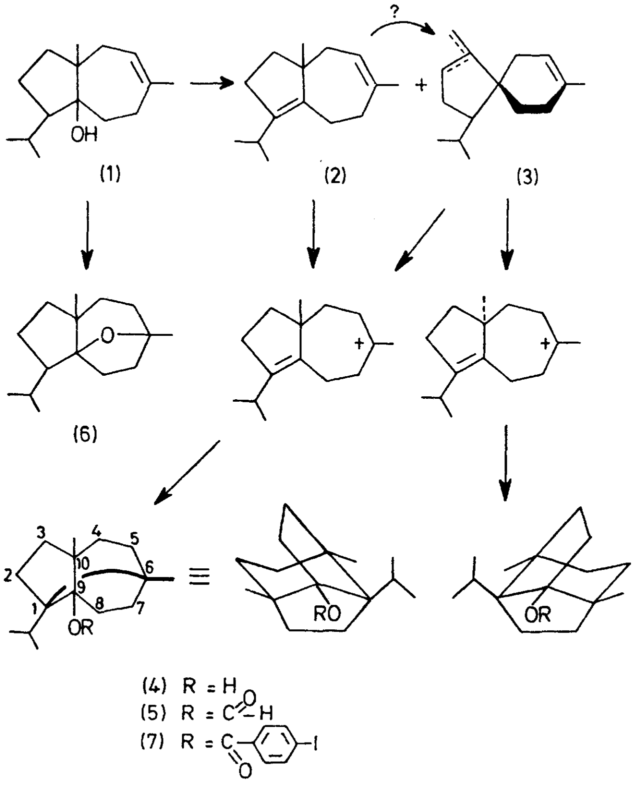
Formic Acid-catalysed Rearrangement of Carotol. *X*-Ray Crystal Structure of the *p*-Iodobenzoate of One of the Alcohols Formed

By L. H. Zalkow,* M. G. Clower, Jr., M. Gordon J. Smith, D. VanDerveer and J. A. Bertrand
(*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia* 30332)

Summary Formic acid-catalysed rearrangement of carotol (**1**) gives, among other products, the alcohol (**4**); *X*-ray crystal structure determination of its *p*-iodobenzoate (**7**) showed that the ester contained enantiomeric forms of (**4**).

We recently described the conversion of carotol (**1**) into daucene (**2**) and acoradienes (**3**) with either thionyl chloride or 90% formic acid.[1] Further investigation of the reaction in 90% formic acid revealed that the initially formed (**2**) and (**3**) disappeared with time and five other products were detected by g.l.c. and separated by column chromatography on silica gel: (a) two isomeric olefins, $C_{15}H_{24}$, which have not been fully characterised yet, (b) the ether (**6**) ν_{max} 1110 and 1040 cm^{-1}; δ 0·73 (3H, s), 0·85 (3H, d, *J* 6 Hz), 1·13 (3H, d, *J* 6 Hz), and 1·22 (3H, s); ^{13}C n.m.r. spectrum: δ 44·0 (quaternary C), 77·3 (quaternary ether C), and 92·8 (quaternary ether C) p.p.m.; plain negative o.r.d. curve, $[\phi]_{589}$ − 39·1° (*c* 3·39, $CHCl_3$),† (c) the alcohol (**4**), m.p. 46—47 °C; ν_{max} 3450, 1070, and 1020 cm^{-1}; δ 0·85 (3H, s), 0·93 (3H, s), 1·02 (3H, d, *J* 7 Hz), 1·15 (3H, d, *J* 7 Hz), and 1·42 (1H, m); ^{13}C n.m.r. spectrum: δ 47·4, 48·5, 60·2, and 91·7 (all quaternary C's); plain positive o.r.d. curve, $[\phi]_{589}$ +54·8° (*c* 5·67, $CHCl_3$);† and (d) the formate (**5**), b.p. 83—87 °C (bath) at 0·1mmHg, ν_{max} 1730, 1180, and 1150 cm^{-1}; δ 0·83 (3H, s), 0·97 (3H, s), 0·98 (3H, d, *J* 7 Hz), 1·07 (3H, d, *J* 7 Hz), 8·13 (1H, s); ^{13}C n.m.r. spectrum: δ 45·9, 50·0, 61·8, and 101·1 (all quaternary C's); plain positive o.r.d. curve, $[\phi]_{589}$ 71·9° (*c* 4·52, $CHCl_3$).



Starting with (**1**), (**2**), (**4**), or (**5**), approximately the same equilibrium mixtures of products were obtained which comprised *ca.* 60% (**4**) and 20% (**5**). Reduction of (**5**) with $LiAlH_4$ gave (**4**). An indication of the structure (**4**) was obtained from the following facts. The i.r., n.m.r. (^1H and ^{13}C), and mass spectra and elemental analysis showed that the substance was a saturated tricyclic tertiary alcohol ($C_{15}H_{26}O$) containing four quaternary carbon atoms and four methyl groups. The ^1H n.m.r. spectrum showed overlapping singlets and doublets which made assignment of the methyl groups difficult, but by use of chemical shift reagents, the methyl signals were separated and it became apparent that there were two methyl groups attached to carbons bearing no hydrogen atoms (quaternary) and an isopropyl group. Besides the high field isopropyl methyl doublets it was possible to see the septet arising from the proton on the tertiary isopropyl carbon and irradiation of this septet caused the isopropyl methyl doublets to coalesce to singlets. Further evidence for the isopropyl group arose from the mass spectrum which showed a base peak at *m/e* 179 ($M^+ - C_3H_7$) and an intense peak (78%) at 161 ($M^+ - C_3H_7 - H_2O$).

The chemical shift studies showed that besides the tertiary isopropyl proton at C-13, four other protons were in close enough proximity to the hydroxyl group to show considerable deshielding. We now recognize these as the β-oriented (*cis* to OH) protons at C-2 and C-3 and both protons at C-8 in (**4**). In addition, the C-10 methyl group (C-11) showed considerable deshielding and one of the isopropyl groups was more deshielded than the other. The C-6 methyl group (C-12) was the least deshielded of all the methyl groups and protons mentioned. However, the structure of (**4**) was unequivocally determined and the above n.m.r. assignments made only after an *X*-ray analysis. The heavy atom derivative was prepared as follows. To the lithium salt of (**4**) (of properties described above), prepared with butyl-lithium in dimethoxyethane, was added *p*-iodobenzoyl chloride. The crude ester (**7**) was purified by chromatography on silica gel until it gave a single spot on t.l.c. and a single peak on g.l.c.; however, capillary melting point determination of randomly selected crystalline material gave a broad melting range, 70—88 °C [later shown to be due to partial racemization of (**4**)], ν_{max} 1725 and 1580 cm^{-1}; δ 0·85 (3H, s), 1·00 (3H, s), 1·05 (6H, d, *J* 6 Hz), and 7·70 (dd, *J* 6 Hz). Some of this crystalline material was reduced with $LiAlH_4$ in ether and gave (**4**), identical with the alcohol (**4**) from which the material was derived (g.l.c. and i.r. and ^1H n.m.r. spectra). The crystalline ester was recrystallized from ethyl acetate and gave some plates,

---

† Satisfactory elemental analyses and mass spectra were obtained for this compound.

one of which (m.p. 101—103 °C) was used for the X-ray analysis.

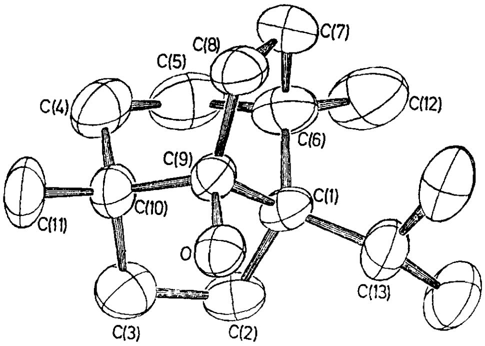


FIGURE. A perspective view of the non-hydrogen atoms in (**7**) with the oxygen atom attached to C–9.

Crystal Data: $C_{22}H_{29}O_2I$, M 452·4, monoclinic, a = 13·21 (1), b = 12·40(1), c = 13·82(1) Å, β = 112·84(1)°, Z = 4, space group $P2_1/c$, R = 0·056 for 2665 reflections with $I > 3\sigma(I)$.

Intensity data were collected on a four-circle computer-controlled diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0·71073Å). The structure was solved using Patterson methods and refined using anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters (5·0) for hydrogen atoms. The structure (Figure) contains no unusual bond distances or angles and is fully consistent with the spectral and chemical data. Because of space group symmetry, the unit cell is required to contain the enantiomeric forms of the compound in equal numbers.

The lack of optical activity of the crystal of the ester (**7**) used in the X-ray analysis led us to investigate the possibility that the alcohol (**4**) racemized on prolonged exposure to formic acid. We thus carried out the reaction of optically active carotol in formic acid for two days, separated the alcohol (**4**) and its formate (**5**) from the other products by chromatography on silica gel and reduced the mixture of (**4**) and (**5**) with $LiAlH_4$ to give (**4**), whose o.r.d. curve was measured. This alcohol was again exposed to formic acid for 12 days and the alcohol isolated as before to give an o.r.d. curve identical to the previous one within experimental error. This isolated alcohol was then exposed to formic acid for 36 days and again after similar isolation procedures, it gave the alcohol (**4**), of identical o.r.d. curve, within experimental error. We then exposed the optically active† acoradiene mixture (**3**), prepared from optically active carotol and free of any daucene (**2**), to formic acid under the same conditions and the alcohol (**4**), isolated, as described above, was optically inactive. We therefore suggest that (**4**) can arise by two pathways, one of which leads to the optically inactive (**4**) *via* the acoradiene (**3**) and the other to the optically active (**4**), of the indicated configuration, *via* (**2**) as illustrated.

We thank the National Science Foundation for a grant towards the purchase of a JEOL PFT-100 Fourier Transform n.m.r. spectrometer.

(*Received*, 1*st March*, 1976; *Com.* 205.)

[1] L. H. Zalkow and M. G. Clower, Jr., *Tetrahedron Letters*, 1975, 75.