Natural Acetylenes. Part XXXIV.[1] Synthesis of C_{11} Ene-diyn-ene Alcohols, Aldehydes, Acids, and Esters

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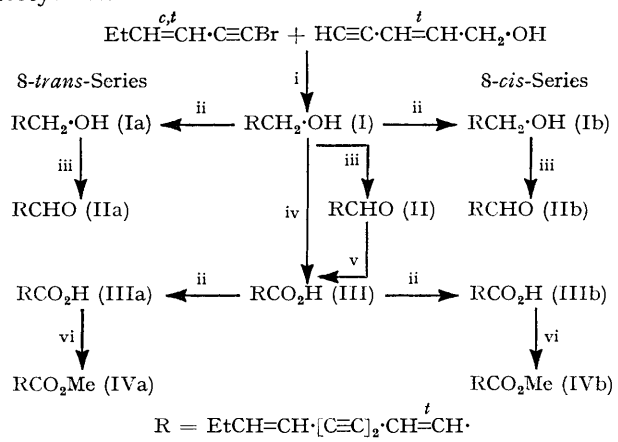
Undeca-*trans*-2.*trans*(and *cis*)-8-diene-4.6-diyn-1-ols have been synthesised and converted into the corresponding aldehydes. acids. and methyl esters.

THE previously unknown C_{11} ene-diyn-ene alcohols (Ia and b), aldehydes (IIa and b), and acids (IIIa and b) and methyl esters (IVa and b) have been synthesised by standard procedures (see Scheme) and fully characterised. They were needed for comparisons with natural acetylenes.



Reagents: i, CuCl–NH_2·OH–$EtNH_2$; ii, crystallisation; iii, MnO_2; iv, CrO_3–Me_2CO; v, Ag_2O–HO^-; vi, MeOH–H^+.

SCHEME

EXPERIMENTAL

Equipment: i.r., Perkin-Elmer 257; u.v., Unicam SP 800; n.m.r., Perkin-Elmer R 14; mass spectra (direct insertion), Atlas CH7; m.p. (corr.), Kofler hot-stage apparatus.

Liquid chromatography: silica gel H.B.L. M60 in columns and Merck $HF_{254+366}$ and $PF_{254+366}$ in 0·3 and 1 mm layers, respectively.

Light petroleum refers to fraction b.p. 40—60°. All reactions were carried out under nitrogen in the dark and all evaporations under reduced pressure.

1-*Bromohex*-3-*en*-1-*yne*.—Hex-3-en-1-yne [2] (0·75 g, 9·4 mmol) and sodium hypobromite [40 ml; prepared from bromine (4·4 ml), water (20 ml), ice (40 g), and sodium hydroxide (8 g)] were shaken for 2 h. The emulsion was left to settle, the aqueous phase was decanted, and the product was washed by decantation (saturated ammonium chloride solution and water). The crude bromohexenyne (1·2 g, 80%), $\nu_{max.}$ (CCl_4) 2180 (C≡C) cm^{-1}, was used directly in the coupling reaction.

Undeca-trans-2,trans-8-*diene*-4,6-*diyn*-1-*ol* (Ia) *and Undeca*-trans-2,cis-8-*diene*-4,6-*diyn*-1-*ol* (Ib).—1-Bromohex-3-en-1-yne (1·5 g, 10 mmol) in methanol (25 ml) was added during 30 min to a stirred suspension of pent-*trans*-2-en-4-yn-1-ol (0·82 g, 10 mmol), hydroxylamine hydrochloride (1·5 g), ethylamine (40% aqueous solution; 15 ml), and copper(I) chloride (40 mg) in dimethylformamide (5 ml) at 20°. After 10 min, the mixture was transferred with ether (50 ml) into a solution of potassium cyanide (1 g) in crushed ice (100 g)–water (100 ml). The crude product, a yellow oil (1·3 g), was isolated with ether and chromatographed on silica gel (100 g); ether–light petroleum (1 : 1) eluted the *cis*–*trans*-alcohol mixture (I), a pale yellow oil (0·9 g, 61%). Crystallisation (ether–hexane; −5°;

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[2] A. A. Petrov, Yu. I. Porfireva, and G. I. Semenov, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1258.

3 days) gave *undeca*-trans-2,trans-8-*diene*-4,6-*diyn*-1-*ol* (Ia) as needles (83 mg), m.p. 48·5° (Found: C, 82·7; H, 7·65%; M^+, 160. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%; *M*, 160), $\lambda_{max.}$ 312·5 (ε 19,900), 293 (25,200), 276 (16,700), 261 (8400), 247 (23,600), 237 (36,000), and 231·5 (31,800) nm, $\nu_{max.}$ (CCl_4) 3620 (OH free), 3470br (OH bonded), 2208 and 2130 (C≡C), 1623 (CH=CH), and 950 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·95 (t, *J* 7·5 Hz, $CH_3{\cdot}CH_2$), 7·78 (dq, *J* 7·5 and 6·4 Hz, $CH_3{\cdot}CH_2{\cdot}CH$=), 3·64 (dt, *J* 6·4 and 16 Hz, *trans*-$CH_2{\cdot}CH$=CH), 4·48 (d, *J* 16 Hz, *trans*-CH=CH·C≡C), 4·21 (d, *J* 15·8 Hz, *trans*-CH=CH·$CH_2{\cdot}$OH), 3·62 (dt, *J* 15·8 and 4·7 Hz, *trans*-CH=CH·$CH_2{\cdot}$OH), and 5·83 (d, *J* 4·7 Hz, $CH_2{\cdot}$OH), *m/e* 160 (M^+, 95%), 145 (M^+ −15, 12%), 129 (M^+ −31, 17%), 117 (M^+ −43, 64%), 115 (M^+ −45, 100%), and 91 (M^+ −69, 75%).

The mother liquor of the above crystallisation was cooled to −40°, the deposited solid was separated by centrifugation, and the liquid was concentrated; repeated crystallisations of the residue (ether–hexane, −40°) gave *undeca*-trans-2,cis-8-*diene*-4,6-*diyn*-1-*ol* (Ib) as needles (150 mg), m.p. *ca.* 10° (Found: C, 82·25; H, 7·6%; M^+, 160. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%; *M*, 160), $\lambda_{max.}$ 313 (ε 20,000), 293·5 (25,200), 276·5 (16,500), 261·5 (8500), 247 (23,700), 238 (32,400), and 231·5 (31,800) nm, $\nu_{max.}$ (CCl_4) 3620 (OH, free), 3470br (OH bonded), 2208 and 2130 (C≡C), 1625 (CH=CH), and 950 (*trans*-CH=CH) cm^{-1}, $\nu_{max.}$ (CS_2) 730 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·95 (t, *J* 7·5 Hz, $CH_3{\cdot}CH_2$), 7·64 (dq, *J* 7·5 and 7·5 Hz, $CH_3{\cdot}CH_2{\cdot}$CH=), 3·95 (dt, *J* 10·8 and 7·5 Hz, *cis*-$CH_2{\cdot}CH$=CH), 4·54 (d, *J* 10·8 Hz, *cis*-CH=CH·C≡C), 4·23 (d, *J* 15·8 Hz, *trans*-CH=CH·$CH_2{\cdot}$OH), 3·64 (dt, *J* 15·8 and 4·7 Hz, *trans*-CH=CH·$CH_2{\cdot}$OH), and 5·83 (d, *J* 4·7 Hz, $CH_2{\cdot}$OH), *m/e* 160 (M^+, 100%), 145 (10%), 129 (14%), 117 (67%), 115 (100%), and 91 (85%).

Undeca-trans-2,trans-8-*diene*-4,6-*diyn*-1-*al* (IIa) *and Undeca*-trans-2,cis-8-*diene*-4,6-*diyn*-1-*al* (IIb).—The alcohols (Ia and b) (50 mg, 0·31 mmol) in dichloromethane (50 ml) were shaken separately with manganese dioxide (500 mg) for 2 h. Filtration of the mixture (Celite) and concentration of the filtrate gave the corresponding crude aldehydes. These were purified by repeated chromatography on 1 mm layers (ether–light petroleum, 1 : 9; two runs). The pure aldehydes (40 mg, 80%) were pale yellow oils which rapidly turned brown in light. *Undeca*-trans-2,trans-8-*diene*-4,6-*diyn*-1-*al* (IIa) distilled at 60—70° (block) and 0·01 mmHg, R_F (2,4-dinitrophenylhydrazone spray) 0·33 (ether–light petroleum, 1 : 9; two elutions), 0·49 (dichloromethane), 0·27 (carbon tetrachloride; three elutions), $\lambda_{max.}$ 339 (rel. *E* 1·7), 318 (2·08), 298sh (1·6), 281sh (1·0), 261·5 (2·34), 249 (2·62), and 237sh (2·4) nm, $\nu_{max.}$ (CCl_4) 2700 (CHO), 2200 and 2145 (C≡C), 1688 (aldehyde CO), and 960 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·92 (t, 3H, *J* 7·5 Hz, $CH_3{\cdot}CH_2$), 7·75 (dq, 2H, *J* 7·5 and 6·5 Hz, $CH_3{\cdot}CH_2{\cdot}$CH=), 3·55 (dt, 1H, *J* 6·5 and 16 Hz, *trans*-$CH_2{\cdot}CH$=CH), 4·40 (d, 1H, *J* 16 Hz, *trans*-$CH_2{\cdot}$CH=CH), 3·35—3·5 (m, 2H, *trans*-CH=CH·CHO), and 0·43 (d, 1H, *J* 6·0 Hz, CHO), *m/e* 158 (M^+, 100%), 143 (M^+ −15, 7%), 129 (M^+ −29, 64%), 115 (M^+ −43, 100%), 104 (M^+ −54, 31%), and 87 (M^+ −71, 53%). *Undeca*-trans-2,cis-8-*diene*-4,6-*diyn*-1-*al* (IIb) distilled at 50—60° (block) and 0·01 mmHg, R_F (2,4-dinitrophenylhydrazone spray) 0·32 (ether–light petroleum, 1 : 19; two elutions), 0·47 (dichloromethane), 0·27 (carbon tetrachloride; three elutions), $\lambda_{max.}$ 339 (rel. *E* 1·7), 318 (2·14), 298sh (1·62), 281sh (1·0), 261·5 (2·34), 249 (2·67), and 237sh (2·4) nm, $\nu_{max.}$ (CCl_4) 2700 (CHO), 2200 and 2145 (C≡C), 1688 (aldehyde CO), and 960 (*trans*-CH=CH) cm^{-1}, $\nu_{max.}$ (CS_2) 775 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·92 (t, 3H, *J* 7·5 Hz, $CH_3{\cdot}CH_2$), 7·62 (dq, 2H, *J* 7·5 and 7·5 Hz, $CH_3{\cdot}CH_2{\cdot}$CH=), 3·81 (dt, 1H, *J* 7·5 and 10·8 Hz, *cis*-$CH_2{\cdot}CH$=CH), 4·44 (d, 1H, *J* 10·8 Hz, *cis*-$CH_2{\cdot}$CH=CH), 3·23—3·65 (m, 2H, *trans*-CH=CH·CHO), and 0·42 (d, 1H, *J* 6 Hz, CHO), *m/e* 158 (M^+, 100%), 143 (7%), 129 (68%), 115 (100%), 104 (33%), and 87 (56%).

Undeca-trans-2,trans-8-*diene*-4,6-*diynoic Acid* (IIIa) *and Undeca*-trans-2,cis-8-*diene*-4,6-*diynoic Acid* (IIIb).—(*a*) Chromic acid (8N; 5 ml) was added dropwise to a cooled (0°), stirred, solution of the *cis–trans*-alcohol mixture (I) (250 mg, 1·6 mmol) in acetone (20 ml). After 10 min, more chromic acid (1 ml) was added and stirring was continued at 0° (5 min) and then without cooling (5 min) before water (50 ml) was added and the products were transferred into ether (4 × 50 ml). The combined ether layers were extracted with saturated sodium hydrogen carbonate solution (3 × 50 ml); this was acidified, and the *cis–trans*-acid mixture (III), a crystalline solid (117 mg, 42%), m.p. 60—100°, was isolated with ether. Crystallisation, first from dichloromethane–hexane and then from carbon tetrachloride–hexane, gave *undeca*-trans-2,trans-8-*diene*-4,6-*diynoic acid* (IIIa) as needles (35 mg), m.p. 143—145° (Found: C, 76·05; H, 6·1%; M^+ 174. $C_{11}H_{10}O_2$ requires C, 75·85; H, 5·8%; *M*, 174), $\lambda_{max.}$ 330 (ε 14,800), 311 (11,700), 257 (20,900), and 246 (25,100) nm, $\nu_{max.}$ (CCl_4) 2208 and 2138 (C≡C), 1697 (acid CO), and 955 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·92 (t, *J* 6·5 Hz, $CH_3{\cdot}CH_2$), 7·76 (dq, *J* 7·5 and 6·5 Hz, $CH_3{\cdot}CH_2{\cdot}$CH=), 3·52 (dt, *J* 6·5 and 16 Hz, *trans*-$CH_2{\cdot}CH$=CH), 4·36 (d, *J* 16 Hz, *trans*-$CH_2{\cdot}$CH=CH), 3·03 (d, *J* 16 Hz, *trans*-CH=CH·CO_2H), and 3·64 (d, *J* 16 Hz, *trans*-CH=CH·CO_2H), *m/e* 174 (M^+, 100%), 145 (M^+ −29, 12%), 131 (M^+ −43, 25%), 128 (M^+ −46, 40%), 117 (M^+ −57, 25%), 103 (M^+ −71, 31%), and 87 (M^+ −87, 30%).

Concentration of the combined mother liquors from the crystallisation of the all-*trans*-acid (IIIa) and repeated crystallisations of the residue from hexane gave *undeca*-trans-2,cis-8-*diene*-4,6-*diynoic acid* (IIIb) as needles (41 mg), m.p. 85—88° (Found: C, 75·65; H, 5·95%; M^+, 174. $C_{11}H_{10}O_2$ requires C, 75·85; H, 5·8%; *M*, 174), $\lambda_{max.}$ 330 (ε 14,300), 311 (16,800), 257 (19,400), and 246 (24,800) nm, $\nu_{max.}$ (CCl_4) 2208 and 2138 (C≡C), 1697 (acid CO), and 960 (*trans*-CH=CH) cm^{-1}, $\nu_{max.}$ (CS_2) 730 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·92 (t, *J* 7·5 Hz, $CH_3{\cdot}CH_2$), 7·63 (dq, *J* 7·5 and 7·5 Hz, $CH_3{\cdot}CH_2{\cdot}$CH=), 3·89 (dt, *J* 7·5 and 10·8 Hz, *cis*-$CH_2{\cdot}CH$=CH), 4·49 (d, *J* 10·8 Hz, *cis*-$CH_2{\cdot}$CH=CH), 3·13 (d, *J* 16 Hz, *trans*-CH=CH·CO_2H), and 3·74 (d, *J* 16 Hz, *trans*-CH=CH·CO_2H), *m/e* 174 (M^+, 100%), 145 (14%), 131 (26%), 128 (46%), 117 (35%), 103 (35%), and 87 (32%).

(*b*) The freshly prepared crude *cis–trans*-aldehyde mixture (II) [from the *cis–trans*-alcohols (I) (120 mg, 0·8 mmol) and manganese dioxide (1·2 g) in dichloromethane (50 ml)], freshly precipitated and washed silver oxide (from 1·7 g of silver nitrate), and potassium hydroxide (44 mg, 0·8 mmol) were shaken in methanol–water (9 : 1; 50 ml) for 24 h. The solids were filtered off, the filtrate was acidified, and the crude acids (III) were isolated with ether; the off-white solid residue (98 mg) was crystallised from dichloromethane–hexane at −70° and gave the *cis–trans*-acid mixture (III) (83 mg, 64%), m.p. 60—100°.

Methyl Undeca-trans-2,trans-8-*diene*-4,6-*diynoate* (IVa) *and Methyl Undeca*-trans-2,cis-8-*diene*-4,6-*diynoate* (IVb).—

The acids (IIIa and b) (30 mg, 0·17 mmol) were esterified separately at 20° with sulphuric acid in methanol (1 : 25; 25 ml). The crude esters were isolated with ether, purified by repeated chromatography on 1 mm layers (ether–light petroleum, 1 : 19), and crystallised from hexane at −70°. *Methyl undeca*-trans-2,trans-8-*diene*-4,6-*diynoate* (IVa) melted below 10°, R_F 0·34 (ether–light petroleum, 1 : 19), 0·34 (dichloromethane–light petroleum, 3 : 7), 0·40 (ethyl acetate–light petroleum, 3 : 100; two runs), $\lambda_{max.}$ 335 (15,800), 314 (19,000), 300sh (16,000), 259 (22,600), 247·5 (26,700), and 234·5 (27,000) nm, $\nu_{max.}$ (CCl_4) 2205 and 2125 (C≡C), 1730 (ester CO), 1612 (CH=CH), and 957 (*trans*-CH=CH) cm^{-1}, τ (CCl_4) 8·94 (3H, t, *J* 7·5 Hz, CH_3·CH_2), 7·80 (2H, dq, *J* 7·5 and 6·4 Hz, CH_3·CH_2), 3·64 (1H, dt, *J* 6·4, and 16 Hz, *trans*-CH_2·CH=CH), 4·45 (1H, d, *J* 16 Hz, *trans*-CH_2·CH=CH), 3·25 (1H, d, *J* 15·8 Hz, *trans*-CH=CH·CO_2Me), 3·77 (1H, d, *J* 15·8 Hz, *trans*-CH=CH·CO_2Me), and 6·30 (3H, s, CO_2Me), *m/e* 188 (M^+, 100%), 173 (M^+ −15, 33%), 157 (M^+ −31, 29%), 129 (M^+ −59, 20%), 115 (M^+ −73, 33%), and 87 (M^+ −101, 32%).

Methyl Undeca-trans-2,cis-8-*diene*-4,6-*diynoate* (IVb) melted below 10°, R_F 0·34 (ether–light petroleum, 1 : 19), 0·34 (dichloromethane–light petroleum, 3 : 7), and 0·40 (ethyl acetate–light petroleum, 3 : 97; two runs), $\lambda_{max.}$ 335 (ε 15,800), 314 (19,300), 300sh (16,100), 259 (23,300), 247·5 (27,300), and 234·5 (24,000) nm, $\nu_{max.}$ (CCl_4) 2205 and 2130 (C≡C), 1730 (ester CO), 1613 (CH=CH), and 955 (*trans*-CH=CH) cm^{-1}, $\nu_{max.}$ (CS_2) 730 (*cis*-CH=CH) cm^{-1}, τ (CCl_4) 8·94 (3H, t, *J* 7·5 Hz, CH_3·CH_2), 7·64 (2H, dq, *J* 7·5 and 7·5 Hz, CH_3·CH_2), 3·89 (1H, dt, *J* 7·5 and 11 Hz, *cis*-CH_2·CH=CH), 4·49 (1H, d, *J* 11 Hz, *cis*-CH_2·CH=CH), 3·24 (1H, d, *J* 15·8 Hz, *trans*-CH=CH·CO_2Me), 3·76 (1H, d, *J* 15·8 Hz, *trans*-CH=CH·CO_2Me), 6·30 (3H, s, CO_2Me), *m/e* 188 (M^+, 100%), 173 (29%), 157 (29%), 129 (22%), 115 (37%), and 87 (43%).

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