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Preparation of Ethyl 19-Bromononadecanoate by a Mixed Coupling Reaction

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Woolford *et al.*[1] prepared several long-chain ω-bromofatty esters from mixtures of ω-bromofatty acids and methyl hydrogen esters by a mixed coupling reaction. However, the yields of the desired cross-coupling products were generally low, and it was difficult to separate the coupling products by distillation. Therefore, two modifications of the procedure were attempted in this investigation: A) the ethyl hydrogen ester[2] was used instead of the methyl hydrogen ester and B) the coupling products were separated by column chromatography, not by distillation.

In the present investigation, 5: 1 to 1 : 5 mixtures of 11-bromoundecanoic acid (I) and ethyl hydrogen sebacate (II) were used for the electrolysis. By the electrolysis, ethyl 19-bromononadecanoate (III), 1,20-dibromoeicosane (IV), and diethyl octadecanedioate (V) were obtained as the coupling products. The coupling products were successfully separated by column chromatography on silica gel.

The lowest yield of III (29%) was given by an equimolar mixture of I and II, but the yield was increased when an excess of I or II was employed. The best yield in the present experiments was 54%; it was obtained from a 1 : 5 mixture of I and II. The largest amount of III, however, was given by an equimolar mixture of I and II.

For the identification of the coupling products, TLC on silca gel was preferable to GLC. Their R_f-values were as follows: IV, 0.80; III, 0.47; V, 0.25 (methyl ethyl sebacate, 0.37; methyl 11-bromoundecanoate, 0.15).

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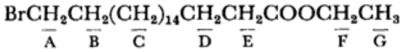
[1] R. G. Woolford, W. Arbic and A. Rosser, *Can. J. Chem.*, **42**, 1788 (1964).

[2] H. Agata and A. Tanaka, *Yakugaku Zasshi (J. Pharm. Soc. Japan)*, **76**, 960 (1956).

The IR spectrum of III showed bands at 1740 cm^{-1} (ester carbonyl group) and 645 cm^{-1} (C–Br linkage[3]). The NMR spectrum of III showed chemical shifts at 5.96 τ (F), 6.68 τ (A), 7.81 τ (E), 8.19 τ (B), 8.46 τ (D), 8.73 τ (C), and 8.77 τ (G).



$$\underset{A}{BrCH_2}\underset{B}{CH_2}\underset{C}{(CH_2)_{14}}\underset{D}{CH_2}\underset{E}{CH_2}COO\underset{F}{CH_2}\underset{G}{CH_3}$$

Experimental

TLC was conducted on a silica-gel plate (0.25 mm, Merck, G, No. 7731), with ligroin (bp 85—115°C)-acetone (50 : 1, v/v) as the solvent. For the detection of the spots, the plate was sprayed with a 10% phosphomolybdic acid-ethanol solution and then heated at 140°C.

The IR spectra were recorded with a Perkin-Elmer 337 Grating Infrared Spectrophotometer in a KBr disk.

The NMR spectra were recorded with a Varian 100-HA Spectrometer for a 10% carbon tetrachloride solution, with tetramethylsilane as the internal reference.

Materials. The I was prepared from 10-undecenoic acid.[4] Mp, 52°C (50°C[4]). The II was obtained from sebacic acid and diethyl sebacate.[5] Bp, 150—154°C/1 mmHg (bp 183—187°C/6 mmHg[5]); mp 35.5—36.5°C (34—36°C[5]).

The IV was prepared from I by electrolysis,[6] and the crude product was recrystallized from ligroin with small amounts of silica gel for decolorization. Mp, 68.5—69°C (67.4—68°C[7]). The V was prepared from II by electrolysis. The crude product was distilled *in vacuo*, and a fraction boiling at 192—194°C at 1 mmHg was recrystallized from ethanol. Mp, 47—47.5°C (46.9—47.8°C[8]).

Procedures. The cell used was a 500 m*l* measuring cylinder fitted with a thermometer and two parallel platinum plates electrodes (4×3 cm) placed about 2 mm apart. The cell was surrounded with ice water to maintain the internal temperature within the range of 40—45°C.

Three and eithteen hundredth grams of I (0.012 mol), 13.82 g of II (0.06 mol), and 0.16 g of sodium (0.007 atom) were dissolved in 176 m*l* of methanol. A current of about 1.5 A was passed through for three times the theoretical time while the mixture was being stirred with a magnetic stirrer.

After the unreacted materials had been removed by washing with 5% potassium bicarbonate solution, the product mixture was distilled *in vacuo* to separate the non-coupling products as the distillate. The coupling products remaining as a residue (9.2 g) were separated by column chromatography on silica gel (110 g), with ligroin as the solvent.

The first fraction, melting at 65—68°C, was recrystallized from ligroin; white plate crystals were thus obtained. The crystals, which melted at 68.5—69°C, were shown to be IV by a study of their TLC, IR, and NMR spectra. The yield was 8% based on the moles of I employed. A mixed-melting-point determination with an authentic sample showed no depression.

The second fraction, melting at 47—49°C was recrystallized from ethanol; white flaky crystals were thus obtained. The crystals, which melted at 49.5—50°C, were shown to be III by elemental analysis, and by a study of their TLC, IR, and NMR spectra. The yield was 54% based on the moles of I employed.

Found: C, 62.40; H, 10.26; Br, 19.55%. Calcd for $C_{21}H_{41}O_2Br$: C, 62.21; H, 10.19; Br, 19.71%.

The third fraction, melting at 43—46°C, was distilled *in vacuo*; the distillate was recrystallized from ethanol to obtain white large flaky crystals. The crystals, which melted at 47—47.5°C, were shown to be V by a study of their TLC, IR, and NMR spectra. The yield was 57% based on the moles of II employed. A mixed-melting-point determination with an authentic sample showed no depression.

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3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., Ltd., London (1958), p. 331.

4) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

5) Y. Iwakura and K. Uno, "Yuki-kagobutsu Gosei-ho (Organic Syntheses, Japan)," Vol. 10, Giho-do, Tokyo (1958), p. 47.

6) R. G. Woolford, *Can. J. Chem.*, **40**, 1846 (1962).

7) H. Korshing, *Chem. Ber.*, **86**, 943 (1953).

8) V. N. Belov, E. K. Smol'yaninova, E. A. Ogordnikova, V. M. Rodionov, N. P. Solov'eva, G. E. Svadkovskaya and N. N. Shevyakova, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Sintet. i Natural. Dushistykh Veshchestv*, **1958**, No. 4, 3; *Chem. Abstr.*, **53**, 15969a (1959).