1170, 1090, 1050, 910 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (1 H, s), 7.14–7.17 (2 H, m), 6.77–6.82 (1 H, m), 4.00 (3 H, s), 2.85–2.95 (4 H, m), 2.45 (3 H, s), 1.68 (1 H, br s).

Acknowledgment. We thank the National Institutes of Health (GM-31349) for financial support.

Registry No. 1, 57-27-2; 3, 111976-12-6; 4, 75611-13-1; 6, 7169-37-1; 7, 1521-38-6; 8, 7169-06-4; 12, 58131-63-8; 13, 111976-11-5; vinyl chloroformate, 5130-24-5.

A Transannulation Route to the [5.5.5.7]Fenestrane Ring System of Laurenene

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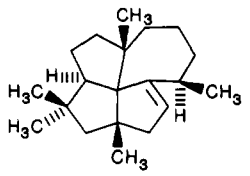
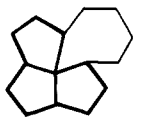
The diterpene hydrocarbon laurenene (1), isolated in 1979 from *Dacrydium cupressinum* by Corbett and coworkers, is unique among natural products in being the only fenestrane known to occur in nature.[1] The presence of a novel tetracyclic framework composed of three five-membered rings and a seven-membered ring, embellished with five asymmetric carbon centers and a network of methyl groups, makes laurenene an attractive target of synthesis. Basic to the synthesis of the natural product is the methodology for the construction of the [5.5.5.7]-fenestrane ring system 2 present in it. While the synthesis of several [4.4.4.5], [4.4.5.5], [5.5.5.5], and larger fenestranes have been reported[2,3] in recent years, the synthetic entry into the ring system 2 has not yet appeared in the literature.[3] We describe here a novel approach that has led to the attainment of a derivative of 2, albeit as a mixture of stereoisomers.



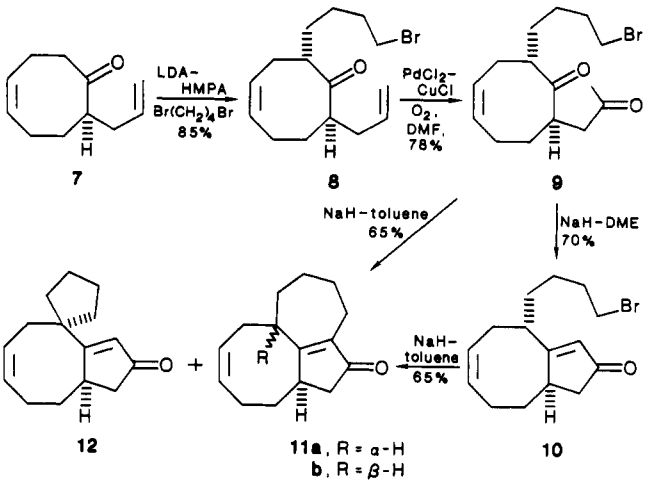
1



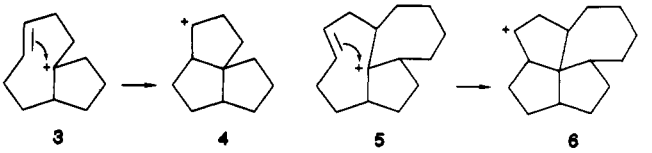
2

At the very outset, we recognized the carbocyclic ring system 2 as an angular triquinane (heavy lines) spanning a four-carbon bridge on the methylenes adjacent to the spirocenter. It was therefore tempting to adopt our general cationic transannulation approach[4] (3 → 4) to the angular triquinanes as the synthetic stratagem for the construction of the fenestrane ring system 2. Consequently, generation

Scheme I



of the bridged tricyclic cation 5 and its cyclization to 6 became our main concern.



3 4 5 6

Readily available[4,5] allylcyclooctenone 7 was selected as the starting point and regioselectively alkylated with 1,4-dibromobutane, under kinetically controlled conditions, to furnish the trans-dialkylated cyclooctenone 8, Scheme I. The allyl group in 8 was transformed into an acetonyl side chain through Wacker-type oxidation employing the Tsuji reaction conditions[4,6] to furnish the 1,4-diketone 9 in good yield. Internal aldol cyclization of 9 was achieved with sodium hydride under controlled conditions to deliver the bicyclic enone 10 as a single isomer. The structure of 10 was fully secured through its characteristic ^{13}C NMR lines at δ 207.6, 187.2, and 126.0 due to a β,β-disubstituted cyclopentenone moiety.[4,7]

The next step was crucial and required the four-carbon bridge formation through intramolecular bromide displacement from the α-position of the enone moiety in 10. This was realized through the dienolate generation with sodium hydride in refluxing toluene. A mixture of three tricyclic enones 11a,b and 12 (1:1) was obtained. The same mixture of three enones could be obtained directly from the diketone 9 on treatment with large excess of sodium hydride in boiling toluene. However, hydrogenolysis of the bromide in 9 was noticed as a competing reaction under these conditions. The three enones 11a,b and 12 could be separated through a combination of column chromatography and HPLC. The gross structure of 11a and 11b and their epimeric nature could be discerned from their spectral data. But, it was not possible to distinguish between them and, therefore, the epimeric mixture 11a,b was deployed for further reactions. The unwanted spiro enone 12 was readily identified on the basis of a quaternary sp^3 carbon resonance at δ 54.3 (s) in the ^{13}C NMR spectrum besides other complementary data.

With the acquisition of the tricyclic enones 11a,b, attention was turned toward the key transannular cyclization step 5 → 6. The enone mixture was exposed to a variety of protic acids (CF_3COOH, aqueous $HClO_4$, CF_3SO_3H) and

(1) (a) Corbett, R. E.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1774. (b) Corbett, R. E.; Couldwell, C. M.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1791. (c) Hanton, L. R.; Simpson, J.; Weavers, R. T. *Aust. J. Chem.* **1983**, *36*, 2581.

(2) For a recent review, see: Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399. For some of the leading references in the area, see: Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, 4315. Mitschka, R.; Cook, J. M.; Weiss, U. *J. Am. Chem. Soc.* **1978**, *100*, 3973. Luyten, M.; Keese, R. *Helv. Chim. Acta* **1984**, *67*, 2242. Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 5732.

(3) (a) For an approach toward laurenene, see: Crimmins, M. T.; Mascarella, S. W.; Bredon, L. D. *Tetrahedron Lett.* **1985**, *26*, 997. Crimmins, M. T.; Mascarella, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 3435 and private communication. (b) After completion of this manuscript, total syntheses of (±)-laurenene were reported: Tsunoda, T.; Amaike, M.; Tambunam, U. S. F.; Fujise, Y.; Ito, L.; Kodama, M. *Tetrahedron Lett.* **1987**, *28*, 2537. Crimmins, M. T.; Gould, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 6199.

(4) Mehta, G.; Rao, K. S. *J. Am. Chem. Soc.* **1986**, 108, 8015.

(5) Apparau, M.; Barrella, M. *Tetrahedron* **1978**, *4*, 1817.

(6) Tsuji, J.; Schimizu, I.; Yamamoto, K. *Tetrahedron Lett.* **1976**, 2975.

(7) Mehta, G.; Pramod, K.; Subrahmanyam, D. *J. Chem. Soc., Chem. Commun.* **1986**, 247.

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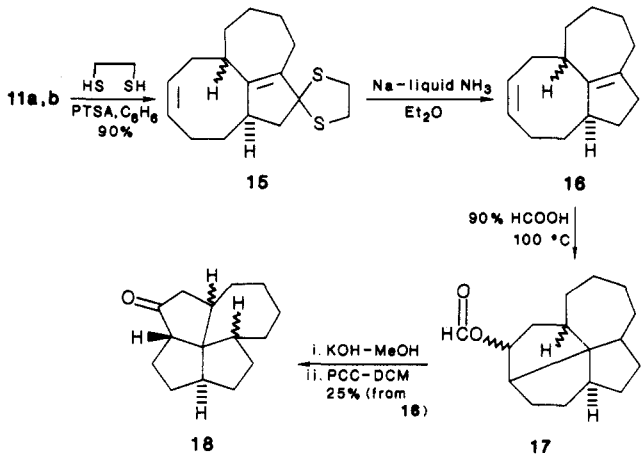
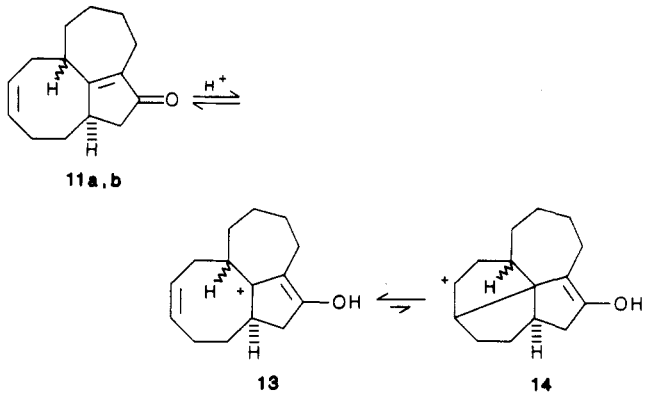
Scheme II



Lewis acids (BF_3, $SnCl_4$, Me_3SiI) but no cyclization product resulted. It is reasonable to speculate that either the derived cation **13** cannot attain the geometry for effective



π-overlap or the equilibrium concentration of the tetracyclic secondary carbonium ion **14** is very unfavorable compared to the allylic tricyclic ion **13**. We therefore decided to employ the tricyclic olefin **16** for the cyclization. Deoxygenation of the enone mixture was effected via the ethylene thioacetal **15** and metal–ammonia reduction, Scheme II. The crude olefin **16** was directly subjected to formolysis in 90% formic acid. The resulting tetracyclic formates **17** were hydrolyzed and oxidized with PCC to furnish the [5.5.5.7]fenestranone **18** as an epimeric mixture (3:1 by HPLC), which could not be seperated. The HRMS established the molecular formula of **18** as $C_{15}H_{22}O$ and hence its tetracyclic nature. The IR spectrum of **18** exhibited a strong band at 1730 cm^{-1} (cyclopentanone) and showed absence of unsaturation in the ^1H and ^{13}C NMR spectra. Further, the ^{13}C NMR spectrum of **18** exhibits marked resemblance to that of closely related tricyclo-[6.3.0.$0^{4,8}$]undecan-5-one.[4] For example, **18** has carbonyl resonances at δ 224.6 and 223.9 characteristic of cyclopentanone and more or less same as in related tricyclic ketone δ 223.5.

In summary, we have demonstrated the feasibility of the transannular cyclization route for the construction of the tetracyclo[7.5.1.$0^{4,15}$.$0^{12,15}$]pentadecane (5.5.5.7-fenestrane) framework. However, the stereochemical course of the reaction could not be defined.

Experimental Section[8]

2-(4-Bromo-1-butyl)-8-allylcyclooct-4-en-1-one (8). Into a 100-mL three-necked flask fitted with a dry N_2 inlet, septum, and mercury seal was introduced *n*-butyllithium (30 mL, 30 mmol, in hexane) and the flask was cooled to −78 °C. Diisopropylamine (3.5 g, 34.6 mmol) was added dropwise and the resulting slurry was stirred for 45 min, and 20 mL of dry dimethoxyethane was added. A solution of allyl ketone **1** (4 g, 24 mmol) in 20 mL of dry dimethoxyethane was then added through a syringe and the reaction mixture was brought to −20 °C. 1,4-Dibromobutane (5.4 g, 25 mmol) in 10 mL of dry HMPA was added and the reaction mixture was allowed to attain room temperature and stirred overnight. The reaction mixture was then quenched with water and extracted with ether (4 × 40 mL). The ethereal layer was washed successively with water and 5% HCl and dried over Na_2SO_4. The solvent was removed to give 8 g of crude product which was charged on a silica gel (120 g) column. Elution with 1% ethyl acetate–petroleum ether furnished the alkylated ketone **8**, 6.2 g (85%): bp 150 °C/1 Torr; IR (neat) ν_{max} 3060, 3010, 1690 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.9–5.4 (3 H, m), 5.2–4.8 (2 H, m), 3.36 (2 H, J = 7 Hz, t), 3.0–1.0 (16 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 217.1, 135.8, 130.9, 129.0, 116.9, 57.4, 46.5, 38.2, 33.2, 32.3, 31.9, 29.7, 28.0, 26.2, 25.6. Anal. Calcd for $C_{15}H_{23}OBr$: C, 60.23; H, 7.69. Found: C, 60.20; H, 7.72.

2-(4-Bromo-1-butyl)-8-(2-oxopropyl)cyclooct-4-en-1-one (9). Palladium chloride (1 g), cuprous chloride (7.5 g, 75 mmol), 30 mL of dimethylformamide, and 8 mL of H_2O were taken into a 250-mL pressure bottle and preactivated by shaking under an O_2 blanket for 1 h. A solution of **8** (4 g, 13.3 mmol) in 10 mL of dry dimethylformamide was added and the contents were shaken for 3 h at room temperature in an O_2 atmosphere. The reaction mixture was quenched with 10% HCl and was extracted with ether (4 × 40 mL). The ethereal solution was washed with water and dried over Na_2SO_4. The solvent was removed to give 5.2 g of crude product which was charged on a silica gel (100 g) column. Elution with 20% ethyl acetate–petroleum ether furnished the diketone **9**, 3.2 g (78%): bp 150 °C/0.15 Torr; IR (neat) ν_{max} 3020, 1690 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.62 (2 H, J = 6 Hz, t), 3.36 (2 H, J = 7 Hz, t), 2.08 (2 H, s), 3.0–1.0 (16 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 214.1, 205.8, 130.0, 129.1, 57.5, 47.2, 40.7, 33.4, 32.3, 31.9, 30.0, 27.6, 26.0, 25.3. Anal. Calcd for $C_{15}H_{23}O_2Br$: C, 57.14; H, 7.35. Found: C, 57.10; H, 7.30.

2-(4-Bromo-1-butyl)bicyclo[6.3.0]undeca-1(11),4-dien-10-one (10). Sodium hydride (150 mg, as 50% dispersion in oil, 3 mmol) was placed in a 25-mL, three-necked flask equipped with a magnetic pellet, dry N_2 inlet, condenser with mercury seal, and septum. The dispersion was twice washed with dry petroleum ether and the residue was suspended in 8 mL of dry dimethoxyethane. A solution of diketone **9** (100 mg, 0.3 mmol) in 5 mL of dry dimethoxyethane was added dropwise. The resulting solution was heated at 50–60 °C for 1.5 h, after which it was quenched with 5% HCl and extracted with ether (3 × 10 mL). The ethereal solution was washed with water and dried over Na_2SO_4. Removal of solvent gave 90 mg of crude enone which was purified by passage through a silica gel (8 g) column. Elution with 20% ethyl acetate–petroleum ether furnished pure bicyclic bromo enone **10**, 66 mg (70%): IR (neat) ν_{max} 3040, 1710, 1630 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.8 (1 H, br s), 5.44 (2 H, J = 6 Hz, t), 3.36 (2 H, J = 7 Hz, t), 3.3–1.0 (16 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 207.6, 187.2, 133.4, 130.1, 126.0, 45.1, 44.2, 39.3, 33.6, 33.2, 32.6, 31.9, 30.4, 25.7, 25.2. Anal. Calcd for $C_{15}H_{21}OBr$: C, 60.61; H, 7.12. Found: C, 60.67; H, 7.14.

Tricyclo[7.5.1.$0^{4,15}$]pentadeca-4(15),11-dien-3-one (11a,b): Preparation from 9. Sodium hydride (100 mg, as 50% dispersion in oil, 2 mmol) was placed in a 25-mL, three necked flask equipped with dry N_2 inlet, pellet, condenser with mercury seal, and septum. The mineral oil was removed by washing twice with dry petroleum ether and the residue was suspended in 4 mL of dry toluene. A solution of diketone **9** (50 mg, 0.16 mmol) in 5 mL of dry toluene was added dropwise. The resulting yellow solution was refluxed for 6 h, after which it was quenched with 5% HCl and extracted with ether (3 × 10 mL). The ethereal solution gave 35 mg of an oily residue. TLC (20% ethyl acetate–petroleum ether) showed the presence of two components. The mixture was charged on a silica gel (10 g) column. Elution with 10% ethyl acetate–petroleum ether furnished the less polar component, which was found to be a 3:2 mixture of epimers **11a** and **11b** by HPLC (Lichrosorb SI 60 (7 μm), 250 mm × 4 mm, 25 bar, 254 nm, dichloromethane, LKB Model 2211). Separation of this mixture

(8) For a general writeup, see: Mehta, G.; Rao, K. S. *J. Org. Chem.* **1985**, *50*, 5537.

gave 7 mg and 5 mg of **11a** and **11b**. The major compound **11a** or **11b** was bulb-to-bulb distilled at 160 °C/0.25 Torr: IR (neat) ν_{max} 3020, 1690, 1620 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.8–5.4 (2 H, m), 3.2–1.0 (18 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 207.7, 184.3, 143.8, 130.7, 128.4, 45.1, 43.9, 40.2, 39.3, 35.7, 35.4, 30.6, 25.6, 24.8, 22.5. The minor compound **11a** or **11b**: IR (neat) ν_{max} 3010, 1690, cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.64 (2 H, t), 3.0–1.0 (18 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 208.1, 182.8, 143.2, 130.9, 127.7, 43.6, 42.7, 42.3, 34.9, 32.4, 31.2, 26.1, 26.0, 24.8, 22.2. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.32; H, 9.57. Further elution of the column with the same solvent gave the spiro enone **12**, 13 mg (which was bulb-to-bulb distilled at 170 °C/0.6 Torr): IR (neat) ν_{max} 3020, 1700, 1610 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.85 (1 H, br s), 5.48 (2 H, J = 6 Hz, t), 3.4–1.2 (17 H, series of m); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 208.7, 191.6, 130.9, 130.4, 126.0, 54.3 (s), 45.5, 41.7, 39.9, 35.6 (2C), 33.7, 25.7, 23.8, 23.6. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.15; H, 9.34.

Preparation of 11a,b from 10. Sodium hydride (60 mg, as 50% dispersion in oil, 1.2 mmol) was placed in a 25-mL, three-necked flask equipped with dry N_2 inlet, pellet, condenser with mercury seal, and septum. The mineral oil was removed by washing twice with petroleum ether and the residue was suspended in 4 mL of dry toluene. A solution of bromo enone **10** (45 mg, 0.15 mmol) in 4 mL of dry toluene was added dropwise. The resulting solution was refluxed for 1 h, after which it was quenched with 5% HCl and extracted with ether (3 × 10 mL). The ethereal solution was washed with water and dried over Na_2SO_4. Removal of solvent gave a residue (35 mg), which was found to be identical (TLC, IR, NMR) with that obtained in the above experiments.

3,3-(Ethylenedithio)tricyclo[7.5.1.0^{4,15}]pentadeca-4-(15),11-diene (15). A solution of the tricyclic enones **11a,b** (120 mg, 0.5 mmol) and ethanedithiol (0.2 mL) in 10 mL of dry benzene in the presence of catalytic amount of *p*-toluenesulfonic acid was heated at reflux for 8 h. The organic layer was washed successively with water and 5% $NaHCO_3$ and dried over Na_2SO_4. Removal of solvent gave 150 mg of crude compound which was filtered through a silica gel (8 g) column to remove impurities. Elution with 10% benzene–petroleum ether furnished the thioacetal **15**, 143 mg (90%) (which was bulb-to-bulb distilled at 140–150 °C/0.2 Torr): IR (neat) ν_{max} 3010, 730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.7–5.4 (2 H, m), 3.4–3.0 (4 H, m), 3.0–1.2 (18 H, series of m). Anal. Calcd for $C_{17}H_{24}S_2$: C, 69.80; H, 8.27. Found: C, 69.79; H, 8.2.

Tetracyclo[7.5.1.0^{4,15}.0^{12,15}]pentadecan-11-one (18). To a vigorously stirred mixture of 30 mL of liquid NH_3 and sodium (25 mg, 1.0 mmol) kept at −40 °C was carefully added thioacetal **15** (100 mg, 0.32 mmol) in 4 mL of ether. The reaction mixture was warmed and ammonia allowed to evaporate. The residue was dissolved in pentane (30 mL) and the organic layer was washed with water and dried over Na_2SO_4. The crude oily residue obtained after removal of solvent [IR (neat) ν_{max} 3020, 1460 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 5.8–5.4 (2 H, m), 3.0–1.0 (20 H, series of m)] was dissolved in 1 mL of 85% HCOOH and heated at 90 °C for 4 h. The reaction mixture was poured into ice-cold water and extracted with ether (4 × 10 mL). The ethereal layer was washed with 5% $NaHCO_3$ and dried over Na_2SO_4. Removal of solvent gave 70 mg of a crude mixture of formate esters (IR 1730 cm^{-1}) and unreacted hydrocarbon. The hydrocarbon impurity was removed by passing through a small silica gel column and the formate esters (20 mg) were dissolved in 2 mL of 10% methanolic KOH, diluted with two drops of H_2O, and refluxed for 2 h. The reaction mixture was diluted with water and extracted with ether (2 × 10 mL). The ethereal layer was washed with water and dried over Na_2SO_4. Removal of solvent gave 18 mg of a crude hydroxy compound: IR (neat) ν_{max} 3450 cm^{-1}. The hydroxy compound was dissolved in 1 mL of dry dichloromethane and was added dropwise to a solution of 35 mg PCC in 1 mL of dichloromethane at 0 °C. The reaction mixture was brought to room temperature and allowed to stir for 1 h. The resulting dark-brown residue was diluted with ether (10 mL) and filtered through a Florosil pad and repeatedly washed with dichloromethane. Removal of solvent left a dark residue that was charged on a silica gel (8 g) column. Elution of the column with 10% ethyl acetate–petroleum ether furnished the tetracyclic ketone **18** as colorless oil, 16 mg, which was shown by HPLC (Lichrosorb SI 60 (7 μm), 250 mm × 4 mm, 25 bar, 226 nm, *n*-hexane) to be a 1:3 mixture of epimers. The ketone **18**, which was bulb-to-bulb distilled at 120 °C/0.2 Torr, was characterised as follows: IR (neat) ν_{max} 1730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.8–1.0 (22 H, m); ^{13}C NMR (25.0 MHz, $CDCl_3$) significant peaks observed at δ 224.6, 223.9, 64.2, 60.6, 59.1, 52.6, 51.8, 43.9, 42.6, 40.7, 39.6, 37.7, 36.7, 35.9, 35.5, 34.6, 32.6, 31.6, 30.9, 26.4; exact mass calcd (M^+) 218.1665, found 218.1691. Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.09. Found: C, 82.41; H, 10.20.

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Registry No. **1**, 72779-23-8; **7**, 110307-69-2; **8**, 111975-91-8; **9**, 111975-92-9; **10**, 111975-93-0; **11a**, 111975-94-1; **11b**, 111975-95-2; **12**, 111975-96-3; **15** (isomer 1), 111975-97-4; **15** (isomer 2), 111976-01-3; **16** (isomer 1), 111975-98-5; **16** (isomer 2), 111976-02-4; **17**, 111975-99-6; **18**, 111976-00-2.

Ritter Reactions. 3. A Simple Entry into the 3-Azatricyclo[5.3.1.0^{4,9}]undecane System[1]

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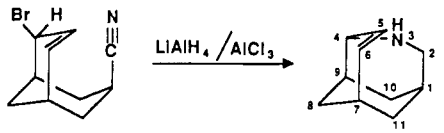
In 1979 Hassner et al.[2] reported that reduction of the bromo nitrile **1** produced a 56% yield of the tricyclic compound **2** via an intramolecular allylic halide displacement. Since this report, this reaction has remained the



sole example of the preparation of the 3-azatricyclo[5.3.1.0^{4,9}]undecane[3] skeleton. We now report a simple and effective means of synthesizing derivatives of this ring system using typical Ritter reaction[4] conditions.

Addition of 2,6-dimethylenebicyclo[3.3.1]nonane[5] (**3**) to a mixture of acetonitrile and concentrated sulfuric acid led to the isolation of a single product with mass ion m/z^+ 248 and composition $C_{15}H_{24}N_2O{\cdot}H_2O$ in 63% yield. If this monohydrate was heated above its melting point under low pressure, the material resolidified as the anhydrous compound. The latter is hygroscopic and slowly reverts to the hydrated form on exposure to the atmosphere.[6] The increase of 100 in the molecular weight of the anhydrous

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(2) Hassner, A.; Morgan, T. K.; McLaughlin, A. R. *J. Org. Chem.* **1979**, *44*, 1999.
(3) *Chemical Abstracts* nomenclature is based on 3,6-methanoquinoline.
(4) Krimen, L. I.; Cota, D. J. *Org. React. (N.Y.)* **1969**, *17*, 213.
(5) (a) Bishop, R.; Landers, A. E. *Aust. J. Chem.* **1979**, *32*, 2675. (b) Landa, S.; Kiefmann, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 1005. (c) Dovgan, N. L.; Likhotvorik, I. R.; Davidenko, N. P.; Yurchenko, A. G. *Zh. Org. Khim.* **1982**, *18*, 1774.
(6) Although the hydrated form gave a combustion analysis that was almost correct for a monohydrate, it is not certain at this stage whether it is a stoichiometric compound. It is clear, however, from ^1H and ^{13}C NMR data that in solution this material is a hydrated form of the imine **10** rather than having the carbinolamine structure $RC(OH)(CH_3)NHR^1$.

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