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The Preparation of Ethyl 18-Nonadecenoate by a Mixed Coupling Reaction

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Long-chain terminal olefinic fatty esters are useful intermediates for the syntheses of various long-chain compounds. However, no paper reporting a simple preparation of the esters has been appeared. Concerning the electrolysis of terminal alkenoic acid, the preparation of 1,19-eicosadiene from 10-undecenoic acid by electrolysis with platinum electrodes has been attempted by Weedon *et al.*,$^{1)}$ but the diene was contaminated by its positional isomers of the double bond. On the other hand, a 1,19-eicosadiene-rich-product was obtained when a platinum anode and a mercury cathode were used.$^{2)}$

In the present study, mixtures of 10-undecenoic acid (I) and ethyl hydrogen sebacate (II) were electrolyzed with platinum anode and a mercury cathode (procedures A and B) or with platinum electrodes (procedure C). The molar ratios of I to II employed were from 2 : 1 to 1 : 5. The coupling products were successfully separated by elution chromatography on silica gel.

Typical conditions of electrolysis, together with the products, are shown in Table 1. By procedure A, the desired ester, III, was obtained. The 45% yield of III was given by a 1 : 5 mixture of I and II. On the other hand, the largest weight percentage of III was given by an equimolar mixture of I and II. In procedure B, ester-exchange reaction of III and V proceeded. In procedure C, difficulty in obtaining unsaturated coupling compounds was experienced. The X, XI, and XII fractions comprised some positional isomers of the double bond. The key reaction may be illustrated as follows:

$$\underset{\text{(I)}}{CH_2{=}CH(CH_2)_8COOH} + \underset{\text{(II)}}{HOOC(CH_2)_8COOC_2H_5} \rightarrow$$

$$\underset{\text{(III)}}{CH_2{=}CH(CH_2)_{16}COOC_2H_5} + \underset{\text{(IV)}}{CH_2{=}CH(CH_2)_{16}CH{=}CH_2}$$

$$+ \underset{\text{(V)}}{H_5C_2OOC(CH_2)_{16}COOC_2H_5}$$

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1) D. G. Bounds, R. P. Linsteasd and B. C. L. Weedon, *J. Chem. Soc.*, **1953**, 2393.

2) R. F. Gardwood, C. J. Scott and B. C. L. Weedon, *Chem. Commun.*, **1965**, No. 1, 14.

Table 1. Reaction procedures and products

Procedure		A	B	C
Substrate (mol)	I	0.05	0.05	0.05
	II	0.05	0.05	0.05
MeOH (m*l*)		207	207	207
Sodium (atom)		0.10	0.10	0.01
Current (A)		1	1	1
Current density (A/cm^2)		0.15	0.15	0.11
Terminal voltage (V)		30—100	30—100	30—100
Reaction time (hrs)		5.5	5.5	5.5
Reaction temp. (°C)		30—35	45—50	40—45
Products (%)	III*	24	—	—
	IV*	22	21	—
	V*	25	—	27
	VI*	—	23	—
	VII*	—	24	—
	VIII*	—	—	27
	IX*	—	—	23
	X*	—	—	2
	XI*	—	—	0.6
	XII*	—	—	0.9

* III, Ethyl 18-nonadecenoate; IV, 1,19-eicosadiene; V, diethyl 1,18-octadecanedioate; VI, methyl 18-nonadecenoate; VII, dimethyl 1,18-octadecanedioate; VIII, ethyl nonadecanoate; IX, eicosane; X, ethyl nonadecenoates; XI, eicosenes; XII, eicosadienes.

Experimental

The GLC was carried out by means of a Hitachi Gas Chromatograph K-23 on a column packed with 20% poly(diethylene glycol succinate) on Chromosorb WAW. The IR spectra were recorded with a Hitachi EPI-S2 Infrared Spectrophotometer in a KBr disk or in a liquid film. The IR spectra of III, IV, and VI showed bands assigned to terminal double bond at 3064—3053, 1825—1820, 1645—1640, 1420—1416, 1302—1298, 990—988, and 908—904 cm^{-1}. The spectra of III, V, VI, VII, and VIII showed a band assigned to the ester carbonyl group at 1740—1738 cm^{-1}. The NMR spectra were recorded with a JEOL JNM C-60HA NMR Spectrometer for a 10% carbon tetrachloride solution. The NMR spectra of III, VI, and VIII showed peaks at τ 5.07 (a, triplet). 4.3 (b, multiplet), 7.94—7.96 (c, doublet), 8.73 (d, singlet), 7.75—7.80 (e, unsymm. triplet), 5.96 (f, quartet), 8.74 (g, unsymm. triplet), 6.39 (h, singlet), and 9.11 (i, unsymm. triplet).

$$\underset{\bar{a}}{CH_2}=\underset{\bar{b}}{CH}\underset{\bar{c}}{CH_2}\underset{\bar{d}}{(CH_2)_{14}}\underset{\bar{e}}{CH_2}COO\underset{\bar{f}}{CH_2}\underset{\bar{g}}{CH_3}\ \text{(III)},$$

$$\underset{\bar{a}}{CH_2}=\underset{\bar{b}}{CH}\underset{\bar{c}}{CH_2}\underset{\bar{d}}{(CH_2)_{14}}\underset{\bar{e}}{CH_2}COO\underset{\bar{h}}{CH_3}\ \text{(VI)},$$

$$\underset{\bar{i}}{CH_3}\underset{\bar{d}}{(CH_2)_{16}}\underset{\bar{e}}{CH_2}COO\underset{\bar{f}}{CH_2}\underset{\bar{g}}{CH_3}\ \text{(VIII)}$$

Oxidative ozonolysis was carried out according to the procedure of Ackman *et al.*[3] The cleavage products were elucidated by GLC.

Materials. Commercially-available Compound I was rectified by vacuum distillation; bp 121°C/1 mmHg. Compound II was prepared according to the procedure used in our previous experiments;[4] bp 150—154°C/1 mmHg; mp 35.5—36.5°C.

Procedures. Cells fitted with a platinum anode and a mercury cathode[5] (procedures A and B) and with platinum electrodes[4] (procedure C) were surrounded with water in order to maintain the electrolyte at the required temperature.

In procedure C, the current direction was changed every 3 sec. The products were treated as in our previous experiments,[4] and the coupling products were separated into three fractions by elution chromatography on silica gel with ligroin (bp 85—115°C) and then with methanol.

Products from Procedure A. The first fraction, mp 20—20.5°C (19.5—20°C[1]), was shown to be IV by elemental analysis and by its iodine value, along with the results obtained from its GLC, ozonolysis, and IR and NMR spectra. The second fraction, white crystals; mp 30—30.5°C (from ethanol), was shown to be III by its iodine and saponification values and also by a study of its GLC and ozonolysis, together with a study of its IR and NMR spectral data.

Found: C, 77.58; H, 12.39%. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42%.

The third fraction was shown to be V by comparing it with the specimen obtained by the procedure used in our previous experiments.[4]

Products from Procedure B. The first fraction was composed of IV; this was established by comparing it with the authentic compound obtained in the above paragraph. The second fraction, white crystals; mp 32—32.5°C (from ethanol), was shown to be VI by its iodine and saponification values and by a study of its GLC and ozonolysis, together with a study of its IR and NMR spectral data.

Found: C, 77.51; H, 12.30%. Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.34%.

The third fraction, white crystals; mp 59—59.5°C (57—58°C[6]) (from ethanol), was shown to be VII by elemental analysis and also by a study of its GLC, together with a study of its IR and NMR spectral data.

Products from Procedure C. The first fraction was shown to be a mixture of IX, XI, and XII by means of GLC, together with a study of its IR and NMR spectral data. The ozonolysis of XI gave a mixture of 1-, 2-, and 3-eicosenes, while XII gave a mixture of 1,19-, 1,18-, 1,17-. 2,18-, 2,17-, and 3,17-eicosadienes. The second fraction was shown to be a mixture of VIII and X, by GLC and by a study of its IR and NMR spectral data. The ozonolysis of X gave a mixture of ethyl 18-, 17-, 16-, 15-, and 14-nonadecenoates. The third fraction was successfully identified as V.

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4) Y. Suhara and S. Miyazaki, This Bulletin, **42**, 3022 (1969).

5) N. Dihn-Nguyen, *Acta Chem. Scand.*, **12**, 585 (1958).

6) S. Swann, Jr., and W. E. Garrison, Jr., "Organic Syntheses," Vol. 41, p. 33 (1961).