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The Coupling Mode of Propargyl Undecynoate in a Cupric Acetate Monohydrate-Pyridine System

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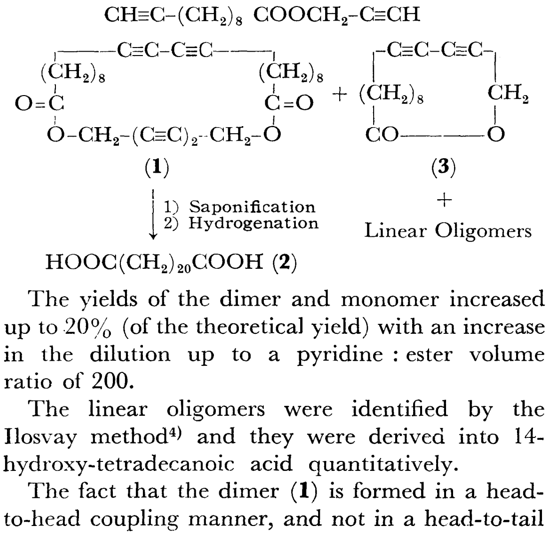
It is well known that α,ω-diyne compounds are oxidatively coupled and that cyclic compounds containing α,γ-diyne units are formed in cupurous chloride-ammonia water[1] and cupric acetate-pyridine systems.[2]

However, the coupling mode of diyne esters into cyclic oligomers —whether diynes undergo the coupling in a head-to-head or in a tail-to-head manner— has not yet been established.

In the oxidative coupling reaction of propargyl undecynoate in a cupric acetate monohydrate-pyridine system,[3] we have found that, among the possible cyclic oligomers, the dimer results only from a head-to-head coupling reaction, and that linear oligomers are given in a head-to-tail coupling reaction. The structure of the dimer was identified according to the following scheme:



The yields of the dimer and monomer increased up to 20% (of the theoretical yield) with an increase in the dilution up to a pyridine : ester volume ratio of 200.

The linear oligomers were identified by the Ilosvay method[4] and they were derived into 14-hydroxy-tetradecanoic acid quantitatively.

The fact that the dimer (**1**) is formed in a head-to-head coupling manner, and not in a head-to-tail manner, can be explained by considering that, according to the Dale rule[5] concerning the conformational stability of macrocyclic compounds, the dimer (**1**), which has a strain-free conformation, can exist more stably than the other possible dimer, formed in a head-to-tail coupling manner.

The different formation modes of the cyclic dimer and the linear oligomer still remain to be elucidated.

Experimental[*1]

Propargyl Undecynoate. This was prepared by the esterification method of Black and Weedon[6]; bp 128—130°C/2 mmHg: d_{20}^{20} 0.9442; n_{D}^{20} 1.4624.

Oxidative Coupling of Propargyl Undecynoate. Into a mixture of cupric acetate monohydrate (30 g, 0.15 mol) and pyridine (1.4 *l*), a solution of the propargyl undecynoate (5 g, 0.023 mol) in 100 m*l* of pyridine was stirred, drop by drop, at 55—60°C over a 3-hr period. The reaction mixture was concentrated to *ca.* 300 m*l* at 55—60°C under a pressure of 20—30 mmHg and then cooled. Seven hundred m*l* of an aqueous solution of 15% hydrochloric acid previously cooled with ice were then added to the concentrated solution. The resulting solution was extracted with ether (100 m*l* × 5). The ethereal solution was washed with 200 m*l* of an aqueous solution of 5% sodium carbonate and dried over Na_2SO_4. By the removal of the ether from the solution, an oily product (4.8 g) was obtained.

Separation of Products. The product showed three spots, with R_f values of 0.0, 0.47, and 0.77, by t.l.c. on a silica-gel layer (thickness, 0.25 mm) with a mixed

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[1] F. Sondheimer and Y. Amiel, *J. Amer. Chem. Soc.*, **78**, 4178 (1956).

[2] G. Eglinton and A. R. Galbraith, *Chem. Ind.* (London), **1956**, 737.

[3] F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Amer. Chem. Soc.*, **81**, 4600 (1959).

[4] L. Ilosvay, *Ber.*, **32**, 2697 (1899).

[5] J. Dale and A. J. Habert, *J. Chem. Soc.*, **1963**, 73.

[*1] The infrared (IR) spectra were obtained with a Nihon-Bunko IR-spectrometer, Model IR-S. The ultraviolet (UV) spectra were taken in ethanol with a Hitachi spectrometer, EPS-2. The nuclear magnetic resonance (NMR) spectra were determined in carbon tetrachloride and acetone at 60 Mc with a Nihon-Denshi. NMR spectrometer, JMN C-60. The chemical shifts are described in values relative to tetramethylsilane as the internal standard. The multiplicity of signals is indicated in abbreviated form; *s* for singlet, and *m* for multiplet. The molecular weight was measured in methyl ethyl ketone with a vapor-pressure osomometer, Model 301-A (Mechrolab, Inc.). The silica-gel layers used for the thin-layer chromatography(t.l.c.) were made from Silica Rider (silica-gel with 12—14% calcium sulfate, purchased from Daiichi Pure Chemicals) and were activated at 105°C for 1.5 hr.

[6] H. K. Black and B. C. L. Weedon, *J. Chem. Soc.*, **1953**, 1785.

solvent of *n*-hexane and ether (7 : 3 v/v).

A suspension of silica-gel (100—200 mesh, 250 g) in *n*-hexane was poured in a tube (2.4 cm in diameter and 1200 cm long). Then, a solution of the product (4.8 g) in *n*-hexane was passed through the column and subsequently eluted with *n*-hexane - ether (7 : 3 v/v, 1.5 *l*). The effluent was divided into 25 m*l* × 60 fractions using an auto-fraction collector. The elution speed was 100 m*l* per hour. Products with R_f value of 0.77 and 0.47 appeared in the fractions of Nos. 20—25 and Nos. 36—40 respectively; each of them gave 0.95 or 0.99 g of a white solid after the evaporation of the solvent *in vacuo*. A product with an R_f value of 0.0 remained in the column. After the elution, the silica-gel column was extracted with ether and then with acetone in a Soxhlet apparatus. Thus, by the removal of the solvent from the extract, ether- and acetone-soluble portions were obtained in yields of 2.4 g and 0.3 g respectively.

Identification. In order to collect a sufficient amount of aliquot for analysis, the above-described procedures were repeated twice within the limits of experimental error.

Cyclic Compounds Dimer (1). The dimer crystals had a melting point of 94.5—95.5°C. The IR spectrum, $\nu_{\max}$ (KBr); 2190, 2280($-C\equiv C-C\equiv C-$), and 1745 ($>C=O$) cm^{-1}. The UV spectrum, $\lambda_{\max}$ (CH_3OH) mμ (ε): 214(1272), 222(868), 233(1047), 245(1058), 258 (628), 267(185), 284(115). The NMR spectrum, τ (CCl_4): 5.25 (s, $-C\equiv C-C\equiv C-CH_2-O-$), 7.65 (m, $-CH_2-C-O$), 8.51 (m, $-CH_2-$). The saponification value was 256.9 (Calcd 256.8). Found: C, 76.94; H, 8.26%. Calcd for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31%. The dimer (**1**) (a 1-g portion of the dimer separated by column chromatography) was saponified with 10 m*l* of an ethanolic 0.5N potassium hydroxide solution. The resultant solution was acidified with an aqueous solution of 10% hydrochloric acid, and then extracted with ether (20 m*l* × 5). The ethereal solution was dried over Na_2SO_4 and then evaporated to give white crystals (1.2 g) as a residue. The crystals were hydrogenated in ethyl acetate (50 m*l*) at room temperature over 5% Pd-on-charcoal (100 mg) to give docosanedioic acid (**2**) (mp 126°C; acid value, 302.8 (theoretical value 302.7)), the identity of which was confirmed by observing no depression of the melting point when it was mixed with an authentic sample prepared from methyl undecynoate by the McCrae method,[7] further, the crystals were examined by t.l.c. (thickness of silica-gel layer, 0.25 mm; developing solvent, a mixture of *n*-hexane, ether and acetic acid (50 : 40 : 1 v/v); the chromatogram, after being sprayed with an aqueous sulfuric acid solution (1 : 1), was heated at 150°C for 30 min); they exhibited only one spot with the R_f value of 0.42 of docosanedioic acid, and not the spot with the R_f value of 0.24 of 14-hydroxytetradecanoic acid.

Monomer (3). The lactone (**3**) (1.0 g, 0.0045 mol) was recrystallized twice from *n*-hexane (5 m*l*) to give white crystals (500 mg); mp 41°C. The IR spectrum, $\nu_{\max}$ (KBr): 2140, 2240($-C\equiv C-C\equiv C-$), and 1750 ($>C=O$) cm^{-1}; the UV spectrum, $\lambda_{\max}$ (CH_3OH) mμ (ε): 219(897), 232(684), 245(624), 258(659), 273(601): the NMR spectrum, τ(CCl_4): 5.25(s, $-C\equiv C-C\equiv C-CH_2-O-$), 7.65(m, $-CH_2-C=O$), 8.51(m, $-CH_2-$). The saponification value was 257.0 (Calcd 256.8). Found: C, 76.76: H, 8.36%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

The crystals (200 mg) were hydrogenated over a 5% Pd-on-charcoal catalyst (50 mg) in ethyl acetate (50 m*l*) to yield cyclo-tetradecanolide (mp 28°C), the identity of which was confirmed by comparison with the IR spectrum and gaschromatogram of an authentic, commercially-available sample.

Linear Oligomer. A solution of a 0.3-g portion of the combined ether and acetone-soluble fraction in 40 m*l* of a mixed solvent of acetone-ether was shaken with a solution of the Ilosvay reagent,[4] consisting of cuprous chloride (1 g), ammonium carbonate (5 g), 28% ammonia water (5 m*l*), and water (20 m*l*). The precipitates thus formed were filtered off. The evaporation of the oily layer separated from the filtrate gave no product, indicating no contamination of cyclic oligomers in the products.

Upon the t.l.c. of the product obtained by the hydrolysis, followed by hydrogenation over the Pd-on-charcoal of the linear oligomer, only one spot, with a R_f value of 0.24, appeared; we may thus conclude that the linear oligomer is formed by a coupling of the esters only in a head-to-tail manner.

Moreover, the ether-soluble portion (2.3 g) was saponified with 50 m*l* of an ethanolic 1N potassium hydroxide solution. The resulting solution was acidified with an aqueous solution of 10% hydrochloric acid, and then extracted with ether (20 m*l* × 4). The product (2.3 g) obtained by the removal of the solvent from the ether solution dried over Na_2SO_4 was hydrogenated at 10 kg/cm^2 of hydrogen over Pd-on-charcoal; 14-hydroxytetradecanoic acid, mp 95°C, was thus obtained in a 95% yield.

The IR spectrum, $\nu_{\max}$ (KBr): 3300($HC\equiv C-$), 2280 and 2150($-C\equiv C-C\equiv C-$) and 1745($>C=O$) cm^{-1}. The NMR spectrum, τ(acetone): 5.05(s, $-C\equiv C-C\equiv C-CH_2-O-$), 7.65(m, $-CH_2-C=O$) and 8.65(m, $-(CH_2)_8-$).

These spectral data were in good agreement with those of the linear oligomer prepared by the Sondheimer method.[8]

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[7] W. McCrae, *Tetrahedron*, **20**, 1773 (1964).

[8] F. Sondheimer and Y. Amiel, *J. Amer. Chem. Soc.*, **81**, 6301 (1959).