

Dehydrogenation of Fatty Acids to the Corresponding $\alpha\beta$ -Unsaturated Derivatives

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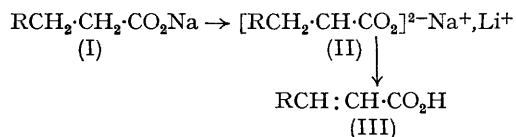
Summary The α -anions of linear fatty acids can be dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone to give exclusively the (*E*)- $\alpha\beta$ -unsaturated derivatives.

RECENTLY it has been reported that α -metallated carboxylic acids may be oxidized with oxygen alone to the α -hydroxyacids,¹ and with oxygen in the presence of copper(II) salts to the corresponding dimers.²

We report here that the α -anions of linear fatty acids (II) prepared from (I) by treatment with $\text{Pr}^1_2\text{NLi}^3$ in tetrahydrofuran-hexamethylphosphoramide undergo a ready dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone⁴ (DDQ) to the corresponding (*E*)- $\alpha\beta$ -unsaturated acids (III).

No reaction was observed on treating the fatty acids or their sodium salts with DDQ under a variety of conditions. An important feature of this new dehydrogenation reaction

is its complete stereoselectivity leading exclusively to the (*E*)-isomer.



R = Me, Pr^n , $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_9\text{H}_{19}$

In a typical experimental procedure a solution of 10 mmol of DDQ in dry benzene was added dropwise over 15 min to a stirred solution of 10 mmol of (II), obtained by treating the sodium salt of the fatty acid with an equimolar amount of Pr^1_2NLi in tetrahydrofuran containing 30 mmol of hexamethylphosphoramide under argon. The reaction mixture was heated under reflux for 3 h and worked-up.

The acid fraction was esterified by diazomethane and the ester was separated from DDQ by extraction with hexane or distillation under vacuum.

The reaction seems to be general for linear fatty acids. Butanoic, hexanoic, octanoic, and dodecanoic acid give the corresponding $\alpha\beta$ -unsaturated acids (III) in a yield of about 30% as determined by g.l.c. Since a considerable amount of unchanged starting material was always recovered, the actual yield of the fatty acid converted was correspondingly higher.

Low yields of $\alpha\beta$ -unsaturated acids have also been obtained on substituting DDQ with 10-phenylisoalloxazine. This new dehydrogenation procedure, which passes through the oxidation of a carbanionoidic species, could represent a model of the flavin-promoted enzymatic dehydrogenation of fatty acids.

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