tinued at 94° for 1.25 hr., whereupon all the zinc had dissolved. Dilution with water, filtration, and recrystallization from hexane afforded 1.94 g. of *androstan-17β-ol-16-one* (VII), m.p. 137–139.5°, $[\alpha]_D$ −144.7° (chloroform). The analytical specimen showed a m.p. of 139–141°, $\lambda_{max}^{CHCl_3}$ 2.84 and 5.72 μ, $\lambda_{max}^{CH_3OH}$ 297 mμ, log ε 1.67; R.D. in methanol (*c*, 0.10): $[\alpha]_{589}$ −162°, $[\alpha]_{322.5}$ −4158°, $[\alpha]_{277.5}$ +4055°, $[\alpha]_{256}$ +2665°.

Anal. Calcd. for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.22; H, 10.57.

Acetylation of 5.33 g. of VII with acetic anhydride–pyridine and crystallization from methanol provided 5.16 g. of *androstan-17β-ol-16-one acetate* (VIII), m.p. 152.5–153.5°. The analytical specimen, obtained by double sublimation at 130°/0.02 mm., exhibited a m.p. of 153–153.5; $\lambda_{max}^{CHCl_3}$ 5.68, 5.73, and 8.05 μ, $\lambda_{max}^{CH_3OH}$ 294–300 mμ, log ε 1.59.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.82; H, 9.73; O, 14.94.

A solution of 3.00 g. of the above acetate VIII in 100 cc. of dry tetrahydrofuran was added dropwise over a period of 15 min. to a stirred solution of 5.77 g. of calcium in 750 cc. of liquid ammonia. The mixture was stirred for an additional 15 min. and the blue color was discharged with methanol. The ammonia was allowed to evaporate overnight and the residue was taken up in ethyl acetate, washed with water, and evaporated. The resulting semisolid (2.24 g.) containing an appreciable amount of androstan-16-ol[20] was directly oxidized for 15 min. at 7° in acetone solution (160 cc.) in the presence of 3.0 g. of anhydrous sodium sulfate with 3.00 cc. of 8*N* chromium trioxide in sulfuric acid.[21] The crude product was chromatographed on neutral alumina and the hexane eluted material was recrystallized from methanol to give 1.52 g. of *androstan-16-one* (IX), m.p. 108–109.5°. Two distillations at 150°/0.02 mm. yielded the analytical sample, m.p. 109–110°, λ_{max}^{KBr} 5.74 μ, $\lambda_{max}^{CH_3OH}$ 290 mμ, log ε 1.55; R.D. in methanol (*c*, 0.114): $[\alpha]_{589}$ −224°, $[\alpha]_{322.5}$ −4050°, $[\alpha]_{320}$ −4003°, $[\alpha]_{312.5}$ −4592°, $[\alpha]_{272.5}$ +4203°, $[\alpha]_{260}$ +3407°.

Anal. Calcd. for $C_{19}H_{30}O$:C, 83.15; H, 11.02. Found: C, 82.74; H, 10.86.

The *dibenzylmercaptal* was prepared as described above for androstan-17-one (IV) in acetic acid solution with benzyl mercaptan and concentrated hydrochloric acid. Recrystallization from isopropyl alcohol afforded colorless crystals, m.p. 79–81°, $[\alpha]_D$ +8.7° (chloroform), which did not exhibit any carbonyl band in the infrared.

Anal. Calcd. for $C_{33}H_{44}S_2$: C, 78.51; H, 8.79. Found: C, 78.38; H, 8.67.

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(20) For similar results in some related calcium-ammonia reductions see J. A. Zderic and A. Bowers, *Ciencia* (*Mex*), 20, 23 (1960).

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New Catalysts for the Conversion of Isocyanates to Carbodiimides

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Aluminum isopropoxide and a variety of metal naphthenates have been found to be catalysts for the conversion of isocyanates to carbodiimides and carbon dioxide, as shown in Table I.

$$2\ \text{ArNCO} \xrightarrow[\text{cat.}]{\Delta} \text{CO}_2 + \text{ArN}{=}\text{C}{=}\text{NAr}$$

Although these new catalysts appear less active than the phosphorus compounds,[2] they are somewhat more readily available.

At temperatures above 255° 1-naphthylisocyanate yielded the carbodiimide and carbon dioxide in the absence of an external catalyst.[3] The evolution of carbon dioxide was an autocatalytic reaction, accelerated by the carbodiimide. However, at these high temperatures the carbodiimide was unstable and formed oligomers.[3] In the metal ion-catalyzed reactions of Table I, on the other hand, carbon dioxide evolution followed a pseudo-first-order rate law, and high yields of carbodiimide were obtained at temperatures slightly above 135°.

Isocyanates are known to form complexes with metal alcoholates.[4] The intermediate leading to the formation of carbon dioxide might involve a complex of the metallic catalyst with the isocyanate or with the unsymmetrical isocyanate trimer.[5] The symmetrical isocyanate trimer is thought to be a coproduct rather than an intermediate in carbodiimide formation. A recent paper[6] reports that at room temperature the metal naphthenates are excellent catalysts for trimer formation; however, at the somewhat higher temperatures of the current work the predominant product was the carbodiimide.

The inactivity of 1,4-diaza[2.2.2]bicyclooctane (DABCO) as a catalyst (Table I) indicates that the ability to catalyze other reactions[7] of isocyanates is not always accompanied by the ability to catalyze the conversion of isocyanates to carbodiimides.

EXPERIMENTAL

To a mixture of freshly distilled isocyanate and solvent was added the catalyst, and the mixture was heated at reflux under a stream of dry nitrogen. Organic materials were removed from the sweep stream (postreaction system) by passing it through traps cooled by Dry Ice–acetone, and carbon dioxide was determined by passage through tared Ascarite-filled weighing tubes. Removal of unchanged isocyanate and solvent from the reaction mixture by evaporation under reduced pressure gave a mixture of catalyst and

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[1] From the Ph.D. thesis, University of Delaware, of Robert E. Read, Armstrong Cork Co. Research Fellow, 1957–1960.

(2) T. W. Campbell and J. J. Verbanc, U. S. Patent 2,853,473, Sept. 23, 1958, *Chem. Abstr.*, 53, 10126 (1959); W. J. Balon, U. S. Patent 2,853,518, Sept. 23, 1958, *Chem. Abstr.*, 53, 5202 (1959); K. C. Smeltz, U.S. Patent 2,840,589, June 24, 1958, *Chem. Abstr.*, 52, 16290 (1958).

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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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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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