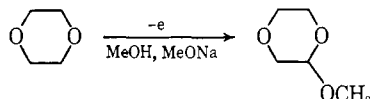


Organic Synthesis by Electrolysis. V. Anodic Alkoxylation of Aliphatic Saturated Ethers

Sir:

Previously, the anodic alkoxylation reaction of aliphatic saturated ethers has been suggested in the study on the anodic reaction of cyclohexyl isocyanide.¹ In the present study, we wish to report some results on this novel alkoxylation reaction. In the preliminary study, the electrolysis of a methanolic solution of dioxane using sodium methoxide as a supporting electrolyte gave monomethoxylated dioxane as the anodic product.



Accordingly, the anodic methoxylation of some aliphatic saturated ethers was studied in preparative scale, and the results are shown in Table I in which the reactions were not necessarily carried out under the optimum reaction condition. The products were isolated by gas chromatographic techniques and identified by spectroscopic methods and elemental analysis.

other hand, both cationic and radical mechanisms have been suggested to rationalize the anodic side chain substitution reactions. Moreover, a radical mechanism has been proposed for the allylic substitution reaction.

Two mechanisms would be conceivable for the present alkoxylation reaction of ethers. The first step of each mechanism could be classified as follows: (1) anodic oxidation of the ether to a cationic species, and (2) hydrogen abstraction from the α position of the ether by an anodically generated radical.

The controlled potential electrolysis of dioxane at 1.65 V vs. sce in methanol using ammonium nitrate as a supporting electrolyte gave the expected methoxylated dioxane in a reasonable yield, while the substitution of ammonium nitrate by lithium perchlorate did not give the product. Although the oxidation potentials of dioxane and the supporting electrolytes are uncertain, ammonium nitrate is known to be oxidized at low potential.⁴ Moreover, the fact that the electrolysis of III or IV in methanol did not give any product suggests that ethers are not oxidized under the present reaction condition.

Thus, the experimental results imply that the ether was methoxylated by mechanism 2 and the radical

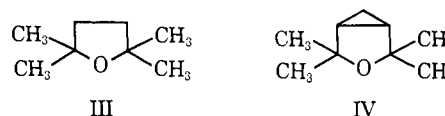
Table I. Anodic Methoxylation of Ethers

Ether ^d	Product	Supporting electrolyte ^d	Current, ^a A	Time, hr	Yield, %
		CH ₃ ONa	1.5	30	28
		NH ₄ NO ₃	0.5	22	9.7
		Salt ^b	0.5	22	10.3
		CH ₃ ONa	1.5	12	21
C ₂ H ₅ (CH ₂)CHOCH ₂	C ₂ H ₅ (CH ₂)C(OCH ₃) ₂				
		CH ₃ ONa	1.0	27.5	26
(CH ₃) ₂ CHOCH(CH ₃) ₂	(CH ₃) ₂ CHOC(CH ₃) ₂ OCH ₃	CH ₃ ONa	1.5	17.5	10
		CH ₃ ONa	1.0	16	24.3
		CH ₃ ONa	1.0	15	16.3
		NH ₄ NO ₃	0.5	26	3.9
		CH ₃ ONa	1.0	15	8.5

^a Terminal voltages were 18~25 V. ^b Tetraethylammonium *p*-toluenesulfonate. ^c Ethanol was used as the solvent. ^d Concentrations of ethers and supporting electrolytes were 2.5 M.

Anodic acetoxylation, cyanidation, methoxylation, and isocyanation of both nuclear and side chains of aromatic compounds have been studied by several workers,² and some allylic substitution reactions have been reported in the previous study.³ Most of the nuclear substitution reactions have been explained by a cationic mechanism where the aromatic substrate was oxidized to a cationic species at the anode. On the

which abstracts hydrogen from the α position of the ether is generated from the supporting electrolyte. The



substitution reactions of aliphatic saturated ethers by radical mechanism (Kharasch reaction), in which the

- (1) T. Shono and Y. Matsumura, *J. Am. Chem. Soc.*, **90**, 5937 (1968).
 (2) V. D. Parker and B. E. Burgert, *Tetrahedron Letters*, 3341 (1968), and references cited therein.
 (3) T. Shono and T. Kōsaka, *ibid.*, 6207 (1968).

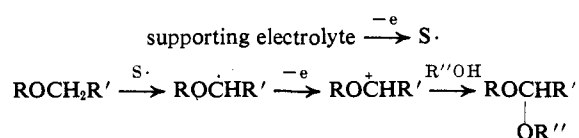
- (4) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **88**, 4657 (1966).

oxidation process of the radical to the cation is involved, have been reported by several workers.⁵ Relative reactivities of some typical ethers in the methoxylation by Kharasch reaction and in anodic methoxylation are indicated in Table II.

Table II. Relative Reactivities (per α Hydrogen)

	Tetra- Dioxane	hydropropan ethyl ether	<i>t</i> -Butyl ethyl ether
Kharasch reaction	1	1.9	4.4
Anodic reaction	1	2	4

Although the establishment of the reaction mechanism in the present study seems rather premature, this anodic alkoxylation reaction may involve the abstraction of α hydrogen from ethers by anodically generated radicals and subsequent anodic oxidation of the ethereal radicals to cations. Further study on the



reaction mechanism is currently in progress.

Acknowledgment. We are extremely grateful to Professor R. Oda of Kyoto University for his kind encouragement.

(5) G. Sosnovsky and S. Lawesson, *Angew. Chem.*, **76**, 218 (1964); S. Lawesson and C. Berglund, *Arkiv Kemi*, **17**, 465 (1961).

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Received March 12, 1969

The [1ⁿ]Ferrocenophanes

Sir:

The reaction of a transition metal halide with a hydrocarbon dianion made up of two linked cyclopentadienyl anions might be anticipated to give a polymeric metallocene in which hydrocarbon rings and metal atoms alternate,¹ a process we call polygemination.² Up until now only two characterized polymers have been made by this method, and both are only dimers.^{1,3} We have in this way now prepared a trimer, tetramer, and pentamer, the first well-characterized polygeminate oligomers larger than dimers.⁴

Their precursor is the easily prepared⁵ bis(cyclopentadienyl)methane (I). When the hydrocarbon I is added to a tetrahydrofuran solution of *n*-butyllithium in hexane at 0° and after 10 min poured onto anhydrous ferrous chloride, a dark reaction product forms from which has been isolated thus far the dimer (II), [1.1]-

(1) (a) T. J. Katz, V. Balogh, and J. Schulman, *J. Am. Chem. Soc.*, **90**, 734 (1968); (b) T. J. Katz and J. Schulman, *ibid.*, **86**, 3169 (1964).

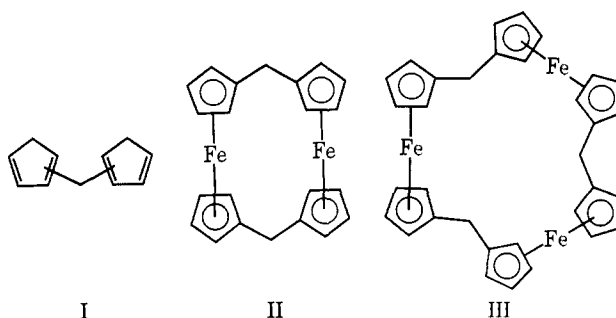
(2) Latin *geminus*, twin.

(3) A. Lüttringhaus and W. Kullick, *Makromol. Chem.*, **44-46**, 669 (1961).

(4) A polymeric material, not characterized, but believed to be larger than a dimer was described by Lüttringhaus and Kullick.³

(5) It is made in a few related ways, such as by the reaction of sodium cyclopentadienide with methylene chloride: H. Schaltegger, M. Neuenchwander, and D. Meuche, *Helv. Chim. Acta*, **48**, 955 (1965).

ferrocenophane,⁶ the trimer (III), [1.1.1]ferrocenophane, the corresponding tetramer, [1.1.1.1]ferrocenophane, and the pentamer, [1.1.1.1.1]ferrocenophane.⁷ The first three, which are crystalline, analyze correctly for



carbon, hydrogen, and iron; the fourth, which is still amorphous, does not quite.

The structures of these ferrocenophanes are proven by their spectroscopic properties. The nmr spectra (Table I) of all exhibit resonances attributable to the ring and methylene protons in the required intensity ratio of 4:1. That the difference in chemical shifts of the ring protons^{6,10} would decrease with increased polymerization and vanish as in 1,1'-dimethylferrocene¹¹ or diferrocenylmethane¹² is confirmed. The infrared spectra of the ferrocenophanes are remarkably similar. The mass spectra exhibit the required parent peaks: in the dimer at *m/e* 396, in the trimer at 594, in the tetramer at 792, and in the pentamer at 990.

Table I. Proton Nmr Spectra of the [1ⁿ]Ferrocenophanes^a

<i>n</i>	Ring proton chemical shifts	Methylene proton chemical shifts	Measured intensities
2	5.77 (t), 5.96 (t) ^b	6.53 (s) ^b	2.0:2.0:1.0
3	5.99 (t), 6.06 (t) ^b	6.42 (s) ^b	3.93:1.07
4	5.97 (s) ^c	6.30 (s) ^c	3.99:1.01
5	6.12 (s) ^b	6.76 (s) ^b	4.05:0.95

^a s = singlet; t = approximately a distorted triplet. ^b In CS₂ (room temperature). ^c In toluene-*d*₆ at 100°

The dimer, recrystallized from acetone, melts (evacuated capillary) at 245–248°,¹³ and the trimer, from carbon disulfide, at 278.5–280.5°; the tetramer, from toluene, darkens at *ca.* 265° and partially melts at *ca.*

(6) Previously made from ferrocene itself: W. E. Watts, *J. Organometal. Chem.*, **10**, 191 (1967).

(7) The notation³ becomes cumbersome for large oligomers, and a simple variant would be to use the notation [1ⁿ]ferrocenophane, where the superscript denotes the degree of polymerization. The next member would thus be [1⁶]ferrocenophane, read as sexiferrocenophane. An alternative notation for the quinqueferrocenophane is, of course, [1-11]-ferrocenophane.⁹

(8) (a) B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964; (b) W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

(9) Tally marks, used by primitive man: "World Book Encyclopedia," Vol. 14; Field Enterprises Educational Corp., Chicago, Ill., 1968, p 452.

(10) (a) J. S. McKechnie, B. Bersted, I. C. Paul, and W. E. Watts, *J. Organometal. Chem.*, **8**, P29 (1967); (b) W. E. Watts, *J. Am. Chem. Soc.*, **88**, 855 (1966); (c) T. H. Barr and W. E. Watts, *Tetrahedron*, **24**, 6111 (1968).

(11) K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Am. Chem. Soc.*, **85**, 970 (1963).

(12) E. W. Neuse and K. Koda, *Bull. Chem. Soc. Jap.*, **39**, 1502 (1966).

(13) Lit.⁶ mp 254–256°