CONCLUSIONS

1. We have established conditions for the reaction of bromophenylacetylene with copper(I) cyanide whereby the yield of phenylcyanoacetylene can be increased from 37 to 80%.

2. The reaction of phenylcyanoacetylene and cyanoacetylenic alcohols with 1,2- and 1,3-glycols does not terminate with the formation of substituted β -organyloxyacrylonitriles; the latter undergo intramolecular cyclization to the corresponding 2-(cyanomethyl)-1,3-dioxolanes and 1,3-dioxanes.

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CU(I) SALTS AS CATALYSTS OF ACETYLENE CONDENSATION

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In the presence of K_2CO_3 , Cu(I) salts in pyridine efficiently catalyze the substitution of aromatic halogen by alkynyl groups [1]

$$\operatorname{Arl} \xrightarrow{\operatorname{HC} \cong \operatorname{CR}}_{\operatorname{K_2CO_5, Cu (I), C_8H_5N}} \operatorname{ArC} \cong \operatorname{CR}$$

Here we report some results of a further examination of this reaction.

The activity of Cu(I) salts in this condensation far exceeds that of metallic copper, which we suggested earlier as catalyst [2, 3]. Replacement of Cu by the equivalent quantity of CuI considerably intensifies the reaction (Table 1).

The catalytic activity of CuCl is identical to that of CuI, but the latter is preferable, since it excludes the possibility of partial conversion of the more reactive aromatic iodide to the chloride by halogen exchange [7]. The Cu(I) salts are much more active than Cu₂O, probably because of their better solubility in pyridine. Thus under identical conditions the reaction time for condensation of methyl o-iodobenzoate (I) and phenylacetylene (II) in the presence of Cu₂O is 9-10 h as against 3.5 and 17 h with CuI (CuCl) and Cu, respectively



The rate of reaction depends on the quantity of the Cu(l) salt. The reaction time for condensation of (l) with (ll) diminishes from 12 h to 40 min as the quantity of CuI is changed from 0.03 to 4 moles per mole of (l) (Fig. 1).

The nature of the base affects the catalytic action of the Cu(l) salts. For example, the reaction time for condensation of (l) with (II) increases by a factor of ~ 8 if, other things being equal, K₂CO₃ is replaced by KHCO₃.

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ou or or in with HO-CH th the Flesence of Cut and Cutl	o-CH3OOGGeH4 p-CH3OOGGeH4 g-CsH4N pyridyl b-C3H4N p, C3H4N	$I_{5} \qquad C(CH_{3})_{2}OR' * \qquad C(CH_{3})_{2}OR' \qquad CH(OC_{2}H_{3})_{2} \qquad \beta-C_{5}H_{4}N \qquad C(CH_{3})_{2}OR' \qquad C(CH_{3})_{2}OR'$	95 93 88 83 90 77	,	5 3,5† 23† 1 1-1,5 11 18,5	[4] 8 [4] [†] 65-75 [4] [†] 4,5 [5] 6-6,5 [5] 40-42 [6] 22 [†]
	H, p-CH300CCaH,	C(CH ₃) ₂ OR' * C(CH ₃) ₂ OR'	95 93		3,5 † 23 †	8 [4]† 65–75 [4]†
A THE TO MOMPONE	0-CH300CC	C ₆ H ₅	80		3,5	17 [4]
	Ar	æ	Yield, 🌾	Reaction time, h	Cuľ	Cu

TABLE 1. Condensation of Arl with $HC \equiv CR$ in the Presence of Cul and Cu(l)

With twice the quantity of HC = CR (3 moles per mole Arl).



Fig. 1. Dependence of the reaction time for condensation of methyl o-iodobenzoate (I) with phenylacetylene (II) on the quantity of catalyst.

 $[*]R = CH(CH_3)OC_2H_5.$

Moreover, K_2CO_3 is also more effective than Na_2CO_3 , $CaCO_3$, KF, etc. The failure of earlier attempts to use CuI as catalyst for preparing tolans from anylacetylenes and iodobenzenes probably stemmed from the low efficiency of the chosen condensing base, tertiary amines [8].

Condensation in the presence of Cu(I) salts is accompanied by the appearance of the characteristically colored copper(I) acetylides in the reaction mixture. Furthermore, the minimum reaction time is almost identical to the reaction time of the iodide with the copper(I) acetylide. Separate experiments revealed that under the conditions of condensation but in the absence of the aryl iodide, the conversion of phenylacetylene (II) to copper(I) phenylacetylide is not more than 30% over a period of 2.5 h. Equally, significant quantities of the phenylacetylide are not formed without K_2CO_3 . All this undoubtedly implicates acetylides as intermediates in the catalytic reaction.* The function of the condensing base is probably to ensure that the copper(I) acetylide is formed in the requisite quantity and at an adequate rate. The nature of the base probably controls both the position of the equilibrium and the rate of this stage and thus affects the rate of the entire process.

Having discovered the catalytic activity of Cu(I) salts, we naturally wondered whether the action of metallic copper was due to the presence of oxidized species. Estimates based on the figures of Table 1 and Fig. 1 show that the rate of reaction observed in the presence of copper would require the presence of ~0.02 g-atom Cu(I) per mole ArI. This would represent a content in the metallic catalyst of ~5 wt. % of Cu(I) compounds based on Cu_2O . Such a small quantity of Cu(I) could easily be formed either by oxidation of the catalyst during preparation or in the course of condensation by processes such as Ullmann coupling.

To find the extent to which Cu(I) is formed, we treated the copper powder used as catalyst [12] in an inert atmosphere with pyridine. After filtration, the reaction between (I) and (II) was carried out in the filtrate; we added neither metallic copper nor a Cu(I) salt but only K_2O_3 to the solution of reactants in pyridine. Under these conditions (I) condensed with (II) but rather more slowly than would be usual in the presence of copper. The use of pyridine specially deoxygenated before the run further increased the reaction time. Consequently, the activated specimens of the metallic catalyst contain pyridine-soluble oxidized copper species, which to a considerable extent are also responsible for its catalytic action.

However, we found simultaneously that copper powder after repeated treatment with pyridine also retains its catalytic activity and scarcely differs in efficiency from freshly prepared copper. In this context we repeated these experiments in modified form: We treated the copper beforehand not with pure pyridine but with a pyridine solution of iodide (I) and, after filtration, we carried out the acetylene condensation in the filtrate without adding the catalyst. The reaction time was the same in this case and in the presence of copper powder, which on the one hand definitely confirms that Cu(I) is the active component of the metallic copper catalyst and on the other hand means that part of the CU(I) is formed by direct interaction of Cu with ArI, i.e., probably in the side reaction of coupling of aryl iodides.

The intensification of acetylene condensation by Cu(l) salts markedly simplifies the preparation of monoand polyethynylarenes



by the method suggested earlier [12, 13]. Thus we synthesized without difficulty 3,5-diethynylpyridine (V) in 50% overall yield from 3,5-diiodopyridine (III) and 3-methyl-3-(1-methyl-2-oxabutyloxy)-1-butyne (IV) (Table 1) [14]. In some cases condensation of halogen derivatives and acetylenic alcohols with an unprotected hydroxyl group became possible. For example we were able to prepare 1-(o-methoxycarbonylphenyl)-3-methyl-1-butyn-3-ol (VI) [4] directly from 2-methyl-3-butyn-2-ol (VII) and (I) in 90% yield with a reaction time of 2.5 h



However, the condensation with an unactivated halide [15] - o-iodoanisole – under the same conditions was more complicated and proceeded only to 50% completion, whereupon it terminated, apparently because of the decomposition of the intermediate substituted copper(I) acetylide. During this reaction the original red acetylide

*The mechanism of condensation of aryl iodides with substituted copper(I) acetylides is discussed [9-11].

precipitate was slowly converted to a dark-colored compound of unknown structure, which did not react with the aryl iodide and exploded when heated in the dry state.

EXPERIMENTAL

2-(Methoxycarbonyl)tolan. a) Compound (I) (5.2 g), (II) (3.1 g), powdered K_2CO_3 (5.2 g), and CuI (1.9 g) in pyridine (50 ml) were heated at 115-117°C in an atmosphere of N₂ until (I) disappeared (GLC). After cooling, the reaction mixture was diluted with ether, washed with dilute HCl and water, and dried over MgSO₄. 2-(Methoxycarbonyl)tolan [4] was purified by chromatography on Al_2O_3 (activity II) in benzene; the yield and reaction time are given in Table 1.

b) Compound (I) (5.2 g) was condensed with copper(I) phenylacetylide (3.3 g) [9] in pyridine (50 ml) under reflux; the reaction time was 40 min.

Formation of Copper (I) Phenylacetylide under the Condensation Conditions. Compound (II) (1 g), CuI (1.9 g), and K_2CO_3 (2.5 g) in pyridine (25 ml) were refluxed in an atmosphere of N_2 for 2.5 h, whereupon the mixture was diluted with ether (0.5 liter) and filtered. The filtrate was washed with dilute HCl and water and dried over K_2CO_3 . Removal of ether gave a mixture (0.5 g) of (II) and diphenyldiacetylene, which were identified by TLC and GLC. The precipitate of copper (I) phenylacetylide and inorganic salts was separated by filtration, washed with ether and water, and shaken with a mixture of dilute HCl and ether. The ethereal layer yielded (II) (0.3 g).

Compound (II) (1 g) and CuI (5 g) in pyridine (25 ml) was refluxed for 2.5 h. After the same treatment the ethereal solution gave (II) (0.8 g) contaminated with a small quantity of diphenyldiacetylene. The ethereal extract derived by decomposing the precipitated inorganic salts with dilute HCl did not contain (II).

Identification of the Active Component of the Metallic Copper Catalyst. a) Copper powder (0.70 g) and K_2CO_3 (2 g) in pyridine (50 ml) were refluxed for 3 h in an atmosphere of N_2 ; the supernatant liquid was carefully transferred by syringe to another flask. After purging with N_2 , (I) (5.2 g), (II) (6.1 g), and K_2CO_3 (5.2 g) were added and the condensation was carried out. The reaction terminated after 14 h. The precipitated copper and K_2CO_3 after decantation of pyridine were carefully washed with water, acetone, and ether; copper (0.62 g) was recovered.

Use of pyridine distilled in a stream of N_2 immediately before the run increased the duration of the reaction to 36 h when this procedure was employed with an atmosphere of Ar.

b) Condensation was carried out in pyridine as before, starting with (I) in addition to copper and K_2CO_3 ; (II) and a second portion of K_2CO_3 were added to the solution after removal of the copper. The condensation terminated after 8 h.

Acetylene Condensation. The condensations of the compounds listed in Table 1 and of (I) and o-iodoanisole with (VII) were carried out under the same conditions as (I) and (II) in the preparation of 2-(methoxycarbonyl)tolan.

An analytical sample of β , β' -bis[3-methyl-3-(1-methyl-2-oxabutyloxy)butyn-1-yl] pyridine was further purified by preparative TLC on Al₂O₃ (activity II) in CHCl₃, n_D^{20} 1.5069. Found: N 3.59%. C₂₃H₃₃NO₄. Calculated: N 3.62%. IR spectrum (CCl₄, ν , cm⁻¹): 2235 (C=C); 1053, 1080, 1125, 1155 (C=O-C=O-C).

 $\begin{array}{l} \beta,\beta'-\text{Bis}\,(3-\text{methyl-}3-\text{hydroxybutyn-}1-\text{yl})\text{pyridine.} \quad \beta,\beta'-\text{Bis}\,(3-\text{methyl-}3-1-\text{methyl-}2-\text{oxabutyloxy})\text{butyn-}1-\text{yl})\text{pyridine} \quad (920 \text{ mg}) \text{ was hydrolyzed in acidic aqueous dioxane at 20°C [13] to give the diol (560 mg, 96.5\%), mp 120-121°C (from CCl₄). Found: N 5.88\%. C₁₅H₁₇NO₂. Calculated: N 5.76\%. IR spectrum (CHCl₃, <math>\nu$, cm⁻¹): 2235 (C = C); 3607, 3390 br (OH).

3.5-Diethynylpyridine (V). A carefully powdered mixture of β , β '-bis(3-methyl-3-hydroxybutyn-1-yl)pyridine (200 mg) and KOH (35 mg) was heated in a vacuum sublimation apparatus at 130°C (1 mm). The sublimed (V) was chromatographed on Al₂O₃ (activity II) in CHCl₃ and repeatedly sublimed. The yield of (V) was 70 mg (67%), mp 76-76.5°C. Found: N 11.10%. C₃H₅N. Calculated: N 11.02%. IR spectrum (CCl₄, ν , cm⁻¹): 3315 (C=CH), 2120 (C=C). PMR spectrum (CH₂Cl₂, δ , ppm): 3.50 (C=CH); 7.88 (γ =H); 8.62 (α =H).

CONCLUSIONS

1. We have carried out the acetylene condensation of several aromatic iodo compounds in the presence of CuI and K_2CO_3 . We have established the distinctive features of the proposed catalytic scheme.

2. The active components of the metallic copper catalyst are Cu(I) compounds.

3. Catalytic substitution of aromatic halogen by alkynyl groups involves the intermediacy of copper (I) acetylides.

4. We have synthesized 3,5-diethynylpyridine by condensation of 3,5-diiodopyridine with 3-methyl-3-(1-methyl-2-oxabutyloxy)-1-butyne followed by hydrolysis and alkaline cleavage of the diol.

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FLUORINE-CONTAINING HETEROCUMULENES

15*. BIS(TRIFLUOROMETHYL)KETENE N~(BENZENESULFONYL)IMINE

IN REACTIONS WITH VINYL ETHYL ETHER AND PHENYLACETYLENE

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UDC 542.91:547.318' 161:547.538.241

Bis (trifluoromethyl) ketene N-phenylimine reacts with vinyl ethers and phenylacetylene as a heterodiene; the reaction involves the aromatic ring of the ketenimine and forms fluorine-containing quinolines. The intermediate four-membered cyclic compounds could not be isolated [2, 3]. The reactivity of fluorine-containing ketenimines varies inversely with the basicity of the nitrogen [4]. Consequently, we would expect bis (trifluoromethyl) ketene N- (benzenesulfonyl) imine (I) [5] to be particularly reactive; ketenimine (I) is also convenient for examining the behavior of a cumulated system of double bonds in cycloaddition reactions, since the C-N bond is not conjugated with the aromatic ring.

Here we report a study of the reactions of ketenimine (I) with vinyl ethyl ether and phenylacetylene. Ketenimine (I) reacts violently with vinyl ethyl ether at room temperature with tar formation; this can be obviated by carrying out the reaction in ethereal solution. The reaction forms the unstable product of 1,2-cycloaddition to the C = N bond of the ketenimine – azetidine (II). Analogy with the results of [6] suggests that azetidine (II) is in equilibrium with betaine (III). In fact, betaine (III) reacts as a 1,4-dipolar system in α -addition to cyclohexyl isocyanide (cf. [7]) to form the stable iminopyrrolidine (IV)

* For communication 14, see [1].

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