

## 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*- $\alpha\beta$ -Mono-unsaturated aldehydes have not previously been prepared,<sup>1</sup> although such di-unsaturated aldehydes are known.<sup>2</sup> The published preparations of *trans*-pent-2-enal<sup>3,4</sup> 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<sup>+</sup> 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.<sup>5</sup> Gas chromatography was carried out with the aid of a Griffin and George mark IID apparatus,

<sup>1</sup> R. A. Raphael and F. Sondheimer, *J.*, 1951, 2693.

<sup>2</sup> E. E. Boehm and M. C. Whiting, *J.*, 1963, 2541.

<sup>3</sup> R. Kuhn and C. Grundmann, *Ber.*, 1937, 70, 1894.

<sup>4</sup> U.S.P. 2,628,257 (*Chem. Abs.*, 1954, 48, 1423).

<sup>5</sup> B. W. Nash, D. A. Thomas, W. K. Warburton, and T. D. Williams, preceding Paper.

modified to accommodate a  $\beta$ -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)<sup>6</sup> and m. p. 65—66° (from ethanol)<sup>7</sup>]. The diol (200 g.) was converted<sup>8</sup> into *cis*-4-chlorobut-2-en-1-ol, b. p. 83—89°/14 mm.,  $n_D^{25}$  1.4838 (lit.,<sup>8</sup> b. p. 79—81°/11 mm.,  $n_D^{25}$  1.4837),  $\nu_{\max.}$  (CS<sub>2</sub>) 762 cm.<sup>-1</sup> (includes C—Cl) (C:C, *cis*-). The  $\alpha$ -naphthylurethane had m. p. 78.5—79.5° (from hexane),  $\nu_{\max.}$  (CS<sub>2</sub>) 762 cm.<sup>-1</sup> (Found: C, 65.7; H, 5.1; Cl, 12.7; N, 4.8. C<sub>15</sub>H<sub>14</sub>ClNO<sub>2</sub> 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<sup>8</sup> 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.,<sup>8</sup> b. p. 137—139°/760 mm.,  $n_D^{20}$  1.4360),  $\nu_{\max.}$  790 cm.<sup>-1</sup> (C:C, *cis*-); retention time 12.5 min. The  $\alpha$ -naphthylurethane had m. p. 78—80° (from hexane),  $\nu_{\max.}$  (CS<sub>2</sub>) 765 cm.<sup>-1</sup> (C:C, *cis*-) (Found: C, 75.2; H, 6.7; N, 5.5. C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub> 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<sup>9</sup> (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<sub>2</sub>) 735 (C:C, *cis*-), 1685 cm.<sup>-1</sup> (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 m $\mu$  ( $\epsilon$  29,000),  $\nu_{\max.}$  (Nujol) 744 cm.<sup>-1</sup> (C:C, *cis*-) (Found: C, 50.9; H, 8.0; N, 30.0. C<sub>6</sub>H<sub>11</sub>N<sub>3</sub>O 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 m $\mu$  ( $\epsilon$  29,100),  $\nu_{\max.}$  (CHBr<sub>3</sub>) 980 cm.<sup>-1</sup> (C:C, *trans*-) (Found: C, 50.2; H, 4.5; N, 21.0. Calc. for C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: 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<sub>2</sub>) 960 cm.<sup>-1</sup>] (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.,<sup>10</sup> b. p. 113°/11 mm.,  $n_D^{22}$  1.4422),  $\nu_{\max.}$  (CS<sub>2</sub>) 968 cm.<sup>-1</sup>; it was also prepared by the same method in 88% yield from *trans*-1,4-dichlorobut-2-ene [which had  $\nu_{\max.}$  (CS<sub>2</sub>) 965 cm.<sup>-1</sup>].

*trans*-But-2-ene-1,4-diol.—*trans*-1,4-Diacetoxybut-2-ene was converted<sup>7</sup> in 90% yield into *trans*-but-2-ene-1,4-diol, b. p. 89—92°/0.7 mm.,  $n_D^{21}$  1.4678 (lit.,<sup>11</sup> b. p. 102—104°/2.5 mm.,  $n_D^{20}$  1.4775),  $\nu_{\max.}$  (CHBr<sub>3</sub>) 978 cm.<sup>-1</sup> (C:C, *trans*-). The dibenzoate had m. p. 100—101° (from ethanol) (lit.,<sup>11</sup> 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<sub>2</sub>) 967 cm.<sup>-1</sup>. The  $\alpha$ -naphthylurethane had m. p. 96—97° (from hexane),  $\nu_{\max.}$  (CS<sub>2</sub>) 970 cm.<sup>-1</sup> (Found: C, 65.3; H, 5.3; Cl, 12.8; N, 5.2. C<sub>15</sub>H<sub>14</sub>ClNO<sub>2</sub> 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; <sup>12</sup> b. p. 138—139°/760 mm.,  $n_D^{20}$  1.4347<sup>18</sup>),  $\nu_{\max.}$  (CS<sub>2</sub>) 968 cm.<sup>-1</sup>; retention time 11 min. It was 96% pure (gas chromatography). The  $\alpha$ -naphthylurethane had m. p. 77—80° (from hexane) (depressed by the corresponding *cis*-derivative),  $\nu_{\max.}$  (CS<sub>2</sub>) 970 cm.<sup>-1</sup> (Found: C, 75.5; H, 6.7; N, 5.6. C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub> 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

<sup>6</sup> A. W. Johnson, *J.*, 1946, 1014.

<sup>7</sup> C. S. Marvel and C. H. Young, *J. Amer. Chem. Soc.*, 1951, **73**, 1066.

<sup>8</sup> J. Colonge and G. Poilane, *Bull. Soc. chim. France*, 1955, 953.

<sup>9</sup> J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J.*, 1952, 1094.

<sup>10</sup> P. Grünanger and D. Grieco, *Gazzetta*, 1958, **88**, 296.

<sup>11</sup> I. N. Nazarov, S. M. Makin, and B. K. Kruptsov, *Zhur. obshchei Khim.*, 1959, **29**, 3983 (*Chem. Abs.*, 1960, **54**, 19,462).

<sup>12</sup> F. Semeniuk and G. L. Jenkins, *J. Amer. Pharmaceut. Assoc. (Sci. Edn.)*, 1948, **37**, 118 (*Chem. Abs.*, 1948, **42**, 5410).

<sup>13</sup> W. M. Laver and L. S. Benton, *J. Org. Chem.*, 1959, **24**, 804.

*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;<sup>14</sup> b. p. 48–52°/55–65 mm.,  $n_D^{21}$  1.4389<sup>10</sup>),  $\nu_{\max}$  (CS<sub>2</sub>) 972 (C:C, *trans*-), 1692, 2710 cm.<sup>-1</sup> (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.,<sup>15</sup> m. p. 159–159.5°),  $\lambda_{\max}$  263 m $\mu$  ( $\epsilon$  29,700),  $\nu_{\max}$  (CHBr<sub>3</sub>) 980 cm.<sup>-1</sup>; the *trans*-semicarbazone had m. p. 177–178° (depressed by the semicarbazone of *cis*-pent-2-enal) (lit.,<sup>14</sup> m. p. 175–177°),  $\lambda_{\max}$  263 m $\mu$  ( $\epsilon$  29,700),  $\nu_{\max}$  (CS<sub>2</sub>) 980 cm.<sup>-1</sup>.

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<sub>2</sub>) 972 cm.<sup>-1</sup>.

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<sup>14</sup> C. Jutz, *Chem. Ber.*, 1958, **91**, 1867.

<sup>15</sup> E. E. Royals and K. C. Brannock, *J. Amer. Chem. Soc.*, 1954, **76**, 1180.

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