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A NOVEL STEREOSPECIFIC REDUCTION OF ALKYNES TO ALKENES

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Summary : Zinc-copper couple in boiling methanol reduces alkynes to olefins in nearly quantitative yields. Terminal acetylenes are converted to terminal ethylenes, whereas disubstituted acetylenes are transformed to (Z)-olefins.

In continuation of our investigations[1,2] on the reactions of zinc-copper couple as a reducing agent, we have discovered another method for stereospecific reduction of carbon-carbon triple bonds to (Z)-olefins.

Catalytic hydrogenations with various poisoned catalysts have been widely used to obtain cis-olefins with just acceptable yields[3-6]. Levin et al[7] used lithium in tetrahydrofuran at -78° to convert diphenylacetylene to cis-stilbene quantitatively. In like manner, Jardine et al[8] reduced diphenylacetylene to cis-stilbene using a ruthenium-based catalyst. Our method consists in just heating the alkyne with zinc-copper couple in methanol.

Generally the compound to be reduced (1g) is treated in boiling methanol (300 ml) with Zn-Cu couple prepared from zinc dust[9] for various times. The reactions are monitored by T.L.C. After cooling, the exhausted couple is filtered off and the filtrate evaporated under reduced pressure to about one third of the original volume. The latter is then extensively diluted with distilled water and extracted twice with methylene chloride or ether (50 ml each time). The combined fractions are dried over anhydrous $MgSO_4$ and evaporated to dryness. The yield is generally more than 95%. There are no traces of any trans isomer present in the reaction product, nor any unchanged starting material as detected by nmr spectroscopy.

We were able to reduce the following compounds :

Alkyne	Product	Reaction time
Phenylacetylene	styrene	3 - 4 hrs
Diphenylacetylene	cis-stilbene	5 - 6 hrs
2-butyn-1,4-diol	cis-buten-1,4-diol*	1 - 2 hrs
3-methyl 1-pentyn-3-ol	3-methyl 1-penten-3-ol	9 - 10 hrs
3,8-dimethyl 4,6-decadiyn-3,8-diol	cis-(3,8-dimethyl 4,6-decadien-3,8-diol)	22 - 24 hrs

* The yield is just about 57%, the compound being very highly retained by the couple.

All reaction products were characterised by nmr, ir and uv spectroscopy. Further investigations are in progress.

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