## Dimerisation of Polyacetylenic Aldehydes with Elimination of Carbon Monoxide

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Hexa-2.4-diynal, octa-2.4-diynal, and octa-2.4.6-triynal (R[C≡C]<sub>n</sub>•CHO) dimerise in concentrated solution with evolution of carbon monoxide, to give products of the type  $R[C\equiv C]_{n-1} \cdot CH = C(CHO) \cdot [C\equiv C]_n R$ ; above 100° even phenylpropargyl aldehyde reacts analogously. Both geometrical isomers of the 'dimers' were detected and characterised.

A recent publication by Gorgues and Levas<sup>1</sup> describing the dimerisation of 5-phenylpenta-2,4-diynal (Id) with elimination of carbon monoxide, prompts us to report our findings on analogous aldehydes, which we have been using in the synthesis of natural polyacetylenes. Concentrated solutions of the aldehydes (Ia-c) were observed to undergo a striking change in u.v. absorption and concurrently a second carbonyl stretching band appeared in the i.r. spectrum at higher frequency.

From hexa-2,4-diynal (Ia) a stable crystalline product was obtained to which was assigned the structure (IIa). Analysis and mass spectrometry indicated a molecular formula C<sub>11</sub>H<sub>8</sub>O, the hydrogen atoms being assigned by magnetic resonance to two propynyl groups, an ethylenic proton coupled to one of them, and an aldehydic proton. Oxidation to an acid followed by esterification and hydrogenation gave an ester identical with the ester (III) prepared by a malonic ester synthesis. Completely analogous spectral data were obtained for the products from the aldehydes (Ib) and (Ic), which are correspondingly formulated as (IIb) and (IIc). Phenylpropargyl aldehyde, which has long been known<sup>2</sup> to lose carbon monoxide on attempted distillation at atmospheric pressure, gives the aldehyde (IV) above 100°. But-2-ynal slowly oxidises <sup>3</sup> at room temperature; as yet we have not detected any ' dimer ' in this instance.

When a solution of the dimer [(IIa), m.p. 93–94°] was kept in light or chromatographed on silica gel, equilibrium was established with a geometrical isomer (m.p. 74-78°). These are distinguished by the very different chemical shifts of their aldehydic protons, unusually large for the primary product. The (Z)-configuration,<sup>4</sup> in which the aldehydic proton is deshielded by the triple bond in the *cis*-position <sup>5</sup> was assigned to

<sup>1</sup> A. Gorgues and E. Levas, Compt. rend. (C), 1968, 266, 41.

<sup>2</sup> L. Claisen, Chem. Ber., 1898, **31**, 1021.

<sup>3</sup> M. P.-L. Viguier, Compt. rend., 1911, 152, 1491.

<sup>4</sup> The use of (E)- and (Z)- has been described by J. E. Blackwood, C. L. Gladis, K. L. Loening, A. E. Petrarca, and J. E. Rush, J. Amer. Chem. Soc., 1968, 90, 509.

this isomer. (Similar effects have recently been observed <sup>6</sup> with the geometrical isomers of

 $Me[C=C]_{2}$ ·CH=C(SCH\_{3})·CHO]. Confirmation of this assignment was given by a nuclear Overhauser effect

$$\begin{array}{ccc} RC \equiv C \cdot C \equiv C \cdot CHO & RC \equiv C \cdot CH \equiv C(CHO) \cdot C \equiv C \cdot C \equiv CR \\ (I) & (II) \end{array}$$

a, R = Me; b,  $R = [CH_2]_2Me$ ; c,  $R = C \equiv CMe$ ; d, R = Ph

$$\begin{array}{c} \operatorname{Me}[\operatorname{CH}_2]_3 \cdot \operatorname{CH}(\operatorname{CO}_2\operatorname{Me}) \cdot [\operatorname{CH}_2]_4\operatorname{Me} & \operatorname{Ph}\operatorname{CH}=\operatorname{C}(\operatorname{CHO}) \cdot \operatorname{C}=\operatorname{CPh} \\ (\operatorname{III}) & (\operatorname{IV}) \end{array}$$

experiment.<sup>7</sup> An enhancement of ca. 20% of the aldehydic proton signal was observed on double irradiation of the vinylic proton signal of (E)-5-formyldec-4-ene-2,6,8-trivne, but no effect was observed with the (Z)-isomer. No coupling was apparent between the aldehydic and vinylic protons in either of the isomers, the line width remaining constant on irradiation. Thus the enhancement was not a decoupling effect. Further, an enhancement of the vinylic proton quartet was observed (though less readily measured) on double irradiation of the aldehydic proton signal in the (E)-isomer. Analogous chemical shifts (Table) were

Chemical shifts  $(\tau)$  of aldehydic protons in the geometrical isomers of the ' dimers '

observed for the aldehydic protons in the isomeric dimers from octa-2,4-diynal (Ib) and octa-2,4,6-triynal (Ic). The n.m.r. data quoted by Gorgues and Levas<sup>1</sup>

<sup>5</sup> L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1959, p. 114.

<sup>6</sup> F. Bohlmann and H.-C. Hummel, Chem. Ber., 1968, 101, 2506.

7 F. A. L. Anet and A. J. R. Bourn, J. Amer. Chem. Soc., 1965, 87, 5250.

## EXPERIMENTAL

U.v. and i.r. spectra were recorded on Unicam SP 800 and Perkin-Elmer 237 spectrophotometers respectively. N.m.r. spectra were obtained on Perkin-Elmer R10 and R14 spectrometers. Mass spectra were determined on an A.E.I. MS9 mass spectrometer with a direct insertion probe.

M.p.'s (corrected) were determined on a Kofler hot-stage apparatus. The silica gel used in column chromatography refers to Whatman SG31. Merck silica gel HF254 and  $PF_{254 + 366}$  were used in t.l.c. (0.3 and 1 mm. thick layers respectively). 10% Poly(ethyleneglycol succinate) on Embacel  $(1500 \times 4 \text{ mm. column})$  was used as stationary phase with argon as carrier gas (flow 50 ml./min.) in g.l.c.

Manganese dioxide was freshly prepared 8 and its activity tested on cinnamyl alcohol. Light petroleum refers to fraction b.p. 40-60°.

Hexa-2,4-diynal (Ia).9-A solution of hexa-2,4-diyn-1-ol 10 (500 mg.) in methylene chloride (100 ml.) was shaken with manganese dioxide (5 g.) for 4 hr. After filtration the concentrated solution was introduced onto a silica gel column. Elution with methylene chloride gave hexa-2,4-diynal (305 mg., 62%) which was stored in dilute solution;  $\lambda_{max.}$  (CH<sub>2</sub>Cl<sub>2</sub>) 288 ( $\epsilon$  8500), 272 ( $\epsilon$  9500), 257 ( $\epsilon$  6000), 245 nm. ( $\epsilon$  2500);  $\nu_{max.}$  (CH<sub>2</sub>Cl<sub>2</sub>) 2228 (C=C) and 1657 cm.<sup>-1</sup> (C=O);  $\nu_{\text{max.}}$  (CS<sub>2</sub>) 1670 cm.<sup>-1</sup> (C=O);  $\tau$  (CCl<sub>4</sub>) 7.89 (s, CH<sub>3</sub>) and 0.81 (s, CHO).

Octa-2,4-diynal (Ib). This was obtained analogously in 55% yield;  $\lambda_{max}$  (ether) 288 ( $\varepsilon$  7000), 272 ( $\varepsilon$  8500), 257 ( $\varepsilon$  5500), and 245 nm. ( $\varepsilon$  3000);  $\nu_{max}$  (CCl<sub>4</sub>) 2220, 2120 (C=C) and 1660 cm.<sup>-1</sup> (C=O);  $\tau$  (CCl<sub>4</sub>) 8.95 (t, J 7 Hz,  $CH_3$ ), ca. 8.40 (m,  $CH_3 \cdot CH_2 \cdot CH_2$ ), 7.60 (t, J 6 Hz,  $CH_2 \cdot C \equiv C$ ), and  $0 \cdot 82$  (s, CHO).

Octa-2,4,6-triynal (Ic).<sup>11</sup> This was obtained analogously and was extremely unstable;  $\lambda_{max}$  (ether) 338 (relative E 0.65), 313 (1.0), 294 (0.70), 278 (0.30), 262 (0.10), 233 (7.0), and 226 nm. (7.0);  $\tau$  (CCl<sub>4</sub>) ca. 7.95 (s, CH<sub>3</sub>), and 0.80 (s, CHO)

Phenylpropargyl Aldehyde. This was prepared by the method of Allen and Edens; <sup>12</sup>  $\lambda_{max}$  (ether) 285sh, 275 ( $\epsilon$  16,500), 264sh, and 234 nm. ( $\epsilon$  8500);  $\tau$  (CCl<sub>4</sub>) ca. 2.54 (m, aromatic H) and 0.60 (s, CHO).

But-2-ynal. This was also obtained by manganese dioxide oxidation as above (40% yield);  $\nu_{max.}$  (CH<sub>2</sub>Cl<sub>2</sub>) 1665 cm.<sup>-1</sup> (C=O);  $\tau$  (CCl<sub>4</sub>) 7.92 (s, CH<sub>3</sub>) and 0.90 (s, CHO).

Dimerisation of Hexa-2,4-diynal.-A solution of hexa-2,4-diynal (150 mg.) in methylene chloride (1 ml.) was kept in the dark at 20° for 1 week (carbon monoxide was detected <sup>13</sup> when the flask was flushed with nitrogen). The solvent was removed and the residue was extracted with boiling light petroleum (10 ml.). The solution was cooled and gave pale yellow needles of (Z)-5-formyldec-4-ene-2,6,8-triyne (IIa) (26 mg.), m.p. 93-94° (Found: C,

<sup>8</sup> J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, J. Chem. Soc., 1952, 1094.

E. R. H. Jones, L. Skatteböl, and M. C. Whiting, J. Chem. Soc., 1958, 1054. <sup>10</sup> W. Chodkiewicz, Ann. Chim. (France), 1957, **13**, 819.

83.8; H, 5.3%; M, 156.0578  $\pm$  0.0004. C<sub>11</sub>H<sub>8</sub>O requires C, 84.6; H, 5.2%; M, 156.0575),  $\lambda_{\max}$  (ether) 319 ( $\varepsilon$  15,600), 268 ( $\varepsilon$  4700), 260sh, 251 ( $\varepsilon$  6200), 239 ( $\varepsilon$  6100), 227 nm. (<br/>є 4500);  $\nu_{\rm max}$  (CS2) 1695 cm.<sup>-1</sup> (C=O);  $\tau$  (CDCl3) 7·99 (s,<br/> CH3·C=C·C=C), 7·85 (d, J 2·5 Hz, CH3·C=C·CH=C), 3·09 (quartet, J 2.5 Hz, CH=C), -0.06 (s, CHO);  $\tau$  (CCl<sub>4</sub>) 7.98, 7.87, 3.21, and 0.03.

The part of the crude product insoluble in light petroleum plus the recrystallisation residues were chromatographed from methylene chloride on a silica-gel column and rechromatography on a 1-mm. thick silica-gel layer gave hexa-2,4-diynal (10 mg.) and a mixture of dimer isomers (44 mg.);  $\tau$  (CCl<sub>4</sub>) 0.03 [9 parts (Z)-isomer] and 0.60 [1 part (E)-isomer]. Repeated chromatography followed by recrystallisation from light petroleum gave the pure isomers. (E)-5-Formyldec-4-ene-2,6,8-triyne had m.p. 74-78°;  $\lambda_{max.}$ (ether) 317 (z 12,200), 255 (z 8200), and 242 nm. (z 5600);  $p_{\text{max.}}$  (CS<sub>2</sub>) 1705 cm.<sup>-1</sup> (C=O);  $\tau$  (CDCl<sub>3</sub>) 7.96 (s,

 $CH_3$ ·C=C·C=C), 7.80 (d, J 2.5 Hz,  $CH_3$ ·C=C·CH=C), 3.28 (quartet, J 2.5 Hz, CH=C), and 0.58 (s, CHO);  $M^+$  156.

Dimerisation of Octa-2,4-diynal.-A solution of the aldehyde (Ib) (660 mg.) in ether (1.5 ml.) was kept in the dark at 20° for 1 week. Chromatography of the reaction mixture (1-mm. layer, 5% ether in light petroleum) gave octa-2,4-diynal (35 mg.) and 7-formyl-tetradec-6-ene-4,8,10-triyne (IIb) (210 mg.) as a 10 : 1 mixture (n.m.r.) of (Z)-(E)-isomers which failed to crystallise;  $\lambda_{max}$  (ether) 325 ( $\epsilon$  21,000), 273 (\$ 6500), 263sh (\$ 7500), 254 (\$ 8000), 242 (\$ 7500), and 230 nm. ( $\epsilon$  6500);  $\nu_{max}$  (CCl<sub>4</sub>) 2220 and 2200 (C=C), 1698 cm.<sup>-1</sup> (CO);  $\tau$  (CCl<sub>4</sub>) 8.95 (t, J 6 Hz, CH<sub>3</sub>·CH<sub>2</sub> twice), ca. 8.40 (m, CH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub> twice), ca. 7.62 (m, CH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·C≡C twice), 3.17 (t, J 2.5 Hz,  $CH_2 \cdot C = C \cdot CH = C$ ), 0.60 and 0.01(ss, CHO, in ca. 1:10 ratio); m/e 212 (21%,  $M^+$ ), 184 (100%,  $M^+$ -CO). The dimer gave a semicarbazone (60%) yield), m.p. 155-157° (methanol-water) (Found: C, 71.1; H, 7.0%;  $M^+$  269.  $C_{16}H_{19}N_3O$  requires C, 71.35; H 7.1%; M 269);  $\lambda_{max.}$  (ether) 329 ( $\epsilon$  35,200), 317 ( $\epsilon$  35,500), 276 (ε 17,300), 259sh, 231 nm. (ε 15,200); τ (CDCl<sub>3</sub>) 9.00 (t, J 6.5 Hz, CH3. CH2 twice), ca. 8.45 (m, CH3. CH2. CH2 twice), ca. 7.65 (m,  $CH_3 \cdot CH_2 \cdot CH_2 \cdot C \equiv C$  twice), 4.08 (s, NH<sub>2</sub>), 3.79 (t, J 1.5 Hz, CH<sub>2</sub>C=C·CH=C), 2.10 (s, CH=N), -0.20 (s, N·NH·CO, disappears on addition of  $D_{2}O$ ).

Dimerisation of Octa-2,4,6-triynal.-A solution of the aldehyde (Ic) (200 mg.) in dichloromethane (1 ml.) was kept in the dark at 20° for 1 week. Chromatography (silica gel, light petroleum-ether) gave starting material (10 mg.) and 7-formyltetradec-6-ene-2,4,8,10,12-pentayne (IIc) (80 mg.) as a 1:1 mixture (n.m.r.) of the (Z)-(E) isomers. Rechromatography of the dimer-fraction (1-mm. layer, 10% ether in light petroleum) gave the crystalline but very unstable  $(\tilde{E})$ -isomer from the slower moving band;  $\lambda_{max}$ . (ether) 375 (z 34,500), 354 (z 38,500), 300 (z 23,500), 282 ( $\epsilon$  15,500), and 232 nm. ( $\epsilon$  98,000);  $\nu_{max}$  (CCl<sub>4</sub>) 2230, 2190 and 2140 (C=C), and 1705 cm.^{-1} (CO);  $\tau$  (CCl<sub>4</sub>) 7.92 (s, CH<sub>3</sub>), 7.84 (s, CH<sub>3</sub>), 3.21 (s, CH=C), 0.56 (s, CHO); M<sup>+</sup> 204. From the faster moving band, a 2:1 mixture of the (Z)-(E)isomers, also crystalline and very unstable, was obtained but not further purified;  $\lambda_{max.}$  (ether) 380 (z 23,000), 358 (z 31,500), 308sh, 283 (z 8400), and 234 nm. (z 87,500);  $v_{max}$  (CCl<sub>4</sub>) 2230, 2190 and 2150 (C=C), and 1720 cm.<sup>-1</sup>

<sup>11</sup> F. Bohlmann, W. von Kap-herr, C. Rybak, and J. Repplinger, Chem. Ber., 1965, 98, 1736. <sup>12</sup> C. F. H. Allen and C. O. Edens, jun., Org. Synth., Coll.

Vol. 3, 1955, 731.

<sup>13</sup> F. S. Snell and C. T. Snell, 'Colorimetric Methods of Analysis,' D. Van Nostrand, New York, 3rd edn., vol. II, p. 834.

(CO);  $\tau$  (CCl<sub>4</sub>) 7.92 (complex, CH<sub>3</sub>), 3.10 and 3.21 (ss, CH=C), 0.03 and 0.56 (ss, CHO, ratio 2:1);  $M^+$  204.

Dimerisation of Phenylpropargyl Aldehyde.-Phenylpropargyl aldehyde (700 mg.) was heated at 140° for 7 hr. under nitrogen. Effervescence was observed and carbon monoxide was detected in the exit gas.<sup>13</sup> Chromatography on 1-mm. layers (10% ether in light petroleum, multiple development) gave starting aldehyde (240 mg.) and two main fractions, a faster moving one (180 mg.), and a slower moving fraction (100 mg.), interconvertible on repeated chromatography. From the front of the faster moving band one isomer [probably  $(Z_{-})$ ] of 2-formyl-1,4-diphenylbut-1-en-3-yne (IV) was obtained as a liquid;  $\lambda_{max}$  (ether) 322 ( $\epsilon$  12,000) and 259 nm. ( $\epsilon$  9000);  $\nu_{max}$  (CCl<sub>4</sub>) 2750 (CHO), 2240 (C=C), and 1695 cm.<sup>-1</sup> (CO);  $\tau$  (CCl<sub>4</sub>) 2.6 (m, 10 aromatic H), 2·1 (s, CH=C), and 0·17 (s, CHO);  $M^+$  232. This dimer at 20° gave a semicarbazone (30% yield), m.p. 182-184° (decomp.) (methanol-water) (Found: C, 74.9; H, 5.4%;  $M^+ 289$ .  $C_{18}H_{15}N_3O$  requires C, 74.7; H, 5.25%; M 289);  $\lambda_{max.}$  (ether) 318 ( $\epsilon$  13,000) and 285 nm. ( $\epsilon$  11,000). From the rear of the slower moving band the other isomer was eluted;  $\lambda_{max}$  (ether) 329 ( $\epsilon$  12,000) and 258 nm. (11,000); (CCl<sub>4</sub>) 2720 (CHO), 2225 (C=C), and 1705 cm.<sup>-1</sup> (CO); ν<sub>max.</sub>  $\tau$  (CCl<sub>4</sub>) 2.6 (m, 8 ArH and CH=C), 1.92 (m, aromatic ortho-H in C<sub>6</sub>H<sub>5</sub>CH=C), 0.40 (s, CHO);  $M^+$  232.

Methyl 2-n-Butylheptanoate (III).-(a) Chromic acid reagent<sup>14</sup> (0·1 ml.) was added to a cooled solution of (Z)-5-formyldec-4-ene-2,6,8-trivne (15 mg.) in acetone (2 ml.). After 10 min. at  $20^{\circ}$  the crude reaction product was heated under reflux for 30 min. in 4% methanolic sulphuric acid (5 ml.); water was added and the mixture was extracted with ether. The ethereal extract was washed with sodium hydrogen carbonate solution, dried, and stirred with an excess of sodium borohydride for 30 min. to reduce

<sup>14</sup> K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, J. Chem. Soc., 1946, 39.
<sup>15</sup> R. Adams and R. M. Kamm, Org. Synth., Coll. Vol. 1, Joint Press, 1961, 2011.

1941, 250.

 <sup>16</sup> H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wong, A. H. Sommers, and R. W. Danett, *J. Org. Chem.*, 1961, **26**, 644.

any unchanged aldehyde. The unsaturated ester was isolated by t.l.c. [ $\lambda_{max.}$  (ether) 313, 275, 247, and 236 nm.;  $\nu_{max.}$  (CCl<sub>4</sub>) 1725 cm.<sup>-1</sup>] and hydrogenated in ether over Adams' catalyst to give methyl 2-n-butylheptanoate (III)  $(R_{\rm T} \text{ and mass spectrum see below}).$ 

(b) Diethyl malonate was alkylated with n-butyl bromide to give diethyl n-butylmalonate.<sup>15</sup> The latter compound (10.8 g.) was converted into the sodium salt by the method of Zaugg et al.<sup>16</sup> (sodium hydride in dimethyl formamide) and reacted with pentyl bromide (8.9 g.) to yield diethyl n-butyl-n-pentyl malonate (10.1 g.), b.p. 128-129°/2 mm.,  $n_{\rm p}^{18\cdot5}$  1·4339 (lit.,<sup>17</sup> b.p. 185—193°/55 mm.,  $n_{\rm p}$  1·4312). The ester was heated under reflux for 10 hr. with 25% ethanolic sodium hydroxide. n-Butyl-n-pentylmalonic acid, had m.p. 143-144° (decomp.) (from ether-light petroleum) (Found: C, 62·4; H, 9·35. C<sub>12</sub>H<sub>22</sub>O<sub>4</sub> requires C, 62·55; H, 9.6%). The dicarboxylic acid was heated to  $150^{\circ}$ , first at 300 mm. and then at 0.5 mm.; 2-n-butylheptanoic acid distilled at  $128^{\circ}/1$  mm. (lit.,<sup>17</sup> 170--173<sup>o</sup>/28 mm.),  $n_{\rm p}^{19\cdot5}$ 1.4340. Its amide, prepared via the acid chloride had m.p. 117.5-118° (from light petroleum) (lit., 18 92°) (Found: C, 71.25; H, 12.65; N, 7.75. Calc. for C<sub>11</sub>H<sub>23</sub>NO: C, 71.3; H, 12.55; N, 7.55%). The methyl ester (III), prepared in 4% methanolic sulphuric acid at 65° had b.p. 118-119°/23 mm. (Found: C, 72.05; H, 12.25. C12H29O2 requires C, 71.95; H, 12.05%).

The specimens of the ester (III) prepared by routes (a)and (b) had the same retention time  $(13.8 \text{ min.}, 76^{\circ})$  in g.l.c. and showed an identical fragmentation pattern in their mass spectra ( $M^+$  200, base peak m/e 87, prominent peaks m/e 144 and 130).

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