

CONVERSION OF PINANE SKELETON INTO STRAINED BICYCLO[2.1.1] HEXANE SYSTEM.

PINACOL-TYPE REARRANGEMENT OF  $\alpha$ -PINENEGLYCOL TOSYLATE\*

Takayuki SUGA, Toshifumi HIRATA, Tsuyoshi SHISHIBORI, and Tamon MATSUURA

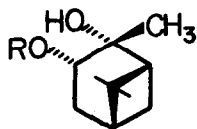
Department of Chemistry, Faculty of Science, Hiroshima University,

Hiroshima, Japan

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$\alpha$ -Pineneglycol monotosylate II derived from I (1) was treated with methanolic potassium hydroxide. The main product from II was found to be a member of the bicyclo[2.1.1] hexane series. This observation is the first example of ring contraction of a member of the pinane group to this highly strained ring system.

cis- $\alpha$ -Pineneglycol monotosylate (II), m.p. 75-76°C, was treated with methanolic potassium hydroxide in methanol at 65°C for 3 hrs. An oily reaction mixture was obtained, which was subjected to gas chromatography (column: DEGS, NGS, and PEG-6000), thin-layer chromatography, and then elution chromatography on a silicagel column. In this manner, the reaction mixture was found



I: R=H

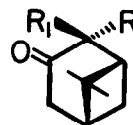
II: R=Ts



III: R=COCH<sub>3</sub>, R<sub>1</sub>=H

IV: R=COOH, R<sub>1</sub>=H

V: R, R<sub>1</sub>=O



VI: R=CH<sub>3</sub>, R<sub>1</sub>=H

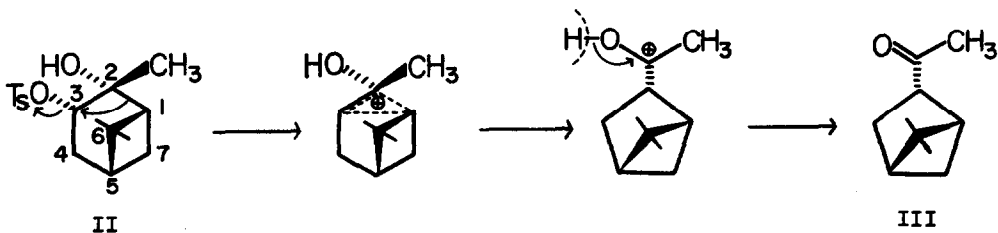
VII: R=H, R<sub>1</sub>=CH<sub>3</sub>

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to consist of the ring-contracted ketone, (+)-2( $\alpha$ -acetyl-5,5-dimethylbicyclo[2.1.1]hexane (III) (50 % yield), *cis*- $\alpha$ -pineneglycol (I) (26 %), pinocamphone (VI) (5.6 %), isopinocamphone (VII) (0.9 %) and two unidentified products (5.6 and 8.5 %, respectively).

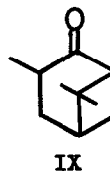
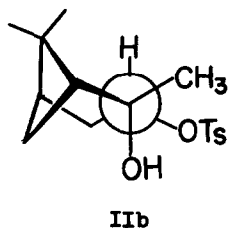
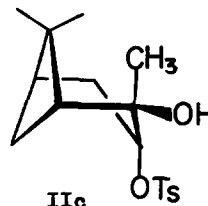
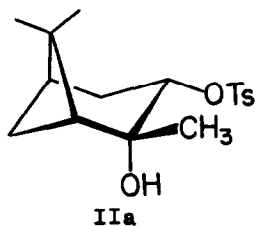
Evidence for structure III of the ring-contracted ketone was obtained as follows: the ketone  $[\alpha]_D^{25} +16.2^\circ$  (c 0.48, MeOH);  $M^+ 152$  (2);  $\nu_{\max}^{\text{liq.}}$  1710 (C=O), 1386 and 1369, 1178 (gem-dimethyl) and 1357  $\text{cm}^{-1}$  ( $\text{CH}_2\text{CO}$ ); nmr (3): 0.81, 1.27, 2.09 (s, 3H) and 2.84 (m, 1H,  $\text{>CHCO-}$ );  $\lambda_{\max}^{\text{MeOH}}$  280  $\mu\text{m}$  ( $\epsilon$  35.2) was oxidized with sodium hypobromite to afford 5,5-dimethylbicyclo[2.1.1]hexane-2( $\alpha$ -carboxylic acid (IV) (m.p. 54-55°C, lit. (4) m.p. 55.0-55.5°C;  $\nu_{\max}^{\text{KBr}}$  1693  $\text{cm}^{-1}$ ), which was further converted into 5,5-dimethylbicyclo[2.1.1]hexan-2-one (V) ( $\nu_{\max}^{\text{liq.}}$  1750  $\text{cm}^{-1}$ ; 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. (5) 155.5-156.0°C) following Meinwald's procedure (4).

The same treatment of each of *cis*- $\alpha$ -pineneglycol (I) and 2,3-epoxypinane (VIII) as above gave no reaction product. Accordingly, neither of I nor VIII is an intermediate product to produce the ketone III from the tosylate II. Thus, the formation of III is best explained by the pinacol-type rearrangement as shown below. The pinocamphones VI and VII may be considered to be produced



by migration of the hydroxyl group from C-2 to C-3, followed by 1,2-shift of the hydride ion from C-3 to C-2.

If the reactive conformation of *cis*-glycol tosylate (II) is assumed to be IIa, the ring-contracted ketone III is expected to be readily formed, because the migrating moiety would be anti-coplanar to the leaving group as shown in Newman projection formula (IIb). On the other hand, if the tosylate II is in conformation IIc, 3-methylnopinone (IX) would be expected to be formed because the anti-coplanar migrating group is the methyl group (see IIc), but we have been unable to obtain evidence for the formation of this ketone. Hence the



reactive conformation of cis- $\alpha$ -pineneglycol monotosylate is surely conformation IIa.

#### References

1. H. Schmidt, Chem. Ber., 93, 2485 (1960).
2. The mass spectrum was measured with a Hitachi RMU-6D mass spectrometer by courtesy of Professor K. Nakanishi of Tohoku University in Japan.
3. We are indebted to Dr. E. von Rudloff of the Prairie Regional Laboratory, National Research Council of Canada for measurement of nmr spectrum by a Varian HA-100 spectrometer in carbon tetrachloride with TMS as an internal standard.
4. J. Meinwald and P. G. Gassman, J. Am. Chem. Soc., 82, 5445 (1960).
5. We are grateful to professor J. Meinwald of Cornell University for supplying us with the sample of 5,5-dimethylbicyclo [2.1.1] hexan-2-one 2,4-dinitrophenylhydrazone, m.p. 155.5-156.0°C (4).