Synthetic Studies starting from β-Cyanopropionaldehyde. II. The Syntheses of Aliphatic Aldehydes and ω-Aldehydic Acids

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The preceding paper in this series,[1] dealt with the Kolbe electrolysis of the ethylene acetal of β-formylpropionic acid (II) which had been derived from β-cyanopropionaldehyde (I). Electrolysis of this acetal acid gives the diethylene acetal of adipic dialdehyde (IX). Only a few examples of the Kolbe electrolysis of such aldehydic acids have been recorded[2,3] and the crossed electrolysis of aldehydic acids with ordinary carboxylic acids does not appear to have been described. The present paper involves a further extension of the Kolbe reaction as summarized in the accompanying flow sheet.

Electrolysis of the ethylene acetal of β-formylpropionic acid (II) in the presence of butyric acid was found to give the expected product, caproaldehyde ethylene acetal (III), in 25% yield.

The Kolbe electrolysis of the ethylene acetal (II) with succinic acid monobutyl ester

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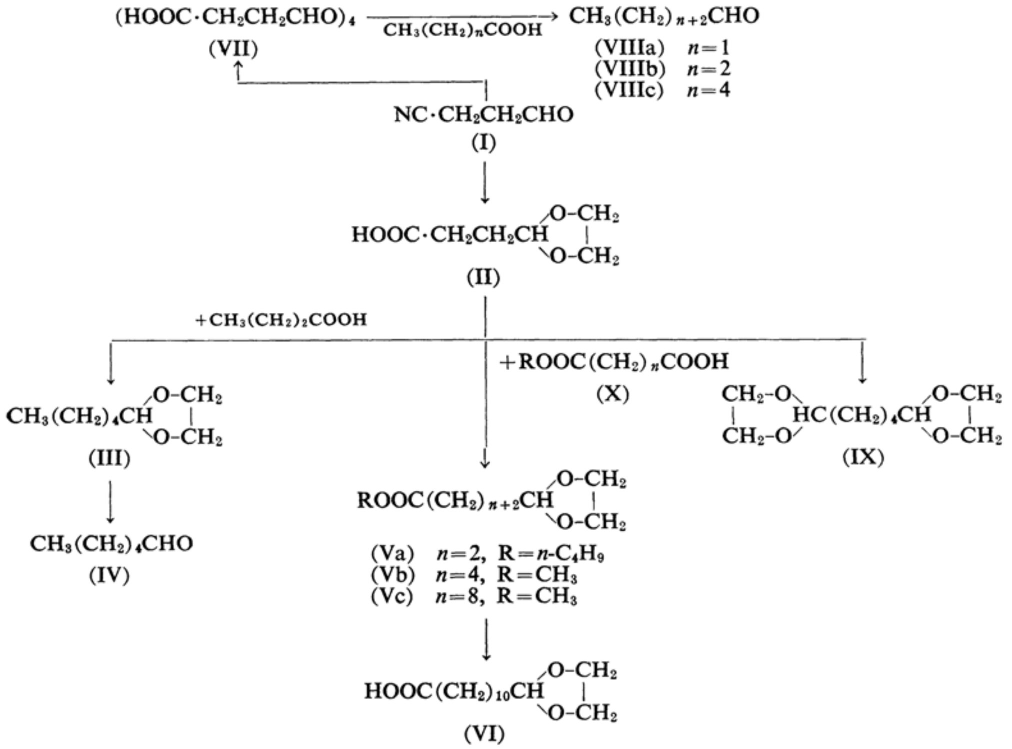
[1] S. Motoki, S. Satsumabayashi and I. Tajima, This Bulletin, 37, 646 (1964).

[2] M. Stoll and A. Rouvé, *Helv. Chim. Acta*, 20, 525 (1937).

[3] A. Wohl and H. Schweizer, *Ber.*, 39, 890 (1906).



gave the ethylene acetal of adipinaldehydic acid butyl ester (Va). When the monomethyl ester of succinic acid was used, the boiling points of the three products (adipinaldehydic acid methyl ester ethylene acetal, dimethyl adipate and adipic dialdehyde diethylene acetal) were too close to isolate the expected aldehydic acid by fractional distillation.

Similar electrolysis of a mixture of adipic acid monomethyl ester and an excess of the acetal (II) gave suberinaldehydic acid methyl ester ethylene acetal (Vb), whereas the compound II and an excess of monomethyl adipate led to a mixture which was difficult to separate. In the latter case, separation of Vb from the large amount of dimethyl sebacate formed was unsuccessful.

Crossed electrolysis of the acetal (II) with sebacic acid monomethyl ester afforded ω-formylundecylic acid methyl ester ethylene acetal (Vc) without any difficulties in separation.

As seen in Table I, the yields of ω-aldehydic acids are better in the presence of II excess of than in the presence of excess of monoesters. ω-Aldehydic acids are generally inaccessible compounds* the properties of which have rarely been described in the literature⁴⁾, so these electrolytic reactions starting from β-cyanopropionaldehyde may provide a new convenient synthetic route.

On the other hand, the cyclic tetramer (VII)⁵⁾ of β-formylpropionic acid has recently been prepared by the hydrolysis of β-cyanopropionaldehyde tetramer. Since the tetramer (VII) is more easily accessible than the previously reported β-formylpropionic acid ethylene acetal¹⁾ and is inert to oxidation, its possible usefulness in a Kolbe reaction was examined.

Attempted electrolysis of the tetramer itself turned out to be unsuccessful, but the tetramer underwent a normal Kolbe reaction in the presence of fatty acids to give the corresponding aldehydes in relatively good yields; the results are summarized in Table II. In general, it is known that the Kolbe reaction of a polybasic acid results in olefine formation or in evolution of oxygen at the anode, rather than in the formation of a coupling product. As VII can be regarded formally as a polybasic acid, the results obtained here seem to be of much interest.

Experimental

Materials. — β-Formylpropionic acid ethylene acetal (II) was obtained by hydrolysis of β-cyanopropionaldehyde ethylene acetal as reported in the

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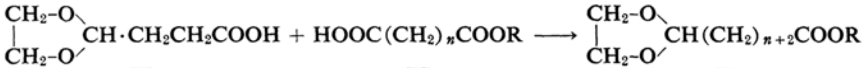
* ω-Formylundecylic acid is a new compound.

4) F. C. Pennington, W. D. Celmer, W. M. McLamore, V. V. Bogert and I. A. Solomons, *J. Am. Chem. Soc.*, **75**, 112 (1953).

5) J. Kato, T. Komatsu, T. Ito, H. Wakamatsu and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 548 (1962).

TABLE I



$$\begin{matrix}CH_2\text{-}O\diagdown\\ |\qquad\quad CH\cdot CH_2CH_2COOH\\ CH_2\text{-}O\diagup\end{matrix} + HOOC(CH_2)_nCOOR \longrightarrow \begin{matrix}CH_2\text{-}O\diagdown\\ |\qquad\quad CH(CH_2)_{n+2}COOR\\ CH_2\text{-}O\diagup\end{matrix}$$

(II) (X) (V)

	n	R	B. p.	M. p.	Yield, %	Molar ratio II : X
Va	2	*n*-C_4H_9	110—113°C/1 mmHg	Liquid	26.2	1 : 3
Vb	4	CH_3	115—116°C/2 mmHg	Liquid	40.5	3 : 1
Vc	8	CH_3	140—142°C/1 mmHg	26—27°C	23.1	1 : 3
					42.5	3 : 1

	Molecular formula	Analysis		2,4-Dinitrophenyl hydrazone*		
				M. p.	Analysis	
		Calcd.	Found		Calcd.	Found
Va	$C_{12}H_{22}O_4$	C: 62.58 H: 9.63	C: 62.40 H: 9.77	78°C orange yellow needles	C: 52.45 H: 6.05 N: 15.29	C: 52.27 H: 6.29 N: 15.50
Vb	$C_{11}H_{20}O_4$	C: 61.09 H: 9.32	C: 61.08 H: 9.48	86—87°C orange yellow needles	C: 51.13 H: 5.72 N: 15.90	C: 51.19 H: 6.18 N: 16.12
Vc	$C_{15}H_{28}O_4$	C: 66.14 H: 10.36	C: 66.42 H: 10.57	72°C orange yellow needles	C: 55.87 H: 6.91 N: 13.72	C: 56.32 H: 7.18 N: 13.95

* Treatment of the acetal ester (V) with ethanolic solution of 2,4-dinitrophenylhydrazine in the usual manner precipitated the 2,4-dinitrophenylhydrazone of the corresponding aldehyde ester gradually.

TABLE II

$$(HOOC\cdot CH_2CH_2CHO)_4 + CH_3(CH_2)_nCOOH \longrightarrow CH_3(CH_2)_{n+2}CHO$$

(VII) (VIII)

	n	B. p.	Yield*		2,4-Dinitrophenylhydrazone		
					M. p.	Analysis	
			g.	%	°C	Calcd.	Found
VIIIa	1	101—102°C	8.2	47.5	105	N: 21.04	N: 21.11
VIIIb	2	131—132°C	8.3	43.8	103	N: 19.99	N: 19.74
VIIIc	4	58—59°C/9 mmHg	10.8	42.1	106	N: 18.17	N: 18.31

* Based on the β-formylpropionic acid tetramer (VII).

previous paper.1) Monoesters of succinic, adipic and sebacic acid were prepared by the method given in Org. Syn.6) Succinic acid monobutyl ester, b. p. 136—137°C/3 mmHg. Adipic acid monomethyl ester, b. p. 162°C/10 mmHg. Sebacic acid monomethyl ester, b. p. 170—174°C/4 mmHg, m. p. 40°C.

Apparatus. — Electrolysis was carried out with the apparatus previously described.1)

***n*-Caproaldehyde Ethylene Acetal (III).**—Twenty grams (0.137 mol.) of II and 35 g. of butyric acid (0.4 mol.) were electrolyzed in 130 ml. of methanol containing 3.1 g. of potassium hydroxide until the electrolyte became slightly alkaline. At the end of the electrolysis the solvent was removed and the residue was washed with water, extracted with ether and dried over anhydrous sodium sulfate. Fractional distillation of the extract gave 5 g. of III, b. p. 78—80°C/34 mmHg, yield 25.4%. Found: C, 66.39; H, 11.41. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18%.

III was mixed with the same amount of 3% hydrochloric acid and refluxed for one hour. After hydrolysis, the organic layer was extracted with ether and dried over anhydrous sodium sulfate. By distillation caproaldehyde (IV) was obtained. B. p. 130 — 131°C. 2,4 - Dinitrophenylhydrazone, m. p. 106°C.

Found: C, 51.12; H, 6.09; N, 20.03. Calcd. for $C_{12}H_{16}O_4N_4$: C, 51.42; H, 5.75; N, 19.99%.

Adipinaldehydic Acid Butyl Ester Ethylene Acetal (Va), Suberinaldehydic Acid Methyl Ester Ethylene Acetal (Vb) and ω-Formylundecylic Acid Methyl Ester Ethylene Acetal (Vc). — A mixture of II and the monoester of the dibasic acid was electrolyzed in methanol, to which sufficient potassium hydroxide had been added to neutralize about 10% of the total acid. At the end of the electrolysis, the solvent was removed and the residue

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6) S. Swann, R. Oehler and R. J. Buswell, "Organic Syntheses," Coll. Vol. II, 276 (1943).

was washed with water, extracted with ether and dried. Fractional distillation gave the results shown in Table I.

ω-Formylundecylic Acid Ethylene Acetal (VI). — Ten grams of Vc was saponified by refluxing for 3 hr. with 20 ml. of a 50% methanolic solution containing 2 g. of sodium hydroxide. Methanol was then removed by distillation and the aqueous solution was acidified to pH 3 with dilute hydrochloric acid. The crude product which precipitated was recrystallized from 50% aqueous methanol to give 7.7 g. of pure VI, m. p. 73—75°C, yield 81.1%.

Found: C, 65.19; H, 10.28. Calcd. for $C_{14}H_{26}O_4$: C, 65.08; H, 10.14%.

***n*-Valeraldehyde (VIIIa), *n*-Caproaldehyde (VIIIb) and *n*-Caprylaldehyde (VIIIc).** — Twenty grams of β-formylpropionic acid tetramer (VII) and 0.6 mol. of a fatty acid were electrolyzed in 130 ml. of methanol containing 4,5 g. of potassium hydroxide. At the end of the electrolysis, the solvent was removed and the residue was directly hydrolyzed by refluxing with 20 ml. of 5% sulfuric acid for 3 hr. The oily product which separated was taken up in ether and dried over anhydrous sodium sulfate. Distillation of the extract gave the results shown in Table II.

Summary

Electrolysis of the ethylene acetal of β-formylpropionic acid with butyric acid gave caproaldehyde ethylene acetal as a result of crossed coupling. Crossed electrolysis with monoesters of succinic, adipic and sebacic acid were then studied. The expected products, adipinaldehydic, suberinal dehydic and ω-formylundecylic acid, were obtained as their ethylene acetal ester respectively. As ω-aldehydic acids are usually inaccessible compounds, these electrolytic reactions may provide a new convenient synthetic route.

Furthermore, it has been found that the tetramer of β-formylpropionic acid underwent the normal electrolytic reaction in the presence of fatty acids and the corresponding aliphatic aldehydes were obtained in relatively good yields.

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