Tetrahedron Letters No.41, pp. 3587-3588, 1969. Pergamon Press. Printed in Great Britain.

1,4 REDUCTION OF A CONJUGATED IMINOENOLETHER WITH COMPLEX METAL HYDRIDES

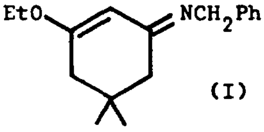
S.W. Breuer and Paul Yates

Department of Chemistry, University of Lancaster, Lancaster, England.

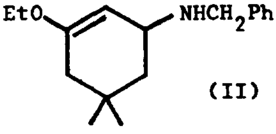
(Received in UK 11 July 1969; accepted for publication 8 August 1969)

In the course of synthetic study we prepared the enamine from dimedone and benzylamine[1] and reacted it with ethyl iodide. As expected[2], the O-ethylated product (I), an iminoenolether, was formed. As this compound is the vinylogue of an imidate, we wished to compare some of its chemical properties with those of simple imidates. The recent publication by Borch[3] reporting the reduction of imidates to amines with sodium borohydride prompted us to look at the reaction of the iminoenolether (I) with sodium borohydride. The reduction proceeded smoothly to give one main product in more than 80% yield, which could be formally derived from the starting material by the addition of 2H. This was shown by the integration of the NMR spectrum and by the fact, that under acidic conditions it could be converted into 5,5-dimethyl-cyclohex-2-ene-1-one, isolated as the DNP derivative[4].

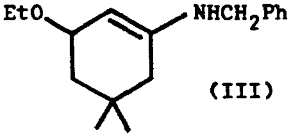
The reduction could proceed either via 1,2 or 1,4 addition leading to the enolether (II) or the enamine (III) respectively, but the latter, derived from a primary amine, would certainly tautomerise to give the imine (IV). The product had the following spectroscopic properties.



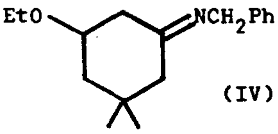
(I)



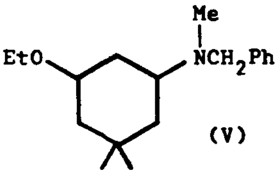
(II)



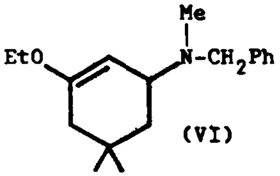
(III)



(IV)



(V)



(VI)

In the infrared a strong band at 1660 cm^{-1} could be due either to the azomethine system or an enolether but there was no absorption in the NH region. In the NMR, apart from signals characteristic of both possible structures (e.g. aromatic protons, ethoxy group, gem-dimethyl group), the N-benzyl methylenes appeared as a singlet at 6.22τ and there was a broad peak corresponding to one proton at 5.43τ which could be assigned either to the olefinic proton of an enolether or the C$\underline{H}$-O proton in the imine (IV). On this evidence we favoured the imine structure (IV), but felt that additional evidence was required before the enolether structure (II) could be eliminated.

This was obtained by reacting the borohydride reduction product with methyl iodide and reducing the methiodide with sodium borohydride. The product from the imine (IV) would be expected to be N-benzyl-N-methyl 3,3-dimethyl-5-ethoxycyclohexylamine (V) whereas from the enolether (II) these reactions should give 3-(N-benzyl,N-methylamino)-5,5-dimethyl-1-ethoxycyclohexene (VI). Spectroscopic and analytical data clearly showed the former to be the case, placing the imine structure (IV) for the original reduction product beyond doubt.

In a parallel reaction the iminoenolether (I) was reduced with lithium aluminium hydride, and the product obtained in 80% yield, was identical with that obtained from the borohydride reduction. To the best of our knowledge, this is the first instance of a conjugated system being reduced with complex metal hydrides to give a product arising from 1,4 addition only.

Satisfactory elemental analyses, IR, UV, and NMR spectra have been obtained for all new compounds.

References

(1) G.O. Dudek and R.H. Holm, J.Amer.Chem.Soc., <u>84</u>, 2691 (1962).

(2) N.J. Leonard and J.A. Adamcik, J.Amer.Chem.Soc., <u>81</u>, 595 (1959).

(3) R.F. Borch, Tetrahedron Letters, (1968), 61.

(4) A.W. Allan, R.P.A. Sneeden and J.M. Wilson, J.Chem.Soc., 2186, (1959).