

25.4 g. (0.2 mole) of oxalyl chloride, and 1.2 g. (0.005 mole) of benzoyl peroxide was heated under reflux for twenty-four hours. Fractionation of the mixture yielded 19.0 g. of cyclohexane carboxylic acid chloride, a yield of 65%. Several grams of less volatile material which remained in the distillation vessel gave the usual reactions of acid chlorides, and, apparently, consisted largely of the higher carboxylated derivatives of cyclohexane.

In a similar manner, chlorocyclohexane yielded a mixture of chlorocyclohexane carboxylic acid chloride in 60% yield, and *n*-heptane formed a mixture of octanoic acid chlorides in 50% yield.

Summary

1. The photolysis of oxalyl chloride in the presence of paraffin hydrocarbons leads to the formation of acid chlorides—a reaction involving the direct substitution of hydrogen by the $-\text{COCl}$

group. Cyclohexane, methylcyclohexane, chlorocyclohexane, methylcyclopentane, *n*-pentane, *n*-heptane and isoöctane undergo the reaction.

2. Organic peroxides catalyze a similar *dark* reaction between paraffin hydrocarbons and oxalyl chloride.

3. In both instances it is postulated that the reaction proceeds by means of a chain involving chlorine atoms and alkyl free radicals.

4. The study of the action of oxalyl chloride on pyruvic acid, benzoylformic acid and benzoyl peroxide supports the conclusion that the keto-acid chlorides are not intermediates in the reaction mechanism.

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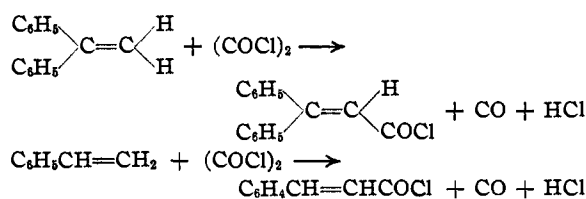
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Carboxylation. II. The Reaction of Oxalyl Chloride with Unsaturated Hydrocarbons

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Under the influence of light, or in the presence of organic peroxides, oxalyl chloride reacts with the paraffin hydrocarbons to form carboxylic acid chlorides. This interesting reaction involving the direct introduction of the chloroformyl group ($-\text{COCl}$) into the paraffin hydrocarbons already has been described.² The present paper deals with the reaction between oxalyl chloride and unsaturated hydrocarbons.

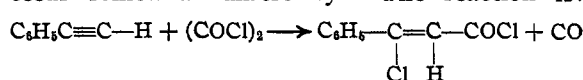
Neither light nor peroxides have any apparent effect upon the action of oxalyl chloride with unsaturated compounds. In the absence of these agents oxalyl chloride reacts with certain olefinic derivatives; gentle refluxing of a mixture of the two components is sufficient to bring about reactions similar to the following:



1,1-Diphenylethylene, styrene, α -methylstyrene, and 1-methylcyclohexene have been shown to

react in this manner. The products are β -phenylcinnamoyl chloride, cinnamoyl chloride, β -methylcinnamoyl chloride, and 1-methylcyclohexene-2-carboxylic acid chloride, respectively. The yields vary from better than 50% for 1,1-diphenylethylene to approximately 6% for 1-methylcyclohexene.

The reaction of phenylacetylene (the only representative of the acetylene series tested) proceeds somewhat differently. The reaction is:



Most of the unsaturated compounds tested do not react with oxalyl chloride under such mild conditions.³ Cyclohexene, trimethylethylene, stilbene, cetene, octene, and 1,2-dichloroethylene, for example, gave negative results. A comparison of the two groups of hydrocarbons indicates that a highly polar double (or triple) bond is a prerequisite for reaction. Those compounds which readily add reagents of the halogen acid type by a polar mechanism ("normal" addition)

(3) These studies of carboxylation form a part of the broader research program dealing with the reactions of atoms and free radicals in solution. The primary object of the present investigation was to determine whether the reactions of oxalyl chloride with olefins proceed through mechanisms involving intermediates of the free radical type. Therefore, the reaction of oxalyl chloride with olefins under the influence of reagents such as aluminum chloride and boron fluoride was not investigated although the yields in the presence of these catalysts might have been higher than those here recorded.

(1) This paper is part of a dissertation submitted by Stephen S. Kane to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Kharasch and Brown, *THIS JOURNAL*, **64**, 329 (1942).

react with oxalyl chloride; those which add such reagents less easily do not react with oxalyl chloride under the mild conditions of the experiments here described.

In view of this observation and because the reaction is neither promoted by the usual catalysts for reactions involving atoms and free radicals nor inhibited by the usual inhibitors of such reactions, it is concluded that the mechanism involved is probably of the polar type involving bond scissions without rupture of the electron pair.

Experimental Part

Materials.—Oxalyl chloride was prepared from anhydrous oxalic acid and phosphorus pentachloride.⁴ Stilbene was obtained by the dehydration of the alcohol formed by the action of benzylmagnesium chloride with benzaldehyde,⁵ and 1,1-diphenylethylene was prepared in a similar manner from the alcohol formed from phenylmagnesium bromide and ethyl acetate.⁶ 1-Methylcyclohexene was obtained by the dehydration of 2-methylcyclohexanol,⁷ and phenylacetylene was prepared from cinnamic acid by the standard procedure.⁸ The other olefins investigated are commercially available chemicals; they were carefully purified before use.

1,1-Diphenylethylene and Oxalyl Chloride.—The apparatus consisted of a simple reflux system with a ground glass joint between the flask and the condenser. A small bubble counter attached to the top of the condenser allowed the course of reaction to be followed by watching the evolution of gas. In a typical experiment, 6.5 g. of diphenylethylene and 4.5 g. of oxalyl chloride were gently heated under reflux for three to four hours. The brown viscous product was diluted with benzene; then the solution was extracted several times with a solution of sodium carbonate. Acidification of the alkaline extract gave 4 g. (50% yield) of a white precipitate which was identified as β -phenylcinnamic acid by its m. p. of 160–162° and its neut. eq. of 225 (the accepted values are 162 and 224, respectively).

Styrene and Oxalyl Chloride.—From 9.5 g. of oxalyl chloride and 28 g. of styrene heated under the reflux for twenty-four hours, there was obtained 1.0 g. (9% yield)

(4) Staudinger, *Ber.*, **41**, 3563 (1908). See also Kharasch and Brown, *This Journal*, **64**, 329 (1942).

(5) "Organic Syntheses," **17**, 90 (1937).

(6) "Organic Syntheses," **6**, 32 (1926).

(7) Sabatier, *Compt. rend.*, **138**, 1323 (1904).

(8) "Organic Syntheses," **2**, 67 (1922).

of cinnamic acid, identified by its m. p. of 129–131° and its neut. eq. of 148 (the accepted values are 132 and 148, respectively).

Phenylacetylene and Oxalyl Chloride.—From 4.0 g. of phenylacetylene and 5.0 g. of oxalyl chloride was obtained 1.1 g. (16% yield) of an acid, identified as the higher melting form of β -chlorocinnamic acid by its constants: m. p. 139–141°, neut. eq. 180 (the accepted values are 143 and 182.5, respectively).

Effect of Experimental Conditions on Yield.—A large number of carboxylation experiments were carried out on 1,1-diphenylethylene in order to determine the effect of the reaction conditions upon the yield. In each instance, the reaction was carried out and the product isolated as already described.

At room temperature, no appreciable reaction occurred in twenty-four hours. As the temperature of the reaction mixture was raised, the rate of formation of the acid increased, but the yield was not markedly affected. The addition of benzoyl peroxide to the reaction mixture lowered the yield to less than 25%. The decrease appears to be due primarily to polymerization of the olefin, a reaction which is catalyzed by peroxide. The yields were slightly less if the reaction mixture was illuminated, probably because of polymerization of the olefin induced by light.

Summary

1. In the reaction between oxalyl chloride and such olefins as 1,1-diphenylethylene, styrene, α -methylstyrene, and 1-methylcyclohexene the chloroformyl group replaces a hydrogen on one of the doubly-bonded carbon atoms. The reaction is: $\text{RHC}=\text{CH}_2 + (\text{COCl})_2 \rightarrow \text{RHC}=\text{CHCOCl} + \text{CO} + \text{HCl}$. Phenylacetylene reacts somewhat differently. The reaction is: $\text{C}_6\text{H}_5\text{C}\equiv\text{CH} + (\text{COCl})_2 \rightarrow \text{C}_6\text{H}_5\text{C}(\text{Cl})\text{C}=\text{CHCOCl} + \text{CO}$.

2. Under the conditions described, cyclohexene, trimethylethylene, stilbene, cetene-1, octene-1, and 1,2-dichloroethylene do not react with oxalyl chloride.

3. The factors influencing the rate of the reaction and the yield indicate that the reaction probably proceeds through a polar mechanism.

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