slopes (run 5 *vs.* run 1). However, when the glycol chain length became too long ($x = 12$, run 6), the ester crystallized at low temperatures. In runs 7 to 15, the acyl groups were different. The long-chain glycol with $x = 12$ again gave a relatively high pour point, but this could be overcome by increasing the difference in the acyl chain length (runs 14 and 15).

Diesters from β,β-Disubstituted Propanediols (II, Table II). Durr and coworkers (*2*) reported high thermal stabilities for similar esters. Based on pour points and viscosities at −40° F., Type II has relatively poor low-temperature fluidity. ASTM slopes are relatively high. This probably results from lack of free rotation and chain flexibility caused by bunching of the alkyl substituents near the carboxyl groups. One product, run 18, had a low pour point, but this was achieved only because its molecular weight was lower than the other products of Type II.

Diesters from Polyethylene Glycols (III, Table III). Where comparisons between compounds of similar molecular weights are available (runs 22, 23, 25, and 26), the ester from the longer-chain polyethylene glycols had lower ASTM slopes and pour points. The ether oxygens apparently contribute increased chain flexibility. MacPhail (*4*) has recently described several closely related esters.

Diesters from 2,2,3,3,4,4-Hexafluoropentanediol (IV, Table IV). Viscosities increase as the acyl groups become larger. While run 27 still had good low-temperature fluidity, runs 28 and 29 became progressively worse. ASTM slopes were relatively high. The approximate densities increased with increasing fluorine content. Snead and Gisser (*5*) have demonstrated superior thermal and oxidative stability for related esters.

Comparison of Types I to IV. If one considers diethylene glycol as a pentanediol in which the center methylene group has been replaced by an ether oxygen, a comparison between the various pentanediol esters of neodecanoic acid ($R = C_9H_{19}$) can be made. Based on pour points and viscosities at −40° F., the best low-temperature fluidity was obtained by Type I, followed by Types III, IV, and II (runs 2, 23, 28, and 16).

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Selective Hydrogenation of the Double Bond in Unsaturated Aliphatic Isocyanates

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Unsaturated aliphatic isocyanates were hydrogenated selectively in high yields to their saturated counterparts over palladium or platinum catalysts at ambient temperatures and low pressures (10 to 40 p.s.i.). Continued reduction beyond the point of theoretical hydrogen uptake resulted in a gradual loss of isocyanate content with concomitant formation of the appropriately substituted formamide and symmetrical urea. Catalyst activity apparently was destroyed during this sluggish secondary reaction, because hydrogen uptake ceased at relatively low levels of conversion of the isocyanate function.

As PART of a program directed toward utilizing the double bond in olefinic isocyanates as a selective reaction site, we decided to explore the possibility of catalytically hydrogenating various unsaturated aliphatic mono- and diisocyanates to their saturated counterparts, as illustrated for the diisocyanate case by Equation 1. This transformation was of interest to us academically as an example of a novel selective reaction of olefinic isocyanates and commercially as a potential route to certain polymer-forming diisocyanates whose olefinic precursors were more readily accessible.

$$OCN{-}R_1{-}\underset{R_3}{\underset{|}{C}}{=}\underset{R_4}{\underset{|}{C}}{-}R_2{-}NCO \xrightarrow{H_2/cat.} OCN{-}R_1{-}\underset{R_3}{\underset{|}{C}H}{-}\underset{R_4}{\underset{|}{C}H}{-}R_2{-}NCO \qquad (I)$$

There are only a few reported examples of reactions occurring selectively at the double bond site in olefinic isocyanates. These include bromination (*2*), Diels-Alder adduction (*5*), silane addition in the presence of chloroplatinic acid (*9*), bromotrichloromethane addition in the presence of free radical catalysts (*1*), and vinyl polymerization and/or copolymerization (*3, 4, 6*). Inasmuch as the principal interest in olefinic isocyanates has been as intermediates for the preparation of vinyl polymerizable urethanes, the paucity of data on selective reactions at the double bond site is understandable.

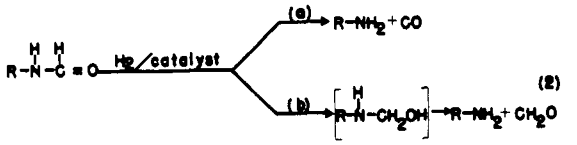
Since the behavior of the isocyanate function under conditions of noble metal type catalytic hydrogenations had never been described in the literature, no basis existed for predicting the ease with which this functional group might add hydrogen, relative to that of a carbon-carbon double bond. Whereas by analogy with other "twinned" double bond functions, such as those present in ketenes and carbodiimides, the isocyanate group might be expected to add hydrogen too rapidly to permit a selective reaction, the double bond selectivity observed in the reduction of unsaturated aliphatic nitro compounds (*7, 8*) suggested that our objective was not totally unreasonable.

Results indicate that a variety of olefinic isocyanates in fact can be catalytically hydrogenated to their saturated counterparts with a high degree of selectivity, using reaction conditions typical of those employed for laboratory-scale hydrogenations over palladium metal catalysts. Although palladium metal on various supports was the principal catalyst used in this work, results obtained from a single run employing platinum oxide suggest that this catalyst may be equally effective. All reductions were carried out at ambient temperatures and hydrogen pressures of 10 to 40 p.s.i.g., using an active metal catalyst concentration of 0.5 to 1.0%, based on the quantity of olefin charged. The only special consideration to be noted in these particular hydrogenations is that of solvent choice. Due to the high reactivity of isocyanates toward active hydrogen compounds in general, the hydrogenation solvent employed must be of the nonreactive type and should have a low water content. The commercially available "Polyurethane Grade" of ethyl acetate (less than 0.05% water; Union Carbide Corp.) produced good results without further drying. This solvent was used for all hydrogenations except that of VIIA, which was carried out neat in order to avoid solvent-product separation problems. The apparatus and general procedure followed are described in greater detail in the Experimental section.

Olefinic isocyanates I-VII embrace five different types of double bonds; namely, the cyclic (I), bicyclic (II, III), α,β-unsaturated ester (IV, V), substituted cyclic (VI), and terminal acyclic types (VII). Hydrogenation proceeded smoothly in all cases except that of VI, where the uptake rate was low and the saturated product decomposed vigorously—internal kettle temperature reached 400° C.—during attempted distillation under conditions comparable to those used for refining the saturated counterparts I and II. This behavior is consistent with side reactions of the isocyanate groups with by-product formamides and ureas which are present when selectivity is poor in the hydrogenation step. A lower than usual level of selectivity in the reduction of VI is not totally unexpected, in the sense that the catalyst concentration was low and the double bond function was of the trisubstituted type. Except for VI, the yields realized were excellent (Table I) and would be essentially quantitative if allowances were made for mechanical losses during workups.

A typical plot of hydrogen uptake rate *vs.* time is shown in Figure I, the olefin used being 2-isocyanatomethylbicyclo[2.2.1]-heptene (IIIA). Although the curve breaks sharply at the point corresponding to saturation of the double bond, it does not completely level off. Intentionally prolonged hydrogenation in this case led to cessation of uptake after the absorption of 1.26 moles of hydrogen. Workup of this reaction mixture afforded 3 components; namely, 1) the expected saturated product (IIIB), 2) bicyclo[2.2.1]hept-2-ylmethyl formamide, and 3) *N,N'*-(bicyclo[2.2.1]hept-2-ylmethyl) urea. The formamide was characterized by its infrared spectrum and by microanalysis, and the urea by microanalysis and comparison with an authentic sample (no depression of melting point).

These results suggest that the initial product formed upon reduction of the isocyanate function is the corresponding formamide. This species apparently undergoes hydrogenolysis to an amine, which subsequently condenses with saturated isocyanate to produce a symmetrical urea. In the hydrogenolysis step, catalyst activity is lost, presumably by the generation of either carbon monoxide or formaldehyde via path (a) or (b) below. When simple (nonolefinic) aromatic isocyanates, such as phenyl isocyanate, were subjected to these hydrogenation conditions, hydrogen uptake ceased at extremely low levels of —NCO group consumption. No reduction of any olefinic isocyanates of the aromatic series was attempted; hence, the authors cannot comment on the applicability of this reaction to such materials.



(2)

Although this study was by no means exhaustive in nature, the data suggest that selective reduction of olefinic aliphatic isocyanates is a reasonably general and satisfactory preparative route to saturated isocyanates. Practically speaking, the real utility of the reaction is limited to those cases wherein an unsaturated precursor of a desired isocyanate is more readily accessible than is the saturated compound itself. The Diels-Alder adducts are an excellent case in point.

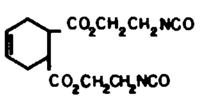
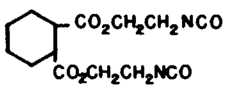
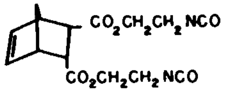
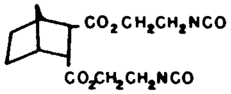
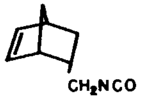
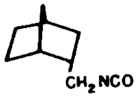
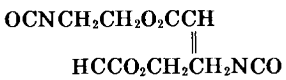
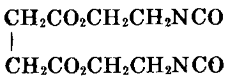
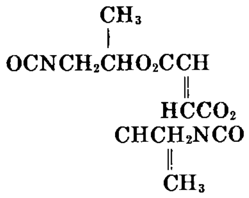
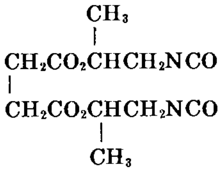
EXPERIMENTAL

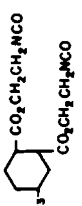
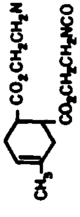
The hydrogenation apparatus was of the Paar reciprocating shaker type and utilized a jacketed 250-ml. steel pressure bottle supplied with cylinder hydrogen through a small stainless steel tank, which was calibrated for a pressure drop of 285 p.s.i.g. per mole of hydrogen. Internal temperature was measured with a thermocouple inserted into a thermowell located below the liquid level in the bottle. Temperature control, although seldom required in these small-scale runs, was achieved by passing a stream of air through the jacket of the bottle.

Melting points were determined with a Mel-Temp (Laboratory Devices, Inc.) capillary tube apparatus and are uncorrected. Microanalyses were performed by the Analytical Section of the Research and Development Department of Union Carbide Chemicals Division, South Charleston, W. Va. Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer.

With the exception of allyl isocyanate, which was purchased from Aldrich Chemical Co., all of the olefinic

Table I. Selective Reduction of the Double Bond in Unsaturated Aliphatic Isocyanates

Olefin (Compound No.)	Product (Compound No.)	Catalyst, Conc., %[a]	B.P., ° C./Mm.	n_D^{30}	Yield, %	Empirical Formula	Microanalysis,		Phenylureylene derivative			
											Microanalysis,	
							Calcd., %	Found, %	M.p., ° C. (solvent)	Empirical formula	Calcd., %	Found, %
 (IA)	 (IB)	Pd/C, (0.84)	144/0.09	1.4761	83.3	$C_{14}H_{18}N_2O_6$	C, 54.19 H, 5.81 N, 9.03	C, 54.26 H, 5.87 N, 8.99	160–161.5 (DMF/H_2O)	$C_{26}H_{32}N_4O_6$	C, 62.90 H, 6.46 N, 11.28	C, 62.44 H, 6.51 N, 11.26
 (IIA)	 (IIB)	Pd/Al_2O_3, (0.62)	160/0.05	1.4870	89.9	$C_{15}H_{18}N_2O_6$	C, 55.90 H, 5.59 N, 8.70	C, 55.13 H, 5.62 N, 9.17	170–172 (EtOAc)	$C_{27}H_{32}N_4O_6$	C, 63.74 H, 6.30 N, 11.02	C, 63.52 H, 6.39 N, 11.24
 (IIIA)	 (IIIB)	Pd/C, (0.67)	41/0.05	1.4767	90.1	$C_9H_{13}NO$	C, 71.52 H, 8.61	C, 71.60 H, 8.73	182.5–183.5 (CH_3OH)	$C_{15}H_{20}N_2O$	C, 73.77 H, 8.19 N, 11.47	C, 73.14 H, 8.24 N, 11.63
		PtO_2, (0.82)	59/1.5	1.4769	80.0		N, 9.27	N, 9.29	176–178[b] (EtOAc)	$C_{17}H_{28}N_2O$[b]	C, 73.83 H, 10.15 N, 10.15	C, 73.84 H, 10.22 N, 9.90
 $\begin{array}{l} OCNCH_2CH_2O_2CCH \\ \quad\quad\quad\quad \Vert \\ \quad HCCO_2CH_2CH_2NCO \end{array}$ (IVA)	 $\begin{array}{l} CH_2CO_2CH_2CH_2NCO \\ \vert \\ CH_2CO_2CH_2CH_2NCO \end{array}$ (IVB)	Pd/C, (0.80)	144/0.24	1.4615	89.3	$C_{10}H_{12}N_2O_6$	C, 46.86 H, 4.69 N, 10.94	C, 47.03 H, 4.82 N, 11.05	171–172.5 (DMF/H_2O)	$C_{22}H_{26}N_4O_6$	C, 59.75 H, 5.88 N, 12.67	C, 60.19 H, 6.07 N, 12.41
 $\begin{array}{l} \quad CH_3 \\ \quad \vert \\ OCNCH_2CHO_2CCH \\ \quad\quad\quad\quad \Vert \\ \quad\quad\quad HCCO_2 \\ \quad\quad CHCH_2NCO \\ \quad\quad \Vert \\ \quad\quad CH_3 \end{array}$ (VA)	 $\begin{array}{l} \quad CH_3 \\ \quad \vert \\ CH_2CO_2CHCH_2NCO \\ \vert \\ CH_2CO_2CHCH_2NCO \\ \quad \vert \\ \quad CH_3 \end{array}$ (VB)	Pd/C, (0.50)	137/0.23	1.4568	95.8	$C_{12}H_{16}N_2O_6$	C, 50.70 H, 5.64 N, 9.86	C, 50.68 H, 5.62 N, 9.89	. . .	. . .	. . .	. . .

 (VIA)	 (VIB)	Pd/C, (0.5–1.0)[c]	Decomposed[d]	. . .	. . .	$C_{15}H_{20}N_2O_6$	. . .	. . .	. . .	. . .	. . .	. . .
$CH_2=CHCH_2NCO$ (VIIA)	$CH_3CH_2CH_2NCO$ (VIIB)	Pd/C[e] (0.67)	87/760	1.3934	74.4	C_4H_7NO	C, 56.47 H, 8.23 N, 16.47	C, 56.62 H, 8.26 N, 16.38	113.5–114.5[f] (50/50 benzene/ cyclohexane)	$C_{10}H_{14}N_2O$	C, 67.43 H, 7.86 N, 15.73	C, 67.49 H, 7.83 N, 15.71

[a] Weight per cent of active metal, based on amount of isocyanate charge. Ethyl acetate solvent unless otherwise noted.
[b] Amine used to form this derivative was 2-aminomethylbicyclo [2.2.1] heptane.
[c] Hydrogenation started with 0.5% catalyst; increased to 1.0% after one hour.
[d] Product decomposition under distillation conditions similar to those used to refine IB, IIB, IVB, and VB.
[e] Hydrogenation carried out neat.
[f] Literature value is 114–116° C. from ethanol solvent.

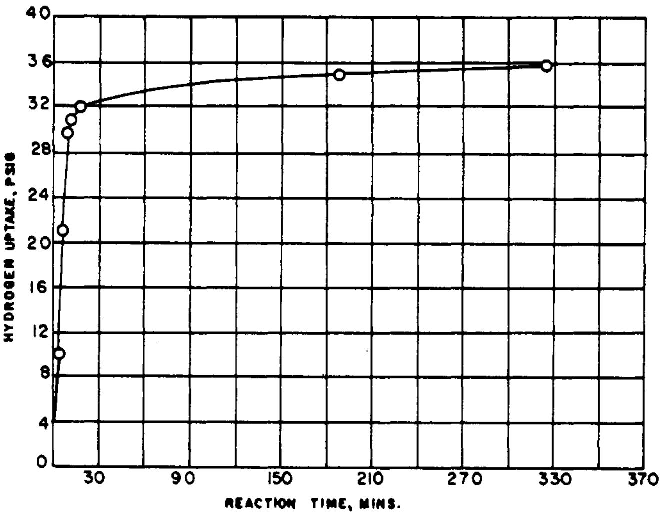


Figure 1. Prolonged hydrogenation of 2-isocyanatomethyl bicyclo[2.2.1]heptene over Pd/C catalyst at 25° C./30 p.s.i.

Olefin charge, 15 grams, 0.1 mole
Catalyst, 5% Pd-on-carbon
Catalyst charge, 2.0 grams
Solvent, ethyl acetate
Theo. H_2 uptake for $>C=C<$, 28.5 p.s.i.g.

isocyanates utilized in this study were prepared in this laboratory, using procedures described in U. S. Patents **3,141,900** and **3,231,595,** French Patent **1,370,869,** and Belgian Patent **635,604.** The ethyl acetate solvent used was the commercial "Polyurethane Grade" (< 0.05% water) available from Union Carbide's Chemicals and Plastics Division. The supported palladium catalysts were all 5% active materials purchased from Matheson, Coleman and Bell, and the platinum oxide catalyst was 83.7% active material purchased from Engelhard Ind.

Procedure. The first description below is typical of the experimental procedure followed throughout for preparative purposes; physical properties and analytical data on the products are given in Table I. The second description is concerned with the effects of prolonged hydrogenation of isocyanates (Figure I).

2-Isocyanatomethylbicyclo[2.2.1]heptane IIIB. To the Paar hydrogenator described above was charged 15.0 grams (0.100 mole) of 2-isocyanatomethylbicyclo[2.2.1]hept-5-ene (IIIA), 2.0 grams of 5% palladium-on-carbon catalyst, and 100 ml. of ethyl acetate. After the system had been purged three times with hydrogen, it was pressured to 30 p.s.i. and rocking was begun at an initial temperature of 23° C. When the gage pressure fell to 10 p.s.i., the system was repressurized to 30 p.s.i. The theoretical quantity of hydrogen was consumed in less than 20 minutes, and the uptake rate then diminished sharply. After an additional 5 minutes of reaction the system was vented, the catalyst was removed by filtration, the solvent was stripped off on a rotary evaporator, and the liquid residue was refined by vacuum distillation through a 6-inch insulated Vigreux column. The refined product (b.p. 41° C./0.5 mm., n_D^{30}, 1.4767) was obtained in 90.1% yield and reacted readily with aniline to afford a phenylureylene derivative (m.p. 182.5–3.5° C.), which failed to depress the melting point of an authentic sample prepared from IIIB, which had been obtained by treating 2-aminomethylbicyclo[2.2.1]heptane with phosgene and reacting the resulting isocyanate with aniline.

Prolonged Hydrogenation of 2-Isocyanatomethylbicyclo-[2.2.1]heptane. The above experiment was repeated, with the exception that the catalyst used was 5% palladium-on-alumina, and the reduction was continued until the hydrogen uptake decreased to a rate of less than 1 p.s.i. in two hours (Figure 1). The total quantity of hydrogen consumed was approximately 1.26 mole per mole of olefin, or 0.26 mole more than the quantity required to saturate the double bond. Following removal of the catalyst by filtration and the solvent by evaporation, the liquid residue was refined by vacuum distillation, as described above. Two liquid fractions and a solid kettle residue were obtained. Fraction 1, representing about 61% of the kettle charge, boiled from 56° to 128° C. at 1.4 to 1.0 mm. and was identified as principally the saturated isocyanate (IIIB). Fraction 2, representing about 26% of the total charge, boiled at 132° C. at 0.85 mm. (n^{30}_{D}, 1.5002) and was indicated by infrared spectrum (amide C=O bands at 6.0 and 6.5 microns and an N—H at 3.05 microns) and microanalysis to be *N*-(2-norbornylmethyl)-formamide.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.59; H, 9.80; N, 9.15.
Found: C, 70.73; H, 9.75; N, 9.10.

The distillation residue, comprising about 13% of the kettle charge, was an impure yellow solid melting from 105° to 153° C. Two recrystallizations from ethyl acetate with decolorizing charcoal present afforded a white crystalline product with a melting point of 176–8° C. Admixture of this product with an authentic sample of *N,N'*-(2-norbornylmethyl) urea caused no depression in melting point.

Anal. Calcd. for $C_{17}H_{28}N_2O$: C, 73.83; H, 10.15; N, 10.15.
Found: C, 73.84; H, 10.22; N, 9.90.

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Alkyl Benzyl Ketones and Hydantoin Derivatives

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Ten alkyl benzyl ketones were prepared by the interaction of phenylacetyl chloride and dialkyl cadmium. Hydantoin derivatives of these ketones were prepared.

TEN ALKYL BENZYL KETONES were synthesized by the interaction of phenylacetyl chloride and the requisite dialkyl cadmium, the synthesis being modeled after a published procedure (*2*). Hydantoin derivatives were prepared from these ketones by the method of Henze and Speer (*3*).

Table I lists the yields of the alkyl benzyl ketones prepared by means of dialkyl cadmiums as well as data on the hydantoin derivatives.

EXPERIMENTAL

Reactants were obtained commercially and used without further purification. Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo. Melting points were determined in a silicone oil bath and are corrected. The following examples illustrate the synthesis of the alkyl benzyl ketones and the 5-alkyl-5-benzylhydantoins.

1-Phenyl-2-heptanone. A mixture of 40 ml. of anhydrous ether and 6.1 grams (0.25 gram-atom) of magnesium was stirred under reflux while 37.8 grams (0.25 mole) of pentyl bromide in 140 ml. of anhydrous ether was added over a 3-hour period; stirring under reflux was continued for an additional hour. The reaction mixture was cooled with an ice bath and 22.4 grams (0.134 mole) of powdered anhydrous cadmium chloride was added over a 5- to 10-minute period, warmed to room temperature, and refluxed on a steam cone for 1 hour. Ether was removed by distillation on a steam cone. To the residue was added 100 ml. of anhydrous benzene and the distillation was continued until about 50 ml. more of distillate was collected. Again 100 ml. of anhydrous benzene was added, the flask was cooled in an ice bath, and 30.9 grams (0.2 mole) of phenylacetyl chloride in

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