The Kolbe Electrolytic Coupling of Ethylenic Carboxylic Acids

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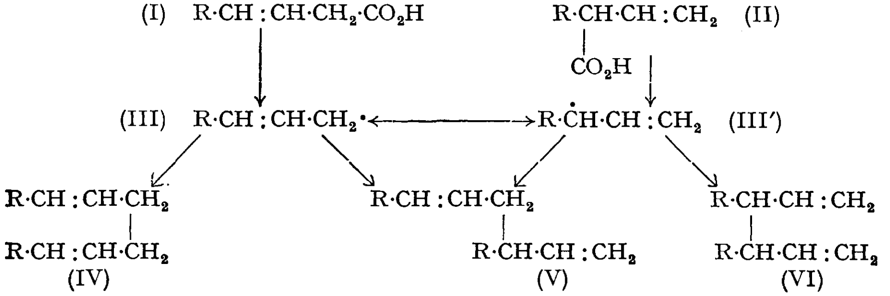
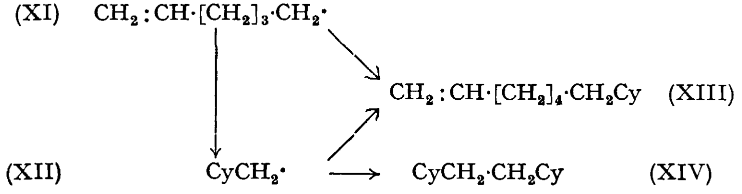
IT is reported[1] that $\alpha\beta$- and $\beta\gamma$-ethylenic acids fail to undergo the Kolbe anodic synthesis, whereas other ethylenic acids couple normally. Both reports require modification.

Electrolysis* of hex-3-enoic (I*a*) and oct-3-enoic acid (I*b*) afforded (35—40%) the mixture of hydrocarbons (IV–VI) to be expected from the three possible modes of dimerisation of the intermediate radicals (III*a* $\longleftrightarrow$ III′*a* and III *b* $\longleftrightarrow$ III′*b*). Separation by g.l.c. (squalane) of the products (IV*a*), (V*a*), and (VI*a*) formed from *cis*- and *trans*-hex-3-enoic acid (I*a*) in the approximate proportions 42 : 45 : 13, and analysis of each fraction by i.r. and g.l.c. ($AgNO_3$–polyethylene glycol), showed that the configuration of the double bond in the starting material was largely (>90%) retained in the products (IV) and (V). This supports the view that allylic radicals possess a defined stereochemistry.[2] The acid (II*b*) gave, as expected, all geometrical isomers of (IV*b*) and (V*b*). Electrolysis of acetic acid in the presence of butadiene[3] gave a mixture of C_{10}-hydrocarbons very similar in composition and stereochemistry to that obtained from *trans*-hex-3-enoic acid (I*a*). Evidently the methyl radicals first formed at the anode add to butadiene to give mainly the *trans*-allylic radical (III*a* $\longleftrightarrow$ III ′*a*). Vinylacetic acid afforded hexa-1,5-diene (*ca.* 15%) on electrolysis; cross coupling of $\beta\gamma$-ethylenic acids is also practicable, for ethyl oct-7-enoate was obtained from a mixture of vinylacetic acid and ethyl hydrogen adipate.



(*a*, R = Et; *b*, R = Bu)

$$\text{(VII)}\quad CH_2{:}CH\cdot CH_2\cdot[CH_2]_n\cdot CO_2H \longrightarrow \begin{cases} CH_2{:}CH\cdot CH_2\cdot[CH_2]_{2n}\cdot CH_2\cdot CH{:}CH_2 & \text{(VIII)} \\ CH_3\cdot CH{:}CH\cdot[CH_2]_{2n}\cdot CH_2\cdot CH{:}CH_2 & \text{(IX)} \\ CH_3\cdot CH{:}CH\cdot[CH_2]_{2n}\cdot CH{:}CH\cdot CH_3 & \text{(X)} \end{cases}$$



Cy = cyclopentyl

Electrolysis of *trans*-hex-4-enoic and *trans*-oct-6-enoic acid gave (*ca.* 35%) the *trans,trans*-dienes (X; n = 2 and 4), no isomers being detected. However, electrolysis of hex-5-enoic acid (VII; n = 2) and undec-10-enoic acid (VII; n = 7) gave the dienes (VIII; n = 2 and 7) contaminated with varying amounts of the positional isomers (IX;

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* Electrolyses were carried out in methanol by standard procedures.[1] Except where stated to the contrary, both electrodes were smooth platinum.

[1] Cf. B. C. L. Weedon, *Adv. Org. Chem.*, 1960, **1**, 1.

[2] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 1961, **83**, 3877.

$n = 2$ and 7) and (X; $n = 2$ and 7).[1] These by-products were not formed when a platinum anode and a mercury cathode were used, a procedure which prevents the electrolyte becoming alkaline.[4]

Electrolysis (Pt or Hg cathode) of hept-6-enoic acid (VII; $n = 3$) gave (*ca.* 40%) three isomers, (VIII; $n = 3$), (XIII), and (XIV) in the approximate proportions 42 : 37 : 21. Formation of the cyclopentyl compounds is noteworthy; it suggests that the intermediate radical (XI) cyclises to the primary (XII) rather than the secondary (cyclohexyl) radical.[5] The cyclisation is irreversible, since cyclopentylacetic acid (like cyclohexylacetic acid, and cyclohexanecarboxylic acid) undergoes Kolbe coupling without detectable ring opening. No cyclic product was obtained on electrolysis (Hg cathode) of oct-7-enoic acid (VII; $n = 4$). The implications of these results will be discussed in the full publication.

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[3] W. B. Smith and H. G. Gilde, *J. Amer. Chem. Soc.*, **1959, 81,** 5325.

[4] N. Dinh-Nguyen, *Acta Chem. Scand.*, 1958, **12**, 585.

[5] Cf. N. O. Brace, *J. Amer. Chem. Soc.*, 1964, **86**, 523; J. I. G. Cadogan, D. H. Hey, and A. Ong Soon Hock, *Chem. & Ind.*, 1964, 753.