

ELECTROCHEMICAL OXIDATION OF SOME
KETENE-S,S-ACETALS.

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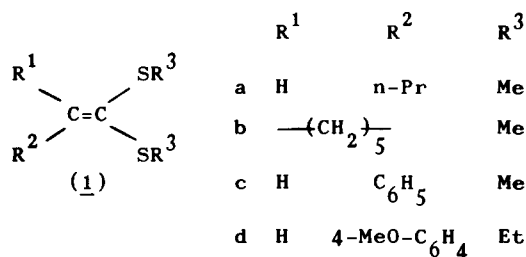
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Recebido em 1/7/87

Abstract: Electrochemical oxidation of ketene-S,S-acetals (1) under controlled potential in aqueous acetonitrile at a platinum anode yielded as main products thiolesters (2), α -thiolated-thiolesters (3), α -hydroxy-thiolesters (4) and dimers (5). In one case the corresponding monosulfoxide was isolated.

Ketene-S,S-acetals are valuable intermediates for organic synthesis.¹ Their hydrolysis products can be carboxylic acids, esters or thiolesters depending upon the experimental conditions. α -Heterosubstituted compounds are obtained under oxidative conditions.²

The anodic oxidation of vinyl sulfides in aqueous acetonitrile yielding α -thiolated aldehydes described by Yijima et al.,³ prompted us to study ketene-S,S-acetals under similar conditions as in these reactions α -thiolated thiolesters could be formed. We now report the preliminary results of these studies.



Cyclic voltammetry (Table 1) in acetonitrile shows that the first anodic peaks of the compounds (1) are irreversible and the

potentials depend upon their structures.

The decrease of the oxidation potentials suggests an increased stability of the cation radicals intermediates due to electro-nic effects.⁴

Table 1. Electrochemical oxidation potentials^a

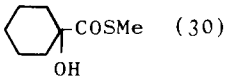
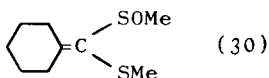
Compound	E _p ^a /V
(1a)	1.65
(1b)	1.58
(1c)	1.55
(1d)	1.45

^a Pt bead anode; reference electrode Ag/AgI; MeCN/0.1M NaClO₄; scan rate 0.2Vs⁻¹

Preparative scale electrolysis, in a divided cell under controlled potential, were carried out in aqueous acetonitrile at a platinum plate anode. Product analysis (Table 2) reveals that main products are thiolesters (2), α -thiolated-thiolesters (3), α -hydroxy-thiolesters (4) and dimers (5). In the case of compound (1d) a keto-thiolester (7d) was isolated probably due to the oxidation of the corresponding hydroxy-derivative (4). It is noteworthy that only compound (1b) yielded the monosulfoxide (6b) which may be due to the lack of an hydrogen linked to the carbon-carbon double bond.

It seems to be clear that structural factors play an important role concerning the type and the distribution of products formed in the anodic oxidation of ketene-S,S-acetals. Further investigations are being undertaken.

Table 2. Controlled-potential electrolysis of ketene-S,S-acetals (1)^a

Compound	Products (% yield) ^b
(1a)	(2a) n-PrCH ₂ COSMe (7) (3a) n-PrCH(SMe)COSMe (13) (4a) n-PrCH(OH)COSMe (7) (5a) (n-PrCH(COSMe) ₂) ₂ (47) ^c
(1b)	(4b)  (30) (6b)  (30)
(1c)	(2c) C ₆ H ₅ CH ₂ COSMe (25) (3c) C ₆ H ₅ CH(SMe)COSMe (25)
(1d)	(3d) 4-MeO-C ₆ H ₄ CH(SET)COSEt (17) (7d) 4-MeO-C ₆ H ₄ COCOSEt (17) (5d) (4-MeO-C ₆ H ₄ CHCOSEt) ₂ (33) ^c

^a Electrolysis conditions: MeCN-H₂O 9:1 (v/v)/0.2M NaClO₄; Pt foil anode (4cm²); 1.5 - 1.8 Fmol⁻¹; [1] = 0.10 - 0.30M; solid NaHCO₃ (2 equiv.) added to the anodic compartment;

^b Isolated by column chromatography after aqueous work-up;

^c Mixture of meso and d,l forms.

Acknowledgments: The authors thank FINEP for financial support and CNPq for a scholarship for one of us (M.P.).

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MÉTODOS ALTERNATIVOS DE FORMAÇÃO DE COMPLEXOS DE DITIOCARBAMATO

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Recebido em 1/7/87

ABSTRACT: ALTERNATIVE METHODS FOR THE FORMATION OF DITHIOCARBAMATE COMPLEXES

Two new methods for the formation of dithiocarbamate complexes are proposed: the direct reaction of CS₂ over amin-copper complexes and the transference of dithiocarbamate groups from dithiocarbamatophosphines to transition metal ions. The possible mechanisms for these reactions are discussed.

INTRODUÇÃO

Há grande interesse na química de ditio-carbamato-complexos, principalmente devido à sua potencial ação fungicida e anti-tumor. Os ligantes ditio-carbamato são em geral preparados pela ação de CS₂