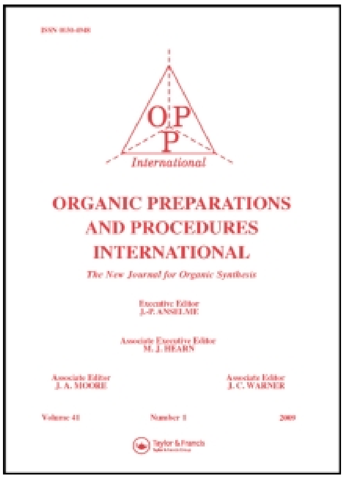

ORGANIC PREPARATIONS AND PROCEDURES INTERNATIONAL

The New Journal for Organic Synthesis

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Volume 41 Number 1 2009

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED PREPARATION OF DIETHYL 1,4-DIHYDROXY-CYCLOHEXA-1,4-DIENE-2,5-DICARBOXYLATE

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To cite this Article Moore, J. A.(1972) 'AN IMPROVED PREPARATION OF DIETHYL 1,4-DIHYDROXY-CYCLOHEXA-1,4-DIENE-2,5-DICARBOXYLATE', Organic Preparations and Procedures International, 4: 1, 31 — 34

To link to this Article: DOI: 10.1080/00304947209356796

URL: http://dx.doi.org/10.1080/00304947209356796

ORGANIC PREPARATIONS AND PROCEDURES INT. 4(1), 31-34 (1972)

AN IMPROVED PREPARATION OF DIETHYL 1,4-DIHYDROXY-CYCLOHEXA-1,4-DIENE-2,5-DICARBOXYLATE[1]

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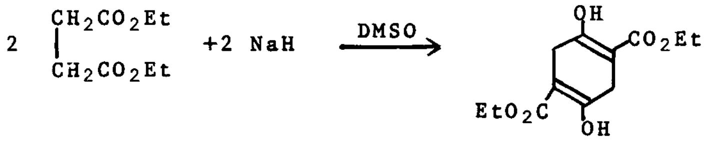

The product of the base-catalyzed self condensation of diethyl succinate was first isolated by Fehling,[2] but it was not characterized. The structure of this compound has been contested over the years and it has been considered both as a diketone and a bis-enol. Nmr spectroscopy unequivocally supports the bis-enol form under normal conditions (on the nmr time-scale).

The condensation has been carried out using alkali metals, alkoxides, ammonia and secondary amines.[3] The use of NaH in diethyl ether has been recommended for this reaction, but no experimental details were given.[4] In our hands, those procedures using alkoxides in alcohol or inert solvents suffer from the fact that, for reasonably short reaction times (i.e., up to 6 hr.), yields were unsatisfactory. In addition, the thick, difficultly stirred reaction mixture complicates the procedure. Although the use of NaH in ether improved the yield of product,[5] it also required extended reaction times. The volatile and flammable nature of ether makes its use for reactions requiring long periods of reflux a problem and a potential hazard.

We now report that the use of NaH in dry dimethyl sulfoxide (DMSO)[6] as solvent increases the yield of pure product to better than an average of 80%, in only 3 hr. at moderate temperatures.

EXPERIMENTAL[7]

The reaction should be done in a good hood because dimethyl sulfide is evolved during the reaction and subsequent neutralization. DMSO, 250 ml, (freshly opened bottle) was added to NaH-mineral oil dispersion, 48g (1.0 mole), (nominally 50% in NaH, Callery Chemical Co.) in a 2ℓ,[8] 3-necked flask fitted with a nitrogen inlet tube and thermometer (y-shaped adapter), mechanical stirrer and a vented dropping funnel protected with a calcium chloride drying tube. The apparatus had been previously flushed with N_2 while being heated with a Bunsen flame and had been allowed to cool under a N_2 atmosphere. The suspension was stirred vigorously at room temperature for 30 min. and had taken on a yellowish cast. The flask was immersed in an ice-water bath and when the temperature had reached about 10°C, commercial diethyl succinate (Aldrich), 87g, (0.5 mole) was added at a drop rate of about 2 drops/sec., so that the addition was completed in about 30 min. Stirring was continued for about 45 min., when the suspension thickened to a yellow granular mass. Another 125 ml of DMSO was added to the reaction mixture and the ice water bath was removed. The suspension was stirred for 10 min. and another 125 ml of DMSO was added. The temperature of the suspension was 25°. Stirring was continued at ambient temperature for 30 min. and then at 60° (water bath) for another 30 min. At the end of this time the tan suspension was cooled in an ice-bath and cautiously neutralized with 6N hydrochloric acid. The precipitated product was filtered and washed with water until the odor of HCl was no longer detectable. The greyish powder[9] obtained at this stage is contaminated with some mineral oil but is suitable for further reaction. If purification is deemed necessary, the crude product is stirred with cyclohexane, filtered, air-dried (54-58g, 85-90%, mp. 124-129°) and recrystallized from absolute ethanol or acetone to give pale yellow needles, 51-54g, 80-85%, mp. 130-131° (lit.[3c,4] 127-128°, 130-131°), IR (KBr) 3400 (OH), 1675, 1220 ($-\overset{O}{\overset{\|}{C}}-O-$), 1640 ($>C=C<^{O-}$), 1320, 1060, 790 (split band) cm^{-1}; UV (EtOH) λ_{max} = 237 mμ; fluorescence $\lambda_{max} = 433^{EtOH}_{m\mu}$ (λ_{ex} = 255 mμ); NMR ($CDCl_3$) δ 1.25 (t, 6 CH_3), δ 3.17 (s, 4 $-CH_2-$, ring), δ 4.29 (q, 4 $-CH_2-$ ester), δ 12.3 (s, 2, OH).

ACKNOWLEDGEMENT: The author acknowledges his indebtedness to Dr. F.C. Wedler and Mr. P. Sheffer for the fluorescence spectra and to Mr. J.E. Kelly for the nmr spectra.

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1. In its long history this compound has developed an impressive list of aliases: diethylsuccinylosuccinate; diethyl 1,4-cyclohexanedione-2,5-dicarboxylate; 2,5-dicarboethoxy cyclohexane-1,4-dione; succinosuccinic acid diethyl ester; diethyl 2,5-dihydro-3,6-dihydroxyterephthalate; 1,4-diethoxy carbonyl-2,5-dihydroxy-1,4-cyclohexadiene; 2,5-dioxo-1,4-cyclohexanedicarboxylic acid diethyl ester.

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7. Melting points are uncorrected and were obtained with a Thermolyne melting point apparatus. Infrared spectra were recorded as KBr pellets with a Perkin Elmer Model 137 Infracord. Ultraviolet spectra were recorded on a Unicam Model Sp.800A spectrophotometer. Fluorescence spectra were recorded on a Baird Atomic Spectrophotometer Model SF-1. Nuclear magnetic resonance spectra were recorded on a Varian Model T-60 spectrometer with tetramethyl silane as the internal standard.

8. The large reaction vessel is necessary for good temperature control and because of foaming.

9. It is imperative to exclude oxygen from the reaction mixture until the product has been precipitated. The appearance of a pronounced yellow color indicates that oxidation has occurred.

(Received December 6, 1971; in revised form January 29, 1972)