

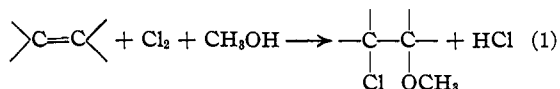
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Chlorination of Olefins in Reactive Solvents with *t*-Butyl Hypochlorite¹

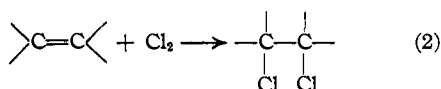
BY CARL F. IRWIN AND G. F. HENNION

Introduction

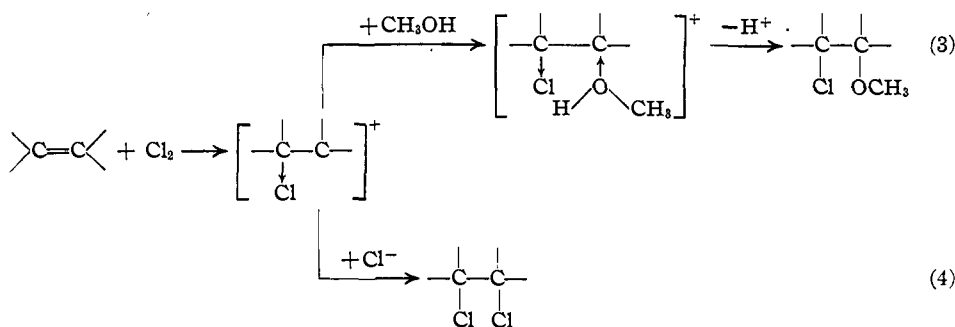
The previous six papers in this series¹ describe chlorination reactions of some unsaturated compounds in reactive solvents, *i. e.*, solvents which may participate in the over-all reactions, *e. g.*



When free chlorine is used in such processes the products are contaminated seriously with the compounds formed by the addition of chlorine only.



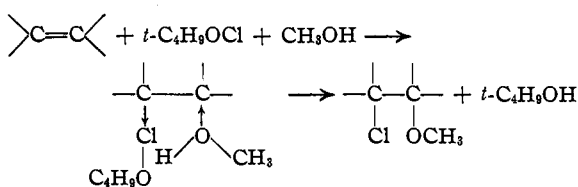
The extent of reaction (2) presumably depends on the chloride ion concentration of the reacting system. The two reaction mechanisms may be formulated on an electronic basis as follows



Some investigators have attempted to suppress (2) by neutralization of the hydrogen chloride formed or better by fixation of the chloride ion as an insoluble precipitate. Mercuric oxide,² silver nitrate,³ calcium carbonate,⁴ and ammonia⁵ have been used in this way. When no fixing agent is used the competing reactions proceed as shown in Table I where yield data are given for the chlorination of three olefins in methanol solution.

Reactions of type (1) or (3) may be favored also by the use of a chlorinating agent having only

“positive” or electrophilic halogen. The solvent then becomes the nucleophilic reagent. In this way β -halo-ethers and similar compounds may be prepared through the action of trinitro-bromomethane,⁶ monochlorourea,⁷ or *N,N*-dichlorobenzene sulfonamide.⁸ Some time ago the authors successfully employed *t*-butyl hypochlorite as the source of chlorine for the preparation of several methyl β -haloalkyl ethers.



The literature revealed that Harford had recently used this reagent for the preparation of chlorohydrin esters⁹ and chlorohydrins¹⁰ by reaction in acetic acid solution and in the presence of

water, respectively. When this work was nearly completed, a third Harford patent¹¹ disclosed the use of *t*-butyl hypochlorite for the preparation of

TABLE I
REACTION OF CHLORINE WITH OLEFINS IN METHANOL^a

Olefin	Wt., g.	Wt., g.	Product % Composition	
			Dichloride	Chloroether
Cyclohexene	82	92.8	17.6	82.3
1-Heptene	98	119.7	31.6	68.3
3-Hexene	42	40.1	34.7	65.2

^a Four moles methanol per mole of olefin; temperature held at 30–35°.

(1) Paper 7 on halogenation in reactive solvents; previous paper, *THIS JOURNAL*, **62**, 1368 (1940).

(2) Carius, *Ann.*, **126**, 197 (1863).

(3) Meinel, *ibid.*, **516**, 231 (1935).

(4) Petrov, *Acta Univ. Voronegisis*, **8**, No. 2, 59 (1935); *C. A.*, **32**, 4525 (1938).

(5) Petrov and Morgun, *ibid.*, **8**, No. 2, 54 (1935); *C. A.*, **32**, 4525 (1938).

(6) Schmidt and Bartholome, *Ber.*, **57B**, 2039 (1924).

(7) Detouef, *Bull. soc. chim.*, **31**, 102 (1922).

(8) Likhosherstov, *et al.*, *J. Gen. Chem.* (U. S. S. R.), **8**, 370 (1938); *C. A.*, **32**, 5369 (1938). *Cf.*, *ibid.*, **32**, 4524, 4525, 6623 (1938).

(9) Harford, U. S. Patent 2,054,814 (Sept. 22, 1938).

(10) Harford, U. S. Patent 2,107,789 (Feb. 8, 1938).

(11) Harford, U. S. Patent 2,207,983 (July 16, 1940).

TABLE II
 PRODUCTS FROM *t*-BUTYL HYPOCHLORITE REACTIONS

Olefin	Solvent	Product	Yield, %	°C.	B. p., Mm.	n_D^{20}	d_4^{20}	Chlorine, % Calcd. Obsd.	
Propylene	MeOH	1-Cl-2-MeO-propane	22.4	100-101 ^a	743	1.4147 ^a	1.0057 ^a		
Propylene	MeOH ^b	1-Cl-2-MeO-propane	56.2						
Trimethyl- ethylene	MeOH ^b	2-Cl-3-Me-3-MeO-butane	38.0	134-135	749	1.4279	0.9759	26.0	25.6
Trimethyl- ethylene	MeOH ^b	2-Cl-3-Me-3-MeO-butane	45.2 ^c						
2-Pentene	MeOH ^b	2-Cl-3-MeO-pentane	77.7	75-77	100	1.4246	0.9665	25.9	26.4
Cyclohexene	MeOH ^b	1-Cl-2-MeO-cyclohexane	66.3	73-74	20	1.4648	1.0646	23.9	25.1
3-Hexene	MeOH ^b	3-Cl-4-MeO-hexane	62.8	94-95	98	1.4288	0.9548	23.6	24.3
1-Heptene	MeOH	1-Cl-2-MeO-heptane	40.5	123	100	1.4330	.9473	21.6	23.4
2-Pentene	EtOH ^b	2-Cl-3-EtO-pentane	57.0	69-70	50	1.4236	.9454	23.6	25.6
1-Heptene	EtOH ^b	1-Cl-2-EtO-heptane	70.4	98	28	1.4320	.9283	19.8	21.2
1-Heptene	<i>n</i> -PrOH ^b	1-Cl-2-PrO-heptane	59.7	104-105	20	1.4337	.9197	18.4	19.7
1-Heptene	<i>n</i> -BuOH ^b	1-Cl-2-BuO-heptane	59.7	128-129	30	1.4359	.9104	17.1	17.0
Ethylene	HO(CH ₂) ₂ Cl	2,2'-di-Cl-diethyl ether	60.8 ^d	176-178 ^e	752	1.4568 ^e	1.2135 ^e		
Ethylene	HOAc	1-Cl-2-AcO-ethane	53.2	141-142 ^f	738	1.4235 ^f	1.1460 ^f		
Propylene	HOAc	1-Cl-2-AcO-propane	72.0	147-149	745	1.4223	1.0788	26.0	25.9
Trimethyl- ethylene	HOAc	2-Me-2-AcO-3-Cl-butane	22.4 ^g	99-101	100	1.4320	1.0400	21.5	21.7
2-Pentene	HOAc	2-Cl-3-AcO-pentane	65.0	73-75	20	1.4299	1.0331	21.5	22.5
3-Hexene	HOAc	3-Cl-4-AcO-hexane	58.8	124-126	100	1.4340	1.0159	19.9	20.2
1-Heptene	HOAc	1-Cl-2-AcO-heptane	55.6	119-120	20	1.4367	0.9969	18.4	18.7
Propylene	PhOH ^h	1-Cl-2-PhO-propane	35.5	110-113	22	1.5218	1.1020	20.8	20.1
1-Heptene	PhOH ⁱ	1-Cl-2-PhO-heptane	38.4	138-140	8	1.5053	1.0198	15.6	14.4

^a Dewael, *Bull. Soc. Chim. Belg.*, **39**, 395-401 (1930). ^b *p*-Toluenesulfonic acid (0.5 g.) added as catalyst. ^c Reaction carried out at a low temperature (5°C.). ^d Corrected for 5.7 g. of recovered ethylene chlorohydrin. ^e Kamm and Waldo, *THIS JOURNAL*, **43**, 2223 (1921). ^f Weber, Hennion and Vogt, *ibid.*, **61**, 1457 (1939). ^g In addition there was obtained 36.3 g. of 2-Cl-3-Me-2-butene, a 47.5% yield; b. p. 91-92° (741 mm.), n_D^{20} 1.4320, d_4^{20} 0.9096. ^h Dissolved in 225 ml. benzene. ⁱ Dissolved in 100 ml. benzene.

chlorohydrin ethers. Meanwhile the present authors had prepared a variety of chloroethers and esters by the *t*-butyl hypochlorite method, using notably primary alcohols, acetic acid and phenol as reactive solvents.¹² The reactions appear to be acid-catalyzed, as was observed previously¹⁰ in the chlorohydrin synthesis. We have found small amounts of *p*-toluenesulfonic acid effective in improving the processes both in reaction rate and yield. The reagents and products are listed in Table II.

Experimental

Reagents.—*t*-Butyl hypochlorite was prepared by a modification of the method of Chattaway.¹³ Chlorine was introduced well below the surface of a cold aqueous solution of *t*-butyl alcohol and sodium hydroxide (in a molar ratio of 1:2) contained in a three-necked, round-bottom flask equipped with a liquid-seal stirrer, chlorine inlet and an exit tube. Chlorine was introduced until no more was absorbed. The reaction mixture separated into two layers. The upper oily layer was saved. The hypo-

chlorite was washed with strong sodium carbonate solution and dried over calcium chloride just before use.¹⁴

Propylene and ethylene were the ordinary commercial chemicals. 1-Heptene was prepared by the procedure of Kistiakowsky;¹⁵ b. p. 93-95° (753 mm.), n_D^{20} 1.3999, d_4^{20} 0.694. 3-Hexene was obtained from the Jackson Laboratory of the du Pont Company and was redistilled; b. p. 66-67° (744 mm.), n_D^{20} 1.3910. Cyclohexene was prepared by the method of Dehn and Jackson;¹⁶ b. p. 83-83.5° (750 mm.), n_D^{20} 1.4470. Trimethylethylene was prepared by dehydration of *t*-amyl alcohol; b. p. 35-36° (745 mm.), n_D^{20} 1.3818. 2-Pentene was prepared by dehydrating diethyl carbinol; b. p. 35-36° (752 mm.), n_D^{20} 1.3857. The other chemicals were reagent grade or the equivalent.

Reaction of Chlorine with Olefins in Methanol.—Olefins were treated with chlorine in methanol solution by the method of Norris, Vogt and Hennion¹⁷ and the reaction mixture treated in a similar manner. Each prod-

(14) *t*-Butyl hypochlorite should be handled with care. It is particularly susceptible to photochemical decomposition which may occur with explosive violence. Certain of its reactions also are dangerously vigorous. In the present work washed and dried *t*-butyl hypochlorite was used without distillation. Containers were stored in a refrigerator and were brought into the laboratory only after they were well wrapped in towels. Bright light was avoided at all times.

(15) Kistiakowsky, *THIS JOURNAL*, **58**, 139 (1936).

(16) Dehn and Jackson, *ibid.*, **55**, 425 (1933).

(17) Norris, Vogt and Hennion, *ibid.*, **61**, 1460 (1939).

(12) The products reported in this paper are for the most part new compounds and are not described in the older literature or in the Harford patents.

(13) Chattaway, *J. Chem. Soc.*, **123**, 2999 (1923).

uct, a mixture of dichloride and chloroether, distilled over a very narrow temperature and refractive index range, and could not be separated by fractionation through a glass helix packed, total-condensation, partial take-off type column, the packed section having the dimensions 33×1.5 cm. Percentage composition of the product was determined by analysis for total chlorine and this was checked by extraction of the chloroether with concentrated sulfuric acid in which the dichlorides are not soluble.

The following procedures for the hypochlorite reactions illustrate the various modifications used.

Preparation of β -Chloroisopropyl Methyl Ether.—The apparatus consisted of a wide mouthed bottle of about 500 ml. capacity, equipped with a dropping funnel, a reflux condenser, a thermometer which extended to within 3 cm. of the bottom and a gas diffuser which extended to the bottom of the bottle. One-half gram *p*-toluenesulfonic acid was dissolved in 64 g. (2 moles) of methyl alcohol and the solution placed in the bottle. Propylene was then passed into the solution while 54.2 g. (0.5 mole) of *t*-butyl hypochlorite was added slowly through the dropping funnel. The solution was not allowed to become very yellow (concentration of hypochlorite kept low) and the temperature was kept at 10°. After all the hypochlorite was added and no more propylene would dissolve, the reaction mixture was poured into a large excess of water, the whole extracted with ether, the ether layer washed with water, dilute sodium carbonate solution, and dried over calcium chloride. The ether was removed by distillation and the residue fractionated through the column described above.

Preparation of 3-Chloro-4-acetoxyhexane.—A solution of 100 g. of acetic acid and 84 g. (1 mole) 3-hexene was placed in a 1-liter, 3-necked, round-bottom flask equipped with a liquid-seal stirrer, a reflux condenser and a dropping funnel. Over a period of two hours 108.5 g. (1 mole) of

t-butyl hypochlorite was added to this solution, with stirring, and the temperature maintained at 30° by external cooling. The reaction mixture was treated as described above except that extraction with ether was not necessary.

Preparation of β -Chloroisopropyl Phenyl Ether.—A solution of 47 g. (0.5 mole) of phenol in 225 ml. of dry benzene was prepared and placed in the apparatus described for the preparation of β -chloroisopropyl methyl ether. Propylene was passed into the solution and 54.2 g. (0.5 mole) of *t*-butyl hypochlorite added over a period of seven to eight hours. After no more propylene would dissolve, the product was poured into water and the benzene layer separated. The benzene extract was washed repeatedly with water, four times with 15% sodium hydroxide, dried over calcium chloride and fractionated.

Miscellaneous.—The other experiments were conducted on a 0.5 to 1.0 mole scale. Reaction temperatures varied from about 5 to 60° depending on the reactive solvent used; cooling was used for the vigorous reactions and heat supplied for those which seemed to be slow. The solvent was used in considerable excess (2 to 6 moles per mol of olefin) while the hypochlorite was always the theoretical amount.

Acknowledgment.—The junior author (C. F. I.) gratefully acknowledges assistance given by the Organic Chemicals Division of the du Pont Company.

Summary

t-Butyl hypochlorite has been found to be an effective reagent for the preparation of chlorohydrin ethers and esters by reaction with olefins and alcohols, phenol or acetic acid. Twenty products are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Solvent Effects in Addition Reactions. II. Addition of Hydrogen Bromide and Chloride to α -Pinene

BY G. F. HENNION AND CARL F. IRWIN

Introduction

In a previous communication¹ it was shown that the character of the solvent influences tremendously the relative rates at which hydrogen bromide and chloride add to cyclohexene and 3-hexene. Under comparable conditions of concentration and temperature these reactions are exceedingly rapid in non-donor solvents and very slow in solvents which act as electron donors. This may be taken to mean that the reactions are most rapid in those solvents in which the hydrogen halides are least soluble.

(1) O'Connor, Baldinger, Vogt and Hennion, *THIS JOURNAL*, **61**, 1454 (1939).

It was thought of interest to repeat these studies with a more reactive olefin. α -Pinene was selected for this purpose since it is known to react (upon heating) even with ammonium chloride, forming bornyl chloride with release of ammonia.²

Solutions of hydrogen bromide (approximately 0.15 *M*) in seven solvents were prepared and these treated with stoichiometric amounts of α -pinene. Relative reaction rates were determined by periodic analyses of the solutions.

In the order of decreasing reaction rates the solvents arrange themselves as follows: chloro-

(2) Aschan, *Översikt Finska Vetenskaps Soc. Förh.*, **88**, 9 (1919); *C. A.*, **14**, 3654 (1920).