ACYLATION OF ACETYLENE COMPOUNDS IN THE PRESENCE OF DIVALENT COPPER SALTS AND CHELATES

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The reaction of acid chlorides with terminal acetylene compounds to form α-acetylenic ketones proceeds readily in the presence of catalytic amounts of CuI or CuCl and one equivalent of triethylamine (TEA) in hydrocarbon solvents [1, 2]. It is known that Cu(II) salts form acetylides, so one can assume that they can catalyze the acylation of acetylenes. In this work this problem was investigated because of the significantly better solubility of Cu(II) compounds in organic solvents.

The catalytic action of Cu(II) salts of the acylation of 3-methyl-3-methoxy-1-nonyne (I) by isobutyryl chloride (II) was studied (Table 1). The reaction was carried out in benzene or toluene at 20-50°C under an inert atmosphere. The base was TEA [1.25-2 moles per mole of (I)]. The reaction proceeds most readily with catalytic amounts [0.05-0.1 mole per mole of (I)] of the following salts: $CuCl_2$, $CuCl_2 \cdot 2H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $CuSO_4$, and $Cu(C_{17}H_{35}COO)_2$ with a reaction time of 3-6 h, yielding 68-83% of 2,6-dimethyl-6-methoxy-4-dodecyn-3-one (III). Use of the basic salts $Cu(OH)_2$, $Cu(OH)_2 \cdot CuCO_3$, and $CuSO_3 \cdot 5H_2O$ decrease the yield of (III) to 37-42% and the reaction time increses to 10-20 h.

Both anhydrous and hydrated copper chloride were used with success in the acylation of (I), 3-methyl-methoxy-1-butyne (IV), and phenylacetylene (V) by trimethylacetyl (VI) and benzoyl (VII) chlorides. The yields of ketones (VIII)-(XI) reached 64-95% (Table 2). One can expect that in the presence of Cu(II) a competing reaction, the oxidative condensation of the terminal acetylene compound, may occur. In fact, upon reaction of (I) with (VI) in the presence of $Cu(CH_3COO)_2 \cdot H_2O$ in addition to acetylenic ketone (VIII) (64.5%) 7,12-dimethyl-7,12-dimethoxy-8,10-octadecadiyne was produced which was identical with the dimer obtained from (I) by oxidative condensation. Since the reaction is conducted in an inert atmosphere, the yield of dimer is determined by the amount of Cu(II) acetate consumed. Therefore, under the reaction conditions Cu(II) is reduced to Cu(I), which also catalyzes the reaction.

However, it is known that $CuCl_2$ under analogous conditions does not oxidize acetylene compounds [3] and therefore Cu(II) can catalyze the condensation of acetylenes with acyl chlorides.

In order to explore the use of Cu(II) chelate compounds in this reaction, Cu(II) complexes with acetylacetone $Cu(acac)_2$ and aminovinyl ketones were obtained:

TABLE 1. Conditions of the Reaction (I) + (II) = (III)

Cu(II) compound	Amt., moles/mole of (I)	T., °C	Time, h	Yield of (III), %
$CuCl_2$ anhydrous	0,05	25	3	68,5
$CuCl_2 \cdot 2H_2O$	0,05	23	6	72,3
$CuCl_2 \cdot 2H_2O$	0,05	45–50	6	78,5
$Cu(CH_3COO)_2 \cdot H_2O$	0,1	45–50	3	82,8
$Cu(CH_3COO)_2 \cdot H_2O$	0,025	18	12	
		40–50	3	77,0
$CuSO_4 \cdot 5H_2O$	0,1	40–50	10	37,4
$CuSO_4$ anhydrous	0,1	40–50	7	77,0
$Cu(C_{17}H_{35}COO)_2$	0,05	40–50	3	77,0
$Cu(OH)_2 \cdot CuCO_3$	0,1	40–50	20	40,7
$Cu(OH)_2$	0,1	40–50	13	42,4
$Cu(acac)_2$	0,1	50–55	6	56,3
(XIV)	0,05	50–55	3	73,5

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TABLE 2. Acetylenic Ketone Products of the Type (VIII)-(XI) and (XVII), (XVIII)

Obtained ketone	Acylation catalyst (0.10 mole/mole of substrate)	T., °C	Time, h	Yield of ketone, %
(VIII)	$CuCl_2 \cdot 2H_2O$	45–50	6	70,3
	$CuCl_2$ anhydrous	23	4	73,0
	$Cu(CH_3COO)_2 \cdot H_2O$	50–60	3	64,5
	(XIV) *	50–60	6	86,0
	$Cu(acac)_2$	50	30	84,1
(IX)	$CuCl_2$ anhydrous	25	3,5	84,9
(X)	$CuCl_2 \cdot 2H_2O$	55–60	2	90,1
	$CuCl_2$ anhydrous	40	3,5	88,4
(XI)	$CuCl_2 \cdot 2H_2O$	55	8	64,3
	$CuCl_2$ anhydrous	50–55	4	76,2
(XVII)	$CuCl_2$ anhydrous	40	8	95,6
	$Cu(acac)_2$	60	6	83,8
	(XVI) *	60	6	82,5
(XVIII)	$CuCl_2$ anhydrous	50	12	43,5
	$Cu(acac)_2$ *	50–60	7	45,9
	(XV) *	50–60	7	59,0

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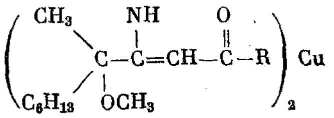
*0.05 mole of chelate per mole of acetylene substrate.

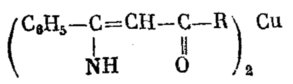
TABLE 3. Characteristics of Chelastes (XIII)-(XVI)

Compound	mp, °C (from CH_3OH)	Cu found, %	Molecular formula	Cu calc., %
(XIII)	79–83	11,2	$(C_{15}H_{28}NO_2)_2Cu$	10,8
(XVI)	117–119	10,5	$(C_{16}H_{30}NO_2)_2Cu$	10,6
(XV)	130–132	14,4	$(C_{12}H_{14}NO)_2Cu$	14,4
(XVI)	193–195	13,7	$(C_{13}H_{16}NO)_2Cu$	13,6



$$\left(\begin{matrix} CH_3 \\ C_6H_{13} \end{matrix} \!\!> C(OCH_3)-\overset{NH}{C}=CH-\overset{O}{\overset{\|}{C}}-R\right)_2 Cu$$

(XIII), (XIV)



$$\left(C_6H_5-\underset{NH}{C}=CH-\underset{O}{\underset{\|}{C}}-R\right)_2 Cu$$

(XV), (XVI)

$R = CH(CH_3)_2$ (XIII), $C(CH_3)_3$ (XIV); $CH(CH_3)_2$ (XV); $C(CH_3)_3$ (XVI)

The choice of chelate, which was used in catalytic quantities (0.05 mole per mole of acetylene compound), was determined by the structure of the final acetylenic ketone. Thus, in the acylation of (I) by acyl chloride (VI) chelate (XIV) was used. In addition, the catalytic action of $Cu(acac)_2$ was verified. The results are shown in Tables 1-3.

In the acylation of (I) by acyl chlorides (II) and (VI) the chelates of aminovinyl ketones (XIII) and (XIV) were found to be more active catalysts than $Cu(acac)_2$. Thus, the reaction of (I) with (II) in the presence of chelate (XIII) is complete in 3 h and the yield of (III) is 73.5%, while for completion of this reaction with $Cu(acac)_2$ 6 h is necessary and the yield of ketone (III) is 56.3%. One can assume that the high activity of chelates (XIII) and (XIV) is due to their solubility in benzene, and even after addition of (I) the reaction mixture remains homogeneous. By interaction of (I) with (VI) we obtained (VIII) in 84.1% yield. However, for complete reaction 30 h was needed. It was observed that the order of addition of the reactants influences the product yield. Addition of TEA to the mixture containing the complex before addition of the acetylene component adversely affects the reaction and the yield of (VIII) is 54.5% (30 h, 50°C).

Compound (V) reacts with (VI) at 40-60°C in 6-8 h in the presence of (XVI), $Cu(acac)_2$, and $CuCl_2$ (anhydrous) to form (XVII) (yield 82-95%). With the use of acyl chloride (II) the yield of (XVIII) is only 43-59%. The decrease in yield can be explained by the formation of ketone dimer from (II) in the TEA medium.

EXPERIMENTAL

Gas–liquid chromatography was carried out on a Chrom-4 chromatograph (column 2.5 × 3 mm with 5% PEGA on 0.25-0.36 mm Sterchamol, carrier gas N_2). The methyl esters of tertiary acetylenic alcohols and Cu(II) chelates were obtained by the methods of [4, 5]. The properties of chelates (XIII)-(XVI) are shown in Table 3.

2,2-Dimethyl-6-methoxy-4-dodecyn-3-one (III). to 100 ml of benzene or toluene 0.85 g (0.005 mole) of $CuCl_2 \cdot 2H_2O$, 16.8 g (0.1 mole) of ester of (I), 12.6 g (0.125 mole) of TEA, and 13.2 g (0.125 mole) of the acyl chloride of (II) were added. The mixture was stirred for 6 h at 45-50°C under Ar or N_2. the reaction was followed by gas–liquid chromatography. The reaction mixture was decomposed with water, extracted with ether, and dried with Na_2SO_4. Compound (III) was obtained in amount of 17.5 g with yield of 73.5%. The conditions of reaction with other salts and chelates are shown in Table 1. Acetylenic ketones (III), (VIII)-(X), (XVII), and (XVIII) were identical with those cited in [1, 6]. The conditions of synthesis of ketones (VIII)-(X) and (XVII)-(XVIII) are shown in Table 2.

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CONCLUSIONS

Salts and chelates of bivalent copper effectively catalyze the formation of acetylenic ketones from terminal acetylene compounds and carboxylic acid chlorides in the presence of tertiary amines.

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CLEAVAGE OF ETHERS AND ESTERS BY PHOSPHORUS HALIDES

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The cleavage of ethers, including cyclic ones, by the simultaneous action of PBr_3 and concentrated HBr under aprotic conditions at 120-150°C has already been discussed [1]. Thus, the corresponding mono- and dibromides (in the case of a cyclic ether) are formed, and no resinification takes place. The individual action of PBr_3 and concentrated HBr do not lead to cleavage of the ethers, and therefore the formation of a more active cleaving reagent, phosphorous acid bromide, can be assumed to take place:

$$PBr_3 + H_2O \rightarrow [HOPBr_2] \rightarrow HPOBr_2$$

A reaction scheme has been proposed, according to which a donor–acceptor interaction and the formation of an O–P bond are accompanied by intramolecular nucleophilic substitution by the S_Ni mechanism. It was assumed that the cleavage of the O–C bond and the substitution of O by Br takes place primarily at the C atom bound to the alkyl substituent with the bromine atom taking the place of the oxygen atom, indicating an S_N2 mechanism. This was confirmed by the fact that 2-ethylthiolane is obtained from 2-ethyltetrahydrofuran, without admixture of an isomer.

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