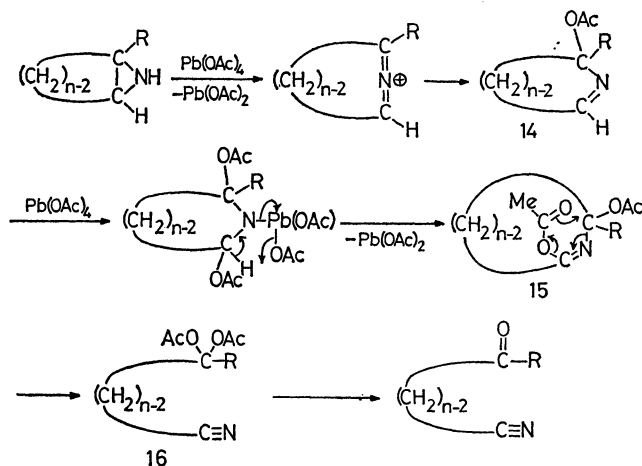


Table 2. In contrast to the above results, 7-azanorcarane (**10c**) was recovered unchanged under the typical condition, but the reaction at reflux of dichloromethane gave a product tentatively assigned as 7,7'-bi-7-azanorcarane (**13**).

The mechanism of the novel transformation can be understood by the following scheme involving two moles of lead tetraacetate. A cyclic 2-azaallene cation is readily susceptible to nucleophilic attack of acetate anion to give **14**. Addition of lead tetraacetate on the C=N bond in **14** followed by elimination yields **15**. Facile thermal rearrangement affords a *gem*-diacetate **16**, characterized by the spectrometry of the crude product (1735—1744 cm^{-1} , $\delta \sim 2.0$ (singlet)). Purification upon silica gel tlc induces the hydrolysis of **16** to give the corresponding ω -cyano carbonyl compound. Obviously **10c** should give a nitrenium ion which can not be isomerized to a seven-membered azaallene cation due to the strain. This accounts for the formation of **13**.

The transformation of an olefin into an ω -cyanoaldehyde has been previously achieved by the addition of nitrosyl chloride and the following Beckmann rearrangement.¹³ The present method is more generally applicable, as the 2-substituted aziridines are easily obtained from cyclic ketone oximes by means of the Neber reaction¹⁴ proceeding in the presence of Grignard reagents or organolithiums.



Experimental

IR spectra were recorded on a Shimadzu IR-27 G spectrometer, mass spectra on a Hitachi RMU-6L machine, and PMR spectra on a Varian EM 360 spectrometer (60 MHz) in carbon tetrachloride solution. All the temperatures recorded are uncorrected.

Oxidation of Amines **1**, **2**, and **3** with Lead Tetraacetate. A General Procedure.

To a solution of lead tetraacetate (490 mg, 1.1 mmol) in dichloromethane (20 ml) an amine (1.0 mmol) dissolved in dichloromethane (5 ml) was added dropwise under a nitrogen atmosphere at -78°C . The mixture was then gradually warmed up to room temperature in *ca.* 10 hr. Isolation of the product was accomplished by concentration of the reaction mixture, followed by preparative tlc. The product was identified by the comparison of its spectral data with those of the authentic specimen. The results are summarized in Table 1. The yields were estimated either by

TABLE 1. OXIDATION OF **1**, **2**, AND **3**

Amine	Oxidant	Product	Yield (%)
<i>trans</i> - 1	$\text{Pb}(\text{OAc})_4$	$\text{PhCH}=\text{CHCHO}$	79 ^{a)}
<i>trans</i> - 1	NaOCl	$\text{PhCH}=\text{CHCHO}$	34 ^{a)}
<i>cis</i> - 1	$\text{Pb}(\text{OAc})_4$	$\text{PhCH}=\text{CHCHO}$	84 ^{a)}
2	$\text{Pb}(\text{OAc})_4$	$\text{PhC}\equiv\text{N}^{\text{c)}$	69 ^{b)}
2	NaOCl	$\text{PhC}\equiv\text{N}$	21 ^{b)}
3	$\text{Pb}(\text{OAc})_4$	PhCHO	42 ^{b)}

a) Isolation yield. b) Estimated by gas chromatographic assay. c) The accompanying ethylene was identified as 1,2-dibromoethane.

the isolation or glc assay as indicated.

Oxidation of Amines *trans*-1 and 2 with Sodium Hydrochlorite. An amine (0.6 mmol) was added to ice-cooled commercially available aqueous sodium hypochlorite (5% content, 5.2 g) at 0°C . The mixture was stirred at 0°C for 10 min and then at room temperature for 1 hr. Extractive work-up with ether gave a crude product which was treated with silver perchlorate (166 mg) in acetone (5 ml) for a night. The results are listed in Table 1.

Oxidation of 2,3-Polymethyleneaziridines. A Typical Procedure: Aziridine **6a** (197 mg, 1.0 mmol) dissolved in dichloromethane (4 ml) was added to a solution of lead tetraacetate (1.00 g, 2.3 mmol) in dichloromethane (15 ml) under a nitrogen atmosphere at -40°C . Precipitation of lead diacetate immediately occurred. The mixture was gradually warmed up to room temperature in 6 hr and then concentrated *in vacuo*. The product **7a** (171 mg, 82% yield) was separated from lead diacetate by preparative tlc on silica gel (*n*-hexane/ether 3 : 1, R_f 0.4). The yields and the physical properties of the products are collected in Table 2.

1-Methyl-13-azabicyclo[10.1.0]tridecane (6a). A methylmagnesium iodide solution prepared from methyl iodide (11.4 g, 80 mmol) and magnesium (2.0 g, 82 mmol) in ether (20 ml) was diluted with toluene (20 ml) and then cyclododecanone oxime (3.94 g, 20 mmol) was added. Ether was removed by heating the mixture and the remaining toluene solution was heated to reflux overnight. The mixture was poured into ice-cooled aqueous ammonium chloride and extracted with benzene. Work-up and distillation at $89-90^\circ\text{C}/0.1$ mmHg gave the aziridine **6a** (2.19 g, 56% yield), mp $33.0-33.5^\circ\text{C}$ (*n*-hexane). IR (neat): 3250, 888 cm^{-1} , PMR: δ 0.9—2.4 (m+s (δ 1.17), methylenes, methyl and methine), mass: m/e 195 (M^+), 194 (M^+-1), 180 (M^+-15). Found: C, 79.8; H, 13.2; N, 7.4%. Calcd for $\text{C}_{13}\text{H}_{25}\text{N}$: C, 79.9; H, 12.9; N, 7.2%.

1-Phenyl-13-azabicyclo[10.1.0]tridecane (6b). Cyclo-dodecanone oxime (5.91 g, 30 mmol) and toluene (70 ml) were added to an ethereal solution of phenyllithium (prepared from lithium dispersion (1.75 g) in ether (50 ml) and bromobenzene (18.8 g, 120 mmol)). The resulting suspension was concentrated to remove ether and heating was continued for 24 hr (bath temperature 140°C). Work-up and column chromatography (silica gel, *n*-hexane/ether 1 : 1) afforded **6b** (6.19 g, 80%), mp $55-56^\circ\text{C}$ (*n*-hexane). IR (Nujol): 3230, 1604, 1580, 763, 701 cm^{-1} , PMR: δ 0.5 (br s, 1H, NH), 0.8—2.2 (m, 21H, methylenes and methine), 7.10 (s, 5H, Ph). Mass: m/e 257 (M^+), 256 (M^+-1), 148 (100%). Found: C, 83.8; H, 10.8; N, 5.7%. Calcd for $\text{C}_{18}\text{H}_{27}\text{N}$: C, 84.0; H, 10.6; N, 5.4%.

13-Azabicyclo[10.1.0]tridecane (6c). A mixture (*ca.* 1 : 1) of *cis*- and *trans*-cyclododecene (1.66 g, 10 mmol) was treated with silver isocyanate (2.0 g, 13 mmol) and iodine (2.54 g, 10 mmol) in tetrahydrofuran (20 ml) in a similar

TABLE 2. LEAD TETRAACETATE OXIDATION OF AZIRIDINES **6**, **8**, **10** AND **11**, AND THE PHYSICAL PROPERTIES OF THE PRODUCTS

Aziridine	Product	Yield(%)	Bp or Mp	IR (cm ⁻¹) ^{a)}	NMR (δ)
6a	7a^{b)}	82	110 °C/0.09 mmHg (bath temp)	2260, 1713	0.9—2.0 (m, 16H, methylenes), 1.98 (s, 3H, Me), 2.1—2.5 (m, 4H, CH ₂ CO and CH ₂ CN)
6b	7b^{c)}	85	54—550C (<i>n</i> -hexane)	2270, 1678 ^{d)} 1600, 1580	1.0—2.0 (m, 16H, methylenes), 2.27 (t, <i>J</i> =6 Hz, 2H, CH ₂ CN), 2.90 (t, <i>J</i> =6 Hz, 2H, CH ₂ CO), 7.2—7.7 (m, 3H, Ph- <i>m,p</i>), 7.8—8.1 (m, 2H, Ph- <i>o</i>)
6c	7c^{e)}	58	2,4-DNPH ^{f)} 91—92 °C	2725, 2250 1723	1.0—2.0 (m, 16H, methylenes), 2.0—2.6 (m, 4H, CH ₂ CO and CH ₂ CN), 9.77 (t, <i>J</i> =1.8 Hz, 1H, CHO)
8a	9a^{g)}	58	120 °C/2.5 mmHg	2260, 1711	1.0—2.0 (m, 8H, methylenes), 2.06 (s, 3H, Me), 2.2—2.6 (m, 4H, CH ₂ CO and CH ₂ CN)
8b	9b^{h)}	46	41—41.5 °C (<i>n</i> -hexane)	2255, 1677 ^{d)} 1600, 1580 742, 727, 690	0.8—2.0 (m, 8H, methylenes), 2.28 (t, <i>J</i> = <i>ca</i> 6 Hz, 2H, CH ₂ CN), 2.90 (t, <i>J</i> =6 Hz, 2H, CH ₂ CO), 7.0—7.6 (m, 3H, Ph- <i>m,p</i>), 7.8—8.1 (m, 2H, Ph- <i>o</i>)
8c	9cⁱ⁾	29	100 °C/0.07 mmHg 2,4-DNPH ^{j)} 75—77 °C	2730, 2255 1722	1.0—2.0 (m, 8H, methylenes), 2.0—2.8 (m, 4H, CH ₂ CO and CH ₂ CN), 11.07 (t, <i>J</i> =1.4 Hz, 1H, CHO)
11a	12a^{k)}	82	140—145 °C/6 mmHg (bath temp)	2260, 1716	0.6—2.0 (m, 14H, methylenes), 2.09 (s, 3H, Me), 2.1—2.6 (m, 4H, CH ₂ CN and CH ₂ CO)
10c	13^{l)}	—		955, 840, 790	0.8—2.0 (m)

a) Neat unless otherwise stated. b) Mass: *m/e* 209 (M⁺). Found: C, 74.6; H, 11.1; N, 6.7%. Calcd for C₁₃H₂₃NO: C, 74.6; H, 11.1; N, 6.7%. c) Mass: *m/e* 291 (M⁺). Found: C, 79.9; H, 9.3; N, 5.2%. Calcd for C₁₈H₂₅NO: C, 79.7; H, 9.3; N, 5.2%. d) Nujol. e) Mass: *m/e* 195 (M⁺). f) Lit., 90—92 °C (Ref. 13). g) Mass: *m/e* 153 (M⁺). Found: C, 70.4; H, 10.0; N, 9.2%. Calcd for C₉H₁₅NO: C, 70.6; H, 9.9; N, 9.1%. h) Mass: *m/e* 215 (M⁺). Found: C, 78.1; H, 8.2; N, 6.4%. Calcd for C₁₄H₁₇NO: C, 78.1; H, 8.0; N, 6.5%. i) Mass: *m/e* 139 (M⁺). j) Lit., 76—77 °C (Ref. 13). k) Mass: *m/e* 195 (M⁺). Found: C, 73.6; H, 11.1; N, 7.2%. Calcd for C₁₂H₂₁NO: C, 73.8; H, 10.8; N, 7.2%. l) Mass: *m/e* 192 (M⁺).

manner as the reported procedure¹⁵⁾ to obtain methyl 2-iodocyclododecanecarbamate, mp 108—109.5 °C (*n*-hexane), IR (Nujol): 3200, 1692, 1536 cm⁻¹. Found: C, 45.9; H, 7.2; N, 3.7%. Calcd for C₁₄H₂₆INO₂: C, 45.8; H, 7.1; N, 3.8%.

The carbamate (1.11 g, 30 mmol) was heated in methanol (40 ml) and water (8 ml) containing sodium hydroxide (2.4 g, 60 mmol) for 2 hr. Work-up followed by distillation at 120—130 °C (bath temperature)/0.2 mmHg gave the aziridine **6c** (490 mg, 90% yield), mp 46.5—47.5 °C (*n*-hexane), IR (neat): 3250, 969, 874 cm⁻¹. Found: C, 79.4; H, 12.9; N, 7.8%. Calcd for C₁₂H₂₃N: C, 79.5; H, 12.8; N, 7.7%.

1-Methyl-9-azabicyclo[6.1.0]nonane (8a). Cyclooctanone oxime (2.82 g, 20 mmol) was treated with methylmagnesium iodide (*ca.* 80 mmol) in toluene (10 ml) and ether (25 ml) in a similar manner as **6a** to give **8a** (1.92 g, 51% yield), bp 54 °C/4 mmHg. IR (neat): 3250, 830 cm⁻¹, PMR: δ 1.0—2.4 (m+s (δ 1.15)), mass: *m/e* 139 (M⁺), 138 (M⁺ - 1). Found: C, 77.3; H, 12.5; N, 9.8%. Calcd for C₉H₁₇N: C, 77.6; H, 12.3; N, 10.1%.

1-Phenyl-9-azabicyclo[6.1.0]nonane (8b). The aziridine was obtained in 62% yield, bp 103—105 °C/0.1 mmHg. IR (neat): 3230, 1601, 1496, 931, 809, 760, 742, 701 cm⁻¹, PMR: δ 0.7—2.7 (m, 14H), 7.0—7.7 (m, 5H), mass: *m/e* 201 (M⁺), 200 (M⁺ - 1). Found: C, 83.4; H, 9.7; N, 6.7%. Calcd for C₁₄H₁₉N: C, 83.5; H, 9.5; N, 7.0%.

Aziridines 8c and 10c. The aziridines were prepared according to the literature.¹⁶⁾

1-Methyl-12-azabicyclo[9.1.0]dodecane (11a). The aziridine was obtained by the similar method from cycloundecanone oxime in 71% yield, bp 160—165 °C/22 mmHg. IR (neat): 3250, 894 cm⁻¹, PMR: δ 0.2—0.7 (br. s, 1H), 0.7—2.3 (m+s (δ 1.18), 22H), mass: *m/e* 181 (M⁺). Found: C, 79.5; H, 12.8; N, 7.7%. Calcd for C₁₂H₂₃N: C, 79.4;

H, 12.9; N, 7.6%.

Alternative Preparation of 12-Cyano-2-dodecanone (7a).

Ethyl acetoacetate (1.30 g, 10 mmol) was added to sodium hydride (10 mmol) suspended in dimethoxyethane (20 ml). After the evolution of hydrogen gas ceased 1,9-dibromononane (2.86 g, 10 mmol) was added to the resulting pale yellow solution. Stirring at room temperature for two days, followed by chromatographic separation of the crude product, gave 12-bromo-3-ethoxycarbonyl-2-dodecanone (0.62 g, 54% yield based on the consumed dibromide). The alkylate was dissolved in 95% aqueous dimethyl sulfoxide (10 ml) containing sodium cyanide (9.50 g), and the solution was heated at 160—165 °C for 3 hr. Extractive work-up and the subsequent purification by preparative tlc (silica gel, ether/*n*-hexane 1 : 3, R_f 0.4—0.5) afforded **7a** (0.11 g, 28% yield). All the spectral data were identical with those of the oxidation product.

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