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TRANSFORMATION REACTIONS OF α-PINENE II
MAGNETIC ANISOTROPY OF THE CYCLOBUTANE SYSTEM

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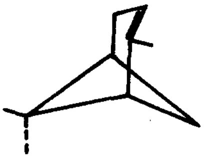
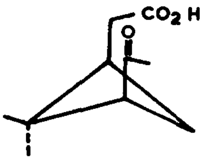
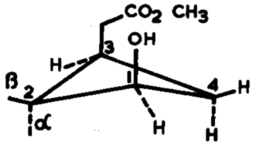
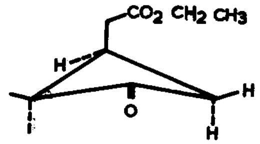
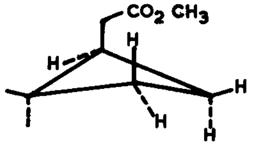
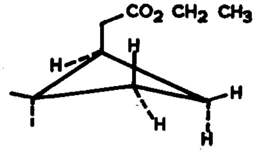
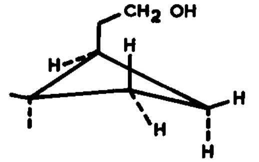
In the course of our study on the transformation reactions of α-pinene (1) we had occassion to examine the NMR spectra of the substituted cyclobutanes III to VI (Table 1), prepared from α-pinene (I) via pinonic acid (II).


I



II

Puckered conformations with quasi-axial and equatorial substituents (2-6) for the cyclobutanes III-VI follow from the bridged half-chair Y-shaped geometry of α-pinene (7). The stereochemistry of the hydroxy function in III is in accordance with the well understood retention of configuration (8) during Baeyer-Villiger cleavage.

CYCLOBUTANE		Gem-dimethyl signals[a] (in c/s)	Remarks[b]
Str.	Conformation		
III		α-63 (3H,s) β-54 (3H,s)	Ref (1)
IV		α-63 (3H,s) β-72 (s) $[-CO_2CH_2\underline{CH_3}-$ 75(t,J 7 Hz)] } (6H)	
Va		α-63 (s) β-57 (d,J 7 Hz) } (6H)	IR (neat): 1742 cm^{-1} (ester C=0) n_D^{27} 1.4258
Vb		α-64 (s) $[-CO_2CH_2\underline{CH_3}-$ 73(t,J 7 Hz)] } (6H) β-56 (3H,d,J 7.5 Hz)	IR (neat): 1739 cm^{-1} (ester C=0) n_D^{22} 1.4292
VI		α-63 (s) β-57 (d,J 8 Hz) } (6H)	IR (neat): 3500 cm^{-1} (-OH)

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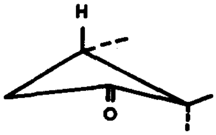
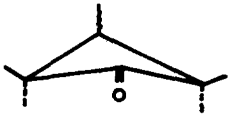
[a] The NMR spectra are taken on Varian A-60 spectrometer (CCl_4) at 60-Mc by courtesy of Dr. Sukh Dev of the National Chemical Laboratory, Poona (India). The chemical shifts are expressed in c/s downfield with TMS as internal reference.

[b] All the compounds studied are homogeneous by TLC and VPC and analysed correctly.

The NMR data for compounds III-VI assembled in Table 1 confirm the findings of the Japanese investigators (6) that (i) the chemical shift of the 'axial' α-methyl protons is more or less unaffected by structural variations at other centres and (ii) the axial α-methyl proton resonance signals (63-64 c/s) uniformly appear at fields lower than those of the 'equatorial' β-methyl protons occurring at 54-57 c/s, in the absence of functional groups that may influence otherwise. The downfield shift of the equatorial methyl protons has been demonstrated by appropriate changes in the fused cyclobutane systems studied by the Japanese workers. The pronounced downfield shift of the signal of the equatorial β-methyl protons when C-1 is trigonal (compound IV in Table 1) with no corresponding change in the α-methyl signal confirms the observations of Nakagawa *et al.* (6) in a remarkable way. While the chemical shift difference (α- *vs* β-methyl protons) observed in ring fused cyclobutane systems is reported to be approximately 0.4 ppm, in the case of the less strained cyclobutanes (III-VI) under study, the difference however, is found to be not more than 0.15 ppm, the difference arising due to the inherent upfield signals of axial methyl protons in these compounds.

It will be interesting to examine the methyl proton signals of 2,2,3-trimethylcyclobutanone (VII) and 2,2,3,4,4-pentamethylcyclobutanone (VIII) reported by Conia *et al.* (9) (Table 2) in the light of the conclusions drawn from the present study. It may be noted that the methyl proton signals for the axial methyl (63-64 c/s) and the equatorial methyl adjascent to the carbonyl (72 c/s) (Table 1) are in agreement with the values, 61.2-64.2 c/s and 69 c/s respectively observed in VII and VIII by Conia (Table 2). This has enabled us to assign the signals for the various methyl protons as shown in Table 2. The equatorial C-3 secondary methyl in VII is further shifted downfield with respect to the normal value (56-57 c/s Table 1) because of the influence of C-1 carbonyl. The conformation VII deduced on the basis of NMR is indeed in agreement with such a formulation arrived at on the basis of ORD by Conia (4). The assignment of C-3 secondary methyl in VIII (optically inactive) is somewhat ambivalent, presumably on account of the high degree of substitution.

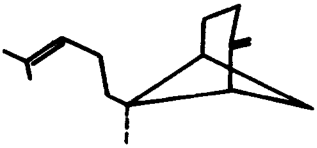
TABLE 2

CYCLOBUTANE		Gem-dimethyl signals (in c/s)	Sec-methyl signals (in c/s)	Assignment[a]
Str.	Conformation			
VII		61.2 (3H,s) 69 (3H,s)	68.4 (3H,d)	61.2 2-axMe 69 2-eqMe 68.4 3-eqMe
VIII		61.8 (6H,s) 69 (6H,s)	64.2 (3H,d)	61.8 2,4-ax$(CH_3)_2$ 69 2,4-eq$(CH_3)_2$

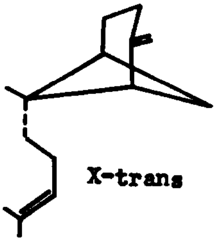
[a] Proposed by the present authors.

The considerable upfield signal for the axial methyl protons noted already *vide supra* for the unfused cyclobutanes (61-64 c/s) compared to the same in fused cyclobutanes (6) (70-80 c/s) is also confirmed by the examples cited from Conia's work.

Another interesting application of these deductions arising from the present study and that of Nakagawa *et al.* (6) would be in the assignment of the configuration of β-bergamotene. Two forms [*cis*-(IX) and *trans*-(X)] are possible for the naturally occurring sesquiterpene (10). Recently Gibson and Erman (11) synthesized stereospecifically *cis*-β-bergamotene (IX), in which



IX-cis



X-trans

the methyl protons (on saturated carbon) appeared as a singlet at 73 c/s. However, in the naturally occurring β-bergamotene the methyl protons singlet (57 c/s) is at 16 c/s higher upfield consistent with its equatorial configuration (cf. the eq Me proton signals at 54-57 c/s for compounds III-VI, Table 1), thus supporting the *trans*-structure (X) for the natural β-bergamotene on the basis of NMR.

A novel observation encountered in this study is the doublet signal (splitting) of the quaternary β-methyl protons (56-57 c/s, J 7-8 Hz) in the three compounds Va, Vb and VI (Table 1). These compounds differ from the others by the presence of the C-1 axial proton. The possibility of a long range (4σ) coupling (12-14) to explain the above observed C-2 equatorial methyl splitting is under study.

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