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.

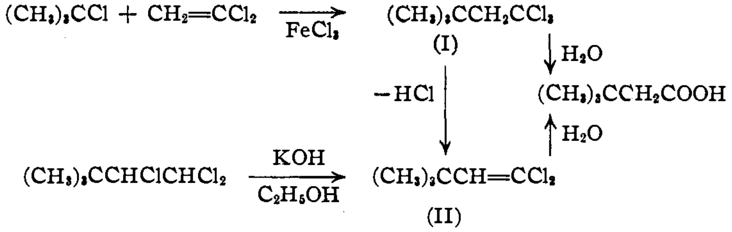
RIVERSIDE, ILL. RECEIVED JULY 22, 1948

[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.



$$\begin{tikzcd}
(CH_3)_3CCl + CH_2{=}CCl_2 \arrow[r, "FeCl_3"'] & (CH_3)_3CCH_2CCl_3 \text{ (I)} \arrow[dd, "-HCl"'] \arrow[dr, "H_2O"] & \\
& & (CH_3)_3CCH_2COOH \\
(CH_3)_3CCHClCHCl_2 \arrow[r, "KOH", "C_2H_5OH"'] & (CH_3)_3CCH{=}CCl_2 \text{ (II)} \arrow[ur, "H_2O"'] &
\end{tikzcd}$$

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).

TABLE I

CONDENSATION OF SATURATED CHLORIDES WITH VINYLIDENE CHLORIDE

Method	Reactants: Satd. RCl	Reactants: Chloride, g.	Reactants: $CH_2{=}CCl_2$,[a] g.	Catalyst MX	G.	Temp., °C.	Duration, hr.	Chief products: Compd.	Chief products: G.	Chief products: %	Higher boiling prod., g.
T	*t*-BuCl	98	93	$FeCl_3$	2	−10 to 10	0.8	I	119	65	
								II	19	13	1
T	*t*-BuCl	47	40	$FeCl_3$	1	8 to 23[b]	0.5	I	11	14	
								II	38	60	1
S	*i*-PrCl	95	117	$AlCl_3$	9[c]	1 to 20[c]	3.0	III	51	30	
								V	48	30	15
T	*c*-$C_6H_{11}Cl$	67	50	$AlCl_3$	2	...[d]	..[d]	IV	45	48	
								V	21	30	11
S	*c*-$C_6H_{11}Cl$	140	114	$AlCl_3$	6	0 to 20	1.5	IV	64	30	
								V	48	30	21

[a] Obtained from The Dow Chemical Co., redistilled immediately before use. [b] The catalyst was added to the mixture of reactants cooled to 8° by immersion in an ice–water-bath. The temperature rose to 23° and then dropped to 10° in two minutes. It was permitted to set at about this temperature for twenty minutes more, after which it was washed, dried and distilled. [c] The mixture of reactants was added during one and one-half hours to a stirred suspension of 4 g. of aluminum chloride in 62 g. of *n*-pentane at 1–3°. Additional catalyst (5 g.) was added and the temperature was permitted to rise (stirring continued) to 20° during the next one and one-half hours. [d] The catalyst was added to the mixture of reactants at −70° and the temperature was permitted to rise. A sudden reaction occurred at −20°; the temperature rose to 35° for a moment and then dropped to −10° when immersed in the bath at −78°. The total reaction time was three to four minutes.

TABLE II

PROPERTIES OF THE POLYCHLORO PRODUCTS

Compd.	Formula	B. p., °C.	B. p., 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. Cl	Found C	Found H	Found Cl
I	$(CH_3)_3CCH_2CCl_3$	64–65	18	166–167	1.4608	1.1644	44.6	44.6	38.00	5.85	56.15	38.26	6.03	55.75
II	$(CH_3)_3CCH{=}CCl_2$	55–56	39	138–139	1.4537	1.0588	39.2	39.1	47.06	6.59	46.35	46.90	6.71	46.20
III	$(CH_3)_2CHCH{=}CCl_2$	50–51	71	118–119	1.4454	1.0686	34.6	34.6	43.19	5.80	51.01	43.21	5.84	50.92
IV	*c*-$C_6H_{11}CH{=}CCl_2$	95–96	19	204–205	1.4948	1.1236	46.3	46.4	53.63	6.76	39.61	53.86	7.11	39.35
V	CH_3CCl_3	...	..	73–74	1.4375									

[a] Calculated from boiling point under reduced pressure using nomograph prepared for hydrocarbon conversions. This was found to give accurate results for halogenated hydrocarbons. [b] Microanalyses by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

1,1-Dichloro-3,3-dimethyl-1-butene (II).—The hydrolysis of 12 g. of this dichloride was carried out using the same procedure as was used for the trichloride. The sealed tube broke during the heating. The product which was recovered from the autoclave was made alkaline and ether extracted. About 5 g. of unreacted dichloride was recovered from the ether. Acidification of the alkaline solution yielded 1.5 g. of organic acid, m. p. 0–5°, the *p*-phenylphenacyl ester of which melted at 92°. There was no depression of the melting point of this ester when it was mixed with the corresponding derivative of the acid derived from 1,1,1-trichloro-2,2-dimethylbutane.

Further evidence in support of the structure assigned to dichlorodimethylbutene was obtained by showing that the same compound was obtained by the dehydrochlorination of 1,1,2-trichloro-3,3-dimethylbutane (prepared by the condensation of *t*-butyl chloride with *cis*-dichloroethylene[4]). Fifteen grams (0.08 mole) of the trichloride was added to a solution of 10 g. (0.18 mole) of potassium hydroxide in 40 cc. of ethanol. The temperature rose to 45° and potassium chloride began to precipitate out. The mixture was permitted to set overnight, the potassium chloride (6 g., 0.08 mole) was filtered off, and the filtrate was washed, dried and distilled. There was obtained 6.0 g. (0.04 mole) of product boiling at 55° at 40 mm. (138°

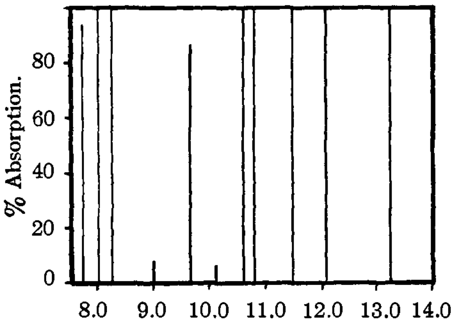

Fig. 1.—Infrared absorption spectrum of 1,1-dichloro-3,3-dimethyl-1-butene.

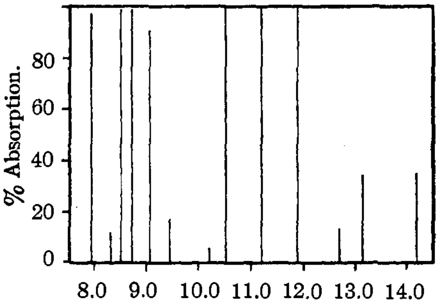

Fig. 2.—Infrared absorption spectrum of 1,1-dichloro-3-methyl-1-butene.

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[4] L. Schmerling, THIS JOURNAL, 68, 1655 (1946).

at 760 mm.); n^{20}_D 1.4530. The infrared absorption spectrum[5] of this product was identical with that of II (Fig. 1).

1,1-Dichloro-3-methyl-1-butene (III).—The infrared spectrum of this compound was identical with that of the product obtained by the dehydrochlorination of 1,1,2-trichloro-3-methylbutane, the condensation product of isopropyl chloride and *cis*-dichloroethylene[4] (Fig. 2). The dehydrochlorination of 17 g. (0.10 mole) of the trichloride by the procedure described above for the dehydrochlorination of 1,1,2-trichloro-3,3-dimethylbutane yielded 6 g. (0.08 mole) of potassium chloride and 6.5 g. (0.05 mole) of product boiling at 115–116° at atmospheric pressure; n^{20}_D 1.4460.

1,1-Dichloro-2-cyclohexylethylene (IV).—Hydrolysis of 10 g. of this compound by heating with 100 g. of water at 275° for four hours yielded 5 g. of an organic acid boiling at 244–247° and melting at 28–29°. It yielded an amide melting at 166–167°. The reported[6] properties of cyclohexaneacetic acid are: b. p. 245–247°; m. p. ranging from 27 to 32–33°; amide, m. p. 168°, 171–172° (cor.).

Acknowledgment.—The author wishes to thank Mr. J. P. West for assistance in this work.

Summary

The condensation of *t*-butyl chloride with vinylidene chloride in the presence of ferric chloride yields a mixture of 1,1,1-trichloro-3,3-dimethylbutane and 1,1-dichloro-3,3-dimethyl-1-butene, the relative amounts of the two products depending chiefly on the reaction temperature.

The aluminum chloride catalyzed condensation of the secondary chlorides, isopropyl chloride and cyclohexyl chloride, with vinylidene chloride yields as major products the unsaturated dichlorides, 1,1-dichloro-3-methyl-1-butene and 1,1-dichloro-2-cyclohexylethylene respectively. 1,1,1-Trichloroethane, formed by the hydrochlorination of vinylidene chloride is a by-product in both cases.

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[5] The author is indebted to Dr. W. S. Gallaway, Physics Department, Universal Oil Products Company, for the infrared absorption analyses reported in this paper. For a description of the procedure used, see THIS JOURNAL, **69**, 1124 (1947).

[6] Beilstein, 4th ed., Vol. IX, p. 14.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ST. VINCENT COLLEGE]

Furfuryl and Thenylalkylamines from Schiff Bases[1,2]

BY BERTIN L. EMLING, J. E. BEATTY AND J. R. STEVENS

A number of secondary amines have been prepared[3] by the action of organomagnesium halides on Schiff bases. However, since none of the furfurylideneamines or thenylideneamines have as yet been utilized in this type of reaction, it was decided to investigate their behavior. Six isomeric alkylfurfurylamines have been prepared as represented by the equations

$$C_4H_3OCHO + H_2N{-}R' \xrightarrow{(-H_2O)}$$

$$C_4H_3O{-}CH{=}N{-}R' + RMgBr \xrightarrow{\text{(hydrolysis)}}$$

$$C_4H_3OCH(R){-}NHR' \quad (1)$$

One thenylamine, $C_4H_3S{-}CH(C_2H_5){-}NH(C_4H_9)$, was also prepared from thenylidenebutylamine and ethylmagnesium bromide. The Schiff bases prepared and used in the syntheses are listed in Table I. The methyl- and ethylfurfurylideneamines were prepared by Schwabbauer[4] who lists only their boiling points. The remaining Schiff bases are not described in the literature. Table II lists the furfurylamines, synthesized from the Schiff bases, and their α-naphthylurea derivatives. The ureas were prepared from the amines and α-naphthyl isocyanate.

TABLE I

N-ALKYLFURFURYLIDENEAMINES

Amine	B. p., °C.	Mm.	Yield, %	n^{20}_D	d^{20}_4	N Analyses, % Calcd.	Found
Methyl	53	16	85	1.5269	1.025	12.8	12.6
Ethyl	67	18	86	1.5170	0.988	11.4	11.2
Propyl	87-88	21	90	1.5105	0.967	10.2	10.1
Butyl	90	13	90	1.5057	0.950	9.26	9.21
Amyl	104–105	10	85	1.5024	0.940	8.48	8.35
Butyl[a]	112-113	13	90	1.5459[b]	0.990[b]	12.0	11.9[c]

[a] Thenylideneamine. [b] n^{25}_D and d^{25}_4. [c] *Anal.* Calcd. for $C_9H_{13}S$: S, 19.2. Found: S, 19.1.

Gilman, Kirby and Kinney[3c] reported a case of 1,4-addition to benzophenone anil under reaction conditions involving high temperature and a long period of heating. While we were of the opinion that 1,2-addition to the carbon–nitrogen structure took place under the mild conditions used in our reactions we desired to prove this. For this purpose one of the furfurylamines was synthesized from furan

$$C_4H_4O + (C_2H_5CO)_2O \xrightarrow{ZnCl_2}$$

$$C_4H_3O{-}COC_2H_5 \xrightarrow{NH_2OH}$$

$$C_4H_3O{-}C(NOH)C_2H_5 \xrightarrow[C_2H_5OH]{Na}$$

$$C_4H_3O{-}CH(NH_2)C_2H_5 + C_4H_9I \xrightarrow{\text{xylene}}$$

$$C_4H_3O{-}C(H)(NHC_4H_9)(CH_2CH_3) \quad (I)$$

The amine, I, was not isolated but reacted in ligroin with α-naphthyl isocyanate to give the corresponding urea, 1-butyl-1-(α-ethylfuryl)-3-(α-naphthyl)-urea.

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[1] Presented before the Organic Division at the 114th meeting of the American Chemical Society, Washington, D. C., Aug. 30–Sept. 3, 1948.

[2] The authors wish to acknowledge the assistance of John Heid, Harvey Patterson, Glenn Johnson, Ernest Goral, Thomas Solomon and Walter Hubis in some of the experimental work.

[3] (a) Campbell, *et al.*, THIS JOURNAL, **70**, 3868 (1948); (b) Moffett and Hoehn, *ibid.*, **69**, 1792 (1947); (c) Gilman, Kirby and Kinney, *ibid*, **51**, 2252 (1929).

[4] Schwabbauer, *Ber.*, **35**, 410–415 (1902).