Tricyclic Olefins from Solvolysis of Longicamphenilyl Tosylate

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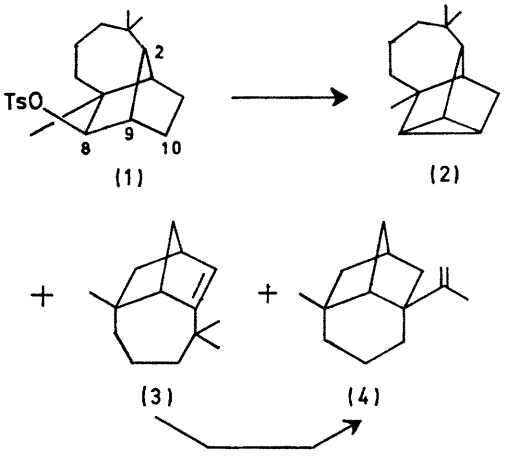
Summary Acetolysis of longicamphenilyl tosylate affords, in addition to norlongicyclene and acetate products, the novel *endo*-bridged tricyclic olefins (**3**) and (**4**).

THE reactions of longifolene and its derivatives are characterized by a remarkable propensity for skeletal rearrangements and transannular effects.[1] We have found yet another rearrangement pathway in the solvolysis of longicamphenilyl tosylate (**1**).[2]

Buffered acetolysis (50°, 24 h) of (**1**) gives a mixture of acetates (40%) and hydrocarbons (57%). The latter can be separated by chromatography into three components: the known[3] norlongicyclene, (**2**) (27%), (**3**) [62%, τ 4·33 (d, 1H, J 3 Hz), 8·85, 8·92, and 9·01 (3 s, 3 H each); m/e 190 (M^+, 24%), 108 (100%)], and olefin (**4**) [11%, ν_{max} 890 cm^{-1}, τ 5·28 (m, 2 H), 8·30 (m, 3 H), 9·03 (s, 3 H); m/e 190 (M^+, 68%), 80 (100%)]. Hydroboration of (**3**) with diborane in tetrahydrofuran, followed by treatment with alkaline hydrogen peroxide, produces a secondary alcohol (**5**) [70%, m.p. 158—159°, τ 6·27 (d, 1 H, J 5·5 Hz)] along with 18% of a tertiary alcohol. The acetate of (**5**) is, in fact, one component of the solvolysis mixture. Oxidation of (**5**) to the corresponding ketone (**6**) (ν_{max} 1735 cm^{-1}) and lithium aluminium hydride reduction furnishes an isomeric alcohol (**7**) [τ 5·61 (2 d, J 8·5, 4·5 Hz)]. The coupling constants quoted for the carbinyl protons of the two alcohols are consistent with *exo,endo* coupling in (**5**) and *exo,exo* and *exo*–bridgehead coupling in (**7**).[4]

The *endo*-bridged structure (**3**), 3,7,7-trimethyltricyclo-[6,2,1,$0^{3,9}$]undec-8(11)ene, has been confirmed by means of an independent synthesis of the parent tricyclic hydrocarbon (**8**), the hydrogenation product of (**3**). Treatment of longicamphenilone (**9**) with potassium t-butoxide in

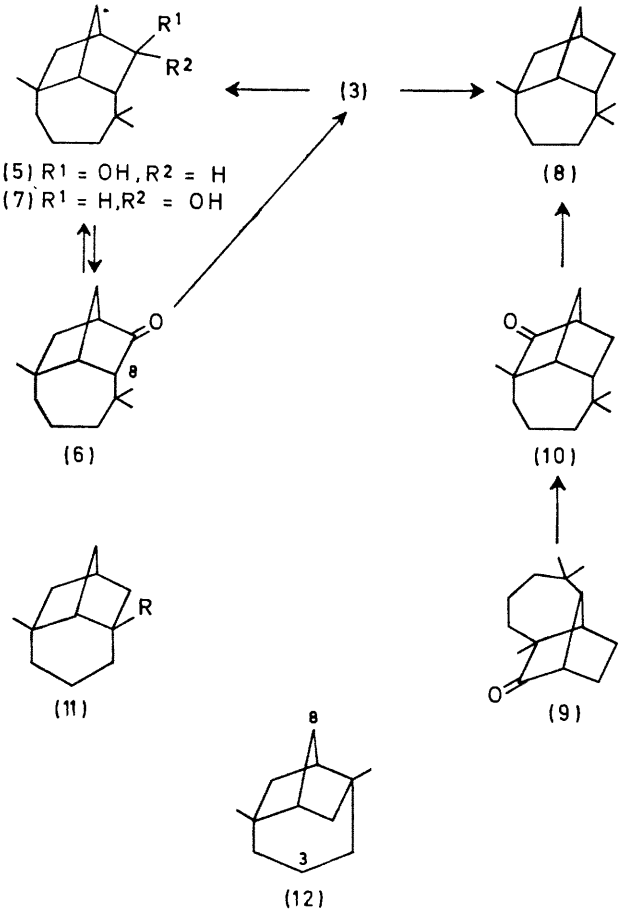
t-butyl alcohol (275°, 14 h) effects homoenolate rearrangement[5] to a 7 : 1 mixture of (**9**) and (**10**). Wolff–Kishner reduction of a 3 : 1 mixture of these ketones gave a hydrocarbon (*ca.* 25%) identical to (**8**) according to g.l.c. and n.m.r. comparison.†



SCHEME 1

A close structural relationship between the two isomeric olefins is indicated by the conversion of (**3**) into (**4**) in formic acid (24 h, 25°). The structure of (**4**) as 3-isopropenyl-7-methyltricyclo[5,2,1,$0^{3,8}$]decane has been established by degradation to the symmetrical hydrocarbon (**11**; R = Me). Ozonolysis to the methyl ketone (**11**; R = COMe) [τ 7·83, 9·01 (2 s, 3 H ea)] followed by Baeyer–Villiger oxidation with buffered peroxyacetic acid yields the tertiary acetate (**11**; R = OAc) [τ 8·04, 9·00 (2 s, 3 H ea)]; the absence of absorption from protons on carbon bearing an acetoxy-group in the n.m.r. spectrum requires a quaternary isopropenyl group. The carbinol (**11**; R = CH_2OH) (m.p. 41·5—43°) was obtained from the methyl ketone by degradation to the carboxylic acid (**11**; R = CO_2H) with sodium hypobromite, then reduction with lithium aluminium hydride. Wolff–Kishner reduction of the corresponding aldehyde, (**11**; R = CHO), gave the optically inactive hydrocarbon (**11**; R = Me), $[\alpha]_D$ 0 ± 1°, (*c* 1·59, CCl_4) $\tau_{100\ MHz}$ 7·86 (br s, 1 H), 9·07 (s, 6 H), *m/e* 164 (M^+)]. The appearance of the unique downfield bridgehead proton absorption (τ 7·86) in the n.m.r. spectrum of this tricyclic hydrocarbon conclusively eliminates the structural alternative with the three-carbon *endo*-bridge diagonally linked across the norbonane base, (**12**). The two-fold symmetry axis (through C-3 and C-8) of (**12**) renders the two bridgehead protons (as well as all other proton pairs) chemically equivalent; furthermore (**12**) should exhibit optical activity.

The rearrangement pathway from (**1**) to (**3**) is most simply pictured as a 10 → 8 hydride shift, followed by 9 → 10 methylene migration, then elimination of the C-2 proton. Although (**3**) contains a bridgehead double bond, the strain would appear from molecular models to be only



SCHEME 2

slightly greater than that of norbornene itself. It is interesting to note that aprotic decomposition of the tosylhydrazone of (**6**) regenerates (**3**) to the complete exclusion of norlongicyclene (**2**).[6]

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† A smaller amount of norlongifolane (8%), recovered longicamphenilone (**9**; 35%), and longicamphenilol (17%) were also obtained.

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