

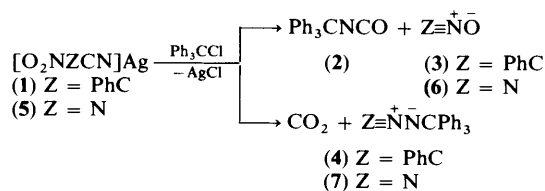
## Alkylation of Nitrocyanamide. A New Synthesis of Isocyanates

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Thirteen alkyl halides (primary, secondary, and tertiary aliphatic including alicyclic, aralkyl, and hetero-alkyl systems) and certain non-vicinal dihalides on treatment with silver nitrocyanamide are converted into the corresponding isocyanates (63–95%). Intermediate alkyl nitrocyanamides, spectroscopically detected, thermolysed ( $-20$ – $80$  °C) to the expected isocyanates. In certain examples silver nitrocyanamide is generated *in situ* from sodium nitrocyanamide and silver nitrate. Silver nitrocyanamide does not react with cyclopropyl bromide, acetyl chloride, toluene-*p*-sulphonyl chloride, phenacyl bromide and 2-bromomethyldioxolane (27), and the ethylene acetal (28) of 1-bromo-4-iodopentacyclo-[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one. Silver nitrocyanamide reacts with 4,6-bis(bromomethyl)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octane-2,8-dione (26), to give an intractable mixture. Vicinal dihalides give erratic results without detectable formation of vicinal di-isocyanates: unisolated 2-bromoethyl isocyanate (tentative assignment) has been detected in a product mixture from ethylene dibromide; an expected rearrangement during the reaction with 1,2-dibromocyclobutane, brought about the formation of 4-bromobut-3-enyl isocyanate isolated as ethyl 4-bromobut-3-enylcarbamate in low yield; and 1,2-dibromocyclohexane gives 2-bromocyclohexyl isocyanate isolated as ethyl *N*-(2-bromocyclohexyl)-carbamate in low yield.

Direct conversion of an alkyl halide offers an attractive, but rarely encountered, synthesis of an isocyanate. Trimerization of an isocyanate precluded its isolation when produced from an organic halide and an alkali cyanate in an aprotic solvent, *e.g.* dimethylformamide; however, methoxymethyl, allyl, and but-2-enyl isocyanates and methylene di-isocyanate were similarly obtained and isolated.<sup>1a</sup> In a mathematical description of the reaction maximum conversion (87.02%) of benzyl chloride, when treated with potassium cyanate, was achieved at 175 °C in *N,N*-dimethylacetamide with a copper powder catalyst.<sup>1b</sup>

Recognition that trityl chloride and silver phenylcyanomethylene nitronate (1) gave trityl isocyanate (2) and benzonitrile *N*-oxide (3) by one pathway and carbon dioxide and benzonitrile *N*-tritylimide (4) by a competitive pathway<sup>2,3</sup> permitted the prediction that a similar tritylation of silver nitrocyanamide (5) would give trityl isocyanate (2) along with nitrous oxide (6) and/or trityl azide (7) along with carbon dioxide, Scheme 1. The prediction was partially

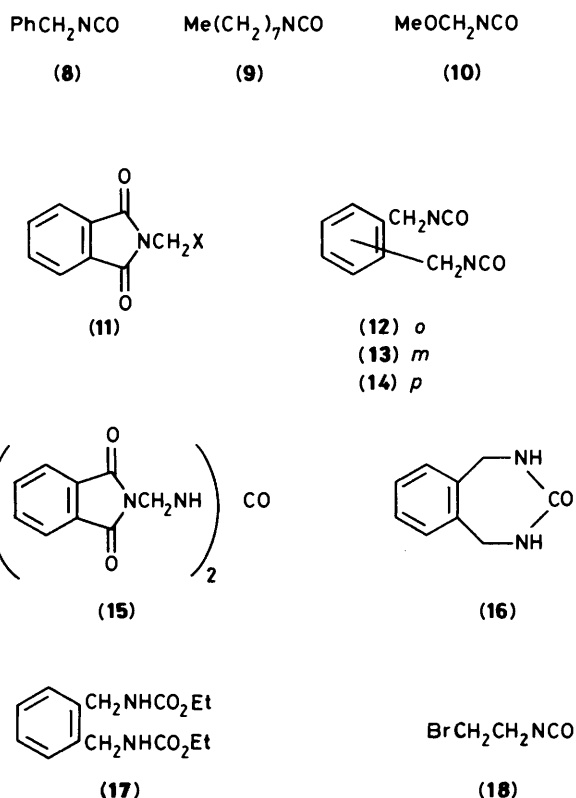


Scheme 1.

fulfilled when the isocyanate (2) was obtained nearly quantitatively from the salt (5); the formation of trityl azide (7), nitrous oxide, and carbon dioxide was not detected.<sup>4,5</sup> The present report describes extensions of this new reaction to provide preparations of isocyanates of various structures and gives some limits on its applicability.

## Results

**Primary Alkyl Systems.**—Silver nitrocyanamide efficiently converted the appropriate primary halide into benzyl, octyl, methoxymethyl, and phthalimidomethyl isocyanates (8)–(11) ( $\text{X} = \text{NCO}$ ), and *o*-, *m*-, and *p*-xylene- $\alpha,\alpha'$ -diyl di-isocyanates



(12)–(14) (Table). The previously unknown isocyanates (11;  $\text{X} = \text{NCO}$ ) and (12) gave expected derivatives: bis(phthalimidomethyl)urea (15), 2,3,4,5-tetrahydro-1*H*-2,4-benzodiazepin-3-one (16) and diethyl *o*-xylene- $\alpha,\alpha'$ -dicarbamate (17). Unidentified, presumably oligomeric, material formed from the xylene-diyl di-isocyanates after a few hours. A di-isocyanate was not obtained from 1,2-dibromoethane; instead treatment with silver nitrocyanamide brought about a very slow but efficient conversion into 2-bromoethyl isocyanate (18) (tentative identification).

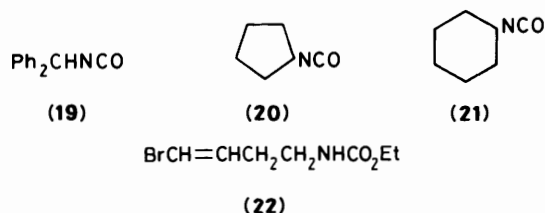
Table. Isocyanates from halides and silver nitrocyanoamide

Halide	Solvent	Temp. (°C)	Time (h)	Isocyanate <sup>a</sup>	Yield (%)	M.p. (°C) or b.p. (°C) [Torr] <sup>b</sup>
PhCH <sub>2</sub> Br	C <sub>6</sub> H <sub>6</sub>	25	24	(8)	78	65[4] <sup>c</sup>
n-C <sub>8</sub> H <sub>17</sub> I <sup>d</sup>	C <sub>6</sub> H <sub>6</sub>	80	20	(9)	75	60[3.5] <sup>e</sup>
MeOCH <sub>2</sub> Br	Et <sub>2</sub> O	35	4	(10)	84	90[760] <sup>f</sup>
(11; X = Br)	C <sub>6</sub> H <sub>6</sub>	80	1	(11; X = NCO)	81	g
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> Br) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	80	3	(12)	90	h
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> Br) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	80	3	(13)	94	i
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> Br) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	80	3	(14)	82	44 <sup>j</sup>
Ph <sub>2</sub> CHBr	C <sub>6</sub> H <sub>6</sub>	25	15	(19)	74	148[4] <sup>k</sup>
<i>c</i> -C <sub>5</sub> H <sub>9</sub> Br	Et <sub>2</sub> O	35	4	(20) <sup>l</sup>	95	m
<i>c</i> -C <sub>6</sub> H <sub>11</sub> Br	C <sub>6</sub> H <sub>6</sub>	25	24	(21)	70	58[8] <sup>n</sup>
Ph <sub>3</sub> CCl	PhMe	-20	4	(2) <sup>o</sup>	84	91 <sup>p</sup>
Me <sub>3</sub> CBr	Et <sub>2</sub> O	25	4	(24)	63	67[760] <sup>q</sup>
(25; X = Br)	C <sub>6</sub> H <sub>6</sub>	25	4	(25; X = NCO)	89	147 <sup>r</sup>

<sup>a</sup> Each isocyanate showed an i.r. absorption near 2 260 cm<sup>-1</sup> (NCO) and was in complete agreement with the structure required by its <sup>1</sup>H n.m.r. data.

<sup>b</sup> Values shown were in agreement with literature data cited. <sup>c</sup> Ref. 8. <sup>d</sup> Octyl bromide gave the isocyanate (9) (5%). <sup>e</sup> H. J. Niclas and D. Martin, *Tetrahedron*, 1978, **34**, 703. <sup>f</sup> W. J. Kauffman, *J. Org. Chem.*, 1974, **39**, 2472. <sup>g</sup> Isolated as the urea (15), see the Experimental section. <sup>h</sup> Isolated as the cyclic urea (16) and as the urethane (17), see the Experimental section. <sup>i</sup> On isolation from the product mixture the isocyanate, as an oil, showed  $\nu_{\max}$  (neat) 2 260 cm<sup>-1</sup> (NCO);  $\delta$ (CDCl<sub>3</sub>) 7.23 (4 H, s, ArH), and 4.30 (4 H, s, CH<sub>2</sub>);  $m/z$  (70 eV) at 188 ( $M^+$ ). Attempted distillation was unsuccessful [lit.,<sup>16</sup> b.p. 159–162 °C (12 Torr)]. <sup>j</sup> M.p. 46.5 °C.<sup>16</sup> <sup>k</sup> J. J. Donleavy and J. English, *J. Am. Chem. Soc.*, 1940, **62**, 218. <sup>l</sup> The isocyanate (20) was isolated by gas chromatography. Attempted purification by distillation resulted in explosions. <sup>m</sup> A b.p. of 145–146 °C was reported by D. F. Hayman, V. Petrow, and O. Stephenson, *J. Pharm. Pharmacol.*, 1964, **16**, 538. <sup>n</sup> N. Bortnick, L. S. Luskin, M. D. Hurwitz, and A. W. Rytina, *J. Am. Chem. Soc.*, 1956, **78**, 4358. <sup>o</sup> A comparable conversion was carried out in methylene dichloride at 0 °C for 1 h. <sup>p</sup> L. W. Jones and C. D. Hurd, *J. Am. Chem. Soc.*, 1921, **43**, 2422. <sup>q</sup> A. Danopoulos, M. Avowin, and S. Peraskewas, *Synthesis*, 1985, 682. <sup>r</sup> H. Stetter and C. Wulff, *Chem. Ber.*, 1962, **95**, 2302.

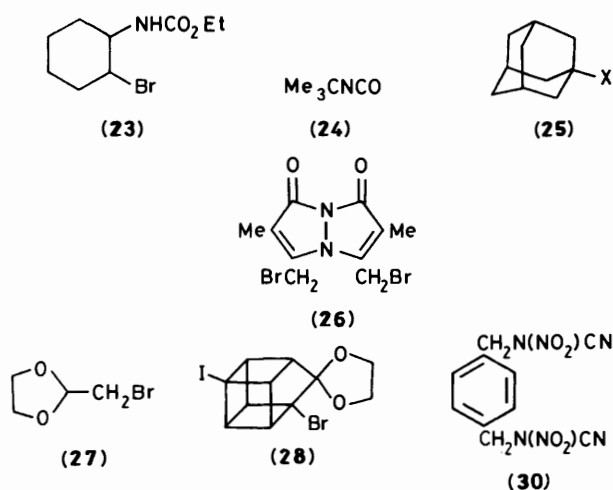
**Primary and Secondary Alkyl Systems.**—Secondary halides afforded benzhydryl, cyclopentyl, and cyclohexyl isocyanates (19)–(21) (Table). Explosions obtained on heating samples of the crude cyclopentyl isocyanate (20) from repeated preparations were attributed to presumed trace quantities (undetected by i.r. and n.m.r. spectroscopy) of the intermediate cyclopentyl-nitrocyanoamide. The isocyanate (20) was isolated by non-preparative gas chromatography.



A carbon-skeleton rearrangement was encountered in the inefficient conversion of 1,2-dibromocyclobutane into 4-bromobut-3-enyl isocyanate, subsequently converted into ethyl *N*-(4-bromobut-3-enyl)carbamate (22) for structure confirmation. Related rearrangements of cyclobutyl and cyclopropylmethyl systems have been reported.<sup>6</sup> In contrast, 1,2-dibromocyclohexane and silver nitrocyanoamide gave a mixture that contained a moderate yield of 2-bromocyclohexyl isocyanate. The latter was converted into ethyl *N*-(2-bromocyclohexyl)carbamate (23).

**Tertiary Alkyl Systems.**—Tertiary halides afforded trityl, *t*-butyl, and adamantan-1-yl isocyanates (2), (24), and (25), (X = NCO) (Table).

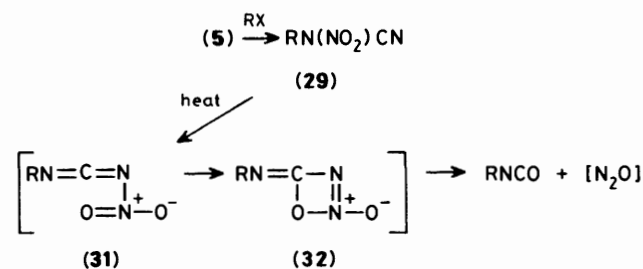
**Halides that did not give Isocyanates.**—An intractable mixture was obtained from 4,6-bis(bromomethyl)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octane-2,8-dione (26)<sup>7</sup> and silver nitrocyanoamide. Cyclopropyl bromide, acetyl chloride, toluene-*p*-sulphonyl chloride, phenacyl bromide, 2-bromomethyldioxolane (27) and the ethylene acetal (28) (we thank Professor R. M. Moriarty for a generous sample) of 1-bromo-4-iodopentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one failed to react with silver



nitrocyanoamide at 80 °C for 20 h. To understand the scope of the reaction more completely further investigations are underway.

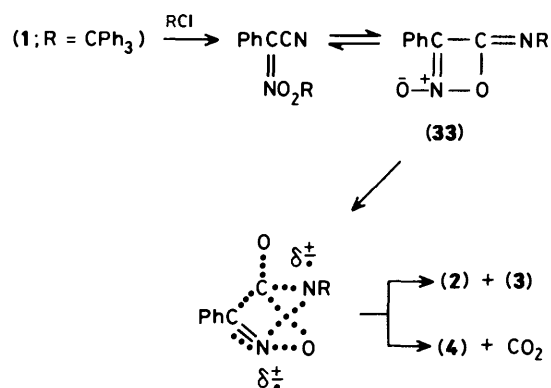
### Discussion

It has been shown that the conversion, Scheme 1, Z = N, proceeds via an intermediate alkylnitrocyanoamide (29), Scheme 2, by stopping a reaction after a short time to detect i.r.



Scheme 2.

absorption at 2 200 ( $C\equiv N$ ) and 1 270  $cm^{-1}$  ( $N-NO_2$ ). As the reaction proceeded, these peaks disappeared and intense absorption at 2 260  $cm^{-1}$  (NCO) developed. Benzylnitrocyanamide (29) ( $R = PhCH_2$ ) and *p*-xylene- $\alpha,\alpha'$ -diylbisnitrocyanamide (30) were each isolated in high yield and were readily thermolysed quantitatively to benzyl isocyanate (8)<sup>8</sup> and *p*-xylene- $\alpha,\alpha'$ -diyl di-isocyanate (14). Thermolysis of acyl- and sulphonyl-nitrocyanamides to acyl and sulphonyl isocyanates has recently been reported.<sup>9</sup> A structure assignment in favour of benzylnitrocyanamide (29;  $R = PhCH_2$ ) rather than the isomeric carbodi-imide (31;  $R = PhCH_2$ ) was determined by the <sup>13</sup>C chemical shift signal at 104.38 p.p.m. in the centre of the range 100–110 p.p.m. attributed to the  $NC\equiv N$  group and outside the range 120–130 p.p.m. assigned to the  $-N=C=N-$  group.<sup>10</sup> The assumption that each alkylnitrocyanamide underwent thermal isomerization to an undetected *N*-alkyl-*N'*-nitrocarbodi-imide (31) followed by ring closure and dissociation provided a straightforward explanation for the formation of the isocyanate, Scheme 2. A similar sequence was proposed to account for the thermal conversion of triphenylmethyl phenylcyanomethylene nitronate,<sup>2–4</sup> Scheme 3. At this



Scheme 3.

time, a rationale for bond switching in the intermediate (33) (implicated to account for product formation) and its suppression in intermediate (32) cannot be offered.

## Experimental

Instruments included a Pye–Uicam SP 200 i.r. spectrophotometer, a Varian A-60 spectrometer, and an AEI Scientific Apparatus Limited MS30 mass spectrometer. G.c. data was obtained from an HP-5790 instrument with an HP-3390A integrator (column: 3% OVB-17 on 80/100 Gas Chrom Q stainless steel: 6 ft  $\times$  1/8 in; carrier gas nitrogen; column temperature 50–200 °C, with f.i.d.). Elemental analyses were obtained from Micro-Tech. Laboratories, Skokie, IL. The organic halides listed in the Table, acetyl chloride, tosyl chloride, phenacyl bromide, 1,2-dibromoethane, 1,2-dibromocyclohexane, 2-bromomethyldioxolane, and cyclopropyl bromide were obtained from the Aldrich Chemical Company, 4,6-bis(bromomethyl)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octane-2,8-dione (26),<sup>7</sup> the ethylene ketal (28)<sup>11</sup> of 1-bromo-4-iodopentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonan-9-one and 1,2-dibromocyclobutane<sup>12</sup> were obtained according to methods in the literature cited. Sodium nitrocyanamide was obtained from *N*-methyl-*N*-nitroso-*N'*-nitroguanidine by treatment with sodium hydroxide in alcohol.<sup>13</sup> It is recommended that the operation be carried out in a well-ventilated hood to eliminate the possible accumulation of diazomethane, a by-product. The sodium salt was converted into silver nitrocyanamide by treatment with

silver nitrate in water. To avoid handling neat silver nitrocyanamide (explosive) the salt was kept moist with solvent.<sup>13</sup> Silver nitrocyanamide prepared *in situ* from an equimolar mixture of sodium nitrocyanamide (non-explosive)<sup>13</sup> and silver nitrate was successfully used in one example.

*Conversion of Halides into Isocyanates: General Procedure.*—Silver nitrocyanamide (10.0 g, 0.05 mol) and anhydrous magnesium sulphate (1.0 g) were suspended in anhydrous benzene (30 ml) and stirred under nitrogen. A solution of benzyl bromide (8.5 g, 0.05 mol) in anhydrous benzene (20 ml) was added in drops and the mixture was stirred at room temperature for 24 h. The exclusive formation of benzyl isocyanate was shown by a single peak in the g.c. analysis of the liquid phase. Inorganic salts and the solvent were removed to give the crude product (5.9 g, 90%), distillation of which (65 °C, 4 Torr) afforded pure benzyl isocyanate (5.2 g, 78%), identified spectroscopically (i.r. and n.m.r.) by direct comparison with data from an authentic sample.<sup>8</sup> Similar treatment converted other alkyl and aralkyl halides into isocyanates (Table). When silver nitrocyanamide was prepared *in situ* from sodium nitrocyanamide and equimolar silver nitrate and the reaction time with *N*-phthalimidomethyl bromide was arbitrarily increased to 3 h, the yield of the isocyanate (11;  $X = NCO$ ), isolated as the urea (15), was 80%. This result was nearly identical with the efficiency obtained in the reaction with isolated silver nitrocyanamide (Table).

Phthalimidomethyl isocyanate (11;  $X = NCO$ ) treated with aqueous acetone gave the urea (15), m.p. 244–245 °C;  $\nu_{max}$ (KBr) 3 320 (NH), 1 770, and 1 700  $cm^{-1}$  ( $C=O$ );  $\delta[(CD_3)SO]$  7.86 (4 H, s, ArH), 6.97 (1 H, t, *J* 6 Hz, NH), and 4.90 (2 H, d, *J* 6 Hz,  $CH_2$ ) (Found: C, 60.15; H, 3.65; N, 12.45. Calc. for  $C_{19}H_{14}N_4O_5$ : C, 60.31; H, 3.70; N, 14.81%). Similar treatment of *o*-xylene- $\alpha,\alpha'$ -diyl di-isocyanate with aqueous acetone afforded the cyclic urea (16), m.p. > 280 °C (lit.,<sup>14</sup> m.p. 300 °C),  $\nu_{max}$ (KBr) 3 320 and 3 240 (NH) and 1 660  $cm^{-1}$  ( $C=O$ );  $\delta(CF_3CO_2H)$  7.27 (4 H, d, ArH) and 4.53 (4 H, s,  $CH_2$ ).

*Diethyl o-Xylene- $\alpha,\alpha'$ -dicarbamate (17).*—*o*-Xylene- $\alpha,\alpha'$ -diyl di-isocyanate (1.0 g, 5.3 mmol) was treated with absolute ethanol (4 ml) and pyridine (1 drop) at 65 °C for 0.5 h. Removal of unchanged ethanol gave diethyl *o*-xylene- $\alpha,\alpha'$ -dicarbamate (17) (1.30 g, 87%) as colourless crystals, m.p. 117–118 °C from ethanol;  $\nu_{max}$ (KBr) 3 300 (NH) and 1 680  $cm^{-1}$  (CO);  $\delta(CDCl_3)$  7.15–7.45 (4 H, m, ArH), 5.50 (2 H, s, NH), 3.80–4.57 (8 H, m,  $CH_2$ ), and 0.87–1.77 (6 H, m, Me) (Found: C, 59.8; H, 7.25; N, 9.85. Calc. for  $C_{14}H_{20}N_2O_4$ : C, 59.98; H, 7.19; N, 9.99%).

*Reaction of 1,2-Dibromoethane with Silver Nitrocyanamide.*—Silver nitrocyanamide (10.0 g, 52 mmol), anhydrous magnesium sulphate (1.0 g), and 1,2-dibromoethane (4.7 g, 25 mmol) were stirred under nitrogen and heated in an oil bath at 85–90 °C for 4 days. Anhydrous ether (50 ml) was added and the mixture was filtered. Ether was removed to leave an unresolved mixture that contained a detectable amount of an isocyanate;  $\nu_{max}$ (neat) 2 260  $cm^{-1}$  (NCO);  $\delta(CDCl_3)$  3.70 (4 H, s,  $BrCH_2CH_2Br$ ), 3.60 (2 H, t, *J* 6 Hz,  $CH_2Br$ ), and 3.57 (2 H, t, *J* 6 Hz,  $CH_2NCO$ );  $m/z$  (70 eV) 186, 188, 190 ( $M^+$  for  $BrCH_2CH_2Br$ ), 149 and 151 ( $M^+$  for  $BrCH_2CH_2NCO$ ).

*Reaction of 1,2-Dibromocyclobutane and Silver Nitrocyanamide.*—Silver nitrocyanamide (5.1 g, 26 mmol) and anhydrous magnesium sulphate (1.0 g) were suspended in anhydrous benzene (20 ml) and stirred under nitrogen. 1,2-Dibromocyclobutane (2.8 g, 12.5 mmol) was added and the mixture was heated at 80 °C for 120 h. The removal of inorganic salts and the solvent left an impure isocyanate (1.4 g) as a yellow oil,  $\nu_{max}$ (neat) 2 260  $cm^{-1}$  (NCO). Treatment of this with absolute

ethanol (2 ml) containing anhydrous pyridine (4 drops) at 65 °C for 0.5 h gave a new oil, (1.3 g), which did not contain an isocyanate,  $\nu_{\max}(\text{neat})$  3 340 (NH) and 1 700  $\text{cm}^{-1}$  (CO). Purification by column chromatography [silica gel; elution with dichloromethane-hexane (1:1)] gave ethyl 4-bromobut-3-encylcarbamate (**22**) as a pale yellow liquid (0.52 g, 19%);  $\nu_{\max}(\text{neat})$  3 300 (NH) and 1 680 (CO)  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  1.03—1.23 (t, 3, CH<sub>3</sub>), 2.10—2.57 (2 H, m, CH<sub>2</sub>), 3.00—3.36 (2 H, m, CH<sub>2</sub>), 3.86—4.23 (2 H, m, OCH<sub>2</sub>), 4.83 (1 H, s, NH), and 6.00—6.17 (2 H, m, CH=CH);  $\delta_{\text{C}}(\text{CDCl}_3)$  156.60 (CO), 134.42, 131.24 (=CHBr), 109.91, 106.39 (=CH), 60.68 (OCH<sub>2</sub>), 39.54, 39.21 (CH<sub>2</sub>N), 33.37, 30.31 (CH<sub>2</sub>), and 14.44 (Me);  $m/z$  (70 eV) 221 and 223 ( $M^+$ ) (Found: C, 37.8; H, 5.4; N, 7.1; Br, 35.85. Calc. for C<sub>7</sub>H<sub>12</sub>BrNO<sub>2</sub>: C, 37.86; H, 5.44; N, 6.31; Br, 35.98%).

**Reaction of 1,2-Dibromocyclohexane with Silver Nitrocyanoamide.**—Silver nitrocyanoamide (5.1 g, 26 mmol) and anhydrous magnesium sulphate (1.0 g) were suspended in anhydrous benzene (20 ml) and stirred under nitrogen. *trans*-1,2-Dibromocyclohexane (6.0 g, 24 mmol) was added and the mixture was heated at 80 °C for 48 h. The removal of inorganic salts and solvent left a yellow liquid (4.4 g);  $\nu_{\max}(\text{neat})$  2 250 (NCO) and 2 200  $\text{cm}^{-1}$  (CN). Treatment of this with absolute ethanol (4 ml) and pyridine (2 drops) at 65 °C for 0.5 h gave an oil [(4.5 g),  $\nu_{\max}(\text{neat})$  3 290 (NH), 2 200 (CN), and 1 680  $\text{cm}^{-1}$  (CO)] that afforded two products on flash chromatography. Elution with dichloromethane-hexane (1:1) afforded an unidentified material as colourless prisms (2.0 g, 32%), m.p. 65—66 °C;  $\nu_{\max}(\text{KBr})$  2 200  $\text{cm}^{-1}$  (CN);  $\delta(\text{CDCl}_3)$  1.07—2.67 (8 H, m, CH<sub>2</sub>), 3.80—4.27 (1 H, m, CHBr), and 5.20 (1 H, br, CHN or CHO) (Found: C, 34.5; H, 4.15; N, 15.9; Br, 32.2. Calc. for C<sub>7</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>Br: C, 33.89; H, 4.06; N, 16.94; Br, 32.21%). Further elution with methanol afforded ethyl *N*-(2-bromocyclohexyl)-carbamate (**23**) as a yellow crystalline solid (1.3 g, 22%), m.p. 107—109 °C;<sup>15</sup>  $\nu_{\max}(\text{KBr})$  3 285 (NH) and 1 680  $\text{cm}^{-1}$  (CO);  $\delta(\text{CDCl}_3)$  1.00—1.53 (3 H, t, Me), 2.00—2.63 (8 H, m, CH<sub>2</sub>), 3.43—4.00 (2 H, m, CHBr and CHN), 3.87—4.27 (2 H, q, OCH<sub>2</sub>), and 5.27 (1 H, s, NH);  $\delta_{\text{C}}(\text{CDCl}_3)$  155.82 (CO), 60.55 (OCH<sub>2</sub>), 56.26 and 55.61 (CHBr and CHN), 36.62, 32.98, 25.95, and 24.07 (CH<sub>2</sub>), and 14.38 (Me);  $m/z$  (70 eV) 249 and 251 ( $M^+$ ).

Reaction of silver nitrocyanoamide (26 mmol) and *trans*-1,2-dibromocyclohexane (12 mmol) also gave a mixture that contained the unidentified solid, C<sub>7</sub>H<sub>10</sub>N<sub>3</sub>O<sub>2</sub>Br, m.p. 65—66 °C and 2-bromocyclohexyl isocyanate [identified as ethyl *N*-(2-bromocyclohexyl)carbamate].

**Preparation of Alkyl Nitrocyanoamides.**—Benzyl bromide (3.4 g, 20 mmol) was added in drops to a solution of silver nitrocyanoamide (4.0 g, 21 mmol) in acetonitrile (15 ml) at 0 °C under nitrogen. Immediate precipitation of silver bromide was observed. The mixture was stirred for 1 h and filtered. The solvent was removed under reduced pressure without heating. The residue was triturated in chloroform (50 ml). Unchanged silver nitrocyanoamide was removed by filtration and the clear chloroform solution was concentrated to give benzyl nitro-

cyanamide (**29**; R = PhCH<sub>2</sub>) (3.2 g, 91%), m.p. 47—48 °C;  $\nu_{\max}(\text{KBr})$  2 220 (C≡N), 1 600 and 1 270 (N-NO<sub>2</sub>)  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.43 (5 H, s, ArH) and 5.03 (2 H, s, CH<sub>2</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  130.46, 129.81, 129.15, 128.83 (ArC), 104.38 (C≡N), and 55.74 (CH<sub>2</sub>);  $m/z$  177 ( $M^+$ ) (Found: C, 54.55; H, 3.45; N, 23.85. Calc. for C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>: C, 54.24; H, 3.95; N, 23.73%).

*p*-Xylene- $\alpha,\alpha'$ -diyl dibromide (2.6 g, 10 mmol) was treated with a solution of sodium nitrocyanoamide (2.2 g, 20 mmol) and silver nitrate (3.4 g, 20 mmol) in acetonitrile (15 ml) for 4 h to give the bisnitrocyanoamide (**30**) (2.48 g, 90%), m.p. 88—89 °C;  $\nu_{\max}(\text{KBr})$  2 220 (C≡N), 1 600 and 1 270 (N-NO<sub>2</sub>)  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.50 (4 H, s, ArH) and 5.10 (4 H, s, CH<sub>2</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  132.60, 129.94 (ArC), 104.38 (NCN), and 55.21 (CH<sub>2</sub>);  $m/z$  (70 eV) 276 ( $M^+$ ) (Found: C, 43.35; H, 3.0; N, 29.2. Calc. for C<sub>10</sub>H<sub>8</sub>N<sub>6</sub>O<sub>4</sub>: C, 43.48; H, 2.90; N, 30.43%).

**Conversion of Alkyl Nitrocyanoamides into Isocyanates.**—Benzyl nitrocyanoamide (1.0 g, 6 mmol) was dissolved in dry benzene (10 ml) and refluxed for 10 h. Removal of benzene afforded benzyl isocyanate (0.7 g, 93%). Similarly, refluxing a solution of *p*-xylene- $\alpha,\alpha'$ -diylbisnitrocyanoamide (1.0 g, 4 mmol) in benzene for 2 h gave *p*-xylene- $\alpha,\alpha'$ -diyl di-isocyanate (0.65 g, 96%), m.p. 43—44 °C (lit.,<sup>16</sup> m.p. 46 °C).

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