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REDUCTION OF ALPHA BETA UNSATURATED KETONES WITH LITHIUM ALUMINIUM HYDRIDE-ALUMINIUM CHLORIDE.

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Solutions of $LiAlH_4$ with a molar excess of $AlCl_3$ in ether make excellent reagents for the direct reduction of diaryl ketones, aryl alkyl ketones and certain alcohols to the corresponding hydrocarbons[1-4]. The reactive species are believed to be $AlHCl_2$ and AlH_2Cl, which act both as Lewis acids and hydride donors[5]. Reduction of alpha beta unsaturated ketones under similar conditions yields derivatives of propene, but the mechanisms by which reduction proceeds have not been clearly established and appear to be dependent on the structure of the substrate. When the geometry of the carbon chain is fixed, e.g. the enone forms part of a ring, the position of the olefinic bond remains unchanged[6-8]. This suggests that the carbonyl group alone may be involved, as in the reduction of simple ketones. For reduction of chalcones, by contrast, Brown _et al._[9] reported that migration of the olefinic bond takes place and proposed a mechanism whereby initial reduction to the saturated alcohol is followed by dehydration. More recently, Wigfield and Taymaz[10] obtained two isomeric derivatives of propene from the reduction of ethyl _p_-methoxycinnamate and suggested the formation of a resonance-stabilised carbonium ion prior to hydride attack.

We have prepared two isomeric propenones, 2-naphthyl styryl ketone _1_ and phenyl 2-(2-naphthyl)vinyl ketone _2_ [11] and three reduction products of each, namely the allylic alcohols _3_ and _4_, the saturated alcohols _5_ and _6_, and the propenes _7_ and _8_. The allylic alcohols were prepared by Braude and Gore's method[12]; the saturated alcohols by reducing _1_ or _2_ with sodium borohydride-pyridine[13], and the propenes either from the allylic alcohols by reducing the sulphur trioxide-pyridine complex with $LiAlH_4$ [14] or from the saturated alcohols by warming with

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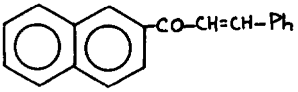
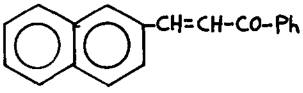
$KHSO_4$[11]. The identity of each product was confirmed by Mass Spectrometry.



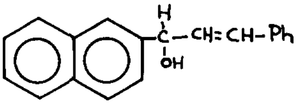
1

m.p. 105°
(lit[12] 102°)



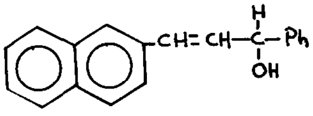
2

m.p. 155°
(lit[12] 154°)



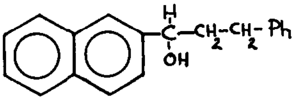
3

m.p. 77°
(lit[12] 75°)
m/e 260,244



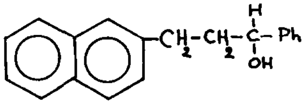
4

m.p. 74-75°
(lit[12] 76°)
m/e 260,244



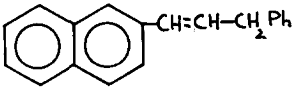
5

m.p. 64°
(lit[11] 62.5-64°)
m/e 262



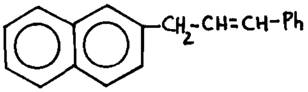
6

m.p. 69°
m/e 262



7

m.p. 64.5°
(lit[11] 63-64°)
m/e 244,229



8

m.p. 44-45°
(lit[11] 39-40°)
m/e 244,229

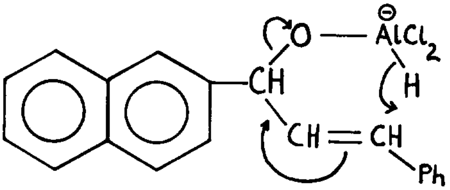
Direct reduction of 1 and 2 to the propenes 7 and 8 was carried out by adding the powdered propenone over 5 minutes to a well stirred excess of $LiAlH_4$-$AlCl_3$ (1:3) in ether at 20° under nitrogen and allowing the reaction to proceed for a further 5 minutes or 48 hours (Table 1). The isomeric propenes were readily separated from the alcoholic products by chromatography on alumina and separated from a little polymeric material by distillation (b.p. 166-171°/0.01mm). Mixtures of the propenes were analysed most satisfactorily by comparing their infrared spectra with those of a series of authentic calibration mixtures, with particular reference to the peak at 785 cm^{-1} given by 7 but not by 8. Analysis by ultraviolet spectroscopy[11] gave similar results but was tedious, while satisfactory separation of 7 from 8 by gas liquid chromatography was not achieved.

From the results presented in Table 1 it appears that the initial reduction products of 1 and 2 are in each case the allylic and, to a much lesser extent, the saturated alcohols. Subsequent reaction of the saturated alcohols is slow and each yields, as expected, the propene

Table 1 Reductions with lithium aluminium hydride-aluminium chloride (1:3).

Substrate	Time of reaction	Products (%)	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
<u>1</u>	10 minutes		12	-	47	32
	48 hours		-	-	54	33
<u>2</u>	10 minutes		-	10	31	47
	48 hours		-	-	31	56
<u>3</u>	10 minutes		-	-	55	37
<u>4</u>	10 minutes		-	-	34	54
<u>5</u>	10 minutes		96	-	Trace	-
	46 hours		-	-	74	-
<u>6</u>	10 minutes		-	95	-	Trace
	48 hours		-	-	-	79

showing overall migration of the olefinic bond. Subsequent reaction of the allylic alcohols is fast and each also gives the propene in which the olefinic bond has migrated as the major product. An S_N2 hydride displacement, such as is believed to occur in the reduction of simple alcohols and ketones[1], would not involve migration of the olefinic bond, while an intermediate carbonium ion would be expected to yield a common mixture of the two isomers. While one or both of these mechanisms undoubtedly contributes in part to the overall yield, neither can explain the predominance in each reduction of the propene showing migration of the olefinic bond. A possible reaction route, reduction of the allylic to the saturated alcohols followed by dehydration[9], does not appear to take place to any significant degree, and the most probable explanation is the intermediacy of a cyclic transition state of the type :



That such a transition state is not possible when the enone has a fixed trans configuration also provides an explanation as to why olefinic bond migration is not observed in the $LiAlH_4$ - $AlCl_3$ reduction of such systems[6-8]. An S_N2 hydride substitution appears to be the most important mechanistic route in these reactions.

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REFERENCES :

1 B.R.Brown and A.M.S.White, J. Chem. Soc., 3755 (1957).

2 R.F.Nystrom and C.R.A.Berger, J. Amer. Chem. Soc., 80, 2896 (1958).

3 J.Blackwell and W.J.Hickinbottom, J. Chem. Soc., 1405 (1961).

4 J.H.Brewster, S.F.Osman, H.O.Bayer, and H.B.Hopps, J. Org. Chem., 29,121 (1964).

5 E.C.Ashby and J.Prather, J. Amer. Chem. Soc., 88, 729 (1966).

6 J.Broome, B.R.Brown, A.Roberts, and A.M.S.White, J.Chem. Soc., 1406 (1960).

7 N.Basu, U.R.Ghatak, G.Sengupta, and P.C.Dutta, Tetrahedron, 21, 2461 (1965).

8 J.Bridgemen, E.R.H.Jones, G.D.Meakins, and J.Wicha, Chem. Commun., 898 (1967).

9 M.M.Bokadia, B.R.Brown, D.Cobern, A.Roberts, and G.A.Somerfield, J. Chem. Soc., 1658 (1962).

10 D.C.Wigfield and K.Taymaz, Tetrahedron Letters, 4841 (1973).

11 D.R.Ross and E.S.Waight, J. Chem. Soc., 6710 (1965).

12 E.A.Braude and P.H.Gore, J. Chem. Soc., 41 (1959).

13 K.Iqbal and W.R.Jackson, J. Chem. Soc. (C), 616 (1968).

14 E.J.Corey and K. Acniwa, J. Org. Chem., 34. 3667 (1969).