# *Elimination of Water from Glycols. Dehydration of Racemic 1 : 4-Glycols Derived from Acenaphthene.*

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[Reprint Order No. 4679.]

5-β-Ethoxycarbonylpropionylacenaphthene with methyl- and ethyl-magnesium iodide yields the expected 1 : 4-glycols, which with dilute sulphuric acid or anhydrous copper sulphate give tetrahydrofuran derivatives.

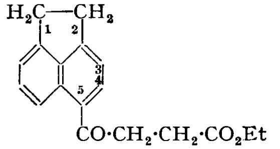
The rearrangement of pinacols and α-glycols occurring on elimination of water has been much studied. In this laboratory the examination of the mechanism of such rearrangements has been facilitated by using optically active substituted hydrobenzoins, and has led to optically active epoxides, diepoxides, ketones, and aldehydes (McKenzie and Roger, *J.*, 1924, **125**, 844, 2148; Roger and McKenzie, *Ber.*, 1929, **62**, 272; Roger and McKay, *J.*, 1933, 332; Roger and Roberts, *J.*, 1937, 1753).

Recently we had occasion to examine the action of Grignard reagents on 5-β-ethoxycarbonylpropionylacenaphthene (I). With methyl- and ethyl-magnesium iodide we obtained the expected 1 : 4-glycols (II; R = Me and Et) respectively.

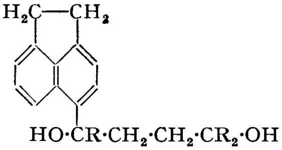
Phenyl-, *cyclo*hexyl-, and α-naphthyl-magnesium bromide yielded only intractable oils; these usually contained some unchanged ester as long heating was avoided.

1 : 4-Glycols have not received the same attention as their α-counterparts. Lieben (*Monatsh.*, 1902, **23**, 60) reviewed the limited data then available and stated that, in general, 1 : 4-glycols yielded tetrahydrofuran derivatives, without intramolecular rearrangement, on treatment with dilute mineral acids. In a recent review of the literature Shepherd (Thesis, St. Andrews, 1951) reports that, of twenty-nine 1 : 4-glycols prepared and dehydrated in the intervening years, twenty-five yielded substituted tetrahydrofurans, and the remaining four gave unsaturated alcohols or diolefins.

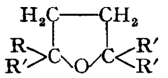
In the present work dehydration of (II; R = Me or Et) by boiling dilute sulphuric acid or a suspension of anhydrous copper sulphate in boiling ethanol gave the tetrahydrofuran derivatives predicted by Lieben's hypothesis, *viz.* (III; R = 3-acenaphthenyl, R′ = Me and Et). Similarly, Kloetzel (*J. Amer. Chem. Soc.*, 1940, **62**, 3045) showed that dehydration of the 5 : 6 : 7 : 8-tetrahydro-1-naphthyl analogue of (II; R = Me) gave the furan derivative (III; R = tetrahydronaphthyl, R′ = Me). The dehydration products (III) possess a centre of asymmetry, and it is hoped in a further communication to deal with the dehydration of optically active 1 : 4-diols.



(I)



(II)



(III)

## EXPERIMENTAL

5-β-Carboxypropionylacenaphthene was prepared by the method of Fieser and Peters (*Org. Synth.*, 1940, **20**, 1). Esterification with ethanol–sulphuric acid gave the *ethyl ester* in good yield as needles (from ethanol), m. p. 75—76° (Found : C, 76·8; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

*2-5′-Acenaphthenyl-5-methylhexane-2 : 5-diol.*—A suspension of the foregoing ester (5 g.) in dry ether (100 ml.) was slowly added, with ice-cooling, to the Grignard reagent prepared from methyl iodide (15 g.). The reaction mass was allowed to reach room temperature, refluxed for 1 hr., and decomposed with ice and dilute sulphuric acid. The product, isolated in the usual way, was a yellow oil (5·3 g.) which was dissolved in hot light petroleum (b. p. 60—80°) containing sufficient ethanol for miscibility. On cooling, a solid separated which, after recrystallisation from the above solvent mixture, gave *2-5′-acenaphthenyl-5-methylhexane-2 : 5-diol* as rectangular prisms (1·6 g.), m. p. 125—126° (Found; C, 80·2; H, 8·5. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·5%). This glycol gave a blood-red colour with concentrated sulphuric acid.

*3-5′-Acenaphthenyl-6-ethyloctane-3 : 6-diol.*—A similar reaction (initially at −10°; then at 15° for 72 hr.) gave *3-5′-acenaphthenyl-6-ethyloctane-3 : 6-diol* as rectangular prisms, (2·4 g. from 10 g. of ester), m. p. 112·5—113·5° (Found : C, 81·1; H, 9·2. $C_{22}H_{30}O_2$ requires C, 81·0; H, 9·2%). This also gave a blood-red colour with concentrated sulphuric acid.

*2-5′-Acenaphthenyltetrahydro-2 : 5 : 5-trimethylfuran.*—(*a*) 2-5′-Acenaphthenyl-5-methylhexane-2 : 5-diol (2 g.) was refluxed for 4 hr. with 20% (vol.) sulphuric acid (25 ml.), then cooled and extracted with ether. The combined extracts were washed with 5% aqueous sodium hydrogen carbonate and then with water. After being dried, the extract yielded a viscous oil which solidified. Recrystallisation from ethanol gave *2-5′-acenaphthenyltetrahydro-2 : 5 : 5-trimethylfuran* as rectangular plates, m. p. 68·5—69° (Found : C, 85·4 ; H, 8·4. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%).

The compound gave a brilliant red colour with concentrated sulphuric acid. It did not decolorize bromine in carbon tetrachloride, react with sodium in dry ether, or form a 2 : 4-dinitrophenylhydrazone.

(*b*) The diol (1 g.) was refluxed for 2 hr. with a suspension of freshly prepared anhydrous copper sulphate (2·5 g.) in absolute ethanol (50 ml.). The mixture was then poured into water (200 ml.) and stirred until all the copper sulphate had dissolved; the resulting turbid liquid was extracted with ether. The extract, after being washed with water and dried, gave a viscous oil (0·8 g.) which afforded the tetrahydrofuran derivative, m. p. and mixed m. p. 68·5—69°.

*2-5′-Acenaphthenyl-2 : 5 : 5-triethyltetrahydrofuran.*—By both methods 3-5′-acenaphthenyl-6-ethyloctane-3 : 6-diol gave *2-5′-acenaphthenyl-2 : 5 : 5-triethyltetrahydrofuran* as rectangular plates, m. p. 63—64° (Found : C, 85·6; H, 9·2. $C_{22}H_{28}O$ requires C, 85·7; H, 9·1%), its chemical properties being similar to those of the trimethyl analogue.

Attempts to dehydrate these glycols with glacial acetic acid and iodine gave only viscous tars.

We thank the Department of Scientific and Industrial Research for the award of a maintenance allowance to one of us (D. M. S.).

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[*Received, September 25th,* 1953.]