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PRELIMINARY NOTE

# Preparation and Reactions of 2-Chloroperfluorocyclobutenyl Copper Reagent

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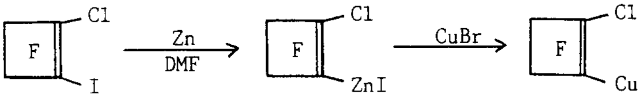
## SUMMARY

2-Chlorotetrafluorocyclobutenyl copper reagent was prepared via copper(I) bromide metathesis from the corresponding zinc reagent which was readily obtained from 1-chloro-2-iodo-3,3,4,4-tetrafluorocyclobutene by the direct reaction with zinc metal in DMF. The copper reagent was used to synthesize alkyl and acyl derivatives of tetrafluorocyclobutene.

Previous studies on fluorinated vinyl zinc reagents[1-3] and their applications for the preparation of copper reagent[4] have been reported. Most of these concentrated on acyclic systems. Our work has focussed on the preparation and synthetic applications of cyclic fluorinated vinyl copper reagents. We have found that 1-chloro-2-iodotetrafluorocyclobutene reacted quantitatively with activated zinc powder in DMF at room temperature. This reaction was quite exothermic and proceeded to completion within one hour. The zinc reagent exhibited good thermal stability. Even at 80°, it showed no appreciable decomposition after three days. By the addition of copper(I) bromide to the filtered solution of zinc reagent below 0°, the copper



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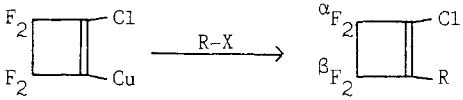
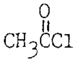
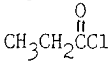
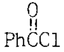
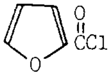
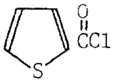
reagent was formed with 92% yield as determined by $^{19}F$ NMR*. The copper reagent was found to be quite stable at room temperature. The results from the reactions of the copper reagent with alkyl or acyl halides are summarized in Table I.

TABLE I.



| R-X | Temp. | Time(h) | Yield(%)$^a$ | b.p(°C/mmHg) | $^{19}F$ NMR(δ ppm)$^b$ α | β |
|---|---|---|---|---|---|---|
| $CH_3I$ | r.t | 120 | 42 | 82-83 | 113.0 | 113.7 |
| PhI | r.t | 120 | 47 | 70-71/3 | 112.0 | 113.0 |
| $PhCH_2Br$ | r.t | 48 | 78 | 78-80/3 | 111.8 | 113.4 |
| $CH_2{=}CHCH_2Cl$ | r.t | 10 | 87 | 117 | 112.8 | 114.3 |
|  $CH_3\overset{O}{\overset{\|}{C}}Cl$ | -20°-r.t | 5 | 43 | 64-66/50 | 113.8 | 111.2 |
|  $CH_3CH_2\overset{O}{\overset{\|}{C}}Cl$ | -20°-r.t | 5 | 58 | 66-67/20 | 113.5 | 110.6 |
|  $Ph\overset{O}{\overset{\|}{C}}Cl$ | -20°-r.t | 5 | 53 | 76-77/1 | 113.2 | 106.8 |
|  | -20°-r.t | 5 | 38 | 58-60/1.5 | 113.2 | 106.9 |
|  | -20°-r.t | 5 | 32 | 70-72/1.5 | 113.3 | 107.1 |

[a] Isolated yields. Yields are based on starting 1-chloro-2-iodotetrafluorocyclobutene.

[b] Chemical shifts are upfield from $CFCl_3$. All measurements were made in $CDCl_3$ using $CF_3COOH$ as external standard. All signals are multiplets.

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* $^{19}F$ NMR chemical shifts: Zinc reagent; -110.2(m), -103.7(m)
Copper reagent; -109.6(m), -102.9(m) ppm.

The yields were quite good for benzyl bromide and allyl chloride where the reactants contain active halogens. However, the reaction proceeded very slowly for $CH_3I$ and PhI. Some tar remained at the end of the experiments due to the decomposition of copper reagent.

Previously, Park[5] reported a synthetic method to obtain alkyl derivatives of tetrafluorocyclobutene, in which 1,2-dichlorotetrafluorocyclobutene was alkylated by Grignard reagents. The present method offers versatility and facility of reaction. Zinc and copper reagents were prepared under mild conditions and a wide variety of reactants could be used. With the present method, we were able to obtain acylated derivatives which have not been previously reported in the literature. An investigation is underway to improve the yields using various solvents.

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3 S.W.Hansen, T.D.Spawn, and D.J.Burton, J. Fluorine Chem., 35 (1987) 415.
4 D.J.Burton and S.W.Hansen, J. Am. Chem. Soc., 108 (1986) 4229.
5 J.D.Park and R.Fontanelli, J. Org. Chem., 28 (1963) 258.