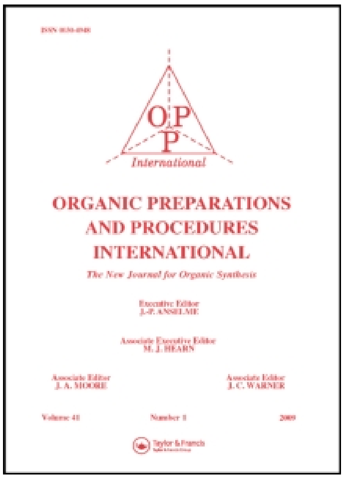

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A DRY MEDIUM SYNTHESIS OF 1-CYCLOHEXENE CARBOXALDEHYDE

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To cite this Article Hogg, J. L. , Goodwin, T. E. and Nave, D. W.(1978) 'A DRY MEDIUM SYNTHESIS OF 1-CYCLOHEXENE CARBOXALDEHYDE', Organic Preparations and Procedures International, 10: 1, 9 — 11
To link to this Article: DOI: 10.1080/00304947809354997
URL: http://dx.doi.org/10.1080/00304947809354997

ORGANIC PREPARATIONS AND PROCEDURES INT. 10(1), 9-11 (1978)

A DRY MEDIUM SYNTHESIS OF 1-CYCLOHEXENE CARBOXALDEHYDE

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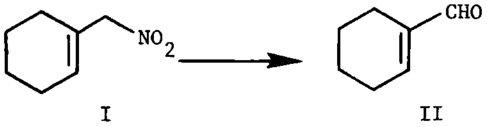
1-Cyclohexene carboxaldehyde (II) has found use as an intermediate for organic synthesis[1] and as the precursor for compounds of value in kinetic studies involving enzyme models.[2] Previous preparations have involved, inter alia, formylation of 1-lithiocyclohexene[3] (26%) and titanous ion-mediated hydrolysis of 1-nitromethylcyclohexene (I) (55%).[4] Keinan and Mazur[5] have recently reported a remarkable new procedure to effect the synthetically-valuable nitro to carbonyl conversion (i.e. the Nef reaction[6]). We now report the use of this "dry medium" technique for the facile conversion of 1-nitromethylcyclohexene (I) to 1-cyclohexene carboxaldehyde (II) in 82% yield using sodium methoxide-activated silica gel as both a reaction medium and a reagent. This yield was obtained from a 120 hrs exposure at ambient temperature, while a 4 hrs exposure at 80° decreased the yield to ∿ 40 percent. Adaptations of this procedure should be generally useful for the preparation of other 1-cycloalkene carboxaldehydes.



EXPERIMENTAL

Infrared spectra were measured with a Beckman Model IR-8 Grating Spectrometer. ^{1}H NMR spectra were recorded on dilute solutions in deuteriochloroform ($CDCl_3$) using tetramethylsilane (TMS) as internal standard on a Varian Model T-60 spectrometer. Boiling points are uncorrected.

1-Nitromethylcyclohexene (I).[7] This procedure is adapted from that of Eckstein, Sacha and Urbanski.[8,9] A stirring mixture of 70.4g (0.71 mole) of cyclohexanone, 112.0g (1.8 moles) of nitromethane, 8.0 ml of piperidine, and 300 ml of benzene was refluxed under a Dean-Stark trap for 16 hours. Solvent was distilled at atmospheric pressure and the residue was distilled to provide a 70% yield of 1-nitromethylcyclohexene (I) as a pale yellow liquid, bp. 49-52°/0.35-0.45 Torr; IR (neat film) 1552 and 1376 (s, NO_2), C-N stretch 930 (m), CNO bending 661 (s) cm^{-1}; nmr ($CDCl_3$) δ 1.62 (m, 4, methylenes), 2.05 (m, 4, allylic methylenes), 4.73 (s, 2, $-CH_2NO_2$), 5.83 (broad, s, 1, vinyl H).

Methoxide-activated Silica Gel.- This procedure is essentially that of Keinan and Mazur.[5] A solution of sodium methoxide in methanol (prepared from 2.3g (0.1g-atom) of sodium in 200 ml of anhydrous methanol) was added to 200g of dry silica gel (Baker Reagent; 60-200 mesh). Solvent was slowly removed on a rotary evaporator (water aspirator) and the residue dried for 12 hours at 250°. The dry reagent was stored in a sealed brown bottle.

1-Cyclohexene carboxaldehyde (II).- 1-Nitromethylcyclohexene (I), 1.0g (0.014 mole) was added dropwise to 100g of dry, methoxide-activated silica gel and thoroughly mixed by rotation. The mixture was placed in sealed brown bottles, allowed to remain undisturbed for 120 hrs at ambient temperature, then packed into a glass chromatographic column (8 by 30 cm) and eluted with 1 ℓ. of ether. Evaporation of the solvent and distillation of the orange residual liquid provided the desired aldehyde (II) as a colorless liquid (0.65g, 82%), bp. 68-72°/12 Torr; lit.[3] 72° /15 Torr ; IR (neat film) 2730 (m, aldehyde C-H), C=O 1685 (s), C=C 1645 (s) cm^{-1}. nmr ($CDCl_3$) δ 1.65 (m, 4, $-CH_2-$), 2.21 (m, 4, allylic-CH_2-), 6.66 (m, 1, vinyl H), 9.35 (s, 1, aldehyde H).

Acknowledgement.- We wish to thank the Robert A. Welch Foundation for financial support of this work and for the undergraduate scholarship provided for DWN.

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(Received August 29, 1977; in revised form October 25, 1977)