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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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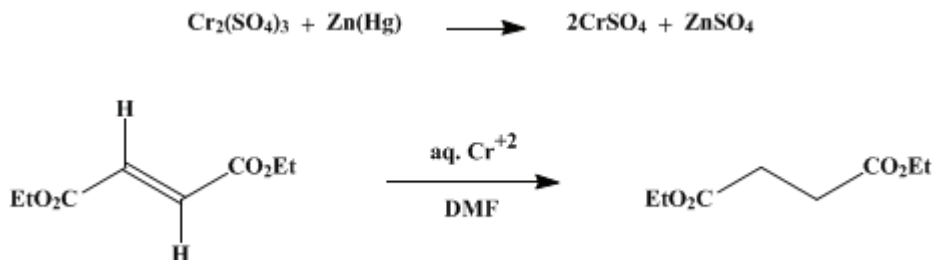
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Organic Syntheses, Coll. Vol. 5, p.993 (1973); Vol. 49, p.98 (1969).

REDUCTION OF CONJUGATED ALKENES WITH CHROMIUM (II) SULFATE: DIETHYL SUCCINATE

[Succinic acid, diethyl ester]



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1. Procedure

A. *Chromium(II) sulfate solution.* A 3-l., three-necked flask fitted with a gastight mechanical stirrer and nitrogen inlet and outlet stopcocks is charged with 300 g. (ca. 0.55 mole) of hydrated chromium(III) sulfate (Note 1), 2 l. of distilled water, 75 g. (1.15 g. atoms) of mossy zinc (Note 2), and 4.0 ml. (54 g., 0.27 g. atom) of mercury (Note 3). After the flask has been flushed with nitrogen for 30 minutes, the mixture is warmed in a water bath to about 80° (Note 4) with stirring for 30 minutes under a nitrogen atmosphere to initiate reaction. Then the mixture is stirred at room temperature under a nitrogen atmosphere for an additional 30 hours, at which time the originally green reaction mixture has been converted to a clear, deep blue solution. While a nitrogen atmosphere is maintained over the reaction solution, the mechanical stirrer is removed and replaced with a nitrogen outlet (Note 5). The third neck of the reaction flask is fitted with a short adapter closed with a rubber septum (Note 6).

The solution is standardized by withdrawing 5.0-ml. aliquots into a hypodermic syringe (Note 6) fitted with a relatively wide-bore needle and flushed with nitrogen before use. The aliquots are quenched by injecting them into 10 ml. of aqueous 1M ferric chloride solution in an Erlenmeyer flask under a nitrogen atmosphere. After 2 minutes the flow of nitrogen is stopped, and the resulting solution is diluted with 50 ml. of water and titrated with 0.1N ceric sulfate to the ferrous ion-phenanthroline end point (Note 7). Solutions prepared in this fashion are usually 0.55M in chromium(II) species (Note 8) and are stable for years, if they are protected from reaction with oxygen.

B. *Reduction of diethyl fumarate.* A 1-l. three-necked flask is equipped with a magnetic stirring bar, an addition funnel with a pressure-equalizing tube, a stopcock connected to a mercury trap, and a rubber septum (Note 9). The addition funnel is charged with a solution of 13.87 g. (0.080 mole) of diethyl fumarate (Note 10) in 137 ml. of dimethylformamide (Note 11). A nitrogen line is connected to the top of the addition funnel and the system is thoroughly flushed with nitrogen (Note 12). With a hypodermic syringe, 318 ml. (0.175 mole) of the previously described 0.55M chromium(II) sulfate solution (0.175 mole) is added to the reaction flask through the rubber septum. After the stirrer has been started, the diethyl fumarate solution is added rapidly. The solution immediately turns green and the reduction is complete in 10 minutes (Note 13). The resulting solution is diluted with 100 ml. of water and 30 g. of ammonium sulfate is added. The mixture is shaken with four 150-ml. portions of ether, and the combined ether extracts are washed with three 50-ml. portions of water and then dried over magnesium sulfate. After the ether has been removed by distillation through a 60-cm. Vigreux column, the residual liquid is distilled through a short Vigreux column to separate 12.4–13.2 g. (88–94%) of diethyl succinate (Note 14); b.p. 129° (44 mm), *n*_D²⁵ 1.4194.

2. Notes

1. Mallinckrodt analytical reagent, [chromium\(III\) sulfate](#) crystals, $\text{Cr}_2(\text{SO}_4)_3(\text{H}_2\text{O})_x$, were employed. Repeated preparations with this substance have indicated its average formula weight to be 542.
2. Either Baker and Adamson or Mallinckrodt reagent grades of mossy [zinc](#) have been used interchangeably.
3. Distilled [mercury](#) was employed.
4. Warming is not always essential, but a more rapid reduction occurs routinely if the reaction is initiated by warming. In some cases a longer heating period may be required.
5. In order to maintain an oxygen-free atmosphere over the solution, it is essential that all standard taper joints be adequately lubricated and that the various joints be held together with rubber bands, wire, or springs.
6. Transfers are conveniently made by maintaining a slightly positive [nitrogen](#) pressure in the reaction vessel before the aliquots are removed and using an adapter consisting of a standard taper joint sealed to a wide-bore stopcock. The short length of glass tubing above the stopcock is fitted with a securely fastened rubber septum. The rubber septum above the stopcock is pierced with the hypodermic syringe, and then the stopcock is opened to place a slightly positive [nitrogen](#) pressure in the small septum-capped chamber. This procedure forces the plunger of the syringe out and sweeps any remaining [oxygen](#) from the syringe. The syringe plunger is replaced and the syringe needle is pushed below the surface of the solution. The internal [nitrogen](#) pressure forces liquid into the syringe until slightly more than the desired amount is obtained. The syringe is then withdrawn and inverted and the excess solution is expelled into an absorbent paper. Finally, the syringe containing the desired volume of solution is emptied into a reaction vessel under a [nitrogen](#) atmosphere.
7. The preparation of the indicator solution is described by Kolthoff and Sandell.² The red-brown to green end point is easily observed.
8. Solutions of higher or lower concentrations can be prepared by adjusting the amounts of reagents.
9. Though unnecessary for this reduction, it is more usually convenient for [chromium\(II\) sulfate](#) reductions to fit the rubber septum to a stopcock adapter of the type described in (Note 6).
10. [Diethyl fumarate](#) was purchased from either Eastman Organic Chemicals, Inc., or Aldrich Chemical Company and used without purification.
11. Baker reagent grade [dimethylformamide](#) was used without further purification.
12. The submitters recommend that the system be flushed with a slow stream of [nitrogen](#) for 30 minutes.
13. The kinetics of this reduction have been reported.³ The reaction is easily followed by withdrawing aliquots and analyzing them for [chromium\(II\)](#) content.
14. [Diethyl succinate](#) is the sole product of the reduction. The yield reflects the efficiency of the workup. The distilled product gives a single sharp peak on gas chromatography employing a column packed with Carbowax 20M suspended on Chromosorb P. On this column the checkers found the retention times of [diethyl fumarate](#) and [diethyl succinate](#) to be 38.8 minutes and 43.6 minutes, respectively.

3. Discussion

Aqueous solutions of [chromium\(II\) sulfate](#) have been prepared from [chromium\(III\) sulfate](#) by reduction with [zinc](#) powder³ and from [potassium dichromate](#) by reduction with amalgamated zinc and [sulfuric acid](#).⁴ Solid [chromium\(II\) sulfate pentahydrate](#) can be obtained from the reaction of highly purified [chromium](#) metal with concentrated [sulfuric acid](#).⁵ The present procedure is especially simple since it avoids filtration of [zinc powder](#) and avoids the acid present in the dichromate reduction.

[Chromium\(II\) sulfate](#) is a versatile reagent for the mild reduction of a variety of bonds. Thus aqueous [dimethylformamide](#) solutions of this reagent at room temperature couple benzylic halides,^{3,6} reduce aliphatic monohalides to alkanes,⁶ convert vicinal dihalides to olefins,⁷ convert geminal halides to carbenoids,⁸ reduce acetylenes to *trans*-olefins,⁹ and reduce α,β -unsaturated esters, acids, and nitriles to the corresponding saturated derivatives.¹⁰ These conditions also reduce aldehydes to alcohols.⁷

The reduction of [diethyl fumarate](#) described in this preparation illustrates the mildness of the reaction conditions for the reduction of acetylenes and α,β -unsaturated esters, acids, and nitriles.

The reduction of [diethyl fumarate](#) to [diethyl succinate](#) has also been effected with [diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate](#)¹¹ and by catalytic hydrogenation.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 821](#)

References and Notes

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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

amalgamated zinc

[sulfuric acid \(7664-93-9\)](#)

[ether \(60-29-7\)](#)

[oxygen \(7782-44-7\)](#)

[nitrogen \(7727-37-9\)](#)

[mercury \(7439-97-6\)](#)

[zinc,
zinc powder \(7440-66-6\)](#)

[ferric chloride \(7705-08-0\)](#)

[diethyl fumarate \(623-91-6\)](#)

[ammonium sulfate \(7783-20-2\)](#)

[diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate \(1149-23-1\)](#)

[potassium dichromate \(7778-50-9\)](#)

[chromium\(III\) sulfate \(15244-38-9\)](#)

magnesium sulfate (7487-88-9)

chromium (7440-47-3)

dimethylformamide (68-12-2)

Diethyl succinate,
Succinic acid, diethyl ester (123-25-1)

ceric sulfate (13590-82-4)

CHROMIUM(II) SULFATE

chromium(II)

chromium(II) sulfate pentahydrate