TABLE I

THE CATALYZED CONVERSION OF ISOCYANATES TO CARBODIIMIDES

| Metal Salt, Moles × $10^5$ | | Isocyanate, Moles | | Solvent,[a] Moles | Time, Hr. | $CO_2$, % | Carbodiimide, % |
|---|---|---|---|---|---|---|---|
| None | | NI[b] | 0.0415 | 0.325 | 43 | 2 | |
| Al[c] | 50.0 | NI | 0.0415 | 0.325 | 72 | 98 | 93[d] |
| Mn[e] | 174. | NI | 0.1590 | 0.325 | 157 | 92 | 90[d] |
| Fe[e] | 4.8 | NI | 0.0524 | 0.450 | 95 | 29 | |
| Co[e] | 8.0 | NI | 0.0673 | 0.325 | 48 | 4 | |
| Cu[e] | 11.9 | NI | 0.0478 | 0.325 | 165 | 12 | |
| Pb[e] | 131 | NI | 0.0249 | 0.405 | 46 | 11 | |
| Al[c] | 30.0 | MDI[f] | 0.0249 | 0.405 | 93 | 67 | 64[g] |
| Al[c,h] | 20.0 | MDI[f] | 0.0129 | 0.221 | 20 | 56 | 41[i] |
| DABCO[j] | 71.0 | NI | 0.041 | 0.024 | 19 | 0 | |

[a] Dried and distilled xylene mixture, b.p. 135–137°, used at reflux temperature under nitrogen. [b] 1-Naphthylisocyanate. [c] Aluminum isopropoxide, which must be freshly distilled. [d] Di-1-naphthylcarbodiimide, m.p. 89–90°. [e] Metal naphthenate solution in hydrocarbon solvent (Nuodex Corp.), dried before use; concentration calculated for metal ion. [f] Methylenebis(4-phenylisocyanate). [g] Product, 3.8 g., had strong carbodiimide band (4.75 μ) and bands characteristic of isocyanate (4.4 μ) and of isocyanate trimer (5.9 μ). [h] Solvent was dried and distilled tetralin in this case. [i] Product, 1.3 g., had strong band at 4.75 μ and weak bands at 4.4 μ and 5.9 μ. [j] 1,4-Diaza[2.2.2]bicyclooctane, Houdry Process Corp.

products. The *N,N'*-di-1-naphthylcarbodiimide[8] was a green oil that solidified on cooling to a tan solid. The solid carbodiimide was extracted with hot ether and the insoluble isocyanate trimer filtered off. Cooling of the ether filtrate gave the carbodiimide as white needles, m.p. 89–90°. The polymeric products [from methylenebis(4-phenylisocyanate)] were washed with ether or petroleum ether (b.p. 30–60°) before obtaining infrared spectra. The polymers were a mixture of materials soluble and insoluble in cold xylene. The insoluble portion was similar to the product reported by Dyer and Newborn,[9] whereas the soluble portion more closely corresponded to the recently reported low molecular weight polycarbodiimide-isocyanates.[10]

Although aluminum isopropoxide had the highest activity, manganese naphthenate was the preferred catalyst due to the formation of fewer by-products than with the naphthenate. The alcoholate gave products contaminated with isocyanate trimer and traces of isopropyl *N*-naphthylcarbamate.

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(8) A. Huhn, *Ber.*, **19**, 2405 (1886).

(9) E. Dyer and G. E. Newborn, *J. Am. Chem. Soc.*, **80**, 5495 (1958).

(10) P. Fischer and E. Meisert, Ger. Patent 1,092,007, Nov. 3, 1960.

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## Cyclohexanecarboxaldehyde from the Selective Hydrogenation of 3-Cyclohexene-1-carboxaldehyde

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Cyclohexanecarboxaldehyde has been prepared by many methods. However, the reported methods require a multistep synthesis or a single step synthesis under rather extreme conditions (*e.g.*, the oxo process). The selective hydrogenation of readily available 3-cyclohexene-1-carboxaldehyde (the Diels-Alder adduct of butadiene and acrolein) was reported by Heilbron *et al.*[1] However, their process involved slurrying the aldehyde with Raney nickel and then hydrogenating the "treated aldehyde" with a palladium on calcium carbonate catalyst. This method was recently repeated by Nazarov and Zaretskaya.[2]

We wish to report that 3-cyclohexene-1-carboxaldehyde may be selectively hydrogenated to cyclohexanecarboxaldehyde in 81% yield and 99.0% purity (gas chromatography) using commercially available 5% palladium on carbon catalyst (Baker and Co., Inc.) without a prior treatment as described by Heilbron *et al*,[1] provided one uses proper reaction conditions and a hydrogenation vessel with good agitation. A reaction temperature of 75–80° and a hydrogen pressure of 200 lb./in.$^2$ appeared to be the optimum conditions in our experiments. The hydrogenation stopped abruptly when an equimolar amount of hydrogen had been absorbed. Higher reaction temperatures gave increasingly higher amounts of cyclohexanemethanol. No solvents were used in this study and pressures in excess of 200 lb./in.$^2$ were not investigated.

This hydrogenation was carried out in a Parr Series 4500 medium pressure stirrer type pressure reaction apparatus. Hydrogenation in a rocker bomb was unsuccessful; the reaction rate was so slow at a reaction temperature of 75–80° and at a pressure of 200 lb./in.$^2$ that the method was impractical. The selectivity of hydrogenation in the rocker apparatus was decreased when the attempt was made to increase the rate of hydrogenation by increasing the reaction temperature.

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(1) I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).

(2) I. N. Nazarov and I. I. Zaretskaya, *Zhur. Obshcheĭ Khim.*. 27, 624 (1957), English translation.

Apparently the conditions of this selective hydrogenation of 3-cyclohexene-1-carboxaldehyde to cyclohexanecarboxylaldehyde are more critical than for the similar type of hydrogenation of the myrcene-methacrolein Diels-Alder adduct to the saturated aldehyde. Kitchens[3] was able to hydrogenate this adduct to the saturated aldehyde in the presence of palladium on carbon catalyst in a rocker bomb and reported a satisfactory hydrogenation temperature range of 50–150° and a preferred temperature of 100°.

## EXPERIMENTAL[4]

*Hydrogenation of 3-cyclohexene-1-carboxaldehyde to cyclohexanecarboxaldehyde.* Into a Parr Series 4500 1-l. medium pressure stirrer-type, electrically heated pressure reaction apparatus was placed 330 g. (3.00 moles) of 3-cyclohexene-1-carboxaldehyde (prepared by the Diels-Alder reaction of butadiene and acrolein), b.p. 54–56° (15–16 mm.), $n_D^{25}$ 1.4691, 98.6% pure *via* gas chromatography, and 5 g. of 5% palladium on carbon catalyst (Baker and Co., Inc.). The compound was hydrogenated at a temperature of 75–80° and at 200 lb./in.$^2$ of hydrogen pressure. The hydrogenation was interrupted whenever the exothermic heat of reaction carried the reaction temperature above 80° and then resumed when the heat had dissipated and the temperature was below 75°. The hydrogenation was complete in 8 hr. under these experimental conditions. The reaction time was reduced to 2.5 hr. by using a special heating mantle equipped with cooling tubes for circulation of water to dissipate the heat. The catalyst was collected on a Büchner funnel and the crude product was distilled through an 18-in. Vigreux column under reduced pressure to give 272 g. (81%) of center cut cyclohexanecarboxaldehyde, 99.0% pure (gas chromatography), b.p. 57–59° (22–24 mm.), $n_D^{25}$ 1.4490, $n_D^{20}$ 1.4514 (lit.[2] b.p. 62–63° (25 mm.), $n_D^{20}$ 1.4512).

The semicarbazone of the product was recrystallized twice from ethanol-water mixtures to give fine white needles, m.p. 170–171° (lit. melting points range from 166–167°[2] to 178°[5]). The 2,4-dinitrophenylhydrazone crystallized from an ethanol–ethyl acetate mixture as bright yellow plates, m.p. 171–173° (lit.[2] m.p. 172°).

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(3) G. C. Kitchens, U. S. Patent **2,842,598** (July 8, 1958).

(4) Boiling points and melting points are uncorrected. Gas chromatography analyses were performed by E. O. Camehl of The Dow Chemical Co. Spectroscopy Service Laboratory.

(5) A. Tillotson and B. Houston, *J. Am. Chem. Soc.*, **73**, 221 (1951).

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## Reaction of Dimethyl Sulfoxide with Grignard Reagents

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There have been several reports of the reaction of dimethyl sulfoxide with various reagents. The reaction with thionyl chloride or acid chlorides yields chlorinated methyl sulfides,[1,2] and the reaction with acid anhydrides yields acyloxymethyl sulfide.[3,4]

Dimethyl sulfoxide is also characterized as an oxidizing agent, yielding aldehydes from some halides such as substituted benzyl bromides or higher alkyl halides,[5,6] and converting organic sulfides to the corresponding sulfoxides.[7]

The reaction of phenylmagnesium bromide and methyl *p*-tolyl sulfoxide has been reported by Potter[8] to give a tolyl benzyl sulfide in which the phenyl group from the Grignard reagent has replaced a hydrogen of the methyl group in the sulfoxide.

It is expected that the same reaction may occur with a simple sulfoxide such as dimethyl sulfoxide (DMSO). In the present work such reactions were carried out between dimethyl sulfoxide and ten Grignard reagents. Sulfides were obtained in all cases.

$$H_3CSOCH_3 + RMgX \longrightarrow H_3CSCH_2{-}R + Mg(OH)X$$

R = alkyl, aralkyl, and aryl group.

As described in the Experimental, when alkyl Grignard reagents (R = ethyl, *n*-propyl, and *n*-butyl) were used, considerable amounts of olefin were evolved during the reaction.

The reaction of dimethyl sulfoxide with benzylmagnesium chloride did not yield the expected methyl $\beta$-phenylethyl sulfide but methyl *o*-methylbenzyl sulfide, indicating a rearrangement.

In the case of aryl and aralkyl halides (R = phenyl, *o*-tolyl, *p*-tolyl, *p*-anisyl, *p*-bromophenyl, and $\beta$-phenylethyl), the resulting sulfides had their methylthiomethyl group in the position of the halogen of the parent halides. The reaction product from *o*-tolyl-magnesium bromide and dimethyl sulfoxide—*i.e.*, methyl *o*-methyl-benzyl sulfide was identical with the product obtained from benzylmagnesium chloride and dimethyl sulfoxide.

The yield of sulfide obtained from the reaction of dimethyl sulfoxide with Grignard reagent of *p*-dibromobenzene was low, because in anhydrous ether the conversion of this halide to the Grignard reagent was low. Therefore, this sulfide could be identified only in the form of the corresponding sulfone.

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(1) S. A. Heininger and J. Dazzi, *Chem. Eng. News*, **35**, No. 9, 87 (1957).

(2) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

(3) W. R. Sorenson, *J. Org. Chem.*, **24**, 978 (1959).

(4) (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959). (b) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

(5) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).

(6) I. M. Hunsberger and J. M. Tien, *Chem. & Ind.*, 88 (1959).

(7) S. Searles, Jr., and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).

(8) H. Potter, 137th Meeting, American Chemical Society, Cleveland, Ohio, April 5–14, 1960, p. 30.