NOTES

536. *The Preparation of* cis- *and* trans-*Pent-2-enal*

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We required *cis*- and *trans*-pent-2-enal as intermediates. *cis*-αβ-Mono-unsaturated aldehydes have not previously been prepared,[1] although such di-unsaturated aldehydes are known.[2] The published preparations of *trans*-pent-2-enal [3,4] gave in our hands impure products. We therefore treated the known *cis*- and the known *trans*-but-2-ene-1,4-diol with thionyl chloride to obtain the corresponding chloro-alcohols; these reacted with methylmagnesium bromide to give *cis*- and *trans*-pent-2-en-1-ol, respectively. Oxidation of these alcohols by manganese dioxide gave the required aldehydes, with little loss of steric purity.

When *cis*-pent-2-enal was treated with perchloric acid in ether for three days, the *trans*-isomer was produced, but there was much decomposition also. The isomerisation was also catalysed by Zeo-Karb-225 resin (H^+ form), but was incomplete (80%) after 4 days; treatment with hydrogen chloride in ether gave a saturated chloro-aldehyde, which decomposed on distillation. Trifluoroacetic acid in ether did not catalyse the interconversion. The *cis*-aldehyde when treated with 2,4-dinitrophenylhydrazine under acid conditions gave only the *trans*-derivative.

Experimental.—Thin-layer chromatography was carried out as previously described.[5] Gas chromatography was carried out with the aid of a Griffin and George mark IId apparatus,

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[1] R. A. Raphael and F. Sondheimer, *J.*, **1951**, **2693**.
[2] E. E. Boehm and M. C. Whiting, *J.*, 1963, 2541.
[3] R. Kuhn and C. Grundmann, *Ber.*, 1937, **70**, 1894.
[4] U.S.P. 2,628,257 (*Chem. Abs.*, 1954, **48**, 1423).
[5] B. W. Nash, D. A. Thomas, W. K. Warburton, and T. D. Williams, preceding Paper.

modified to accommodate a β-ray argon ionisation detector; it was fitted with a 4-ft. column packed with 15% diglycerol/72—85 mesh Celite and maintained at 55°. Argon inlet-pressure was 10 p.s.i. Melting points are corrected. Ultraviolet spectra were measured in ethanol.

cis-4-*Chlorobut*-2-*en*-1-*ol*.—*cis*-But-2-ene-1, 4-diol (L. Light & Co.) had b. p. 95—100°/1·5 mm., n_D^{27} 1·4771. The dibenzoate (needles from ethanol) had m. p. 66—67° [lit., m. p. 69—70° (from aqueous methanol) [6] and m. p. 65—66° (from ethanol) [7]]. The diol (200 g.) was converted [8] into *cis*-4-chlorobut-2-en-1-ol, b. p. 83—89°/14 mm., n_D^{25} 1·4838 (lit.,[8] b. p. 79—81°/11 mm., n_D^{25} 1·4837), $\nu_{max.}$ (CS_2) 762 cm.$^{-1}$ (includes C–Cl) (C:C, *cis*-). The α-*naphthylurethane* had m. p. 78·5—79·5° (from hexane), $\nu_{max.}$ (CS_2) 762 cm.$^{-1}$ (Found: C, 65·7; H, 5·1; Cl, 12·7; N, 4·8. $C_{15}H_{14}ClNO_2$ requires C, 65·3; H, 5·1; Cl, 12·9; N, 5·1%).

cis-*Pent*-2-*en*-1-*ol*.—*cis*-4-Chlorobut-2-en-1-ol was converted [8] into *cis*-pent-2-en-1-ol, b. p. 72—76°/50 mm., n_D^{24} 1·4380, in 56% yield. Redistillation gave the alcohol (98% pure by gas chromatography), b. p. 135—137°, n_D^{25} 1·4350 (lit.,[8] b. p. 137—139°/760 mm., n_D^{20} 1·4360), $\nu_{max.}$ 790 cm.$^{-1}$ (C:C, *cis*-); retention time 12·5 min. The α-*naphthylurethane* had m. p. 78—80° (from hexane), $\nu_{max.}$ (CS_2) 765 cm.$^{-1}$ (C:C, *cis*-) (Found: C, 75·2; H, 6·7; N, 5·5. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%).

cis-*Pent*-2-*enal*.—*cis*-Pent-2-en-1-ol (8·0 g.) was stirred with manganese dioxide [9] (80 g.) in ether (400 ml.) at 25° for 1 hr. Ether was removed from the filtered solution through a 40-cm. Vigreux column, and the residue was distilled, giving *cis*-pent-2-enal (3·25 g., 42%), b. p. 58—60°/85 mm., n_D^{26} 1·4413, $\nu_{max.}$ (CS_2) 735 (C:C, *cis*-), 1685 cm.$^{-1}$ (CO·C:C); retention time 14 min. This aldehyde was *ca*. 90% pure (gas chromatography). The *semicarbazone* had m. p. 180—182° (from aqueous methanol), $\lambda_{max.}$ 266—267 mμ (ε 29,000), $\nu_{max.}$ (Nujol) 744 cm.$^{-1}$ (C:C, *cis*-) (Found: C, 50·9; H, 8·0; N, 30·0. $C_6H_{11}N_3O$ requires C, 51·0; H, 7·9; N, 29·8%). The *trans*-2,4-dinitrophenylhydrazone (orange-red needles from chloroform–methanol) had m. p. 163—165°, $\lambda_{max.}$ 374 mμ (ε 29,100), $\nu_{max.}$ ($CHBr_3$) 980 cm.$^{-1}$ (C:C, *trans*-) (Found: C, 50·2; H, 4·5; N, 21·0. Calc. for $C_{11}H_{12}N_4O_4$: C, 50·0; H, 4·6; N, 21·2%).

trans-1,4-*Diacetoxybut*-2-*ene*.—*trans*-1,4-Dibromobut-2-ene (L. Light & Co.) [$\nu_{max.}$ (CS_2) 960 cm.$^{-1}$] (100 g.) and potassium acetate (137 g.) in acetic acid (137 ml.) were refluxed for 5 hr. to give *trans*-1,4-diacetoxybut-2-ene (6·2 g., 77%), b. p. 78—81°/0·7 mm., n_D^{22} 1·4415—1·4420 (lit.,[10] b. p. 113°/11 mm., n_D^{22} 1·4422), $\nu_{max.}$ (CS_2) 968 cm.$^{-1}$; it was also prepared by the same method in 88% yield from *trans*-1,4-dichlorobut-2-ene [which had $\nu_{max.}$ (CS_2) 965 cm.$^{-1}$].

trans-*But*-2-*ene*-1,4-*diol*.—*trans*-1,4-Diacetoxybut-2-ene was converted [7] in 90% yield into *trans*-but-2-ene-1,4-diol, b. p. 89—92°/0·7 mm., n_D^{21} 1·4678 (lit.,[11] b. p. 102—104°/2·5 mm., n_D^{20} 1·4775), $\nu_{max.}$ ($CHBr_3$) 978 cm.$^{-1}$ (C:C, *trans*-). The dibenzoate had m. p. 100—101° (from ethanol) (lit.,[11] m. p. 99—100°).

trans-4-*Chlorobut*-2-*en*-1-*ol*.—Treatment of *trans*-but-2-ene-1,4-diol with thionyl chloride, as described above for the *cis*-compound, gave *trans*-4-chlorobut-2-en-1-ol (55%), b. p. 75—78°/10 mm., n_D^{24} 1·4790, $\nu_{max.}$ (CS_2) 967 cm.$^{-1}$. The α-*naphthylurethane* had m. p. 96—97° (from hexane), $\nu_{max.}$ (CS_2) 970 cm.$^{-1}$ (Found: C, 65·3; H, 5·3; Cl, 12·8; N, 5·2. $C_{15}H_{14}ClNO_2$ requires C, 65·3; H, 5·1; Cl, 12·9; N, 5·1%).

trans-*Pent*-2-*en*-1-*ol*.—Prepared in 54% yield from *trans*-4-chlorobut-2-en-1-ol in the same way as the *cis*-isomer, this had b. p. 74—74·5°/45 mm., $n_D^{22.5}$ 1·4335 (lit., b. p. 50—55°/12 mm., n_D^{25} 1·4325; [12] b. p. 138—139°/760 mm., n_D^{20} 1·4347 [13]), $\nu_{max.}$ (CS_2) 968 cm.$^{-1}$; retention time 11 min. It was 96% pure (gas chromatography). The α-*naphthylurethane* had m. p. 77—80° (from hexane) (depressed by the corresponding *cis*-derivative), $\nu_{max.}$ (CS_2) 970 cm.$^{-1}$ (Found: C, 75·5; H, 6·7; N, 5·6. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%).

trans-*Pent*-2-*enal*.—*trans*-Pent-2-en-1-ol (1·0 g.) was stirred with manganese dioxide (10 g.) in ether (50 ml.) at room temperature for 2·5 hr. The product, isolated as for the *cis*-isomer, was

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trans-pent-2-enal (380 mg.), b. p. 80—81°/160 mm., n_D^{21} 1·4400 (lit., b. p. 62—64°/80 mm., n_D^{22} 1·4469;[14] b. p. 48—52°/55—65 mm., n_D^{21} 1·4389[10]), $\nu_{max.}$ (CS_2) 972 (C:C, *trans*-), 1692, 2710 cm.$^{-1}$ (CO·C:C), retention time 18 min. It was *ca.* 90% pure (gas chromatography). The *trans*-2,4-dinitrophenylhydrazone (from ethanol) had m. p. 161—162° (not depressed by a sample prepared from *cis*-pent-2-enal) (lit.,[15] m. p. 159—159·5°), $\lambda_{max.}$ 263 mμ (ε 29,700), $\nu_{max.}$ ($CHBr_3$) 980 cm.$^{-1}$; the *trans*-semicarbazone had m. p. 177—178° (depressed by the semicarbazone of *cis*-pent-2-enal) (lit.,[14] m. p. 175—177°), $\lambda_{max.}$ 263 mμ (ε 29,700), $\nu_{max.}$ (CS_2) 980 cm.$^{-1}$.

Oxidation of *trans*-pent-2-en-1-ol (7·9 g.) and removal of ether gave the undistilled aldehyde in *ca.* 90% yield; this was similar in its steric purity to the distilled aldehyde just described (infrared spectrum).

Isomerisation of cis-*Pent-2-enal.*—*cis*-Pent-2-enal (800 mg.) in ether (25 ml.) was treated with 60% perchloric acid (1 drop) and left for 3 days at room temperature. The solution was washed with sodium hydrogen carbonate solution and with water, then dried, and evaporated to a residue which was distilled (the distillation was accompanied by much decomposition) to give *trans*-pent-2-enal (230 mg., 29%), b. p. 56°/70 mm., n_D^{25} 1·4375, $\nu_{max.}$ (CS_2) 972 cm.$^{-1}$.

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