

probably because of accompanying dissociation into its components.

A mixture of 13.4 cc. of α,α' -lutidine, 13.13 cc. of pyridine, was treated with 13.3 cc. of boron fluoride. A white solid formed. The supernatant liquid was distilled out and identified as α,α' -lutidine by its vapor pressure (6 mm. at 23°). In several trials the recovery corresponded to 77% of the α,α' -lutidine added. The presence of an appreciable amount of pyridine in the volatile product could not be demonstrated. Thus, toward boron fluoride, α,α' -lutidine acts as a weaker base than pyridine.

Summary

1. Trimethylamine forms more stable addition compounds than does pyridine with hydrogen

chloride, hydrogen bromide, borine, and boron trifluoride, whereas with trimethylboron, pyridine forms the more stable compounds.

2. α,α' -Lutidine acts as a stronger base than pyridine toward hydrogen chloride, whereas toward boron trifluoride, pyridine acts as a stronger base.

3. These reactions are explained on the basis of steric strains produced by steric hindrance of the groups about the coordinating central atoms.

4. The significance of the results to the concept of free rotation is discussed.

CHICAGO, ILLINOIS

RECEIVED OCTOBER 25, 1941

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

Carboxylation.¹ I. The Photochemical and Peroxide-catalyzed Reactions of Oxalyl Chloride with Paraffin Hydrocarbons²

BY M. S. KHARASCH AND HERBERT C. BROWN³

The chemical inertness of the paraffinic hydrocarbons as compared with those of the aromatic series has long been a cherished conviction of the organic chemist. The availability and widespread utilization of nitric and sulfuric acids as laboratory reagents probably accounts for this belief. Because these acids react differently toward the two classes of hydrocarbons (under ordinary laboratory conditions), it was natural for the early workers to conclude that the aromatic hydrocarbons were reactive and the aliphatic hydrocarbons inert. That this classification has persisted can be attested by examination of a number of textbooks of organic chemistry. But it is now becoming evident that the term "reactivity" must be carefully defined if it is to have any significant meaning. Reactivity or lack of it as broad terms applying to classes of substances must be abandoned, unless the reactions which are used as the criteria of reactivity are carefully specified. Thus, recent studies of the paraffin hydrocarbons have brought forth abundant evidence that they can be isomerized,

halogenated, sulfonated, and (as will be shown in this paper) carboxylated with the aid of reagents which have little or no effect on aromatic hydrocarbons.

This apparent anomaly is probably due to the fact that substitution reactions in the two series tend to take place by reactions which, in general, follow mechanisms of two distinct types. Substitution reactions in the aromatic series indicate that the mechanism is one involving ionic or polar intermediates. On the other hand, substitution into paraffin hydrocarbons appears to occur most readily by means of chain reactions operating through atom and free radical intermediates.

In the course of the work under way in this Laboratory on chain reactions in solution involving atoms and free radicals, it appeared desirable to investigate means of introducing the carboxyl group directly into aliphatic hydrocarbons. A possible approach to the problem was suggested by the postulated occurrence of the $\cdot\text{COCl}$ free radical as an intermediate in certain photochemical reactions, notably in the formation of phosgene⁴ and in the photochemical decomposition of both phosgene⁵ and oxalyl chloride.⁶ Accordingly, a study of the reaction of phosgene and oxalyl chloride with paraffin hydrocarbons under appropriate experimental conditions was under-

(1) No convenient expression is available for referring to the direct introduction of the chloroformyl group ($-\text{COCl}$) into organic compounds. Rather than coin a new word, the term "carboxylation" has been extended to include this reaction.

(2) Preliminary communication: Kharasch and Brown, *THIS JOURNAL*, **62**, 454 (1940).

(3) Part of the work described in this paper was carried out while H. C. B. was the holder of an Eli Lilly Post-Doctorate Fellowship (1938-1939). The authors wish to express their appreciation to the Eli Lilly Company for the support which made this investigation possible.

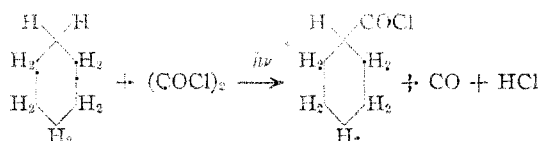
(4) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B2**, 459 (1929).

(5) Montgomery and Rollefson, *THIS JOURNAL*, **56**, 1089 (1934).

(6) Krauskopf and Rollefson, *ibid.*, **58**, 443 (1936).

taken. This paper describes the use of oxalyl chloride as a carboxylating agent; the results obtained with phosgene and diphosgene will be reported later.

In the dark (and in the absence of the peroxides) oxalyl chloride does not react with such typical saturated hydrocarbons as *n*-heptane and cyclohexane even at the boiling point of the mixtures. But if light is not excluded, reaction readily occurs at room temperature with the formation of an acid chloride and the liberation of carbon monoxide and hydrogen chloride. The over-all reaction may be represented as



This reaction appears to be general for the paraffinic and cycloparaffinic hydrocarbons. Among the compounds studied by us which have been found to react may be mentioned *n*-pentane, *n*-heptane, isoöctane, cyclopentane, cyclohexane, methylcyclohexane and chlorocyclohexane. Toluene and similar aromatic hydrocarbons with side chains do not react to any appreciable extent.⁷

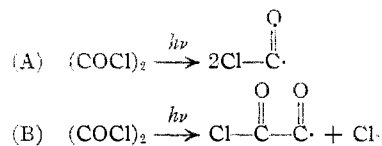
The yields, in those instances which have been carefully studied, appear to be quantitative. That is, within the accuracy of the experimental procedure, a molecule of acid chloride is produced for each molecule of oxalyl chloride. The conversions, on the other hand, vary considerably: from a few per cent. for methylcyclohexane or *n*-heptane to nearly fifty per cent. for cyclohexane itself. The chief cause of low conversions appears to be the formation of colored matter in the reaction mixture. This shields the oxalyl chloride from the effective radiation, thereby decreasing the rate or completely stopping the reaction. This view is supported by two experiments. If a small quantity of this colored material from one reaction mixture (it concentrates in the residue upon fractionation), is added to a fresh reaction mixture, little or no reaction occurs. On the other hand, conversions are markedly increased by illuminating freshly distilled hydrocarbon and oxalyl chloride in what might be termed a continuous process.

Attempts to find catalysts for the photochemical reaction were unsuccessful. Among the substances which have been tested are thiophenol,

pyridine, 2-mercaptothiazole, dioxane, ethyl ether, and iodine.

Inert solvents, such as carbon tetrachloride, have no apparent effect upon the course of the reaction beyond reducing the rate slightly. This effect may be attributed to a decrease in the concentration of the reactants. Benzene, however, strongly inhibits the reaction, apparently by the absorption and degradation of the effective radiation. The fact mentioned earlier that toluene and related hydrocarbons do not undergo the reaction to any appreciable extent is therefore due, in part,⁸ to the presence of the aromatic ring and its effect upon the transmission of the radiation required for the activation of the oxalyl chloride.

As a result of their study of the photolysis of oxalyl chloride in the vapor phase, Krauskopf and Rollefson⁶ concluded that the primary act involves the decomposition of the oxalyl chloride into atoms and free radicals. Two processes are postulated. At low wave lengths (2537 Å.) the reaction is believed to proceed predominantly through the rupture of the carbon-to-carbon bond (A); at high wave lengths (3650 Å.) the predominant process is believed to involve the breaking of the carbon-to-chlorine bond (B).



The absorption of light by oxalyl chloride dissolved in a paraffin hydrocarbon probably results in the same primary step (or steps). Following this primary dissociation, the photolytic fragments must either react rapidly with the solvent or else recombine. According to the Franck-Rabinowitch hypothesis⁹ the photolytic fragments in the liquid phase will be trapped in a cage of solvent molecules and will have but little opportunity to escape and participate in independent secondary processes. The photolysis of oxalyl chloride in an inert solvent should be an exceedingly slow process. This conclusion was tested and verified. The photolysis of oxalyl chloride diluted with carbon tetrachloride is so slow that no appreciable decomposition is observed under conditions leading to 50% reaction in cyclohexane.

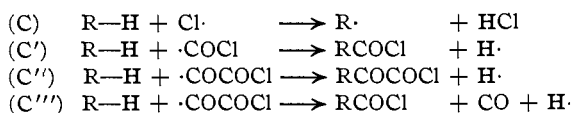
Of the possible reactions (C, C', C'' and C''') of the photolytic fragments with a paraffin hydro-

(8) The reactivity of the aralkyl free radicals such as benzyl, $\text{C}_6\text{H}_5\text{CH}_2\cdot$, must also be considered, Ref. 7.

(9) Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

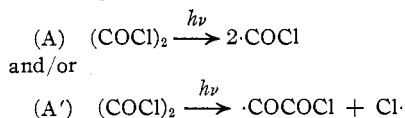
(7) Kharasch, Kane and Brown, forthcoming publication.

carbon, that involving the reaction of a chlorine atom to form a free radical (C) is by far the most probable from considerations of the energy involved.

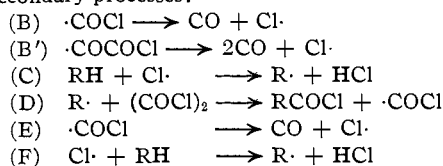


The free alkyl radical must then react either with the remaining photolytic fragment or fragments, or attack another oxalyl chloride molecule, initiating a chain reaction. Until the quantum yield of this reaction is determined, the question cannot be answered unequivocally. However, evidence is available that the reaction is a chain of moderate length. The mechanism we wish to propose for this reaction involves a chain reaction initiated by the chlorine atoms produced as a result of the absorption of the light quanta.

Primary process:



Secondary processes:



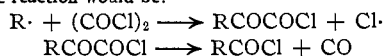
The possible chain-breaking steps are obvious and need not be described.

Several points concerning this mechanism remain to be discussed. In deciding that the free alkyl radical reacts with the oxalyl chloride molecule at the carbon-to-carbon bond to form an acid chloride, rather than at the carbon-to-chlorine bond to form the keto-acid chloride,¹⁰ we are influenced by the following experiments which demonstrate that the α -keto-acid chloride is not an intermediate.

(1) Pyruvic acid, when treated with oxalyl chloride under the conditions of the carboxylation experiments, yields neither the simple keto-acid chloride nor acetyl chloride, but a product of low volatility, which has been tentatively identified as a condensation product of two moles of pyruvyl chloride with one of oxalyl chloride.

(2) Benzoylformic acid by the same treatment

(10) The reaction would be:



yields benzoylformyl chloride which is stable under the experimental conditions.

(3) The decomposition of benzoyl peroxide (a reaction which is postulated to proceed through the formation of free phenyl radicals) in oxalyl chloride forms benzoyl chloride in excellent yield. Neither benzoylformyl chloride nor phenyl chloride could be isolated from the reaction mixture.

This last experiment suggested the possibility of initiating the chain reaction between oxalyl chloride and these paraffin hydrocarbons *in the dark* by the addition of small quantities of organic peroxides. This was tested and verified. The addition of small quantities of benzoyl peroxide to a reaction mixture of cyclohexane and oxalyl chloride induced a reaction in which the conversion was practically complete and the yield, based on oxalyl chloride, of the mono-COCl derivative of cyclohexane was 65%. (Considerable quantities of other substances were formed. These appeared to be the higher carboxylated derivatives, but they were not studied in any detail.) The reaction was extended to other hydrocarbons with similar results. The chain length appears to be rather short, since for satisfactory results about 5 mole per cent. of benzoyl peroxide must be used. We believe that the mechanism is similar to that outlined for the photochemical reaction, the chains being initiated by free radicals produced in the thermal decomposition of the peroxide.

Experimental Part

Methods.—In the preliminary experiments² the hydrocarbon and oxalyl chloride were heated gently under reflux and illuminated by a 300-watt tungsten lamp. No particular precautions were taken to control the intensity of the illumination or to confine it to any particular part of the reaction mixture. Since it appeared desirable to have comparative data on the effect of experimental conditions upon the ease of carboxylation, this procedure was modified, and the experiments reported in this paper were made as follows.

The hydrocarbon and oxalyl chloride, in a ratio of 2 moles to 1, were placed in an elongated flask (Pyrex) fitted by means of a ground glass joint to an efficient condenser. Several of these flasks were fixed in positions equidistant from a mercury arc lamp and illuminated, usually for a period of twenty hours. The illumination was restricted to the liquid phase by carefully shielding the vapor phase. Although no particular effort was made to control the temperature of the reaction mixture, it was found to remain fairly constant in the range from 30 to 35°. As a check upon the reproducibility of the experimental conditions, one of the flasks in each of the experiments was filled with a standard reaction mixture of 0.2

mole of cyclohexane and 0.1 mole of oxalyl chloride. The extent of the reaction, as measured by the yield of the acid chloride from these standard mixtures, rarely varied by more than 10%.

In these experiments the analysis of the reaction mixture was carried out by fractionation, and the acid chloride was isolated, weighed, and identified by standard methods. The loss in weight of the reaction mixture (due to the formation and escape of the gases, carbon monoxide and hydrogen chloride) was found to parallel closely the extent of reaction as determined by fractionation, and in preliminary experiments it was used as a means of following the effect of varying conditions upon the course of the reaction.

Materials.—Oxalyl chloride was prepared from anhydrous oxalic acid and phosphorus pentachloride.¹¹ It was found possible to carry out the preparation without impairment of the yield in quantities five times that recommended by Staudinger and in a considerably shorter time (twenty-four hours), provided the oxalic acid was very finely ground and thoroughly mixed with the phosphorus pentachloride.

The hydrocarbons used in this work were all either commercial products or prepared by standard procedures; they were carefully purified before use.

Photochemical Carboxylation of Hydrocarbons.—A typical experiment with cyclohexane is reported. Cyclohexane, 16.8 g. (0.2 mole), and oxalyl chloride, 12.7 g. (0.1 mole), were placed in the elongated flask (Pyrex) and illuminated by a low pressure mercury vapor lamp (Pyrex) for twenty hours. The loss in weight of the reaction mixture was 4.2 g., indicating that a 60% conversion had occurred. Fractionation of the reaction mixture resulted in the recovery of 5.7 g. (0.045 mole) of oxalyl chloride (b. p. 60–65°) and 8.0 g. (0.055 mole) of cyclohexane-carboxylic acid chloride (b. p. 175–180°; redistilled, b. p. 180–181° mncor.). The acid chloride was identified by a determination of the neutralization equivalent and the preparation of an amide which melted at 185–186°.

Methylcyclohexane¹² yielded 2.9 g. of product [b. p. 107–112° (50 mm.)], which reacted with aqueous ammonia to form an amide. This amide melted over a wide range and was apparently a mixture of isomers. *Anal.* Calcd. for $\text{CH}_3\text{C}_6\text{H}_{10}\text{CONH}_2$: N, 9.93. Found: N, 10.1.

From chlorocyclohexane¹² 3.2 g. of higher boiling material was obtained which was identified as the —COCl substitution product by treatment with aqueous ammonia and analysis of the resulting amide.

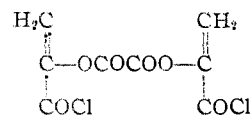
Cyclopentane¹² yielded 2.8 g. of cyclopentane-carboxylic acid chloride [b. p. 85–88° (60 mm.)] which was identified by the preparation of the amide, melting at 177–178°.

The quantity of acid chloride obtained from methylcyclopentane¹² was comparatively small, less than 0.5 g. The low conversion in this and other instances appeared to be, to a large extent, limited by the coloring of the reaction mixture. To test this hypothesis a reaction mixture of methylcyclopentane and oxalyl chloride was heated under reflux and the water-clear stream of condensed hydro-

drocarbon and oxalyl chloride illuminated as it returned to the reaction flask. The conversion was increased sixfold.

n-Pentane, *n*-heptane and isoöctane also gave rather poor conversions. Little was done in these instances beyond establishing the fact that an acid chloride with the correct neutralization equivalent was formed.

Pyruvic Acid and Oxalyl Chloride.—Pyruvic acid was fractionated and the middle fraction [b. p. 82–84° (40 mm.)] collected. To 17.6 g. (0.2 mole) of this material and 16.0 g. of benzene (diluent) contained in a round-bottomed flask, 101.6 g. (0.8 mole) of oxalyl chloride was added carefully. After the first evolution of gas had ceased, the mixture was heated gently under reflux for five hours. The excess oxalyl chloride, 63.0 g. (0.5 mole) was recovered by distillation through a short column and the benzene removed under reduced pressure. Thus 0.3 mole of oxalyl chloride had reacted with 0.2 mole of pyruvic acid. The product was a yellow moderately viscous liquid, which could not be distilled at temperatures as high as 130° (20 mm.). It reacted vigorously with water and with methyl alcohol, giving off fumes of hydrogen chloride. From the aqueous solution oxalic acid was isolated, and the phenylhydrazone of pyruvic acid (decomposing at 190–191°) was precipitated by phenylhydrazine. The neutralization equivalent was determined as 46.6. The following is a possible structure for the compound:



The investigation was not carried further since the results already indicated it to be highly improbable that the keto-acid chlorides could be intermediates in the carboxylation reaction.

Benzoylformic Acid and Oxalyl Chloride.—Benzoylformic acid,¹³ 15.0 g. (0.1 mole), and oxalyl chloride, 50.8 g. (0.4 mole), were heated under reflux for six hours. A 75% yield of benzoylformyl chloride [b. p. 91° (9.5 mm.)]¹⁴ was isolated from the reaction mixture by distillation and identified by the determination of its neutralization equivalent, 83.6 (calcd., 84.2), and by the isolation of the phenylhydrazone of benzoylformic acid (m. p. 157–158°) from the aqueous solution.

Benzoyl Peroxide and Oxalyl Chloride.—Benzoyl peroxide, 24.2 g. (0.10 mole), and excess oxalyl chloride, 76.2 g. (0.6 mole), were heated under reflux in the dark for twenty-four hours. After removal of the unreacted oxalyl chloride, the mixture was carefully fractionated under reduced pressure. Practically all of the higher boiling material distilled at 100 to 110° (50 mm.), and was identified as benzoyl chloride, after redistillation, by means of its physical constants and the preparation of benzamide (m. p. 129–130°). The yield was 70%. No phenyl chloride or benzoylformyl chloride could be isolated. A small quantity of material which did not distill under 200° (50 mm.) was not further studied.

Peroxide-Catalyzed Carboxylation of Hydrocarbons.—A mixture consisting of 25.2 g. (0.3 mole) of cyclohexane,

(11) Staudinger, *Ber.*, **41**, 3563 (1908).

(12) The experiment was carried out as described for cyclohexane above: 0.2 mole of hydrocarbon and 0.1 mole oxalyl chloride.

(13) "Organic Synthesis," **8**, 68 (1928).

(14) Acree, *Am. Chem. J.*, **50**, 393 (1913), reports b. p. 125° (9 mm.).

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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RECEIVED OCTOBER 25, 1941

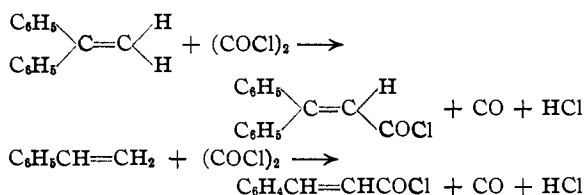
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

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

BY M. S. KHARASCH, STEPHEN S. KANE¹ AND HERBERT C. BROWN

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.

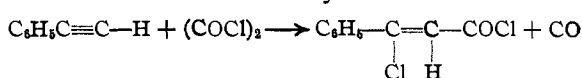
Neither light nor peroxides have any apparent effect upon the action of oxalyl chloride with unsaturated compounds. In the absence of these agents oxalyl chloride reacts with certain olefinic derivatives; gentle refluxing of a mixture of the two components is sufficient to bring about reactions similar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