

Table 1. Variations with solvent composition of δ for H-1, H-3 and H-5 of three methyl 2,3,4,6-tetra-O-acetyl- β -D-hexopyranosides.

	CDCl ₃	CDCl ₃ /(CD ₃) ₂ SO		(CD ₃) ₂ SO
		5:2	1:1	
<i>galacto</i> configuration				
H-1	4.39	4.48	4.54	4.59
H-3	4.99	—	—	5.04
H-5	3.91	—	—	4.09
<i>gluco</i> configuration				
H-1	4.43	4.52	4.59	4.68
H-3	5.21	5.23	5.24	5.26
H-5	3.70	3.82	(3.89) ^a	(3.98)
<i>manno</i> configuration				
H-1	4.56	4.72	4.78	4.84
H-3	5.04	—	—	(5.09)
H-5	3.66	—	—	3.86

^a Values in parentheses are less accurate due to overlapping signals or second-order effects and those not given could not be determined, for the same reasons.

at the centre of frequency of the presumed H-5 signal (identified from its chemical shift and spin coupling pattern) caused a simplification of the H-6 and H-6' signals and a sharpening of the H-4 broad doublet. Irradiation at δ 5.18 (H-2) caused the presumed H-1 signal to collapse into a singlet. The converse collapse of the presumed H-2 triplet into a doublet when irradiating at the presumed H-1 frequency was also observed. Irradiation at the H-4 frequency caused collapse of the H-3 signal (dd) into the expected doublet. The following assignments were therefore made: δ values: H-1 4.39, H-2 5.18, H-3 4.99, H-4 5.39, H-5 3.91, H-6 and H-6' 4.10-4.22. First-order coupling constants: $J_{1,2}$ 8 Hz, $J_{2,3}$ 10 Hz, $J_{3,4}$ 4 Hz, $J_{4,5} < 1$ Hz.

Methyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside. Solvent CDCl₃/(CD₃)₂SO 5:1. Using decoupling techniques similar to those described above, the following assignments were made: δ values: H-1 4.51, H-2 4.89, H-3 5.23, H-4 5.00, H-5 3.80, H-6 4.08, H-6' 4.28. First-order coupling constants: $J_{1,2}$ 8 Hz, $J_{2,3}$ 8 Hz, $J_{3,4}$ 8 Hz, $J_{4,5}$ 8 Hz, $J_{5,6}$ 3 Hz, $J_{5,6'}$ 5 Hz, $J_{6,6'}$ 12 Hz.

Methyl 2,3,4,6-tetra-O-acetyl- β -D-mannopyranoside. Solvent CDCl₃. Using decoupling techniques similar to those described above, the following assignments were made: δ values: H-1 4.56, H-2 5.48, H-3 5.04, H-4 5.26, H-5 3.66, H-6 4.13, H-6' 4.33. First-order coupling constants: $J_{1,2} < 1$ Hz, $J_{2,3}$ 4 Hz, $J_{3,4}$ 10 Hz,

$J_{4,5}$ 10 Hz, $J_{5,6}$ 4 Hz, $J_{5,6'}$ 6 Hz, $J_{6,6'}$ 12 Hz. The various integrals and shift gradients were in accordance with the above assignments.

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Studies on the Kolbe Electrolysis. XI.* Racemization of Optically Active sec-Butyl Radicals in a Mixed Coupling Reaction

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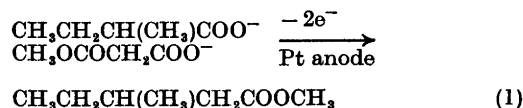
In the preceding article of this series,¹ the mixed Kolbe coupling between radicals from ethyl hydrogen (+)-ethylmethylmalonate and isovaleric acid was found to give ethyl ethylisobutylmethylacetate which was racemic to an extent of at least 99.98%. From the theoretical point of view, one possible objection against this system is that the radical center of the optically active radical is strongly conjugated with an ethoxycarbonyl group, thus (1) providing a strong driving force for the radical to attain a planar structure and (2) causing a weakening of any chemisorption bond between the radical and the electrode surface (platinum). Both factors would de-

* Part X. See Ref. 1.

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crease any tendency for the formation of a product with at least partially retained configuration, postulated to be the outcome of a mechanism involving a strong chemisorptive interaction between the initially formed radical and the electrode.^{2,3}

The mixed coupling reaction between optically active *sec*-butyl radicals from (+)-2-methylbutanoic acid and methoxycarbonylmethyl radicals from methyl hydrogen malonate (eqn. 1) is not marred with the problem indicated above. We now report that methyl 3-methylpentanoate formed in this reaction



is completely racemized, in spite of the fact that the optically active radical is of purely hydrocarbon type.

Optically pure (+)-2-methylbutanoic acid was prepared by oxidation of (-)-2-methyl-1-butanol in "purple benzene".⁴ It was then electrolyzed together with methyl hydrogen malonate in a 3:1 ratio (several test runs with inactive material showed that the formation of methyl 3-methylpentanoate was suppressed when the reaction was run with an excess of monomethyl malonate) in methanolic solution, the acid mixture being neutralized by potassium hydroxide to an extent of ca. 3%. Methyl 3-methylpentanoate was isolated from the product mixture by preparative GLC, $[\alpha]_{578}^{25}$ being $0.000 \pm 0.002^\circ$. An ORD curve in ethanol indicated no rotation down to 220 nm. Optically pure methyl 3-methylpentanoate has $[\alpha]_{589}^{25} = \pm 7.57^\circ$ (neat).⁵ Thus, complete racemization had taken place during the coupling process, and no conclusion regarding the possible intervention of chemisorbed radicals can be drawn from this experiment. As stressed before,¹ only the positive establishment of a retention mechanism would be conclusive in this respect.

Experimental. (+)-2-Methylbutanoic acid. Potassium permanganate (144 g, 0.90 mol), water (1250 ml), benzene (300 ml), tetrabutylammonium bromide (15 g, 0.047 mol) and (-)-2-methyl-1-butanol was stirred vigorously for 24 h at room temperature. Then sodium pyrosulfite and sulfuric acid was added in small portions (the flask being immersed in an ice-bath) until a clear solution was obtained. The benzene layer was separated and the acidic aqueous phase extracted with three portions of benzene. The combined benzene extracts were evaporated and the residual oil dissolved in aqueous sodium carbonate. This solution was extracted with two portions of ether to remove neutral components. Acidification, ether extraction, and distillation gave (+)-2-methylbutanoic acid, b.p. 76–78 °C/15

mmHg (10.5 g, 34%), $[\alpha]_{578}^{25} = 18.2^\circ$ (neat; lit.⁶ $[\alpha]_{589}^{27} = 17.9^\circ$).

Mixed coupling of (+)-2-methylbutanoic acid and methyl hydrogen malonate. This reaction was carried out as described previously^{7,8} with (+)-2-methylbutanoic acid (18.6 g, 0.182 mol), methyl hydrogen malonate (7.2 g, 0.061 mol), methanol (100 ml), and potassium hydroxide (0.45 g, 0.008 mol). After electrolysis at 1.0 A for 10.5 h, water (400 ml) was added and the mixture extracted with pentane (2 × 200 ml). After drying with magnesium sulfate, the pentane was distilled off through a Vigreux column. The residual oil (6.0 g) was subjected to preparative GLC (6 m × 10 mm 20% SE-30 on Chromosorb W), pure methyl 3-methylpentanoate being collected in low yield (0.327 g, 4%). This sample showed $[\alpha]_{578}^{25} = 0.000 \pm 0.002^\circ$ (c 12.8, methanol).

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