944. *Double Pinacol-type Rearrangement Leading to a 1,4-Diketone*

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During work on *sym*-dicyclohexylethane derivatives[1] the *meso*- and racemic forms of the tetraol (I) containing *cis*-1,2-diol grouping were prepared. The conversion of the corresponding ditosylates (II) into the diketone (IV) by a double pinacol-type rearrangement is now described.

OWEN *et al.*[2] studied the reaction of alicyclic *cis*- and *trans*-secondary 1,2-diol monotosylates with bases, and found that the *cis*-compounds are converted into ketones. The presence

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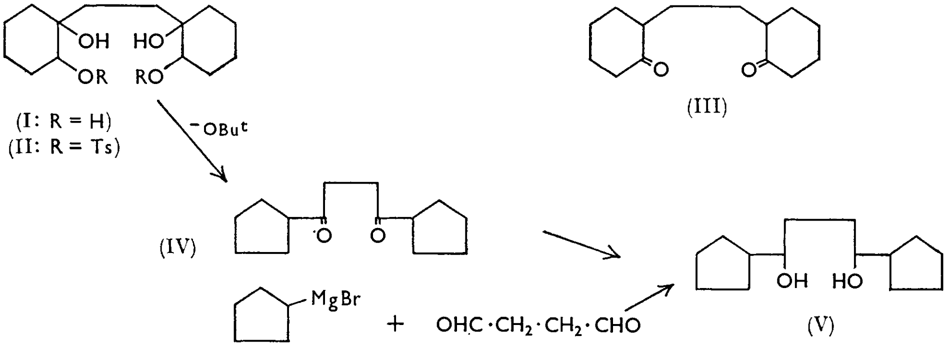
[1] E. Ghera, M. Gibson, and F. Sondheimer, *J. Amer. Chem. Soc.*, 1962, **84**, 2953.

[2] M. F. Clarke and L. N. Owen, *J.*, 1949, 315; L. N. Owen and G. S. Saharia, *J.*, 1953, 2582; M. E. Ali and L. N. Owen, *J.*, 1958, 2119.

of a tertiary hydroxyl group in the *cis*-1,2-diol monotosylate system can cause a pinacol-type rearrangement,[3] which, in the case of compound (I), could lead to the diketones (III) or (IV). We expected the 1,4-diketone (IV) to be the preferred product, as the condition of antiparallel relationship of departing and migrating groups is essential in such rearrangements.



On treatment with tosyl chloride each of the isomers of the tetraol (I) yielded the corresponding ditosylate (II) (isomer A, m. p. 150—151°; isomer B, m. p. 146—147°). Either of the isomers of the ditosylate (II) on treatment with potassium t-butoxide in t-butyl alcohol at room temperature gave *ca.* 80% of a liquid diketone, characterised as the bis-semicarbazone (m. p. 190—191°). As expected, this diketone was not identical with diketone (III),[1] and structure (IV) is assigned to it. Reduction of the diketone (IV) with lithium aluminium hydride gave the crystalline diol (V) in almost quantitative yield.*

The structure of compound (V) and, consequently, of diketone (IV) was confirmed by an independent synthesis. Cyclopentyl bromide was converted into the Grignard reagent, which was condensed with succinaldehyde in tetrahydrofuran.† The crystalline fraction which could be separated by chromatography from the resulting mixture of products was identical in all respects with the diol (V).

Experimental.—Chromatograms were carried out with Merck " acid-washed " alumina.

1,2-*Bis*-(1,2-cis-*dihydroxycyclohexyl*)*ethane* 2′,2″-*ditosylate* (II) (*isomers A and B*). Tosyl chloride (450 mg.) was added to an ice-cooled solution of 120 mg. of the tetraol (I) (isomer A) in 2·5 c.c. of pyridine and set aside for 16 hr. at room temperature. The solution was poured into water and the solidified product was filtered, dried, and dissolved in benzene. The insoluble part was eliminated by filtration and the benzene solution was concentrated to small volume and diluted with hexane. Cooling produced 192 mg. (72%) of the ditosylate (II) (isomer A) as plates, m. p. 146—148°. Recrystallisation from hexane–benzene (4 : 1) gave the analytical sample, m. p. 150—151° (Found: C, 59·1; H, 6·75. Calc. for $C_{28}H_{38}O_8S_2$: C, 59·35; H, 6·75%).

Treatment of the tetraol (I) (isomer B) with tosyl chloride under the same conditions produced an almost identical yield of the ditosylate (II) (isomer B) as prisms, m. p. 146—147° (Found: C, 59·55; H, 6·82%).

The infrared spectra (KBr discs) of the two isomers of the ditosylate (II) were distinctly different.

1,4-*Dicyclopentylbutane*-1,4-*dione* (IV). The ditosylate (II) (100 mg., isomer A) was dissolved in 3 c.c. of dry benzene and added to a solution of potassium (20 mg.) in t-butyl alcohol (8 c.c.) under nitrogen, with stirring. The solution was set aside at room temperature for 3 hr. Addition of water and ether extraction gave a residue which was chromatographed on 6 g. of alumina. Elution with pentane–ether (4 : 1) yielded 31 mg. (79%) of the diketone (VI) as a

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* The crude diol may consist of a mixture of two diastereoisomers, as judged from the substantial difference in melting point before and after crystallisation (see Experimental section).

† To our knowledge succinaldehyde has never before been used in a Grignard reaction.

[3] See, *e.g.*, N. L. Wendler, *Tetrahedron*, 1960, **11**, 213; R. B. Bates, G. Büchi, T. Matsura, and R. R. Schaffer, *J. Amer. Chem. Soc.*, 1960, **82**, 2327; Y. Mazur and M. Nussim, *ibid.*, 1961, **83**, 3911; E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, *ibid.*, 1964, **86**, 478.

colourless oil with a strong carbonyl band at 5·86 μ in the infrared ($CHCl_3$). The bis-semicarbazone was obtained in almost quantitative yield and on crystallisation from methanol formed prisms, m. p. 190—191° (Found: C, 56·9; H, 8·5; N, 25·1. Calc. for $C_{16}H_{28}N_6O_2$: C, 57·1; H, 8·4; N, 25·0%).

An almost identical result was obtained when the experiment was carried out with the ditosylate (II) (isomer B).

1,4-*Dicyclopentylbutane*-1,4-*diol* (V). (*a*) *By reduction of compound* (IV). A solution of the diketone (IV) 50 mg. in 5 c.c. of dry ether was added to 60 mg. of lithium aluminium hydride in 5 c.c. ether and the mixture was stirred for 3 hr. A saturated solution of sodium sulphate was then added, followed by solid sodium sulphate. Filtration followed by washing with chloroform and evaporation of the filtrates yielded 50 mg. of crystalline product, m. p. 121—135°, which showed one homogeneous spot on thin-layer chromatography. Crystallisation from acetone raised the melting point to 160—161° (Found: C, 74·35; H, 11·55. Calc. for $C_{14}H_{26}O_2$: C, 74·3; H, 11·6%).

(*b*) *From cyclopentylmagnesium bromide and succinaldehyde.* The Grignard reagent was prepared from 1·5 g. of cyclopentyl bromide and 0·24 g. magnesium in ether solution. The commercially available succinaldehyde (30% solution in water, K & K Laboratories Inc.) was extracted with ether and the ether solution was dried ($MgSO_4$) and evaporated under reduced pressure. The succinaldehyde thus obtained was partly polymerised, according to the refractive index (n_D^{22}, 1·446). Without further purification the dialdehyde (0·6 g.) in dry tetrahydrofuran (25 ml.) was added dropwise to the Grignard reagent with external ice-cooling. After the addition was completed the mixture was refluxed for 3 hr., hydrolysed with ammonium chloride solution, and extracted with ether. Evaporation of solvents under reduced pressure afforded 0·6 g. residue, which yielded on chromatography a crystalline compound (40 mg.), eluted with benzene–ether 3 : 2. After crystallisation from acetone the compound had m. p. 159—160°, and was identical with compound (V) (infrared spectra, thin-layer chromatography, and mixed m. p.).

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