REACTION OF COPPER ACETYLIDES WITH α-IODOPYRIDINE

I. L. Kotlyarevskii, V. N. Andrievskii, and M. S. Shvartsberg

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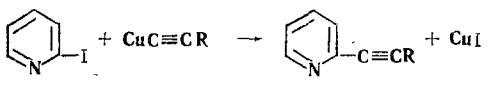
In the case of α-iodopyridine, it is shown that reaction of copper acetylides with iodopyridines can be used to introduce acetylenic substituents into the pyridine ring.

The reaction between copper acetylides and aryl iodides [1–3] has been suggested for introducing substituents containing a triple bond into aromatic compounds. Recently this method was successfully used for synthesizing acetylenic derivatives of furan and thiophene, among them naturally-occurring compounds [4]. It was natural to assume that reaction of copper acetylides with iodopyridine will proceed similarly, and that particularly with α and γ isomers, where the halogen atoms are more mobile. We checked this assumption with α-iodopyridine.



R=C_6H_5 (I); p-$CH_3OC_6H_4$ (II); p-$O_2NC_6H_4$ (III); n-C_4H_9 (IV); p-$C_6H_5C_6H_4$ (V); p-$C_6H_5C_6H_4C{\equiv}C$— (VI).

If copper phenylacetylide reacts completely with iodobenzene in boiling pyridine in 10 hours [3], then in the case of α-iodopyridine under the same conditions reaction is complete in 1 hour. For other acetylides the time of reaction with α-iodopyridine is also 1–2 hours. An exception is copper p-nitrophenylacetylide (7 hours). The yields of acetylenes I–V are 52–95%. The low yields of diacetylene VI (7%) is probably connected with the instability of the corresponding diacetylide. I is not found to be formed when a mixture of phenylacetylene, α-iodopyridine, and Cu_2Cl_2 are heated in pyridine.

EXPERIMENTAL

α-Iodopyridine was prepared by the method of [5], from α-aminopyridine, yield 56.2%, bp 85° (5 mm).

2-Phenylethynylpyridine (I). 4.3 Cu phenylacetylide, was added, with stirring, to a solution of 5 g α-iodopyridine in 70 ml dry pyridine, under N, and the whole heated to 120°. The orange-brown solution which formed after some minutes turned to a transparent yellow solution. The heating at 120° was continued for 1 hr, when practically all the α-iodopyridine reacted (the course of the reaction was checked by thin-layer chromatography on Al_2O_3.) After cooling, the reaction products were poured into 300 ml dilute HCl (1:2) plus ice, the mixture stirred for 30 min, filtered, the residue dissolved in 20 ml petrol ether (bp 40–60°), and chromatographed over Al_2O_3 (II activity). I was eluted with $CHCl_3$, and vacuum-distilled. The pyridinacetylenes II–VI were synthesized similarly. Yields and physical constants of the compounds prepared are given in the table.

2-p-Diphenylylethynylpyridine (V). Prepared from 9.5 g/Cu p-diphenylylacetylide and 7 g *L*-iodopyridine. After treating the reaction products with HCl, the precipitate, containing the hydrochloride of V, was filtered off, mixed with 200 ml 20% KOH, the V extracted with benzene, and the benzene solution chromatographed on Al_2O_3, the eluant being ether. The pyridylacetylene VI was isolated similarly.

Yields and Physical Constants of Compounds Prepared

Compound no.	Reaction time, hr	Bp, °C (pressure, mm) Mp, °C	IR spectrum $\nu_{C\equiv C}$, cm^{-1}	Formula	N, % Found	N, % Calculated	Yield, %
I	1	162—164 (3)[6]	—	—	—	—	85.8
II	2	*	2224	$C_{14}H_{11}NO$	6.69	6.69	67.8
III	7	155.5—156 5[7]	—	—	—	—	52.0
IV	1	79—81 (1)**	2230	$C_{11}H_{13}N$	9.04	8 79	94.6
V	1	119.5—120.5 (petrol ether)	2225	$C_{19}H_{13}N$	5.63	5.49	54.0
VI	2***	135—136 benzene + petrol ether 1:3)	2223	$C_{21}H_{13}N$	4.83	5.01	7.0

*n_D^{20} 1.6645. Picrate mp 161–162° (ex 50% acetone). Found: N 12.68%. Calculated for $C_{14}H_{11}NO \cdot C_6H_3N_3O_7$: N 12.78%.

**n_D^{20} 1.5397. Picrate mp 85–86° (ex 60% MeOH). Found: N 14.21%. Calculated for $C_{11}H_{13}N \cdot C_6H_3N_3O_7$: N 14.43%.

***Time of heating at 120°.

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Institute of Chemical Kinetics and Combustion, Siberian Division AS USSR, Novosibirsk