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THE PINACOL REARRANGEMENT OF CYCLOPENTYLCYCLOHEPTANE-1,1'-DIOL

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Abstract—When cyclopentylcycloheptane-1,1'-diol was heated with dilute acid, the major product was spiro [5.6] dodecan-1-one. The diene, 1-(1-cyclopentenyl)cycloheptene, was a minor product, and no spiro [4.7] dodecan-6-one was found.

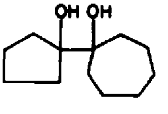
THE pinacols of several cycloalkanes have been reported and converted to a mixture of a spiro ketone and a diene[1–4] (Table 1). That ring size is one of the structural features influencing the degree of ring expansion in the reaction of alicyclic glycols with dilute acid was indicated by a study of cyclopentylcyclohexane-1,1'-diol.[4] The purpose of the present investigation was to continue the study of the influence of ring size on the degree of ring expansion, and cyclopentylcycloheptane-1,1'-diol (I) was chosen for that purpose.

TABLE 1. PINACOL REARRANGEMENT OF ALICYCLIC GLYCOLS

Glycol	% Spiro ketone[a]	% Diene
Bicyclobutyl-1,1'-diol	100[b]	
Bicyclopentyl-1,1'-diol (II)	86[c]	10–15[g]
Cyclopentylcyclohexane-1,1'-diol (XIII)	19·8[d]	80·2
Bicyclohexyl-1,1'-diol	12·7[e]	88[h]
Bicycloheptyl-1,1'-diol (III)	1·25[f]	98·75
Bicyclooctyl-1,1'-diol	1·83[f]	98·17

[a] All percents represent composition of the product mixtures isolated; per cent yields are less. [b] Diene not reported.[1] [c] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.* **76**, 2753 (1954). [d] Consists of two ketones. See Ref. 4. [e] Isolated as the semicarbazone.[3] [f] See Ref. 2. [g] Isolated as the maleic anhydride adduct.[2] [h] E. de B. Barnette and C. A. Lawrence, *J. Chem. Soc.* 1104 (1935).

Preparation of I was accomplished by pinacol reduction of a mixture of cyclopentanone and cycloheptanone. Since the product proved to be an inseparable mixture I, II and III, rearrangement was carried out on the impure glycol. A mixture of five products was obtained (Table 2).



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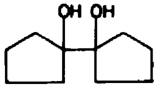

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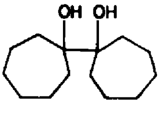

III

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[1] E. Vogel, *Chem. Ber.* **85**, 25 (1952).

[2] D. S. Greidinger and D. Ginsberg, *J. Org. Chem.* **22**, 1406 (1957).

[3] Qudrat-i-Khuda, *J. Indian Chem. Soc.* **16**, 525 (1939).

[4] R. D. Sands and D. G. Botteron, *J. Org. Chem.* **28**, 2690 (1963).

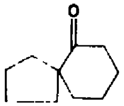
Table 2. Pinacol rearrangement of cyclopentylcycloheptane-1,1'-diol

	Percentage yield from			
Product	Impure I[a]	Pure I[c]	Pure II[c]	Pure III[c]
IV	1·1		14·9	
V	6·5		85·1	
VI	10·9	14·5		
VII	64·2	85·5		
VIII	0·0	0·0		
IX	17·2			100
X	0·0[b]			0

[a] These percentages represent the composition of the 40 g of product mixture obtained from 65 g of the glycol. [b] Traces of X were once isolated as the 2,4-dinitrophenylhydrazone. [c] Calculated from the percentages determined for the impure glycol.

The composition of the product mixture was determined by gas chromatography. The components of the mixture were identified by comparison with authentic samples. Compounds VI, VII and VIII have not been reported previously.

IV



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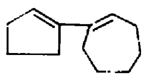

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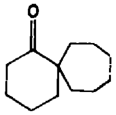

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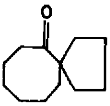
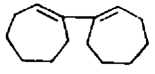


VIII



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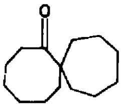
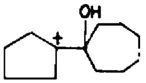
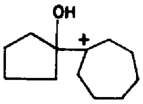


X



XI



XII

Table 2 shows that cyclopentylcycloheptane-1,1'-diol (I) is far better able to rearrange than it is able to form the diene and that rearrangement involves expansion of the five-membered ring only. Since product composition is the result of a competition between ring expansion and proton loss involving the internal strains of the reversibly formed carbonium ions,[4] the product composition depends on the relative internal strains of XI and XII. Although either carbonium ion could return to the glycol (I),[5] the more strained ion is more apt to form product. The ease of formation of XI and XII should be nearly the same, with XI slightly favoured,[6] but with the more highly strained five-membered ring[7] unrelieved, XII is the more strained of the two carbonium ions.

The less strained XI can return to I, lose a proton and water to form the diene, or

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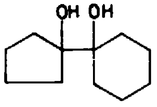
[5] M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.* **81**, 1498 (1959); C. J. Collins, *Quart. Rev.* **14**, 357 (1960).

[6] Blased on the relative rates of hydrolysis of the 1-methyl-1-chlorocycloalkanes, H. C. Brown, R. S. Fetcher and R. B. Johannesen, *J. Amer. Chem. Soc.* **73**, 212 (1951).

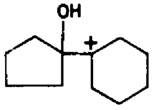
[7] A five-membered ring is more strained than a seven-membered ring, R. Spitzer and H. M. Huffman, *J. Amer. Chem. Soc.* **69**, 211 (1947).

undergo ring expansion. Since ring expansion does not offer any relief of strain to the seven-membered ring,[8] diene formation is the fate of any XI that does not return to I. This is consistent with the reaction of III, where diene formation is nearly exclusive.

It is the more strained XII that determines the product composition. Its strain can be relieved by proton loss with diene formation and by ring expansion. Ring expansion to a strainless six-membered ring is the preferred method of strain relief. This is consistent with the reaction of II where the same per cent expansion of the five-membered ring is found.



XIII



XIV

This preference for rearrangement instead of diene formation was not observed in the case of cyclopentylcyclohexane-1,1'-diol (XIII).[4] In that case, the more strained carbonium ion, XIV, was more strained than the parent glycol because formation of the ion resulted in eclipsed conformations in the six-membered ring. With two highly strained rings, XIV was so strained that it most often lost a proton and formed the diene before the orientation necessary for rearrangement could take place.

In the present case, however, the more strained carbonium ion, XII, is less strained than its parent glycol because formation of the ion results in a de-eclipsing of bonds and hence a reduction of strain in the seven-membered ring. Therefore, with only the five-membered ring highly strained, XII can exist long enough for the orientation leading to rearrangement to take place, and rearrangement, not proton loss with diene formation, is the major course of the reaction.

EXPERIMENTAL

*Preparation of cyclopentylcycloheptane-*1,1'*-diol.* A solution of 62 g $HgCl_2$ in a mixture of 316 ml (300 g, 3·57 moles) cyclopentanone and 380 ml (400 g, 3·57 moles) cycloheptanone was slowly added to a boiling mixture of 800 ml benzene and 132 g Al turnings. The mixture was refluxed 3 hr after the completion of the addition, hydrolysed by the addition of 500 ml water and another 800 ml benzene, and then refluxed for another 2 hr. The mixture was filtered while hot, the residue was washed with benzene, and the benzene was removed from the filtrate by distillation. Recrystallization of the cooled residue from ligroin (60–90°) gave 161 g impure glycol. m.p. 63–64°.

*Rearrangement of cyclopentylcycloheptane-*1,1'*-diol.* The impure glycol (65 g) was refluxed with 25% H_2SO_4 for 2 hr. Ether extraction was followed by washing with $NaHCO_3$ aq and water and drying of the ether solution ($MgSO_4$). Evaporation of the ether gave 40 g residue.

Preparation of reference compounds. Compounds IV and V were obtained from II and compound IX from III. Compounds VII and VIII were prepared by the method of Mousseron *et al.*[9] (a) *Spiro*[5.6]*dodecan-*1*-one* (VII) was isolated in small yield by a chromatographic separation of the product mixture from the reaction of hexamethylene bromide with cyclohexanone. The resulting colourless liquid boiled at 114–116°/8 mm, n_D^{21} 1·4878. 2,4-dinitrophenylhydrazone (yellow) m.p. 127°. (Found: C, 80·12; H, 11·07 $C_{12}H_{20}O$ requires: C, 80.00; H, 11·11%; Found: C, 59·79; H, 6·59. $C_{18}H_{24}N_4O_4$ requires: C, 60.00; H, 6·67%.)

(b) *Spiro*[4.7]*dodecan-6-one* (VIII) was obtained in small yield by the reaction of tetramethylene bromide with cyclo-octanone. The colourless, chromatographically pure, liquid boiled at 103–104°/8 mm, $n_D^{28\cdot 5}$ 1·4872. 2,4-dinitrophenylhydrazone (brown) m.p. 127–28°. (Found: C, 59·88; H, 6·62. $C_{18}H_{24}N_4O_4$ requires: C, 60·00; H, 6·67%.)

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[8] An eight-membered ring is more strained than a seven-membered ring (Ref. 7).

[9] M. Mousseron, R. Jacquier and H. Christol, *C.R. Acad. Sci. Paris* **239**, 1805 (1954).

Analysis of the reaction mixture. The rearrangement mixture was analysed by gas chromatography using a 10-ft column of Dow-Corning silicone stopcock grease on Johns-Manville Chromsorb. The identification of the compounds was done on the reaction mixture, the reaction mixture after the dienes had been removed with maleic anhydride, and on the ketones regenerated from the semicarbazones. Separation of the reaction products was accomplished with an Aerograph A-700 Autoprep, using a 10-ft. by $\frac{3}{8}$-in column packed with 20% Dow-710 on acid washed 60/80 mesh Chrom. W.

Compound VII, after the chromatographic separation from the reaction mixture, had a b.p. and refractive index identical with those of the reference compound. Its 2,4-dinitrophenylhydrazone showed depression of m.p. when mixed with that of VIII but not when mixed with that of VII.

Compound VI, 1-(1-*cyclopentenyl*)*cycloheptene*, was identified as a diene because it was removed from the product mixture with the other dienes by maleic anhydride. After the chromatographic separation, it was a colourless liquid boiling at 108°/7 mm, n_D^{22} 1·5317. (Found: C, 88·65; H, 11·12. $C_{12}H_{18}$ requires: C, 88·88; H, 11·12%.)

The percentage composition of the reaction mixture was determined by weighing the peaks in the chromatographic analysis. The reliability of this method of analysis is confirmed by the agreement of the values for the rearrangements of II and III shown in Table 2 compared with the previously reported values shown in Table 1.