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Preparation of Ethyl 19-Bromonadecanoate 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 ester²⁾ 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-bromonadecanoate (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.

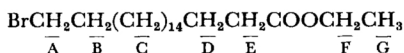
The lowest yield of III (29%) was given by an equimolar mixture of I and II, but the yield was increased when an excess of I or II was employed. The best yield in the present experiments was 54%; it was obtained from a 1:5 mixture of I and II. The largest amount of III, however, was given by an equimolar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

For the identification of the coupling products, TLC on silica 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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The IR spectrum of III showed bands at 1740 cm^{-1} (ester carbonyl group) and 645 cm^{-1} (C-Br linkage³⁾). 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).



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°C⁴⁾). The II was obtained from sebacic acid and diethyl sebacate.⁵⁾ Bp, 150–154°C/1 mmHg (bp 183–187°C/6 mmHg⁵⁾); mp 35.5–36.5°C (34–36°C⁵⁾).

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°C⁷⁾). 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°C⁸⁾).

Procedures. The cell used was a 500 ml 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 eighteen 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 ml 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 $\text{C}_{21}\text{H}_{41}\text{O}_2\text{Br}$: 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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