1, CHCH=CH), 6.06 (d of d, 1, J = 10 and 5 Hz, CHCH=CH), 6.66 (d of d, 1, J = 10 and 2 Hz, CHCH=CH), and 6.85–6.70 (m, 9, ArH).

The filtrate from the above yellow solid and the mother liquors from recrystallization were combined and worked up as usual. The organic product was chromatographed over 400 g of alumina. From the second fraction eluted with benzene–ether (4:1) was obtained 7.6 g (52%) of orange solid, mp 121–128°. On recrystallization from benzene–petroleum ether (bp 60–100°) and four times from benzene–ethanol a portion of **13a**, mp 146.0–147.5°, ir (KBr) 1630, 1610 cm^{-1}, was obtained. However, after the melting point had been taken the remelting point was 131–135°. The NMR of the 147° form in $CDCl_3$ showed the following: δ 1.37 (d, 3, J = 6 Hz, $CHCH_3$), 1.83 (s, 3, SCH_3), 3.32 (q, 1, J = 6 Hz, $CHCH_3$), 6.60 (d, 1, J = 10 Hz, CH=CHCO), and 7.10–8.25 (m, 10, ArH, CH=CHCO). The lower melting samples of **13a** showed two doublets ($CHCH_3$) at δ 1.37 and 1.47, the remaining NMR spectrum being similar to that of the high-melting **13a**. When the lithio derivative of **11a** was treated with **4** at 0° only 45% of **16**[8] was isolated.

Dimethyl[α-methyl-*o*-(9-phenalenonyl)benzyl]sulfonium Tetrafluoroborate (14a). In a reaction of **13a** (820 mg) with CH_3I, etc., entirely similar to that for the conversion of **13** to **14**, except that the reaction with CH_3I was run for 2 hr, there was obtained 850 mg (80%) of **14a**,* mp 218–220° dec, having the expected ir and NMR spectra. All attempts to obtain benzo[*a*]pyrene derivatives by treatment of **14a** with CH_3ONa in MeOH failed to yield appreciable amounts of any pure substance.

Registry No.—**4**, 548-39-0; **5**, 34824-58-3; **6**, 55669-59-5; **7**, 55669-60-8; **8**, 55669-61-9; **9**, 50-32-8; **10**, 55669-62-0; **10** picrate, 55669-63-1; **11**, 19614-11-0; **11a**, 55669-64-2; **12**, 55669-65-3; **12a**, 55669-66-4; **13**, 52288-10-5; **13a** isomer 1, 55669-67-5; **13a** isomer 2, 55721-20-5; **14**, 52288-12-7; **14a**, 55669-69-7; ethylene dibromide, 106-93-4; tris(dimethylamino)phosphine, 1608-26-0; *o*-(methylthiomethyl)phenyllithium, 52288-09-2; phenalenone dimer, 55669-48-2; $AgBF_4$, 14104-20-2; *o*-bromoethylbenzene, 1973-22-4.

References and Notes

(1) This work was supported by grants from the National Science Foundation (GP 12445) and the U.S. Public Health Service (07394).

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Alkaline Hydrolysis of Cationic Di- and Trimethylthiopurines

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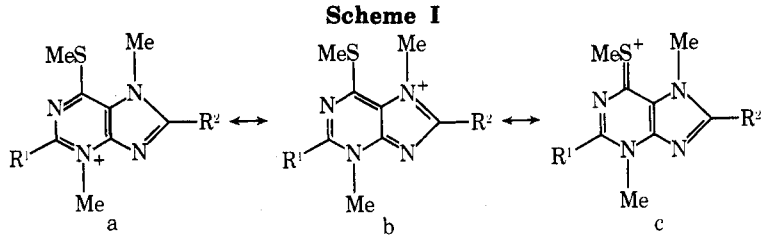
Di- and trimethylthiopurines, which bear two *N*-methyl substituents, exist as resonating cations in which the charge spreads over both rings. Alkali hydrolyzes the methylthio groups in a fixed order, which for 3,7-dimethyl-2,6,8-trimethylthiopurinium cation is 2, 6, 8. Hydrolysis of dimethylthiopurinium cations follows the same order.

In a previous study on di- and trimethylthiopurines it was found that those derivatives, which can form anions, are not attacked by alkali. On the other hand, the *N*-methyl homologs exist above pH 7 only as neutral molecules and thus can be hydrolyzed, the sequence of the reaction being determined by the position of the *N*-alkyl group.[1] It was assumed that the polarized form of the latter creates a positive center which directs the hydroxyl ion to the nearest SMe-substituted carbon atom.

Di- and trimethylthiopurines bearing two *N*-alkyl substituents are resonating cations (Scheme I), their structure being independent of pH in the range 0–14. Consider, for

Scheme I



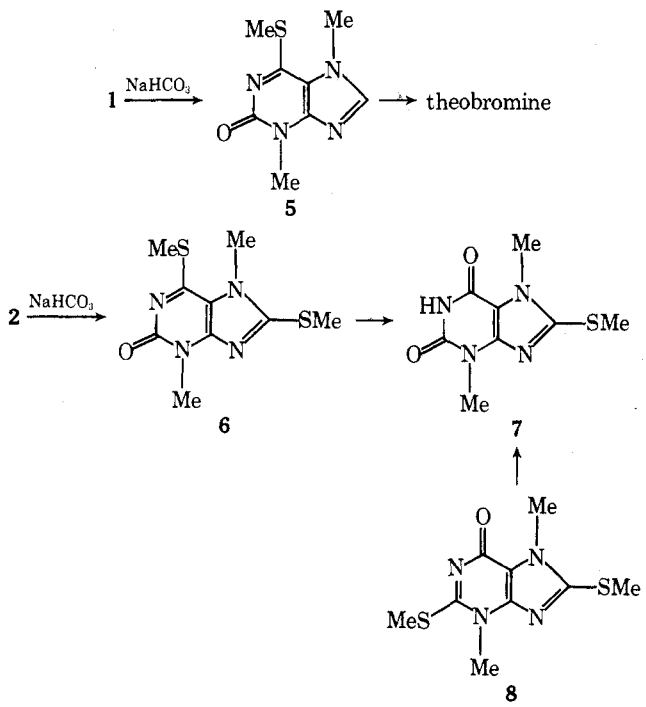
1, R^1 = SMe; R^2 = H
2, R^1 = R^2 = SMe
3, R^1 = H; R^2 = SMe

instance, the three mesomeric forms of 3,7-dimethyl-2,6,8-trimethylthiopurinium cation **2**. Form a would lead to alkaline hydrolysis of the 2-SMe group; in mesomer b, the 8-methylthio substituent should be replaced first; and in c attack should be directed toward position 6. Similarly in 3,7-dimethyl-2,6-dimethylthiopurinium cation **1**, OH^- should attack mesomer a at the 2–3 bond to cause hydrolysis of the 2-SMe group, while in form c nucleophilic substitution should involve position 6. In mesomer b of **1**, OH^- may be directed, inter alia, toward the 6–7 region and thus may again split off the 6-SMe group. This possibility is suggested by the observation that a 7-methyl group in 2,6-dimethylthiopurine directs attack to position 6.[1] Finally, in 3,7-dimethyl-6,8-dimethylthiopurinium cation **3** we may expect attack at position 8 for mesomer b and at C-6 for mesomer c (see Scheme I). However, in this case, predictions about mesomer a are ambiguous because of the remoteness of the positive center from the SMe-substituted positions.

The question arises whether nucleophilic attack will take simultaneously two (or three) different courses or whether a specific resonance form of the cations **1–3** will be preferred in the transition state.

We have observed that in compounds **1** and **2**, position 2 is attacked by alkali to yield **5** and **6**, respectively (Scheme II), indicating preference of mesomer a, containing an aromatic pyrimidine ring. In these two cases, very mild conditions had to be used to avoid further reactions. Thus in 2 *N* NaOH, **5** was converted to theobromine and **6** to the xanthine derivative **7**[2] (Scheme II).

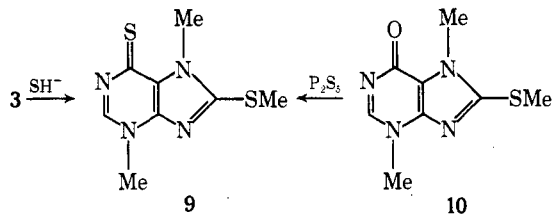
Scheme II



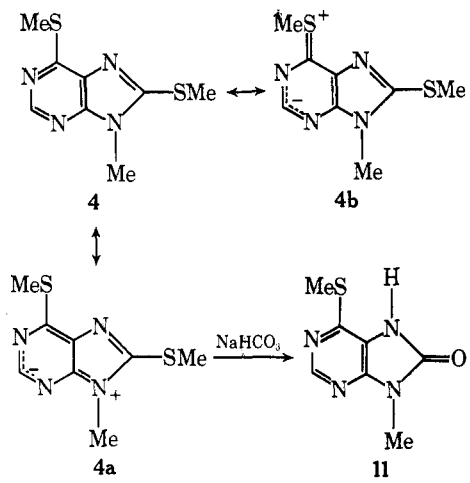
Hydrolysis of **3**, even under very cautious conditions, led to degradation products, presumably by ring opening. We have used instead thiohydrolysis, which converts **3** quantitatively into 3,7-dimethyl-8-methylthio-6-thioxopurine (**9**, Scheme III). Thus in **2**, the methylthio group at position 2 is most susceptible to nucleophilic attack. When this substituent is removed, as in **3**, then the 6-methylthio group exhibits the greater reactivity. Thus the overall sequence of reactivities in **2** is **2**, 6, 8, just as in 3-methyl-2,6,8-trimethylthiopurine.[1]

We have also found that in 9-methyl-6,8-dimethylthiopurine (**4**), the 8-methylthio group undergoes hydrolysis by hot sodium bicarbonate to yield **11**[3] (Scheme IV). This shows that attack at C-8 is definitely possible; the direction of nucleophilic attack is determined by the 9-methyl substituent, i.e. the mesomeric effect of the NMe group (**4a**) is more powerful than that of the SMe substituent (**4b**).

Scheme III



Scheme IV



Identification of Reaction Products. 3,7-Dimethyl-6-methylthio-2-oxopurine (**5**)[4] and 9-methyl-6-methylthio-8-oxopurine (**11**)[3] are known compounds. The structure of **6**[2] can be derived (a) from comparison of its uv spectrum with that of 3-methyl-6,8-dimethylthio-2-oxopurine[1] (Table I); and (b) from the fact that both **6** and its isomer, 3,7-dimethyl-2,8-dimethylthiohypoxanthine (**8**),[2] are hydrolyzed to the same xanthine derivative **7**[2] (Scheme II). Since the structure of **8** has been established before,[5] this conversion confirms the structure assigned to **6**. It should also be noted that introduction of a 2-oxo group shifts the 3-Me signal from 4.22 in **3** to 3.70 ppm in the cation of **6** (Table I), while the 7-Me substituent is shielded only little.

3,7-Dimethyl-8-methylthio-6-thioxopurine (**9**) was identical with the product resulting from thiation of 3,7-dimethyl-8-methylthiohypoxanthine (**10**)[6] (Scheme III).

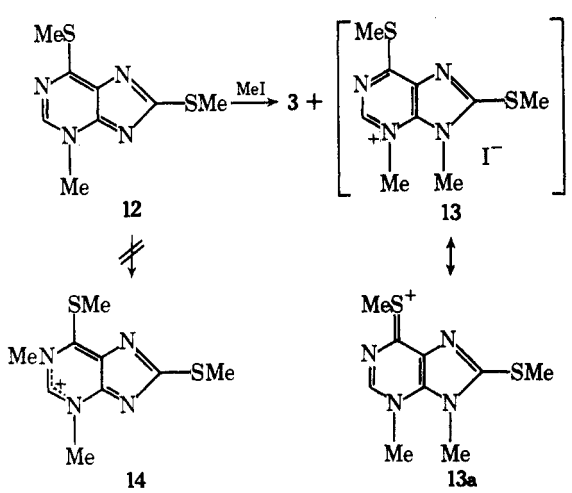
Observations on the Methylation of 3-Methyl-6,8-dimethylthiopurine (12). Methylation of **12** gave a mixture, from which pure **3** was isolated as the main product. The water-insoluble portion contained, inter alia, a small amount of an isomer, identified as the 3,9-dimethyl derivative **13** (Scheme V). The NMR spectrum of either compound showed two NMe and two SMe bands (Table I). Neither in **3** nor in **13** can the new *N*-methyl group be located at N-1 because formation of the "fixed cation" **14**[7] would move the 2-H signal downfield by about 1 ppm[8,9]. Such a large shift of the 2-H band is observed, e.g., for protonation of **9**, $\Delta\delta(N\text{–}C)_{2H}$ = 0.99 ppm (see Table I and Scheme VI, **9d**). However the actual displacement of δ_{2H} for the transition **12** (neutral form) → **3** is only 0.33, and for the conversion **12** (neutral form) → **13**, 0.59 ppm. It should also be noted that protonation of **12** leads to $\Delta\delta$(N–

Table I
Comparison of Spectral Data for Structure Determination of Reaction Products

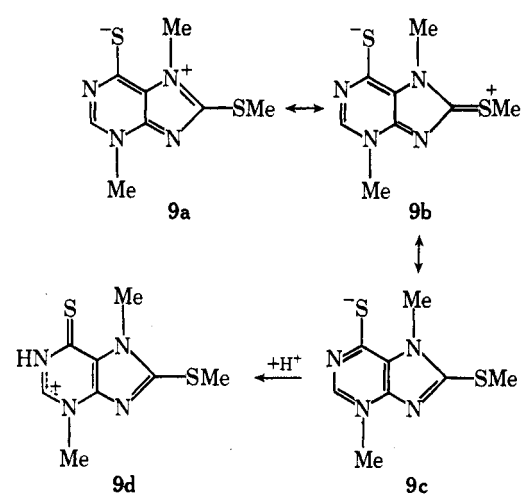
Compd	Molecular form used	λ_{max}, nm	2-H	δ, ppm[a] NMe		SMe		
A. 6,8-Dimethylthiopurines								
3-Methyl- (**12**)	N	259, 340	8.68	4.11		(6) 2.82	(8) 2.74	
	C	259, 285, 340	9.10	4.22		2.89	2.89	
9-Methyl- (**4**)	N		8.81	3.50		(6) 2.85	(8) 2.78	
	C	248, 331	9.02	3.97		2.95	3.12	
3,7-Dimethyl- (**3**)	C	258, 290, 343	9.01	(3) 4.22	(7) 4.02	(6) 2.89	(8) 2.84	
3,9-Dimethyl- (**13**)	C	*b*	9.27	(3) 4.54	(9) 4.24	(6) 2.94	(8) 3.15[c]	
B. 2,6-Dimethylthiopurines								
3,7-Dimethyl- (**1**)	C	332	8.88	(3) 4.27	(7) 4.16	(2) 2.99	(6) 2.99	
3,7-Dimethyl-8-methylthio- (**2**)	C	227, 294, 358		(3) 4.11	(7) 4.08	(2) 2.97	(6) 2.97	(8) 2.97
C. Oxo Derivatives								
3,7-Dimethyl-6-methylthio-2-oxopurine (**5**)	N	272, 319		(3) 3.56	(7) 4.06	2.69		
	C	258, 343		3.75	4.12	2.85		
3-Methyl-6,8-dimethylthio-2-oxopurine	N	342		3.52		(6) 2.65	(8) 2.61	
	C	279, 370		3.78		3.02	2.91	
3,7-Dimethyl-6,8-dimethylthio-2-oxopurine (**6**)	N	340		(3) 3.65	(7) 3.95	(6) 2.87	(8) 2.70	
	C	285, 373		3.70	3.96	2.92	2.88	
9-Methyl-6-methylthio-8-oxopurine (**11**)	N	224, 297.5	8.66	3.52		2.76		
	C	237, 320.5	8.96	3.63		2.93		
3,7-Dimethyl-8-methylthio-6-thioxopurine (**9**)	N	270, 357	8.44	(3) 3.94	(7) 4.33	2.88		
	C	273, 367	9.43	4.11	4.02	2.88		

[a] All measurements in D_2O at 70°. Figures in parentheses indicate the assignment of the signals to a specific methyl group. Assignment of the SMe signals is based on comparison with known compounds, in which unequivocal identification of these bands was possible, and is thus arbitrary. [b] This substance was not isolated in pure form. The NMR spectrum was determined with the impure product, containing small amounts of 3. [c] This assignment is based on the assumption that the neighboring 9-methyl substituent deshields the 8-SMe group as in the cation of 4. However, 13 cannot form a mesomer like **4B** in Scheme VII. On the other hand, 13a (Scheme V) represents a possible resonance form of this cationic purine. Therefore the low-field signal of 3.15 ppm may actually belong to the 6-SMe group.

Scheme V



Scheme VI



$C)_{2H}$[10] = 0.42 (Table I), indicating again formation of a resonating cation, similar to forms a–c in Scheme I, by protonation at N-7. Thus alkylation and protonation of 12 take a similar course.

The above conclusions are supported by measurement of the nuclear Overhauser effect (NOE). Irradiation of 3 with the frequency of its 3-Me band (δ 4.22) causes a 40% increase in the area underneath the 2-H signal, while use of the 7-methyl frequency has no marked effect. For the same reason, only one NMe group (δ 4.54) in 13 can neighbor 2-H (NOE 50%). It is concluded that 3 and 13 can only be the 3,7- and 3,9-dimethyl derivatives. Since the structure of 3 is established by its thiohydrolysis to compound 9, 13 must be the 3,9 isomer. This assignment receives further support from comparison of the δ_{3Me} and δ_{9Me} values of 13 with those of its congeners 12 and 4 in their protonated forms (Table I). The two *N*-methyl signals are shifted downfield in 13 by 0.32 and 0.27 ppm, respectively, in accordance with earlier observations on other 3,9-dimethylated purines.[8,11] On the other hand, in the 3,7-dimethyl derivatives, the presence of a second NMe substituent has very little influence on the position of a given *N*-methyl band (compare, e.g., the δ_{3Me} values of 3 and of the cation of 12).

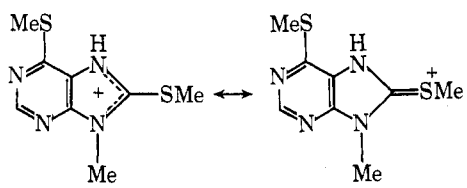
If the second methylation product of 12 were the fixed 1,3-dimethyl cation 14 (Scheme V), we should expect rapid H–D exchange of 2-H upon dissolution in D_2O.[12,13] The ab-

Table II
Alkaline Hydrolysis of Methylthiopurines and Physical Constants of the Products Formed

No.	Compd used	Alkaline hydrolysis[a] Time, min	Temp, °C	Product[b] formed	Mp or dec, °C	Solvent for crystn	Crystal form	R_f[c]	Fluorescence[d]
1	3,7-Dimethyl-2,6-dimethylthiopurinium cation	20	90	5[e]	300	Water	Needles		Violet
2	3,7-Dimethyl-2,6,8-trimethylthiopurinium cation	20	90	6	225–226	Ethanol	Needles	(B) 0.69	Violet
3	3,7-Dimethyl-6,8-dimethylthiopurinium cation[f]	30	0	9	295	Water	Rods	(A) 0.72 (B) 0.73 (C) 0.71	Yellow
4	9-Methyl-6,8-dimethylthiopurine	180	100	11[g]	272	1-Butanol	Rectangular plates	(B) 0.75 (C) 0.75	Light blue

[a] For the method used see Experimental Section. [b] The new compounds 6 and 9 gave satisfactory analyses of C, H, N, S. [c] For solvents A, B, and C see Experimental Section. [d] Under a Mineralight uv lamp. [e] See ref 14. [f] This compound underwent thiohydrolysis to 9. [g] See ref 3.

Scheme VII
Cation of 4



sence of such an effect is satisfactorily explained by the 3,9-dimethyl structure.

The steric interference between the two *N*-methyl groups in **13** presumably is responsible for the marked deshielding of the 8-SMe substituent (see Table I).

The relative proportion of **3** and **13**, resulting from methylation of **12**, shows that electrophilic attack at N-7 is much faster than at N-9, i.e., the combined steric effect of 3-Me and 8-SMe is much stronger than the combined influence of the 6- and 8-SMe substituents.

NMe and SMe Signals in the NMR Spectra (Table I). The NMR spectra of **3** and of the cation of **12** are very similar, indicating protonation of the latter at N-7, as mentioned above. In the cation of **12**, $\Delta\delta$(N–C) of 3-Me = 0.11 and 8-SMe = 0.15 ppm. **4** also attaches a proton at N-7, but this process displaces the 9-Me signal downfield by 0.47 ppm and the 8-SMe band by 0.34 ppm. As shown in Scheme VII, the cation of **4** bears a fixed charge in the imidazole ring. Here the resonance form B may be responsible for the considerable deshielding of the 8-methylthio group; a similar canonical form cannot be formulated for **13**.

In the cation **9d**, the 7-methyl signal is shifted *upfield* by 0.31 ppm. This surprising change may be explained by inspecting Scheme VI. Protonation at N-1 creates a fixed charge in the pyrimidine moiety and thus eliminates any participation of 7-NMe$^+$ (as, e.g., in **9a**) in the polarized forms of the neutral molecule.

Assignment of the 3- and 7-methyl signals in the compounds used was based on NOE, whenever the two signals were sufficiently apart. Furthermore, in **9**, the 3-methyl band was broader and of lower amplitude than the 7-methyl signal, both in the neutral form and in the cation. This effect is due to splitting of the 3-Me signal by the neighboring 2 hydrogen.

Experimental Section

All melting points are uncorrected. Microanalyses were performed by F. Strauss, Oxford, England. For chromatography on Whatman paper No. 1 by the descending method, the following solvents were used: A, 1-butanol–acetic acid–water (12:3:5 v/v); B, 2-propanol–DMF–concentrated ammonia (13:5:2 v/v); C, ethanol–DMF–water (3:1:1 v/v). Spots were located by their fluorescence under a Mineralight uv lamp (λ ~254 nm).

Uv spectra were measured on a Hitachi Perkin-Elmer Model 124 spectrophotometer, and NMR spectra on a Jeol MH-100 instrument, using TSP (sodium 3-trimethylsilylpropionate-*2,2,3,3-d*$_4$ of Merck Sharp and Dohme, Canada) as internal standard. Unless stated otherwise, NMR measurements were carried out in $(CD_3)_2SO$–D_2O (9:1) at 70°.

General Procedure for Hydrolysis of Methylthiopurines. A suspension of the purine was stirred and, if necessary, heated with an aqueous solution of sodium bicarbonate. The precipitate was removed by filtration and purified, as indicated in Table II; yield 80–90%. In the case of hydrolysis of **4**, the product **11** was soluble at pH 8 and was precipitated by addition of acetic acid.

Purines. The following compounds were prepared by known methods: **1**,[1] **2**,[1] **5**,[14] **7**,[2] **8**,[2] **11**,[3] and **12**.[9]

I. Synthesis of 3,7-Dimethyl-6,8-dimethylthiopurinium Cation 3 and Its 3,9-Dimethyl Isomer 13. A suspension of 3-methyl-6,8-dimethylthiopurine (**12**, 0.5 g) in acetonitrile (50 ml) was stirred and refluxed with methyl iodide (3 ml) for 3 hr. The solvent was removed in vacuo and the residue was stirred with water for 15 min.

A. The water-soluble portion was lyophilized and the residue was converted into the picrate of **3**: yellow cubes (ethanol); 0.5 g, mp 177°; λ_{max} (pH 0) 258, 290, 342 nm (log ϵ_{max} 4.33, 4.19, 4.61); R_f (A) 0.68, (C) 0.60.

Anal. Calcd for $C_{15}H_{15}N_7O_7S_2$: C, 38.4; H, 3.2; N, 20.9; S, 13.6. Found: C, 38.4; H, 3.2; N, 20.8; S, 13.4.

B. From the red, water-insoluble portion, a second product **13** was separated by paper chromatography. Its NMR spectrum was determined (Table I), but the amount was insufficient for purification and analysis.

Thiohydrolysis of 3 to 9. **3** (100 mg) was dissolved at 0° in concentrated ammonia that had been saturated with hydrogen sulfide; H_2S gas was bubbled through the solution for another 30 min. The precipitate (**9**) that had formed (50 mg, 80%), was purified by paper chromatography and then recrystallized from water as yellow rods, mp 295° (see Table II).

The chromatogram revealed the presence of small amounts of a second product, λ_{max} (pH 0) 250, 373 nm; (pH 6) 282, 372 nm; R_f (A) 0.30, (B) 0.60; orange fluorescence. The spectral data resemble those of 3-methyl-6,8-dithiopurine.[15] Therefore the by-product of the thiohydrolysis of **3** is most probably 3,7-dimethyl-6,8-dithioxopurine.

Synthesis of 3,7-Dimethyl-8-methylthio-6-thioxopurine (9).

A solution of 3,7-dimethyl-8-methylthiohypoxanthine (10,[6] 100 mg) and phosphorus pentasulfide (200 mg) in pyridine (10 ml) was refluxed for 30 min. The solvent was removed in vacuo and the residue was treated with boiling water for 30 min. The insoluble portion was recrystallized from water. The physical properties of this compound were identical with those of the product resulting from thiohydrolysis of 3 (see Table I).

II. Hydrolysis of 6 to 3,7-dimethyl-8-methylthioxanthine (7). A suspension of 6 in 2 *N* NaOH was stirred and refluxed for 20 min. The clear solution was acidified with acetic acid. The precipitate was identified by comparison with an authentic sample of 7.[2]

9-Methyl-6,8-dimethylthiopurine (4). A. 9-Methyl-8-thiohypoxanthine. An intimate mixture of 5-amino-6-hydroxy-4-methylaminopyrimidine[16] (2 g) and thiourea (6 g) was heated to 250° for 45 min and then to 280° for 15 min. The cake was dissolved in dilute NaOH and the solution was neutralized with acetic acid. Repeated reprecipitation and finally recrystallization from water gave colorless needles (56%): mp >300° dec; λ_{max} (pH 1) 234 sh, 289 nm (log ϵ_{max} 4.30); R_f (B) 0.48, (C) 0.51; violet fluorescence.

Anal. Calcd for $C_6H_6N_4OS$: C, 39.6; H, 3.3; N, 30.8; S, 17.6. Found: C, 40.0; H, 3.1; N, 30.6; S, 17.3.

B. 9-Methyl-6,8-dithiopurine. A mixture of 9-methyl-8-thiohypoxanthine (5 g) and phosphorus pentasulfide (20 g) in pyridine (800 ml) was refluxed for 3.5 hr. Already after the first 20 min a homogeneous solution was obtained. After removal of the solvent in vacuo, the mixture was heated with water (150 ml) for 2.5 hr. The brown, insoluble portion was dissolved in 1 *N* NaOH and the product was precipitated by addition of glacial acetic acid. Final purification was by ammonia–acetic acid: yield 45%; mp >300° dec; λ_{max} (pH 1) 269, 357 nm (log ϵ_{max} 4.47, 4.42); λ_{max} (pH 8) 263, 337 nm (log ϵ_{max} 4.23, 4.39); R_f (B) 0.68, (C) 0.66; yellow fluorescence.

Anal. Calcd for $C_6H_6N_4S_2$: C, 36.4; H, 3.0; N, 28.3; S, 32.3; Found: C, 36.4; H, 3.1; N, 28.1; S, 32.35.

C. 9-Methyl-6,8-dimethylthiopurine (4). A solution of the foregoing dithio derivative (2 g) in 5% NaOH (30 ml) was stirred with methyl iodide (3 ml). After 5 min, a white precipitate formed as colorless needles (ethanol): mp 166°; yield 75%; λ_{max} (pH 0) 248, 331 nm; R_f (B) 0.83, (C) 0.75; sky-blue fluorescence.

Anal. Calcd for $C_8H_{10}N_4S_2$: C, 42.5; H, 4.4; N, 24.8; S, 28.3. Found: C, 42.5; H, 4.5; N, 25.0; S, 28.5.

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Registry No.—**1**, 55800-42-5; **2**, 55800-43-6; **3**, 55800-44-7; **3** picrate, 55800-45-8; **4**, 55800-46-9; **5**, 38759-27-7; **6**, 40848-24-6; **9**, 55800-47-0; **10**, 55800-48-1; **11**, 42930-79-0; **12**, 39008-31-6; **13**, 55800-49-2; 3-methyl-6,8-dimethylthio-2-oxopurine 39013-78-0; phosphorus pentasulfide, 1314-80-3; 9-methyl-8-thiohypoxanthine, 55800-50-5; 5-amino-6-hydroxy-4-methylaminopyrimidine, 45751-74-4; thiourea, 62-56-6; 9-methyl-6,8-dithiopurine, 55800-51-6.

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Solvolysis of *exo*- and *endo*-2-Bicyclo[3.2.0]hept-6-enyl Tosylates and the Corresponding 1,4,4- and 4,4,6-Trimethyl Derivatives. Steric and Conformational Effects on the Ring Enlargements of the Resulting Carbocations[1]

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The kinetics of acetolysis and the products from solvolysis in acetic acid, aqueous acetone, and 4.0 *M* sodium methoxide in methanol of the title compounds were determined. An exo/endo rate ratio, corrected for the observed yield of products formed via a solvent-assisted pathway during acetolysis of the endo tosylate, of 2400 was observed. Solvolysis of the endo tosylate yields unrearranged exo-2-substituted and ring-enlarged products, with product ratios dependent on the nucleophilicity of the solvolysis medium. Solvolysis of the exo tosylate yields only products derivable from the ring-enlarged 7-norbornenyl cation. Acetolysis of the *exo*-1,4,4- and 4,4,6-trimethylbicyclo[3.2.0]hept-6-enyl tosylates has been shown to yield small amounts of the corresponding unrearranged exo 2-acetates. The differences in the rates for ring enlargement of the first formed cations from these solvolyses are explained in terms of steric and conformational effects.

Winstein[3] and Tufariello[4] have elegantly delineated two routes which result in direct formation of the 7-norbornenyl cation (Ib). The π route involves solvolysis of *anti*-7-norbornenyl tosylate (Ia, X = OTs)[3a,b] or treatment of the corresponding alcohol (Ia, X = OH) with fluorosulfonic acid (FSO_3H) at low temperatures.[3c,d] The other, termed the σ route, involves treatment of *endo*-tricyclo[3.2.0.0^{2,7}]hept-3-yl methyl ether (II, X = OMe) with dilute acid[3c] or FSO_3H