

CHLORODECARBOMETHOXYLATION AND DECHLOROCARBOMETHOXYLATION BROUGHT ABOUT BY HALIDE IONS

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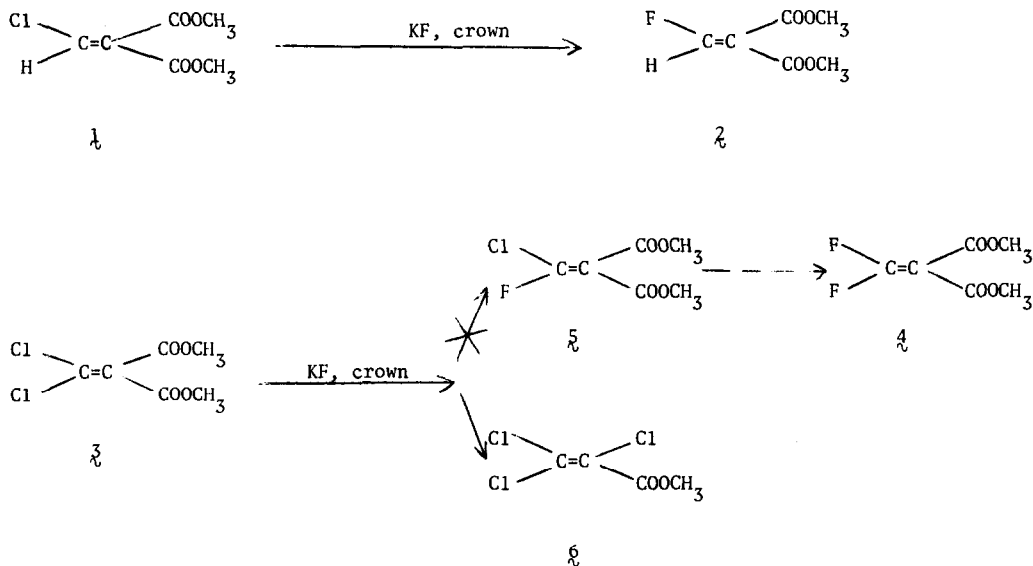
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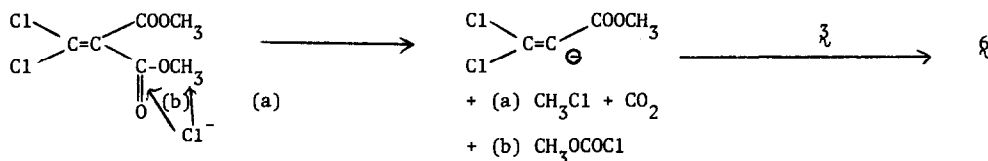
We report novel chlorodecarbomethoxylation and dechlorocarbomethoxylation elimination reactions of polycarbomethoxy-ethylenes and -ethanes brought about by halide ions in dipolar aprotic solvents or neat.

Unsaturated Esters - Whereas dimethyl 2-chloroethylene-1,1-dicarboxylate reacts with potassium fluoride in presence of dicyclohexyl-18-crown-6 to form dimethyl 2-fluoro-ethylene-1,1-dicarboxylate λ ,¹ dimethyl 2,2-dichloroethylene-1,1-dicarboxylate ξ under the same conditions (sulfolane, 150°C, 30 mm) gave neither dimethyl 2,2-difluoroethylene-1,1-dicarboxylate μ nor the partially reacted dimethyl 2-chloro-2-fluoroethylene-1,1-dicarboxylate η .

Surprisingly the only isolated product was methyl 1,2,2-trichloroethylene-1-carboxylate ζ ² (70% yield if we assume that 2 molecules of starting material give one of product):

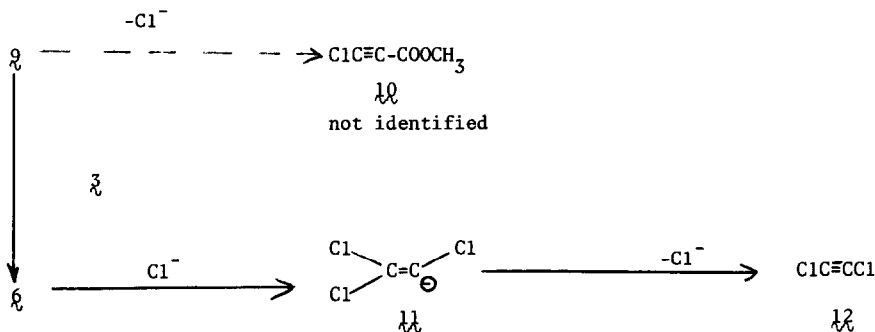


Replacing potassium fluoride by potassium chloride gave a similar result. Disproportionation of starting olefin ξ to the isolated methyl trichloroethylene-carboxylate ζ and to trimethyl 2-chloroethylene-1,1,2-tricarboxylate η was excluded as a possible reaction course; compound η was synthesized independently³ and shown to be absent from the reaction mixtures. We favor a mechanism involving formation of a vinyl carbanion ϱ through attack of halide ion at either (a) methyl or (b) carbonyl in the carbomethoxy group. Such vinyl carbanions are well known through the work of K \ddot{O} brich.⁴ Decarboalkoxylation of geminal diesters and β -ketoesters has been observed in wet dimethyl sulfoxide in presence or absence of sodium chloride by Krapcho.⁵

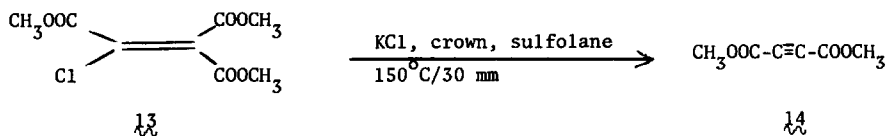


Rise in pressure during the reaction corresponds to the loss of volatile products; however, due to the probable decomposition of methyl chloroformate into carbon dioxide and methyl chloride under the reaction conditions, we have not attempted to distinguish between paths (a) and (b).

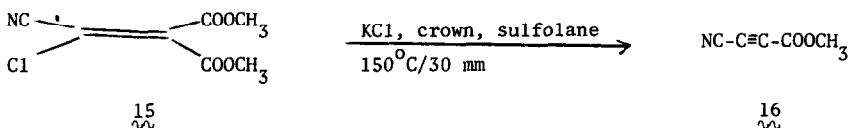
Beside abstracting Cl^+ , anion ϱ might be expected to lose Cl^- to form methyl chloroacetylene-carboxylate $\lambda\lambda$. While we did not detect $\lambda\lambda$, a trace of dichloroacetylene $\lambda\lambda$, probably arising via the analogous anion $\lambda\lambda$,⁶ could be identified.



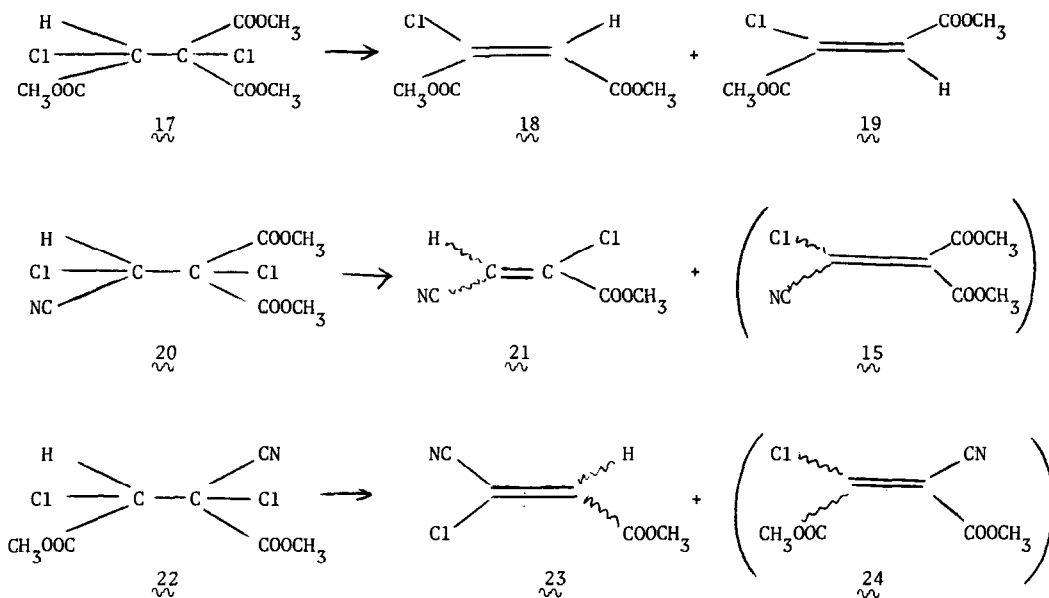
Similarly, dechlorocarbomethoxylation of trimethyl 2-chloroethenetricarboxylate $\lambda\lambda$ gave dimethyl acetylenedicarboxylate $\lambda\lambda$ in 7% yield.



The hitherto unknown methyl cyanoacetylenecarboxylate 16 was obtained in 16% yield from dimethyl 2-chloro-2-cyanoethylene-1,1-dicarboxylate 15:



Saturated Esters - Analogous elimination reactions were observed with saturated esters under milder conditions. Vacuum distillation of trimethyl 1,2-dichloroethane-1,1,2-tricarboxylate 17 in presence of tetraethylammonium chloride gave a mixture of dimethyl chloromaleate 18 and fumarate 19 in 58% yield. Dimethyl 1,2-dichloro-2-cyanoethane-1,1-dicarboxylate 20¹ gave methyl 1-chloro-2-cyanoacrylate 21 (mixture of isomers, isolated in purity in 36% yield) and dimethyl 2-cyano-2-chloroethene-1,1-dicarboxylate 15 (containing the acrylate; total yield 72%; relative abundance of 21:15, 64:36). Dimethyl 1,2-dichloro-1-cyanoethane-1,2-dicarboxylate 22 gave methyl 2-cyano-2-chloroethene-1-carboxylate 23 (isolated in purity in 36% yield, the major isomer being a solid) and dimethyl 1-cyano-2-chloroethene-1,2-dicarboxylate 24 (in 28% yield; relative abundance of 23:24, 56:44). Compounds 15 and 24 arise by normal dehydrochlorination induced by halide ions.



Conclusion - Dechlorocarbomethoxylation and chlorodecarbomethylation are new reactions which appear to possess considerable generality, and which also display synthetic utility in certain cases.

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2. All new compounds were identified by spectroscopical methods and gave satisfactory elemental analysis; compound ~~2A~~ was always contaminated by small amounts of ~~2C~~.
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