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A SERENDIPITOUS SYNTHESIS OF (1SR,6RS)-1-METHYL-8,8-ETHYLENEDIOXY-BICYCLO[4.4.0]DECAN-2-ONE. INTRAMOLECULAR TRANSACETALIZATION INDUCED BY A "WRONG LABELLED HYDROGENATION CATALYST".

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It has been established beyond any reasonable doubt that selective acetalization at the unconjugated carbonyl group of the Wieland-Miescher ketone (1→2), followed by catalytic hydrogenation at normal conditions over 10% Pd-on-carbon, in 96% ethanol solution, affords selectively the cis-decalone 3 (m.p. 54.5-56.5º)[1].

In connection with an attempted new stereoselective synthesis of patchouli alcohol, we have repeated once and again the reported sequence with no troubles at all[2], the cis-decalone 3 being isolated in high yield. However, recently, owing to the fact that the necessary catalyst in our laboratory was exhausted, we had to resort to a brand new "Palladium auf Aktivkhole - 10% Pd Hydrerungskatalysator" labelled bottle, and we found that the hydrogenated product showed small but significant differences in the NMR spectrum, the peak of the methylenes acetal group appearing at δ 3.89 instead of 3.99 observed for decalone 3. Moreover, the angular methyl group of the new product showed greater sensibility to Eu(FOD)$_3$ than that of the decalone 3: δ_{CH_3} = 7.25 ppm/eq in contrast with δ_{CH_3} = 3.95 ppm/eq for the latter. On the other hand, mass spectrometry revealed that the new product was isomeric with cis-decalone 3 (M$^+$ = 224.1) and, in fact, both compounds gave, after acid hydrolysis, the same cis-decalin-1,6-dione 4 (m.p. 64-66º)[3]. Accordingly, the new product was identify as (1SR,6RS)-1-methyl-8,8-ethylenedioxybicyclo[4.4.0]decan-2-one (5), m.p. 74-6º, which had been already prepared from the Wieland-Miescher ketone (1) by a four step sequence[4]. We can conclude that an intramolecular transacetalization, concomitant with hydrogenation, took place -probably through a process involving a boat conformation and catalyzed by some kind of "acidic" impurity (Fig. 1). In fact, when a drop of aqueous concentrated HCl was added to an ethanol solution of cis-decalone 3, transacetalization 3→5 was observed to occur in 90% yield after 1.5 h (94% yield with gaseous HCl in DME). This finding led us to guess that the "wrong labelled catalyst" was probably PdCl$_2$-on-carbon, which on hydrogenation affords Pd[5] and highly active gaseous HCl-on-carbon. Two further experiments seem to confirm this hypothesis:

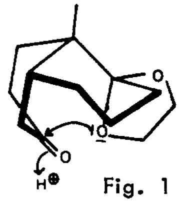
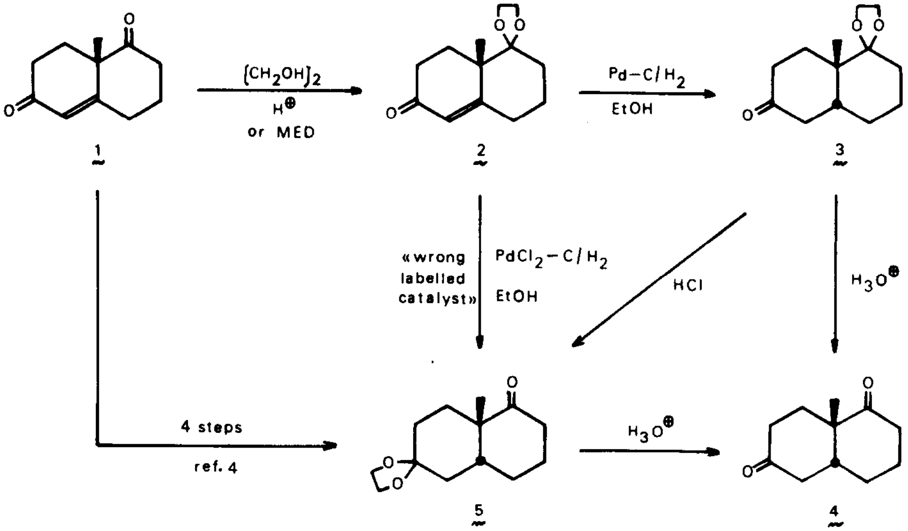


Fig. 1

1) Catalytic hydrogenation of the unsaturated ketone **2** with the "wrong labelled catalyst" previously hydrogenated and washed thoroughly with ethanol and dried, afforded the normal *cis*-decalone **3**.

2) Catalytic hydrogenation of the same unsaturated ketone **2** with freshly prepared 10% PdCl$_2$-on-carbon[5] gave the isomerized *cis*-decalone **5**.

However, careful GLC analyses of the hydrogenated crude samples[6] showed that the "wrong labelled catalyst" was always more active (**5**:**3** ratio = 91:9) than the freshly prepared 10% PdCl$_2$-on-carbon catalyst (**5**:**3** ratio = 78:22), probably due to a higher quality of the support used in the former.



NOTES AND REFERENCES

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2. P. Camps, R.M. Ortuño and F. Serratosa, *Tetrahedron*, **32**, 2583 (1976).
3. C.B.C. Boyce and J.S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).
4. R.F. Church, R.E. Ireland, and D.R. Shridhar, *J. Org. Chem.*, **27**, 707 (1962).
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6. Some hydrolyzed dione **4** was always detected by GLC (10-17%). On the other hand, both catalysts are much less active working in microscale quantities (less than 40 mg).

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