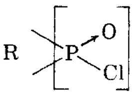
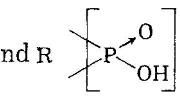
aluminum chloride per olefinic bond. When a functional group which complexes with aluminum chloride is also present, such as the carboxylate group in methyl oleate, an additional mole of aluminum chloride must be used. The intermediate complex is decomposed with aqueous methanol, and the product is isolated from methylene chloride solution after drying with sodium sulfate.

The reaction products thus obtained contain one atom of phosphorus per (original) double bond; stability to hydrolysis and failure to observe P—O—C bonding in the 10-μ region of the infrared indicate that the phosphorus is bonded directly to carbon. Absorption at 8 μ, however, confirms the presence of the P → 0 group. Loss of unsaturation, indicated by infrared analysis and iodine value determination, suggests that the reaction occurs at the double bond.

The products isolated as described above contain varying amounts of chlorine, up to one chlorine per double bond, depending on the structure of the starting olefin. This chlorine is labile and the chlorides are readily hydrolyzed to monobasic phosphorus-containing acids. Elemental analyses indicate the formula



for the acid chloride and



for the acid. While the exact attachment of the phosphorus to the carbon skeleton has not been established completely at this time, it is apparent that to fulfill the natural valence requirements of phosphorus, the products must be either polymeric, cyclic, or have a P—H bond. The first possibility was eliminated, since ebullioscopic molecular weight determinations of the acid and the methyl ester from 2,4,4-trimethyl-2-pentene indicated monomeric structures with some association. The other possibility, presence of a P—H bond, was eliminated because of the stability of the compound to oxidation with bromine and the absence of supporting NMR and infrared data. A detailed report on the structure of the product obtained from 2,4,4-trimethyl-2-pentene will be the subject of a forthcoming publication.

Some typical examples are given below:

2,4,4-Trimethyl-2-pentene yielded a crystalline material, (I), m.p. 74–75°. [*Anal.* Calcd. for $C_8H_{16}POCl$: C, 49.36; H, 8.29; P, 15.92; Cl, 18.22. Found: C, 49.80; H, 8.45; P, 15.90; Cl, 18.20]. The compound (I) is readily hydrolyzed to a monobasic acid (II), m.p. 75–76°. [*Anal.* Calcd. for $C_8H_{16}PO_2H$: C, 54.53; H, 9.73; P, 17.58; neut. equiv., 176.2; mol. wt., 176.2. Found: C, 54.89; H, 9.72; P, 16.07; neut. equiv., 176.0; pK 2.85; mol. wt. (ebullioscopic in acetone), 302, indicating *ca.* 50% association.] Reaction of I with sodium methoxide yields the methyl ester, m.p. 35–36°, b.p. 78°/0.7 mm. [*Anal.* Calcd. for $C_8H_{16}PO_2CH_3$: sap. equiv., 190.2; mol. wt. 190.2; Found: sap. equiv., 190.6; mol. wt. (ebullioscopic in acetone), 201.] Reaction of II with thionyl chloride regenerates the acid chloride (I).

A commercial nonene (a propylene trimer) gave an oil with the following analysis: Calcd. for $C_9H_{18}POCl$: P, 14.9; Cl, 17.0. Found: P, 13.9; Cl, 15.3. Hydrolysis yielded a chlorine free acid. (*Anal.* Calcd. for $C_9H_{18}PO_2H$: neut. equiv., 190.6; Found: neut. equiv., 210.) Methyl oleate yielded an oil with the following analysis: Calcd. for $C_{19}H_{36}PO_3Cl$: P, 8.6; Cl, 9.4; sap. equiv., 189; Found: P, 8.3; Cl, 3.6; sap. equiv., 210. The low value for chlorine indicates that extensive hydrolysis of the acid chloride occurs during decomposition of the complex.

The above constitute the first reported examples of the addition of phosphorus trichloride to olefins under ionic conditions and obviously differ from the well known Friedel-Craft reaction between aromatic compounds and phosphorus trichloride. In the latter case, a dibasic acid results on hydrolysis, and the aromatic character of the molecule is not affected; on the other hand, in the reaction with olefins, saturated monobasic acids are formed.

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ARMOUR AND CO.
SOAP RESEARCH DEPARTMENT
1355 WEST 31ST ST.
CHICAGO 9, ILL.
ERIC JUNGERMANN

ARMOUR INDUSTRIAL CHEMICAL CO.
RESEARCH LABORATORY
MCCOOK, ILL.
JOSEPH J. MCBRIDE, JR.

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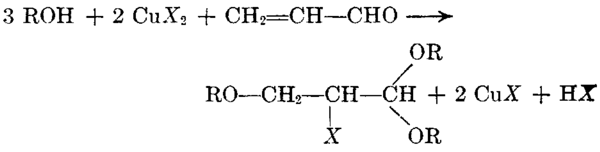
Halogenation of Unsaturated Aldehydes with Cupric Halides

Sir:

In the course of another investigation, α,β-unsaturated aldehydes have been found to reduce cupric to cuprous halides in alcoholic media.[1] The reaction provides a convenient route to β-alkoxy-α-haloaldehydes or their acetals.



$$3\ ROH + 2\ CuX_2 + CH_2{=}CH{-}CHO \longrightarrow RO{-}CH_2{-}\underset{X}{\underset{|}{CH}}{-}CH(OR)_2 + 2\ CuX + HX$$

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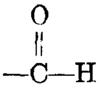
[1] The reduction of cupric chloride by acetone in aqueous media has been reported; V. Kohlshutter, *Ber.*, **27**, 1170 (1904). The kinetics of the reaction were found to be complex; J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

Thus, in a typical experiment, a mixture of acrolein (0.12 mole), anhydrous cupric bromide (0.40 mole), and 500 ml. of ethanol was refluxed for 3 hr. with stirring. The cooled mixture was filtered from cuprous bromide, and the resulting solution was concentrated *in vacuo* to a volume of 100 ml. To the concentrate was added 500 ml. of petroleum ether (b.p. 60–68°) and 500 ml. of water. After shaking, the mixture was filtered again. The combined yield of cuprous bromide was (0.22 mole) 92%. The hydrocarbon phase was washed free of copper salts and acids, dried, and concentrated. Fractionation of the product concentrate afforded colorless 2-bromo-1,3,3-triethoxypropane I (b.p. 112.8°/14 mm., lit.[2] b.p. 104–107°/13 mm.) in 67% yield.

Similarly, in methanolic media, 2-bromo-1,3,3-trimethoxypropane (II) was obtained (40%, b.p. 60°/2 mm., *Anal.* Found: C, 33.5; H, 6.1; Br, 37.8; mol. wt., 211). The same reaction could be carried out at room temperature. The infrared spectra of I and II were similar and showed the characteristic acetal doublet and ether bands (1070–1185 cm.$^{-1}$). The structure of I and thus II was substantiated by conversion of I with alcoholic potassium hydroxide to 1,3,3-triethoxypropene-1[2](III) and thence with semicarbazide to pyrazole-*N*-carboxamide[3] (m.p. sublimed material, 140.5°. *Anal.* Found: C, 43.1; H, 4.7; N, 38.2). *N*-2,4-Dinitrophenylpyrazole prepared from III had a melting point and mixed melting point identical with an authentic sample.

The reaction of acrolein with excess cupric chloride in refluxing *t*-butyl alcohol afforded the novel β-*t*-butoxy-α,α-dichloropropionaldehyde (IV) (20%, b.p. 40–41°/2 mm.[4]). The infrared spectrum of IV demonstrated the presence of a *t*-butoxy moeity (878, 1110, 1190, 1370, 1395 cm.$^{-1}$) and an α-halo aldehyde grouping (C=O, 1750 cm.$^{-1}$  $\overset{\overset{\displaystyle O}{\|}}{—C}—H$, 2700 cm.$^{-1}$). The NMR spectrum of the product aldehyde showed only three hydrogen resonances (CHO at 370, O—CH_2 at 158, and $(CH_3)_3$-C at 48 c.p.s.; tetramethylsilane reference) with peak areas in the approximate ratio of 1:2:13. There was no splitting. The dihaloaldehyde (IV) rapidly forms a crystalline monohydrate (V) upon exposure to the atmosphere (m.p. 66.5–67° from petroleum ether, b.p. 60–68°. *Anal.* Found: C, 38.9; H, 6.5; Cl, 32.3) which can be smoothly oxidized with neutral permanganate to β-t-butoxy-α,α-dichloropropionic acid (VI) (m.p. 81–82°, cyclohexane. *Anal.* Found: C, 39.0; H, 5.6; Cl, 31.7; eq. wt., 218). The infrared spectrum of the latter (C=O 1745 cm.$^{-1}$) is nearly identical with that of the unsubstituted (C=O 1715 cm.$^{-1}$) β-*t*-butoxypropionic acid[5] (VII). Under identical conditions methacrolein, cupric chloride, and *t*-butyl alcohol afforded β-*t*-butoxy-α-chloroisobutyraldehyde (VIII) (32%, b.p. 43/6–47°/5 mm. *Anal.* Found: C, 53.1; H, 8.4; Cl, 19.5) and a white crystalline solid, $C_{12}H_{22}Cl_2O_4$ (20%), of as yet uncertain structure. The infrared spectra of IV and VIII are virtually identical.

The fact that β-alkoxy-α-halopropionaldehydes are readily obtained by this procedure suggests that copper salts may be effective catalysts for alcohol additions to carbonyl conjugated olefins.[6] The α-halogenation would then reasonably proceed through the enol form of the β-alkoxyaldehyde. In accord with this latter contention, propionaldehyde and *n*-butyraldehyde[7] reduced cupric to cuprous chloride in *t*-butyl alcohol media, but no definable organic chlorides were isolable. However, *n*-butyraldehyde reacted smoothly with cupric bromide in ethanol to yield 2-bromo-1,1-diethoxypropane (IX) (41%, b.p. 81–83°/12 mm., lit. b.p. 88–91°/21 mm.[8] *Anal.* Found: C, 43.2; H, 7.7; Br, 34.9).

The probable wide scope of these reactions is indicated by the conversion of acrylonitrile in one step to ethyl, α,α-dibromo-β-ethoxypropionate (X) upon exposure to cupric bromide in refluxing ethanol. The infrared spectrum of X (b.p. 49–53°/1 mm. *Anal.* Found: C, 27.1; H, 4.1; Br, 51.5, 53.8; C=O, 1745 cm.$^{-1}$) was nearly superimposable upon that of the unhalogenated ester (C=O, 1720 cm.$^{-1}$).

Acknowledgment. The author is indebted to Dr. G. M. Coppinger for many valuable discussions, and to Mr. F. L. Rodgers for assistance with the experimentation. Thanks are also tendered to Drs. J. L. Jungnickel and C. A. Reilly for obtaining and interpreting the NMR spectrum of IV.

SHELL DEVELOPMENT CO.
EMERYVILLE, CALIF.
C. E. CASTRO[9]

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[2] R. W. Price and A. Moos, *J. Am. Chem. Soc.*, **67**, 207 (1945).

[3] A Dornow and K. Peterlein, *Ber.*, **82**, 257 (1949) report m.p. 136.5°.

[4] Higher boiling fractions polymerized upon standing and were not investigated. None of the yields reported in this work should be considered as the maximum attainable since optimum conditions for these transformations have not been sought.

[5] The previously undescribed acid VII (b.p. 92°/2 mm. *Anal.* Found: C, 57.5; H, 9.5; eq. wt., 144) was prepared by saponification of the ester obtained from potassium *t*-butoxide and ethyl β-chloropropionate in cold *t*-butyl alcohol.

[6] *t*-Butyl alcohol could not be induced to add to acrolein under the influence of a variety of acids and bases.

[7] It should be noted that under identical conditions crotonaldehyde which should not add *t*-butyl alcohol as readily as acrolein, and therefore, not form an enol reacted at best only very slowly.

[8] R. G. Jones, E. C. Kornfeld, K. C. McLaughlin, and R. C. Anderson, *J. Am. Chem. Soc.*, **71**, 4002 (1949).

[9] Department of Nematology, University of California, Riverside, Calif.