453. *The Stepwise Hydrogenation of Dimethyl Docosa*-10 : 12-*diynedioate.*

By J. P. Riley.

Dimethyl docosa-10 : 12-diynedioate has been synthesised by oxidative coupling of the cuprous derivative of methyl undec-10-ynoate. Hydrogenation of the conjugated diacetylenic ester over Raney nickel at 100° yields dimethyl docosa-10-ynedioate and docosa-10-enedioate simultaneously. Before appreciable amounts of the fully saturated ester are formed all the monoyne is converted into monoene. Only an insignificant amount of conjugated diene is formed during the hydrogenation, in contrast with the findings of other workers using other types of diacetylenic compounds. Both the *cis*- and the *trans*-mono-olefins are produced; they have been characterised by oxidation of the corresponding acids to their dihydroxy-compounds.

The seed oil of *Onguekoa Gore* Engler has been claimed (Steger and van Loon, *Rec. Trav. chim.*, 1940, **59**, 1156; Castille, *Annalen*, 1939, **543**, 104) to contain among its component fatty acids a conjugated diacetylenic acid (isanic acid; octadec-17-ene-9 : 11-diynoic acid). During an investigation of this oil it was thought desirable to study the hydrogenation of a typical long-chain conjugated diacetylene, since few such compounds had been investigated. Kuhn and Wallenfels (*Ber.*, 1938, **71**, 1889) and Zal'kind and Gversiteli (*J. Gen. Chem.*, *U.S.S.R.*, 1939, **9**, 971) showed that hydrogenation of diacetylenic glycols $(OH\cdot CRR'\cdot C{:}C\cdot)_2$ over palladium yielded the corresponding diethylenic glycol, but over platinum or nickel only the fully saturated glycols. Ott and Schroter (*Ber.*, 1927, **60**, 624) hydrogenated diphenyldiacetylene over nickel in ether and obtained solely *cis-cis*-diphenylbutadiene; use of palladium resulted in a mixture of diphenylbutadienes (*cis-trans* 68%; *cis-cis* 25%; *trans-trans* 0·17%). Lauer and Gensler (*J. Amer. Chem. Soc.*, 1945, **67**, 1171) found that dodeca-2 : 10-diynedioic acid was smoothly hydrogenated at room temperature in the presence of Raney nickel to dodecanedioic acid.

For the present investigation dimethyl docosa-10 : 12-diynedioate was synthesised by oxidative coupling of methyl undecynoate (cf. Bowden, Heilbron, Jones, and Sergeant, *J.*, 1947, 1579), and its identity proved by a molecular-weight determination and oxidation to sebacic acid. The ester, which was a stable colourless solid, showed the characteristic ultra-violet absorption bands of low-intensity (cf. Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 2003). The corresponding acid and its *p*-bromophenacyl ester were rapidly but partly converted into pink and blue polymers respectively (cf. Armitage *et al.*, *loc. cit.*).

The pure diacetylenic ester with a 7·5% solution of potassium hydroxide in ethylene glycol at 180° (60 minutes; cf. Hilditch, Morton, and Riley, *Analyst*, 1945, **70**, 67) was converted into a substance showing absorption at 283 and 235 mμ ($E^{1\%}_{1\,\mathrm{cm.}}$ 87·0 and 92·0 respectively).

The diacetylenic ester was hydrogenated at 100° by using Raney nickel since these are the conditions usually employed for fatty acid derivatives. Fractions withdrawn during the reaction were analysed as follows: (i) Unchanged diacetylenic compound was estimated by alkali-isomerisation followed by spectrophotometry at 283 mμ. (ii) Conjugated diene was determined from the absorption of the fraction at 232 mμ after deduction of the absorption due to the unchanged diacetylene. (iii) Fully saturated ester was determined by acetone–permanganate oxidation followed by removal of acidic oxidation products. (iv) Monoacetylenic ester and monoethenoid ester were determined from the amount of hydrogen absorbed, after allowance had been made for the other products. Compounds containing diene or enyne unsaturation show strong selective absorption in the region 226—232 mμ ($\varepsilon_{\mathrm{max.}}$ *ca.* 28,000 and 15,000 respectively). When absorption due to unchanged diyne is taken into account it is seen (Fig. 1) that the total amount of unsaturation of this type in each fraction never exceeds 5% and in fractions 1—3 is less than 3%. For calculations all absorption in this region has been assumed to arise from a conjugated diene, though there is probably a mixture of diene and enyne.

These analyses, shown in Fig. 2, indicated that the initial product of the hydrogenation was dimethyl docosa-10-ynedioate (II), formed by the addition of two molecules of hydrogen. After approximately 25% of the theoretical amount of hydrogen had been absorbed (*i.e.*, 1 mol.), formation of the ethylenic compound (III) set in at the expense of both the di- and the mono-acetylenic compound, increasing to a maximum of 83% at 75% hydrogenation. Beyond this stage the fully saturated dimethyl docosanedioate (IV), which had hitherto been produced in very small amounts, was formed by addition of hydrogen to (III).

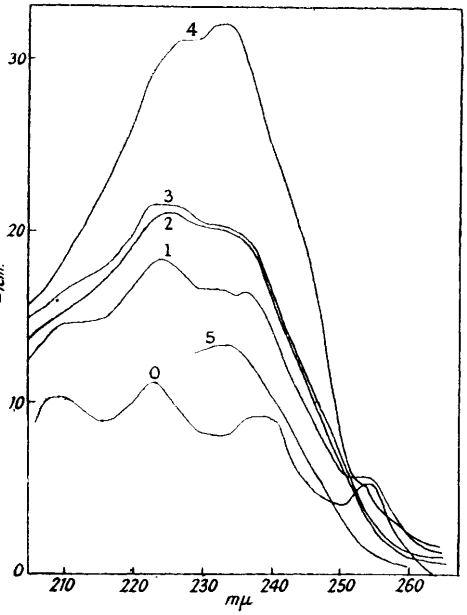

FIG. 1.
Absorption spectra of fractions.

$$\underset{\text{(I)}}{MeO_2C\cdot[CH_2]_8\cdot C{:}C\cdot C{:}C\cdot[CH_2]_8\cdot CO_2Me} \xrightarrow{2H_2} \underset{\text{(II)}}{MeO_2C\cdot[CH_2]_8\cdot C{:}C\cdot[CH_2]_{10}\cdot CO_2Me} \xrightarrow{H_2}$$

$$\underset{\text{(III)}}{MeO_2C\cdot[CH_2]_8\cdot CH{:}CH\cdot[CH_2]_{10}\cdot CO_2Me} \xrightarrow{H_2} \underset{\text{(IV)}}{MeO_2C\cdot[CH_2]_{20}\cdot CO_2Me}$$

To determine whether the monoacetylene had been formed by Thiele addition of 2 molecules of hydrogen and triple bond shift (which would yield $MeO_2C\cdot[CH_2]_9\cdot C{:}C\cdot[CH_2]_9\cdot CO_2Me$), a 50% hydrogenated fraction was oxidised with potassium permanganate in acetone; the only dibasic acids recovered were sebacic and dodecanedioic acids, showing that triple-bond shift had not occurred.

Attempts were made to identify the monoacetylenic compound by iodination but the resultant di-iodo-compound was too unstable for analysis.

After absorption of 78% of the theoretical amount of hydrogen the product was fractionally crystallised from acetone at low temperatures; it yielded approximately equal amounts of the *cis*- and the *trans*-form of dimethyl docosa-10-enedioate (III), which were characterised by hydrolysis and oxidation to the corresponding dihydroxy-acids. The position of the double bond in both isomers was confirmed by oxidation. The infra-red absorption spectra of the isomers were practically identical, owing perhaps to the fact that the compounds are almost symmetrical, symmetrical vibrations not being infra-red active.

The formation of both a *cis*- and a *trans*-ethylene by hydrogenation of an acetylene is very unusual, since the normal product is only the *cis*-isomer. Thus Gonzalez (*Anal. Fis. Quim.*, 1926, **24**, 156), using a nickel catalyst, obtained oleic and erucic acid (both *cis*) by hydrogenation of stearolic and behenolic acid respectively. These observations have been confirmed and extended to other types of compounds by many later workers. The method has been frequently employed for the synthesis of the naturally occurring (*cis*-)-isomers of fatty acids. Adkins and Billica (*J. Amer. Chem. Soc.*, 1948, **70**, 695) on the other hand claimed to have hydrogenated stearolic acid to elaidic acid (identified by melting point only), by using W6 Raney nickel. Ott (*Ber.*, 1928, **61**, 2119) found that in the presence of highly active catalysts, such as platinum black, only *cis*-isomers were formed, but with less active or poisoned catalysts variable amounts of the *trans*-isomer were also produced.

In the present work, the monoethenoid ester could have arisen either by direct addition of 3 mols. of hydrogen to the diacetylene, or by addition of 1 mol. to the previously formed monoacetylenic compound (II). The latter reaction would probably give solely the *cis*-isomer; the former on the other hand might yield the equilibrium mixture of *cis*- and *trans*-forms. The rate of hydrogenation revealed no discontinuity until only saturated and monoethenoid compounds were present.

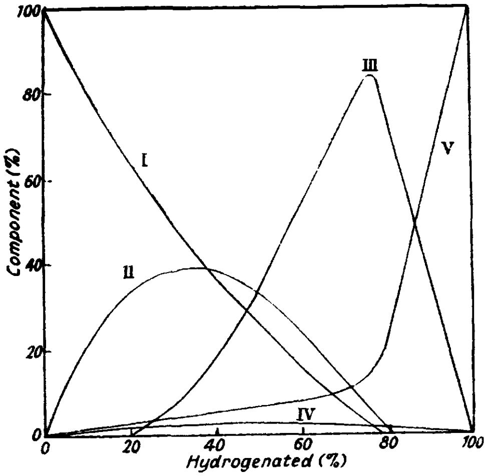

FIG. 2. *Composition of hydrogenated fractions.*

I. Dimethyl docosa-9 : 11-diynedioate.
II. Dimethyl docosa-9-ynedioate.
III. Dimethyl docos-9-enedioate.
IV. Dimethyl docosa-9 : 11-dienedioate.
V. Dimethyl docosanedioate.

Earlier studies of the hydrogenation of conjugated diacetylenic compounds have yielded as first product the conjugated diene, but the compounds investigated contained another functional group (hydroxyl or phenyl) adjacent to the triple bonds which might have affected the course of reaction.

EXPERIMENTAL

Preparation of Dimethyl Docosa-10 : 12-*diynedioate.*—10 : 11-Dibromoundecanoic acid (450 g.) was dehydrobrominated with aqueous potassium hydroxide (62%) at 150° for 8 hr. The liberated crude undecynoic acid (360 g.) was esterified at room temperature with methyl alcohol containing 1% of concentrated sulphuric acid. The resultant ester, fractionated *in vacuo* to separate it from hydroxylated and polymerised products, gave methyl undec-10-ynoate (289 g.), b. p. 90°/1 mm., n_{D}^{15} 1·4506 [Found: I.V. (Wijs), 155·5; I.V. (Toms), 248·1. Calc. for $C_{12}H_{20}O_2$: I.V., 249·0].

Methyl undec-10-ynoate (120 g.) in ethyl alcohol (800 ml.) was added dropwise with constant stirring to a solution of cuprous chloride (160 g.), ammonium chloride (280 g.), and hydrochloric acid (8 ml.) in water (1200 ml.). The mixture was heated to 55° and a current of air passed through it until the yellow-green precipitate of the cuprous derivative of the acetylenic ester had almost disappeared (2½ hr.). The cold mixture was poured into water and extracted with ether. The ethereal layer was washed several times with water and filtered to remove copper salts. The crude diacetylenic ester (116 g.), recovered by evaporation, was crystallised first from ether (10 ml./g.) at −70°, and then from ether (30 ml./g.) at −50°. The yield of pure dimethyl docosadiynedioate, m. p. 42·5°, was 92·5 g. [Found: C, 74·1; H, 9·8%; I.V. (Wijs, 0·1 g., 30 min.), 121·0; I.V. (Toms), 132·7; I.V. (hydrogenation), 260·0; sap. equiv., 194·7; *M* (Rast), 383·5. Calc. for $C_{24}H_{38}O_4$: C, 73·8; H, 9·8%; I.V., 260·3; sap. equiv., 195·2; *M*, 390·5]. Absorption max. (in EtOH) : 210, 223, 239, and 254 mμ (ε 400, 435, 366, and 216 respectively). After the ester had been heated with 7·5% potassium hydroxide in ethylene glycol at 180° for 60 min. (Hilditch *et al.*, *loc. cit.*), absorption maxima appeared at 235 and 283 mμ ($E^{1\%}_{1\,\text{cm.}}$ 92·0 and 87·0 respectively).

The ester (1·04 g.) was oxidised with potassium permanganate (8 g.) in acetone (20 ml.). Hydrolysis then gave 0·43 g. of sebacic acid, m. p. (from water) and mixed m. p. 130—131°.

The dimethyl ester was hydrolysed with alcoholic potassium hydroxide. The recovered acid, recrystallised from alcohol, was a white powder, m. p. 114—115°, which soon became covered with an insoluble pink polymer (Found : C, 72·7; H, 9·1. Calc. for $C_{22}H_{34}O_4$: C, 72·8; H, 9·4%).

The potassium salt of the acid was refluxed with an excess of an aqueous-alcoholic *p*-bromophenacyl bromide. The resultant *p*-bromophenacyl ester formed colourless plates, m. p. 103—104° (from alcohol), which rapidly became blue (Found : Br, 21·1. Calc. for $C_{38}H_{44}O_6Br_2$: Br, 20·9%).

Hydrogenation.—The dimethyl ester (59 g.) was hydrogenated at 100° in the presence of *ca.* 1 g. of Raney nickel (Pavlic and Adkins, *J., Amer. Chem. Soc.*, 1946, **68**, 1471). The apparatus consisted of a three-necked flask fitted with a mechanical stirrer (*ca.* 1300 r.p.m.) operating through a packed gland, and with a tube reaching to the bottom of the flask, by means of which samples could be withdrawn without stopping the hydrogenation. Fractionation of the product gave the results shown in Table 1. The results of permanganat oxidatione (Table 2) and of analysis discussed on p. 2193 gave the compositions shown in Table 3.

TABLE 1.

Fraction	Wt. (g.)	Hydrogenated * (%)	I.V.†	$E^{1\%}_{1\,\text{cm}}$ at (mμ) 232	254	283 ‡
0	—	0	121	8·33	5·54	87·0
1	5·11	20	106·7	16·70	5·80	53·7
2	5·60	40	102·2	20·33	5·00	33·5
3	13·87	50	80·9	20·41	3·71	22·9
4	3·00	65	70·1	32·20	3·65	7·9
5	23·05	78	56·7	13·20	3·20	—
6	8·00	100	0·6	—	—	—
Total	58·63					

* Expressed as a percentage of the volume of hydrogen required for complete saturation (*i.e.*, 4 mols.).

† I.V. (Wijs), sample wt. 0·1 g., reaction time 30 min.

‡ After alkali-isomerisation at 180° for 60 min.

TABLE 2.

Fraction	Wt. oxidised (g.)	Wt. of dibasic acid recovered (g.)	Wt. of unoxidised material (g.)	I.V. of unoxidised material	Saturated material (%)
0	1·04	0·43	0·01	—	—
1	4·22	—	0·147	13·6	3·0
2	3·83	2·71	0·221	11·1	5·1
3	13·13	10·25	0·961	5·8	6·8
4	1·74	1·18	0·155	9·4	7·7
5	15·74	—	2·55	2·0	15·6

TABLE 3. *Percentage composition of fractions.*

Fraction	Hydrogenated (%)	Saturated	Monoene	Monoyne	Conj. diene	Conj. diyne
0	0	0	0	0	0	100
1	20	2·9	0	33·9	1·5	61·7
2	40	5·2	18·1	38·5	2·0	38·5
3	50	6·8	37·9	26·9	2·1	26·3
4	65	7·7	61·5	18·0	3·7	9·1
5	78	14·3	82·3	1·9	1·5	—
6	100	100·0	0	0	0	0

Further Examination of Fractions.—*Fraction* 3. (i) Oxidation. The dimethyl esters of the dibasic acids from the acetone–permanganate oxidation of fraction 3 (see Table 2) were fractionated under reduced pressure through a micro-fractionation column, with results shown in Table 4.

Fraction 3.1. The acids obtained by hydrolysis had m. p. 84—98°, raised to 97—98° by crystallisation [mixed m. p. with azelaic acid (m. p. 103°), 92—93°]. They probably consisted of sebacic acid contaminated with small amounts of lower dicarboxylic acids which are always formed during acetone–permanganate oxidations.

TABLE 4.

Fraction	Wt. (g.)	B. p./*ca.* 1 mm.	Sap. equiv.	Fraction	Wt. (g.)	B. p./*ca.* 1 mm.	Sap. equiv.
3.1	1·765	—90°	105·9	3.5	1·109	108°	118·1
3.2	1·227	90—96	110·0	3.6	1·093	116	122·0
3.3	1·203	96—103	116·4	3.7	1·579	117 *	124·0
3.4	1·140	103	115·2	3.8	0·376	Residue	143·6

* Falling.

Fractions 3.3 and 3.4. The combined acids (1·79 g.) from these fractions were crystallised twice from water, and twice from ethyl acetate, yielding 0·46 g. of sebacic acid, m. p. and mixed m. p. 128—130°. The soluble material recovered from the second crystallisation from water, on recrystallisation, yielded 0·03 g. of acids, m. p. 106—108° [mixed m. p. with undecanedioic acid (m. p. 109°), 93°].

Fraction 3.5. The acids (0·398 g.) yielded on crystallisation 0·080 g. of sebacic acid and 0·130 g. of acids, m. p. 100—107°, not identical with undecanedioic acid.

Fraction 3.6. The recovered acids (0·92 g.) were boiled with water and the insoluble acids (0·15 g.) recrystallised from ethyl acetate at 0°, yielding dodecanedioic acid (0·12 g.), m. p. and mixed m. p. 128°. A small fraction of m. p. 107—108°, not identical with undecanedioic acid, was obtained by repeated crystallisation of the acids soluble in boiling water.

(ii) Iodination. The acids from fraction 3 were iodinated as described by James and Sudborough (*J.*, 1907, **91**, 104); the di-iodo-compound which was obtained as pale yellow plates partly decomposed before analysis (Found: I, 36·5%. Calc. for $C_{22}H_{38}O_4I_2$: I, 40·9%).

Fraction 5. This was crystallised from acetone at low temperatures, with results shown below:

Fraction	Wt. (g.)	I.V.	Soluble in $COMe_2$	Insoluble in $COMe_2$
S_1	6·02	39·5	—	10 pts. at 0°
L_2	1·64	57·5	10 pts. at 0°	15 „ −30°
L_3	2·20	64·7	15 „ −30°	10 „ −30°
L_4	2·70	64·1	10 „ −20°	10 „ −30°
L_5	1·68	64·1	12 „ −20°	10 „ −20°
S_5	6·57	64·6	—	12 „ −20°

Fraction S_5 was dimethyl *trans*-docos-10-enedioate, m. p. 31—32°, n_D^{40} 1·4523 (Found: sap. equiv., 197·6; I.V., 64·6. Calc. for $C_{24}H_{44}O_4$: sap. equiv., 198·2; I.V., 64·5).

Fraction L_3 was substantially pure dimethyl *cis*-docos-10-enedioate, n_D^{40} 1·4523 (Found: C, 72·7; H, 11·0%; sap. equiv., 200·0; I.V., 64·7. Calc. for $C_{24}H_{44}O_4$: C, 72·6; H, 11·2%; sap. equiv., 198·2; I.V., 64·5).

The unsaturated dicarboxylic acids obtained by hydrolysis of fractions L_3 and S_5 were oxidised to the corresponding dihydroxy-acids by dilute aqueous permanganate (cf. Lapworth and Mottram, *J.*, 1925, **127**, 1628); results are:

	cis.	*trans.*
M. p. of docos-10-enedioic acid	64°	73—74°
Wt. oxidised (g.)	0·851	0·872
Wt. (g.) of crude dihydroxy-acid	0·695	0·692
M. p. of pure dihydroxy-acid	154—155°	127·5—128·5°
Found (%)	C, 65·7; H, 10·2	C, 66·0; H, 10·3

Calc. for $C_{22}H_{42}O_6$: C, 65·6; H, 10·5%.

Acetone–permanganate oxidations were carried out on the ester fractions (*a*) S_1, (*b*) L_2, L_3, L_4, and L_5 combined (*cis*-ester), and (*c*) S_5 (*trans*-ester). The dibasic acids obtained in (*b*) and (*c*) were then converted into methyl esters and distilled. Results are as below. The ester fractions thus obtained were hydrolysed and the acids examined.

Fraction 5C3 (0·62 g.), on repeated crystallisation from water, chloroform and ethyl acetate, yielded sebacic acid (0·06 g.), m. p. and mixed m. p. 130°.

Fraction 5C5 (0·41 g.) on crystallisation from hot water and ethyl acetate yielded dodecanedioic acid (0·02 g.), m. p. and mixed m. p. 127°. A further fraction had m. p. 106—108°, not identical with undecanedioic acid, m. p. 109°.

Fraction 5T3 (0·41 g.) on repeated crystallisation from water, ethyl acetate, and chloroform gave sebacic acid (0·02 g.), m. p. and mixed m. p. 129°. A further fraction had m. p. 110° (mixed with undecanedioic acid, 94°).

Fraction	S_1	*cis* (L_2—L_5)	*trans* (S_5)
Wt. oxidised (g.)	5·69	5·78	4·27
Wt. of unoxidised ester (g.)	1·85	0·56	0·14
Wt. of dibasic acids (g.)	—	4·76	3·92

Dimethyl esters.

cis			*trans*		
Fraction	Wt. (g.)	Sap equiv.	Fraction	Wt. (g.)	Sap. equiv.
5C1	0·909	111·1	5T1	0·407	112·3
5C2	0·711	113·8	5T2	0·505	113·5
5C3	0·739	116·4	5T3	0·518	115·1
5C4	1·066	119·6	5T4	0·537	117·8
5C5	0·499	122·8	5T5	0·631	119·4
5C6	0·326	130·0	5T6	0·716	124·0
			5T7	0·214	141·1
Total	4·250		Total	3·528	

Fraction 5T6 (0·54 g.), by crystallisation from water and ethyl acetate, yielded dodecanedioic acid (0·17 g.), m. p. and mixed m. p. 127°. A more soluble fraction had m. p. 108—110° but was not identical with undecanedioic acid.

Fraction 6. This (5·3 g.; I.V. 0·6), crystallised from acetone (53 ml.) at room temperature, yielded dimethyl docosanedioate (4·74 g.), m. p. 71° (Found: C, 72·2; H, 11·4%; sap. equiv., 197·6. Calc. for $C_{24}H_{46}O_4$: C, 72·3; H, 11·6%; sap. equiv., 198·2). The acid (0·78 g.; m. p. 125—126°) recovered after hydrolysis of the dimethyl ester (0·98 g.) was recrystallised from alcohol (140 ml.) at room temperature and gave docosanedioic acid (0·63 g.), m. p. 125—125·5°. Published m. p.s vary notably for the acid (120—122° to 126·9—127·1°) and its dimethyl ester (67—68° to 70·2—71°).

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