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THE ANODIC OXIDATION OF 1,3-DIENES[1)]

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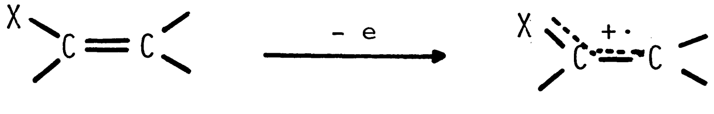
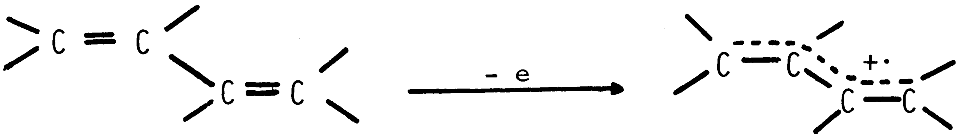
The anodic oxidation of isoprene, piperylene, cyclopentadiene, or 1,3-cyclohexadiene in methanol or acetic acid brought about mainly the nucleophilic 1,4-addition of the solvent molecule to the diene. On the other hand, 1,3-cyclooctadiene gave a considerable amount of the product substituted at the allylic position along with the addition product.

In the course of our studies on the anodic oxidation of a series of aliphatic compounds, it has been clarified that the anodic oxidation of an olefin is initiated by an electron transfer from the unsaturated bond to the anode[2)] and hence the lowering of the oxidation potential of the unsaturated system brought by introduction of an electron donating substituent such as acetoxy,[3)] alkoxy,[4)] or dialkylamino[5)] is desirable in the anodic reaction.



X : Electron donating group

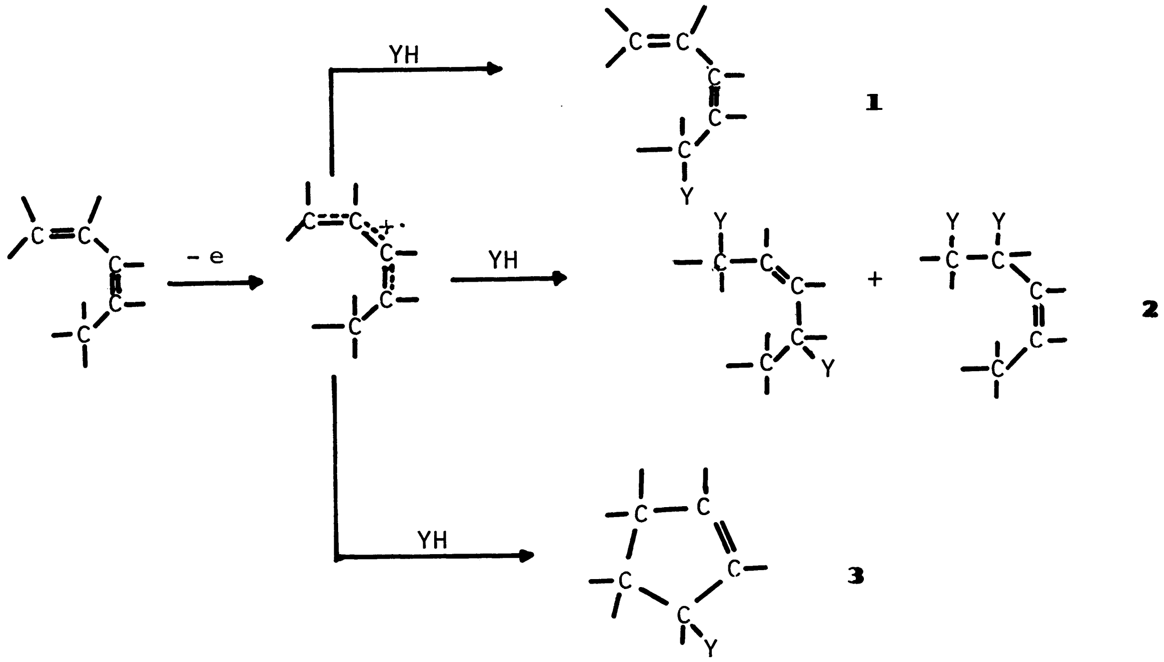
From this point of view, the anodic oxidation of some 1,3-dienes was studied with some expectation of its application to organic syntheses.



The electrooxidation of 1,3-cyclohexadiene in methanol was the only hitherto known reaction in which the 1,3-diene gave a small amount of a mixture of 1,2 and

1,4-addition products.[6)] Generally, three types of products, namely, a product substituted at the allylic position (type **1**), an oxidative addition product (type **2**), or an intramolecularly cyclized product (type **3**), may be yielded in the anodic oxidation of a 1,3-diene as shown in the Scheme I.

Scheme I.



The results obtained in anodic oxidations of isoprene, piperylene, cyclopentadiene, 1,3-cyclohexadiene and 1,3-cyclooctadiene in methanol or acetic acid are shown in Table 1. Excepting 1,3-cyclooctadiene, the oxidation of 1,3-dienes gave products of type **2** in which 1,4-addition was predominant. On the other hand, a considerable amount of type **1** product was yielded together with the product of type **2** in the reaction of 1,3-cyclooctadiene. Especially, the lower nucleophilicity of acetic acid than methanol might be one of the reasons of the increase in formation of the product substituted at the allylic position.[2)] Formation of the product of type **3** from the intermediate 2,4-cyclooctadienyl cation **4** was not detected in the present anodic reaction, whereas this cyclized product has usually been observed in the solvolytic reaction.[7)] This kind of

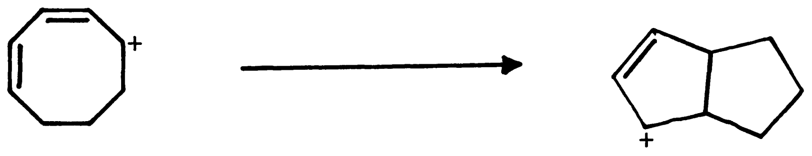


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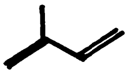
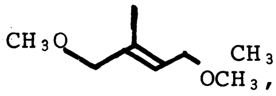
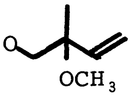
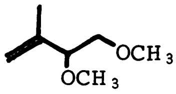
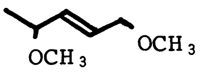
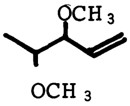
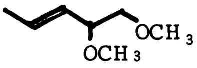
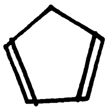
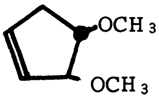
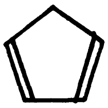
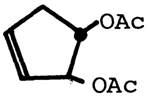
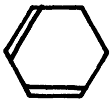
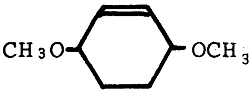
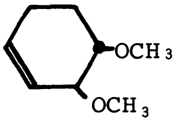
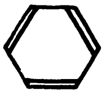
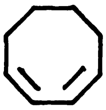
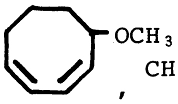
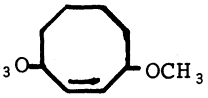
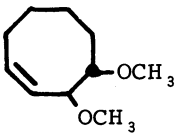
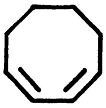
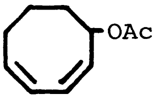
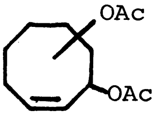
Table 1

1,3-Diene	Solvent	Anode potential (V. vs SCE)	Product(Current efficiency, %)
	CH_3OH	1.4 - 1.55	 (18.6),  (12.5),  (4.0)
	CH_3OH	1.35-1.5	 (42.5),  (14.7),  (11.0)
	CH_3OH	1.2 - 1.4	 (50.6)[a],  (6.1)
	CH_3COOH	1.7 - 1.8	 (45.0)[a],  (6.0)
	CH_3OH	1.0 - 1.2	 (47.2)[a],  (11.8),  (2.8)
	CH_3OH	1.3 - 1.5	 (23.5),  (41.0)[a],  (8.2)
	CH_3COOH	1.8 - 1.9	 (53.6),  (16.6)

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a) Equimolar mixture of trans and cis isomers.

inhibition for such an intramolecular reaction may be one of the characteristics of electrode reactions,8) which may take place at the heterogeneous interface of the solution and the electrode.

The predominant formation of 1,4-addition products from 1,3-dienes in moderate yields would afford a considerable potentiality to organic syntheses. Especially, the facile introduction of acetoxy groups into 1,4-positions of cyclopentadiene would be a remarkable tool in the syntheses of some useful natural products containing cyclopentane structure such as rethrolones and jasmone.

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