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REGIOSELECTIVE REDUCTIVE ELIMINATION OF ARYLOXYMETHYLETHYNYLCARBINOLS - SYNTHESIS OF ARYLOXYMETHYLALLENES

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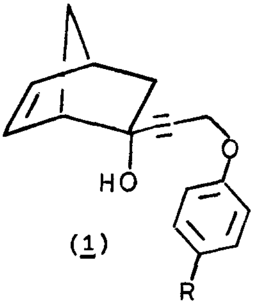
Abstract- Exclusive formation of allenes and alkenols during the reduction of aryloxymethylethynylcarbinols and ethynylcarbinols respectively, with lithium aluminiumhydride, is being reported.

Several reports have appeared in the literature on the reduction of ethynylcarbinols with LiAlH$_4$. This is one of the well known methods for the synthesis of trans-alkenols [1]. In a few instances, a mixture of allene and alkenols has been reported[2,3], the ratio of the allene to alkenols being dependant upon various factors viz., (i) the reaction time[4] (ii) drastic reaction conditions i.e., at 160°C[2] (iii) solvents used[4] (iv) structural features of the molecule[4].

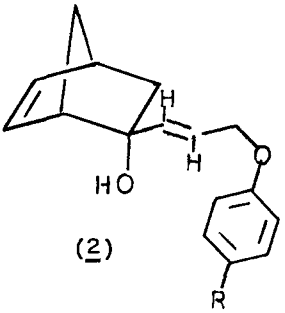
Exclusive formation of allenes in the reduction of ethynylcarbinols with LiAlH$_4$ under milder conditions has not been reported so far.

In this communication, we describe the synthesis of aryloxymethylallenes by the reduction of aryloxymethylethynylcarbinols with LiAlH$_4$.

In connection with our project in the area of sequential and competitive Claisen and retroene transformations, we were interested in the synthesis and rearrangement of the hitherto unknown compounds 1 and 2.



(1)

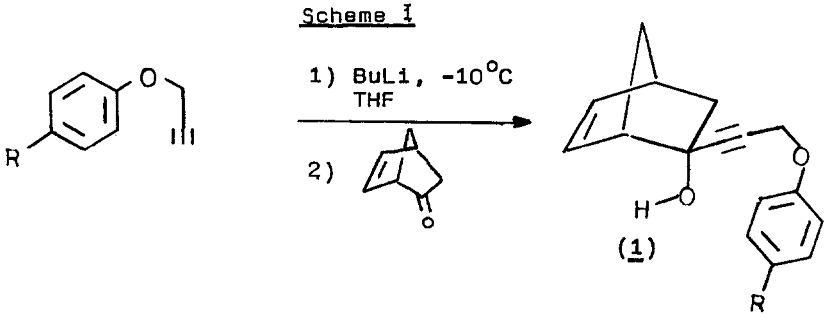


(2)

Based on the numerous literature reports, we sought to prepare the required trans-vinylcarbinols 2 by the reduction of the ethynylcarbinols 1 with LiAlH$_4$.

The endo alcohols 1a-d[5] have been synthesised in 85-91% yield (Scheme I) by the addition of butyl lithium (1.2 equiv.) to aryl propargyl ether (1 equiv.) in THF at -10°C followed by addition of norbornenone (1 equiv.).

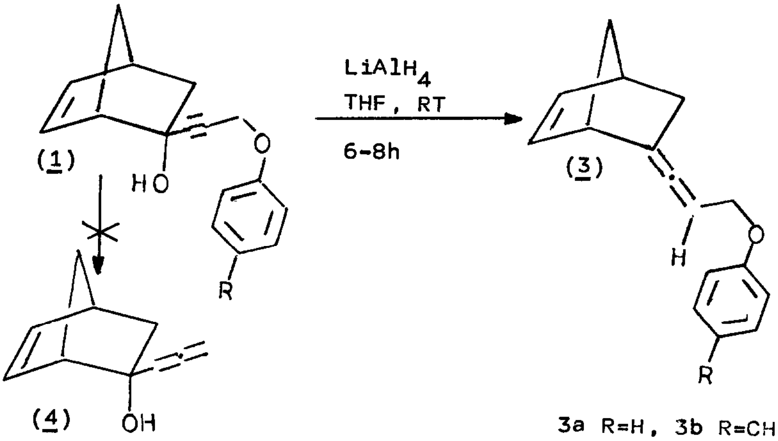
Scheme I



1a R=H, 1b R=CH$_3$,
1c R=OCH$_3$, 1d R=Cl

The reduction of the 2-(exo-1-phenoxypropynyl)bicyclo[2.2.1] hept-5-ene-endo-2-ol 1a with LiAlH$_4$ in THF at room temperature for 6h afforded the allene 3a exclusively as a single isomer, in 92% yield (Scheme II), whose stereochemistry has been tentatively fixed on mechanistic considerations (Scheme V). Neither the expected compound 2a nor the allene 4[6] arising by the reductive elimination of the phenoxide group, was formed even in minor amounts. Similarly the reduction of the other carbinols 1b-d also furnished only the aryloxymethylallenes 3b-d[7] in 90-95% yield.

Scheme II

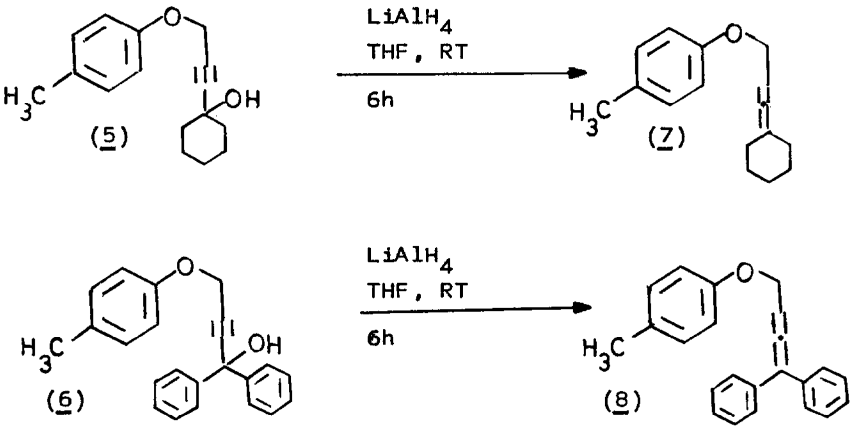


3a R=H, 3b R=CH$_3$,
3c R=OCH$_3$, 3d R=Cl

This anomolous behaviour may be due to solvents, or due to structural features and other factors. But the reaction in diethyl ether also afforded the same products viz., the allenes 3a-d, as in THF, at room temperature.

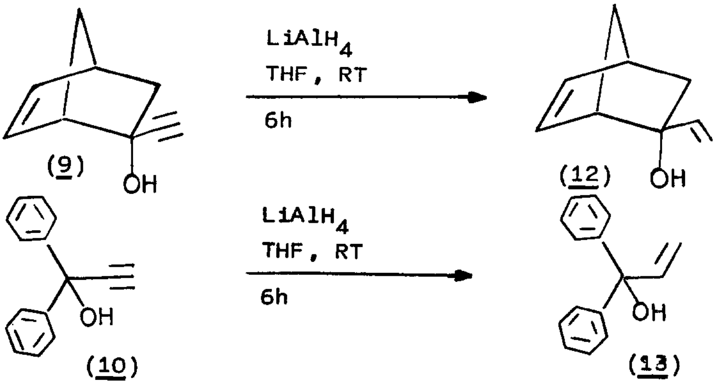
That this reaction is not uniquely undergone by norbornyl systems, but is a general one, was borne out by the other examples studied. Thus under similar conditions, the carbinols 5 and 6, also afforded only the respective allenes viz., 7 and 8 (Scheme III).

Scheme III

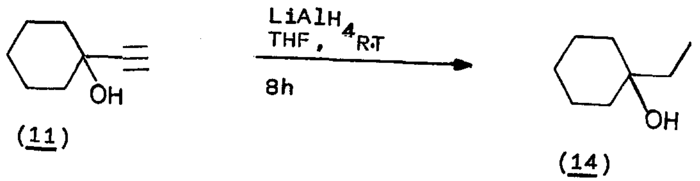


It is however, important to note that the ethynylcarbinols 9 and 10 under similar reduction conditions furnished only the respective vinylcarbinols 12 and 13, while 11 afforded the ethylcarbinol 14[8]. None of the corresponding allenic derivatives was formed (Scheme IV).

Scheme IV

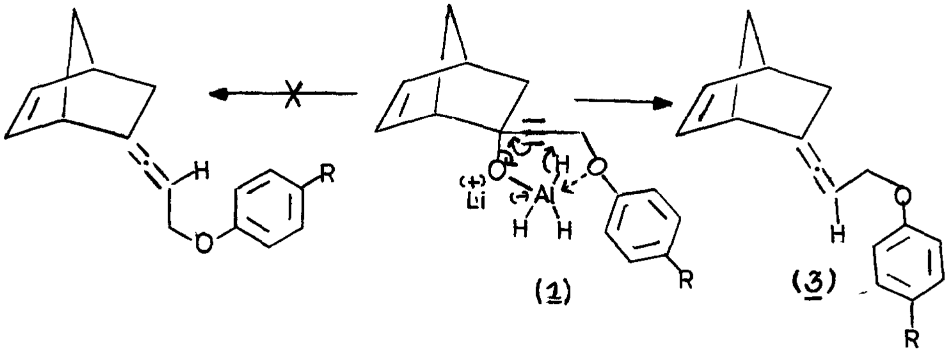


Scheme IV



Based on these findings, the formation of the allene 3 can be rationalised as outlined in Scheme V. The mechanism proposed would also account for the regioselective and stereoselective formation of only one allenic product, viz., 3. In the case of simple ethynylcarbinols, the reduction takes the normal course giving the olefinic compounds, since the internal solvation of the alkoxyaluminium hydride intermediate is not possible.

Scheme V



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4. Blunt J.W., Hartshorn M.P., Munro M.H.G., Lee Tin Soong, Thompson R.S. and Vaughan J., J.Chem.Soc., Chem.Commun ., 1980, 820.
5. Selected ^{1}H-NMR data for 1b (90 Mhz, $CDCl_3$): δ1.2-1.5(2H,m),δ2.1(2H,m), δ2.2(3H,s),δ2.7-2.9(2H,m),δ4.5(2H,s),δ5.8-6.1(2H,m) andδ6.7(4H, dd).
6. The reductive elimination of tetrahydropyranyloxy group in tetrahydropyranyloxymethylcarbinols by $LiAlH_4$ is known to give allenes, see Cowie J.S., Landor P.D., and Landor S.R., Chem.Commun., 1969, 541.
7. Selected ^{1}H-NMR data for 3b(90 Mhz, $CDCl_3$): δ1.2-1.5(2H,m),δ2.1(2H,m), δ2.2(3H,s),δ2.8(2H,m)δ4.7(2H,d)δ 5.4(1H,t)δ 5.8-6.1(2H,m), andδ6.7(4H,dd).
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