

The Properties of *cis*-2-Methyl-2-enals

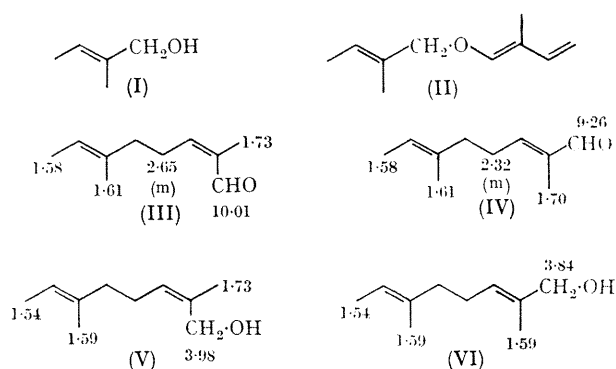
By A. F. THOMAS* and M. OZAINNE

(Research Laboratory, Firmenich & Cie., Geneva, Switzerland)

RECENT reports on *cis*-2-methyl- $\alpha\beta$ -unsaturated aldehydes,^{1,2} show that they can be identified by the chemical shift of the aldehydic proton at δ ca. 10.0 p.p.m.,[†] as compared to 9.25–9.30 for the *trans*-isomer.^{1,2} The *cis*-compounds are said to be unstable, but their rate of conversion into the *trans*-isomer, and the conditions for this are not known. In view of a recent report suggesting that this conversion may be rapid and complete under certain conditions,² and that natural α - and β -sinensals might be originally *cis*-isomers,³ we now present evidence that (a) *cis*-aldehydes are not necessarily so easily converted in the absence of suitable catalysts, and (b) the sinensals are *trans*- at C-2.

The Claisen–Cope double rearrangement of the diene ether (II) of *trans*-2-methylbut-2-enol (I),³ gave an aldehyde mixture which contained about 20% *cis*- and 80% *trans*-aldehyde [(III) and (IV), respectively], estimated by integration of the aldehyde proton signals in the n.m.r. spectrum. Apparently this proportion was correct, since immediate reduction of the mixture by lithium aluminium hydride in ether produced a 1:4 mixture of *cis*- and *trans*-alcohols that was readily separable by g.l.c.,[‡] and gave n.m.r. signals [shown on the formulae (V) and (VI)] which agree with structural attributions made for similar alcohols by Chan *et al.*² The original aldehyde mixture appeared (g.l.c.) to have the same composition as that indicated by n.m.r. spectrometry and reduction to the alcohols; the *cis*-aldehyde (III) has the shorter retention time on our polar columns. There was no indication at any time that a third

isomer (with a different geometry about the other double bond) was present.



We enriched the amount of *cis*-isomer present by chromatography on a column of silica gel in a Nylon tube.⁴ The *cis*-aldehyde under these conditions has a slightly shorter retention time than the *trans*-aldehyde. The mixture from the lowest (most developed) fraction of the column was eluted and distilled on a spinning-band column; the first fractions (b.p. 94–95°/10 mm.) contained 65% of the *cis*-isomer (g.l.c.). This proportion was not appreciably changed by distillation, either alone or with ethyl borate, or by preparative t.l.c. on silica gel. Heating the mixture with

[†] N.m.r. spectra were measured for solutions in CCl₄ (unless otherwise stated) with tetramethylsilane as internal reference.

[‡] G.l.c. was carried out with Carbowax on Chromosorb W columns at 150° with the evaporator at 180–200°.

mercuric acetate alone, even after 8 hr. at 100°, left more than 50% *cis*-aldehyde in the mixture, although when sodium carbonate was added, the amount fell to 53% in 5 hr. The various isomerizations occurring on g.l.c. of similar *cis*-aldehydes^{3,§} possibly take place either on the surface of the evaporation chamber, or on particular supports; we have no evidence that our g.l.c. is perfect in this respect, only that isomerization is not extensive. In fact the *cis*-aldehyde (III) was never obtained completely pure; even after gas chromatographic purification it still contained about 10% *trans*-aldehyde.

In view of the slowness of the isomerization in the presence of sodium acetate, we attempted to prepare a semicarbazone of the *cis*-aldehyde by the standard procedure. The semicarbazone of the *trans*-aldehyde is much less soluble in methanol, and was readily purified by crystallization; m.p. 173—174°. From the more soluble fractions, a semicarbazone, apparently pure, m.p. 121—123°,

was isolated by repeated crystallization from aqueous ethanol. The n.m.r. spectra of these semicarbazones (in [²H₆]dimethylsulphoxide-CCl₄) showed them to be uncontaminated with one another (thus eliminating the possibility of *syn*- and *anti*-isomers, which would equilibrate in solution⁵), and to differ in one major aspect that permits analysis of the mixtures. The C-1 methine signal of the *cis*-isomer was at 7.92 p.p.m., whereas that of the *trans* was at 7.47 p.p.m. Both signals were present in the original mixture of semicarbazones. There was also a slight shift of the C-2 methyl group (1.83 p.p.m. for the *cis*-isomer and 1.80 p.p.m. for the *trans*), but this is insufficient for analysis of a mixture.

We therefore feel that since the original isolation⁶ of the sinensals involved no technique that produces a rapid isomerization of *cis*- to *trans*- at C-2, the accepted all-*trans* structures are correct.⁷

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§ Relevant literature is given in ref. 2. Dr. E. sz. Kovats, (EPUL Lausanne) reports that neral is partly isomerized to geranial on g.l.c. (personal communication).

¹ (a) R. Ruegg, A. Pfiffner and M. Montavon, *Recherches*, 1966, 3; (b) E. Bertele and P. Schudel, *Helv. Chim. Acta*, 1967, 50, 2445; (c) A. F. Thomas, *Chem. Comm.*, 1968, 1657.

² K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, 1968, 33, 3382.

³ A. F. Thomas, *Chem. Comm.*, 1967, 947 and unpublished work.

⁴ B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

⁵ For n.m.r. spectra of semicarbazones, and comments on *syn-anti*-isomerism, see G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *J. Amer. Chem. Soc.*, 1964, 86, 3351.

⁶ K. L. Stevens, R. E. Lundin, and R. Teranishi, *J. Org. Chem.*, 1965, 30, 1690; R. A. Flath, R. E. Lundin, and R. Teranishi, *Tetrahedron Letters*, 1966, 295.

⁷ For additional proof of the structures of the sinensals described see ref. 1b, and G. Büchi and H. Wüest, *Helv. Chim. Acta*, 1967, 50, 2445. The latter also give a table of chemical shifts of β -protons in unsaturated carbonyl compounds, though it has been pointed out (ref. 2) that this proton signal does not differ much between *cis*- and *trans*- $\alpha\beta$ -unsaturated aldehydes.