



Fig. 1. A reciprocal plot of the initial rate at the "pre-steady" state against concentration of the substrate.

The solution of LADH ($4 \mu\text{N}$) + NAD^+ ($100 \mu\text{M}$) was rapidly mixed with various concentrations of ethanol (○) or benzylalcohol (●) in 0.1 M glycine-NaOH buffer, pH 9.0 at 23°C.

summarized in Table 1. The "burst" of the oxidation of ER by acetaldehyde or benzaldehyde corresponded to the stoi-

Table 1. Rate constants of the LADH reactions at pH 9.0.

Rate constants	Ethanol	Benzylalcohol
k_2' ($\mu\text{M}^{-1}\text{sec}^{-1}$)	0.0045	0.065
k_{-1}' (sec^{-1})	20	—
k_{-3} (sec^{-1})	100	6.4

chiometric formation of one mole of bound NAD^+ per one active site of LADH while the reduction of EO by ethanol or benzylalcohol corresponded to less than one mole of bound NADH per one active site of LADH. However, the stoichiometry of EO + alc as judged from the size of the "burst reaction" is rather uncertain, since the size of the "burst reaction" is quenched in the presence of large excess of alcohols. Our value $k_{-3} = 100 \text{ sec}^{-1}$ at pH 9 is in essential agreement with J. Shore's 130 sec^{-1} at pH 7.³

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Electrolytic Cleavage of β -Ketosulfones

II.* Cleavage of Some α -Substituted β -Ketosulfones

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In Part I of the present series,¹ the electrolytic reductive cleavage of some β -ketosulfones to give ketones was described. Of the eight different β -ketosulfones studied in Part I,¹ all except one that had an α -methyl group, were unsubstituted in the α -position. In order to investigate the generality of the reaction, the work has now been extended to include some further β -ketosulfones carrying various substituents in the α -position, namely, methyl, ethyl, benzyl, and carbethoxymethyl. The substituted β -ketosulfones have been prepared by the ion pair extraction technique.²

The electrolytic reductive cleavage of the substituted compounds has been carried out using the same conditions as before¹ (mercury cathode, aqueous dimethylformamide, pH 7.8, undivided cell). In the work-up of the benzyl ketones, however, ether instead of pentane was used. This demanded more washing with water in order to

* For Part I, see Ref. 1.

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Table 1. Reduction potentials and reaction yields for compounds $R^1COCH(R^2)SO_2R^3$.

R ¹	Substituents		Potential V vs. SCE	% Yield, ketone		% Yield, dimer
	R ²	R ³		Crude	Pure	
C ₆ H ₅	CH ₃	CH ₃	-1.50	—	51	40 (crude)
»	»	C ₂ H ₅	-1.50	—	57	37 »
»	»	CH ₂ C ₆ H ₅	-1.50	—	69	30 »
»	»	CH ₂ COOC ₂ H ₅	-1.50	88	61	2.5 (pure)
p-CH ₃ OC ₆ H ₄	C ₆ H ₅	CH ₃	-1.50	82	43	—
»	»	C ₂ H ₅	-1.50	—	74	—
»	»	CH ₂ C ₆ H ₅	-1.50	—	69	—
»	»	CH ₂ COOC ₂ H ₅	-1.60	—	72	—
n-C ₆ H ₁₃	»	CH ₃	-2.00	89	65	—
»	»	C ₂ H ₅	-2.05	85	65	—
»	»	CH ₂ C ₆ H ₅	-1.80	91	72	—
»	»	CH ₂ COOC ₂ H ₅	-2.00	92	75 ^a	—
CH ₂ C ₆ H ₅	»	CH ₃	-1.80	93	63	—
»	»	C ₂ H ₅	-1.90	84	64	—
»	»	CH ₂ C ₆ H ₅	-1.80	95	69 ^b	—
»	»	CH ₂ COOC ₂ H ₅	-1.75	94	66 ^c	—

^a This compound is believed to be new. Boiling point 76°C/0.5 mm.

^b Melting point 41°C. Beilsteins Handbuch der organischen Chemie describes this compound as an oil at room temperature.

^c This compound is believed to be new. Boiling point 92°C/0.03 mm.

remove the dimethylformamide than when pentane was used.

The reduction potential and percentage yield of products for all compounds are given in Table 1. In the runs with β -ketosulfones at a cathode potential more negative than -1.80 V vs. SCE, it was observed that the current yield was less than 100 % (2F/mole). This is probably due to some electrode reaction of the supporting electrolyte. The average time for a run was about 4 h.

In Part I of this series,¹ the occurrence of γ -diketones as by-products upon electrolysis of β -ketosulfones was reported. These diketones are presumably formed *via* free radical dimerization.² We were therefore not surprised to observe "dimer" formation with some of the present compounds as well. It was impossible to obtain some of the dimers formed in a pure state from the reaction mixtures (see Table 1). However, the NMR spectra of the crude products indicate that they are mixtures of *meso*- and *DL*-forms. One of the dimers could be obtained crystallized. This is a mixture of *meso*- and *DL*-forms according to NMR.

As seen from Table 1, the yields in some cases decrease markedly upon purification.

The reason is simply that the compounds char badly upon distillation. For preparative purposes, however, it is unnecessary to distill the compounds since they are relatively pure immediately upon extraction from the electrolyte (95–98 % by GLC and NMR).

The melting points of the compounds (with three exceptions, see Table I) were in accordance with those reported in the literature. The NMR spectra of all compounds were in complete accordance with the proposed structures. No further analyses were therefore considered necessary.

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