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PINACOL-TYPE REARRANGEMENTS IN THE PINANE SERIES: A FACILE ENTRY INTO THE BICYCLO[2.1.1]HEXANE SYSTEM

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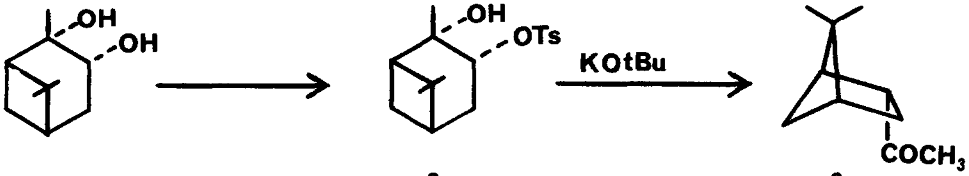
In spite of the current interest in the highly strained bicyclo[2.1.1]hexane system, there is no efficient, non-photochemical synthesis of this system from readily available compounds.[1] The only purely chemical entries into this intriguing ring system involve either long synthetic routes or proceed in very poor yield.[2] We wish to report the first example of the chemical conversion of a pinane derivative to a bicyclo[2.1.1]hexane derivative by a route which provides information on the conformation and reactivity of pinane derivatives.

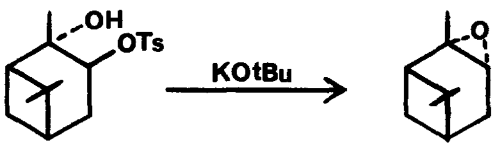
Treatment of diol 1, readily obtained by hydroxylation of α-pinene,[3] with *p*-toluenesulfonyl chloride in pyridine afforded the crystalline *cis*-monotosylate 2,[4] whose nmr spectrum (CCl_4) showed, *inter alia*, singlet methyl absorptions at δ 2.45, 1.25, 1.18 and 0.93 and a doublet of doublets at δ 4.84 (1H, CHOTs, J = 10 and 6 Hz). Monotosylate 2 reacted readily with potassium *t*-butoxide in *t*-butyl alcohol at 65° to give the ring contracted ketone, 2α-acetyl-5,5-dimethylbicyclo[2.1.1]hexane (3)[5] in 60% isolated yield. The ring contracted ketone 3 exhibits nmr absorption at δ 2.85 (1H, mult., $>CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}$) and singlet methyl absorptions at δ 2.10, 1.29 and 0.83 and has an infrared spectrum identical with that of an authentic sample.[6]



1

2

3



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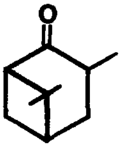

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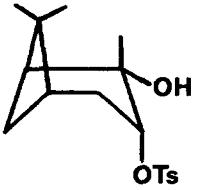
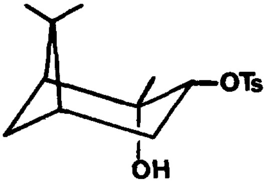
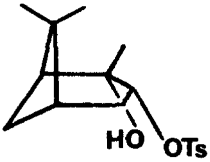


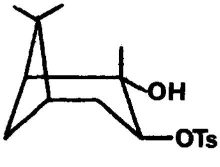
2a



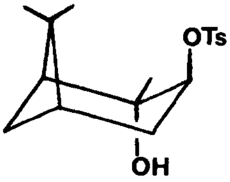
2b



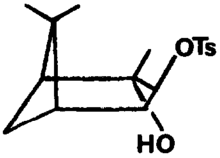
2c



4a



4b



4c

In contrast, when the non-crystalline *trans*-monotosylate **4**, obtained from the corresponding diol[3], was treated with potassium *t*-butoxide in *t*-butyl alcohol α-pinene oxide (**5**) was obtained.

Because it is well established that in base catalyzed pinacol-type rearrangements the migrating group should bear an *anti*-coplanar relationship to the leaving group and that epoxide formation occurs most readily from a diaxial relationship between the alkoxide ion and the leaving group, these results clearly exclude **2a** and **4a** as the *reactive* conformations of the two monotosylates. If conformation **2a** were important for monotosylate **2**, methyl migration would be expected to give 2-methylnopinone (**6**) and we have been unable to detect either isomer of **6** in the reaction product. Similarly, if conformation **4a** were important for monotosylate **4**, ring contraction would be expected, but again we have been unable to detect this product in the crude reaction mixture.

Although the high selectivity observed in these reactions is readily explained by reactive conformations **2b** and **4b** for the two monotosylates it is not possible to exclude the flattened planar conformations **2c** and **4c**. In conformation **2c**, it would appear that there should be an equal probability for either ring contraction or methyl migration, but the transition state for methyl migration may be energetically unfavorable because of the development of a severe interaction between the migrating methyl group and the C-9 methyl group. Similarly in conformation **4c**, ring contraction would require the incipient acetyl group to closely approach the C-9 methyl group. We are currently examining other rearrangements in the pinane series which we hope will clarify the conformational problem.

REFERENCES

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2. Other non-photochemical syntheses not cited in ref. 1 include a) the solvolysis of *exo*-bicyclo[2.2.0]hex-2-yl tosylate, R.N. McDonald and

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3. a) H. Schmidt, Chem. Ber., 93, 2485 (1960).
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4. All new compounds gave satisfactory analytical results.
5. J. Meinwald and P.G. Gassman, J. Amer. Chem. Soc., 82, 5445 (1960).
6. We are indebted to Professor Meinwald for supplying us with the infrared spectrum of 3.