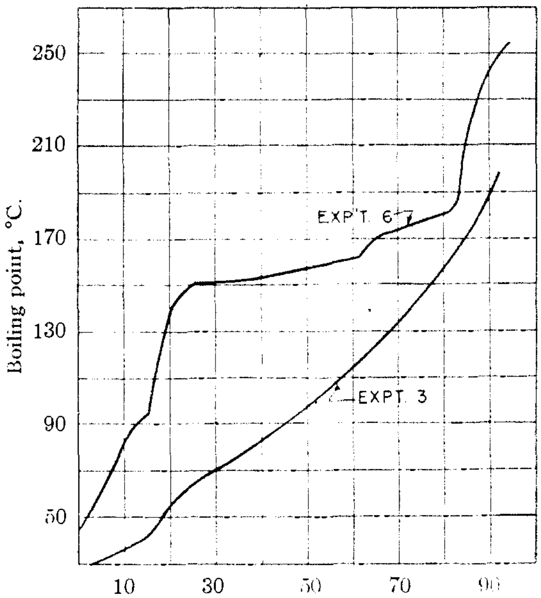

Fig. 1.—Distillation of product from the condensation of isobutane with allyl chloride.

atmospheric pressure (745 mm.) and at 52–53° at 20 mm.; $n^{20}D$ 1.4299; d^{20}_4 0.8825; mol. ref.: calcd. for $C_7H_{15}Cl$, 39.3; obs. 39.4.

Anal. Calcd. for $C_7H_{15}Cl$: C, 62.42; H, 11.24; Cl, 26.34. Found: C, 62.67; H, 11.13; Cl, 25.81.

The anilide[7] prepared from 1-chloro-3,4-dimethyl-, pentane melted at 80–81° (nacreous flakes from dilute ethanol).

Proof of Structure of 1-Chloro-3,4-dimethylpentane.—Thirty grams (0.22 mole) of the chloroheptane was converted to the Grignard reagent in the usual manner. The product was filtered through glass wool. One half of the filtrate was hydrolyzed to heptane by the addition of ice water containing 10 g. of ammonium sulfate and the other half was converted to heptanol by passing oxygen over the surface of the stirred solution for eight hours and then adding an aqueous solution of ammonium sulfate.

The heptane (6 g.) boiled at 88–89°; $n^{20}D$ 1.3920; d^{20}_4 0.6923. These properties are in good agreement with those reported[8] for 2,3-dimethylpentane: b. p. 89.7°, $n^{20}D$ 1.3920; d^{20}_4 0.6952.

The heptanol (8 g.) boiled at 168–169°; $n^{20}D$ 1.4288. It yielded a 3,5-dinitrobenzoate which melted at 51–52° (recrystallized from isopentane at 0°).

Anal. Calcd. for $C_{14}H_{18}N_2O_6$: C, 54.17; H, 5.85. Found: C, 53.81; H, 5.83.

The α-naphthylamine addition compound[9] of the dinitrobenzoate melted at 75–76° (recrystallized from pentane). The α-naphthylurethan of the heptanol was obtained as an oil which was finally crystallized by dissolving it in a minimum of isopentane (about 3–4 cc.) and placing the solution in the refrigerator overnight; hard, white clusters of crystals melting at 41–42° were obtained.

Conversion of the chloroheptane was also accomplished by heating a sealed tube containing 15 g. of the chloride, 100 g. of water, and 3 g. of magnesium oxide at 225° for four hours. Seven grams of heptanol was obtained; b. p. 165–166°; $n^{22}D$ 1.4280.

A sample of authentic 3,4-dimethylpentanol[10] prepared by the reaction of ethylene oxide with the Grignard reagent of 2-bromo-3-methylbutane was obtained from Prof. R. C. Huston. Its 3,5-dinitrobenzoate and the α-naphthylamine addition compound thereof were found to have the same melting points and "mixed melting points" as the analogous derivatives of the alcohol prepared from the chloroheptane.

1,2-Dichloro-4,4-dimethylpentane.—The dichloride boiled with slight decomposition at 173–175° at atmospheric pressure; $n^{20}D$ 1.4450; d^{20}_4 0.9874; mol. ref.: calcd. for $C_7H_{14}Cl_2$, 44.2; obs., 45.6. *Anal.* Calcd. for $C_7H_{14}Cl_2$: C, 49.70; H, 8.34; Cl, 41.96. Found: C, 53.16; H, 8.85; Cl, 38.12. Contamination with paraffin or monochloroheptane is indicated.

Pure 1,2-dichloro-4,4-dimethylpentane prepared[3] by the condensation of *t*-butyl chloride with allyl chloride has the following properties: b. p. 173–175° (745 mm.) and 58–59° (12 mm.); $n^{20}D$ 1.4489; d^{20}_4 1.0259; mol. ref. calcd. for $C_7H_{14}Cl_2$, 44.2; obs., 44.1.

Anal. Calcd. for $C_7H_{14}Cl_2$: C, 49.70; H, 8.34; Cl, 41.96. Found: C, 49.67; H, 8.77; Cl, 41.98.

Proof of Structure of 1,2-Dichloro-4,4-dimethylpentane.—The dichloride reacted very slowly with zinc and alcohol at the reflux temperature (80°). The desired dehalogenation was finally accomplished by carrying out the reaction in a sealed tube at 120°. A 45% yield of heptene was obtained by the reaction of 18 g. of the dichloroheptane with 8 g. of zinc dust and 40 g. of 95% ethyl alcohol. The heptene boiled quite sharply at 71–71.5°; $n^{20}D$ 1.3921. These values are in excellent agreement with the best literature values[7] for 4,4-dimethyl-1-pentene; b. p. 71.8°; $n^{20}D$ 1.3922.

Reaction of 1,2-Dichloro-4,4-dimethylpentane with Isobutane.—The dichloride (30 g.) was added during twenty minutes to a well-stirred mixture of 208 g. of isobutane and 8 g. of resublimed aluminum chloride. The product was stirred for an additional hour after which the upper layer was decanted from the 13.5 g. of red-brown viscous catalyst layer and stabilized. The butane-free liquid product weighed 29 g. Distillation yielded about 4 g. of *t*-butyl chloride (identified as the anilide, m. p. and mixed m. p. 128°), 4 g. of heptane, 1 g. of octane (?), 7 g. of 1-chloro-3,4-dimethylpentane (identified as the anilide, m. p. 80–81°) and 6 g. of unreacted dichloroheptane.

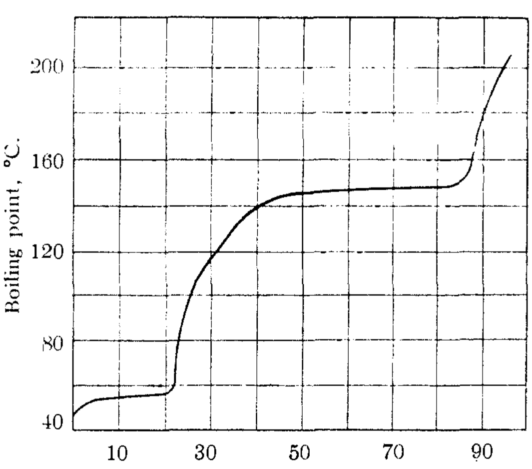

Fig. 2.—Distillation of product of condensation of isobutane with vinyl chloride.

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[7] Prepared according to the method of A. M. Schwartz and J. R. Johnson, THIS JOURNAL, **53**, 1063 (1931); see also H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2117 (1934).

[8] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

[9] Prepared by the method described by P. Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938). This very readily prepared and useful derivative does not seem to have received the wide usage it deserves.

[10] R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941). The author wishes to thank Prof. Huston for the heptanol sample.

Condensation of Isobutane with Vinyl Chloride

Procedure.—Vinyl chloride (80 g.) was bubbled during two hours into a well-stirred mixture of isobutane (340 g.) and aluminum chloride (30 g.), the apparatus being essentially that described above for the allyl chloride experiments. The temperature was that of the refluxing mixture (*i. e.*, about −10 to −8°). The catalyst remained granular until about 80% of the vinyl chloride had been added; little hydrogen chloride was evolved. As the addition was continued, the catalyst began to coagulate and was gradually converted into a red liquid; more hydrogen chloride was evolved. Stirring was continued for ten minutes, after which the upper layer was decanted from the 31 g. of catalyst layer and stabilized. There were recovered 281 g. of butane and 121 g. of liquid product. The soda lime tower gained 4 g. Distillation of the washed liquid product yielded 19 g. of material boiling at 50–55° (n^{20}D 1.376–1.380; density, about 0.75) which consisted of approximately equal amounts of hexane and *t*-butyl chloride (identified as the anilide, m. p. 128°) and 44 g. of product boiling at 145–148° which consisted of 1,1-dichloro-3,3-dimethylbutane (of Fig. 2). There was also obtained about 15 g. of higher boiling compounds.

In another experiment, 8 g. of aluminum chloride, 80 g. of isobutane and 32 g. of vinyl chloride were weighed into a glass liner (cooled in a bath at −78°) for an Ipatieff-type rotating autoclave. The liner was sealed into the autoclave which was then rotated at room temperature four hours after which it was allowed to set overnight. The gaseous material was passed through a soda lime tower (which gained 7 g.) and was collected in a trap immersed in Dry Ice–acetone; 23 g. of condensable gas was obtained. The autoclave was opened and 61 g. of liquid product was separated from 22 g. of red-brown fluid catalyst, washed, dried, and distilled. There was obtained, besides paraffin hydrocarbons, about 8 to 10 g. of 1,1-dichloro-3,3-dimethylbutane contaminated with isoparaffin.

1,1-Dichloro-3,3-dimethylbutane.—The dichlorohexane boiled without decomposition at 146–147° at atmospheric pressure. It melted at −60 to −59°. Other physical properties: n^{20}D 1.4370; $d^{20}{}_4$ 1.0056; mol. ref.: calcd. for $C_6H_{12}Cl_2$, 39.6; obs., 40.3. *Anal.* Calcd. for $C_6H_{12}Cl_2$: C, 46.5; H, 7.75; Cl, 45.75. Found: C, 49.90; H, 8.15; Cl, 42.1. The presence of an impurity (paraffin or chlorohexane) is indicated.

Pure 1,1-dichloro-3,3-dimethylbutane prepared by the condensation of *t*-butyl chloride with vinyl chloride[3] has the following properties: b. p. 148–148°; m. p. −56.5 to −56°; mixed with above dichloride, m. p. −58 to −57°; n^{20}D 1.4389; $d^{20}{}_4$ 1.0262; mol. ref.: obs., 39.7. *Anal.* C, 46.70; H, 7.89; Cl, 45.08.

Proof of Structure of 1,1-Dichloro-3,3-dimethylbutane.—Heating the dichloroneohexane with water in a sealed tube at 300° yielded an aldehyde, b. p. 102–103°. The 2,4-dinitrophenylhydrazone and the dimedon derivative of the aldehyde melted at 146–147° and 162–163°, respectively, proving that the aldehyde was *t*-butylacetaldehyde.[11] The dichloride was, therefore, 1,1-dichloro-3,3-dimethylbutane. The possibility that it was 1,2-dichloro-3,3-dimethylbutane may be eliminated since both chlorine atoms were found to be rather inert (hence, primary) and since the formation of an aldehyde from the 1,2-dichloride would probably be accompanied by rearrangement of the neopentyl carbon skeleton.

Acknowledgment.—The continued interest and advice of Professor V. N. Ipatieff is gratefully acknowledged.

Summary

1. Condensation of isobutane with allyl chloride at about −10° in the presence of aluminum chloride results in a 35–40% yield of 1-chloro-3,4-dimethylpentane and a 13–15% yield of 1,2-dichloro-4,4-dimethylpentane.

2. At a higher temperature, for example 0–5°, the product consists essentially of paraffinic hydrocarbons because of interaction of the chloroheptanes with the isobutane.

3. The principal product of the reaction of isobutane with vinyl chloride at −10° in the presence of aluminum chloride is 1,1-dichloro-3,3-dimethylbutane which is obtained in 40% yield.

4. A reaction mechanism is proposed and evidence in support thereof presented.

(11) H. Brunner and E. H. Farmer, *J. Chem. Soc.*, 1044 (1937).

RIVERSIDE, ILLINOIS RECEIVED DECEMBER 9, 1944

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

Photochemical Investigations. VI. The Photochemical Reaction between Hydrogen and Iodine Monochloride

BY LAWRENCE J. E. HOFER[1,2] AND EDWIN O. WIIG

In the course of a study of the inhibiting effect of iodine monochloride on the hydrogen–chlorine photo-reaction, Rollefson and Lindquist[3] observed in a preliminary experiment that a mixture of hydrogen and iodine monochloride exposed to light of λ 4300 to 5600 Å. absorbed by iodine monochloride did not react to produce hydrogen chloride. Furthermore, a mixture of hydrogen, chlorine and iodine monochloride exposed to light absorbed by iodine monochloride only gave no reaction whereas exposure to light absorbed by chlorine only resulted in the formation of hydrogen chloride. Mellor and Iredale,[4] however, found that 20 mm. iodine monochloride in one atmosphere of hydrogen reacted slowly in the radiation from an ordinary electric light bulb, more rapidly in diffuse daylight and very rapidly in direct sunlight. This observation was confirmed by Ashley and West[5] who observed an easily measurable reaction on exposure of pure hydrogen and iodine monochloride to the light of a mercury arc. In both these investigations the main products were identified as hydrogen chlo-

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(1) Presented at the Atlantic City, N. J., meeting of the American Chemical Society, Sept. 10, 1941.

(2) Abstract from a part of a thesis submitted to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Rollefson and Lindquist, THIS JOURNAL, **52**, 2793 (1930).

(4) Mellor and Iredale, *Nature*, **127**, 93 (1931).

(5) Ashley and West, *ibid.*, **127**, 308 (1931).