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# AN UNUSUAL CLEAVAGE OF A SIDE CHAIN DURING CATALYTIC HYDROGENATION OF SOME OCTALONES

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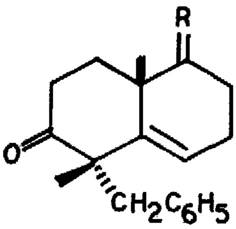
**Summary :** Novel hydrogenolysis of a C-C bond linking a benzyl side chain in some octalones is described.

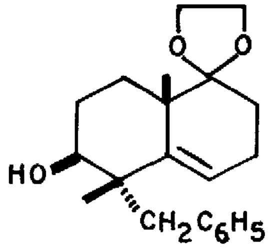
During a synthetic study on diterpenoids, we attempted catalytic hydrogenation of the olefinic bond in octalone (1)[1] in the presence of 10% Pd-C (150 mg/mmol of substrate; EtOH or EtOAc; room temp. and press; 50 hr) and obtained a mixture of decalones arising through loss of the benzyl side chain. Such a C-C bond hydrogenolysis appeared unusual based on an earlier study[2] on closely related compounds, wherein a benzyl substituent had remained unaffected during hydrogenation. However, the recent reports[3] by ApSimon and co-workers do suggest a complex behaviour, possible in related systems under prolonged hydrogenation, and/or, acid-catalysed conditions. Our findings on the above C-C bond cleavage are, therefore, noteworthy towards a better rationalisation of such studies.

Similar debenzylation was observed also in octalones (2) and (3) under the above experimental conditions, whereas the hydroxy compound (4)[4] underwent simply a normal hydrogenation. Toluene was a product, common to above hydrogenolysis reactions. Further, during the preparation of (4) from (1) through reduction with $LiAlH_4$, we obtained small amounts of some debenzylated materials, suggesting thereby that the cleavage involves a hydride ion attack on the benzylic carbon. However, it is not yet clear whether protonation at the carbonyl group occurs prior to hydrogenolysis[5].

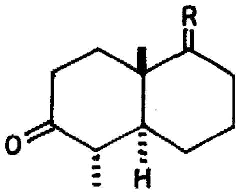
The major product from hydrogenolysis of (1) was characterised as the known _cis_-diketone (7)[6], arising through an unusual deketalisation under the reaction conditions. Further efforts to identify the minor products, furnished small amounts of the known _trans_-diketone (5)[7] and the hitherto unknown _cis_-ketal (8)[8], m.p. 84-85° C. However, spectral analysis of the mother liquors from the above separations revealed the presence of other epimers due to secondary methyl group, but they could not be separated. The diketones, (7) and (5) were also obtained,



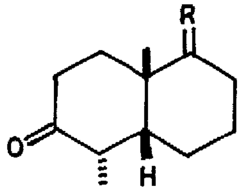
(1); (2); (3)



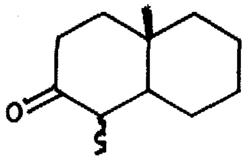
(4)



(5);(6)



(7);(8)



(9)

(1); (6); (8): $R = -O.CH_2.CH_2.O-$

(2); (5); (7): $R = O$; (3): $R = H_2$

as the major and one minor product respectively, from the hydrogenolysis of (2). The decalones arising similarly from (3) failed to separate on chromatography, but the two ring juncture isomers of (9) could be identified following the method[9] of Yanagita and Futaki.

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## References and Notes

1. This compound, b.p. 125-30° C/0.05 mm, and the octalone (3), b.p. 115-20° C/ 0.1 mm, were obtained through alkylation of the corresponding $\alpha,\beta$-unsaturated ketones with benzyl chloride. All new compounds gave expected elemental analyses and spectral data. All compounds describe are racemic.
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3. (a) J. W. ApSimon and I. Toth, Chem. Comm., 67 (1979); (b) J. W. ApSimon, S. Badripersaud, M. L. Post, and E. J. Gabe, Can. J. Chem., 56 , 2150 (1978)
4. The stereochemistry of this compound, m.p. 174-76° C, obtained through $LiAlH_4$-reduction of (1), was assumed based on anologies.
5. B. Miller and L. Lewis, J. Org. Chem., 39 , 2605 (1974).
6. J. D. Yordy and W. Reusch, J. Amer. Chem. Soc., 99 , 1965 (1977).
7. S. W. Pelletier, R. L. Chappell, and S. Prabhakar, J. Amer. Chem. Soc., 90 , 2889 (1968).
8. The structure of this compound was established by its conversion to (7).
9. M. Yanagita and R. Futaki, J. Org. Chem., 21 , 949 (1956).

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