Rearrangement of a Homobrendane to a Perhydro-1,4-methanoindene Skeleton. *X*-Ray Crystal Structure of a Novel Product

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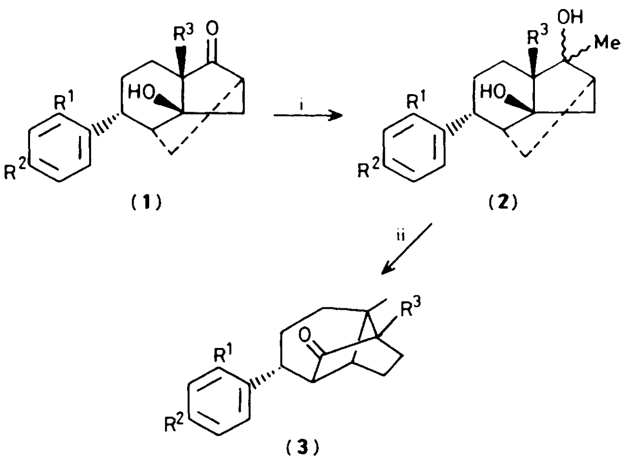
A novel compound obtained by Grignard reaction of the tricyclic hydroxy ketone (**1**) followed by acid treatment has been assigned structure (**3**) on the basis of spectral and *X*-ray crystal structure analyses.

In connection with the total synthesis of *B*-seco-steroids we have discovered a new approach to the synthesis of the tricyclic hydroxy ketone (**1a**),[1] a homobrendane derivative, the structure of which has been established by spectral as well as *X*-ray crystal structure analyses.[2] We now report a novel product formed by acid treatment of the tricyclic diol (**2a**).

Grignard reaction of the tricyclic hydroxy ketone (**1a**) with methylmagnesium iodide afforded compound (**2a**).† Refluxing (1 h) a solution of (**2a**) in benzene containing toluene-*p*-sulphonic acid followed by the usual work-up resulted in a white crystalline solid, m.p. 127 °C, in 97% yield as the sole product. The presence of a five-membered ring carbonyl was evident from its i.r. spectrum ($\nu_{max.}$ 1735 cm^{-1}). Its ^1H n.m.r.



a; $R^1 = R^2 = OMe$, $R^3 = Me$
b; $R^1 = H$, $R^2 = OMe$, $R^3 = Et$

Reagents: i, MeMgI; ii, *p*-$MeC_6H_4SO_3H$, C_6H_6.

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† All new compounds synthesised showed satisfactory elemental and spectral analysis. Spectral data: (**2a**), *m/z* 332, $\nu_{max.}$ (neat) 3460 br., 1610s, and 1590s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.9 (s, 3H), 1.25 (s, 3H), 3.79 (s, 6H), 6.3—6.5 (m, 2H), and 7.1 (d, *J* 7 Hz, 1H). (**3a**), *m/z* 314; $\nu_{max.}$ (Nujol) 1735 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 0.92 (s, 3H), 0.99 (s, 3H), 1.04—2.2 (m, 9H), 2.56 (d, *J* 4.5 Hz, 1H), 3.46 (q, 1H), 3.8 (s, 6H), 6.3—6.54 (m, 2H), and 7.20 (d, 1H); irradiation of the 1H signal at δ 2.56 resulted in the collapse of the quartet at δ 3.46 to a doublet (*J* 4.5 Hz) and irradiation of the quartet resulted in the collapse of the doublet to a singlet; ^{13}C n.m.r. ($CDCl_3$, off-resonance decoupled) singlets at δ 48.76, 57.21, 124.71, 158.19, 159.22, and 222.46; doublets at δ 35.16, 42.80, 55.58, 78.44, 103.47, and 127.85; triplets at δ 23.24, 24.81, 30.34, and 31.64; quartets at δ 9.10, 18.80, and 55.26 (×2). (**1b**), *m/z* 300; $\nu_{max.}$ (Nujol) 3460s and 1730 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.97 (t, *J* 4 Hz, 3H), 2.68—3.18 (m, 1H), 3.71 (s, 3H), and 6.62—7.16 (ABq, *J* 9 Hz, 4H). (**2b**), *m/z* 316; $\nu_{max.}$ (Nujol) 3540s, 3500s, 1610, and 1590 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.99 (t, *J* 5 Hz, 3H), 1.37 (s, 3H), 3.70 (s, 3H), and 6.64—7.19 (ABq, *J* 8 Hz, 4H). (**3b**) *m/z* 298; $\nu_{max.}$ (Nujol) 1735 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.94 (s, 3H), 1.08 (t, *J* 7 Hz, 3H), 2.35 (d, *J* 4.5 Hz, 1H), 3.27 (m, 1H), 3.8 (s, 3H), and 6.85—7.23 (ABq, *J* 8 Hz, 4H); ^{13}C n.m.r. ($CDCl_3$, off-resonance decoupled) singlets at δ 49.39, 60.29, 135.85, 158.01, and 222.21; doublets at δ 40.21, 43.30, 58.65, 113.99, and 128.28; triplets at δ 19.5, 23.13, 24.65, 28.89, and 30.57; quartets at δ 9.61, 18.69, and 55.33.

spectrum showed the presence of two quaternary methyls, two OMe groups, and a 1,2,4-trisubstituted benzene ring. The mutual coupling of the two signals at δ 2.56 (d, 1H) and 3.46 (q, 1H) evident from double irradiation experiments indicated the presence of the group $-CH_2-CH(Ar)-CH(=O)-C-$. Several structures were consistent with the spectral data, and so a single-crystal *X*-ray diffraction study was undertaken. This suggested the structure (**3a**),† but owing to poor crystal quality refinement led to an *R* value of only 0.165.

In studies of the generality of the reaction, compound (**3b**),† which showed spectral properties similar to those of (**3a**), was synthesised from compound (**1b**) and this gave crystals suitable for *X*-ray diffraction studies.‡ A perspective view of the structure is shown in Figure 1. A carbonium ion is generated by the initial protonation of the C-2 hydroxy function, and a series of skeletal rearrangements then give compound (**3**). The perhydro-1,4-methanoindene skeleton is present in many natural products.[4]

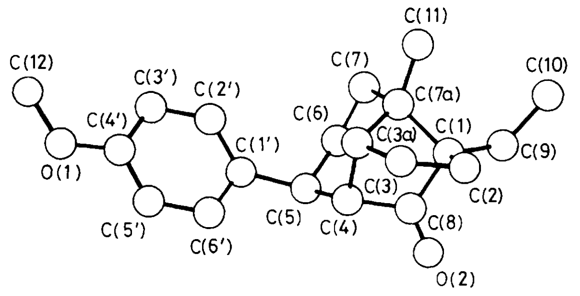

Figure 1. A perspective view of the structure of the perhydromethanoindenone (**3b**).

Received, 7th July 1986; Com. 934

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‡ *Crystal data for* (**3b**): $C_{20}H_{26}O_2$, $M = 298$, monoclinic, space group $P2_1/c$, $a = 8.964(2)$, $b = 12.212(1)$, $c = 14.931(2)$ Å, $\beta = 96.7(2)°$, $Z = 4$, $D_m = 1.211$, $D_c = 1.221$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 0.88$ cm^{-1}. The structure was solved by direct methods using MULTAN 78.[3] Least squares refinement of atomic and positional parameters (anisotropic C and O; isotropic H) yielded a final *R* value of 0.062 for 1426 statistically significant reflections $[|F| > 3.00\,\sigma(|F_o|)]$ measured using an Enraf–Nonius CAD-4 diffractometer (Zr-filtered Mo-K_α radiation, ω–2θ mode). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.