5, phenyl), 5.48 (dd, 1, $J_{1,2}$ = 8.3 Hz, $J_{2,3}$ = 10.5 Hz, C_2 H), 5.41 (s, 1, benzylic), 5.34 (dd, 1, $J_{3,4}$ = 3.6 Hz, C_3 H), 4.20–3.92 (m, 3, C_1 H and CH_2O), 3.98 (t, 1, $J_{4,5}$ = 3.6 Hz, C_4 H), 3.79 (dd, 1, $J_{5,6}$ = 2.7 Hz, C_5 H), 2.64 (m, 1, OH), 2.10 (s, 3) and 2.03 (s, 3) (OAc). This compound was characterized by conversion into **23**.

DL-**Di-*O*-acetyl-1,7-*O*-benzylidene-5-*O*-(methylsulfonyl)-(1,3,4/2,5,6)-4-azido-6-(hydroxymethyl)-1,2,3,5-cyclohexanetetrol (27).** To a solution of **26** (0.17 g) in pyridine (2 mL) was added methanesulfonyl chloride (0.06 mL) at 0 °C, and the mixture was stirred at room temperature. After 4 h, an additional amount of methanesulfonyl chloride (0.05 mL) was added, and then, after 20 h, 0.02 mL of the chloride was added. The reaction mixture was stirred for 20 h and then diluted with chloroform (10 mL). The solution was washed with water and dried. Evaporation of the solvent left crystals which were recrystallized from ethanol to give 0.15 g (74%) of **27** as plates: mp 210–213 °C; NMR δ 5.52 (dd, 1, $J_{1,2}$ = 9 Hz, $J_{2,3}$ = 10 Hz, C_2 H), 5.40 (s, 1, benzylic), 5.25 (dd, 1, $J_{3,4}$ = 4.2 Hz, C_3 H), 4.72 (dd, 1, $J_{4,5}$ = 3 Hz, $J_{5,6}$ = 4.2 Hz, C_5 H), 4.26 (dd, 1, C_4 H), 4.12 (dd, 1, $J_{6,7eq}$ = 7.5 Hz, J_{gem} = 10.5 Hz, C_7 H_{eq}), 3.90 (dd, 1, $J_{1,6}$ = 10.5 Hz, C_1 H), 3.87 (t, 1, $J_{6,7ax}$ = 10.5 Hz, C_7 H_{ax}), 3.14 (s, 3, mesyl), 2.42 (m, 1, C_6H), 2.11 (s, 3) and 2.04 (s, 3) (OAc). Anal. Calcd for $C_{19}H_{23}N_3O_9S$: C, 48.61; H, 4.94; N, 8.95; S, 6.83. Found: C, 48.70; H, 5.02; N, 8.68; S, 6.69.

DL-**Di-*O*-acetyl-3,7-*O*-benzylidene-(1,3,6/2)-6-azido-4-(hydroxymethyl)-4-cyclohexene-1,2,3-triol (28).** A mixture of **27** (150 mg), 1,8-diazabicyclo[5.4.0]undec-5-ene (0.15 mL), and toluene (10 mL) was refluxed for 4.5 h. TLC indicated the formation of one major product (R_f 0.60), along with a minor one [R_f 0.36, 2-butanone–toluene (1:4)]. The reaction mixture was concentrated and the products were fractionated on a silica gel column (6 g) with 2-butanone–toluene (1:7) as an eluant. The major fraction gave crystals, which were recrystallized from ethanol to give 104 mg (87%) of **28** as needles: mp 150–153 °C; NMR δ 7.48–7.23 (m, 5, phenyl), 5.58 (dd, 1, $J_{1,2}$ = 11 Hz, $J_{2,3}$ = 7.5 Hz, C_2 H), 5.57 (d, 1, $J_{5,6}$ = 4.5 Hz, C_5 H), 5.56 (s, 1, benzylic), 5.03 (dd, 1, $J_{1,6}$ = 4.2 Hz, C_1 H), 4.44 (br d, 1, C_3 H), 4.42 (br d, 2, J = 1.2 Hz, CH_2O), 4.32 (br t, 1, C_6 H), 2.10 (s, 3) nnd 2.05 (s, 3) (OAc). Anal. Calcd for $C_{18}H_{19}N_3O_6$: C, 57.90; H, 5.13; N, 11.25. Found: C, 57.66; H, 5.17; N, 10.96.

DL-**Tetra-*O*-acetyl-(1,3,6/2)-6-azido-4-(hydroxymethyl)-4-cyclohexene-1,2,3-triol (29).** A mixture of **28** (23 mg) and 60% aqueous acetic acid (2.5 mL) was stirred at room temperature for 6.5 h. The mixture was concentrated, and the residue was acetylated in the usual way. The product was purified by a short column of alumina with chloroform to give 19 mg (84%) of **29** as a homogeneous oil. The ^{1}H NMR spectrum was superimposable on that of an authentic sample;[10a] R_f 0.43 [2-butanone–toluene (1:5)].

DL-**Tetra-*O*-acetyl-(1,3,6/2)-6-acetamido-4-(hydroxymethyl)-4-cyclohexene-1,2,3-triol** (DL-**Pentaacetylvalienamine, 30).** Compound **29** (45 mg) was reduced with hydrogen sulfide in pyridine (1.5 mL) and water (1.5 mL) for 2 h. The reaction mixture was processed as described for the preparation of **21**. The product was acetylated in the usual way and purified on a silica gel column (2 g) with ethanol–toluene (1:8) to give 38 mg (80%) of **30** as crystals, which were recrystallized from ethanol–ether to afford a pure sample: 20 mg (43%); mp 180.5–181.5 °C (lit.[10a] mp 180–181 °C). The ^{1}H NMR spectrum was superimposable on that of an authentic sample.[10a]

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Registry No. **5**, 70838-35-6; **6**, 70878-41-0; **7**, 74023-99-7; **8**, 74024-01-4; **9**, 74561-02-7; **10**, 77144-65-1; **11**, 77144-67-3; **12**, 77144-66-2; **13**, 77209-45-1; **14**, 84851-92-3; **15**, 77144-68-4; **16**, 84894-17-7; **17**, 77144-71-9; **18**, 77144-72-0; **19**, 77144-73-1; **20**, 77144-69-5; **21**, 77144-70-8; **22**, 77144-76-4; **23**, 77144-74-2; **24**, 77144-75-3; **25**, 77144-64-0; **26**, 84851-93-4; **27**, 84851-94-5; **28**, 84851-95-6; **29**, 74708-35-3; **30**, 74645-52-6.

(25) This compound melted at 127–129 °C, after sintering at 97 °C. Anal. Calcd for $C_{18}N_{21}N_3O_7$: C, 55.24; H, 5.37. Found: C, 55.18; H, 5.71.

Occurrence of Ring Opening in the Reactions of Some 2,6-Disubstituted Purines with Potassium Amide in Liquid Ammonia[1]

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The reaction of 2,6-dichloropurine with potassium amide in liquid ammonia gives three products: 2-chloroadenine, 2,6-diaminopurine, and 4-cyano-5-(cyanoamino)imidazole. We have shown that 2-chloroadenine is formed first. This compound is converted into 4-cyano-5-(cyanoamino)imidazole, which finally gives 2,6-diaminopurine. 2,6-Diaminopurine can also be obtained by conversion of the 4-cyano-5-(cyanoamino)imidazole with methanolic ammonia, but the mechanism of this conversion is different from the one with potassium amide in liquid ammonia. To prove these mechanisms via ^{15}N labeling we have shown that reductive deamination of 2,6-diamino-9-methylpurine with sodium in liquid ammonia removes the amino group at position 6 without ring opening. Reaction of 2-amino-6-chloropurine with potassium amide in liquid ammonia also gives 4-cyano-5-(cyanoamino)imidazole with some 2,6-diaminopurine.

On treatment with potassium amide in liquid ammonia, 2-substituted purines can undergo a ring-opening reaction (S_N(ANRORC) mechanism)[2] involving as initial step the formation of a σ-adduct at position 6.[3] This result induced us to study the behavior of purines substituted at position 2 as well as at position 6 toward liquid ammonia containing potassium amide; we chose 2,6-dichloropurine (**1**) as the first substance in this study. It has been reported that with methanolic ammonia **1** gives 2-chloroadenine (**2**) and that with aqueous ammonia **1** yields 2,6-diaminopurine (**4**).[4]

(1) Part 95 on pyrimidines from this laboratory. For part 94, see van der Plas, H. C.; Charushin, V. N.; van Veldhuizen, A.; submitted for publication in *J. Org. Chem.*

(2) The term S_N(ANRORC) mechanism refers to a nucleophilic substitution involving an addition of the nucleophile, ring opening and ring closure. For a review, see: van der Plas, H. C. *Acc. Chem. Res.* **1978**, *11*, 462.

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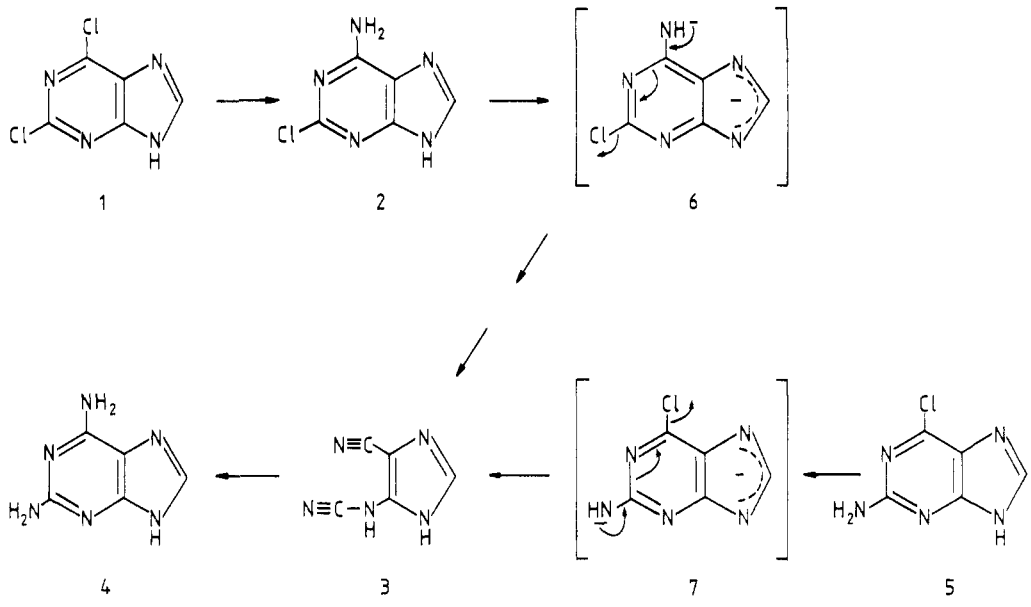
Scheme I



Montgomery and Holum[5] stated that 2-chloro-6-(alkylamino)purines do not react with aqueous ammonia (at 130 °C for 16 h), indicating that a chlorine atom at position 6 is far more reactive than at position 2. The inertness of the chloro atom at position 2 toward nucleophilic displacement is also shown by the conversion of 2,6,8-trichloropurine into 2,8-dichloroadenine with aqueous ammonia[6] and the conversion of 2,8-dichloropurine with aqueous methylamine into 2-chloro-8-(methylamino)-purine.[7] In addition, the very difficult conversion of 2-chloro-6-[(β-imidazol-4-ylethyl)amino]purine with ammonia in butanol into the corresponding amino compound[8] illustrates the low reactivity at position 2.

Results and Discussion

a. Reaction of 2,6-Disubstituted Purines with Potassium Amide. Reaction of 2,6-dichloropurine (1) with potassium amide in liquid ammonia at −33 °C for 20 h gives, besides 40% of starting material, 2-chloroadenine (2, yield 12%), 4-cyano-5-(cyanoamino)imidazole (3, 25%), and 2,6-diaminopurine (4, 13%; Scheme I).

The formation of 2 involves an $S_N(AE)^{ipso}$ mechanism[9] and is in agreement with earlier observations showing that addition of an amide ion to the anion of a purine only occurs at position 6.[3,9] Compound 2 is intermediate in the formation of 3, since reaction of 2 with liquid ammonia containing potassium amide (−33 °C, 20 h) yields indeed 3 (60%) and, in addition, 4 (20%) and 5% of starting material. The formation of 3 from 2 can be explained by an amide-induced deprotonation from both the imidazole ring and the amino group into dianion 6,[10] followed by loss of chloride ion. Such 1,4-dehydrohalogenation reactions are often found in the amination reactions of 6-amino-2-bromopyridine,[11] 3-amino-1-bromoisoquinoline,[11] and possibly 4-amino-2-bromoquinoline.[12] They also occur in the σ-complexes formed between 2-chloropyrimidine and the potassio salts of acetone or pinacolone.[13] 2,6-Diaminopurine (4) is the final product of the reaction of 1 and is not converted further, since 4 was recovered unchanged when reacted with potassium amide in liquid ammonia for 20 h at −33 °C. It is very improbable that 4 is formed from 2 via an $S_N(AE)^{ipso}$ substitution at C-2, since we have shown that attack of an amide ion at position 2 in anionic purines does not take place.[3,9] It is interesting to notice that compounds 3 and 4 are also obtained when reacting 2-amino-6-chloropurine (5) with potassium amide in liquid ammonia (−33 °C, 20 h, yield 70% of 3 and 4). Evidently, in this reaction the opening of the pyrimdine ring can also be explained by a 1,4-dehydrochlorination in dianion 7. To obtain further evidence for the existence of 3 as common intermediate in the amination of 2 and 5, we measured the ^1H NMR spectra of the solutions, which are obtained when compounds 2, 3, and 5 are dissolved in liquid ammonia containing potassium amide at −45 °C. The spectra of all these three solutions were identical, showing only a singlet at δ 6.72. This indicates that 3 is formed immediately when 2 or 5 dissolves. This compound is probably present in the strong basic medium as dianion, formed by loss of the protons from both NH groups.

b. Conversion of 4-Cyano-5-(cyanoamino)imidazole into 2,6-Diaminopurine. In liquid ammonia containing potassium amide the reaction of 3 into 4 proceeds via the addition of an amino group to the cyano group at position 4 in 3, since the intermediate formed could be identified as 4-amidino-5-(cyanoamino)imidazole (8; Scheme II).

Its presence was revealed by TLC, but due to its instability we could only obtain its UV spectrum (λ_{max} (CH_3OH) 315 nm) and its IR spectrum, showing an absorption at 2145 cm^{-1}, which is characteristic of the presence of a conjugated NCN group. These data show that the addition of an amino group has taken place at the C-cyano group and proves that the intermediate is 8 and not 9. We suggest that the addition to the cyanoamino

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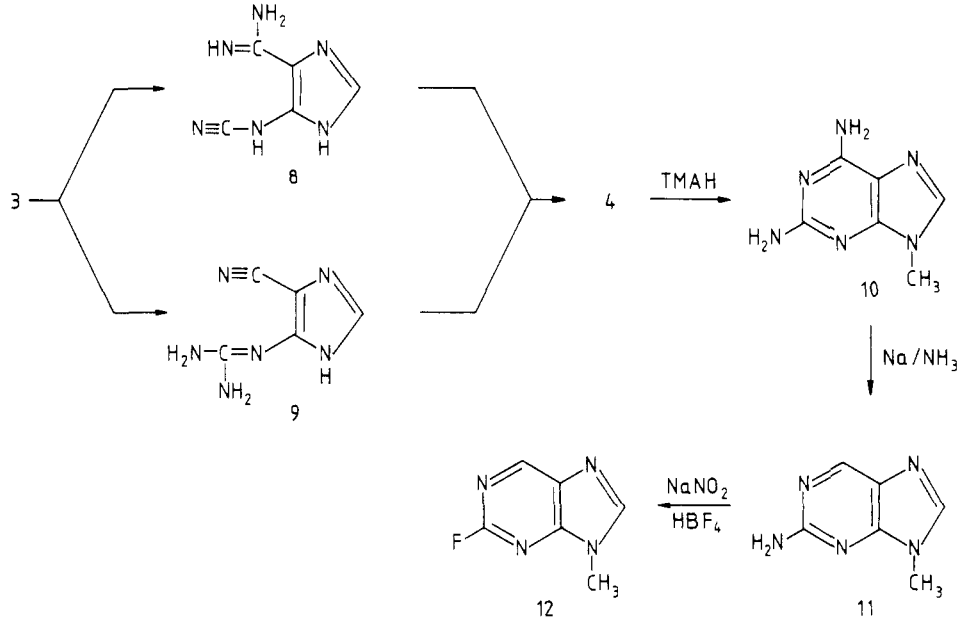
Scheme II



group in **3**, which should have led to intermediate **9**, is prevented due to its presence in a deprotonated form. On heating, **8** is converted into **4**.

A much higher yield of 2,6-diaminopurine (**4**) is obtained when **3** is reacted with methanolic ammonia[14] (5 h at 100 °C in a sealed tube). In this reaction we could not detect an intermediate. The mechanism of the conversion of **3** into **4** in methanolic ammonia was elucidated by the use of ^{15}N-labeled ammonia. To determine to what extent the several positions in **4** are ^{15}N labeled (2- and 6-amino groups, ring nitrogen), we needed a method for the selective removal of the amino groups from **4**. This was achieved successfully by methylation of **4** with tetramethylammonium hydroxide (TMAH) into 2,6-diamino-9-methylpurine (**10**) followed by reductive deamination with sodium in liquid ammonia to give 2-amino-9-methylpurine (**11**);[15] diazotization of **11** yielded 2-fluoro-9-methylpurine (**12**).[16] To ascertain that the deamination of **10** occurs *without* ring opening, we prepared 2,6-diaminopurine being selectively labeled at the 6-amino group (by reacting 2-amino-6-chloropurine with ^{15}N-labeled ammonia] and subjected it to methylation and reductive deamination. The 2-amino-9-methylpurine (**11**) obtained contained no ^{15}N label (% ^{15}N in **10**, 6.2; in **11**, 0.0),[17] which shows that the deamination (**10** → **11**) involves no ring opening.[15] When we applied the reaction sequence (methylation, reductive removal of the 6-amino group, diazotization) to **4** obtained from **3** with ^{15}N-labeled ammonia in methanol, we obtained **10** (% ^{15}N, 4.1), **11** (% ^{15}N, 3.8) and **12** (% ^{15}N, 1.8).[17] These results show that the ^{15}N label in **4** is about equally scrambled over N-1 (52%) and the 2-NH_2 group (48%) and lead to the conclusion that in methanolic ammonia **3** is converted into **4** via **9**. A similar intermediate is postulated in the synthesis of 2-(phenylamino)adenosine.[18]

All data mentioned above indicate that the conversion of **3** into **4** proceeds in liquid ammonia containing potassium amide via **8** and in methanolic ammonia via **9**. This difference in mechanistic pathways is certainly due to the fact that, in the presence of potassium amide, **3** is deprotonated in both the imidazole ring and the NHCN group, directing addition of ammonia to the CCN group, while in methanolic ammonia the addition only takes place at the uncharged cyanoamino group.

In conclusion, we have shown that the reaction of 2,6-dichloropurine (**1**) with potassium amide in liquid ammonia giving 2,6-diaminopurine (**4**) involves the three intermediates **2**, **3**, and **8**.

c. Reactions of 4-Cyano-5-(cyanoamino)imidazole. 4-Cyano-5-(cyanoamino)imidazole (**3**) may be useful as a compound for preparation of some purine derivatives. These reactions also offer additional evidence for the structure of **3**. On reaction with hydrochloric acid in methanol (45 min) **3** gives 2-chloroadenine (**2**).[19] The fact that no 2-amino-6-chloropurine (**5**) is formed shows that the first step in this reaction involves addition to the cyanoamino group rather than addition to the cyano group. When this reaction was carried out with **3** obtained from the reaction of **5** with ^{15}N-labeled potassium amide, we obtained unlabeled **2**, showing that the initial step in the reaction of **5** with potassium amide in liquid ammonia involves anion **7**. A σ-adduct at position 6, already occupied by an amino group, is not formed,[10-12,20] since this should lead to incorporation of label.

Experimental Section

^1H NMR spectra were obtained with a Varian EM 390 instrument using Me_4Si as internal standard. The sample temperature was ca. −50 °C when measuring in liquid ammonia and NH_3 was used as a standard. The spectra were converted to the Me_4Si scale by adding 0.95 ppm. Mass spectra and ^{15}N contents were determined on an AEI MS-902 mass spectrometer. UV spectra were obtained with a Beckman Acta III and a Perkin Elmer 550 instrument and IR spectra with a Perkin Elmer 237 and a Hitachi EPI-G3 instrument.

Preparation of Starting Materials. 2-Amino-6-chloropurine (**5**) was purchased from Aldrich. 2,6-Dichloropurine (**1**)[21] and 2-chloroadenine (**2**)[4] were prepared as described in the literature.

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^{15}N-labeled ammonia was prepared by reacting ^{15}N-labeled ammonium nitrate (from VEB Berlin-Chemie) with potassium hydroxide. 2,6-Diaminopurine (4) was prepared by reacting 2-amino-6-chloropurine (5) with ammonia in a sealed tube for 17 h at 100 °C.[4,5]

Amination Procedure. The amination reactions were carried out in the same manner as described in a previous paper.[22] The products were separated by preparative TLC with mixtures of methanol, chloroform, and water or methanol and chloroform in the presence of aqueous ammonia. The structure of 4-cyano-5-(cyanoamino)imidazole (3) was proved by the following: ^1H NMR (Me_2SO-d_6) δ 6.86 (s); ^{13}C NMR (Me_2SO-d_6) 129.6 (C-2, J = 209.5 Hz), 91.6 (C-4, J = 11 Hz); 153.0 (C-5), 119.4 and 122.7 ppm (NHC≡N and C≡N); UV λ_{max}(CH_3OH) 272 nm; IR (KBr) 2095, 2120, 2160, 2175 cm^{-1}.

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Registry No. 1, 5451-40-1; 2, 1839-18-5; 3, 85029-13-6; 4, 1904-98-9; 8, 85029-14-7; 9, 85029-15-8; 10, 30720-65-1; TMAH, 75-59-2; potassium amide, 17242-52-3.

Studies on the Syntheses of Sesquiterpene Lactones. 8.[1] Syntheses of Saussurea Lactone, 8-Deoxymelitensin, and 11,12-Dehydro-8-deoxymelitensin via a Novel Fragmentation Reaction[2]

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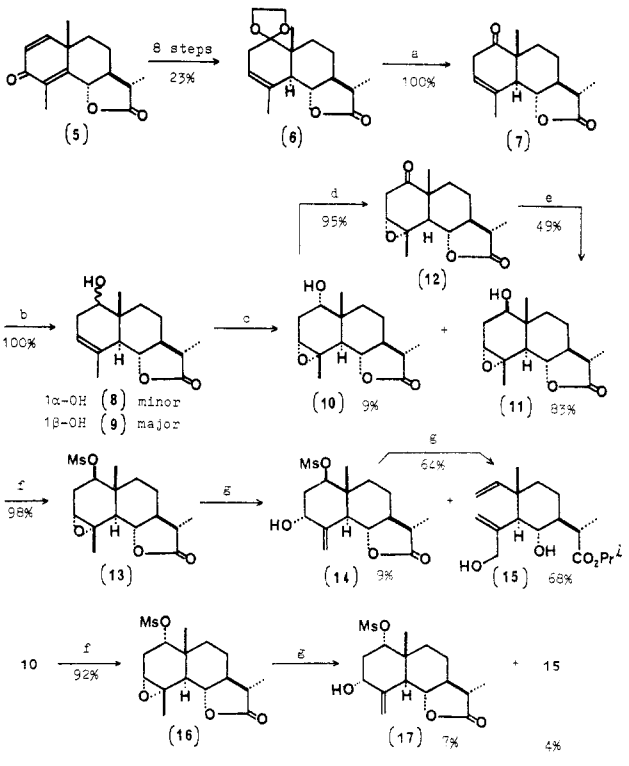
Saussurea lactone (4), 8-deoxymelitiensin (18), and 11,12-dehydro-8-deoxymelitensin (23) have been synthesized from (11*S*)-1,1-(ethylenedioxy)eudesm-3-eno-13,6α-lactone (6) in ten steps, seven steps, and nine steps, respectively. The key step involves a novel fragmentation reaction of (11*S*)-3α,4α-epoxy-1β-(mesyloxy)eudesmano-13,6α-lactone (13) with aluminum isopropoxide in refluxing toluene.

Elemanolides are a small group of natural products, comprising to date ca. 30 varieties.[3] With only a few exceptions the natural products of this class possess a functionality at C_{14} as shown in melitensin (1),[4,5] 11,12-dehydromelitensin (2),[6] and vernolepin (3).[7] In connection with the general synthetic strategy of these natural products, we envisioned an approach which consisted of the fragmentation reaction of appropriately functionalized epoxy mesylates such as compounds **A** and **B** by base as shown in Figure 1. In the present paper we report efficient syntheses of 8-deoxymelitensin (18) and 11,12-dehydro-8-deoxymelitensin (23), which are 8-deoxy derivatives of natural products, and the conversion of 18 to saussurea lactone (4)[8] to demonstrate the utility of this novel fragmentation reaction of an appropriately functionalized epoxy mesylate (13), which was conveniently prepared from α-santonin (5).

Results and Discussion

The starting material is the acetal 6 which can be prepared from α-santonin (5) in 23% yield in 8 steps.[9] Treatment of 6 with boiling 50% aqueous acetic acid for 1 h and 15 min gave the desired β,γ-unsaturated ketone 7 in quantitative yield (Scheme I). The structure of 7 was fully supported by the IR spectrum (1710 cm^{-1}) and the ^1H NMR spectrum [δ 5.59 (1 H, m, $w_{h/2}$ = 9.0 Hz, C_3–H)]. No epimerization of the double bond was observed under these reaction conditions.

Scheme I[a]



[a] (a) 50% AcOH aqueous solution, reflux; (b) LiAl(t-BuO)$_3$H; (c) MCPBA; (d) CrO_3·2Py, CH_2Cl_2; (e) $Zn(BH_3)_2$; (f) MsCl, Py; (g) Al(i-PrO)$_3$, toluene, reflux.

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