Synthesis of Aryl and Heterocyclic Acetylenes *via* Copper Acetylides

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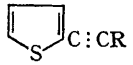
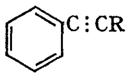
A SIMPLE synthesis of various disubstituted acetylenes, *e.g.*, (I), from copper acetylides and appropriate iodo-heterocyclic derivatives has recently been reported.[1] Unfortunately, monosubstituted acetylenes such as (II) cannot be directly prepared by this method since monocuprous acetylide is unknown. This difficulty can be overcome by the introduction of a substituted cuprous acetylide carrying a readily removable substituent and a synthesis of monosubstituted acetylenes, *e.g.*, (V), based on this approach is now reported.



(I) R=CH_2OH
(II) R=H
(VIII) R=CHO



(III) R=CH_2OH
(IV) R=CHO
(V) R=H

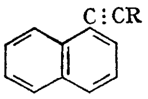
In a typical example, iodobenzene and the cuprous salt of the tetrahydropyranyl ether of prop-2-yn-1-ol were heated under reflux in pyridine solution under nitrogen and the product was hydrolysed with 2N-sulphuric acid to give 3-phenylprop-2-yn-1-ol (III). Heterogeneous oxidation of such $\alpha\beta$-acetylenic alcohols by manganese dioxide in low yield has already been reported;[2] with nickel peroxide[3] in benzene at room temperature the alcohol (III) gave the aldehyde (IV) in 70% yield. On treatment with aqueous methanolic 2N-sodium hydroxide at 50° deformylation[4,5] to phenylacetylene (V) occurred (87%). In the same way the alcohols (I),[1] (VI; m.p. 44°),† and (VII)[6] prepared similarly, were converted into the aldehydes (VIII) (74%),[1] (IX) (b.p. 85—86°/0·5 mm., 81%), and (X) (74%),[1] and then into 2-ethynylthiophen (II) (80%),[7] 1-ethynylnaphthalene (XI) (b.p. 143°/25 mm., 86%), and 5-ethynyl-2,2′-bithienyl (XII) (91%).[6]

The overall sequence (i) could be shortened by direct oxidation of the alcohols with nickel peroxide in aqueous methanolic 2N-sodium hydroxide at 50° to give the corresponding acetylenes in somewhat lower yields (*ca.* 50%).

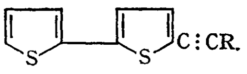
$$\text{(i)}\quad RI \xrightarrow[\text{(2)}\quad H^+]{\text{(1) }CuC{\vdots}C{\cdot}CH_2OTHP} RC{\vdots}C{\cdot}CH_2OH \xrightarrow[C_6H_6]{NiO_2} RC{\vdots}C{\cdot}CHO \xrightarrow{OH^-} RC{\vdots}CH$$

$$\text{(ii)}\quad RI \xrightarrow[\text{(2)}\quad H^+]{\text{(1) }CuC{\vdots}C{\cdot}CH(OEt)_2} RC{\vdots}C{\cdot}CHO \xrightarrow{OH^-} RC{\vdots}CH$$

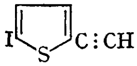
$$\text{(iii)}\quad RI \xrightarrow{CuC{\vdots}C{\cdot}CO_2Et} RC{\vdots}C{\cdot}CO_2Et \xrightarrow[\text{(2) }Cu^{II}]{\text{(1) }OH^-} RC{\vdots}CH$$



(VI) R=CH_2OH
(IX) R=CHO
(XI) R=H



(VII) X=CH_2OH
(X) R=CHO
(XII) R=H



(XIII)

Alternative routes (ii) and (iii) are possible. Sequence (ii)[1] gave the required aldehyde directly but there are some practical difficulties in working up these propargylaldehyde derivatives using this method; in our hands sequence (i) is preferred. Similarly, sequence (iii) is feasible but hydrolysis and cupric-catalysed decarboxylation[8] of the propiolic acids offers no advantage.

This method is an addition to the standard methods of synthesis of monosubstituted aryl and

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† Compounds (VI), (IX), (XI), and (XIII) gave satisfactory analyses; all other compounds were compared with known standards.

heterocyclic acetylenes. No vigorous dehydrohalogenation is required and some inaccessible acetylenes, *e.g.*, (XIII) [m.p. (of mercury derivative) 201—203°] become readily available.

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