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The Condensation of Saturated Halides with Unsaturated Compounds. I. The Condensation of Alkyl Halides with Ethylene[1]

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Although it has long been known[2] that aluminum chloride catalyzes the condensation of polyhaloalkanes (*e. g.*, chloroform and carbon tetrachloride) with polyhaloolefins (*e. g.*, di-, tri- and tetrachloroethylene), the condensation of an alkyl halide (*i. e.*, a monohaloalkane) with a monoolefin or a haloolefin in the presence of a metal halide catalyst has not hitherto been accomplished, chiefly because of the ease with which other reactions, especially polymerization, occur. It has now been found that by proper choice of catalyst and reaction conditions saturated monohalides may be condensed with monoolefinic hydrocarbons to yield pure halohydrocarbons which are of interest as such or as intermediates for the synthesis of desirable derivatives.

The primary reaction is that of the addition of the alkyl group and the halogen atom to the double bond of the olefin, the halogen atom adding to the carbon atom that holds the smaller number of hydrogen atoms.

$$\mathrm{RX + CH_2{=}CHR' \longrightarrow R{-}CH_2CHX{-}R'}$$

The present communication describes the reaction of readily available alkyl chlorides and bromides of lower molecular weight with ethylene. The analogous condensation of higher molecular weight olefins with alkyl halides will be discussed in subsequent papers.

The condensation is catalyzed by the metal halides often referred to as metal halides[3] of the Friedel–Crafts type. Those which will be referred to in the present paper are aluminum chloride, ferric chloride, bismuth chloride, and zinc chloride. The reaction conditions depend on both the catalyst and the reactants used (see Table I). Low temperatures, for example, from about −30 to 0°, are preferred with an active catalyst such as aluminum chloride. Higher temperatures, for example from about 20 to 100°, are necessary with the less active catalysts, bismuth chloride, and zinc chloride.

The reaction of *t*-butyl chloride with ethylene yields 1-chloro-3,3-dimethylbutane as the principal product. No evidence of the formation of isomeric chlorohexanes has been obtained. 1-Chloro-3,3-dimethylpentane is a by-product of the reaction. It is probably formed by the condensation of *t*-amyl chloride, and possibly of isopropyl chloride, with ethylene, these alkyl chlorides having been produced by the disproportionation of *t*-butyl chloride

$$2t\text{-}\mathrm{C_4H_9Cl} \longrightarrow t\text{-}\mathrm{C_5H_{11}Cl} + i\text{-}\mathrm{C_3H_7Cl}$$

The analogous reaction occurs during the reaction of *t*-amyl chloride with ethylene. Thus, when aluminum chloride is used as catalyst at about −5°, there is obtained a 12% yield of the *t*-butyl chloride condensation product, 1-chloro-3,3-dimethylbutane, as well as a 25% yield of the expected chloroheptane, 1-chloro-3,3-dimethylpentane. The formation of *t*-butyl chloride in 18% yield by the action of aluminum chloride on *t*-amyl chloride has been observed by Bartlett and Condon.[4]

The condensation of primary and secondary alkyl halides with ethylene proceeds less rapidly than that of tertiary alkyl halides. As may be seen from the yields tabulated in Table I, the yields of condensation product with *n*-propyl, isopropyl and *s*-butyl chlorides are quite low. There is, however, little side-reaction, and much unreacted alkyl chloride is recovered.

The product obtained by the condensation of isopropyl chloride with ethylene is a chloroheptane rather than the expected isoamyl chloride. The chloroheptane is identical with that obtained by the reaction of *t*-amyl chloride with ethylene and is, therefore, 1-chloro-3,3-dimethylpentane. Its formation may be outlined as follows

$$\mathrm{(CH_3)_2CHCl + CH_2{=}CH_2 \longrightarrow (CH_3)_2CHCH_2CH_2Cl \longrightarrow (CH_3)_2CClC_2H_5}$$

$$\mathrm{(CH_3)_2CClC_2H_5 + CH_2{=}CH_2 \longrightarrow C_2H_5C(CH_3)_2CH_2CH_2Cl}$$

A similar set of reactions occurs in the condensation of *s*-butyl chloride with ethylene. The product is not 1-chloro-3-methylpentane but is, instead, a chlorooctane, the structure of which has not been established. By analogy with the reaction of isopropyl chloride, it may be presumed that the chloride is 1-chloro-3-methyl-3-ethylpentane.

The condensation of *n*-propyl chloride with ethylene yields 1-chloro-3,3-dimethylpentane; isomerization of the primary alkyl chloride to isopropyl chloride apparently precedes the condensation with the olefin. Similarly, the reaction of isobutyl chloride with the olefin proceeds via the formation of *t*-butyl chloride, and the chlorohexane, 1-chloro-3,3-dimethylbutane, is obtained.

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

(2) J. Böeseken and H. J. Prins, *K. Akad. Wetenschappen*, Proceedings of the Section of Sciences, Vol. XIII, 2nd part, 685–687 (1911); *C. A.*, **5**, 3400 (1911). For a review of the subsequent work of Prins and of others, see C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 775–778.

(3) The condensation of polychloromethanes and ethanes with chloroethylenes, on the other hand, is catalyzed by aluminum chloride only [H. J. Prins, *Rec. trav. chim.*, **51**, 1078 (1932)].

(4) P. D. Bartlett and F. E. Condon, private communication.

TABLE I

CONDENSATION OF ALKYL HALIDES WITH ETHYLENE

Expt.	Method of prepn.	Reactants			Catalyst		Temp., °C.	Chief product[a]	Yield[e]	
		Halide	g.	C_2H_4,[b] g.	MX	g.			g.	%
1	A	*t*-BuCl	50[c]	20	$AlCl_3$	5	−15 to −10	$Me_3CCH_2CH_2Cl$ (I)	49	75
2	B	*t*-BuCl	54	...	$FeCl_3$	5	24	(I)	40	57
3	C	*t*-BuCl	680	140	$FeCl_3$	34	− 5 to 5	(I)	490	55
								$EtCMe_2CH_2CH_2Cl$ (II)	30	6
4	B	*t*-BuCl	50	...	$BiCl_3$	10	50	(I)	4	6
5	B	*t*-BuCl	50	...	$BiCl_3$	10	100	(I)	20	30
6	B	*t*-BuCl	50	...	$ZnCl_2$	5	100	(I)	9	14
7	A	*t*-AmCl	150	18	$AlCl_3$	15	−10 to − 2	(II)	48	25
								(I)	20	12
8	A	*i*-PrCl	50[c]	6	$AlCl_3$	5	−18 to −14	(II)	20	23
9	B	*i*-PrCl	58	...	$FeCl_3$	5	24	(II)	8	8
10	B	*i*-PrCl	40	...	$BiCl_3$	10	100	(II)	4	6
11	A	*s*-BuCl	50[c]	26	$AlCl_3$	5	−16 to −10	$C_8H_{17}Cl$[d]	28	35
12	A	*n*-PrCl	75	12	$AlCl_3$	6	2 to 6	(II)	7	5
13	A	*i*-BuCl	50[c]	10	$AlCl_3$	5	−25 to −10	(I)	25	38
14	B	*t*-BuBr	80	...	$FeCl_3$	8	30	$Me_3CCH_2CH_2Br$ (III)	27	28
15	B	*t*-BuBr	88	...	$BiCl_3$	4	70	(III)	24	23
16	A	*t*-AmBr	102[c]	35	$AlCl_3$	3	−23 to −17	$EtCMe_2CH_2CH_2Br$ (IV)	48	40
								$C_9H_{19}Br$	30	20
17	B	*t*-AmBr	100	...	$FeCl_3$	8	40	(IV)	30	25
18	B	*t*-AmBr	100	...	$BiCl_3$	10	50	(IV)	14	12

[a] The identity of each product for which a definite structure is given was confirmed by preparing at least one derivative. [b] Approximate values since the amount of ethylene absorbed was determined by increase in weight of the reaction flask. Part of the increase was sometimes due to physical solution. No attempt was made to determine the amount of ethylene which reacted when Method B was used. [c] *n*-Pentane (50 g.) used as diluent. [d] Presumably $Et_2CMeCH_2CH_2Cl$. [e] Based on the alkyl halide charged. In most cases, much unreacted alkyl halide was recovered. Relatively small amounts of higher boiling by-products were obtained.

TABLE II

PROPERTIES OF THE HALOALKANE PRODUCTS

	Haloalkane	B. p.		B. p., °C. at atm. press.	$n^{20}D$	d^{20}_4	Mol. ref.		Analyses, %					
									Found			Calcd.		
		°C.	Mm.				Obs.	Calcd.	C	H	X	C	H	X
I	1-Chloro-3,3-dimethylbutane[a]	41–41	50	115–115	1.4160	0.8670	34.9	34.7	60.14	10.47	29.64	59.72	10.87	29.41
II	1-Chloro-3,3-dimethylpentane	56–57	30	148–149	1.4299	0.8827	39.3	39.3	62.12	10.73	26.85	62.42	11.24	26.36
	Chlorooctane[b]	51–52	8	173–174	1.4370	0.8863	43.9	43.9	64.24	11.81	24.10	64.60	11.53	23.86
III	1-Bromo-3,3-dimethylbutane[c]	54–54	40	138–138	1.4440	1.1556	37.9	37.6						
IV	1-Bromo-3,3-dimethylpentane	51–52	10	167–168	1.4546	1.1497	42.2	42.2	46.53	8.27	45.33	46.92	8.44	44.63
	Bromononane[d]	60–61	3	205–206	1.4630	1.0950	51.9	51.4	52.28	8.93	38.83	52.16	9.25	38.60

[a] This compound was presumably formed by the chlorination of neohexane but was not isolated in pure state; F. C. Whitmore, H. I. Bernstein and L. W. Mixon, THIS JOURNAL, **60**, 2539 (1938). [b] From the reaction of *s*-butyl chloride with ethylene. Probably 1-chloro-3-methyl-3-ethylpentane. [c] M. Delacre, *Chem. Zentr.*, **77**, I, 1233 (1906); F. C. Whitmore and W. R. Trent (to Mallinckrodt Chemical Works). U. S. Pat. 2,022,485 (November 26, 1935); J. J. Strating and H. J. Backer, *Rec. trav. chim.*, **55**, 903 (1936); P. D. Bartlett and L. J. Rosen THIS JOURNAL, **64**, 545 (1942). [d] From the reaction of *t*-amyl bromide and ethylene (Expt. 16).

Experimental[5]

Condensation of Alkyl Halides with Ethylene

Method A.—The experiment was carried out in a three-necked flask which was equipped with an inlet tube, a mercury-sealed stirrer, and a reflux condenser. The alkyl halide and a diluent, *n*-pentane, when used, were placed in the flask and then cooled to about −60° by immersion in a Dry Ice–acetone-bath. The catalyst was added, the bath was removed, and ethylene was passed into the well-stirred mixture by means of a tube dipping below the surface of the liquid. The temperature of the liquid was permitted to rise until absorption of the olefin began (determined by the difference in rate of bubbling in inlet and exit bubbler). The temperature was then maintained at about that point either until the desired amount of olefin (determined by increase in weight) was absorbed or until absorption no longer occurred. The product was then cooled to about −40°, the liquid product was decanted from the catalyst; washed, dried, and distilled under reduced pressure through a 14-inch total reflux fractionation column.[6]

Method B.—The alkyl halide was weighed into a glass liner, cooled to about −78°, and the catalyst was added. The liner was sealed into an Ipatieff-type rotating autoclave of 850 cc. capacity which was then charged to about 40–50 atmospheres pressure with ethylene. The autoclave was rotated at the desired temperature four hours, more ethylene being added if the pressure fell below 25 atmospheres, allowed to set overnight, and then opened and the product worked up as in Method A.

Method C.—A larger scale experiment was carried out under superatmospheric pressure in an autoclave equipped with a very efficient stirrer (a "turbomixer"). Anhydrous ferric chloride (34 g.) was sealed into the autoclave which

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(5) Microanalyses by Dr. T. S. Ma, University of Chicago.

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

was then cooled in a Dry Ice–acetone-bath; it was evacuated, and *t*-butyl chloride (800 cc., 680 g.) was sucked in. Stirring was started, ethylene was pressed in to 25 p.s.i.[7] pressure and the temperature was permitted to rise to −10° at which point rapid absorption of the olefin occurred. The pressure dropped to 0 and the temperature rose to 8° in one minute. The cooling bath was replaced and ethylene was recharged to 10 p.s.i. The pressure dropped to 0 in one minute. Intermittent recharging of ethylene was continued for one hour, the reaction temperature being maintained at −5 to 5°. At the end of this period, absorption took place slowly even when the ethylene pressure was increased to 100 p.s.i. Stirring was stopped and the liquid product was discharged. There was obtained 810 g. of a pale amber liquid which was washed, dried, and distilled. The recovered catalyst was a coagulated brown solid, wet with liquid product.

Identification of Products

1-Chloro-3,3-dimethylbutane.—The chloride was converted (by means of the Grignard reaction) to neopentylcarbinol which was characterized by its 3,5-dinitrobenzoate, m. p. 83.5°, which yielded an α-naphthylamine addition compound, m. p. 133°. These melting points were in good agreement with those previously reported.[8]

The anilide was prepared from the chlorodimethylbutane by the method of Schwartz and Johnson,[9] white needles from dilute alcohol, m. p. 138–139°.

1-Bromo-3,3-dimethylbutane.—This bromohexane yielded the same anilide as was obtained from 1-chloro-3,3-dimethylbutane; m. p. and mixed m. p., 138–139°.

The carbon skeletal structure of the bromide was confirmed by refluxing it with ethanol in the presence of zinc dust. Neohexane (b. p. 49–50°, $n^{20}D$ 1.3688) was obtained.

1-Chloro-3,3-dimethylpentane.—Conversion of this chloride to the hydroxyl compound (either by heating with water and magnesia at 225° or via the Grignard reagent) yielded a new heptanol, shown to be 3,3-dimethylpentanol by oxidation to the known 3,3-dimethylpentanoic acid.

The 3,3-dimethylpentanol boiled at 78–79° (20 mm.) and 163–164° (745 mm.); $n^{20}D$ 1.4275; d^{20}_4 0.8320; mol. ref. obs. 35.82, calcd. 35.82.

Anal. Calcd. for $C_7H_{16}O$: C, 72.33; H, 13.89. Found: C, 72.01; H, 13.30.

The 3,5-dinitrobenzoate of the heptanol melted at 50–51°.

Anal. Calcd. for $C_{14}H_{18}N_2O_6$: N, 9.03. Found: N, 9.03.

The α-naphthylamine addition compound of the 3,5-dinitrobenzoate melted at 114–115°.

Anal. Calcd. for $C_{24}H_{27}N_3O_6$: N, 9.27. Found: N, 9.15.

Oxidation of the heptanol to **3,3-dimethylpentanoic acid** was accomplished by stirring 6 g. with alkaline permanganate at 0° for four hours and at room temperature for twelve hours. The product was worked up in the customary manner. Distillation yielded 5 g. of the acid, b. p. 201–202°. It was converted to the acyl chloride by reaction with thionyl chloride and thence to the amide,[10] m. p. 76–77° and the anilide,[10] m. p. 105–106°.

The 1-chloro-3,3-dimethylpentane was further characterized by preparing[9] the corresponding anilide, m. p. 95–96°, obtained as soft white needles by recrystallization from methanol.

1-Bromo-3,3-dimethylpentane.—Reduction of this bromide with zinc and alcohol yielded pure 3,3-dimethylpentane, b. p. 86°, the identity of which was confirmed by its infrared spectrum.[11]

The bromoheptane yielded an anilide identical with that obtained from the analogous chloro compound.

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Summary

1. The condensation of alkyl halides with ethylene in the presence of a metal halide of the Friedel–Crafts type yields higher molecular weight primary alkyl halides.

2. *t*-Butyl and *t*-amyl chlorides react with ethylene to yield 1-chloro-3,3-dimethylbutane and 1-chloro-3,3-dimethylpentane, respectively. The analogous products are obtained when the *t*-alkyl bromides are used.

3. Condensation of isopropyl chloride with ethylene yields 1-chloro-3,3-dimethylpentane, the reaction proceeding via the isomerization of the primary product, isoamyl chloride. *s*-Butyl chloride reacts similarly, yielding a chlorooctane believed to be 1-chloro-3-methyl-3-ethylpentane.

4. Isomerization of *n*-propyl chloride and isobutyl chloride to isopropyl chloride and *t*-butyl chloride, respectively, precedes their condensation with ethylene. The respective products are 1-chloro-3,3-dimethylpentane and 1-chloro-3,3-dimethylbutane.

5. A new heptanol, 3,3-dimethylpentanol, is reported.

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[7] P.s.i. signifies pounds per square inch (gage).

[8] P. Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938). The very easily prepared and useful α-naphthylamine addition compounds of 3,5-dinitrobenzoates do not seem to have received the wide usage they deserve.

[9] 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).

[10] N. L. Drake, E. M. Kline and W. G. Rose, *ibid.*, **56**, 2076 (1934).

[11] Analysis by Dr. W. S. Gallaway of this Laboratory.