BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3022—3023 (1969)

Preparation of Ethyl 19-Bromononadecanoate by a Mixed Coupling Reaction

Yasuo SUHARA and Shoji MIYAZAKI

Government Chemical Industrial Research Institute, Tokyo, Shibuya-ku, Tokyo

(Received April 10, 1969)

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).

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).

$$\underset{\text{A}}{\text{Br}}\underset{\text{B}}{\text{CH}_2}\underset{\text{C}}{\text{CH}_2}(\text{CH}_2)_{14}\underset{\text{D}}{\text{CH}_2}\underset{\text{E}}{\text{CH}_2}\text{COO}\underset{\text{F}}{\text{CH}_2}\underset{\text{G}}{\text{CH}_3}$$

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.

We are grateful to Mr. Masaru Yanagisawa for recording the NMR spectra, to Dr. Osamu Yamamoto for his helpful comments on the NMR spectra, and to Kajio Matsuoka and Sukehide Tsuchiya for their assistance in our experimental work.

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).