The Rearrangement of Tricyclic β-Pinene Derivatives

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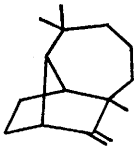
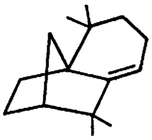
Summary Rearrangement of the tricyclic β-pinene derivatives (**4**) with acid results in migration of the methylene bridge to produce novel tricyclic fenchyl derivatives.

CONTINUING interest in the chemistry of longifolene (**1**), isolongifolene (**2**),[1] and other tricyclic sesquiterpenes[2] prompts us to report our studies of the acid-catalysed rearrangement of tricyclic β-pinene derivatives which provide a synthetic entry to novel tricyclic systems closely related to (**2**) and to other polycyclic terpenes incorporating a bicyclo[2,2,1]heptane ring system.[3]



(**1**)



(**2**)

Diels–Alder reaction of nopadiene (**3**)[4] with maleic anhydride in benzene under reflux gave the tricyclic β-pinene derivative (**4**), m.p. 133·5—134·5.†‡ In analogy to transformations of β-pinene,[5] reaction of (**4**) with acid could generate two rearranged tricyclic products. For example, migration of the *gem*-dimethyl bridge in the carbonium ion derived from (**4**) (with nucleophilic attack of the acid anion concomitant with rearrangement), would lead to the bornyl derivative (**5**). Alternatively, the fenchyl derivative (**6**)§ would be that derived from migration of the methylene bridge.¶ We have found that (**4**) rearranges *via* the latter pathway.

Reaction of (**4**) with hydrogen bromide in benzene at 25°

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† All new compounds gave satisfactory elemental analyses.

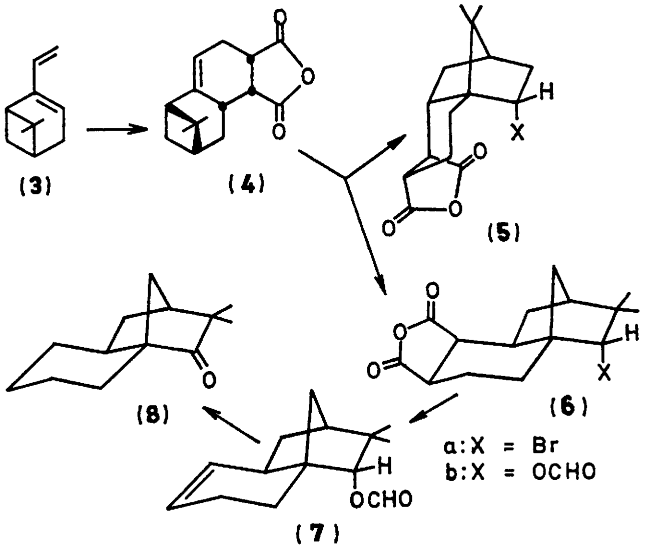
‡ The stereochemistry of this adduct is based on the reasonable assumption that cycloaddition occurs *via* maximum overlap of unsaturated centres and attack from the least hindered side of (**3**).

§ I.U.P.A.C. nomenclature for hydrocarbon systems: (**5**); *cis*-decahydro-9,9-dimethyl-3,8*a*-methanonaphthalene, (**6**); *trans*-decahydro-2,2-dimethyl-3,8*a*-methanonaphthalene.

¶ The enantiomer is represented for better comparison with (**5**).

gave rise to one isolable product (m.p. 138—139°, 50% yield) which is formulated as (**6a**). This structural assignment is based on the n.m.r. spectrum of the adduct which exhibits the anticipated singlet at δ 3·77 (1H) for the C*H*Br proton.[6] Vicinal coupling of the C*H*Br proton in (**5**) would demand higher multiplicity. The rearrangement of (**4**) with formic acid and a trace of sulphuric acid at 25° proceeded in the same manner to give (**6b**), m.p. 202—203°†** in 50% yield (n.m.r. C*H*O·CHO δ 4·38; *gem*-dimethyls δ 0·82, 1·11). Bisdecarboxylation of (**6b**) with lead tetra-acetate in pyridine give (**7**) in 82% yield (n.m.r. C*H*O·CHO δ 4·43; *gem*-dimethyls δ 0·83, 1·15; vinyls δ 5·46). Hydrogenation of (**7**) followed by oxidation with Jones' reagent afforded ketone (**8**) as a liquid which was purified by preparative scale g.l.c. [87% overall yield: ν_{max} (CCl_4) 1739, 1382, 1361 cm.$^{-1}$].

The preferential migration of the methylene bridge when the pinene (**4**) is treated with acid is particularly noteworthy. The extent to which this result reflects a specific protonation of (**4**) and/or that the transition state for rearrangement is late and product-like, cannot be answered at this time.



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** This compound analysed as the diacid.

[1] D. G. Farnum and G. Mehta, *Chem. Comm.*, 1968, 1643.
[2] For a review see W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev.*, 1967, **21**, 331.
[3] J. E. McMurry, *Tetrahedron Letters*, 1969, 55.
[4] C. A. Cupas and W. S. Roach, *J. Org. Chem.*, 1969, **34**, 742.
[5] For a review see D. V. Banthorpe and D. Whittaker, *Quart. Rev.*, 1966, **22**, 373.
[6] M. P. Hartshorn and A. F. A. Wallis, *J. Chem. Soc.*, 1964, 5254; H. Schmidt, M. Muhlstadt, and P. Son, *Chem. Ber.*, 1966, **99**, 2736.