



TABLE I  
 REACTION OF AZIDE WITH ISOCYANIDE<sup>a</sup>

RN <sub>3</sub>	Mmol	R'NC	Mmol	Catalyst	Mmol	R—N=C=N—R'	Yield, <sup>b</sup> %
<i>c</i> -C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	10	<i>t</i> -C <sub>4</sub> H <sub>9</sub> NC	36	Fe(CO) <sub>5</sub>	0.5	<i>c</i> -C <sub>6</sub> H <sub>11</sub> —N=C=N—C <sub>4</sub> H <sub>9</sub> - <i>t</i>	60
<i>c</i> -C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	10	<i>c</i> -C <sub>6</sub> H <sub>11</sub> NC	28	Fe(CO) <sub>5</sub>	0.5	<i>c</i> -C <sub>6</sub> H <sub>11</sub> —N=C=N—C <sub>6</sub> H <sub>11</sub> - <i>c</i>	48
<i>c</i> -C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	10	C <sub>6</sub> H <sub>5</sub> NC	36	Fe(CO) <sub>5</sub>	0.5	<i>c</i> -C <sub>6</sub> H <sub>11</sub> —N=C=N—C <sub>6</sub> H <sub>5</sub>	51
<i>c</i> -C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	10	<i>c</i> -C <sub>6</sub> H <sub>11</sub> NC	37	Cu <sub>2</sub> O <sup>c</sup>	1.0	<i>c</i> -C <sub>6</sub> H <sub>11</sub> —N=C=N—C <sub>6</sub> H <sub>11</sub> - <i>c</i>	2
<i>c</i> -C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	10	<i>c</i> -C <sub>6</sub> H <sub>11</sub> NC	28	None		No reaction	

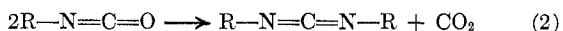
<sup>a</sup> Reactions were carried out at 90° for 24 hr under nitrogen atmosphere. <sup>b</sup> Product yield is based upon the amount of azide. <sup>c</sup> A considerable amount of tar was produced in this reaction.

presence of iron pentacarbonyl, the reaction proceeds smoothly. Cuprous oxide, which has been employed as an effective catalyst in the reactions of isocyanide<sup>1</sup> and of the azide,<sup>2</sup> exhibits a poor catalytic activity in the present reaction. The results of the azide-isocyanide reaction are shown in Table I. It is important to note that only the carbodiimide of the structure as indicated by III is produced and other carbodiimides having structures of R—N=C=N—R and R'—N=C=N—R' are not formed.

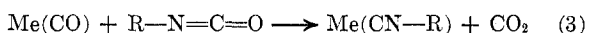
The formation of carbodiimide may be formulated as being the combination of isocyanide and nitrene, which are characterized by lone-pair electrons attached to carbon and nitrogen, respectively. These two species<sup>3,4</sup> are known to form coordination complexes with metal carbonyls. Ligand exchange of iron pentacarbonyl with isocyanide is considered possible in the present reaction conditions.<sup>3a</sup> Therefore, it can be assumed that the isocyanide complex reacts either with azide or nitrene.

Concerning the isocyanide-nitrene reaction, a reaction of cyclohexyl isocyanide with *N*-chloro-*p*-toluenesulfonamide in alkaline methanol has been reported,<sup>5</sup> in which a mechanism of the reaction of isocyanide with an intermediate of *p*-toluenesulfonylnitrene was suggested as one of possible courses.

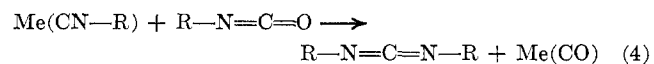
The reaction found in this study can be compared with the metal carbonyl catalyzed condensation of 2 mol of isocyanate, which also produces carbodiimide (eq 2).<sup>6</sup> The condensation of isocyanate has been



explained by the intermediate production of metal isocyanide complex (eq 3) and the subsequent reaction



of this complex with the second molecule of isocyanate (eq 4). In this connection, the azide-isocyanide



(1) (a) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966); *Bull. Chem. Soc. Jap.*, **42**, 3535 (1969). (b) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1217 (1969). (c) T. Saegusa, S. Kobayashi, Y. Ito, K. Hirota, and Y. Okumura, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968).

(2) (a) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967); **89**, 1951 (1967). (b) T. Saegusa, Y. Ito, and T. Shimizu, to be published in *J. Org. Chem.*

(3) (a) W. Hieber and D. V. Pigenot, *Chem. Ber.*, **89**, 193 (1956). (b) L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

(4) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

(5) W. Aumüller, *Angew. Chem.*, **75**, 857 (1963).

(6) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron Lett.*, 1731 (1967).

reaction by iron carbonyl catalyst in the present study might be regarded as the reaction of isocyanide with isocyanate which is formed intermediately from nitrene and the carbon monoxide ligand. This possibility, however, was not supported by a reference experiment in which an equimolar mixture of cyclohexyl azide and iron pentacarbonyl was heated. The gaseous mixture evolved from the heat treated mixture consisted of nitrogen and carbon monoxide. No carbon dioxide was detected. Furthermore, neither cyclohexyl isocyanate nor dicyclohexylcarbodiimide was detected in the reaction mixture. Consequently, the azide-isocyanide reaction is not depicted by eq 3 and 4. Elucidation of the features of this interesting reaction awaits further study.

#### Experimental Section

**Reaction of Cyclohexyl Azide (I) with *tert*-Butyl Isocyanide (IIa).**—To a mixture of IIa (36 mmol) and Fe(CO)<sub>5</sub> (0.5 mmol), I (10 mmol) was added dropwise during 15 min at room temperature under nitrogen atmosphere. The reaction mixture was then heated for 24 hr at 90°. From the reaction mixture the insoluble part was removed by filtration, and the filtrate was distilled *in vacuo* to give a distillate (1.1 g) boiling at 63 ~ 65° (2 mm). The distillate was subjected to glpc analysis. The product was shown to be *tert*-butylcyclohexylcarbodiimide (IIIa, 60%). Compound IIIa was identified by ir and nmr spectra and elemental analysis: ir of IIIa (neat)  $\nu_{\text{N}=\text{C}=\text{N}}$  2160 cm<sup>-1</sup> (vs); nmr (CDCl<sub>3</sub>)  $\tau$  6.50~7.05 (1 H, broad singlet), 7.85~9.0 (10 H, broad multiplet), and 8.70 (9 H, singlet).

*Anal.* Calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>: C, 73.28; H, 11.18; N, 15.54. Found: C, 73.55; H, 11.26; N, 15.82.

**Reaction of Cyclohexyl Azide (I) with Cyclohexyl Isocyanide (IIb).**—The reaction was carried out by a similar procedure. The product was dicyclohexylcarbodiimide (IIIb, 48%). IIIb was identified by comparison of ir and nmr spectra and the glpc retention time with those of the authentic sample.

The reaction of cyclohexyl azide (I) with phenyl isocyanide (IIc) was carried out by a similar procedure. The product, *N*-cyclohexyl-*N*-phenylcarbodiimide (IIIc, 51%), was identified by comparison of ir spectrum and the glpc retention time with those of the authentic sample.

**Reaction of Cyclohexyl Azide (I) with Iron Pentacarbonyl (IV).**—A mixture of I (10 mmol), IV (10 mmol), and acetonitrile (5 ml) in a 50-ml stainless steel pressure tube was heated at 80° for 15 hr. After the reaction, the gaseous products were trapped and analyzed by glpc with a column of silica gel (column temperature 40° for carbon dioxide, -78° for nitrogen and carbon monoxide). Nitrogen (7.5 mmol, 75%) and carbon monoxide (1.3 mmol) were produced. The nonvolatile part of reaction mixture was analyzed by glpc. Dicyclohexylcarbodiimide (IIIb) and cyclohexylisocyanate could not be detected. The nitrene-iron carbonyl complex<sup>4</sup> may have been produced.

**Registry No.**—Carbodiimide (R = *c*-C<sub>6</sub>H<sub>11</sub>; R' = *t*-C<sub>4</sub>H<sub>9</sub>), 1202-53-5; carbodiimide (R = R' = *c*-C<sub>6</sub>H<sub>11</sub>), 538-75-0; carbodiimide (R = *c*-C<sub>6</sub>H<sub>11</sub>; R' = Ph), 3878-67-9; iron pentacarbonyl, 13463-40-6.