Reaction of Patchouli Alcohol with Lead Tetra-acetate; a New, Regiospecific Fragmentation of Patchouli Alcohol

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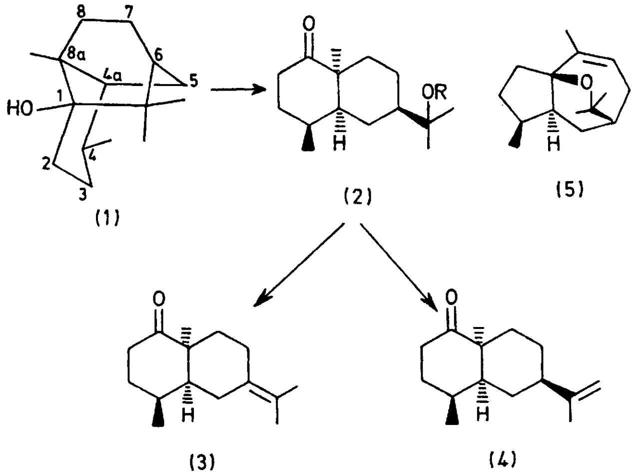
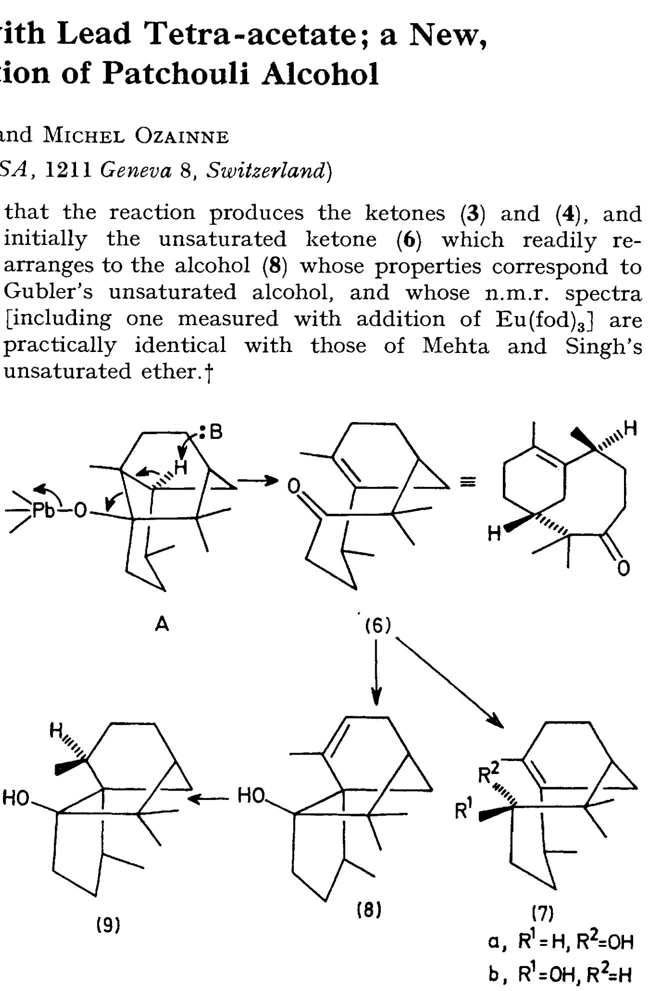
Summary The cyclo-octanone, 2,2,6,8-tetramethylbicyclo-[5.3.1]undec-7-en-3-one (**6**), formed by the action of lead tetra-acetate on patchouli alcohol (**1**), is readily cyclized to 2,2,6,8-tetramethyltricyclo[5.3.1.$0^{3,7}$]undec-8-en-3-ol (**8**).

Reaction of patchouli alcohol (**1**) with lead tetra-acetate was shown by Gubler to give the hydroxylated decalone (**2**, R=H) and its acetate (**2**, R=COMe), olefins (**3**) and (**4**) resulting after longer reaction times.[1] A further unidentified product led to an unsaturated alcohol after g.l.c.[1] Recently, this reaction was reported[2] to give the decalones (**3**) and (**4**), and an unsaturated ether (**5**). We now show that the reaction produces the ketones (**3**) and (**4**), and initially the unsaturated ketone (**6**) which readily rearranges to the alcohol (**8**) whose properties correspond to Gubler's unsaturated alcohol, and whose n.m.r. spectra [including one measured with addition of $Eu(fod)_3$] are practically identical with those of Mehta and Singh's unsaturated ether.†





Patchouli alcohol (**1**), lead tetra-acetate, and calcium carbonate at reflux in benzene for 6 h yielded 40% of

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† The figures quoted by Mehta and Singh (ref. 2) for the signals of the *gem*-dimethyl group are at *ca.* 0·2 p.p.m. higher field than usually associated with such ethers, of which there are several examples (H. Ishii, T. Tozyo, M. Nakamura, and H. Minato, *Tetrahedron*, 1970, **26**, 2751, 2911; M. L. Maheshwari, T. C. Jain, R. B. Bates, and S. C. Bhattacharyya, *Tetrahedron*, 1963, **19**, 1079). Our own experience supports these figures.

ketonic material (b.p. 70—90 °C at 0·001 mmHg), which was (>90%) 2,2,6,8-tetramethylbicyclo[5.3.1]undec-7-en-3-one (**6**), $C_{15}H_{24}O$.‡ The presence of one carbonyl group (i.r. 1695 cm^{-1}, neat; ^{13}C n.m.r. 217·4 p.p.m., compared with 215·9 p.p.m. for cyclo-octanone[3]) and a tetrasubstituted double bond (^{13}C n.m.r. 133·0 and 133·9 p.p.m.) indicates two rings. Of the 4 Me groups, one is secondary (^1H n.m.r. δ 1·03, d, *J* 7 Hz), one is vinylic (δ 1·44), and two are quaternary (δ 1·01 and 1·38). Reduction with $LiAlH_4$ afforded two secondary alcohols (**7a, 7b**) in the ratio 7 : 3. The minor, less polar isomer (on silica gel), formulated as (**7a**), had δ 1·78 (MeC=), displaced by 0·21 p.p.m. per 0·1 equiv. of $Eu(fod)_3$. The major isomer (m.p. 79—81 °C) had δ 1·72, displaced by 0·08 p.p.m. per 0·1 equiv. of $Eu(fod)_3$, and is formulated as (**7b**). Other characteristic signals were observed for the secondary methyl group (δ 0·99 for both isomers, d, *J* 7·5 Hz), the tertiary methyl groups [δ 0·94 and 1·03 for (**7a**); δ 0·90 and 1·02 for (**7b**)], the carbinol proton [δ 3·39 for (**7a**), δ 3·59 for (**7b**)], and one of the protons adjacent to the double bond [δ 2·48 for (**7a**); δ 2·52 for (**7b**)] (geminal coupling, d, *J* 13 Hz in both isomers).

After chromatography on very active silica gel, or gas chromatography with anything but the cleanest apparatus, the ketone (**6**) was transformed into an unsaturated alcohol whose spectroscopic properties correspond to those quoted by Gubler[1] (i.r. 3560 cm^{-1}; ^1H n.m.r. δ 1·67, d, *J* 1·5 Hz, and 5·50). We ascribe structure (**8**) to this substance, based on the ^{13}C n.m.r. spectrum (off-resonance decoupling shows four singlets: 46·8, 62·5, 95·9, and 142·3 p.p.m., and 3 doublets: 35·4, 46·0, and 122·9 p.p.m.). The signal at 95·9 p.p.m. corresponds to a carbon atom adjacent to two quaternary centres, and common to two five-membered rings.§ (Patchouli alcohol has this signal at 75·8 p.p.m.[4]) Catalytic reduction yields the saturated alcohol (**9**), isomeric with patchouli alcohol (**1**), having the signal for the carbinol C atom at 93·8 p.p.m.

Formation of the cyclo-octanone (**6**) presumably occurs by the fragmentation (A), which is probably concerted, since formation of an intermediate C-8a carbonium ion should lead to some $\Delta^{4a,8a}$ olefin. Tranformation of (**6**) into (**8**) appears to be acid-catalysed, and bears some similarity to the very ready cyclization of 1-formyl-5-methylenecyclooctane to a bicyclo[3.3.0]octane.[5]

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‡ Mass spectra and microanalyses support all structures mentioned. N.m.r. spectra were measured in $CDCl_3$; chemical shifts are in p.p.m. downfield from Me_4Si.

§ Several examples of alcohols with a carbinol group common to two five-membered rings are in Y. M. Sheikh, G. Singy, M. Kaisin, H. Eggert, C. Djerassi, B. Tursch, D. Daloze, and J. C. Braekman, *Tetrahedron*, 1976, **32**, 1171. To the value (*ca.* 88 p.p.m.) quoted must be added the amount resulting from the presence of two adjacent quaternary centres (*ca.* 8 p.p.m.), *cf.* the difference between norbornanol [δ 72·5 p.p.m. (G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 1970, **92**, 4627)] and 1,3,3-trimethylnorbornan-2-ol [*endo*; fenchol, 84·8 p.p.m. (F. Bohlmann, R. Zeisberg, and E. Klein, *Org. Magnetic Resonance*, 1975, **7**, 426)].

[1] B. A. Gubler, Promotionsarbeit, E.T.H., Zürich, 1965. We are grateful to Professor G. Büchi (M.I.T.) for drawing our attention to this work.

[2] G. Mehta and B. P. Singh, *Tetrahedron Letters*, 1975, 4495. We are grateful to Dr. G. Mehta for sending a copy of his n.m.r. spectra, measured in CCl_4 with a $CHCl_3$ lock, alone and with addition of $Eu(fod)_3$.

[3] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1347.

[4] A. F. Thomas and W. Thommen, unpublished results.

[5] S. H. Graham and D. A. Jonas, *Chem. Comm.*, 1968, 1091.