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THE FORMATIONS OF COMPLEXES FROM β-KETOSULFONIUM HALIDES AND COPPER HALIDES, AND THEIR REACTIONS WITH ETHYL DIAZOACETATE

Tadashi Sato and Jiro Higuchi
Department of Applied Chemistry, Waseda University, Shinjuku-ku,
Tokyo, Japan

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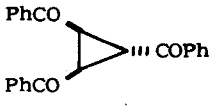
As a continuation of our studies on the reaction between diazo compounds and copper compounds,[1] we investigated the reaction between sulfonium ylide 1 and copper compounds, because sulfonium ylides and diazo compounds have been considered as the same type of compounds in that both belong to a carbenoid.

Trost[2] reported that the ylide 1 afforded *trans*-tribenzoylcyclopropane (2) when treated with $CuSO_4$. An entirely different result was now obtained when copper(II) and copper(I) halides were used in place of $CuSO_4$. Namely, when methanol solutions of 1 and $CuCl_2$ were mixed at room temperature, orange plates 4a of mp 110-120°(dec) were obtained in 42% yield. The other products were methyl benzoate and methyl phenylglyoxylate, but no evidence of 2 was observed in the reaction mixture. We further found that an excellent yield of the complex 4a was obtained when a sulfonium chloride 3a was used instead of 1 in the reaction with $CuCl_2$. The complex 4a dissolved in water to give a blue solution, but the original orange crystals were recovered on evaporation. The complex was stable under the treatment with HCl or SO_2 in methanol, but bubbling of H_2S into the methanol solution resulted in the precipitation of CuS, and 3a was isolated from the solution. The contact with solid KBr resulted in the color-change to purple, presumably because of the exchange of chloride with bromide (cf. complexes 4c-4e).

The same type of complexes (4b-4e) were also prepared from the corresponding sulfonium halides (3) and copper(II) halides as shown in the Table 1. Although the complexes 4a, 4b and 4e were recrystallizable from boiling methanol, the complexes 4c and 4d were unstable under these conditions (*vide*

$Me_2S^+\text{-}CH^-\text{-}COPh$

1



2

$(Me_2S^+\text{-}CH_2COR)\ X^-$

3

$[(Me_2S^+\text{-}CH_2COR)\ X^-]_2\cdot CuX_2$

4

$[(Me_2S^+\text{-}CH_2COR)\ Br^-]\cdot nCuBr$

5
n = 2 for 5c
n = 1 for 5d

$RCOCH = CHCOOEt$

6

a: R = Ph, X = Cl
b: R = p-Tol, X = Cl
c: R = Ph, X = Br
d: R = p-BrC_6H_4, X = Br
e: R = OEt, X = Br
f: R = Me, X = Br

infra), and recrystallized from methanol-ether at room temperature. IR spectra of these complexes showed strong carbonyl bands at 1660-1670 cm^{-1}, and were similar to those of the corresponding sulfonium halides, except a minor difference in finger-print region.

When a methanol solution of 4c was refluxed under nitrogen for 1 hr, a methanol-insoluble pale green complex 5c precipitated. From the mother liquor, phenylglyoxal dimethyl acetal (7), phenacyl bromide and 3c were obtained. In view of the composition of the complex 5c and the formation of 7, we assumed that an oxidation-reduction between ligand and metal atom had occurred. In support of this scheme, complex 5c showed no magnetic moment, while complex 4a showed a normal value of 1.7 B.M. Furthermore, an excellent yield of 5c was obtained when 3c and CuBr were reacted in acetonitrile at 75°.

Similarly, complexes 5d and 5f were prepared in ways as shown in Table 1. Although complexes 5c, 5d and 5f were fairly stable in solid state (can be stored in bottle for one month without so much color-change), an extensive coloring (presumably by oxidation to copper(II)) was observed in solution, and hence, the recrystallization (from acetonitrile) was carried out in the atmosphere of nitrogen.

The reactions of complexes 5c, 5d and 5f with ethyl diazoacetate are noteworthy. When these complexes were reacted with two equivalents of ethyl diazoacetate for 40 min in acetonitrile at room temperature, ethyl trans-β-ketoacrylate derivatives 6c, 6d and 6f were obtained in 65%, 45% and 55%[3] yields, respectively. 6c was identical with the authentic sample,[4] and 6d and 6f gave satisfactory elemental analyses and spectroscopic data. The

Table 1

Complex	State	mp	Reactn condn[a] (yield %)	Elemental analyses[b] C	H	Cu[c]	halogen[d]
4a	orange plate	110-120 (dec)	A (93)	42.22 42.30	4.66 4.61	11.0 11.2	24.6 25.0
4b	yellow needle	105-111 (dec)	A (--)	44.37 44.34	5.12 5.04	10.6 10.7	23.7 23.8
4c	purple flake	125-129 (dec)	A (86)	32.14 32.21	3.44 3.49	8.43 8.52	43.1 42.9
4d	purple flake	145-147 (dec)	A (95)	26.70 26.59	2.72 2.66		
4e	purple flake	77	A (97)	21.19 21.15	3.84 3.82	9.33 9.32	
5c	pale-green needle	156-158 (dec)	B (93) C (98)	21.90 21.95	2.23 2.37		
5d	yellow needle	158-160 (dec)	B (62) C (67)	24.86 24.84	2.62 2.50		
5f[e]	gray powder		D (--)				

a) A: Methanol solutions of 3 and CuX_2 were mixed at room temperature.
B: Acetonitrile solutions of 3 and CuBr were mixed at 75-80°.
C: Methanol solution of the corresponding 4 was refluxed for 2 hr.
D: Methanol solution of 3f and $CuBr_2$ was refluxed for 8 hr.

b) The upper figures refer to the found values and the lower figures to the calculated values.

c) Determined by chelate titration.[5]

d) Determined by Mohr's method.[6]

e) Not obtained in pure state.

reactions were clean and only by-product identified was ethyl bromoacetate. The selectivity of the reaction was less when the complex 4c was used, in which case, diethyl fumarate, diethyl maleate, ethyl bromoacetate, ethyl dibromoacetate and 6c were obtained in various yields depending on the reaction conditions. It is hoped that the reaction could generally be used for the syntheses of olefins by coupling unlike groups to make C-C double bond, and investigations are now under way in this direction. That the reaction proceeded from the complex itself was evident in view of the reaction of 3c with ethyl diazoacetate in the presence of catalytic amounts of $CuSO_4$ or $CuBr_2$, which afforded ethyl bromoacetate and phenacyl bromide as main products accompanied by a small amount of 2, and no evidence of 6c was observed.

The preparations of complexes of Pt, Hg, Sn and Sb with sulfonium salts have been reported.[7] We found that Co(II), Zn(II), Cd(II) halides also afford stable complexes with sulfonium salts, and their characterization and reactions are now being investigated.

References

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