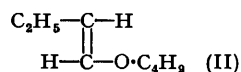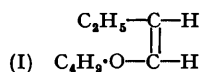**737.** *Preparation and Infra-red Spectra of the Geometrical Isomers of But-1-enyl Butyl Ether.*

By R. H. HALL, A. R. PHILPOTTS, E. S. STERN, and W. THAIN.

But-1-enyl butyl ether, prepared by the catalysed vapour-phase thermal fission of butaldehyde dibutyl acetal, was separated into geometrical isomers by distillation. The constitution of both isomers was proved, and structural isomerism excluded, by hydrogenation to di-*n*-butyl ether and by hydrolysis with cold dilute mineral acid to butaldehyde. The *cis*-configuration was assigned to the lower-boiling, and the *trans*-structure to the higher-boiling isomer, on the basis of infra-red absorption data.

DURING the preparation of but-1-enyl butyl ether, which was required in another investigation, the *cis*- and the *trans*-isomer (I and II, respectively) were separated and characterised. The infra-red absorption spectra of the isomers were also recorded and showed certain interesting features.

$$\text{(I)} \quad \begin{array}{c} \text{C}_2\text{H}_5\text{—C—H} \\ \parallel \\ \text{C}_4\text{H}_9\text{·O—C—H} \end{array} \qquad\qquad \begin{array}{c} \text{C}_2\text{H}_5\text{—C—H} \\ \parallel \\ \text{H—C—O·C}_4\text{H}_9 \end{array} \quad \text{(II)}$$

Thermal fission of butaldehyde dibutyl acetal in the vapour phase at 350° in the presence of *iso*propylsulphate and quinoline (cf. Bramwyche, Mugdan, and the Distillers Co., Ltd.,

B.P. 603,471) yielded a mixture of butanol and the desired ether which could not be separated into its constituents by simple fractional distillation owing to the formation of a constant-boiling mixture; the butanol was readily removed, however, by repeated washing with dilute sodium hydrogen carbonate solution.   In view of the possibility that the residual oil might be a mixture of geometrical isomers, it was submitted to precise fractional distillation under reduced pressure ; two substances, b. p. 35·5°/10·5 mm. and b. p. 41·5°/10 mm., were obtained, which were identified as (I) and (II), respectively, in the following manner.

Both compounds had the composition $C_8H_{16}O$ and absorbed one mol. of hydrogen on catalytic hydrogenation with the formation of di-*n*-butyl ether.   These facts, taken in conjunction with the mode of formation of the compounds, proved that the latter were isomeric butenyl butyl ethers.   The possibility that the ethylenic linkage was not in the 1 : 2-position in one of the isomers was excluded by the formation of butaldehyde *p*-nitro- and 2 : 4-dinitro-phenyl-hydrazone from each substance on treatment of either with aqueous-alcoholic mineral acid
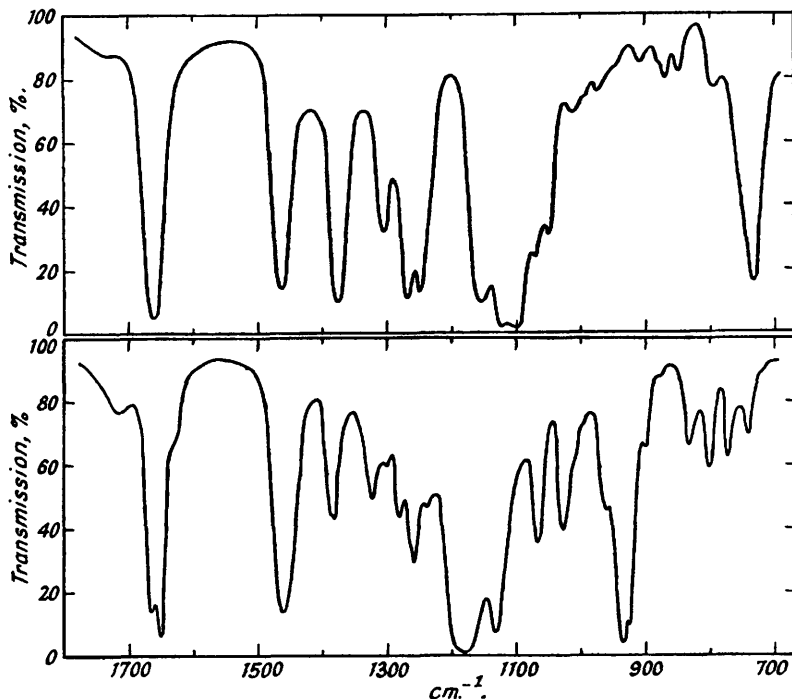

FIG. 1*a*.
cis-*But*-1-*enyl butyl ether*

FIG. 1*b*.
trans-*But*-1-*enyl butyl ether*

solutions of *p*-nitro- and 2 : 4-dinitro-phenylhydrazine, respectively.   The compounds were thus *cis-trans*-isomers of but-1-enyl butyl ether and the final assignment of structure was based on their infra-red absorption spectra.

The CH deformation frequencies in the near infra-red have been used (Sheppard and Sutherland, *Proc. Roy. Soc.*, 1949, **196**, 195) to establish the substitution round an ethylenic double bond.   In particular, frequencies near 970 cm.$^{-1}$ and 700 cm.$^{-1}$ were shown to be characteristic of *trans*- and *cis*-substituted ethylenes, respectively, in hydrocarbons (Andersen and Seyfried, *Analyt. Chem.*, 1948, **20**, 998) and in alcohols where the double bond is separated from the hydroxyl group (Crombie and Harper, *J.*, 1950, 873; Sondheimer, *ibid.*, p. 877). The spectra of crotonaldehyde, crotonic acid, and crotyl alcohol (Philpotts and Thain, to be published) all have a strong band near 970 cm.$^{-1}$ so it is possible that this particular identification rule also applies when an oxygenated group is close enough to the double bond to influence it. The rule is, in fact, used here to assign the *cis*-configuration to the lower-boiling isomer and the *trans*-configuration to the higher-boiling one.

The spectra are shown in the figures.   That of the lower-boiling isomer (Fig. 1*a*) has a broad band at 733 cm.$^{-1}$ compared with 720 cm.$^{-1}$ and 725 cm.$^{-1}$ reported for *cis*-unsaturated alcohols (Crombie and Harper, *loc. cit.*; Sondheimer, *loc. cit.*); since this spectrum (Fig. 1*a*) has no strong band between 850 and 1030 cm.$^{-1}$ the identification as the *cis*-isomer is certain.   In the spectrum

of the higher-boiling isomer (Fig. 1*b*) the only band of sufficiently high intensity to be the " *trans*-band " is at 933 cm.[-1]. This frequency is surprisingly low but the absence of strong absorption near 700 cm.[-1] does give further evidence that the higher-boiling compound is indeed the *trans*-isomer.

The C=C stretching mode absorption is very much stronger in the spectra of the 5-oxanon-3-ene isomers than in those of hydrocarbons of the corresponding type. This increased intensity is also shown in spectra of unsubstituted vinyl ethers, *e.g.*, ethyl vinyl ether (" Nat. Bur. Stand. Catalog of Spectra," No. 143) and butyl vinyl ether (unpublished data of the authors). The *trans*-isomer of but-1-enyl butyl ether has a double band in this region whilst the *cis*-isomer has a single band; this behaviour is similar to that of the hydrocarbons and the frequencies are also similar ($\sim$1660 cm.[-1]). On the other hand the unsubstituted vinyl ethers have a shifted (double) C=C band at 1620 cm.[-1] compared with the single one near 1640 cm.[-1] given by Δ^1-olefins.

Conversion of either isomer into di-*n*-butyl ether results, as expected, in the disappearance of the strong bands characteristic of the olefinic double bond, the saturated ether showing no strong absorption between 700 and 1050 cm.[-1] or between 1500 and 1700 cm.[-1].

EXPERIMENTAL.

All m. p.s and b. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss of Oxford.

The infra-red spectra were recorded (a rock-salt prism being used) on a Perkin–Elmer spectrometer with General Motors Amplifier and Brown Recorder. Lithium fluoride and glass shutters were used at appropriate frequencies with no other correction for scattered radiation. The solutions were 20% by volume in carbon tetrachloride for the range 840—1800 cm.[-1] and in *cyclo*hexane for the range 650—840 cm.[-1]. The cell was approximately 0·1 mm. thick.

Preparation of Butaldehyde Dibutyl Acetal.—A mixture of butaldehyde (250 g.), butanol (1110 g.), concentrated hydrochloric acid (10 c.c.), and methylene dichloride (250 c.c.) was distilled rapidly up a 3-ft. Vigreux column fitted with a phase-separating still-head which continuously decanted the upper (aqueous) layer in the distillate and returned the lower layer to the column as reflux. When no more aqueous layer was being formed (after *ca.* 24 hours) the reaction mixture was cooled, treated with anhydrous sodium acetate (10 g.), and rapidly distilled to free the product from inorganic salts. Subsequent fractionation of the distillate afforded butaldehyde dibutyl acetal (547 g., 78% of theory), b. p. 97—98°/10 mm., n_D^{20} 1·4161 (Adams and Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 1365, give b. p. 213°; Risseghem, *Bull. Soc. chim. Belg.*, 1919, **28**, 376, gives b. p. 105—109°/18 mm., $n_D^{17\cdot5}$ 1·4211, $n_D^{14\cdot6}$ 1·4234).

Preparation of But-1-enyl Butyl Ether.—A mixture of butaldehyde dibutyl acetal (303 g.), quinoline (5·4 g.), and *iso*propyl sulphate (0·27 g.) was passed with nitrogen (4·5 l. per hour at room temp.), at a constant rate for 4¼ hours, through a nearly horizontal, empty glass tube (length 88 cm.; vol. 305 c.c.) heated over 78 cm. of its length by a furnace maintained at 350—355°. The liquid mixture was allowed to run down the entrance of the tube and was vaporised just inside the heated zone. The cooled product was collected in a flask containing quinoline (5 c.c.) and quinol (0·5 g.).

Distillation of the product from a water-bath initially at *ca.* 55 mm. and finally at 10 mm., to free it from high-boiling impurities, gave a colourless distillate (295·1 g.), and left a residue (16·2 g.) consisting partly of unchanged acetal. The main bulk of the distillate (279 g.), after the addition of quinoline (2 c.c.), was washed with successive portions (11 × 600 c.c.) of 0·5% aqueous sodium hydrogen carbonate solution; the final dried (K_2CO_3) oil (159 g.) was treated with quinol (0·15 g.) and quinoline (2 c.c.) and fractionated under reduced pressure through a 50-plate column, the distillate being collected in a number of arbitrary fractions : (i) n_D^{20} 1·4177 (9·1 g.), (ii)—(vii), inclusive, n_D^{20} 1·4179 (61·6 g.), (viii) n_D^{20} 1·4180 (5·2 g.), (ix) n_D^{20} 1·4181 (5·4 g.), (x) n_D^{20} 1·4188 (7·4 g.), (xi) n_D^{20} 1·4196 (10·3 g.), (xii)—(xvi), inclusive, n_D^{20} 1·4199 (50·4 g.).

Fractions (ii)—(vii), inclusive, were pure cis-*but-1-enyl butyl ether*, b. p. 35·5°/10·5 mm., 138·5°/751 mm. (Found : C, 75·05; H, 12·7. $C_8H_{16}O$ requires C, 74·95; H, 12·6%). A sample (504·8 mg.) in dioxan (10 c.c.) shaken in hydrogen in the presence of platinic oxide (Adams's) catalyst (50·8 mg.) absorbed 90·5 c.c. (measured at N.T.P. and corrected for absorption by the catalyst) (theoretical for $C_8H_{16}O|\overline{1}$ is 88·2 c.c.).

Fractions (xii)—(xvi), inclusive, were pure trans-*but-1-enyl butyl ether*, b. p. 41·5°/10 mm., 146·5°/750 mm. (Found : C, 75·25; H, 12·55%). A sample (448·7 mg.) in dioxan (10 c.c.) shaken in hydrogen in the presence of platinic oxide (Adams's) catalyst (51·4 mg.) absorbed 77·6 c.c. (at N.T.P. and corrected for absorption by the catalyst) (theoretical for $C_8H_{16}O|\overline{1}$ is 78·4 c.c.).

The isomers were comparatively stable and could be distilled unchanged at atmospheric pressure. Storage of them in glass vessels at room temperature in diffused daylight for several weeks produced no change in their refractive indices.

If the crude product from the furnace was not washed with dilute sodium hydrogen carbonate solution but was fractionated directly there were obtained (from 207 g. of crude product) : (i) a constant-boiling mixture (170·5 g.), b. p. 28°/11·5 mm., n_D^{20} 1·4123, of butanol and but-1-enyl butyl ether, containing approximately 60% wt./wt. of the ether (estimated by oximation), and (ii) *trans*-but-1-enyl butyl ether (17·2 g.), b. p. 41·5°/10 mm., n_D^{20} 1·4200.

*Conversion of the Isomers into Di-*n-*butyl Ether.*—(a) *cis*-Isomer. The lower-boiling isomer (10·0 g.) was mixed with Raney nickel (*ca.* 2 g. of " paste ") and a little methanol (*ca.* 2 c.c.) and shaken in an

atmosphere of hydrogen until absorption of gas ceased. The catalyst was filtered off, washed with a little methanol, and the combined filtrate and washings were shaken with very dilute sulphuric acid, then with water, and dried (Na_2SO_4), and fractionated to give di-*n*-butyl ether (8·3 g.), b. p. 139·5—140°/750 mm., n_D^{20} 1·3988. An authentic sample of this ether had b. p. 141·1° (corr.)/745 mm., n_D^{20} 1·3988.

(*b*) trans-*Isomer.* Hydrogenation of the higher-boiling isomer (10·05 g.) in a similar manner also afforded di-*n*-butyl ether (8·3 g.), b. p. 139·5—140°/750 mm., n_D^{20} 1·3988, which was shown by examination of its infra-red absorption spectrum to be identical with that obtained in (*a*).

Hydrolysis of the Isomers.—Addition of either isomer to aqueous-ethanolic sulphuric acid containing 2 : 4-dinitrophenylhydrazine gave butaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 121—122° (from ethanol). The m. p. was undepressed in each case on admixture with authentic material, m. p. 121—122°.

With aqueous-ethanolic hydrochloric acid containing *p*-nitrophenylhydrazine each isomer similarly gave butaldehyde *p*-nitrophenylhydrazone, m. p. 89—90° (from ethanol) ; the m. p.s were undepressed on admixture with authentic material, m. p. 89—90°.