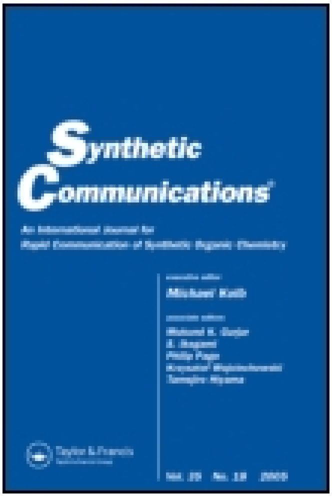

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Isomerisation of Primary Propargyl Alcohols to Vinyl Ketones Mediated by $Hg(OAc)_2$

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ISOMERISATION OF PRIMARY PROPARGYL ALCOHOLS TO VINYL KETONES MEDIATED BY $Hg(OAc)_2$

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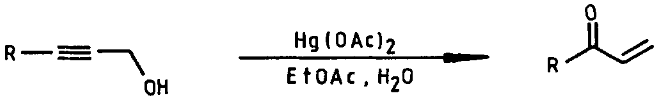
Abstract: Mercuric acetate mediated isomerisation of primary propargyl alcohols to vinyl ketones analagous to Rupe rearrangement is described.

The vinyl ketone is one of the important functional group in organic synthesis especially as a good partner in Diels-Alder, Michael and Baylis Hillman reactions. In the course of the studies on the preparation and utility of propargyl alcohols[1], we have observed an interesting rearrangement of primary propargyl alcohols to vinyl ketones mediated by $Hg(OAc)_2$ (scheme-I), hitherto not possible by conventional Rupe rearrangement[2], wherein only secondary and tertiary propargyl

SCHEME I



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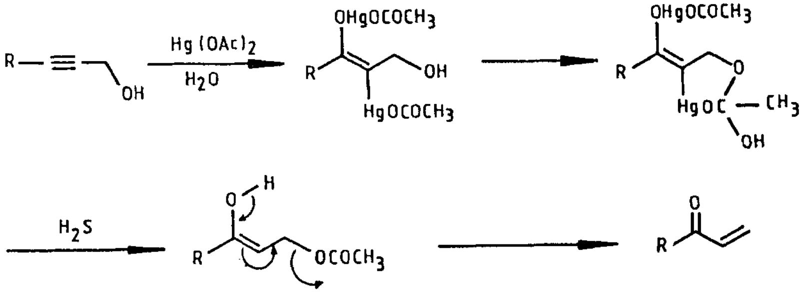
alcohols underwent this kind of transformation. In the case of primary propargyl alcohols[3] harsh conditions ($HgO,H_2SO_4;HgO,HClO_4$)were required for the transformation albeit in low yield.

In the preliminary study, when the the simple 2-decyne-1-ol (entry 1) was treated with excess $Hg(OAc)_2$ in ethyl acetate containing 1 eq. of H_2O and stirring the reaction at ambient temperature for 24 hrs, furnished the corresponding vinyl ketone in 80% yield.

This exclusive formation of vinyl ketone may be rationalised following a logical mechanism, where in $Hg(OAc)_2$ complexes with the acetylenic triple bond, thereby forming carbon-mercury bond with the carbon proximal to the hydroxyl group followed by the sequence of reactions as shown in scheme-II.

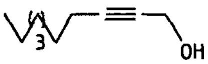
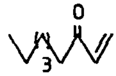
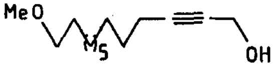
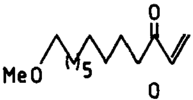
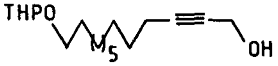
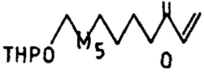
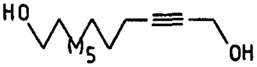
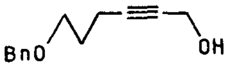
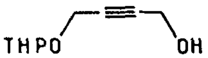
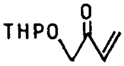
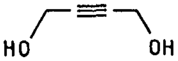
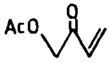
SCHEME II



To test the generality of this transformation a wide variety of propargyl alcohols were treated with $Hg(OAc)_2$ in ethyl acetate to produce the corresponding vinyl ketones in high yields under the described reaction condition, the results being summarised in Table 1.

It is interesting to note that the methyl ester, THP ether, benzyl ether and hydroxyl functionalities survived under the reaction conditions. However, in the case of 1,4-butynediol the free hydroxyl group was acetylated during the rearrangement.

Table 1: Isomerisation of propargyl alcohols to vinyl ketones

ENTRY	PROPARGYL ALCOHOLS	VINYL KETONE	YIELD*
1.			80
2.			82
3.			80
4.			88
5.			80
6.			82
7.			85

* Yields based on isolation of chromatographically homogeneous products.

In conclusion, it is pertinent to mention that a simple protocol has been reported involving mild reaction conditions for convertion of primary propargyl alcohols to vinyl ketones which will have experimental advantages over existing procedure for this important transformation[4].

Typical experimental procedure: To a solutin of 2-decyne-1-ol (0.5g, 3.2 mmol) in ethyl acetate (25ml) and water (0.06ml, 3.2 mmol) was added mercuric acetate (6.2 g, 19.2 mmol) and the reaction mixture was stirred at room temperature for 24 hours. H_2S gas was passed into the reaction mixture to precipitate out mercuric sulphide, filtered and the filterate was washed with water, brine and dried (Na_2SO_4). Purification by silica gel column chromatography afforded 1-decen-3-one (0.4g, 80%).

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4) All new compounds gave satisfactory spectral data including high resolution mass.

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