

## 1,5-Radical Rearrangements during Oxaziridine-Iron(II) Reactions

By Edwin G. E. Hawkins, British Petroleum Company Ltd., Group Research and Development Dept., Epsom Division, Great Burgh, Epsom, Surrey

Reaction of 2'-cyclohexylcyclohexanespiro-3'-oxaziridine with iron(II) sulphate gave, in addition to *N*-cyclohexylhexanamide, considerable amounts of isomeric *NN'*-dicyclohexyldecanedicarboxamides, some of these having a branched-chain structure produced *via* 1,5-radical rearrangements. These, and other, *N*-cyclohexylalkanecarboxamides could be converted into nitriles (or *N*-cyclohexylimides) and olefins by thermal decomposition.

It has been shown that treatment of 2'-alkylcyclohexanespiro-3'-oxaziridines (I) with iron(II) salts gives rise to 5-*N*-alkylcarbamoylpentyl radicals (III), which may (i) abstract hydrogen atoms from other molecules to form 5-*N*-alkylcarbamoylpentanes,<sup>1</sup> (ii) be oxidised (*e.g.* by Cu<sup>II</sup> salts) to 5-*N*-alkylcarbamoylpentenes,<sup>1</sup> (iii) react with certain anions (*e.g.* Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>),<sup>2</sup> (iv) add to reactive olefins (*e.g.* butadiene, acrylonitrile),<sup>3,4</sup> or (v) dimerise.<sup>5</sup> It has been suggested<sup>6</sup> that such radicals are formed *via*

<sup>1</sup> F. Minisci, M. Cecere, and R. Galli, *Gazzetta*, 1968, **98**, 358.

<sup>2</sup> F. Minisci, M. Cecere, and R. Galli, *Chimica e Industria*, 1968, **50**, 225.

<sup>3</sup> F. Minisci, M. Cecere, R. Galli, and A. Selva, *Org. Prepg. Proced.*, 1969, **1**, 11.

<sup>4</sup> F. Minisci, R. Galli, M. Cecere, V. Malatesta, and T. Caronna, *Tetrahedron Letters*, 1968, 5609.

an amino-radical (II) rather than *via* the alkoxy-radical (IV).

The dimeric amide (V; R = Me) was obtained in *ca.* 45% yield on reaction of the oxaziridine (I; R = Me) with iron(II) sulphate.<sup>5</sup> However, alkoxy-radicals can undergo radical (particularly 1,5-) rearrangements;<sup>7</sup> Milas and Perry<sup>8</sup> found that pyrolysis of 1-methyl-1-*t*-butylperoxycyclohexane (VI) gave products (VII) and

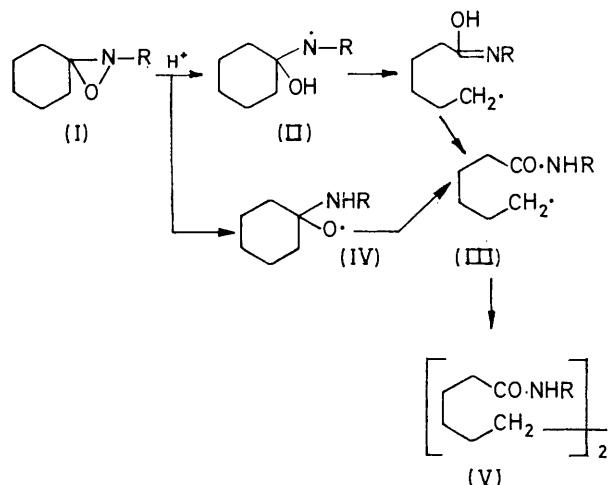
<sup>5</sup> E. Schmitz, R. Ohme, and D. Murawski, *Chem. Ber.*, 1965, **98**, 2516; E. Schmitz and D. Murawski, *ibid.*, p. 2525.

<sup>6</sup> F. Minisci, R. Galli, V. Malatesta, and T. Caronna, *Tetrahedron*, 1970, **26**, 4083.

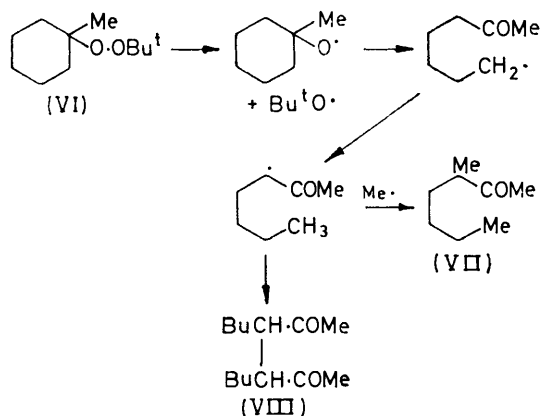
<sup>7</sup> A. Fish, 'Organic Peroxides,' Wiley-Interscience, New York, 1970, vol. I, p. 141.

<sup>8</sup> N. A. Milas and L. H. Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938.

(VIII), formed *via* such 1,5-rearrangement followed by addition of a methyl radical (from the *t*-butoxy-radical) or dimerisation.



In the present work it was found that 1,5-rearrangements also occurred during the reaction of 2'-cyclohexylcyclohexanespiro-3'-oxaziridine (I; R = C<sub>6</sub>H<sub>11</sub>) with iron(II) sulphate. Recrystallisation of the crude dimeric product left after distillation of the *N*-cyclohexylhexanamide (X) (40–45%), gave, in addition to the major constituent [*NN'*-dicyclohexyldodecanediamide (V;

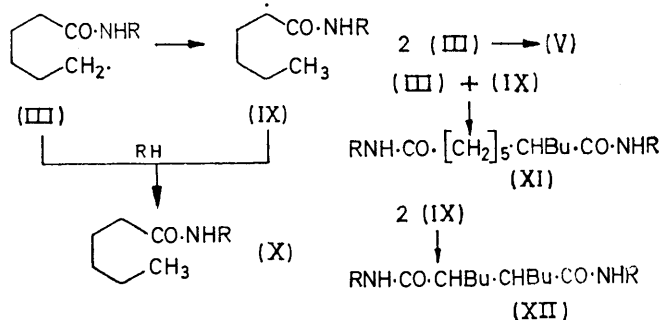


R = C<sub>6</sub>H<sub>11</sub>], a higher-melting diamide mixture shown by n.m.r. and mass spectroscopy to contain compounds with branches consisting of *n*-butyl groups. Analysis of the product from one such experiment by the method described below showed that it contained the amide (X) (41.4%), the diamide (V) (33.5%), *NN'*-dicyclohexyl-2-butyloctanediamide (XI) (18%), and 2,3-dibutyl-*NN'*-dicyclohexylsuccinamide (XII) (6.2%) (R = C<sub>6</sub>H<sub>11</sub> in each case), the last two compounds arising through radical rearrangement.

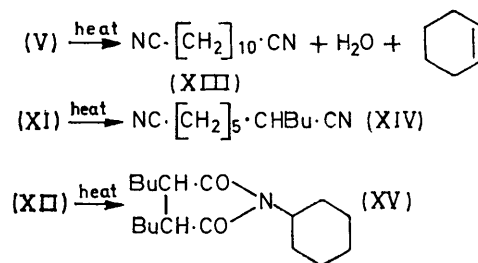
Formation of the products (XI) and (XII) (R = C<sub>6</sub>H<sub>11</sub>) involved 26.7% rearrangement, but both normal and rearranged radicals would provide the monoamide (X; R = C<sub>6</sub>H<sub>11</sub>) by abstraction of hydrogen.

A convenient method for quantitative analysis of the mixture of these amides involved their pyrolysis at 300–

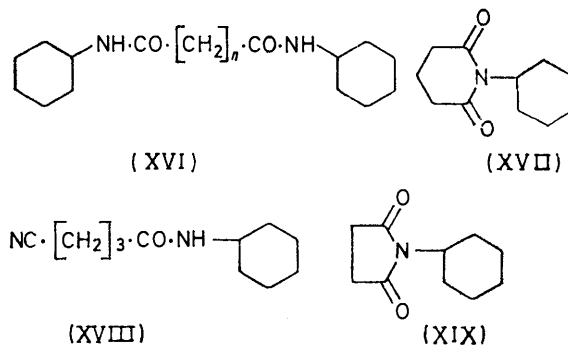
400° for 1–2 h, in the presence of *ca.* 10% boron phosphate (or phosphoric acid), and g.l.c. examination of the products. Under these conditions the monoamide (X; R = C<sub>6</sub>H<sub>11</sub>) was largely recovered, the diamides (V) and



(XI) (R = C<sub>6</sub>H<sub>11</sub>) gave the corresponding dinitriles (XIII) and (XIV), and the diamide (XII; R = C<sub>6</sub>H<sub>11</sub>) was converted into the imide (XV).

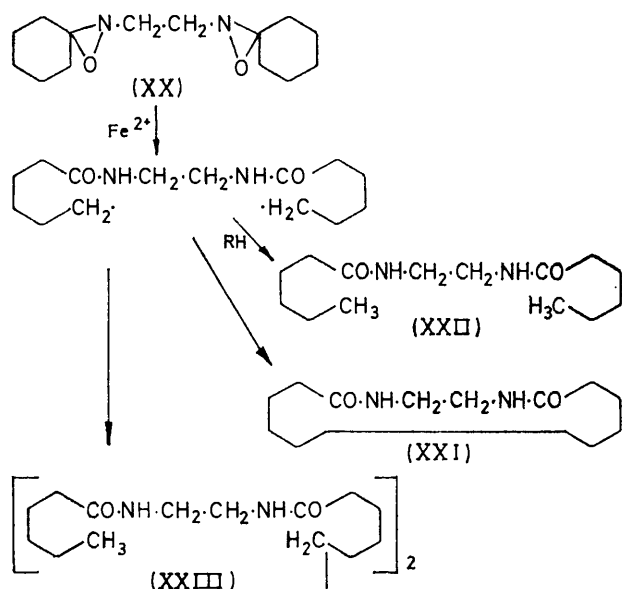


It was found that this reaction proceeded essentially quantitatively with a number of synthetic amides: the diamides (XVI) (*n* = 4–10) gave the corresponding dinitriles, that with *n* = 3 yielded a mixture of the imide (XVII) and nitrile amide (XVIII), that with *n* = 2 was converted completely into the imide (XIX), and the synthetic diamides (XI) and (XII) (R = C<sub>6</sub>H<sub>11</sub>) provided (XIV) and (XV), respectively. Similarly, *N*-cyclohexylbenzamide gave benzonitrile, and 6-chloro-*N*-cyclohexylhexanamide yielded both hex-5-enonitrile



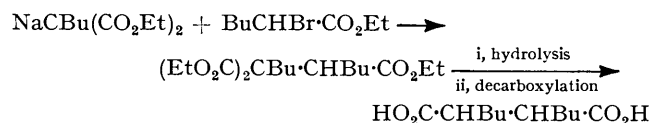
and *N*-cyclohexylhex-5-enamide, but, even on prolonged reaction at temperatures up to 440°, *NN'*-dimethyl- and *NN'*-diethyldodecanediamide only underwent slight decomposition to give complex mixtures containing minor amounts of dodecanedinitrile; on the other hand,

*NN'*-di-*t*-butyldodecanediamide readily yielded the dinitrile and isobutene under normal reaction conditions.



The bisoxaziridine (XX) and iron(II) sulphate provided impure solid products shown by mass spectroscopy to contain compounds C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>, C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>, and C<sub>28</sub>H<sub>54</sub>N<sub>4</sub>O<sub>4</sub>, in accord with the structures (XXI)—(XXIII) of compounds derived from the intermediate diradical.

and (b) 2,3-di-*n*-butylsuccinic acid (isomers, m.p. 169—171<sup>8</sup> and 84—87°), obtained by a similar method:



The amides (Table 1) were obtained by reactions of the corresponding acid chlorides with the requisite primary amines.

*Pyrolysis of Amides.*—Since uncatalysed thermal decomposition of the amides was slow, they were heated, in the presence of boron phosphate (*ca.* 10%) at 340—400°, until no further material distilled over (1—2 h); the distillate was returned to the reaction flask and the total product was fractionated and analysed by g.l.c. and i.r. and n.m.r. spectroscopy. The results are given in Table 2.

Prolonged heating of the amides RNH·CO·[CH<sub>2</sub>]<sub>10</sub>·CO·NHR (R = Me or Et) with boron phosphate at 440° and 1 atm gave a product shown by g.l.c. and mass spectroscopy to contain, in addition to the corresponding dinitrile (<5 and <15%, respectively), a large number of saturated and unsaturated nitriles and amides with a wide range of chain lengths, evidently derived from chain fission and dehydrogenation.

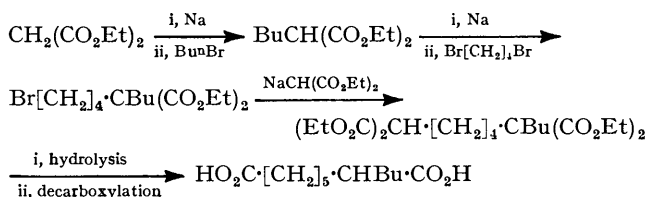
*Reaction of Oxaziridines with Iron(II) Salts.*—(a) 2'-Cyclohexylcyclohexanespiro-3'-oxaziridine. (i) The oxaziridine (18 g) was rapidly added to stirred iron(II) sulphate (heptahydrate) (30 g), sodium acetate (9 g), water (25 cm<sup>3</sup>), and methanol (25 cm<sup>3</sup>) at 25°; the temperature rose to 60°. After 0.5 h the mixture was acidified with dilute sulphuric acid; the solid diamides (12.0 g) were filtered off and washed

TABLE I  
Amides RNH·CO·A·CO·NHR

R	A	M.p. (°C)	Found (%)			Calc. (%)		
			C	H	N	C	H	N
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>10</sub>	189—192	73.55	11.2	7.1	73.45	11.2	7.15
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>8</sub>	196—198	72.55	11.15	7.65	72.5	11.0	7.7
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>7</sub>	177—180	71.85	11.0	8.25	72.0	10.85	8.0
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>6</sub>	214—217	71.6	10.9	8.25	71.4	10.7	8.3
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>5</sub>	190—192	70.6	10.65	8.6	70.8	10.55	8.7
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>4</sub>	239—241	70.15	10.55	9.0	70.1	10.4	9.1
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>3</sub>	214—217	69.5	10.35	9.5	69.4	10.2	9.5
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>2</sub>	244—250	69.1	10.45	9.95	68.6	10.0	10.0
C <sub>6</sub> H <sub>11</sub>	[CH <sub>2</sub> ] <sub>5</sub> ·CHBu	201—203	73.55	11.35	7.05	73.45	11.2	7.15
C <sub>6</sub> H <sub>11</sub>	CHBu·CHBu	333—337			6.95			7.15
		284—287	72.8	11.0	6.8	73.45	11.2	7.15
Me	[CH <sub>2</sub> ] <sub>10</sub>	151—153	66.25	11.1	10.55	65.6	10.95	10.95
Et	[CH <sub>2</sub> ] <sub>10</sub>	150—152			9.45			9.85
Bu <sup>t</sup>	[CH <sub>2</sub> ] <sub>10</sub>	133—135	70.0	11.85	8.3	70.6	11.8	8.25

#### EXPERIMENTAL

The acids used for preparation of the amides were commercially available except for (a) 2-butylsuccinic acid, m.p. 65—67° (Found: acid equiv. 113. C<sub>12</sub>H<sub>22</sub>O<sub>4</sub> requires acid equiv. 115), prepared by normal malonic ester synthesis *via* the route:



with ether, the aqueous phase was extracted with chloroform and the combined ethereal washings and chloroform extract were distilled at 15 mmHg to give fractions (i) (0.2 g), b.p. 40—50°, and (ii) (5.0 g), b.p. 170—210°, and a residue (1.9 g). Fraction (ii) crystallised from petroleum (b.p. 40—60°), gave *N*-cyclohexylhexanamide, m.p. and mixed m.p. 70—72°.

The solid diamides, from this and other experiments, on recrystallisation from chloroform and from ethanol, provided *NN'*-dicyclohexyldodecanediamide, m.p. and mixed m.p. 188—191°. From repeated recrystallisations there was isolated a small quantity of higher-melting solid, m.p. 235—245°, *m/e* 392 (C<sub>24</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>), with fragment ions consistent with *n*-butyl branches; the n.m.r. spectra also

provided evidence for  $\text{MeCH}_2\text{C}^-$  and  $-\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{C}\equiv\text{N})\cdot\text{C}$ - functions.

(ii) The oxaziridine (16 g) was added to stirred iron(II) chloride (tetrahydrate) (25 g), water (25 cm<sup>3</sup>) and methanol (25 cm<sup>3</sup>) at 30°; after stirring for 4 h the solution was acidified with hydrochloric acid and extracted with chloroform; the extract was distilled at 15 mmHg to give fractions (i) (1.1 g), b.p. 40—50°, and (ii) (13.2 g), b.p. 190—220°, and a residue (0.7 g). Fraction (i) was largely cyclohexanone and fraction (ii), crystallised from ether, gave 6-chloro-*N*-cyclohexylhexanamide, m.p. 72—74° (Found: C, 62.8; H, 9.8; N, 6.15.  $\text{C}_{12}\text{H}_{22}\text{ClNO}$  requires C, 62.2; H, 9.5; N, 6.05%), *m/e* 231.

action of the oxaziridine (I; R =  $\text{C}_6\text{H}_{11}$ ) (20 g) with iron(II) sulphate (32 g), sodium acetate (10 g), water (25 cm<sup>3</sup>), and methanol (25 cm<sup>3</sup>) was heated with boron phosphate (2 g) to 400° at 250 mmHg and the product was distilled to give fractions (i) (6.0 g), b.p. 60—105° at 1 atm, and (ii) (13.3 g), b.p. 150—290° at 15 mmHg, and a residue (2.7 g). Fraction (i) was found to consist largely of (wet) cyclohexene with some cyclohexylamine, and, by g.l.c., fraction (ii) contained *N*-cyclohexylhexanamide (58%), dodecanedinitrile (23.0%), the dinitrile (XIV) (13.0%), and the imide (XV) (6.5%).

(b) 6-Chloro-*N*-cyclohexylhexanamide (6 g) and boron phosphate (0.5 g) were heated together at 320—340° and 1 atm; during the ensuing vigorous reaction hydrogen

TABLE 2  
Pyrolysis of amides

Amide	Wt. (g)	BPO <sub>3</sub> Wt. (g)	Temp. (°C) [pressure (mmHg)]	Product		Residue* Wt. (g)		
				Wt. (g)	Composition		Wt. (g)	Composition
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_{10}\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[250]	3.0	4.6	NC[CH <sub>2</sub> ] <sub>10</sub> CN	1.1	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_8\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[280]	3.0	4.4	NC[CH <sub>2</sub> ] <sub>8</sub> CN <i>a</i>	0.4	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_6\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[300]	3.4	4.3	NC[CH <sub>2</sub> ] <sub>6</sub> CN <i>a</i>	0.4	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_4\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[300]	4.2	4.9	NC[CH <sub>2</sub> ] <sub>4</sub> CN <i>a</i>	0.1	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[300]	3.9	3.5	NC[CH <sub>2</sub> ] <sub>2</sub> CN <i>a</i>	0.7	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_0\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—400[1 atm]	1.9	3.9	NC[CH <sub>2</sub> ] <sub>0</sub> CN <i>b</i>	2.5	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	4	0.5	360—380[1 atm]	1.2	1.8	<i>N</i> -Cyclohexyl-glutanamide + NC[CH <sub>2</sub> ] <sub>3</sub> CO·NHC <sub>6</sub> H <sub>11</sub>	0.2	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_2\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	340—380[1 atm]	2.0	5.6	<i>N</i> -Cyclohexylsuccinimide <i>c</i>		
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_6\text{CHBu}\cdot\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	10	1	360—380[250]	2.4	5.4	NC[CH <sub>2</sub> ] <sub>6</sub> CHBu·CN <i>d</i>	0.5	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{CO}\cdot\text{CHBu}\cdot\text{CHBu}\cdot\text{CO}\cdot\text{NHC}_6\text{H}_{11}$	1.4	0.3	340—360[250]		0.7	2,3-Dibutyl- <i>N</i> -cyclohexyl-succinimide	0.2	
$\text{Bu}^t\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_{10}\text{CO}\cdot\text{NHBu}^t$	10	1	300—320[1 atm]	3.1	5.2	NC[CH <sub>2</sub> ] <sub>10</sub> CN	1.2	
$\text{C}_6\text{H}_{11}\text{NH}\cdot\text{COPh}$	10	1	325—345[1 atm]	3.7	4.6	PhCN <i>e</i>	0.2	

*a* Containing some nitrile amide NC[CH<sub>2</sub>]<sub>6</sub>CO·NHC<sub>6</sub>H<sub>11</sub>. *b* Containing unchanged diamide and nitrile amide. *c* Containing traces of a compound C<sub>16</sub>H<sub>26</sub>N<sub>2</sub>O (possibly 1-cyclohexyl-5-cyclohexylimino-2-pyrrolidone. *d* Containing traces of corresponding nitrile acids, nitrile amides, and a compound C<sub>18</sub>H<sub>31</sub>NO<sub>2</sub> (possibly 2-butyl-*N*-cyclohexylsuccinimide). *e* Also a fraction (1.1 g), mainly unchanged amide.

\* After allowance for boron phosphate.

(b) *NN'*-Ethylenebis(cyclohexanespiro-3'-oxaziridine). The bisoxaziridine (9.0 g), in ethanol (50 cm<sup>3</sup>), was added to a stirred mixture of iron(II) sulphate (20 g) in water (20 cm<sup>3</sup>) and concentrated sulphuric acid (5 cm<sup>3</sup>) at <10°, stored at room temperature overnight, and filtered; the filtrate was extracted with chloroform. Evaporation of the solvent afforded a semicrystalline residue (4.3 g), which, on trituration with ethanol-ethyl acetate, provided a solid (A), m.p. ca. 185°. Distillation of the filtrate gave a distillate (1.5 g), b.p. 250—280° at 15 mmHg, and a residue (0.4 g); the distillate afforded a solid (B), m.p. 170—175° (from ethyl acetate). The i.r. spectra of both (A) and (B) showed the presence of secondary amide groups; the major component of (A) had *m/e* 510 [C<sub>28</sub>H<sub>54</sub>N<sub>4</sub>O<sub>4</sub>; probably (XXIII)], and (B) had *m/e* 256 [C<sub>14</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>; probably (XXII)] (mainly), and *m/e* 254 [C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>; probably (XXI)].

*Pyrolysis of the Products.*—(a) The combined solid diamides and residue from the chloroform extract [from re-

chloride was produced. After completion of the reaction (0.5 h) the product was distilled to give fractions (i) (0.6 g), b.p. 70—100° at 1 atm, (ii) (0.6 g), b.p. 70—75° at 15 mmHg, and (iii) (2.4 g), b.p. 170—185° at 15 mmHg, and a residue (1.0 g). I.r. and mass spectroscopy showed that fraction (i) was mainly cyclohexene, fraction (ii) had C≡N, CH<sub>2</sub>=CH, and CH=CH groups and *m/e* 95 (C<sub>6</sub>H<sub>9</sub>N), consistent with isomeric cyanopentenes, and fraction (iii) [*m/e* 195 (C<sub>12</sub>H<sub>21</sub>NO)] was probably largely *N*-cyclohexylhex-5-enamide.

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