that the volatiles are mainly neutral compounds. Hydrocarbons and alcohols would not have been retained under the ammoniacal conditions of evaporation.

In order to obtain a general view of what compounds might possibly be contained in the non-volatile neutral fractions of M30 and M31, a one-dimensional chromatogram was run together with the products of a $Ca(OH)_2$ condensation of formaldehyde.[28,29] This condensation yields mixtures of aldoses and ketoses.[29] In Fig. 6 the approximate range for the various sugars is indicated by their carbon number. The possibility exists that carbohydrates in the triose to hexose range may be formed by electron irradiation.

Discussion

Many of the possible reactions of primitive mixtures have been discussed before.[3–20,30,31] The formation of urea in large amounts in one of the irradiated systems here, with none found in a second system, is noteworthy. Because of the 1,3-nitrogen position, urea is used in pyrimidine synthesis and its possible importance in primitive uracil formation was pointed out recently.[32]

We suggest the synthesis of urea through oxidation by the reactions[32]

$$2HCN + 2OH(H_2O_2) \longrightarrow 2HOCN + H_2O$$

$$HOCN + NH_4OH \longrightarrow (H_2N)_2CO + H_2O$$

the latter being the well known Wöhler synthesis. It is possible that phosphine, or other highly reduced phosphorus compounds, are able to scavenge OH radicals and therefore prevent the formation of urea. From this it follows that urea should be formed upon irradiation of aqueous HCN, and, indeed, this could be confirmed.[2b]

Perhaps the most astonishing result which appeared in this initial examination is the fact that very nearly all, that is over 90%, of the material which has reacted under this set of conditions has been accounted for in terms of discrete and distinct compounds as indicated by the paper chromatographic examination of the products. One might have expected as a major product a more or less continuous spectrum of polymeric material as a result of indiscriminate free radical and ionizing synthesis, but this does not appear to be the case.

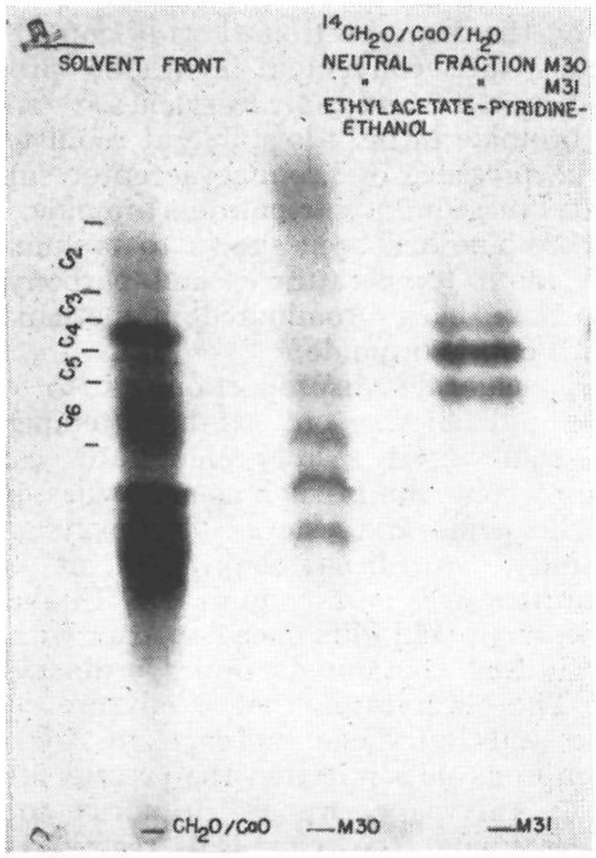

Fig. 6.—Neutral fraction of M30 and M31 in comparison to "formose" from formaldehyde and CaO; solvent: ethyl acetate–pyridine–water 10:3:3.

As yet, we have identified only a few of these compounds, but we are proceeding with the identification of others. It may be expected that as the number of identified chemical species increases, a pattern of chemical transformation under the influence of electron bombardment (as well as other high energy sources) will emerge which will help us in the reconstruction of possible modes of primordial organic synthesis. This will apply to electron beam irradiation and should be extendible to other energy sources such as electric discharge and ultraviolet light as well. These latter two processes have heretofore been considered as the principal energy sources in primordial syntheses.

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(28) R. Mayer and L. Yaescke, *Liebigs. Ann. Chem.*, **635**, 145 (1960).

(29) Unpublished experiments in this Laboratory by R. Ferrier.

(30) S. W. Fox, K. Harada and A. Vegotsky, *Experientia*, **15**, 81 (1959).

(31) S. W. Fox, *Science*, **132**, 200 (1960).

(32) D. Masson, *J. Chem. Soc.*, **91**, 1449 (1907).

[CONTRIBUTION FROM EMERYVILLE RESEARCH CENTER, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Photolyses of Metal Compounds: Cupric Chloride in Organic Media

BY JAY K. KOCHI(1)

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The reactions resulting from the photolysis of cupric chloride in organic solvents have been examined. They can be described as the addition and abstraction reactions of chlorine. Alcohols are converted to carbonyl compounds, olefins to dichlorides and allylic chlorides, and alkanes or aralkanes to the corresponding chlorides. It is tentatively postulated on the basis of the reactivities of substrates and the stoichiometries of the reactions that the photolysis occurs by initial fission to form cuprous chloride and chlorine atoms. Chain termination involves the reaction of cupric chloride with carbon radical intermediates.

Introduction

The relatively accessible oxidation–reduction ranges of copper compounds make them useful agents for electron transfer processes. Thus, cupric ions oxidize iodide, cyanide, sulfite and thiocyanate ions under extremely mild conditions,(2)

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(1) Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.

(2) (a) N. Sidgwick, "Chemical Elements and Their Compounds," Oxford Press, New York, N. Y., 1950, p. 148 ff.; J. Baxendale, D.

similarly, the disproportionations of copper acetylides constitute convenient synthetic procedures for diacetylenes and polyacetylenes.[2b] Although cupric bromide in bulk is stable at room temperature, the presence of bromine acceptor substrates facilitates its reduction to cuprous bromide. Thus, cupric bromide has been shown to brominate olefins at room temperature,[3a] and carbonyl compounds have been brominated in methanol solution with cupric bromide.[3b]

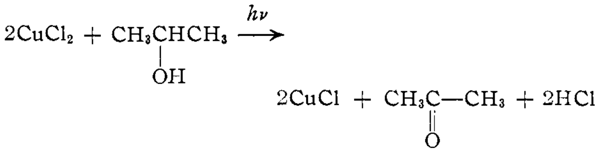
Cupric chloride disproportionates to cuprous chloride and chlorine only at high temperatures; but in solution, it readily chlorinates carbonyl-containing compounds, such as aldehydes, ketones, carboxylic acids and esters.[4] Recently aromatic compounds have been chlorinated at elevated temperatures with cupric chloride.[5] Unlike cupric bromide, cupric chloride does not react with olefins and saturated compounds under ordinary conditions. The observation that a mixture of cupric chloride and butadiene on exposure to sunlight forms cuprous salts initiated the present investigation.[6] In this paper we are primarily concerned with describing the chemical reactions which result from the irradiation of solutions of cupric chloride in *organic media*. A mechanistic study of the photolysis of copper salts in solution will be presented at a later date.

Results

Photolysis of Cupric Chloride in Simple Solvents.—The solubility of cupric chloride in organic solvents is enhanced by lithium chloride.[4] For example, cupric chloride alone is soluble in tetrahydrofuran, acetonitrile and the lower alcohols only to an extent of a few per cent; with the addition of lithium chloride, a 0.5 M solution was easily obtainable. The colors of these solutions varied with the solvent; non-hydroxylic solvents were yellow-brown whereas hydroxylic solvents were generally yellow-green at equivalent concentrations of cupric and chloride ions. The brown solutions are primarily attributed to the presence of higher chloro cupric complexes.[7]

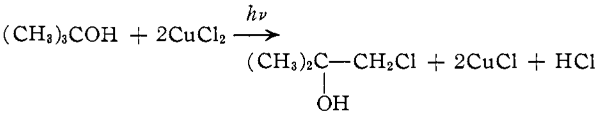
The photolyses were conducted with the unfiltered radiation from a medium pressure mercury lamp through a Vycor vessel at temperatures between 20 and 30°. Acetonitrile and acetic acid were generally unreactive to cupric chloride under these photolytic conditions. n-Butyronitrile, however, reacted readily to form chlorobutyronitriles. Acetonitrile thus served as a useful solvent for investigating the reactions of more reactive compounds.

Isopropyl alcohol was oxidized quantitatively by cupric chloride to acetone. The material balances among cupric, cuprous and chloride ion and acetone and acid indicated the stoichiometry to be



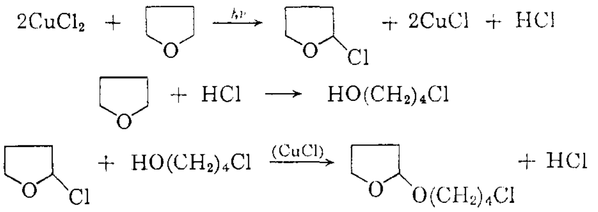
$$2CuCl_2 + CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{h\nu} 2CuCl + CH_3\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3 + 2HCl$$

There was no observed complicating side reaction between acetone and cupric chloride.[4] The low concentration of acetone and the inhibiting effect of acid was undoubtedly responsible for this. Methanol was oxidized to methylal by an analogous reaction but t-butyl alcohol reacted slightly less readily than isopropyl alcohol. The dark brown solution on irradiation was converted to a colorless crystalline mixture. The reaction is



$$(CH_3)_3COH + 2CuCl_2 \xrightarrow{h\nu} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2Cl + 2CuCl + HCl$$

Cupric chloride reacted with tetrahydrofuran at approximately the same rate as it did with isopropyl alcohol. Treatment of the irradiated solution directly with 2,4-dinitrophenylhydrazine reagent (DNP) gave a quantitative yield of γ-hydroxybutyraldehyde dinitrophenylhydrazone. Isolation of the precursors of this aldehyde was difficult. There was obtained in 20% yield a mixture of 2,3-dihydrofuran and 2-chlorotetrahydrofuran. The accompanying product was 2-(4-chlorobutoxy)-tetrahydrofuran (I) isolated in 30% yield. The formations of these products are accounted for by the reactions



I

The acetal I was compared with an authentic compound prepared from the alcohol exchange between 2-butoxytetrahydrofuran and 4-chlorobutanol-1.

Photolysis of Cupric Chloride in the Presence of Hydrocarbons.—A solution of isoprene and acetonitrile reacted with cupric chloride under photolytic conditions to form the isomeric isoprene dichlorides in 76% yield. Titration indicated the absence of acids which result from substitution reactions. The reaction of isoprene in acetonitrile in the presence of acetic acid (3.5 M) and cupric chloride (0.38 M) yielded 89% isoprene dichlorides and less than 5% of chloropentenyl acetates.

Cyclohexene under similar conditions produced 3-chlorocyclohexene and cyclohexene dichloride. Acid titration indicated that 34–37% of the reaction proceeded *via* the former route while the remainder yielded the addition product. Cyclo-

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Westcott, *J. Chem. Soc.*, 2347 (1959); N. Tanaka, M. Kamada, T. Murayama, *Bull. Chem. Soc., Japan*, **31**, 895 (1958); (b) G. Eglinton, A. Galbraith, *Chemistry & Industry*, 737 (1956); D. Behr, G. Eglinton, R. Raphael, *ibid.*, 699 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

(3) (a) G. Coppinger, private communication; (b) A. Fort, *J. Org. Chem.*, **26**, 765 (1961).

(4) J. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

(5) J. Ware and E. Borchert; *J. Org. Chem.*, **26**, 2263, 2267 (1961).

(6) I wish to thank Dr. W. S. Anderson for communicating these results to me.

(7) T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944); E. Doehlemann, H. Fromherz, *Z. physik. Chem.*, **A171**, 353 (1934); G. Spacu and J. Murgulescu, *ibid.*, **A170**, 71 (1934); E. Kosower, *J. Am. Chem. Soc.*, **79**, 1509 (1957).

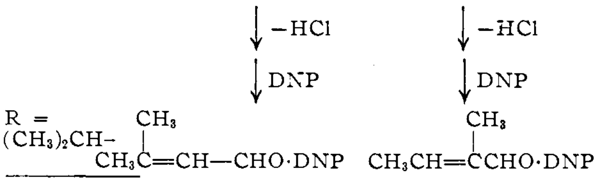
hexene dichloride was isolated in 20% yield and 3-chlorocyclohexene in 35% yield. Cyclohexene was chlorinated with *t*-butyl hypochlorite,[8] by comparison, to yield 3-chlorocyclohexene.

Styrene and cupric chloride reacted in tetrahydrofuran solution to afford styrene dichloride in 87% yield. There was no indication of a mixed styrene-tetrahydrofuran product. Although it is possible that some 2-chlorobutoxy tetrahydrofuran may have been formed (it was not looked for), on the basis of isolated styrene dichloride, a maximum of only 13% cupric chloride could have reacted by this route. When styrene reacted with chlorine at 0° in $CHCl_3$ solution, the predominant products were β-chlorostyrene and styrene dichloride formed in a ratio of 4.5:1.

Toluene in acetonitrile reacted slowly with cupric chloride to form benzyl chloride in 86% (titrated) yield. Benzyl chloride was isolated in 57% yield. In addition there was formed in less than 0.5% yield the isomeric chlorotoluenes and 0.5% bibenzyl.

Although 2,3-dimethylbutane has limited solubility (8–12%) in acetonitrile solutions of cupric chloride, it was possible to chlorinate the mixture over a period of several days. The dilute hexane solution of chlorohexanes contained an 84% yield of the two isomeric chloro-2,3-dimethylbutanes. The chlorohexanes were isolated in 22% yield. Less than 0.2% dichlorohexanes were formed. There was no indication (by G.L.C. analysis) of the presence of hexenes or chlorohexenes in the hexane solution. This obviated the possibility of dehydrochlorination occurring simultaneously; G.L.C. analysis of the hexane solution indicated the ratio of 2-chloro-2,3-dimethylbutane to the 1-chloro isomer to be approximately 0.6. The same ratio of isomers was formed from 2,3-dimethylbutane and chlorine using Russell's procedure.[9]

Photolysis of Cupric Chloride with Isoprene in Reactive Solvents.—The reaction of isoprene in isopropyl alcohol led to a mixture of rather unstable chlorine compounds which could not be isolated pure. In addition to acetone formed in small yields the predominant products were the isoprene dichlorides and chloroisopropoxymethylbutenes, which resulted from the addition of the elements of isopropyl hydrochlorite to isoprene. The latter compounds were unstable and dehydrochlorinated to the two isomeric isopropoxy isoprenes which were identified as the DNP's of the hydrolysis products, tiglaldehyde and senecialdehyde. The postulated reactions[10] can be written as



$$CuCl_2 + C_5H_8 \xrightarrow{ROH} ClCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2OR + ClCH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2OR$$

$$\downarrow -HCl \quad \downarrow DNP$$

$$R = (CH_3)_2CH- \qquad CH_3\overset{CH_3}{\overset{|}{C}}{=}CH{-}CHO\cdot DNP \qquad CH_3CH{=}\overset{CH_3}{\overset{|}{C}}CHO\cdot DNP$$

No mixed products of isopropyl alcohol and isoprene were found. The reaction of isoprene in methanol gave a similarly complex mixture of products. Methanol was competitively oxidized to methylal. The formation of isoprene dichloride and methoxychloropentenes was indicated.

The products from the reaction of isoprene in tetrahydrofuran were those obtained from each component alone, *viz.*, isoprene chloride (18%) and chlorobutoxytetrahydrofuran (10%). In addition there was formed a mixed product, whose structure is postulated to be a chloropentenyltetrahydrofuran.

Discussion

There are several features of the cupric chloride photolysis in organic media which bear consideration. Although quantitative rate measurements were not made, the pattern of reactivities clearly indicates the rate of photoreduction of cupric chloride is dependent on the presence of reactive substrates. Thus acetonitrile and acetic acid, though good solvents for cupric chloride, do not support its reduction. On the other hand, the combination of reactive compounds such as isoprene and cyclohexene in acetonitrile are qualitatively as reactive as isopropyl and methyl alcohols and tetrahydrofuran. Of intermediate reactivity are toluene and dimethylbutane. The limited solubility of dimethylbutane in acetonitrile prevented an assessment of its reactivity. Since an unfiltered mercury radiation was used as a light source, it has not been determined which region of the visible or ultraviolet spectrum is responsible for the photolysis. However, the observation that toluene, a compound quite reactive to free radical chlorinations,[12] is rather unreactive in the photolytic cupric chlorinations is compatible with the inhibitory effect of benzene in tetrahydrofuran under the same conditions. In both cases the presence of an aromatic ring may serve as an internal filter for the photolytic radiations, particularly below 2800 Å. Quantitative measurements, however, are needed to verify these speculations.

The molecular species which is undergoing photolysis appears to be a chlorocupric complex II.[13] The presence of one or more of these complex ions[4] in inorganic media is indicated qualitatively by the

$$Cu^{+2} + nCl^- \rightleftarrows \underset{\text{II}}{CuCl_n^{-n+2}}$$

colors of the solution. Moreover, aqueous cupric chloride solutions of the same concentrations are photolyzed very slowly. Thus, a homogeneous solution of cupric chloride, lithium chloride and allyl alcohol in water on irradiation for 100 hours produced less than 5% cuprous salts. In aqueous solution the chlorocupric complex ions represented

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[8] *Cf.* C. Walling and B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1961).

[9] G. Russell, *ibid.*, **80**, 4987 (1958).

[10] The chloro ethers can arise by one of two paths: (a) isopropoxy radical addition to isoprene followed by reaction with cupric chloride or (b) the alcoholysis of the intermediate isoprene dichloride.[11] Although no direct evidence is at hand, the latter path is preferred.

[11] The heterolysis of organic halides is catalyzed by cuprous chloride (see, *e.g.*, P. Kurtz, *et al.*, *Ann.*, **631**, 21 (1960); M. Farlow, U. S. Patent 2,518,608).

[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 386.

[13] In the absence of quantitative data, the possibility of a binuclear complex, $Cu_2Cl_m^{-m+4}$, cannot be discounted (*vide infra*).

are more highly dissociated than they are in such relatively non-solvating media as acetonitrile.[4]

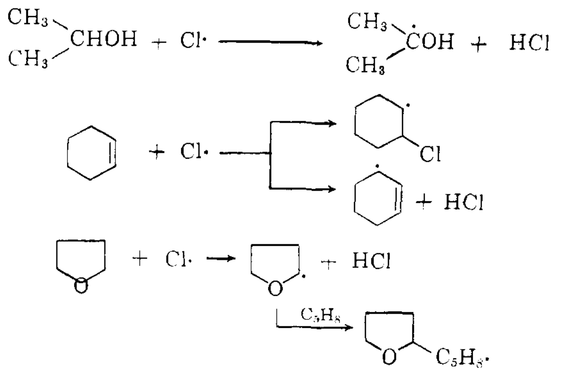
We tentatively postulate that the primary step in the photolysis is

$$\mathrm{CuCl}_n{}^{-n+2} \overset{h\nu}{\rightleftarrows} \mathrm{CuCl}_{n-1}{}^{-n+2} + \mathrm{Cl}\cdot$$

The reversibility of the photolysis step is indicated by the fact that no apparent reaction occurs in either acetonitrile or acetic acid. These solvents are inert to chlorine atoms derived from molecular chlorine.[14]

Secondly, the products of the reaction are characteristic of chlorine atom intermediates. Thus olefins such as isoprene, cyclohexene and styrene form dichloride adducts. Alcohols such as methanol and isopropyl alcohol are converted to the corresponding oxidation products, methylal and acetone. Saturated compounds yield the corresponding halides, such as benzyl chloride from toluene, hexyl chlorides from dimethylbutane and chlorotetrahydrofuran from tetrahydrofuran.

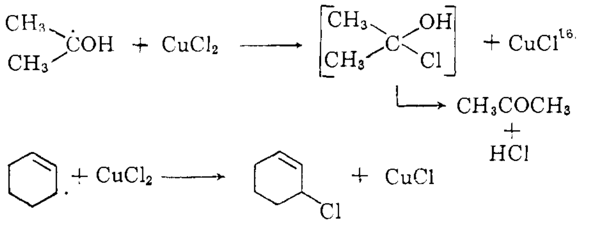
In each case, chlorine atom reactions can be formulated as the second step.



The follow-up reaction is postulated to be one in which cupric chloride serves as a chlorine atom donor to a free radical. The chlorine transfer reaction, employing cupric and ferric halides, have been described recently.[15]

$$\mathrm{R}\cdot + \mathrm{CuCl}_n{}^{-n+2} \longrightarrow \mathrm{RCl} + \mathrm{CuCl}_{n-1}{}^{-n+1}$$

Thus, products observed in the photolysis are consistent with those resulting from the reaction of the free radical intermediates with cupric chloride. For example



$$\mathrm{C_6H_5CH_2}\cdot + \mathrm{CuCl_2} \longrightarrow \mathrm{C_6H_5CH_2Cl} + \mathrm{CuCl}^{17}$$

The selectivity observed in the chlorination of 2,3-dimethylbutane indicates that the species responsible for the abstraction reaction (eq. 28) is essentially the chlorine atom. The isomer distribution between tertiary and primary chlorides has been used by Russell[9] to determine the reactivity of chlorine atoms in various milieu. Since the product distribution is the same for chlorinations with molecular chlorine as it is with cupric chloride, it is assumed that the chain-initiating step is the same in both cases, *viz.*, chlorine atoms. At present this constitutes the best evidence we have for eliminating a charge transfer complex as the reactive chlorinating species. In such a complex III, cuprous chloride

$$[\mathrm{Cl^-}_{n-1}\mathrm{Cu^{II}\ Cl^-} \longleftrightarrow \mathrm{Cl^-}_{n-1}\mathrm{Cu^ICl}\cdot]$$
$$\text{III}$$

could serve as a donor for chlorine atom much as aromatic compounds and carbon disulfide observed by Russell. If such an intermediate were the reactive agent, it would be expected to show enhanced selectivity in hydrogen abstraction reactions, relative to simple chlorine atoms.

The possibility of chlorine molecules as reactive reagents in the photolysis cannot be rigorously discounted at this time.[18] There is some indirect evidence which favors the chlorine atom mechanism. In acetonitrile solution the reaction of isoprene and cupric chloride is largely unaffected by the presence of acetic acid. If isoprene dichloride arose from molecular chlorine, then it would be expected that acetic acid could enter into the reaction to form a chloroacetate. By the chlorine atom mechanism this compound can only arise *via* the slower subsequent solvolysis of isoprene dichloride. Moreover, the products obtained from the addition of molecular chlorine to styrene is primarily *β*-chlorostyrene. From the cupric chloride reaction there is no *β*-chlorostyrene formed, which indicates that a chlorocarbonium ion (or incipient ion) is not formed.

Acknowledgment.—I wish to thank Dr. W. S. Anderson for the original observation which led to these studies and Mr. Fred Rodgers for very helpful technical assistance.

Experimental

Materials. **Cupric chloride** was reagent, Baker and Adamson, $\mathrm{CuCl_2{\cdot}2H_2O}$ heated *in vacuo* to remove water; equiv. wt., 142. **Acetonitrile** was Matheson, Coleman and

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[14] A. Bruylants, M. Tits and R. Danby, *Bull. soc. chim. Belg.*, **58**, 210 (1949); A. Bruylants, M. Tits, C. Dieu and R. Gauthier, *ibid.*, **61**, 266 (1952).

[15] J. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1956); **79**, 2942 (1957); C. Bamford, A. Jenkins and R. Johnson, *Proc. Royal Soc.* (*London*), **A239**, 214 (1957); J. Kumamoto, H. De La Mare and F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

[16] It is conceivable that alcohols react at the hydroxyl group. For example

$$>\mathrm{CHOH} + \mathrm{Cl}\cdot \longrightarrow >\mathrm{CHO}\cdot + \mathrm{HCl}$$
$$>\mathrm{CHO}\cdot + \mathrm{CuCl_2} \longrightarrow >\mathrm{CHOCl} + \mathrm{CuCl}$$
$$>\mathrm{CHOCl} \longrightarrow >\mathrm{C{=}O} + \mathrm{HCl}$$

However, this sequence of reactions is unlikely since *t*-butyl alcohol does not yield acetone and methyl chloride. The *t*-butyl hypochlorite intermediate formed by the oxy radical mechanism does yield these products on photolysis.[1]

[17] Nonhebel has recently treated toluene with cupric halide in a heterogeneous system. The low solubility of cupric halide in toluene precludes the occurrence of the halide transfer reaction with the intermediate benzyl radical. Thus, it is not unexpected that Nonhebel found bibenzyl to be the predominant product (D. C. Nonhebel, *Proc. Chem. Soc.*, 307 (1961)).

[18] For example, it is conceivable that the photodissociation of a binuclear complex, $\mathrm{Cu_2Cl}m^{-m+4}$, or a bimolecular reaction of chlorocupric complexes may lead to chlorine directly. The subsequent photolysis of chlorine molecules would form chlorine atoms.

Bell spectroscopic grade. **Tetrahydrofuran** was du Pont Chemical Co., refluxed and redistilled from $LiAlH_4$ under N_2; b.p. 65–66°. **Isoprene**, Phillips Petroleum Co., polymerization grade, was used as such. **Cyclohexene** Eastman Kodak Co. reagent grade. **2,3-Dimethylbutane**, Phillips Petroleum Co., research grade redistilled was used. **Styrene** was Matheson, Coleman and Bell, redistilled at 90 mm. **Toluene**, J. T. Baker analyzed reagent was used. **Isopropyl alcohol** was Shell Chemical, redistilled from CaH_2.

Analytical Methods.—The determination of the cupric ion was based on the stoichiometric reaction with iodide to produce iodine. The iodine was titrated with standard thiosulfate. Cuprous ion was determined by quenching with ferric nitrate solution and subsequent titration with standard ceric solution. The Volhard analysis for chloride ion was used in reactions where labile alkyl chlorides were formed. The reaction mixture was first quenched in ice-cold ferric nitrate solution and then rapidly extracted with ice-cold pentane to remove the alkyl chlorides. The aqueous solution was analyzed for chloride ion in the usual manner. The ferric nitrate treatment was necessary to oxidize cuprous salts since, in some cases, they were soluble in pentane.

Since cupric ions interfere with the determination of the acid, copper was first precipitated quantitatively with iodide. The liberated iodine was titrated with thiosulfate and the resultant suspension titrated with standard NaOH to the phenolphthalein end-point. In cases where easily hydrolyzed alkyl chlorides were formed, the aqueous cuprous iodide suspension was formed at 0° and then rapidly extracted with *n*-pentane. Centrifuging was necessary in most cases to facilitate the separation of phases. Working rapidly it was possible to effect this separation in 1 to 2 minutes, and with the exception of very labile chlorides the hydrolysis was not a complicating factor.

Qualitative Photolyses.—In order to determine qualitatively the spectrum of reactive substrates, solutions of cupric chloride in sealed Pyrex ampules were exposed to sunlight. Approximately 1 g. of cupric chloride, 0.5 g. of lithium chloride, 8 ml. of inert solvent and 5 ml. of reactant (or 13 ml. of reactive solvent) was exposed to the early winter sunlight. The extent of the reaction was determined by the decolorization (cupric to cuprous) of the solution. Acetonitrile (spectroscopic grade) and acetic acid were unchanged after 20 days. Tetrahydrofuran, methanol, ethanol, isopropyl alcohol and *t*-butyl alcohol were decolorized in 2 to 4 days, with *t*-butyl alcohol the slowest. Acetonitrile solutions containing butadiene, isoprene and cyclohexene were also decolorized after 2 to 3 days. Toluene and 2,3-dimethylbutane in acetonitrile and benzene in tetrahydrofuran were decolorized after 1 to 2 weeks.

Heterogeneous systems were generally quite unreactive. A mixture of butadiene and cupric chloride, although shaken periodically, was practically unreactive (except for slight cuprous chloride formation) for 2 months. Similarly, chloroform and carbon tetrachloride and cupric chloride did not appear to react in 2 months. Although cupric chloride alone was quite insoluble in tetrahydrofuran, it was soluble enough so that a mixture on exposure to sunlight slowly reacted (2 weeks) to form a colorless solution and solid cuprous chloride. The same did not apply to dioxane which was unreactive. In all cases where reaction was evident, the transformation was from a dark brown complex cupric chloride solution or mixture to a clear transparent solution. The transformation is quite dramatic. Exposure of the colorless solution to air, however, resulted in the rapid autoxidation of the cuprous species and concomitant decomposition of the reactive organic chlorides.

Photolyses.—The photolyses were conducted in 500-ml., 1-liter or 2-liter three-necked round-bottom flasks. In the center neck was inserted a water-jacketed Vycor light well. A gas inlet tube and a bubble arrester were connected to the other necks. The light source was a General Electric A100-4 mercury lamp removed from the protective Pyrex sheath. Anhydrous cupric chloride was dissolved in the appropriate solvent with the aid of lithium chloride. The material to be chlorinated was then added to the complex cupric chloride solution and oxygen-free argon was passed over the magnetically stirred solution for 15 minutes. The reaction was then photolyzed keeping the solution under an atmosphere of argon pressure. Samples were periodically extracted to determine the concentrations of the various components.

Acetonitrile.—To a 1-liter reaction vessel containing 850 ml. of acetonitrile, there was added 60 g. of cupric chloride and 25 g. of lithium chloride. The clear dark brown-yellow solution was irradiated nine days at 22–24°. The cupric titer decreased from 25.2 ml. (0.0102 N $S_2O_3^-$) to 24.6 ml. after 125 hr. The cuprous titer increased to 1.2 ml. (0.0986 N Ce^{IV}). In a smaller scale reaction a dark yellow-brown solution of 30 g. of cupric chloride and 10 g. of lithium chloride in 400 ml. of acetonitrile was irradiated at 20–24°. After irradiation for 300 hr., 37% of the cupric salt was reduced. Similar results were obtained with acetic acid.

Isopropyl Alcohol.—A solution (dark green-yellow) of 23.0 g. of cupric chloride and 9.0 g. of lithium chloride in 400 ml. of isopropyl alcohol (freshly redistilled from calcium hydride) was flushed with nitrogen and irradiated at 20–23° for 62 hours at which time the reaction became colorless. One milliliter of the original solution contained the following (by analysis): Cu^{+2}, 0.424 meq.; Cu^+, 0 meq.; Cl, 1.36 meq.; H^+, 0 meq. The irradiated solution contained: Cu^{+2}, 0 meq.; Cu^+, 0.420 meq.; Cl^-, 1.33 meq.; and H^+, 0.395. The irradiated (final) solution was analyzed for carbonyl content (distillation into hydroxylamine hydrochloride) and found to contain 0.18 meq./ml. (theoretical was 0.21 meq.). To a 10-ml. aliquot of the irradiated solution was directly added excess 2,4-DNP reagent in a nitrogen atmosphere and the reaction stirred for 1 hour. Excess ferric nitrate solution was added and the mixture vigorously shaken, poured into water and filtered. The derivative on recrystallization from ethanol was identified as the DNP of acetone (0.413, 0.462 g.; theoretical 0.476 g.). The chloride and acetone balance indicated that the competing reaction between cupric chloride and acetone[4] was negligible under these conditions.

Tetrahydrofuran.—A solution (brown-red) of 80 g. of cupric chloride and 33 g. of lithium chloride in 900 ml. of THF was irradiated at 28–29° until colorless (16 hr.). The colorless solution analyzed for 100% acid and cuprous chloride. The chloride end-point faded rapidly, which indicated the presence of an easily hydrolyzed chloride. A 50-ml. aliquot of the irradiated solution and 50 ml. of water was allowed to stand at room temperature for 6 days. The clear colorless aqueous THF solution was then stirred under nitrogen with 100 ml. of 2,4-DNP reagent overnight, and then added to a solution of 15 g. of ferric ammonium sulfate in 50 ml. of water. The chilled mixture was filtered (3.49 g., theoretical 3.76 g.), and the precipitate recrystallized from absolute ethanol (2.71 g., m.p. 110–114°). Two more recrystallizations yielded yellow needles of the dinitrophenylhydrazone of ω-hydroxybutyraldehyde melting at 115.0–115.5° (lit.[19] m.p. 118°). *Anal.* Calcd. for $C_{10}H_{12}N_4O_5$: C, 44.8; H, 4.5; N, 20.9. Found: C, 44.8; H, 4.6; N, 21.0.

The remainder of the irradiated solution (660 ml.) was vacuum distilled (bath temp. 20°, press. 20 mm.) into a Dry Ice trap. The cuprous chloride residue was extracted with benzene and ether. The organic extracts were combined and washed with ice-cold ferric ammonium nitrate solution, water and dried. Vacuum distillation yielded 15.1 g. of colorless liquid boiling at 77–80° (13 mm.) (n^{25}_D 1.4524). It was 2-(4-chlorobutoxy)-tetrahydrofuran authenticated by a comparison of the infrared spectrum with that of an authentic sample. *Anal.* Calcd. for $C_8H_{15}ClO_2$: C, 53.8; H, 8.5; Cl, 19.8. Found: C, 54.6, 54.4; H, 8.5 8.5; Cl, 16.7, 17.8. It reacted rapidly with 2,4-DNP reagent to form the DNP of ω-hydroxybutyraldehyde. This acetal dissolved slowly in water to give a positive Schiff test, but weak AgCl precipitate. The vacuum distillate (556 g.) consisted mainly of THF. An aliquot was titrated with NaOH (0.289 equiv. acid formed, compared with 0.274 equiv. acid in original reaction mixture). The vacuum distillate was redistilled at 220 mm. to remove THF. The THF distillates, however, were contaminated with materials (dihydrofuran?) which gave a positive Schiff test. The early fractions contained dihydrofuran and HCl since they afforded ω-hydroxybutyraldehyde-DNP. The latter fractions were THF solutions of 2-chlorotetrahydrofuran; they also yielded ω-hydroxybutyraldehyde and decomposed slowly to a black tar. Finally, 2-chlorotetrahydrofuran was isolated (b.p. 26–28° (15 mm.), n^{25}_D 1.4621) in 15% yield. The infrared spectrum was the same as 2-chlorotetrahydrofuran (*vide infra*).

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(19) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 197 (1948).

Synthesis of 2-Chlorotetrahydrofuran.—Tetrahydrofuran (250 ml.) was added to 500 ml. of CCl_4 and de-aerated with nitrogen. Chlorine (83 ml.) was introduced through a sintered glass immersion tube from a measured redistilled supply (1 hour, 83 ml.) at 0 to 10°[20] (bath temp. −30°) into the reaction mixture as it was irradiated with a 100 watt mazda lamp. The solvent and THF were removed and the residual chlorinated material distilled *in vacuo*. There was formed 108 g. of 2-chlorotetrahydrofuran boiling at 34–42° (10 mm.) (n^{25}D 1.4608-1.4658) which darkened rapidly on standing under nitrogen. It reacted with 2,4-DNP reagent to form ω-hydrobutyraldehyde DNP. There was also formed 16 g. of 2,3 dichlorotetrahydrofuran (n^{25}D 1.4725–1.4753) boiling at 48–50° (10 mm.).

Synthesis of 2 Butoxytetrahydrofuran and 3-Chloro-2-butoxytetrahydrofuran.—A mixture of 108 g. of 2-chlorotetrahydrofuran and 16 g. of 2.3-dichlorotetrahydrofuran in 100 ml. of ether was added at 0° to a solution made from 30 g. of sodium in 300 ml. of 1-butanol. The mixture was stirred for 1 hour at 0° and 2 hours at 20° and then poured into an ice–water slurry. The ether extract was washed with dilute NaOH and dried over a mixture of NaOH and $NaHCO_3$. Vacuum distillation yielded 76 g. of 2-butoxytetrahydrofuran boiling at 65–66° (20 mm.) (n^{25}D 1.4213). It yielded a yellow DNP (m.p. 115.0–115.5°). *Anal.* Calcd. for $C_8H_{16}O$: C, 66.7; H, 11.2. Found: C, 66.7; H, 11.2. In addition there was formed 21 g. of 3-chloro-2-butoxytetrahydrofuran boiling at 77–80° (n^{25}D 1.4398–1.4412). *Anal.* Calcd. for $C_8H_{15}O_2Cl$: C, 53.8; H, 8.47; Cl, 19.8. Found: C, 54.7, 54.6; H, 8.6, 8.6; Cl, 19.4. 19.5.

Synthesis of 2-(4-Chlorobutoxy)-tetrahydrofuran.—A solution of 10 g. of 2-butoxytetrahydrofuran and 5.7 g. of 4-chlorobutyl alcohol (Eastman, b.p. 41–42° (8 mm.)) was treated with 1 ml. of a solution consisting of concentrated sulfuric acid (0.1 ml.) and 5 ml. of ether. The mixture was allowed to remain 2 days in the dark and then heated under 50–60 mm. pressure to distil off the 1-butanol. Approximately 1 g. of anhydrous K_2CO_3 was added and the 2-chlorobutoxytetrahydrofuran was obtained (b.p. 54-55° (2.5 mm.), n^{25}D 1.4516–1.4520) in virtually quantitative yields. It readily formed ω-hydroxybutyraldehyde-DNP. *Anal.* Calcd. for $C_8H_{15}O_2Cl$: C, 53.8; H, 8.48; Cl, 19.85. Found: C, 53.8, 53.7; H, 8.5, 8.5; Cl, 20.9, 20.5. Except for a more intense band at 13–14μ the infrared spectrum of 2-(4-chlorobutoxy)-tetrahydrofuran was the same as 2-butoxytetrahydrofuran. Alkoxytetrahydrofurans in general have characteristic absorption bands in the 8–12μ region.

Isoprene in Acetonitrile.—Anhydrous cupric chloride (24 g.) and 8 g. of LiCl was dissolved in 320 ml. of acetonitrile. The solution was swept with nitrogen and 100 ml. of isoprene introduced. The dark yellow-brown solution was photolyzed at 24–25° for 27 hours. The photolyzed solution was light yellow and approximately 5–10 g. of colorless CuCl was precipitated on the sides of the reaction vessel. The colorless solution produced less than 5% acid, which indicated that the reaction went completely by chlorine addition. The irradiated solution was vacuum distilled (bath temp. 25°) leaving a colorless powdery residue (23 g.) which was very lachrymatory. The vacuum distillate was redistilled at 3 mm. to yield 8.5 g. (76%) of isoprene dichloride boiling at 34–36° (3 mm.) (n^{25}D 1.4888). *Anal.* Calcd. for $C_5H_8Cl_2$: C, 43.2; H, 5.8; Cl, 51.0; bromine number, 116. Found: C, 43.0; H, 5.8; Cl, 49.4; 50.7; bromine number, 118.

Cyclohexene in Acetonitrile.—A solution of 60 g. of $CuCl_2$ and 25. g. of LiCl in 1400 ml. of acetonitrile was flushed with nitrogen and 450 ml. of cyclohexene was added. The homogeneous dark yellow-brown solution after irradiation at 27–28° for 36 hours formed a light tan clear solution and approximately 8–10 g. of precipitated CuCl. One ml. of solution originally containing 0.198 meq. of Cu^{+2} produced 0.073 meq. of acid and consumed 0.205 meq. of chloride ions. The amount of acid formed represented 37% of the reaction which proceeded *via* hydrogen abstraction. Chloride ion determination (by titration) indicated that 103% disappeared. The difference (66%) between the chloride ion disappearance and the acid formation represented the amount of the addition reaction. The irradiated solution was cooled to 0° and quickly poured into 1500 ml. of an ice–water slurry. The organic layer was quickly extracted and washed again with 1 liter of an ice–water slurry. The organic layer was washed twice with a ferric solution, once with water and dried over $CaCl_2$ for 15 minutes. Since acetonitrile forms complexes with CuCl, the original aqueous washes were clear and colorless. In the absence of acetonitrile a precipitate of CuCl could be a complicating factor. The excess cyclohexene was removed by vacuum distillation at 75 mm. Further distillation yielded 8.6 g. (35%) of 3-chlorocyclohexene boiling at 47–49° (20 mm.) (n^{25}D 1.4830-1.4838) and 6.5 g. of a fraction which contained cyclohexene dichloride. The cyclohexene dichloride was slightly contaminated with chlorocyclohexene as the analysis shows, but the infrared spectrum was the same as that of an authentic sample (*vide infra*). *Anal.* Calcd. for C_6H_9Cl: C, 61.8; H, 7.28; Cl, 30.4; bromine number, 137. Found: C, 62.0, 60.5; H, 7.8, 7.8; Cl, 30.6, 30.7; bromine number, 132, 130. Calcd. for $C_6H_{10}Cl_2$: C, 47.0; H, 6.6; Cl, 47.1. Found: C, 48.7, 48.2; H, 6.8, 6.7; Cl, 45.2, 45.4.

Cyclohexene (160 ml.) was chlorinated with *t*-butyl hypochlorite (31 g.) in 2 hours at 25–35° using a 100 watt Mazda lamp. The colorless solution was dried with $CaCl_2$ overnight, filtered and distilled. It yielded 22.6 g. of cyclohexenyl chloride boiling at 48–50° (20 mm.) (n^{25}D 1.4862–1.4869). *Anal.* Calcd. for C_6H_9Cl: C, 61.8; H, 7.78; bromine number, 137. Found: C, 62.1, 61.9; H, 7.8, 7.8; bromine number, 132, 130.

Toluene in Acetonitrile.—Cupric chloride (48 g.) and LiCl (20 g.) dissolved in 525 ml. of acetonitrile was flushed with nitrogen. Toluene (300 ml.) was added and the homogeneous dark yellow-brown solution irradiated at 24–28° for 163 hours (total Cu^{+2} was 0.32 equiv.). The reduced solution was a clear light tan solution with approximately 20–30 g. of precipitated cuprous chloride. The mixture was cooled to 0° and added to 1 liter of an ice-water slurry and extracted. The organic phase was washed with dilute ferric solution twice, $NaHCO_3$, and with water and dried over Na_2SO_4. This toluene solution was found to contain 100% (0.159 equiv.) of the bound chlorine. An aliquot reacted with KOH in methanol; the chloride liberated (0.138 equiv.) represented 87% of the chlorine. Toluene was distilled from the solution at 90 mm. Benzyl chloride (12.4 g.) was obtained at 55–59° (10 mm.) (n^{25}D 1.5352–1.5362). The residue (0.85 g.) was analyzed by G.L.C. (5-ft. Apiezon J at 220°. 18.7 min.) to contain benzyl chloride and bibenzyl. The G.L.C. blip was condensed on a salt plate and its infrared spectrum was the same as bibenzyl. Elemental analysis (C, 71.5; H, 6.1; Cl, 22.5) indicated the residue to consist of 80.5% benzyl chloride and 19.5% bibenzyl. *Anal.* Calcd. for C_7H_7Cl: C, 66.5; H, 5.58; Cl, 28.05. Found: C, 66.9, 66.3; H, 5.6, 5.6; Cl, 28.3, 28.5. The benzyl chloride fractions were examined by G.L.C. (6-ft. DC-11 at 100°) for chlorotoluenes. The benzyl chloride (18 minutes) was found to be contaminated by chlorotoluene (12.7 minutes) to the extent of less than 0.5%. The distribution among the isomeric chlorotoluenes was not determined. There was no indication that any benzal chloride or benzotrichloride or any compound containing the –CN group was formed.

2,3-Dimethylbutane in Acetonitrile.—A solution of $CuCl_2$ (51.5 g.) and 20 g. of LiCl in 600 ml. of acetonitrile was flushed with N_2·(Cu^{+2}, 0.343 equiv.). 2,3-Dimethylbutane (250 ml.) was added, but it was soluble in the acetonitrile solution to an extent of only 8–12%. The two-liquid phase system was irradiated with vigorous magnetic stirring for 195 hours at 24–30°. During the irradiation it was necessary to scrape CuCl off the lamp housing. The formation of HCl was evident by the extensive fuming when the vessel was opened to the atmosphere. The irradiated solution consisted of three phases; an upper colorless layer consisting primarily of dimethylbutane, a light green lower acetonitrile solution and precipitated CuCl. A small aliquot of the dimethylbutane solution was removed for G.L.C. analysis. The remainder of the reaction was cooled to 0° and poured into excess ice–water slurry and rapidly extracted. It was washed with ice-cold ferric solution and water and dried over Na_2SO_4. By chlorine analysis of the hexane solution it contained 0.143 equivalent (84%) of bound chlorine. The hexane solutions were analyzed by G.L.C. (5-ft. Apiezon and 5-ft. silicone at 80°) for the two isomeric hexyl chlorides. 1-chloro- and 2-chloro-2,3-dimethylbutane. The ratio, *R*, of the areas of the two chlorides was essentially the same for the crude hexane solution as it was with the washed solution. This indicated that the tertiary chloride was not hydrolyzed during the workup. The ratio of the areas was: *t*-chloride/*p*-chloride, 0.55 (crude hexane solution) and 0.56 (washed

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(20) R. Normant, *Compt. rend.*, **228**, 10 (1948).

solution) on an Apiezon J column, and 0.65 on a silicone column. The washed hexane solution was vacuum distilled to remove unreacted dimethylbutane. The isomeric chlorohexanes (5.9 g.) were obtained as a liquid boiling at 60–67° (100 mm.) ($n^{25}\mathrm{D}$ 1.4196). On the basis of elemental analysis (C, 50.7; H, 8.8; Cl, 38.1), the residue (0.6 g.) was calculated to consist at most of 50% dichlorohexanes. *Anal.* Calcd. for $C_6H_{13}Cl$: C, 59.7; H, 10.88; Cl, 29.4. Found: C, 59.8, 59.8; H, 10.8, 10.8; Cl, 30.0, 30.0. No products containing the CN group were evident.

2,3-Dimethylbutane was also chlorinated at 26° by the method described by Russell.[8] It was chlorinated at two chlorine concentrations, using (A) 2.28 g. and (B) 4.56 g. of chlorine. The crude solution and that after a $NaHCO_3$ wash were analyzed by G.L.C.: solution A: $R = 0.58$ (crude solution) and 0.59 (washed solution) on Apiezon J column; 0.66 on silicone column; solution B: $R = 0.66$ (crude) and 0.69 (washed) on Apiezon J and 0.72 on silicone column.

Styrene in Tetrahydrofuran.—A solution of 60 g. of $CuCl_2$ and 23 g. of LiCl in 500 ml. of THF was flushed with nitrogen and 305 g. of styrene (freshly redistilled) added. The homogeneous dark yellow-brown solution was irradiated at 21–24° for 43 hours. The solution was then chilled to 0° and added to a mixture of 500 ml. of ether and 500 ml. of ice-water at 0°. The ethereal extract was washed with water three times, dried with Na_2SO_4 and the light yellow solution distilled. It gave 32 g. of styrene dichloride boiling at 52–56° (1.2 mm.) ($n^{25}\mathrm{D}$ 1.5452) and 5.9 g. of residue ($n^{25}\mathrm{D}$ 1.5431). *Anal.* Calcd. for $C_8H_8Cl_2$: C, 54.9; H, 4.6; Cl, 40.5. Found: C, 55.13, 55.10; H, 4.27, 4.75; Cl, 39.6.

A solution of 64 g. of styrene in 275 ml. of $CHCl_3$ was chilled to 0° and chlorine (20 ml.) was bubbled through the solution at 0°. The fuming colorless solution was washed with $NaHCO_3$ and dried over $CaCl_2$ overnight. Distillation yielded 55 g. of β-chlorostyrene boiling at 41–46° (2 mm.) ($n^{25}\mathrm{D}$ 1.5497–1.5582),[21] 15.6 g. of styrene dichloride boiling at 51–55° (1.2 mm.) ($n^{25}\mathrm{D}$ 1.5490–1.5487) and 3.2 g. of residue. The infrared spectrum of styrene dichloride was the same as that obtained from the reaction with $CuCl_2$. *Anal.* Calcd. for C_8H_7Cl: C, 69.5; H, 5.1; Cl, 25.6. Found: C, 70.0; H, 5.0; Cl, 24.6.

Isoprene and Tetrahydrofuran.—Cupric chloride (60 g.) and LiCl (25 g.) were dissolved in 500 ml. of THF and 350 ml. (238/68 = 3.56) of isoprene added. The homogeneous dark brown solution was irradiated at 27–28° for 17.5 hours. The original solution which analyzed for cupric ion (0.67 meq. ml.), chloride ion (1.62 meq./ml.), and acid (0) on irradiation contained cuprous ion (0.03 meq./ml.), chloride ion (1.19 meq./ml.) and acid (0.02 meq./ml.). To the irradiated solution was added 200 ml. of *n*-hexane. The mixture was cooled to −30°, and added with strong stirring to excess ferric solution. The clear yellow hexane extract was washed with ice-water, dried over $CaCl_2$ for 10 minutes, and vacuum distilled at 50 mm. The hexane forerun analyzed for 0.18 mole of bound chlorine. The redistillation of the hexane forerun at atmospheric pressure yielded 19 g. of material which turned black on standing. It consisted mainly of isoprene hydrochloride and isoprene dichloride. After the hexane forerun was removed, approximately 20 g. remaining in the kettle was vacuum distilled at 3 mm. It consisted of 6 g. of 2-(4-chlorobutoxy)-tetrahydrofuran (identified as DNP and infrared spectrum). In addition there was isolated 8 g. of 2-(chloropentenyl)-tetrahydrofuran boiling at 56–60° (3 mm.) ($n^{25}\mathrm{D}$ 1.4828–1.4848), which showed bands in the infrared (9–12μ) characteristic of substituted tetrahydrofurans. *Anal.* Calcd. for $C_9H_{15}OCl$: C, 61.9; H, 8.66; Cl, 20.3. Found: C, 61.7, 61.8; H, 8.7, Cl, 19.0, 19.8.

Isoprene and Isopropyl Alcohol.—A solution of 57 g. of $CuCl_2$ and 22 g. of LiCl in 500 ml. of isopropyl alcohol and 400 ml. of isoprene was dark green-yellow. It was photolyzed at 24–25° for 45 hours to yield a pale straw-yellow solution and a small amount (10 g.) of precipitated CuCl. One ml. of solution which contained 0.448 meq. of Cu^{+2} produced 0.443 meq. of Cu^{+} and 0.056 meq. of acid and consumed 0.42 meq. of chloride ion (by titrations). The irradiated solution was qualitatively (G.L.C.) and quantitatively (hydroxylamine hydrochloride) analyzed for acetone. On this basis approximately 85% of the cupric ions reacted to form alkyl chlorides and 15% reacted with isopropyl alcohol to produce acetone. The mole ratio of isopropyl alcohol in the solution was 62%. The irradiated solution was vacuum distilled into a Dry Ice trap (A). The semi-solid residue was taken up in benzene and washed with ferric solution and water at 0°. After removal of the benzene it was vacuum distilled (B). The vacuum distillate A was redistilled at 30 mm. to fractionate the isopropyl alcohol C. The residue was further distilled at 10 mm. It yielded two fractions boiling at 39–43° (10 mm.) (10 g., $n^{25}\mathrm{D}$ 1.4273–1.4298) and 55–60° (10 mm.) ($n^{25}\mathrm{D}$ 1.4668–1.4717, 5 g.). The lower boiling fraction had infrared bands at 8.8, 8.9 and 9.5μ, but no carbonyl or hydroxyl bands. Treatment with 2,4-DNP yielded a red derivative which was recrystallized from ethanol; m.p. 180–181°; (mixed m.p. with senecialdehyde-DNP, 180–181°).[22] *Anal.* Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.58; N, 21.2. Found: C, 49.8; H, 4.5: N, 20.7. G.L.C. (Apiezon J) indicated the lower boiling fraction to be a mixture of compounds, some of which decomposed on the column. One component which was isolated was isopropoxypentene, the adduct of isopropyl alcohol to isoprene (b.p. 54° (40 mm.), $n^{25}\mathrm{D}$ 1.4169). *Anal.* Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.5, 74.1; H, 12.5, 12.4. The other components were probably isopropoxyisoprene (yielded senecialdehyde on hydrolysis) and isoprene hydrochloride. The higher boiling fraction was not examined further. The isopropyl alcohol distillate was treated directly with 2,4-DNP reagent, to form a red derivative. Recrystallization from ethanol–ethyl acetate yielded scarlet crystals (m.p. 216–217°), whose melting point with tiglaldehyde-DNP[23] was undepressed. The absence of carbonyl bands in the infrared indicated that tiglaldehyde was not present as such in solution, but the cold traps contained acetone (as DNP). *Anal.* Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.58; N, 21.2. Found: C, 50.0, 50.1; H, 4.7, 4.7; N, 21.3.

The distillation of B gave a complex mixture of products (boiling range 55–96° (2 mm.), 3 g. $n^{25}\mathrm{D}$ 1.4770–1.4858. *Anal.:* C, 62.66; H, 9–10; Cl, 18–20. Treatment of the lower boiling fractions yielded a yellow DNP (m.p. 150-154°) derived from $C_{10}H_{16}O$. *Anal.* Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.9; H, 6.08; N, 16.9. Found: C, 57.89, 58.83; H, 6.18. 6.20; N, 16.8. It was not identified further.

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[21] R. Biltz, *Ann.*, **296**, 275 (1897).

[22] W. Hickinbottom, *J. Chem. Soc.*, 1368 (1955); M. Julia and J. Surzur, *Compt. rend.*, **238**, 2426 (1954); R. Heilman and R. Glenat. *Bull. soc. chim. France*, 1586 (1955).

[23] Sample from Eastman Kodak Co.