amalgams upon (a) electrolysis, (b) treatment with potassium amalgam.

2. Solid amalgams $Hg_{10}Eu$ and Hg_2Eu_3 were prepared.

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

Chlorination of Ethylenic Compounds Containing a Reactive Group with *t*-Butyl Hypochlorite in Methanol Solution[1]

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Introduction

Irwin and Hennion[1] recently described the addition reactions of *t*-butyl hypochlorite in reactive solvents with a number of ethylenic hydrocarbons. The present work extends this study to some ethylenic compounds containing reactive groups, notably allyl chloride, methallyl chloride, allyl alcohol, cinnamic acid, cinnamaldehyde and crotonaldehyde. Most of the reactions were carried out in excess methanol as a reactive solvent and resulted in the addition of a chlorine atom and the methoxyl group to the unsaturated carbon atoms. In all cases the methoxyl group took the position normally occupied by the negative addendum in directed additions to these compounds.

Certain reactive groups in the ethylenic reagents caused side reactions. The action of *t*-butyl hypochlorite in methanol on allyl alcohol yielded two by-products. The first was found to result from the addition of a chlorine atom and the alloxyl group to allyl alcohol. The same product was obtained by the action of *t*-butyl hypochlorite on allyl alcohol in the absence of methanol. The second by-product was assumed to result from the addition of chlorine and the methoxyl group to the alloxyl group of the first by-product. This conclusion was confirmed by synthesis of the compound by the action of *t*-butyl hypochlorite in methanol on the first by-product. Cinnamic acid gave, besides the expected addition compound, the methyl ester of this product. Crotonaldehyde underwent the expected addition with simultaneous oxidation of the compound thus formed to the acid. Actually, the methyl ester of the acid was isolated. The addition product from cinnamic aldehyde did not appear to be oxidized under these conditions. The reagents, products, yields, etc., are summarized in Table I.

The positions taken by the addenda in these reactions were established in various ways. The structure of the addition compound from allyl chloride was established by the close agreement in physical properties with the 1,3-dichloro-2-methoxypropane reported by Fairbourne.[3] The chloro-methoxyl addition product from allyl alcohol, upon reaction with phosphorus pentachloride, yielded a substance which corresponded satisfactorily with the addition product from allyl chloride. Both of the addition products from cinnamic acid have been described and their structures proved by Jackson.[4] The direction of addition to cinnamaldehyde was proved by oxidizing the addition product to the corresponding acid, which was found to be identical with the acid isolated from the addition reaction with cinnamic acid. In the addition products of crotonaldehyde and methallyl chloride and in the by-products of addition to allyl alcohol the orientations of the addenda were not proved but assigned by analogy.

The procedure used in the addition reactions was nearly uniform except that the temperature was varied slightly according to the reactivity of the ethylenic compound employed.

Experimental

Reagents.—*t*-Butyl hypochlorite was prepared by the method of Chattaway,[5] as modified by Irwin and Hennion.[1]

Allyl chloride, methallyl chloride and allyl alcohol were Shell Chemical Company products. The allyl chloride (b. p. 44°) and methallyl chloride (b. p. 70–71°) were distilled. The other chemicals were reagent grade or the equivalent.

Action of *t*-Butyl Hypochlorite on Allyl Chloride in Methanol Solution.—One-half mole (38.5 g.) of allyl chlo-

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(1) Paper 8 on halogenation in reactive solvents; previous paper, THIS JOURNAL, **63**, 858 (1941).

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(3) Fairbourne, *J. Chem. Soc.*, 2232 (1929).

(4) Jackson, THIS JOURNAL, **48**, 2166 (1926).

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

TABLE I

REAGENTS AND PRODUCTS OF *t*-BUTYL HYPOCHLORITE REACTIONS[a]

		Yield,	B. p.,				Chlorine, %		Molecular wt.	
Ethylenic compd.	Product	%	°C.	Mm.	$n^{20}\text{D}$	d^{20}	Calcd.	Obsd.	Calcd.	Obsd.
Allyl chloride	1,3-Di-Cl-2-MeO-propane	44	154–156	730	1.4542	1.2235	49.6	50.0	143.0	136.7
Methallyl chloride	1,3-Di-Cl-2-MeO-2-methylpropane	35	170	748	1.4595	1.1953	45.2	45.5	157.0	153.4
Allyl alcohol[b]	2-MeO-3-Cl-1-propanol	20	68–69	5	1.4535	1.1879	28.5	29.6	124.6	125.2
	2-Alloxy-3-Cl-1-propanol[c]	7	91–92	10	1.4669	1.1270	23.5	24.0	150.6	154.7
	2-(2-MeO-3-Cl-propoxy)-3-Cl-1-propanol[d]	2	123	5	1.4765	1.2589	32.7	32.4	217.1	216.2
Cinnamaldehyde[e]	2-Cl-3-Ph-3-MeO-propanal	35	114	5	1.5115	1.172	17.9	18.4	198.6	216.0
Crotonaldehyde[e]	Methyl 2-MeO-3-Cl-butanoate	30	67–68	6	1.4382	1.1218	21.3	23.2[f]	166.6	169.9
Cinnamic acid[g]	Methyl 2-Cl-3-Ph-3-MeO-propanoate	24	M. 53–54				15.5	15.8		
	2-Cl-3-Ph-3-MeO-propanoic acid	1	M. 161–162 (uncor.)							

[a] Unless otherwise stated methanol (four moles to one of ethylenic compound) was used as solvent. [b] Two moles of methanol used as solvent. [c] Also obtained in 36% yield by reaction of allyl alcohol with *t*-butyl hypochlorite in the absence of methanol. [d] Also obtained in 50% yield by reaction of 2-alloxy-3-Cl-1-propanol with *t*-butyl hypochlorite in methanol solution. [e] Two moles of *t*-butyl hypochlorite used to one of ethylenic compound. [f] Also % OCH_3, calcd., 37.3; obsd., 40.6. [g] 250 cc. methanol as solvent.

ride and 1 g. of *p*-toluenesulfonic acid (as catalyst) dissolved in two moles (64 g.) of methanol was placed in a 1-liter, 3-necked, round-bottom flask equipped with a liquid-seal stirrer, reflux condenser, dropping funnel and thermometer. One-half mole (54.5 g.) of *t*-butyl hypochlorite was added, a few drops at a time, with stirring. The temperature was kept at about 40° by immersing the flask in a heated water-bath. Total time of addition was about three to four hours. The yellow color of the hypochlorite persisted in the reaction mixture throughout the addition. The mixture was allowed to stand overnight and was washed with water, then with dilute sodium carbonate and again with water. It was dried over calcium chloride and fractionated.

Oxidation of 2-Chloro-3-phenyl-3-methoxypropanal.—A mixture of 15 cc. of water, 8 g. of potassium dichromate, 2.5 g. of the aldehyde and 10 cc. of concentrated sulfuric acid was refluxed two hours. The mixture was then diluted with water and the residue collected on a filter. The residue was purified by solution in 5% sodium hydroxide and precipitation with sulfuric acid. A copious precipitate of fine white crystals was thus obtained. The product was recrystallized from carbon tetrachloride. Melting point and mixed m. p. (uncor.) with 2-chloro-3-phenyl-3-methoxypropanoic acid, 161–162°.

Reaction of 2-Methoxy-3-chloro-1-propanol with Phosphorus Pentachloride.—One-fifth mole (25 g.) of the alcohol was placed in a 200-cc. flask and 23.6 g. (0.114 mole) of phosphorus pentachloride added in small amounts with cooling. After all the halide had been added the flask was allowed to stand about one hour and the contents then poured onto cracked ice. The mixture was stirred, neutralized with caustic and again stirred. The heavy oil that formed was separated, and the remaining water solution extracted with ether and the ether combined with the oil. The ether solution was then washed twice with 200 cc. of water. On distillation about 3 g. of colorless liquid b. p. 158–159° (745 mm.) was obtained ($n^{20}\text{D}$ 1.4562). This was dissolved in ether, washed twice with 5% caustic and twice with distilled water, dried and again distilled; yield, 2 g. of liquid, b. p. 158–159°, $n^{20}\text{D}$ 1.4546, d^{20} 1.224.

Crystallization of 2-Chloro-3-methoxy-3-phenylpropanoic Acid and its Methyl Ester.—Both products were crystallized by the procedure described by Jackson.[4] The ester is best crystallized from 75% methanol at about 35° and allowing the solution to cool in a salt–ice-bath.

Summary

t-Butyl hypochlorite in methanol solution has been found to give methoxy chloro addition with ethylenic chlorides, alcohols, acids and aldehydes. The direction of addition was as predicted by theory. Certain reactive groups in the ethylenic compounds caused the formation of by-products.

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