Asymmetric Selection during Dehydration of Achiral Alcohols in the Presence of (+)-Camphorsulphonic Acid[1]

By STANLEY I. GOLDBERG*
(*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208)
and NATHAN C. MILLER
(*Department of Chemistry, University of South Alabama, Mobile, Alabama*)

Summary Individual dehydration of four *achiral* alcohols, (I), (II), (IV), and (V), in the presence of (+)-camphorsulphonic acid resulted in the formation of optically active olefin in each case.

IN 1921 Wuyts[2] reported an intriguing example of what may now be recognised as asymmetric selection† *via* kinetic resolution: (±)-methylphenylmethanol, after incomplete reaction catalysed by (+)-camphorsulphonic acid, gave, in addition to styrene, recovered alcohol which was found to be optically active. Wuyts' observation indicated a level of chiral influence brought to bear on the system by the optically active acid which was remarkable. It suggested to us the possibility of observing asymmetric selection in acid-catalysed dehydrations of *achiral* alcohols; and, we report here preliminary results of four such experiments.

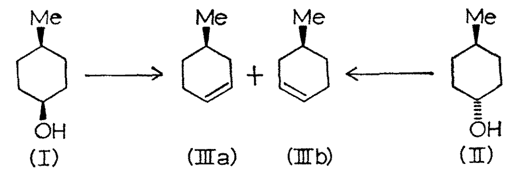
Overall asymmetric selection

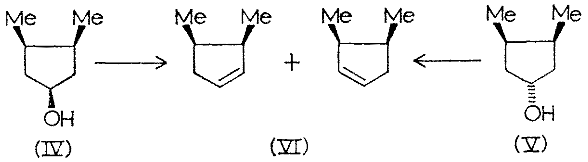
Reactant alcohol	Enriched enantiomer	Product olefin[a] $[\alpha]^{25}_{589}$	$[\alpha]^{25}_{546}$	$[\alpha]^{25}_{365}$
(I)	(IIIb)[d]	−0·177[c]	−0·196[c]	−0·452[c]
(II)	(IIIa)[d]	+0·034[c]	+0·034[c]	+0·077[c]
(IV)	(−)-(VI)[d]	−0·214[c]	−0·268[e]	−0·389[c]
(V)	(−)-(VI)[d]	−0·106[c]	−0·113[e]	−0·364[f]

[a] Specific rotations determined with pure neat samples in 1 dm. tubes. [b] For absolute configuration see ref. 4. [c] ±0·004°. [d] Absolute configuration unknown. [e] ±0·005°. [f] ±0·006°.

Each achiral alcohol‡ [(I),[3] (II),[3] (IV),§ and (V)§] was heated in the presence of (+)-camphorsulphonic acid, and the product olefin was distilled slowly from the reaction mixture. After careful purification, each chiral olefinic product was found to be optically active. The particular enriched enantiomer from each dehydration, along with other relevant data, are given in the Table.

In principle, the rotatory magnitude of each optically active product indicates the degree of asymmetric selectivity which should be the algebraic sum of two independent processes: (i) asymmetric selectivity during the actual olefin-forming reaction, and (ii) kinetic resolution of the resulting mixture of enantiomeric olefins. These processes could be either reinforcing or opposing. In order to evaluate the two separate events, samples of the racemic olefins were submitted to identical reaction conditions used for the alcohols. While no kinetic resolution increment was detected with 4-methylcyclohexene (III) $\{[\alpha]^{25}_{589} + 0{\cdot}004 \pm 0{\cdot}004°\}$, a fairly significant amount occurred with *cis*-2,3-dimethylcyclopentene $\{[\alpha]^{25}_{546} - 0{\cdot}015 \pm 0{\cdot}005°\}$,





---

† Any process that results in an enantiomeric enrichment.

‡ Satisfactory analytical data were determined from each new compound.

§ Unequivocal assignments of structure to these epimeric alcohols have been made, the details of which will be included in a full account of this work.

which means that the actual levels of asymmetric selection for (IV) and (V) were $[\alpha]_{546}^{25}$ −0·253° and $[\alpha]_{546}^{25}$ −0·098°.

The degree of asymmetric selection in the dehydration of *cis*-4-methylcyclohexanol (I) exceeded that of its *trans*-epimer (II) by a factor between five and six, and gave enrichment of the opposite enantiomeric 4-methylcyclohexene [(IIIa) and (IIIb), respectively]; while with the epimeric alcohols (IV) and (V), the all-*cis*-compound again exceeded the level of asymmetric selection displayed by its epimer, but only by a factor of about two, and here both alcohols gave enrichment of the same enantiomer, laevorotatory (VI). This curious pattern appears to be explicable in terms of the *E*1 mechanism, generally accepted for acid-catalysed dehydration, and these points will be discussed in the full presentation of this work.

We thank the National Science Foundation for the support provided to N.C.M., and the donors of the Petroleum Research Fund of the American Chemical Society for a grant.

(*Received, October 2nd*, 1969; *Com.* 1491.)

---

[1] Previous paper in this series: S. I. Goldberg and W. D. Bailey, *J. Amer. Chem. Soc.*, 1969, **91**, 5113.

[2] H. Wuyts, *Bull. Soc. chim. belges*, 1921, **30**, 30.

[3] S. I. Goldberg and F.-L. Lam, *J. Org. Chem.*, 1966, **31**, 2336.

[4] S. I. Goldberg and F.-L. Lam, *J. Org. Chem.*, 1966, **31**, 240.