benzene reagent led exclusively to **18a**, identical to the sample obtained earlier.

From 500 mg (4.2 mmol) of **15**, **18b** was isolated in 97% yield: ^{1}H NMR ($CDCl_3$) δ 6.23 (d with fine splitting, J = 5 Hz, 1), 6.00 (dd, J = 9 and 5 Hz, 1), 5.82 (s, 1), 5.28 (m, 1), 2.30 (d, J = 7 Hz, 2), 2.00 (s, 3), and 1.97 (d, J = 1.5 Hz, 3); m/e calcd 120.0939, found 120.0941.

Cycloaddition of N-phenyltriazolinedione to **18b** in ethyl acetate solution at 0 °C gave **19b** as colorless needles: mp 118.5–120 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 7.37 (br s, 5), 5.70–5.42 (m, 1), 5.03 (t, J = 5.5 Hz, 1), 4.62 (d, J = 2 Hz, 1), 3.45 (s, 3), 1.33 (s, 3), 1.17 (m, 1), 0.43 (d, J = 2.5 Hz, 1), and 0.33 (s, 1); m/e calcd 295.1321, found 295.1320. Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.04; H. 6.04; N, 14.16.

Photoelectron Spectroscopy. The PE spectra have been recorded on a Perkin-Elmer Ltd PS 18 instrument (Beaconsfield, England). The spectra were calibrated with Ar and a resolution of about 20 meV on the Ar line was obtained.

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Registry No.—**11**, 66036-93-9; **12**, 66036-94-0; **13**, 66036-95-1; **14**, 66036-96-2; **15**, 61772-32-5; **16**, 3045-90-7; **17**, 66036-97-3; **18a**, 3045-88-3; **18b**, 61772-26-7; **19a**, 66036-98-4; **19b**, 66036-99-5; **22**, 66037-00-1; **23**, 66037-01-2; 1,4-dimethyl-1,4-cyclohexadiene, 4074-22-0; 2,4-dimethyl-1,4-cyclohexadiene, 4190-06-1; N-phenyltriazolinedione, 4233-33-4.

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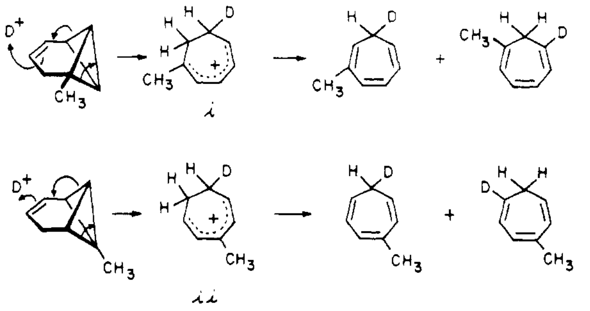
(24) Because of the relative amount of CD_3COOD added and the liberation of H^+ as the rearrangement proceeds, quantitative incorporation of 1 molar equiv of deuterium cannot be expected and is not seen.

(25) The following alternative mechanisms may be legitimately advanced for consideration:



However, they account neither for the exclusivety of product formation nor the absence of observable (^{1}H NMR) sp^2-bound deuterium (note particularly the latent symmetry of ii).

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Isocyanide Reductions. A Convenient Method for Deamination[1]

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Dissolving metal reductions of a number of isocyanides are reported. Dissolving metal reduction of a chiral acyclic isocyanide leads to formation of racemic product. Some stereoselectivity is observed in the reduction of a chiral cyclopropyl isocyanide. Due to the ease of conversion of primary amines to isocyanides and the excellent yields obtained in the dissolving metal reduction of isocyanides, this method is recommended for deamination of primary amines. The mechanism of dissolving metal reduction is discussed.

Ugi and Bodesheim[2] observed the nearly quantitative reduction of isocyanides to their corresponding hydrocarbons by solutions of metals (lithium, sodium, potassium, and calcium) in liquid ammonia. They conjectured that the isocyanide accepted two electrons, by either a one-step or a two-step process, followed by cleavage of the carbon–nitrogen bond.

$$RN{=}C + 2M \xrightarrow{NH_3} RH + MCN + MNH_2$$

Later, Büchner and Dufaux[3] observed that the reductive cleavage of isocyanides occurred in tetrahydrofuran as a solvent as well as in liquid ammonia. These workers postulated a two-step mechanism in which the addition of the first electron leads to formation of an anion radical intermediate which can accept a second electron leading to the formation of a carbanion intermediate and cyanide ions.

$$RN{=}C \xrightarrow{e^-} [RN{=}\dot{C}]^- \xrightarrow{e^-} R{:}^- + CN^-$$

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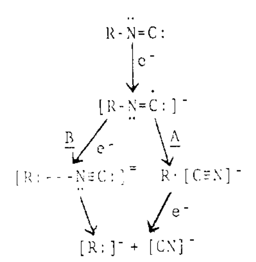
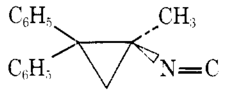
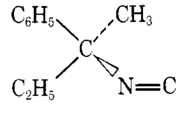


Figure 1. Scheme for the reduction of isocyanides

Our interest in the mechanism of interaction of organohalides with metals[4] prompted the investigation of the reductive cleavage of isocyanides since the results obtained by the early workers[2,3] fitted the reaction scheme proposed for halide reduction.[4,5] This scheme, when applied to the particular case of isocyanides, is depicted in Figure 1.

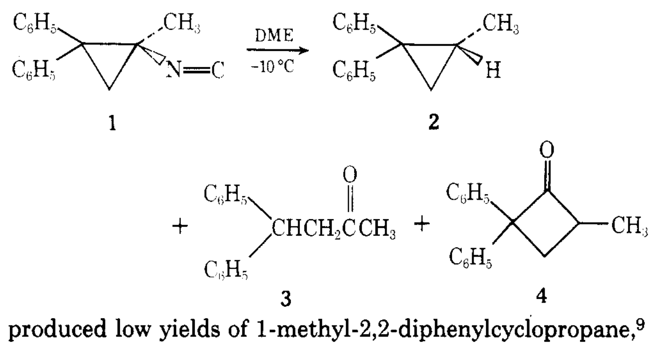
In order to gain some insight into the contribution of path A or path B to the overall reaction, the reduction of a chiral isocyanide whose chiral center is adjacent to the isocyanide moiety was selected for study. If path A were the sole process, the hydrocarbon formed from the free-radical intermediate should be essentially racemic. On the other hand, path B should lead to retention of configuration, if the carbanion intermediate is one whose configuration is stable. This has been shown to be the case for the 1-methyl-2,2-diphenylcyclopropyl anion[5,6] whose configuration is maintained whereas the 1-methyl-2,2-diphenylcyclopropyl radical intermediate, under homogeneous conditions, is unable to maintain its configuration and racemizes rapidly.[7] The stereochemistry of the reductive cleavage of chiral (+)-(*S*)-1-methyl-2,2-diphenylcyclopropyl isocyanide (**1**) and the acyclic (−)-(*S*)-2-phenyl-2-butyl isocyanide (**5**) is the subject of this paper.


(+)-*S*-**1**


(−)-(*S*)-**5**

Results and Discussion

Dissolving Metal Reduction. The chiral isocyanides **1** and **5** have been synthesized previously[8] and their absolute configurations have also been established.[8] The reductive cleavage of **1** by lithium or sodium metal in 1,2-dimethoxyethane produced low yields of 1-methyl-2,2-diphenylcyclopropane,[9] the main products (82–86% of total) being the rearranged 4,4-diphenyl-2-butanone (**3**) and 2,2-diphenyl-4-methylcyclobutanone (**4**).[9] Sodium dissolved in liquid ammonia produced a different set of rearranged products, 1,1-diphenylbutane (**6**) and 3,3-diphenyl-5-methylpyrrolidine (**7**). The reduction of (−)-(*S*)-**5** by a blue solution of sodium (8%) in liquid ammonia or by a bronze solution of sodium (15%) in liquid ammonia yielded the hydrocarbon *sec*-butylbenzene in 92–98% yield but it was totally racemized.



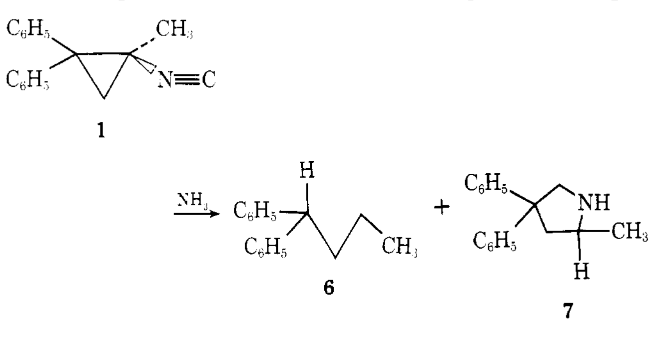


Table I. Sodium Napthalene Reduction of 1-Methyl-2,2-diphenylcyclopropyl Isocyanide in 1,2-Dimethoxyethane

	Yields, %[b]		
$[\mathrm{Na^+Naph^-}]_{\mathrm{cor}}$,[a] M	**2**	**3**	**4**
0.023	92	4	4
0.104	95	2.5	2.5
0.250	94	3	3
0.370	87	6.5	6.5

[a] Corrected according to eq 1. [b] Relative distribution based on peak areas of GLC.

It was found that the amount of rearranged product, obtained in the reduction of **1**, could be drastically diminished when sodium naphthalene in 1,2-dimethoxyethane was used as the reducing medium. Under these conditions **2** was obtained in 87–95% yield and the rearranged products **3** and **4** in 5–13% (Table I).

As was pointed out previously[9] the formation of **3** and **4** as the major products in the reduction of 1 with lithium or sodium dispersion in 1,2-dimethoxyethane was due to the formation of an intermediate 1-lithio- or 1-sodio-1-methyl-2,2-diphenylcyclopropane which then, by α addition, added to the unreacted isocyanide 1. Since the reaction at a metal surface is necessarily much slower than with a homogeneous dissolved metal source, the α addition competes favorably under these conditions but unfavorably in the sodium naphthalene reduction.

Another apparent anomaly is in the reduction of 1 with sodium dissolved in liquid ammonia. Even under these homogeneous conditions the major products formed, 1,1-diphenylbutane (**6**) and 3,3-diphenyl-5-methylpyrrolidine (**7**), resulted from a rearrangement reaction. As has been discussed previously,[9] the initial electron transfer in liquid ammonia is not to the isocyanide moiety but to the benzene ring in 1 which leads to the reductive cleavage of the cyclopropyl ring. However, from the results obtained under aprotic conditions, sodium naphthalene in 1,2-dimethoxyethane, reduction seems to involve an electron transfer to the isocyanide. If our interpretation is correct, this is a unique solvent effect.

The reduction of 1 with sodium naphthalene in 1,2-dimethoxyethane proceeds with overall retention of configuration. The dependence of the retention of optical activity on the sodium naphthalene concentration is shown in Figure 2. The optically pure (+)-(*S*)-1 was added to a 5 mol excess of sodium naphthalene in 1,2-dimethoxyethane at −10 °C. Although varying concentration of sodium naphthalene were used, the 5 mol excess was maintained.

The values for the concentrations used in plotting Figure 2 were corrected according to eq 1 since the measured retention of optical activity for the isolated reduction product was assumed to represent an average value from species generated throughout the course of reduction. The correction also takes into account the relative product distribution shown in Table I by which the α-addition products involve additional consumption of the cyclopropyl isocyanide and therefore a higher final sodium napthalene concentration than predicted from simple stoichiometry.[10]

$$[\mathrm{Na^+\ Naphth^{-}\cdot}]_{\mathrm{cor}} = [\mathrm{Na^+\ Naphth^{-}\cdot}]_{\mathrm{init}} - \tfrac{1}{2}([\mathrm{Na^+\ Naphth^{-}\cdot}]_{\mathrm{init}} - [\mathrm{Na^+\ Naphth^{-}\cdot}]_{\mathrm{final}}) \quad (1)$$

Table II. Experimental Data for the Reduction of (+)-(*S*)-1-Methyl-2,2-diphenylcyclopropyl Isocyanide

Run	$[Na^+Napth]^{-}\cdot_{init}$[a]	$[Na^+Naphth]^{-}\cdot_{corr}$[b]	$[\alpha]^{24}{}_{5461}$ **2**[c]	Optical purity, %[d]
1	0.029 ± 0.005	0.023 ± 0.006	−0.9 ± 0.3	0.6 ± 0.2
2	0.128 ± 0.008	0.104 ± 0.010	−5.4 ± 0.2	3.6 ± 0.1
3	0.310 ± 0.008	0.250 ± 0.014	−13.0 ± 0.2	8.7 ± 0.1
4	0.461 ± 0.008	0.370 ± 0.017	−20 ± 1	13.3 ± 0.6

[a] Mol/L. [b] From eq 1. [c] Specific rotations (*c* 1, $CHCl_3$). [d] Authentic sample[11] of optically pure **2** has $[\alpha]^{24}{}_{5461}$ 150° (*c* 0.8, $CHCl_3$).

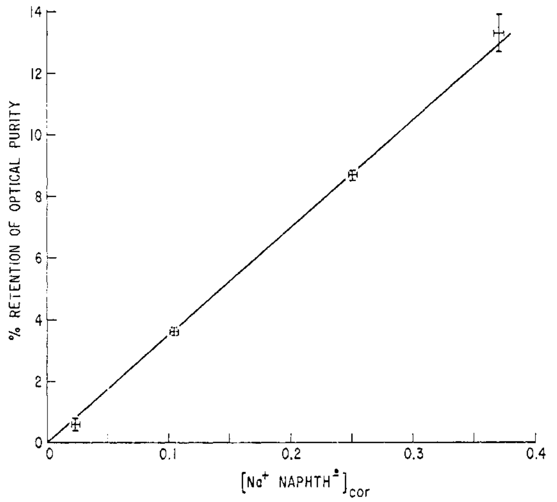
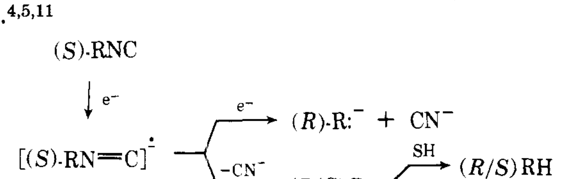


Figure 2. Retention of optical purity in the reduction of 2,2-diphenyl-1-methylcyclopropyl isocyanide to 1,1-diphenyl-2-methylcyclopropane with sodium naphthalene concentration (mol/L).

Qualitatively, two points become evident from the graph in Figure 2. First, there appears to be no residual retention mechanism such as hydrogen abstraction from solvent by a configurationally stable cyclopropyl radical since, if this were the case, extrapolation to zero concentration would have resulted in an intercept. This observation is consistent with previous evidence for the configurational instability of the 2,2-diphenyl-1-methylcyclopropyl radical.[7] Second, the linear relationship exhibited indicates that the overall reduction is probably a two-step process in which an optically active intermediate is short lived and therefore exists only in steady-state concentrations. These two observations lend support to a reduction mechanism similar to the one proposed earlier.[4,5,11]



The initially formed radical anion, of retained configuration, either dissociates to give the racemic radical or is reduced to a carbanion of retained configuration. The degree of retention of configuration in the final product will be dependent on the lifetime of the radical anion. In the metal dispersion reductions the radical anion would be in contact with the metal surface, its potential electron source. This may account for the higher degree of retention of optical purity (67% for sodium dispersion in DME). On the other hand, in the solvated electron systems, radical anion dissociation would be competing with the rate of molecular diffusion of its electron source, in this case sodium naphthalene. Thus, the degree of retention of configuration would be much lower and likewise should be dependent on the concentration of the electron source as was observed in Figure 2.

As one might expect, based on the relative configurational stabilities of the cyclopropyl anion and the acyclic 2-phenyl-2-butyl anion, the reduction of (−)-(*S*)-**5** with excess sodium naphthalene in tetrahydrofuran followed by quenching with carbon dioxide resulted in the formation of racemic 2-methyl-2-phenylbutanoic acid.

From a synthetic viewpoint, the use of sodium naphthalene as a reducing medium for the reduction of isocyanides should be the method of choice. Since both aromatic and alphatic primary amines can be converted to isocyanides conveniently and in high yield,[8,12] this may well turn out to be an excellent method for deamination, the only drawback being that the reduction is not stereospecific.

$$RNH_2 \rightarrow RN{=}C \rightarrow RH$$

Experimental Section[13]

Reduction of (−)-(*S*)-2-Phenyl-2-butyl Isocyanide.[8] The sodium–liquid ammonia reductions were carried out as previously described.[14] The product, *sec*-butylbenzene (bp 172–174 °C), was isolated in 96–98% yield and was racemic.

Reduction of (−)-(*S*)-2-Phenyl-2-butyl Isocyanide with Sodium Naphthalene. Under an argon atmosphere 0.65 g (0.03 g-atom) of sodium and 3.8 g (0.03 mol) of naphthalene in 50 mL of tetrahydrofuran freshly distilled from $LiAlH_4$ were stirred for 1.5 h. The solution was cooled to −5 °C and 0.29 g (0.002 mol) of (−)-(*S*)-2-phenyl-2-butyl isocyanide was added and stirring was continued for 10 min. The solution was cooled with a dry ice–acetone bath and anhydrous carbon dioxide gas was introduced rapidly over a 10-min period and then quenched with aqueous methanol. After ambient temperature was reached the solution was diluted with water. The aqueous layer was washed with methylene chloride and then acidified with hydrochloric acid. The acidified solution was extracted with methylene chloride and the extract was dried (magnesium sulfate). Removal of solvent followed by distillation yielded 0.12 g of 2-methyl-2-phenylbutanoic acid, mp 56–58 °C, whose IR and NMR spectra were identical with those of an authentic sample.[14] The acid was racemic.

Reductions of (+)-(*S*)-1-Methyl-2,2-diphenylcyclopropyl Isocyanide with Sodium Naphthalene. Spheres of sodium were prepared by melting the metal in hot xylene with gentle stirring. Prior to use the solidified spheres were cleaned to a bright metallic finish under argon by sequential washes of THF–methanol (anhydrous), THF, diethyl ether, and finally hexane. Under an argon atmosphere the sodium was reacted at −10 ± 1 °C with a predetermined amount of recrystallized naphthalene in a measured volume of freshly distilled (from $LiAlH_4$) 1,2-dimethoxyethane for 2 h with stirring. The sodium sphere was removed and an additional 5% of naphthalene was added and stirring was continued for 30 min. An aliquot of the solution was removed and titrated for total base content to determine the radical anion concentration and based on the volume of 1,2-dimethoxyethane the total moles of sodium naphthalene was determined. A quantity, equivalent to 20% of the above molar concentration of optically pure (+)-(*S*)-1-methyl-2,2-diphenyl isocyanide,[8] $[\alpha]^{24}{}_{5461}$ 167 ± 1° (*c*, 1.0, $CHCl_3$), was added and the mixture was stirred for 3.0 ± 0.2 min. The reaction mixture was extracted with ether, the ether extract was washed with water and dried over magnesium sulfate, and the solvent was evaporated. VPC analysis (15% SE-33 on 80/100 Chromosorb P, AW) was used to identify and estimate[9] the relative amounts of **2**, **3**, and **4**. The hydrocarbon **2** was isolated by preparative VPC and rotations measured. Table II lists the experimental results.

Registry No.—**1**, 53152-70-8; **2**, 10439-30-2; **3**, 5409-60-9; **4**, 65899-48-1; **5**, 65941-43-1; (±)-*sec*-butylbenzene, 36383-15-0; (±)-2-methyl-2-phenylbutanoic acid, 51018-80-5.

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(10) This correction appears to already assume a linear dependence of retention of optical purity on sodium naphthalene concentration. A nonlinear relationship could still have been detected by the graph of Figure 2 since sodium naphthalene is in a 5 mol excess.
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Synthesis and Deamination of 4-Aminospirohexane

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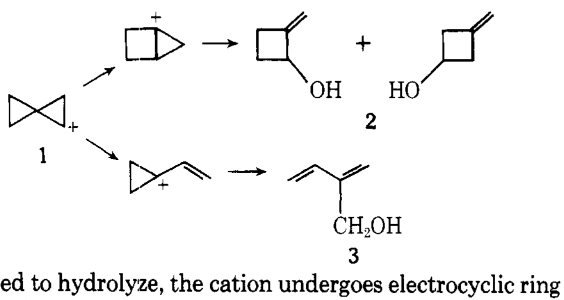
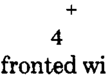
4-Aminospirohexane and 5-aminospirohexane were prepared by direct chlorocarbonylation of spirohexane followed by Curtius degradation. Deamination of 4-aminospirohexane with nitrous acid gave a mixture of spirohexan-4-ol, 2-methylenecyclopentanol, 3-methylenecyclopentanol, cyclohexanone, and several unidentified minor products. This mixture is compared with the products of the 4-spirohexyl cation as generated by solvolysis. 5-Aminospirohexane and nitrous acid gave only spirohexan-5-ol.

Rearrangements of the spiropentyl cation 1 show a remarkable dual behavior, depending upon the mode of generation.[1] When spiropentylamine is deaminated with nitrous acid, the cation rearranges like a cyclopropylcarbinyl cation, giving methylenecyclobutanols 2. When chlorospiropentane is allowed to hydrolyze, the cation undergoes electrocyclic ring opening like a cyclopropyl cation, leading to 2-hydroxymethylbutadiene (3). Although different ways of producing a carbonium ion generally lead to different compositions of the product mixture, the absence of any overlap in products in the above two cases is out of the ordinary, especially considering that both reactions were run in water.



In an effort to see if the same kind of duality of behavior could be found in a closely related system, it was decided to investigate the products from the 4-spirohexyl cation 4. In this case the cation is again confronted with a competition between two favorable types of behavior. As a cyclopropylcarbinyl cation, it could give ring enlargement to a cyclobutyl cation, rearrangement to an isomeric cyclopropylcarbinyl cation, or cleavage to an allylcarbinyl cation. As a cyclobutyl cation, it could give ring contraction or cleavage of the four-membered ring.



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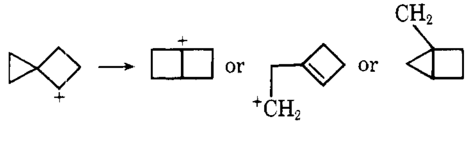
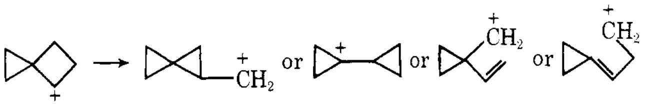
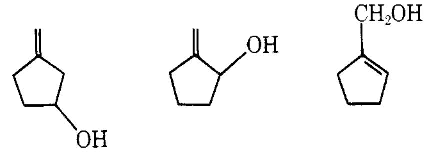
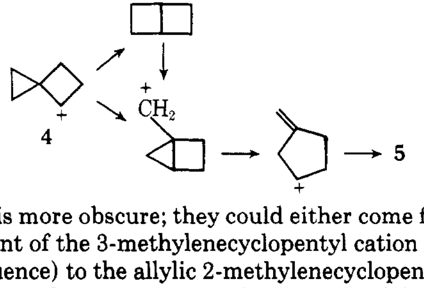


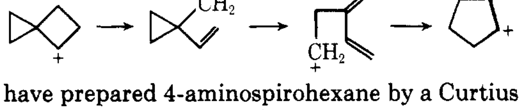


The products from hydrolysis of 4-spirohexyl chloride[2] and 3,5-dinitrobenzoate[3] have already been investigated. The rearranged products are alcohols 5–7, with 5 making up more than half of the mixture. Product 5 seems most likely to have arisen from cyclopropylcarbinyl-type behavior of 4. The origin of 6 and 7 is more obscure; they could either come from a rearrangement of the 3-methylenecyclopentyl cation (from the above sequence) to the allylic 2-methylenecyclopentyl cation or from initial behavior of 4 in the other (cyclobutyl-type) mode.



5; 52-64% 6; 6-15% 7; 0-5%





We have prepared 4-aminospirohexane by a Curtius degradation procedure developed previously for aminospiro-

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