[Contribution from the Research and Development Laboratories, Universal Oil Products Company]

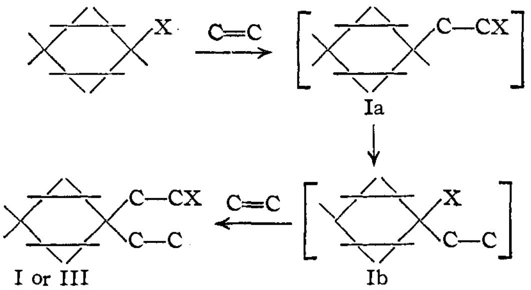
Condensation of Saturated Halides with Unsaturated Compounds. V. Condensation of Cycloalkyl Halides with Ethylene and with Vinyl Halides

By Louis Schmerling

The condensation of alkyl chlorides and bromides with olefins,[1] cycloölefins[2] and haloölefins[3] in the presence of metal halide catalysts was described in previous papers in this series. Examples of the reaction of cycloalkyl chlorides and bromides with ethylene and chloroethylene are given in the present communication (Table I).

The condensation of the tertiary chloride, 1-chloro-1-methylcyclohexane, with ethylene in the presence of aluminum chloride or ferric chloride yielded 1-(2-chloroethyl)-1-methylcyclohexane (II), the product of the addition of the chlorine atom and the 1-methylcyclohexyl group to the double bond of the olefin. Hydrolysis of the chloride yielded an alcohol, presumably 2-(1-methylcyclohexyl)-ethanol.

When the secondary chloride, chlorocyclohexane, was condensed with ethylene, the product was not the expected (2-chloroethyl)-cyclohexane (Ia) but rather 1-(2-chloroethyl)-1-ethylcyclohexane (I) formation of which involved the reaction of two molecular proportions of ethylene



X = Cl or Br

The primary compound, Ia, contains a tertiary carbon atom and readily isomerizes to the tertiary chloride, Ib, which is more reactive than the original secondary chloride and rapidly condenses with ethylene to yield I. Since I does not contain a tertiary carbon atom, it undergoes no further reaction and is, therefore, the principal condensation product. The plausibility of this mechanism and of the structure assigned to the product was indicated by the fact that I was also obtained by the reaction of synthetic 1-chloro-1-ethylcyclohexane (Ib) with ethylene in the presence of aluminum chloride at −10 to 0°.

In a similar manner, the reaction of bromocyclohexane with ethylene in the presence of aluminum chloride produced 1-(2-bromoethyl)-1-ethylcyclohexane (III). That the bromo and chloro compounds had the same carbon skeleton was shown by converting them to the same derivative. Furthermore, condensation of (2-bromoethyl)-cyclohexane (Ia) with ethylene also yielded 1-(2-bromoethyl)-1-ethylcyclohexane, thus furnishing additional evidence in support of the mechanism.

The behavior of the secondary cycloalkyl halides is analogous to that of the secondary alkyl chloride, *s*-butyl chloride, which yielded 1-chloro-3-methyl-3-ethylpentane rather than 1-chloro-3-methylpentane when condensed with ethylene in the presence of aluminum chloride.[1]

The reaction of the halocyclohexanes with ethylene offers a means of synthesizing 1-alkyl-1-ethylcyclohexanes. Thus, reduction of 1-(2-bromoethyl)-1-ethylcyclohexane (III) yielded 1,1-diethylcyclohexane which had not been reported previously.

Condensation of vinyl chloride with chlorocyclohexane, 1-chloro-1-methylcyclohexane, and 1-chloro-1-methylcyclopentane, yielded, respectively, (2,2-dichloroethyl)-cyclohexane, 1-(2,2-dichloroethyl)-1-methylcyclohexane, and 1-(2,2-dichloroethyl)-1-methylcyclopentane. The structure of the (2,2-dichloroethyl)-cyclohexane was proved by hydrolyzing it to cyclohexaneacetaldehyde; that of the 1-(2,2-dichloroethyl)-1-methylcyclohexane was supported by its hydrolysis to an aldehyde identical with that obtained by oxidation of the alcohol prepared via the condensation of 1-chloro-1-methylcyclohexane with ethylene.

(2,2-Dibromoethyl)-cyclohexane was obtained by the reaction of bromocyclohexane with vinyl bromide in the presence of aluminum chloride.

Experimental

Procedures.—The experimental procedures will be summarized very briefly since they were similar to those previously described for the analogous reactions of alkyl halides with ethylene[1] and with haloölefins.[3]

In Method A, ethylene was bubbled through a stirred mixture (cooled to about −60°) of the cycloalkyl halide, *n*-pentane diluent (if used) and the catalyst. The temperature of the mixture was permitted to rise until absorption of the olefin began and was then maintained at about that point for the duration of the experiment.

In Method B, the mixture of reactants (other than ethylene) and catalyst in a glass liner (cooled to about −78°) was sealed into an Ipatieff-type rotating autoclave which was then rotated at room temperature for four hours. When ethylene was used, it was charged to a pressure of 30 atmospheres.

In Method T, the mixture of reactants and catalyst in a large test-tube was shaken manually while the temperature rose gradually from −60° to the temperature of incipient reaction, indicated by the evolution of tiny bubbles of gas. The test-tube was intermittently cooled and warmed until there was little sign of reaction at a temperature at least 10° higher than the original reaction temperature. This method was admittedly crude and was not expected to give the highest possible yields of products;

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[1] L. Schmerling, This Journal, 67, 1152 (1945).

[2] L. Schmerling, *ibid.*, 69, 1121 (1947).

[3] L. Schmerling, *ibid.*, 68, 1650, 1655 (1946).

TABLE I

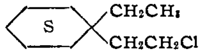
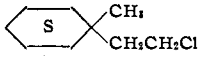
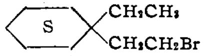
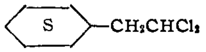
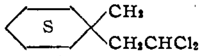
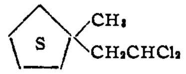
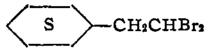
CONDENSATION OF CYCLOALKYL HALIDES WITH ETHYLENE AND VINYL HALIDES

Method	Reactants			Catalyst		Temp., °C.	Duration, hr.	Condensation prod.			Higher boiling prod., g.
	RX[a]	G.	Unsatd. cpd., g.	MX	G.			Compd.	G.	%	
						With ethylene					
A	C_6Cl	50	13[b]	$AlCl_3$	6	−12 to − 8	0.5	I	8	10	9
A	MeC_6Cl	31[c]	15[b]	$AlCl_3$	3	−30 to −25	1.0	II	16	43	12
B	MeC_6Cl	25	10[b]	$AlCl_3$	3	25	4[d]	II	9	30	17
B	MeC_6Cl	15	1[b]	$FeCl_3$	3	25	4[d]	II	2	11	2
A	EtC_6Cl	31[c]	19[b]	$AlCl_3$	5	−10 to 0	1.5	I	11	30	5
A	C_6Br	150[c]	84[b]	$AlCl_3$	10	−20 to −10	1.2	III	65	32	68
A	....[h]	153[c]	21[b]	$AlBr_3$	4	0 to 20	3.0	III	17	10	19
						With vinyl chloride					
T	C_6Cl	120	58	$AlCl_3$	5	−15 to 35[e]	..[e]	IV	65	38	32
B	C_6Cl	50	25	$FeCl_3$	5	23	4[d]	IV	5	7	3
T	MeC_6Cl	33	16	$AlCl_3$	1	−10 to 20	0.2	V	11	23	2
T	MeC_6Cl	50	25	$AlCl_3$	3	−10 to 0	1.0	V	38	52	9
T	MeC_5Cl	16	9	$AlCl_3$	1	0 to 5	0.1	VI	5	20	3
						With vinyl bromide[f]					
T	C_6Br	82	53	$AlCl_3$	1	...[g]	..[g]	VII	24	18	17

[a] C_6Cl and C_6Br = cyclohexyl chloride and bromide, respectively. MeC_6Cl = 1-chloro-1-methylcyclohexane. EtC_6Cl = 1-chloro-1-ethylcyclohexane. MeC_5Cl = 1-chloro-1-methylcyclopentane. [b] Determined by gain in weight of reaction mixture; includes dissolved gas. [c] *n*-Pentane (50 g.) used as diluent. [d] Time during which autoclave was rotated; it was permitted to set at room temperature overnight before it was opened. [e] The reaction mixture was warmed during eight minutes, with intermittent shaking, from −78 to −12°. There was a sudden rise in temperature to 35° even though the reaction tube was immersed in a Dry Ice–acetone-bath. After two minutes at 35–30°, the mixture cooled to −40°. The total reaction time was eleven minutes. [f] Obtained from Westvaco Chlorine Products Corp. [g] The mixture of reactants and catalyst was allowed to warm up from −78 to −40° during six minutes; most of the catalyst dissolved. There was a sudden reaction, the temperature rose to 50° in ten seconds and half of the mixture was blown from the reaction tube. The remaining 67 g. was a deep red solution. The yield shown is that of the product actually isolated. [h] (2-Bromoethyl)-cyclohexane.

TABLE II

PROPERTIES OF THE HALOALKYLCYCLOALKANE PRODUCTS

Compd.	Formula	B. p., °C.	Mm.	B. p. at 760 mm., °C.[a]	n^{20}_D	d^{20}_4	Mol. ref. Calcd.	Mol. ref. Obs.	Analyses[b] Calcd. C	Calcd. H	Calcd. X	Found C	Found H	Found X
I		77–78	3	229–230	1.4750	0.9595	51.0	51.20	...	...	20.31	...	...	20.29
II		59–60	4	202–203	1.4702	0.9626	46.4	46.5	67.25	10.67	22.08	67.20	10.75	22.27
III		86–86	3	239–240	1.4945	1.1854	53.9	53.9	54.78	8.74	36.48	55.13	8.68	36.24
IV		87–87	9	214–214	1.4815	1.1002	46.7	46.8	53.03	7.79	...	53.41	7.92	...
V		79–80	3	228–229	1.4858	1.0941	51.3	51.1	55.37	8.27	36.36	55.22	7.98	36.50
VI		86–87	11	206–208	1.4780	....	46.7	...	53.03	7.79	39.18	52.89	7.84	39.22
VII		100–101	4	252–253	1.5270	1.5729	52.6	52.8	35.30	5.93	58.77	35.95	5.29	58.54

[a] Calculated from boiling point under reduced pressure using nomograph prepared for hydrocarbon conversions. This was found to give accurate results for halogenated derivatives. [b] Microanalyses by Dr. T. S. Ma, then at the University of Chicago, and by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

it had the advantage that the experiments could be carried out quickly.

Materials.—The chloro- and bromocyclohexane were Eastman Kodak Co. products. Vinyl chloride and (2-bromoethyl)-cyclohexane were obtained from The Dow Chemical Company; vinyl bromide, from Westvaco Chlorine Products Corp. The 1-chloro-1-methyl-cyclohexane was prepared in 35% yield by a modification of the method described by Bartlett, Condon and Schneider[4]; an equimolar mixture of methylcyclohexane and *t*-butyl chloride was stirred for one hour with 2% by weight of aluminum chloride at −25 to −10°. The 1-chloro-1-methylcyclopentane and the 1-chloro-1-ethylcyclohexane

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[4] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1534 (1944).

were each obtained in 20% yield in analogous manner. The former boiled at 79–81° at 197 mm. (120–122° at 760 mm.); n^{20}D 1.4452. The latter boiled at 51–53° at 5.5 mm. (183–185° at 760 mm.); n^{20}D 1.4590.

Characterization of the Products

1-(2-Chloroethyl)-1-ethylcyclohexane (I).—The product prepared by the condensation of chlorocyclohexane with ethylene had the same boiling point and refractive index as that obtained by the reaction of 1-chloro-1-ethylcyclohexane with ethylene; the infrared spectra[5] showed that the two were identical (Fig. 1). Furthermore, both were converted to the same anilide, β-(1-ethylcyclohexyl)-propionanilide, by the reaction of the Grignard reagents with phenyl isocyanate[6]; m. p. and "mixed" m. p., 90–91°.

Anal. Calcd. for $C_{17}H_{25}ON$: N, 5.40. Found: N, 5.21.

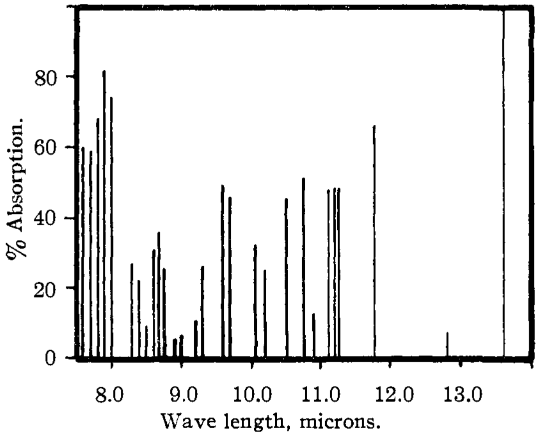

Fig. 1.—Infrared absorption spectrum of 1-(2-chloroethyl)-1-ethylcyclohexane.

1-(2-Bromoethyl)-1-ethylcyclohexane (III).—Both preparations of this compound (*i. e.*, the products of the reaction of ethylene with bromocyclohexane and with (2-bromoethyl)-cyclohexane) yielded the same anilide as did the corresponding chloride (I); m. p. and "mixed" m. p., 90–91°.

The bromide was converted to a new hydrocarbon, 1,1-diethylcyclohexane, by heating a solution of 20 g. (0.09 mole) of the compound in 50 cc. of propanol under reflux for eight hours with 9 g. of zinc granules (which had been pretreated by stirring with a solution of 1 g. of cupric chloride in 30 cc. of water and then washing with ethanol). There was recovered 10 g. (0.07 mole) of liquid boiling at 173–174°; n^{20}D 1.4502.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.62, H, 14.38. Found: C, 85.78; H, 14.20.

1-(2-Chloroethyl)-1-methylcyclohexane (II).—This compound was converted to the corresponding carbinol by heating 8 g. (0.05 mole) with a suspension of 3 g. of magnesium oxide in 110 g. of water in a sealed tube at 225° for four hours. There was obtained 3.5 g. (0.02 mole) of 2-(1-methylcyclohexyl)-ethanol, b. p. 82° at 3 mm.; n^{20}D 1.4686.

Anal. Calcd. for $C_9H_{18}O$: C, 75.98; H, 12.76. Found: C, 76.17; H, 12.49.

The 3,5-dinitrobenzoate derivative of the alcohol melted at 95°.

Anal. Calcd. for $C_{16}H_{20}N_2O_6$: N, 8.33. Found: N, 8.38.

The α-naphthylamine addition compound of the 3,5-dinitrobenzoate melted at 107°.

The alcohol was oxidized by the repeated insertion of a hot, partially oxidized copper wire spiral (heated in flame) in the boiling liquid (0.5 cc.) and its vapor. The product yielded a 2,4-dinitrophenylhydrazone, m. p. 84–85°. There was no depression of the melting point when this derivative was mixed with the analogous derivative prepared, as shown below, from the aldehyde obtained by hydrolyzing 1-(2,2-dichloroethyl)-1-methylcyclohexane (V).

(2,2-Dichloroethyl)-cyclohexane (IV).—A mixture of 13 g. (0.07 mole) of the dichloride, 4 g. (0.1 mole) of magnesium oxide and 100 g. of water in a sealed tube was heated at 250° for four hours. There was obtained 5 g. (0.04 mole) of cyclohexaneacetaldehyde, b. p. 36–37° at 3 mm. (178–179° at atmospheric pressure); n^{20}D 1.4668. The aldehyde yielded a 2,4-dinitrophenylhydrazone, m. p. 114°.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.08.

The melting point of the semicarbazone of the aldehyde depended on the temperature at which the sample tube was inserted in the bath. It ranged from 155–156.5° (insertion at 145°) to 159° (insertion at 158°).

Anal. Calcd. for $C_9H_7ON_3$: N, 22.93. Found: N, 22.50.

Various melting points are reported in the literature for the semicarbazone of cyclohexaneacetaldehyde: 132–134°,[7] 153°,[8] 162°[9] and 171–172°.[10]

1-(2,2-Dichloroethyl)-1-methylcyclohexane (V).—When 21 g. (0.11 mole) of this dichloride was heated at 225° with 4.5 g. (0.1 mole) of magnesium oxide and 100 cc. of water, there was obtained 9 g. (0.06 mole) of aldehyde, presumably 1-methylcyclohexaneacetaldehyde, b. p. 78–80° at 12 mm.; n^{20}D 1.4728. The analytical data indicated that the aldehyde was impure, a possible contaminant being 1-(2-chlorovinyl)-1-methylcyclohexane. No attempt was made to purify the product.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 71.18; H, 10.03.

The semicarbazone and 2,4-dinitrophenylhydrazone derivatives prepared from the impure aldehyde melted at 177–178° and 84–85°, respectively. The latter derivative did not depress the melting point of the analogous derivative of the aldehyde obtained by oxidizing the alcohol prepared by hydrolyzing 1-(2-chloroethyl)-1-methylcyclohexane (II). This may be taken as mutual confirmation of the structures assigned to compounds II and V.

Anal. Calcd. for $C_{10}H_{19}ON_3$ (semicarbazone): N, 21.30. Found: N, 20.82.

Anal. Calcd. for $C_{15}H_{20}O_4N_4$ (dinitrophenylhydrazone): N, 17.49. Found: N, 17.12.

Acknowledgment.—The author wishes to thank Mr. E. E. Meisinger for assistance with part of this work.

Summary

Condensation of the tertiary chlorides, 1-chloro-1-methylcyclohexane and 1-chloro-1-ethylcyclohexane, with ethylene in the presence of aluminum chloride results in the formation of 1-(2-chloroethyl)-1-methylcyclohexane and 1-(2-chloroethyl)-1-ethylcyclohexane, respectively.

Condensation of the secondary cyclohexyl hal-

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(5) The author is indebted to Dr. W. S. Gallaway, Physics Division, Universal Oil Products Company, for the infrared absorption analysis. For a description of the procedure used see THIS JOURNAL, **69**, 1124 (1947).

(6) A. M. Schwartz and J. R. Johnson, *ibid.*, **53**, 1063 (1931); see also, H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2117 (1934).

(7) (a) O. Wallach, *Ann.*, **359**, 313 (1908); (b) E. Venus-Danilova, *Ber.*, **61**, 1954 (1928).

(8) A. Skita, *ibid.*, **48**, 1694 (1915).

(9) F. Sigmund, *Monatsh.*, **49**, 271 (1928).

(10) H. Rupe, W. Messner and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

ides, chlorocyclohexane or bromocyclohexane, with ethylene yields the 1-(2-haloethyl)-1-ethylcyclohexanes, the reaction proceeding via the isomerization and subsequent condensation (with a second molecule of ethylene) of the primary product, (2-haloethyl)-cyclohexane.

(2,2-Dihaloethyl)-cycloalkanes are obtained by the reaction of vinyl chloride (or bromide) with chlorocyclohexane (or bromocyclohexane), 1-chloro-1-methylcyclohexane, and 1-chloro-1-methylcyclopentane.

A number of apparently new products including 1,1-diethylcyclohexane, 2-(1-methylcyclohexyl)-ethanol and crystalline derivatives, and 1-methylcyclohexaneacetyldehyde and crystalline derivatives have been prepared during the characterization of the condensation products.

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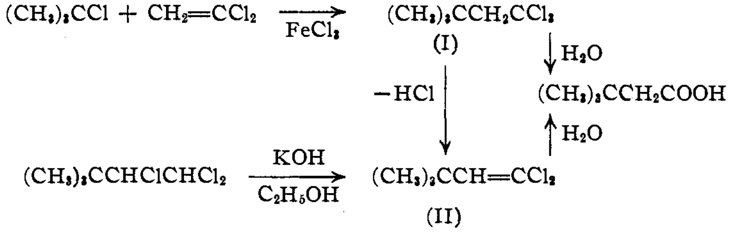
[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Condensation of Saturated Halides with Unsaturated Compounds. VI. Condensation of Alkyl and Cycloalkyl Chlorides with Vinylidene Chloride[1]

BY LOUIS SCHMERLING

The condensation of alkyl chlorides with 1,1-dichloroethylene (*i. e.*, vinylidene chloride) in the presence of metal halide catalysts offers a convenient means for preparing 1,1,1-trichloroalkanes and 1,1-dichloro-1-alkenes. Thus, for example, the ferric chloride catalyzed reaction of *t*-butyl chloride with the dichloroethylene yields both 1,1,1-trichloro-3,3-dimethylbutane (I) and its dehydrochlorination product, 1,1-dichloro-3,3-dimethyl-1-butene (II), the relative amounts of the two products depending on the reaction conditions.



When the temperature was kept at −10 to +10° (chiefly at −10 to 0°), a 65% yield of I and a 13% yield of II were obtained. At a somewhat higher temperature (8–23°) the yields were reversed, a 60% yield of II and a 14% yield of I being obtained.

It is interesting to note that no carbon skeletal rearrangement accompanied the formation of the dichlorohexene by the dehydrochlorination of the 1,1,1-trichloro-3,3-dimethylbutane. Confirmation of the structures of the two products is found in the fact that each yielded *t*-butylacetic acid when heated with water at 275°. The dichloride was shown to be identical with that obtained by the reaction of 1,1,2-trichloro-3,3-dimethylbutane with alcoholic potash.

The reaction of isopropyl chloride with vinylidene chloride at 0–25° in the presence of aluminum chloride resulted in a 30% yield of 1,1-dichloro-3-methyl-1-butene. The primary product, 1,1,1-trichloro-3-methylbutane was obtained in low yield only; the major portion underwent dehydrochlorination to the dichloropentene, the hydrogen chloride adding to the vinylidene chloride to form 1,1,1-trichloroethane which was also obtained in 30% yield. The structure of the 1,1-dichloro-3-methyl-1-butene was indicated by the fact that it was identical with the product of the the dehydrochlorination of 1,1,2-trichloro-3-methylbutane.

The reaction of vinylidene chloride with cyclohexyl chloride in the presence of aluminum chloride proceeded in a similar manner to that with isopropyl chloride. The principal product (30–50% yield) was the dichloroölefin, 1,1-dichloro-2-cyclohexylethylene, rather than the saturated trichloride, 1,1,1-trichloro-2-cyclohexylethane. 1,1,1-Trichloroethane was again obtained as by-product in yield corresponding to the hydrogen chloride evolved during the conversion of the intermediate trichlorocyclohexylethane to the dichlorocyclohexylethylene. Hydrolysis of the dichloride yielded cyclohexaneacetic acid.

Experimental

Procedures.—The procedures were similar to those previously described for the condensation of alkyl halides with haloölefins.[2] In Method T, the mixture of reactants and catalyst in a large test-tube was shaken intermittently at the temperature range shown in the table. In Method S, the mixture of reactants was gradually added to a stirred mixture of the catalyst and *n*-pentane diluent.

Identification of Products.

1,1,1-Trichloro-3,3-dimethylbutane (I).—A sealed tube containing 12.5 g. of the trichloride and 150 cc. of water was heated at 275° for four hours in a rotating autoclave. There was obtained 5.5 g. of organic acid, b. p. 182–183°; $n^{20}D$ 1.4153. It crystallized when cooled to 0°. Its *p*-phenylphenacyl ester melted at 92°. *t*-Butylacetic acid boils at 183°, melts at 6° and yields a *p*-phenylphenacyl ester[3] melting at 92°.

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[1] Preceding paper in this series, THIS JOURNAL, **71**, 698 (1949).

[2] L. Schmerling, *ibid.*, **68**, 1650 (1946).

[3] F. Wrede and A. Rothhaas, *Ber.*, **67**, 739 (1934).