260 g/mol) by titration with perchloric acid (the monoperchlorate separated as crystals) ^{1}H NMR (60 MHz, DMSO-d_6): δ 7.06 (2 H, s), 7. 25 (2 H, dd, J 8.1 and 5.3 Hz), 7.87 (2 H, dd, J 8.1 and 1.5 Hz), 8.40 (2 H, dd, J 5.3 and 1.5 Hz). UV [abs. ethanol (log ε)]: 298 (3.75) 243 (4.14) nm. IR (KBr): 1095 s (C–O–C) cm^{-1}. Anal. $C_{12}H_6N_2OS_2$: C, H, N, S.

(R,S)-1-Methylbenzyl-3-formyl-2(1H)-pyridinethione (*1c*). Glutacondialdehyde sodium salt (120 g) and (*R,S*)-methylbenzyl isothiocyanate (110 g) in dimethyl sulfoxide (500 ml) were heated to 80 °C for 2 h. The reaction mixture was poured in ice-cold water (4 l). The precipitated orange crystals were collected [119 g (73 %)] and recrystallized from methanol/water (510/88). m.p. 103–105 °C. ^{1}H NMR (60 MHz, DMSO-d_6): δ 1.81 (3 H, d, J 6.2 Hz), 7.40 (5 H, s), 7.46 (1 H, q, J 6.8 Hz), 7.78 (1 H, dd, J 6.2 and 1.5 Hz), 8.30 (1 H, dd, J 6.2 and 1.5 Hz), 10.65 (CHO, s). UV [abs. ethanol (log ε)]: 388 (3.49) 3.18 (4.06) 294 sh (3.77) nm. IR (KBr): 1685 (CHO) cm^{-1}. Anal. $C_{14}H_{13}NOS$: C, H, N, S.

1-(2'-Phenylethyl)-3-formyl-2(1H)-pyridinethione. Glutacondialdehyde potassium salt (2.72 g) and 2-phenylethyl isothiocyanate (3.26 g) in *N,N*-dimethylformamide were heated to 100 °C for 4 h. The reaction mixture was evaporated *in vacuo*, water (200 ml) was added and the dark crystals were collected. Trituration with cyclohexane gave orange crystals [2.8 g (50 %)]. Recrystallization from heptane yielded pale orange crystals with m.p. 132–135 °C. ^{1}H NMR (60 MHz, $CDCl_3$); δ 3.28 (2 H, t, J 7.5 Hz), 4.97 (2 H, t, J 7.5 Hz), 6.59 (1 H, t, J 6.9 Hz), 7.35 (5 H, s), 7.53 (1 H, dd, J 6.9 and 1.5 Hz), 7.88 (1 H, dd, J 6.9 and 1.5 Hz), 11.00 (CHO, s). UV [abs. ethanol (log ε)]: 377 (3.36) 320 (4.01) 294 sh (3.72) nm. IR (KBr): 1682 (CHO) cm^{-1}. Anal. $C_{14}H_{13}NOS$: C, H, N, S.

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Studies on the Kolbe Electrolysis. XII.* Complete Racemization of Optically Active Radicals from (—)-2-Methyloctadecanoate in a Mixed Coupling Reaction

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The hypothesis that the Kolbe anodic coupling of carboxylates proceeds *via* adsorbed radicals would seem to demand at least partial retention of configuration in the coupling product from an initially optically active radical.[1–4] Previous experiments to test this idea have, however, resulted in completely racemized coupling products and hence not proved to be conclusive on this point.[5,6] Only if retention is observed would adsorbed radicals be implicated in the mechanism with any degree of certainty.

The explanation put forward by Muck and Wilson [7] for the remarkably selective Kolbe coupling of long-chain carboxylates, parallel stacking of the long alkyl chains perpendicular to the anode surface with concomitant very low mobility of the alkyl radicals formed, suggests yet another possibility to find a system with a maximal propensity toward retention of configuration, if it is indeed possible to find one at all. We now report a study on the mixed Kolbe coupling between D-(–)-2-methyloctadecanoic acid (*1*) and methyl hydrogen malonate (eqn. 1). Both *1* and the product, methyl 3-methylnonadecanoate (*2*), were known with respect to their maximal optical rotation and configuration.[8,9]

$$\underset{1}{RCH(CH_3)COO^-} + MeOCOCH_2COO^- \xrightarrow[R=C_{16}H_{33}]{\text{Pt anode}} \underset{2}{RCH(CH_3)CH_2COOCH_3} \quad (1)$$

After initial experiments with the (+)-isomer to establish the proper reaction conditions, the crucial experiment was run with (–)-*1* and methyl hydrogen malonate in a 1:8 molar ratio in methanol (total salt concentration ~1 M). Both acids were fully neutralized in order to compensate for the difference in pK between them, and a large Hg cathode was used to avoid alkalinization (by amalgamation of the sodium discharged) during the run.[10] The temperature of the electrolyte solution

* Part XI. See Ref. 6.

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was kept at 60 °C and the current density changed from an initial value of 1.0 to 0.1 A cm^{-2}.

After conventional workup the crude product was distilled and a fraction of b.p. 152–175 °C/1 mmHg was collected. Preparative GLC of this material gave pure *2* in a yield of 4.0 %, $\alpha = 0.000 \pm 0.002°$.

Since (−)-*1* and (+)-*2* have the same configuration, it is essential to establish beyond doubt that the product is not contaminated by starting material which accidentally might give a sample with zero optical rotation. GLC analysis of a sample treated with methanol/sulfuric acid at reflux for 5 h showed that the coupling product contained no detectable amount of *1* (< 0.1 %).

The experiment with (+)-*1* likewise gave a completely racemized product, although the less than perfect conditions gave too small and impure a sample to give a completely reliable estimate.

The optical purity of our sample of (−)-*1* was 60.1 %, so that the maximal obtainable value of $[\alpha]_D^{23}$ for *2* would be +2.28°, corresponding to a measured value of α of 0.325° for the product sample isolated. This permits us to conclude that the reaction has proceeded with at least 99.4 % retention, and that we have added yet another piece of evidence, albeit of negative nature, against the adsorbed radical hypothesis, still tenaciously upheld in some quarters.[11] In view of the apparent lack of more ideal systems to study, we can also add the Kolbe reaction to the growing list of electroorganic reactions for which stereochemistry is most notable by its absence.

Experimental. Starting materials. Partially resolved samples of (+)- and (−)-*1* were prepared according to published procedures,[8] $[\alpha]_D^{23}$ +4.32 and −5.65° (chloroform, *c* 8.2 and 11.7), respectively. The only change was in the resolution procedure, in which one recrystallization of the initially precipitated quinine salt was sufficient for the purpose at hand.

*Coupling reaction between (−)-*1 and *methyl hydrogen malonate.* Methyl hydrogen malonate (11.46 g, 0.097 mol), (−)-*1* (3.62 g, 0.0121 mol) and sodium (2.51 g, 0.109 mol) were dissolved in absolute methanol (100 ml). The solution was electrolyzed between a mercury cathode (580 g, area 28 cm^2) and a platinum anode (wire, 1.5 cm^2) at 60 °C (in order to keep all material in solution) for 185 min. The initial current of 1.5 A eventually decreased to 0.2 A.

The reaction mixture was then evaporated to dryness. Water (20 ml) was added, together with some sodium chloride to avoid the formation of an emulsion. The mixture was extracted with ether (4 × 50 ml) and the extracts were dried with anhydrous sodium carbonate. Distillation afforded a fraction (0.52 g) with b.p. 152–175 °C/1 mmHg which contained the desired product (*2*). This material was separated by preparative GLC (Autoprep Model A-700, 3 m × 9 mm 10 % OV-101 on 45–60 mesh Chromosorb B column at 250 °C, He as carrier gas), which gave a pure sample (157 mg, 4 % yield) of *2*, $\alpha = 0.000 \pm 0.002$ (chloroform, *c* 15.7; Perkin-Elmer model 141 spectropolarimeter).

A small sample of the product (45.6 mg) was refluxed with methanol/sulfuric acid (2.0 ml, molar ratio 25:1) for 5 h. GLC on the isolated product showed that < 0.1 % of the starting material could be present in the original sample.

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