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THE SYNTHESIS OF 1-METHYLTRICYCLO[4.4.0.0^{2,7}]DECANES

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Several sesquiterpenoids are now known which possess the tricyclo[4.4.0.0^{2,7}]decane skeleton[1]. Our interest in the total synthesis of these naturally occurring substances led us to examine possible synthetic pathways to this type of tricyclic system. It is the purpose of this communication to report the successful preparation of 1-methyltricyclo[4.4.0.0^{2,7}]decan-8-one (6) in four steps from the Wieland-Miescher ketone (1)[2].

Selective reduction of diketone 1 with sodium borohydride in ethanol yields the unsaturated ketol 2[3], which reacts with p-toluenesulfonyl chloride in pyridine to afford the crystalline tosylate 3 (m.p. 116-117°)*. Hydrogenation of tosylate 3 in the presence of palladized strontium carbonate yields the *cis*-fused keto-tosylate 4 (m.p. 142-143°), which is thus obtained in 55% overall yield from diketone 1. The stereochemical integrity of keto-tosylate 4 was confirmed by its synthesis from the known ketol 5, which may also be obtained from the diketone 1, although by a somewhat more tedious route[3].

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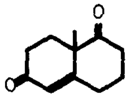
*Satisfactory elemental analyses have been obtained for all new compounds reported herein.

Treatment of compound 4 with one equivalent of methylsulfinyl carbanion in dimethyl sulfoxide[4] leads to the formation of the tricyclic ketone 6 (2,4-dinitrophenylhydrazone, m.p. 174-175°) in 70% yield, along with 3% of the unsaturated ketone 7 (2,4-dinitrophenylhydrazone, m.p. 104-105°), which is also produced in 95% yield by refluxing tosylate 4 in anhydrous pyridine. The liquid ketone 6 affords a crystalline alcohol (8, m.p. 60-61°) when treated with sodium borohydride in absolute ethanol.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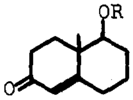
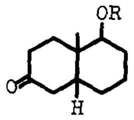
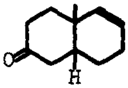

2, R=H

3, R=p-$CH_3C_6H_4SO_2$


4, p-$CH_3C_6H_4SO_2$

5, R=H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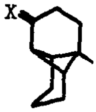
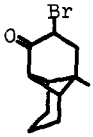

6, X=O

8, X=H,OH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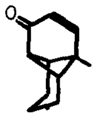
11


9

The tricyclic nature of compound 6 is shown by the fact that it fails to undergo catalytic hydrogenation and does not display olefinic bands in its n.m.r. or i.r. spectra, yet has a mass-spectral molecular weight of 164. That one terminus of the new bridge is adjacent to the carbonyl function is confirmed by the observation that the material quantitatively exchanges two protia for deuteria when treated with 1.4 N NaOD in D_2O at 100° for 44 hours without giving any measurable amount of tri- or tetradeuterated species.

There are two tricyclic ketones which *a priori* might arise from an intramolecular alkylation of an enolate ion derived from the keto-tosylate 4. Structure 6 is favored over the alternative formulation 9 both on mechanistic grounds and from a consideration of the n.m.r. spectra of compound 6 and its dideutero derivative.

An examination of Drieding stereomodels shows that the π-orbital of the enolate ion which would give rise to structure 9 is not suitably oriented for backside displacement of the tosylate group, in contrast to the situation in the enolate ion which leads to structure 6 where such displacement seems likely. The n.m.r. spectra of 6 and dideutero-6 both contain a sharp singlet at 7.46τ, with an integrated intensity corresponding to one proton. We have assigned this band to the bridgehead proton (C_7-H) adjacent to the carbonyl group. Inspection of models reveals that the dihedral angles between the C_7-H bond and the other two bridgehead C-H bonds are both 90°, and thus the proton should be very weakly coupled[5]. In the alternative structure 9, the relevant dihedral angles are 30°, 30°, and 90°, and therefore the analogous hydrogen should be appreciably coupled to two of its neighbors.[5]

In order to rigorously eliminate formulation 9, we envisioned the conversion of the tricyclic ketone into an α,β-unsaturated ketone. Since no α,β-unsaturated ketones derived from 9 are geometrically capable of existence, such a transformation would exclude this formulation from further consideration. Our anticipations were realized when the α-bromoketone 10 (m.p. 94-95°, $\nu_{max}^{CCl_4}$ 1738 cm^{-1}), obtained by the monobromination of 6 with bromine in acetic acid, was dehydrobrominated in refluxing γ-collidine to yield the enone 11 (2,4-dinitrophenylhydrazone, m.p. 164-168°). The structure of compound 11 is secured by its spectra [$\nu_{max}^{CCl_4}$ 1695 1660, 690 cm^{-1}; $\lambda_{max}^{95\%\ C_2H_5OH}$ 252 mμ (ϵ = 3000)*; τ^{CCl_4} 2.69 (one proton doublet, J = 9.2 c.p.s.), 4.30 (one proton double doublet, J = 2.0 c.p.s. and 9.2 c.p.s.), and 7.32 (one proton doublet, J = 2.0 c.p.s.)**]. To ensure against the possibility of rearrangment in the bromination or dehydrobromination steps, enone 11 was hydrogenated in the presence of palladized carbon back to ketone 6.

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*The ultraviolet spectrum of enone 11 may be compared with those of the related compounds mustakone [λ_{max}255 mμ, (ϵ = 5,700)][1b] and verbenone [λ_{max}253 mμ (ϵ = 6,840)].[6]

**The observed 1,4-coupling of 2.0 c.p.s. between the protons at C-7 and C-9 in compound 11 is expected.[7]

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