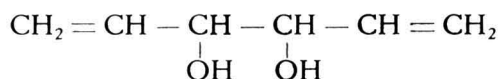


Chemistry. — GRINER's *divinylglycol*. By P. VAN ROMBURGH and W. VAN HASSELT.

(Communicated at the meeting of January 30, 1932.)

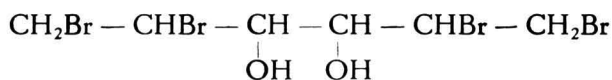
GRINER¹⁾ has obtained divinylglycol by the reduction of acrolein dissolved in diluted acetic acid with zinc covered with a film of copper. An examination of the formula of this compound,



will show that it contains two identical asymmetric carbon atoms.

The existence of two inactive forms, viz. one racemic and the other by internal compensation, is therefore possible. In order to decide which form is represented by GRINER's glycol, LE BEL tried to obtain an active form by growing moulds in a diluted solution of this glycol, but without success. The solution after the experiment was inactive. GRINER concluded therefore that his compound represents the inactive form by internal compensation.

The glycol combines directly with two molecules of bromine, forming a tetrabromide:



occurring in two forms, melting, according to GRINER, resp. at 96° and 174°.

In fact the *i*-divinylglycol may give three inactive tetrabromides viz. one racemic form and two by internal compensation.

If the above mentioned conclusion of GRINER, concerning the configuration of his glycol, is right, the elimination of the bromine from the two different tetrabromides might be expected to result in the recovering of the original *i*-glycol, which, of course, on combining with bromine would again produce a mixture of both the tetrabromides mentioned above.

If, on the other hand, the original glycol should be a mixture of two isomerides, it would be possible to isolate them.

Many years ago one of the authors (v. R.) made preliminary experiments in order to solve this question.

The tetrabromide (m.p. 174°) was refluxed in absolute ethyl alcohol with zinc dust and the recovered glycol (which we denote by A) without

¹⁾ Ann. de Chim. [6] 26, 367 (1892).

further purification was treated with bromine according to GRINER'S method. The tetrabromide obtained in this reaction had an identical melting point with that of the original bromide. A proof of the presence of the isomeride melting at 96° could not be obtained.

It seemed interesting to us first to subject the lower melting tetrabromide to the same reaction, and to isolate the glycols derived from both the isomerides.

The experiments showed, that the glycol (denoted by *B*) derived from the bromide (m.p. 96°) yielded on bromination a tetrabromide with the same melting point without formation of the bromide melting at 174° .

On examination, the two glycols (*A*) and (*B*), obtained by elimination of the bromine, appeared to be quite different. The bromide (m.p. 174°) yielded a glycol (*A*) which solidified at 10° , the other (*B*) on the contrary, at -40° . The physical constants moreover were quite different.

Presumably they represent resp. the racemic and the inactive form of divinylglycol, unless there have been intermolecular rearrangements.

Experimental.

Preparation of the glycol A.

A solution of 25 grams of the tetrabromide (m.p. 174°) in 150 c.c. of absolute ethyl alcohol treated with 30 grams of zinc dust was refluxed for six hours. The reaction mixture was filtered and the alcohol distilled under diminished pressure. Water was added to the residue and the mixture treated with sodium carbonate and filtered. The filtrate was extracted with ether. After removal of the ether there remained about 6 grams of the glycol *A* formed in the reaction.

Addition of bromine to glycol A.

In a two-necked flask, cooled with a mixture of ice and salt and equipped with a mechanical stirrer, the crude glycol, dissolved in 50 c.c. of chloroform, was placed and the stirrer started. Drop by drop bromine was added till the absorption of the bromine stopped. A crystalline white mass separated which was filtered off and dried (weight about 15 grams). The melting point of the crude product was 150° . It was washed with benzene and recrystallised from that solvent. The pure product melted at 172° .

A tetrabromide with the lower melting point (96°) could not be separated.

Preparation of the glycol B.

Using the same technique, 15 grams of the tetrabromide (m.p. 96°) were treated with zinc dust. The glycol *B* formed in this reaction, was dissolved in chloroform and treated with bromine in the manner as described above.

The behaviour of this glycol was quite different from that of glycol *A*.

The chloroform solution did not depose any crystals till the end of the reaction and they only gradually appeared after standing for some time. The melting point of this tetrabromide was 74° and on further recrystallisation 96° .

The tetrabromide melting at 174° could not be demonstrated.

Samples of the glycols *A* and *B* were subjected to fractional distillation. The main fraction showed the following constants :

	Glycol A	Glycol B	
B.P. ^{45mm}	125°	125°	
d_{15}^{18}	1.027	1.016	
n_D^{18}	1.4822	1.4775	
MR _D	31.66	31.73	Calc. for C ₆ H ₁₀ O ₂ $\bar{1}2$ 32.
M.P.	$+ 10^{\circ}$	$- 40^{\circ}$	

A further investigation of the glycol is to follow.

Chemistry. — *Osmosis in systems consisting of water and tartaric acid. I.*
By F. A. H. SCHREINEMAKERS and J. P. WERRE.

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Introduction.

We imagine the composition of a liquid, containing the substances *W* (water) and *X*, represented in the well-known way by a point *a* of the line *WX* (figs. 1 and 2). If we bring an invariant membrane¹⁾, absorbing both substances, into this liquid *a*, then it will get a definite *W*- and *X*-amount, which we represent by the length of the line *aa'* and *aa''* (fig. 1). If we give all compositions, beginning with pure *W* (water) and ending with the pure substance *X*, to this liquid *a*, then point *a'* will proceed along a curve *W'a'X* and point *a''* along a curve *Wa''X'*, which curves we call the *W*- and *X*-curves of the membrane.

We may divide these absorption-diagrams into four groups, depending on the *W*- and *X*-curves having a maximum yes or no [figs. 1—4 of these Proceedings 32, 837 (1929)].

- I. Neither of the two curves has a maximum (fig. 1 l.c.).
- II. Only the *W*-curve has a maximum (fig. 2 l.c.).
- III. Only the *X*-curve has a maximum (fig. 3 l.c.).
- IV. Both curves have a maximum (fig. 4 l.c.).

In fig. 1 of this communication we find a diagram I, in fig. 2 a diagram II; in the last case, however, only the *W*-curve has been drawn, the *X*-curve, not drawn, has a shape as given in fig. 1.

1) F. A. H. SCHREINEMAKERS, Rec.-Trav. Chim. des Pays-Bas, 50, 883 (1931).