

THE COPPER(I) CHLORIDE-ETHANOLAMINE CATALYZED ADDITION
OF POLYFLUORINATED ALKANES TO OLEFINS

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The addition of polyfluorinated alkanes to olefins by peroxide or photochemical initiation has been the subject of much research in recent years (1). However, these two methods of radical initiation have the following disadvantages: (a) telomerization decreases the yield of the 1:1 adduct and makes isolation more difficult; (b) a large excess of the alkane must be employed to minimize telomer formation - this can be costly since the alkane is generally the more expensive and more difficult starting material to obtain; (c) vigorous reaction conditions and special apparatus are often necessary.

Recently, the addition of carbon tetrachloride and chloroform to olefins using copper chloride catalysis has been reported (2,3). This elegant synthetic route has been shown to minimize or eliminate the competing processes of telomer formation and polymerization associated with peroxide catalysis. We have found that similar catalysis using copper(I) chloride and ethanolamine can be employed in the addition of polyfluorinated alkanes to olefins. The results of some of these addition reactions are summarized in Table 1.

TABLE I

| <u>Olefin</u> | <u>Halide</u> | <u>Adduct</u> | <u>% Yield</u> ^a |
|-------------------|---|--|-----------------------------|
| 1-octene | CF ₂ Br ₂ | CF ₂ BrCH ₂ CHBr(CH ₂) ₅ CH ₃ | 68 |
| 1-octene | CF ₂ BrCF ₂ Br | CF ₂ BrCF ₂ CH ₂ CHBr(CH ₂) ₅ CH ₃ | 77 |
| 1-octene | CF ₂ BrCFClBr | CF ₂ BrCFClCH ₂ CHBr(CH ₂) ₅ CH ₃ | 94 |
| 1-octene | CF ₂ ClCFCl ₂ | CF ₂ ClCFClCH ₂ CHCl(CH ₂) ₅ CH ₃ | 62 |
| 1-octene | CF ₃ CClBr ₂ | CF ₃ CClBrCH ₂ CHBr(CH ₂) ₅ CH ₃ | 98 |
| 1-octene | CF ₃ CCl ₃ | CF ₃ CCl ₂ CH ₂ CHCl(CH ₂) ₅ CH ₃ | 83 |
| 1-octene | CF ₃ CBr ₃ | CF ₃ CBr ₂ CH ₂ CHBr(CH ₂) ₅ CH ₃ | 74 |
| 1-octene | CF ₃ CF ₂ CF ₂ I | CF ₃ CF ₂ CF ₂ CH ₂ CHI(CH ₂) ₅ CH ₃ | 57 ^b |
| Ethyl allyl ether | CF ₂ BrCFClBr | CF ₂ BrCFClCH ₂ CHBrCH ₂ OCH ₂ CH ₃ | 78 |
| 2-octene | CF ₂ BrCFClBr | CH ₃ CH(CFClCF ₂ Br)CHBr(CH ₂) ₅ CH ₃ + CH ₃ CHBrCH(CFClCF ₂ Br)(CH ₂) ₅ CH ₃ | 86 ^c |
| Allyl chloride | CF ₃ CClBr ₂ | CF ₃ CClBrCH ₂ CHBrCH ₂ Cl | 47 |

(a) The yield was determined by GLC on a Silicone Rubber Column. All reactions were carried out using a mole ratio of alkane/olefin of 2:1 except where noted. (b) The ratio of halide to olefin was 1:1. In addition to the 1:1 adduct, a 42% yield of CF₃CF₂CF₂CH=CH(CH₂)₅CH₃ was also found. (c) A mixture of both isomers.

A typical procedure is as follows: A mixture of 55.3 g. (0.2 mole) of 1,2-dibromo-1-chloro-1,2,2-trifluoroethane ($\text{CF}_2\text{BrCFClBr}$), 11.2 g. (0.1 mole) of 1-octene, 0.1 g. (0.001 mole) of copper(I) chloride (4), 3.0 g. (0.05 mole) of ethanolamine, and 100 ml. of t-butyl alcohol were refluxed with stirring for 24 hours. After cooling to room temperature, the reaction mixture was diluted with ether and the organic layer was separated. GLC analysis on a silicone rubber column indicated a 94% yield of the adduct based on 1-octene. Subsequent fractionation yielded 27.0 g. (70%) of the pure 1:1 adduct b.p. 88° (0.4 mm.), n_D^{20} 1.4612. Reported for $\text{CF}_2\text{BrCFClCH}_2\text{CHBr}(\text{CH}_2)_5\text{CH}_3$ (5): b.p. 84° (0.3 mm.), n_D^{24} 1.4612.

Structural assignments of the 1:1 adducts are based on elemental analysis, infrared and proton magnetic resonance spectra and on chemical evidence. The latter includes both dehydrohalogenation and dehalogenation of the adducts where appropriate.

Although 1-octene was used as a model olefin for the initial survey of the scope of this reaction, other terminal olefins have been used successfully. In addition, internal olefins, such as 2-octene and cyclohexene, have been employed successfully. Also, reactive olefins such as ethyl allyl ether have given good yields of the 1:1 addition adduct. Telomer formation was not of consequence in any of these reactions.

The data listed in Table I also illustrates that this method can be used successfully with compounds containing a reactive chlorine, bromine, or iodine.

While most of the halogenated alkanes we have examined undergo this addition reaction successfully, some others are worthy of note. For example, 1,2-dibromo-1,1,2,2-tetrachloroethane ($\text{CCl}_2\text{BrCCl}_2\text{Br}$) gave only tetrachloroethylene under these conditions and no 1:1 adduct with 1-octene. In contrast 1,2-dibromo-1,1,2,2-tetrafluoroethane ($\text{CF}_2\text{BrCF}_2\text{Br}$) gave a 77% yield of the 1:1 adduct with 1-octene and gave no tetrafluoroethylene. The reactant alkane must be stable to the catalyst and to the ethanolamine for the addition reaction to be carried out successfully. Also, the attempted addition of 2,3-dibromooctafluorobutane to 1-octene gave only unchanged starting materials under these conditions.

These copper halide catalyzed additions offer extreme simplicity of procedure. The reactions can be generally carried out in all glass apparatus and no special pressure apparatus is required. Also, since the disappearance of the olefin can be conveniently followed by sampling by GLC, reaction times can be reduced to a minimum. Another important point in some cases is that the reaction can be carried out without using large excesses of the expensive halogen reactant. Although the reaction can be carried out successfully using a 1:1 ratio of halogen compound olefin, we have found best results with a 2:1 ratio of these reactants. Even with the

1:1 ratio, however, no significant telomer formation has been observed.

This simple catalysis technique offers much promise for preparing polyfluorinated hydrocarbons, and additional studies are in progress to investigate the scope of this reaction with other fluorinated alkanes and also to investigate this reaction with polyfluorinated olefins.

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References

- (1) For an extensive review of this work, cf. C. Walling, Free Radicals in Solution, John Wiley & Sons, New York, 1957, Chapter 6.

G. Sosnovsky, Free Radical Reactions in Preparative Organic Chemistry, The Macmillian Company, New York, 1964, Chapter 2.
- (2) M. Asscher and D. Vofsi, J. Chem. Soc., 1887 (1963).
- (3) M. Asscher and D. Vofsi, J. Chem. Soc., 3921 (1963).
- (4) For the preparation of Copper(I) Chloride, cf. Inorg. Syn., 2, 1 (1946).

The CuCl is slowly oxidized, by moist air, to yield a green compound $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$. However, this partially oxidized mixture of Cu(I) and Cu(II), was found to be an effective catalyst for these additions.

- (5) P. Tarrant and E. Gilman, J. Am. Chem. Soc., 76, 5423 (1954).