

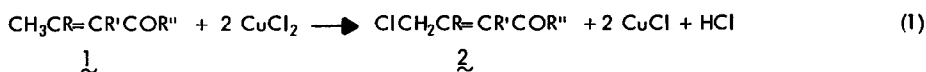
COPPER(II)-CATALYZED γ -CHLORINATION OF α,β -UNSATURATED ALDEHYDES AND KETONES¹

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Lorenzini and Walling² reported α -chlorinations of butyraldehyde and isobutyraldehyde in high yields by stoichiometric amounts of CuCl_2 . Kosower and Wu³ reported α - and γ -chlorinations of unsaturated ketones. We found that α,β -unsaturated aldehydes and ketones were γ -chlorinated stoichiometrically by CuCl_2 in *N,N*-dimethylformamide solution (reaction 1) and that catalytic procedures for this reaction could be used based on regeneration of CuCl_2 from CuCl . Chlorine was used as both oxidant and halogen source (reaction 2), or hydrochloric acid was used as halogen source with an electrode (reaction 3) or oxygen (reaction 4) as oxidant.



1a, 2a: R, R', R'' = H
1b, 2b: R, R'' = H; R' = CH₃
1c, 2c: R, R' = H; R'' = CH₃



One mole of 2-methylcrotonaldehyde (1b) was treated with 2 moles of CuCl_2 in 500 ml *N,N*-dimethylformamide at 75°C for 2 hr. The reaction mixture was diluted with water, and the product was extracted with ether, dried with anhydrous MgSO_4 , and distilled under reduced pressure; it gave a 39% yield of 2b at 33% conversion.⁴

A solution of 1 mole of 1b, 450 ml isopropyl alcohol, 50 ml water, 0.40 mole CuCl_2 , 0.20 mole LiCl , and 0.40 mole hydrochloric acid was stirred while 0.60 mole chlorine gas was admitted over a 2-hr period at 74°C. The rate of addition was controlled to keep the oxidation potential below 0.350 v (platinum vs. saturated calomel electrode) and thus minimize addition to the double bond. Extractive work-up and distillation, as described previously, gave a 64% yield of 2b at 47% conversion.

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A solution of 1 mole of 1b in 450 ml isopropyl alcohol and 400 ml water containing 0.50 mole hydrochloric acid and 0.20 mole CuCl_2 was used as the anolyte in an electrolytic cell. A platinum anode and a lead cathode were separated by a cationic ion-exchange membrane. The catholyte was 1 l. of 0.5 M hydrochloric acid. The anolyte was stirred at 60°C and the anode potential held at +0.7 v vs. a saturated calomel electrode while 1.6 faradays were passed. Extractive work-up and distillation gave a 25% yield of 2b at 22% conversion.

One mole of 1b and 1.20 moles of 12N hydrochloric acid were added simultaneously to a solution of 650 ml acetic acid and 250 ml water containing 0.20 mole CuCl_2 while the solution was stirred rapidly and air was admitted at a rate of 1.5 l./min; the addition was carried out at 75°C over a 1.5-hr period, and stirring and aeration were continued for another 1.5 hr. Extractive work-up and distillation gave a 63% yield of 2b at 55% conversion. Gas chromatograms prior to distillation of the material showed that 2b had been formed in 88% yield at 62% conversion.

The last method was used to γ -chlorinate crotonaldehyde (1a) and 3-penten-2-one (1c). The yield of 2a was 15% (at 14% conversion), and the yield of 2c was 13% (at 8.3% conversion). Similar results were obtained by application of this procedure to saturated compounds: isobutyraldehyde gave 2-chloro-2-methylpropionaldehyde at 19% yield and conversion, and 4-methyl-2-pentanone gave 3-chloro-4-methyl-2-pentanone in 14% yield at 5.7% conversion.

This demonstration that such α - and γ -chlorinations may be made catalytic in copper provides a useful one-step synthetic route to some compounds otherwise difficult to obtain.

REFERENCES

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