co-workers,[10] to give 37 mg (58.4%) of **4** which had the same R_f (0.67) on TLC [cellulose, isobutyric acid–ammonia–water (66:1:33)], on high-pressure liquid chromatography [Waters μBondapak carbohydrate column, 30 cm × 4 mm, CH_3CN–H_2O (85:15), 1.5 mL/min, retention time 6 min, refractive index detector] as an authentic sample of **4**.[13] The NMR spectrum was also identical with that of an authentic sample of **4**.

Registry No.—**1**, 2873-29-2; **2**, 24679-90-1; **3**, 24679-92-3; **4**, 23094-77-1; fluorine, 7782-41-4.

References and Notes

(1) (a) Research carried out at Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration and supported by its Division of Physical Research and Division of Biomedical and Environmental Research and also by the National Institutes of Health (USPHS Grant 2 R01 GM-16, 248-16 S1, and USPHS Grant 1-P07—RR00657-01A1). (b) National Institute of Radiological Sciences, Anagawa, Chiba-City, Japan.

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(13) Authentic samples of **2**, **3**, and **4** were prepared according to the method of Adamson et al.[10] The authors are grateful to Dr. R. H. Hesse for an authentic sample of **4** which served as a spectral and chromatographic standard.

(14) The relative areas of **2** and **3** on GLC do not reflect their isolated yields because **3** undergoes decomposition on GLC.

1,4-Transannular Nitrogen to Carbon Rearrangement Following Intramolecular Carbenoid Insertion. Formation of 6-*trans*-Styryl-3-azabicyclo[3.1.0]hexane

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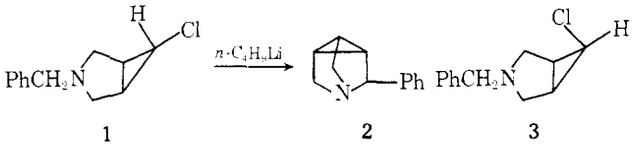
We are reporting a novel nitrogen to carbon transannular rearrangement following a carbenoid insertion reaction. Previously, we reported the formation of 3-phenyl-4-azatricyclo[2.2.1.0^{2,6}]heptane (**2**) from 3-benzyl-6-*exo*-chloro-3-

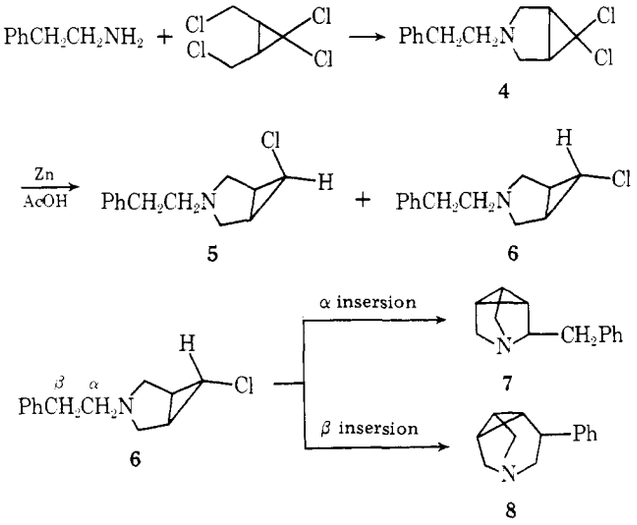


1 2 3

azabicyclo[3.1.0]hexane (**1**) by a proposed intramolecular carbenoid carbon–hydrogen insertion.[2] In addition, it was shown that the epimeric *endo*-chlorocyclopropane (**3**) did not undergo the intramolecular insertion reaction.

To further explore the scope of this reaction, 6-*exo*-chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**6**) was prepared[3] utilizing the procedure previously reported (Scheme I). It was anticipated that reaction of **6** with butyllithium

Scheme I



would yield 3-benzyl-4-azatricyclo[2.2.1.0^{2,6}]heptane (**7**) or 3-phenyl-5-azatricyclo[3.2.1.0^{2,7}]octane (**8**) by intramolecular carbenoid insertions into either the α or β C–H bonds, respectively. Addition of phenethylamine to 1,1-dichloro-*cis*-2,3-bis(chloromethyl)cyclopropane yielded 6,6-dichloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**4**). Reduction of **4** with zinc dust in glacial acetic acid[4] yielded the epimeric *endo*- and *exo*-monochloro isomers **5** and **6**. The exo isomer **6** was the major product (63% yield), whereas **5** was isolated in 5% yield.

When the reaction was carried out by addition of butyllithium solution to an ethereal solution of the exo isomer **6** at room temperature, a solid product having a molecular weight of 185 was isolated in low yield after extensive column chromatography. Spectral data were not consistent with structures **7** or **8**. On the basis of its ^{1}H NMR, IR, and UV spectral characteristics, the substance was determined to be 6-*trans*-styryl-3-azabicyclo[3.1.0]hexane (**9**). The ^{1}H NMR spectrum

9

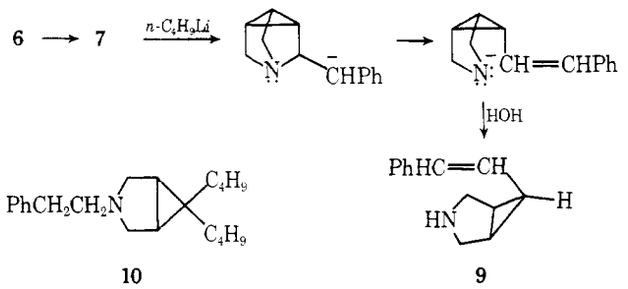
of **9** was characterized by a singlet at δ 1.72 (N–H) which disappeared on addition of D_2O and by olefinic proton absorptions at δ 5.87 (1 H, d of d, $^3J_{vic}$ = 8 Hz, $^3J_{olefinic}$ = 16 Hz) and δ 6.45 (1 H, d, $^3J_{olefinic}$ = 16 Hz). The large value of the olefinic proton coupling constant suggests trans couplings.[5] A multiplet at δ 1.45 (3 H) in the spectrum of **9** indicated that the cyclopropyl ring remained intact. Irradiation at δ 1.45 caused the doublet of doublets at δ 5.78 to collapse to a simple doublet. A singlet at δ 3.03 (4 H) was attributed to the four protons on the carbons adjacent to the nitrogen, in contrast to the ^{1}H NMR spectrum of **2** which was characterized by two sets of unequally coupled doublets of δ 2.28 and δ 2.70 for the protons adjacent to the nitrogen due to the shielding effect of the benzene ring.

The UV maximum of **9** occurred at 248 nm (ε 22 900). This comparatively large value for the extinction coefficient indicated the presence of a strong chromophore which was not seen in previous products and strongly supports the presence of the styryl group. *trans*-β-Methylstyrene, for example, has an absorption maximum of 251 nm (ε 17 000).[6] In the infrared

spectrum, absorptions were observed at 3400 and 2330 cm^{-1} which were attributed to free and associated N–H stretching vibrations, respectively. There were also absorptions at 1637 and 1590 cm^{-1} assigned to the double bond conjugated with an aromatic ring. A weak absorption at 1298 cm^{-1} and a strong one at 960 cm^{-1} support the presence of a trans-substituted double bond.[7]

It appears reasonable that **9** may be formed by hydrogen abstraction and ring opening of the proposed tricyclic compound **7** upon reaction with excess butyllithium present in the reaction mixture (Scheme II). The spectral evidence available

Scheme II



10 **9**

does not permit unequivocal determination of the geometry about carbon 6, but it seems likely that the *trans*-styryl group is endo to the bicyclic ring system providing isomerization has not occurred. The fact that insertion occurs into the C–H bond α to the nitrogen rather than at the β carbon is consistent with the results of Baird and Kaura.[8]

No evidence by ^1H NMR or mass spectral analysis was found for the formation of **9** on reaction of the dichloro compound **4** or the *endo*-chloro isomer **5** with *n*-butyllithium. In the case of **4**, mass-spectral analysis of the reaction mixture indicated the presence of a product, probably **10**, having a mass corresponding to the replacement of the chlorine atoms by two butyl groups. Unreacted starting material accounted for the bulk of the material recovered from the reaction of the endo isomer **5** with *n*-butyllithium. However, a peak at *m/e* 152 did indicate the presence of some material formed by replacement of the chlorine of **5** by a butyl group.

The fact that the *exo*-chloro isomers **1** and **6** yield an intramolecular insertion product or substance resulting from this process, whereas the epimeric *endo*-chloro isomers **3** and **5** do not react or yield butyl derivatives, is consistent with results obtained by Taylor and co-workers[9] and by Goldstein and Dolbier.[10]

Work is currently in progress to determine the mechanism of this interesting rearrangement and to further elucidate the factors influencing and controlling the carbenoid insertion reactions.

Experimental Section

All compounds used as starting materials in the synthetic procedures were obtained either from commercial sources or by known procedures. Reagent grade solvents were used in reactions. Commercial grade solvents were used for column chromatography and extraction procedures. High-resolution proton NMR spectra were recorded on a Varian Model A-60 high-resolution spectrometer. Spin-decoupling experiments were performed on a Varian T-60 equipped with a frequency decoupler. The ^1H NMR spectra were obtained in deuteriochloroform solutions using tetramethylsilane as an internal standard. The ^1H NMR spectra of amine salts were obtained in deuterium oxide (D_2O) solutions using sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 (TSP) as an internal standard. Mass spectra were obtained with a Perkin-Elmer Model RMU-6H mass spectrometer (ionizing voltage 70 eV, inlet temperature 200 °C). Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrophotometer. Liquid samples were run as films between salt (NaCl) plates. Solid samples were run as KBr pellets. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer using methanol as the solvent. A Varian Aerograph Model A-700 equipped with a column of 0.2% OV-1 on glass beads (6 ft × 0.25 in.) was used for gas chromatographic analyses. Silica gel G precoated uniplates (250 μm thickness, 2.5 × 10 cm) from Analtech, Inc., were used for thin-layer chromatographic (TLC) analyses. A short-wavelength ultraviolet lamp (2537 Å) or iodine vapor was used for visualization of zones. For column chromatography, either 60–100-mesh Florisil (Floridin Co.) or 70–230-mesh silica gel 50 (E. Merck) was used. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Compounds which were isolated and purified were analyzed for carbon, hydrogen, and nitrogen content using a Perkin-Elmer Model 240 elemental analyzer, and analyses are within ±0.3% of the theoretical values. Pertinent spectral data are given on those compounds which were isolated and characterized. Unless indicated, spectral data for amines are for the free bases.

1,1-Dichloro-*cis*-2,3-bis(chloromethyl)cyclopropane. A sodium hydroxide solution (390-mL 50% aqueous solution, 7.5 mol) was added dropwise over a period of 4 h to a stirred solution of 1,4-dichloro-*cis*-2-butene (62.5 g, 0.5 mol), chloroform (600 mL, 7.5 mol), and cetyltrimethylammonium bromide (1.0 g, 2.75 mmol). The reaction mixture was stirred at ambient temperature for about 60 h and then poured into 2 L of water. The chloroform layer was separated, washed with water, dried over magnesium sulfate, and concentrated at reduced pressure. The residual oil was vacuum distilled through a 12 × 80 mm column packed with glass helices. The fraction distilling at 123–126 °C (22 Torr) was collected. In a typical reaction, 46.1 g (44.5%) of product was obtained: ^1H NMR ($CDCl_3$) δ 2.22 (2 H, m), 3.67 (4 H, m); IR (film) 1255 cm^{-1} ($-CH_2Cl$); UV λ_{max} (methanol) 239 nm (ϵ 87.5).

Anal. Calcd for $C_5H_6Cl_4$: C, 28.89; H, 2.91; Cl, 68.20. Found: C, 28.57; H, 2.90.

6,6-Dichloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (4). Phenethylamine (6.1 g, 0.05 mol), 1,1-dichloro-*cis*-2,3-bis(chloromethyl)cyclopropane (10.4 g, 0.05 mol), sodium bicarbonate (12.6 g, 0.15 mol), and *n*-butyl alcohol (100 mL) were stirred together and heated at reflux for 36 h. The mixture was cooled and filtered, and the filtrate was concentrated at reduced pressure. The residual oil was chromatographed on a column of Florisil (100 g) using petroleum ether (30–60 °C), benzene, and acetone mixtures to elute the product. The oily product was converted to the hydrochloride salt. Recrystallization from isopropyl alcohol–isopropyl ether gave 4.5 g (35%) of gray-white solid, mp 193–194.5 °C: ^1H NMR ($CHCl_3$) δ 2.25 (2 H, m), 2.70 (4 H, s), 2.86 (2 H, d), 3.15 (2, d of m), 7.25 (5, s); IR (film) 2800 (s, tertiary alkylamine), 1015 cm^{-1} (cyclopropane ring deformation); UV (HCl salt) λ_{max} (methanol) 257 nm (ϵ 179).

Anal. Calcd for $C_{13}H_{16}NCl_3$: C, 53.36; H, 5.51; N, 4.79. Found: C, 53.29; H, 5.50; N, 4.92.

6-Chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane, Endo Isomer 5 and Exo Isomer 6. Zinc dust (14.3 g, 0.22 mol) was added in small portions to a stirred refluxing solution of 6,6-dichloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**4**) (11.0 g, 0.043 mol) in glacial acetic acid (100 mL). Sufficient time was allowed between additions of zinc dust for the foaming to subside. The reaction mixture was stirred at reflux for 18 h and then allowed to cool. The acetic acid solution was decanted from the inorganic material and concentrated at reduced pressure to yield a residue which was treated with 100 mL of 3 N NaOH solution and extracted twice with 100-mL portions of ethyl ether. The ether extract was washed with water, dried over magnesium sulfate, and concentrated to give 8.0 g of crude product which was chromatographed on Florisil using increasing portions of acetone in benzene to elute the components. The first component eluted was shown to be the exo isomer **6** (6.0 g, 63% yield). A second minor component was not isolated or identified. The third component eluted was shown to be the endo isomer **5** (0.5 g, 5.2% yield).

A small portion of each isomer was converted to the hydrochloride salt and recrystallized from isopropyl alcohol–isopropyl ether for elemental analysis.

(a) 6-*exo*-Chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**6**): ^1H NMR ($CDCl_3$) δ 1.70 (2 H, m), 2.37 (2 H, d of m), 2.67 (4 H, s), 3.15 (2 H, d), 3.23 (1 H, s), 7.25 (5 H, s); IR (film) 2790 (s, tertiary alkylamine), 1000 cm^{-1} (m, cyclopropane ring deformation); UV (HCl salt) λ_{max} (methanol) 257 nm (ϵ 184); mp (HCl salt) 201.5–202.5 °C.

Anal. Calcd for $C_{13}H_{17}NCl_2$: C, 60.48; H, 6.64; N, 5.43. Found: C, 60.40; H, 6.64; N, 5.42.

(b) 6-*endo*-Chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**5**): ^1H NMR ($CDCl_3$) δ 1.80 (2 H, m), 2.71 (4 H, s), 2.80 (2 H, d), 3.15 (2 H, d of m), 3.40 (1 H, t), 7.25 (5 H, s); IR (film) 2790 (s, tertiary alkylamine), 1005 cm^{-1} (w, cyclopropane ring deformation); UV (HCl salt) λ_{max} (methanol) 257 nm (ϵ 180); mp (HCl salt) 190–191 °C.

Anal. Calcd for $C_{13}H_{17}NCl_2$: C, 60.48; H, 6.64; N, 5.43. Found: C, 60.46; H, 6.59; N, 5.45.

6-*trans*-Styryl-3-azabicyclo[3.1.0]hexane (9). A butyllithium solution (18.9 mL of 2.4 M hexane solution, 0.045 mol) was added dropwise to a stirred solution of 6-*exo*-chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**6**) (5.0 g, 0.023 mol) in 100 mL of ethyl ether under a nitrogen atmosphere. During addition the reaction became exothermic and mild reflux occurred. The reaction mixture gradually became dark red-brown. Stirring was continued for 16 h and water (50 mL) was then carefully added dropwise to hydrolyze the reaction mixture. The ether solution was separated, dried over magnesium sulfate, and concentrated at reduced pressure to give 4.6 g of oil which was shown by TLC to contain several components. This oil was subjected to molecular distillation at 150 °C (0.01 Torr). On standing, partial crystallization occurred in the distillate. Trituration of the distillate in petroleum ether (30–60 °C) gave an amorphous solid which was collected by filtration. Trituration of this solid with isopropyl ether gave a white solid which was collected by filtration. TLC of this solid shows a single spot (R_f 0.5, 20% methanol in chloroform). The filtrates were combined and evaporated to dryness, and the oily residue was triturated with ethyl ether to give an additional quantity of the white solid. The combined solids were molecularly distilled twice at 150 °C (0.01 Torr) to give about 300 mg (7%) of a white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 1.50 (3 H, m), 1.72 (1 H, s, replaceable by D_2O), 3.03 (4 H, s), 5.87 (1 H, d of d), 6.45 (1 H, d), 7.32 (5 H, s); IR (KBr pellet) 3400, 3230 (m, NH str), 1030 cm^{-1} (w, cyclopropane ring deformation); UV λ_{max} (methanol) 259 nm (ϵ 22 900); mp 82–84 °C.

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.09; H, 8.12; N, 7.54.

Reaction of 6,6-Dichloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (4) with *n*-Butyllithium. In a nitrogen atmosphere, an *n*-butyllithium solution (2.4 mL of 2.4 M hexane solution, 0.006 mmol) was added dropwise to a stirred solution of 6,6-dichloro-3-phenethyl-3-azabicyclo[3.1.0]hexane (**4**) (0.5 g, 0.002 mol) in an anhydrous ether (15 mL) at 0 °C. After the addition was completed, the mixture was stirred for 15 h at room temperature. Water was added and the ether layer was separated, washed once with water, dried, and concentrated at reduced pressure to give a brown oil. Mass-spectral analysis showed the presence of a product having a mass corresponding to replacement of the chlorine atoms by butyl groups.

Reaction of 6-*endo*-Chloro-3-phenethyl-3-azabicyclo[3.1.0]-hexane (5) with *n*-Butyllithium. A solution of 6-*endo*-chloro-3-phenethyl-3-azabicyclo[3.1.0]hexane hydrochloride (**5**) (0.12 g, 0.00047 mol) in 3 mL of water was made basic to litmus by addition of 6 N NaOH solution. This mixture was extracted four times with 5-mL portions of ether. The combined extracts were dried over anhydrous sodium sulfate. Under nitrogen, an *n*-butyllithium solution (0.6 mL, 0.014 mol, 1.6 M hexane solution) was added dropwise with stirring to the dried ether solution of **5** and the mixture was stirred at ambient temperature for 16 h. Water was added and the ether layer was separated, dried ($MgSO_4$), and concentrated at reduced pressure to yield a small quantity of oil which was shown by ^{1}H NMR analysis to be unreacted **5**. Mass-spectral analysis showed, in addition to the parent and fragment ions of the starting material **5**, a peak at *m/e* 152 which could be a fragment arising from a product in which the chlorine was replaced by a butyl group.

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Registry No.—**4**, 62154-20-5; **4** HCl, 62182-98-3; **5**, 62210-63-3; **5** HCl, 62154-16-9; **6**, 62210-64-4; **6** HCl, 62249-34-7; **9**, 62154-17-0; **10**, 62154-18-1; 1,1-dichloro-*cis*-2,3-bis(chloromethyl)cyclopropane, 56505-31-8; 1,4-dichloro-*cis*-2-butene, 1476-11-5; phenethylamine, 64-04-0; *endo*-6-butyl-3-phenethyl-3-azabicyclo[3.1.0]hexane, 62154-19-2.

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A ^{13}C Nuclear Magnetic Resonance Study of *N*-Acetyldaunorubicinol[1]

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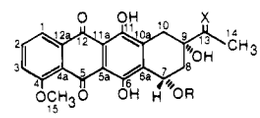
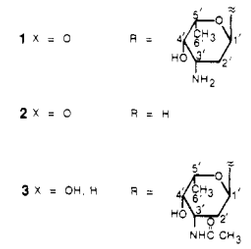
Daunorubicin is an anthracycline antibiotic and is represented by structure **1**. It consists of the tetracyclic quinoid aglycone daunorubicinone **2** in a glycosidic linkage to the





amino sugar daunosamine.[3] Daunorubicin has both well-demonstrated cytotoxic activity[4] and interesting antitumor properties.[5]

In our continuing effort to improve its therapeutic properties and to decrease the undesirable cardiac toxicity of daunorubicin, modification by biotransformation of this antibiotic has been undertaken at the Frederick Cancer Research Center.

To understand the changes that occurred during biotransformation, it was thought that ^{13}C NMR spectroscopy might prove useful in structure elucidation. The ^{13}C NMR spectra of daunorubicin and daunorubicinone were studied, and assignments to all carbons were made (Table I). Using the above-mentioned data it was shown that one of our biotransformed molecules is *N*-acetyldaunorubicinol, represented by structure **3**.

Off-acquisition gated noise decoupling and single-frequency experiments on **2** and chemical shifts reported in the literature[6–9] allowed us to distinguish C-14 (24.5 ppm, q, $^1J_{CH}$ = 130 Hz), C-15 (56.6 ppm, q, $^1J_{CH}$ = 155 Hz), C-8 (35.3 ppm, t, $^1J_{CH}$ = 120 Hz), C-10 (33.1 ppm, t, $^1J_{CH}$ = 120 Hz), C-1 (119.6 ppm, d, $^1J_{CH}$ = 160 Hz), C-2 (135.3 ppm, d, $^1J_{CH}$ = 160 Hz), C-3 (118.3 ppm, d, $^1J_{CH}$ = 160 Hz), and C-7 (61.9 ppm, d, $^1J_{CH}$ = 160 Hz). Single-frequency decoupling experiments on all of the protons of **2** also confirmed the above assignments. The rest of the carbons show only small multiple bond C–H coupling or are singlets. The assignment of carbons 5, 12, 5a, 11a, 6a, 10a, 12a, and 4a was based on published results.[6,10]

Single-frequency decoupling experiments on protons of C-7 and of the amino sugar, together with chemical shifts on model