Dihydro-9*H*(or -ethyl)-carbazol-4(3*H*)-ones (5) and 8,9-Dihydro-7*H*(or -ethyl)-benzo[*c*]carbazol-11(10*H*)-ones (9) (Table III). A mixture of the bromo enaminone (5 mmol), palladium acetate (0.1 mmol), triphenylphosphine (0.2 mmol), and sodium bicarbonate (10 mmol) in DMF (50 mL) was heated. The reaction mixture was filtered through Celite and the solvent was distilled under reduced pressure. The residue was chromatographed on a silica gel column with chloroform.

Preparation of 3-Anisidinocyclohex-2-en-1-ones (11a-e and 14) and 3-Anilinocyclopent-2-en-1-one (15) (Table IV). The arylamine and the β-diketone were treated in a manner similar to that stated above for the general procedure for the bromo enaminones listed in Table I.

General Procedure for Stoichiometric Cyclization of *N*-Arylenaminones. Formation of 1,2-Dihydro-9*H*(or ethyl)-carbazol-4(3*H*)-ones (17 and 18) and 1,2,3,4-Tetrahydrocyclopent[*b*]indol-1-one (19) (Table V). A mixture of the enaminone (5 mmol) and palladium acetate (5 mmol) in an appropriate solvent was refluxed. After cooling to room temperature, the reaction mixture was filtered through Celite and the solvent was evaporated under reduced pressure. The residue was chromatographed on a silica gel column with chloroform.

Preparation of 3-(*N*-Ethylanisidino)cyclohex-2-en-1-ones (16) (Table IV). The secondary enaminone was treated in a manner similar to the general procedure described above for the *N*-ethylenaminones listed in Table II.

Treatment of 3-(4-Methoxyanilino)cyclohex-2-en-1-one (11d) with a Catalytic Amount of Palladium Acetate. A mixture of the enaminone **11d** (1.5 g, 6.9 mmol) and palladium acetate (155 mg, 0.69 mmol) in acetonitrile (50 mL) was refluxed with stirring for 6 h. The reaction mixture was filtered through Celite and the solvent was removed by evaporation. Chromatography of the residue on silica gel ($CHCl_3$) afforded 6-methoxy-1,2-dihydro-9*H*-carbazol-4(3*H*)-one (**17i**) (37 mg, 2.5%) and the unreacted starting material (~80%).

Catalytic Cyclization of 11d with Palladium Acetate in the Presence of Cupric Acetate and Oxygen. A mixture of **11d** (1.0 g, 4.6 mmol), palladium acetate (103 mg, 0.46 mmol), and cupric acetate (84 mg, 0.46 mmol) in acetonitrile (40 mL) was refluxed with bubbling of oxygen for 40 h. After workup according to the above procedure, silica gel column chromatography eluting with chloroform gave **17i** (310 mg, 31%).

Registry No. **1**, 583-68-6; **2a**, 504-02-9; **2b**, 126-81-8; **3b**, 68890-20-0; **3c**, 73825-18-0; **3d**, 73825-19-1; **4a**, 68890-21-1; **4b**, 69083-41-6; **4c**, 73825-20-4; **4d**, 73825-21-5; **5a**, 40429-04-7; **5b**, 73825-22-6; **5c**, 69083-42-7; **5d**, 73825-23-7; **5e**, 73825-24-8; **6**, 20191-75-7; **7a**, 73825-25-9; **7b**, 73825-26-0; **8a**, 73825-27-1; **8b**, 73825-28-2; **9a**, 73825-29-3; **9b**, 73825-30-6; **9c**, 73825-31-7; **10a**, 90-04-0; **10b**, 536-90-3; **10c**, 104-94-9; **10d**, 96-96-8; **10e**, 62-53-3; **11a**, 73825-32-8; **11b**, 61997-80-6; **11c**, 51409-74-6; **11d**, 36646-77-2; **11e**, 73825-33-9; **12**, 14203-46-4; **13**, 3859-41-4; **14**, 73825-34-0; **15**, 73825-35-1; **16a**, 73825-36-2; **16b**, 73825-37-3; **16c**, 73825-38-4; **16d**, 73825-39-5; **17a**, 73825-40-8; **17b**, 73825-41-9; **17c**, 73825-42-0; **17d**, 73825-43-1; **17e**, 73825-44-2; **17f**, 73825-45-3; **17g**, 73825-46-4; **17h**, 73825-47-5; **17i**, 35556-81-1; **17j**, 73825-48-6; **17k**, 73825-49-7; **18**, 73825-50-0; **19**, 61364-20-3; ethyl iodide, 75-03-6; palladium acetate, 3375-31-3; cupric acetate, 142-71-2.

Supplementary Material Available: Spectral characterization data (IR, ^1H NMR, and mass spectral) and C, H, N analyses for all compounds in Tables I–V (11 pages). Ordering information is given on any current masthead page.

Occurrence of the $S_NANRORC$ Mechanism in the Amination of 2-Substituted Purines with Potassium Amide in Liquid Ammonia[1]

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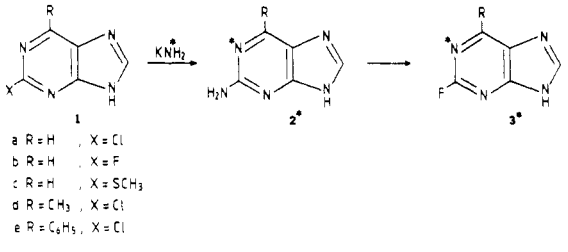
The reactions of 2-chloro-, 2-fluoro- and 2-(methylthio)purine with potassium amide in liquid ammonia lead to the formation of 2-aminopurine. When these reactions are carried out with ^{15}N-labeled potassium amide, *ring*-labeled 2-aminopurine is found. This demonstrates that a ring opening occurs during the amination. Formation of an anionic σ adduct at position 6 is proven by low-temperature NMR spectroscopy, and evidence is obtained for the formation of an open-chain intermediate, although this intermediate could not be isolated in a pure state. Reaction of the open-chain intermediate with hydriodic acid gives the thus far unknown 2-iodopurine. 2-Chloro-6-phenylpurine also reacts via ring opening into 2-amino-6-phenylpurine. However, 2-chloro-6-methyl- and 2-chloro-6,8-di-*tert*-butylpurine are found to be unreactive.

Introduction

We have recently found that purine and its derivatives containing a leaving group at position 6 or 8 easily undergo amination with potassium amide in liquid ammonia.[2,3] From purine and the 6-substituted purines, adenine is obtained, being formed by an addition–elimination reaction at position 6.[2,3] Interestingly 8-chloro- and 8-(methylthio)purine do not undergo amination at position 8, but

Scheme I



at position 6, giving 8-chloroadenine (together with adenine) and 8-(methylthio)adenine, respectively. These reactions have been explained by an initial addition of the amide ion at position 6, leading to a σ adduct, which undergoes either aromatization into 8-chloro- or 8-(methyl-

(1) Part 27 on the $S_NANRORC$ mechanism. For Part 26 see: Rykowski, A.; van der Plas, H. C. *J. Org. Chem.* **1980**, *45*, 881. Pyrimidines, Part 81. For Part 80 see: van der Stoel, R. E.; van der Plas, H. C.; Jongejan, H.; Hoeve, L. *Recl. Trav. Chim. Pays-Bas*, in press.

(2) Kos, N. J.; van der Plas, H. C.; van Veldhuizen, A. *J. Org. Chem.* **1979**, *44*, 3140.

(3) Kos, N. J.; van der Plas, H. C.; van Veldhuizen, A., *Recl. Trav. Chim. Pays-Bas.*, in press.

0022-3263/80/1945-2942$01.00/0

Table I. ^{15}N Contents (Percentages) of Products Obtained in Reaction of Starting Compounds with ^{15}N-Labeled Potassium Amide[a]

starting compd	products: 2-NH_2-6-R-purine	products: 2-F-6-R-purine
2-Cl-purine (1a)	6.2 (5.7) (R = H)	6.4 (5.6) (R = H)
2-F-purine (1b)	6.0 (5.7) (R = H)	5.8 (5.7) (R = H)
2-SCH_3-purine (1c)	4.1 (5.4) (R = H)	4.3 (5.8) (R = H)
2-Cl-6-C_6H_5-purine (1e)	6.1 (5.0) (R = C_6H_5)	5.6 (4.6) (R = C_6H_5)

[a] The numbers in parentheses refer to duplicate experiments; the accuracy of the measurements is ±0.2%.

thio)adenine or a 1,4-tele elimination into adenine.[3] In principle 2-substituted purines are appropriate compounds to give addition at position 6.[2,3] Therefore, these compounds could give 2-aminopurines, via a ring-opening ($S_NANRORC$) mechanism.[4] Several 2-substituted purines were synthesized and their behavior toward potassium amide was studied in order to prove this.

Results and Discussion

2-Chloro-, 2-Fluoro-, and 2-(Methylthio)purine. When 2-chloro- (**1a**) or 2-fluoropurine (**1b**) reacts with potassium amide in liquid ammonia for 20 h and the reaction mixture is worked up as usual,[2] 2-aminopurine (**2**, R = H) is formed in good yield (80% and 60%, respectively) (see Scheme I). 2-(Methylthio)purine (**1c**) gives a similar reaction: after 70 h, 2-aminopurine (**2**, R = H) is obtained in 90% yield. In contrast **1a** and **1c** are expected to be unreactive with aqueous ammonia to give **2** (R = H).[5,6] When the reactions of **1a–c** were followed by TLC, it became evident that in the reactions of all three purines (**1a–c**) a compound is formed which quickly converts into 2-aminopurine (**2**, R = H) during workup. This precursor of **2** (R = H) is the same in all three reactions. This intermediate is not sufficiently stable to be isolated in the pure state, since conversion into **2** (R = H) takes place during isolation. Therefore only an IR spectrum of a mixture of this intermediate and 2-aminopurine could be obtained; it showed an absorption at 2160 cm^{-1}, being characteristic for the presence of a conjugated N–CN group. This result indicates that this intermediate is formed by an opening of the pyrimidine nucleus, which is then followed by cyclization into **2** (R = H). The amination of **1a–c** was carried out with ^{15}N-labeled potassium amide to prove this ring opening. We found that in the labeled 2-aminopurine (**2***, R = H) the label was present exclusively in the ring nitrogens; no trace of ^{15}N was found in the nitrogen of the amino group. This was proven by conversion of **2*** (R = H) into 2-fluoropurine (**3***, R = H) by diazotization in fluoroboric acid[7] and by determining the ^{15}N content in **2*** (R = H) and **3*** (R = H) by using mass spectrometry (Table I).

These results show that an $S_NANRORC$ mechanism[4] operates in the amination of **1a–c**, involving initial addition of the amide ion at position 6 in the deprotonated purine, giving a dianionic σ adduct (**4**, R = H), that can undergo a ring opening into intermediate **5** (R = H).[8] This intermediate **5** (R = H) is stable in the potassium amide/liquid ammonia solution. Addition of ammonium sulfate (necessary to neutralize the potassium amide) gives the neutral species **6** (R = H) in which cyclization of the side chain occurs by an attack of the imino group on the carbon atom of the cyanamino group (see Scheme II).

Scheme II

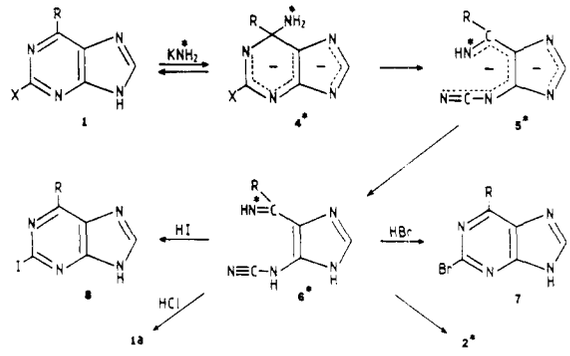


Table II. ^1H NMR Data (δ Values) of 2-Substituted Purines in Liquid Ammonia Containing Potassium Amide

compd	form	H-6	H-8	SCH_3
2-Cl-purine (1a)	anion	8.61	8.11	-
	adduct	5.62	6.85	-
2-Cl-8-D-purine	anion	8.61	-	-
	adduct	5.62	-	-
2-F-purine (1b)	anion	8.54	8.08	-
	adduct	6.08	6.73	-
2-SCH_3-purine (1c)	anion	8.66	8.03	2.57
	adduct	6.23	6.98	2.35
2-SCH_3-8-D-purine	anion	8.66	-	2.57
	adduct	6.23	-	2.35
SCH_3^-		-	-	1.78
2-Cl-6-CH_3-purine (1d)	dianion[a]		6.97	

[a] A CH_2^- signal appeared as two doublets (3.06 and 3.21 ppm, J = 3 Hz).

Addition of the amide ion at position 6 in the purine anion is in full agreement with earlier observations.[2,3] Additional evidence for addition at position 6 was obtained by ^1H NMR spectroscopy. A solution of **1a–c** in liquid ammonia containing potassium amide (0.15–0.5 mmol of **1a–c** in 1 mL of liquid ammonia containing 4–10 equiv of potassium amide) showed first the formation of the anion of **1a–c** and then the formation of a (very short lived) σ adduct as indicated by upfield shifts of 2.4–3.0 ppm for one of the hydrogens[2,3] (Table II). Comparison with the spectra of solutions of 2-chloro-8-deuterio- and 8-deuterio-2-(methylthio)purine in KNH_2/NH_3 proves that the σ-adduct formation takes place at position 6. In the solution of **1c**, after some time a signal appeared at 1.78 ppm assigned to SCH_3^-, formed during the conversion of **4** (R = H, X = SCH_3) into **5** (R = H). The observation that the intermediates obtained from **1a–1c** are identical on TLC indicates that also in the cases of **1a** and **1b** the formation of **5** occurs with loss of Cl^- or F^-, respectively. It is interesting to note that 2-fluoropurine (**1b**) exclusively reacts via a ring-opening mechanism into 2-aminopurine (**2**, R = H), since there are several aminodefluorinations reported in the literature in which the S_NAE mechanism is a more important pathway than the $S_NANRORC$ mechanism.[4,9] The fact that 2-chloropurine reacts via an

(4) The term $S_NANRORC$ mechanism refers to a reaction 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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(8) Kroon, A. P.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1020.
(9) Kroon, A. P.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 227.

$S_NANRORC$ mechanism into 2-aminopurine gives support to the suggestion that the reaction of 2-chloro-7-methyladenine with sodium hydroxide leading to the formation of 2-amino-6-hydroxy-7-methylpurine also proceeds via this mechanism, although an intermediate could never be identified.[10,11]

Reaction of **6** (R = H) with concentrated hydrochloric acid yields 2-chloropurine[8] (**1a**, 87%), while 2-bromopurine (**7**, R = H, 55%) and 2-iodopurine (**8**, R = H, 50%) are formed with hydrobromic and hydriodic acids, respectively. The preparation of 2-iodopurine is of special interest[12] as this compound was unknown until now. Reaction of **6** (R = H) with hydrofluoric acid gave no 2-fluoropurine, but only 2-aminopurine. This can be explained by the lower nucleophilicity of the fluoride ion in comparison with the other halogen ions. Compound **6** obtained in a reaction with ^{15}N-labeled potassium amide gave after treatment with hydrochloric acid 2-chloropurine (**1a**) in which no label was found.

2-Aminopurine. The fact that 2-methylpurine reacts with potassium amide to give 2-methyladenine[1] induced us to react 2-aminopurine (**2**, R = H) with potassium amide in liquid ammonia with the aim to synthesize 2,6-diaminopurine. Even after 20 h we found no product; 2-aminopurine could be recovered quantitatively. This indicates that in contrast to 2-methylpurine both the NH_2 group as well as the imidazole ring in 2-aminopurine are deprotonated yielding a dianion, i.e., a species in which position 6 is effectively deactivated for nucleophilic attack.

2-Chloro-6-substituted Purines. The influence of a substituent at position 6 in 2-chloropurines on the mechanism of the aminodechlorination was also studied. If addition of the amide ion at position 6 is retarded or even prohibited by the presence of the substituent, the replacement of the chlorine atom by the amino group might occur partly or completely via the alternative S_NAE mechanism.

Reaction of 2-chloro-6-methylpurine (**1d**) with potassium amide in liquid ammonia gave after 70 h 6-methylpurine (10%) besides starting material (90%). We explain the absence of a 2-amino compound by the formation of a dianion through proton abstraction of both the NH in the imidazole ring and the methyl group.[2] This dianion is highly deactivated toward nucleophilic attack. An ^1H NMR spectrum of **1d** dissolved in liquid ammonia containing potassium amide indeed showed the presence of a dianion as illustrated by the appearance of the CH_2^- signal as two doublets[2] (Table II). The formation of 6-methylpurine is due to dehalogenation, not unprecedented in a strongly basic medium.[13] We also studied the amination of 2-chloro-6-phenylpurine (**1e**). This compound can only give a *mono*anion and therefore can be expected to react "easier" than **1a** with potassium amide. After 70 h we indeed isolated 2-amino-6-phenylpurine (**2**, R = C_6H_5) in a yield of 80% besides 20% of starting material. When the reaction was carried out with ^{15}N-labeled potassium amide we obtained labeled 2-amino-6-phenylpurine (**2***, R = C_6H_5), which by diazotization[7] yielded 2-fluoro-6-phenylpurine (**3***, R = C_6H_5), containing all the ^{15}N-label (Table I). This shows that the formation of **2** (R = C_6H_5) from **1e** has proceeded via an $S_NANRORC$ mechanism (>90%). Thus despite the presence of a "bulky" group at position 6, the addition takes place at that position. Addition of an amide ion to a position being substituted by a phenyl group is not unprecedented.[9,14] Finally we tested whether the more voluminous *tert*-butyl group at position 6 could change the mechanism of the amination from $S_NANRORC$ to S_NAE. 2-Chloro-6,8-di-*tert*-butylpurine was synthesized, but found to be unreactive, even after 70 h. The same result was reported with 6,8-di-*tert*-butylpurine.[2] Summarizing all the results obtained thus far, we have to conclude that a direct attack of the amide ion at position 2 does not take place even when a leaving group is present at that position. Since we have already shown that position 8 is also completely unreactive toward potassium amide,[3] the conclusion seems justified that a purine derivative that gives a monoanion by deprotonation of the imidazole ring under influence of the amide ion only reacts with the amide ion at position 6. These experimental results are in agreement with data, given in the literature, showing that in anionic purines position 6 is more reactive than position 2 or 8 (see ref 12).

Experimental Section

^{13}C and ^1H NMR spectra were obtained with a Varian XL-100-15 spectrometer, equipped with a Varian 620/L16K computer. ^1H NMR spectra were also recorded on a JEOL C-60H spectrometer, equipped with a JES-VT-3 variable-temperature controller. When the spectrum was measured in Me_2SO-d_6, internal Me_4Si was used as standard. When the spectrum was measured in liquid ammonia, the sample temperature was ca. −50 °C and NH_3 was used as standard. The spectra were converted to the Me_4Si scale by adding 0.95 ppm. Mass spectra and ^{15}N contents were obtained with a Perkin-Elmer 237 and an Hitachi EPI-G3 and UV spectra with a Beckman Acta CIII.

Preparation of Starting Materials. 2-Aminopurine (**2**, R = H) was purchased from Sigma. 2-Chloropurine (**1a**)[15,16] and 2-fluoropurine (**1b**)[7] were prepared as described in the literature. 2-(Methylthio)purine (**1c**) and 2-chloro-6-methylpurine (**1d**) were prepared by reacting 2-(methylthio)-4,5-diaminopyrimidine[6] and 2-chloro-4,5-diamino-6-methylpyrimidine,[17] respectively, with diethoxymethyl acetate.[15,18]

2-Chloro-6-phenylpurine (1e). 2-Chloro-4,5-diamino-6-phenylpyrimidine[16] (0.35 g) was refluxed in 10 mL of diethoxymethyl acetate[18] for 3 h. The solvent was evaporated in vacuo and the residue recrystallized from ethanol: yield 60%; mp 273–274 °C. Anal. Calcd for $C_{11}H_7ClN_4$: C, 57.28; H, 3.06. Found: C, 57.23; H, 3.06.

2-Chloro-6,8-di-*tert*-butylpurine. 2-Chloropurine (650 mg), 150 mg of silver nitrate, and 5.5 g of pivalic acid were dissolved in water (25 mL).[19] With stirring 15 g of ammonium peroxydisulfate dissolved in 30 mL of water was added at 75 °C in 30 min, followed by an additional 30 min of stirring. The solution was made alkaline with aqueous sodium hydroxide and extracted with chloroform. The extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was recrystallized from hexane or aqueous methanol followed by sublimation at 0.1 mm: yield 60%; mp 179–180 °C. Anal. Calcd for $C_{13}H_{19}ClN_4$: C, 58.53; H, 7.18. Found: C, 58.64; H, 7.17.

2-Iodopurine. The crude product obtained by reaction of 2-chloropurine or 2-(methylthio)purine with potassium amide (reaction time 25 and 70 h, respectively) and subsequent treatment with ammonium sulfate and evaporation of the ammonia was immediately treated with 47% hydriodic acid for 1 h. The solution

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(11) Shaw, E. *J. Org. Chem.* **1962**, *27*, 883.
(12) It is suggested that 2-iodopurine cannot be prepared in the usual way through reaction of 2-chloropurine with hydriodic acid. For a review, see: Lister, J. H. *Chem. Heterocycl. Compd.* **1971**, 143–144.
(13) See for example: Rykowski, A.; van der Plas, H. C. *J. Org. Chem.* **1980**, *45*, 881.
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(19) See for the same procedure: van der Plas, H. C.; Koudijs, A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 159.

was neutralized with aqueous sodium hydroxide and continuously extracted with ethyl acetate. Two recrystallizations from water yielded pure 2-iodopurine (50%), mp 233-236 °C. Anal. Calcd for $C_5H_3IN_4$: C, 24.41; H, 1.23. Found: C, 24.38; H, 1.08. The crude product mentioned above yielded 2-chloropurine (87%) with 36% hydrochloric acid and 2-bromopurine (55%) when 47% hydrobromic acid was used. The identity of the 2-chloro- and 2-bromopurine was established by UV and mass spectrometry.

Preparation of 8-Deuteriopurines. 2-Chloro-8-deuteriopurine and 8-deuterio-2-(methylthio)purine were obtained by refluxing 2-chloropurine and 2-(methylthio)purine, respectively, for 4 h in deuterium oxide.[2,3,20] The position of deuteration was proven by NMR spectroscopy.[21,22] For NMR measurements the deuterium-labeled compounds were diluted to about 50% deuterium content.

Amination Procedure. The amination reactions were carried out in exactly the same manner as described in a previous paper.[2] The amination of the compounds **1a-d** gave known products. However, from **1e** 2-amino-6-phenylpurine (**2**, R = C_6H_5), mp 257-259 °C, was obtained. The structure of this product was proven by ^{13}C and ^1H NMR: ^1H NMR ($CDCl_3/CD_3OD$) δ 7.98 (s, 1 H), 7.49 and 8.36 (m, 5 H); ^{13}C NMR (Me_2SO-d_6) 160.3 (C-2), 155.8 (C-4), 123.7 (C-5), 153.0 (C-6), 140.9 (J = 210 Hz, C-8), C_6H_5, 128.3, 129.1, 130.4, 136.3; UV λ_{max}(CH_3OH) 331 nm. Anal. Calcd for $C_{11}H_9N_5$: C, 62.54; H, 4.30. Found: C, 62.28; H, 4.24.

Acknowledgment. This investigation was carried out under the auspices of the Netherlands Foundations for Chemical Research (SON) and with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO). We are indebted to Dr. C. A. Landheer and Mr. W. P. Combé for the mass spectroscopic data, Mr. A. van Veldhuizen for measuring the NMR spectra, Mr. H. Jongejan for carrying out the microanalyses, and Mr. A. Koudijs for the synthesis of 2-chloro-6,8-di-*tert*-butylpurine.

Registry No. **1a**, 1681-15-8; **1b**, 1598-61-4; **1c**, 33512-51-5; **1d**, 1681-19-2; **1e**, 73747-11-2; **2** (R = H), 452-06-2; **2** (R = C_6H_5), 73747-12-3; **3** (R = C_6H_5), 73758-12-0; **7** (R = H), 31458-49-8; **8** (R = H), 28128-16-7; 2-chloro-4,5-diamino-6-phenylpyrimidine, 19796-43-1; 2-chloro-6,8-di-*tert*-butylpurine, 73747-13-4; 2-Cl-8-*D*-purine, 73747-14-5; 2-SCH_3-8-*D*-purine, 73747-15-6.

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1-Nitro-1-(phenylthio)propene as a New Nitro Olefin Reagent for 3-Methylfuran Annulation and Its Application to the Synthesis of Some Furanoterpenoids

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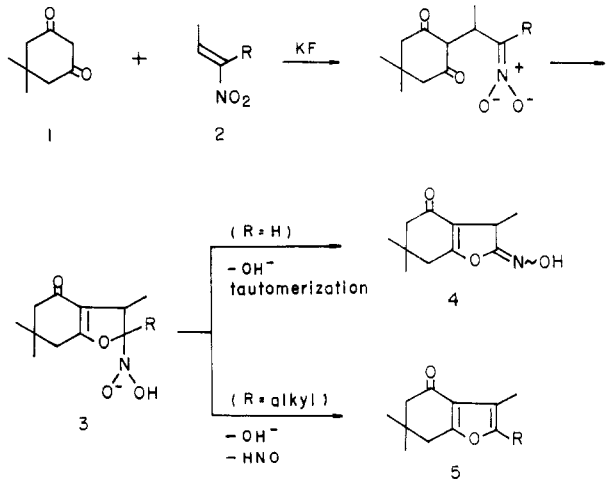
1-Nitro-1-(phenylthio)propene (**9**) was synthesized from (phenylthio)acetic acid (**6**) in five steps. This nitro olefin reacted with dimedone (**1**) with KF catalysis to yield dihydrofurans **10a** and **10b**, both of which were converted to 3-methylfuran **13** on $NaIO_4$ oxidation followed by elimination of benzenesulfenic acid from the resulting sulfoxides in good overall yields. As an application of this reagent, the furanomonoterpenoid evodone (**24**) and the furanosesquiterpenoids ligularone (**25**) and isoligularone (**26**) were synthesized from diones **21** and **34**, respectively. The stereoselective synthesis of dione **34** from the known enone **27** is also described.

Aliphatic, conjugated nitro olefins, readily available from nitroalkanes and aldehydes or ketones[1] or from olefins,[2] are potentially useful synthons, and their synthetic versatility has recently been demonstrated by us[3] and other groups.[2b,4] Our finding[3c] that the KF-catalyzed reaction of 1,3-dicarbonyl compounds and nitro olefins resulted in the direct formation of the 2-alkyl-4-acylfuran system led us to extend this type of reaction to the synthesis of the 3-acyl-4-methylfuran system that has been frequently found in terpenoids. In this paper we describe details on the preparation of the new nitro olefin reagent 1-nitro-1-(phenylthio)propene (**9**) and its reaction with 1,3-diones, leading to the 3-acyl-4-methylfuran system[5] which cul-

Scheme I



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