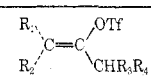
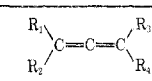
Table I
Preparation and Yields of Allenes *via* Triflates from Ketones

R_1	R_2	R_3	R_4	 Compd	% yield[a]	 Compd	Yield, mg[a] (%)
CH_3	CH_3	H	H	**3**[b]	44	**4**	135 (70)
CH_3	CH_3	D	D	**5**[c]	40	**6**	32 (45)
CD_3	CD_3	H	H	**7**[d]	35	**8**	85 (44)
CH_3CH_2	CH_3	H	H	**9**[e]	44	**10**	580 (85)
CH_3	CH_3	CH_3	H	**11**[f]	41	**12**	320 (76)
CH_3	CH_3	CH_3	CH_3	**13**[g]	48	**14**	130 (79)

[a] Isolated yields. [b] Prepared as previously reported.[5b] [c] Prepared from $(CH_3)_2CDC(O)CD_3$ obtained *via* exchange with D_2O. [d] Prepared from $(CD_3)_2CHC(O)CH_3$ made as previously reported.[7] [e] Prepared from 3-methyl-2-pentanone. [f] Prepared from 2-methyl-3-pentanone. [g] Prepared from 2,4-dimethyl-3-pentanone *via* the silyl enol ether.[5c]

be used directly in the elimination step as all isomers yield the same allene.[6] The procedure may, however, only be used for the preparation of 1,1-di or higher substituted allenes, as elimination from a triflate containing an olefinic hydrogen yields the isomeric acetylene as the major product with only small amounts of allene. Typical examples together with yields are summarized in Table I.

As the data in the table indicate although overall yields are low they represent *isolated yields* of small scale preparations. Moreover, control experiments demonstrated that no rearrangement of the allene to the isomeric acetylene occurs under the reaction conditions employed. The chief

$$(CH_3)_2C{=}C{=}CH_2 \xrightleftharpoons[100^\circ]{\text{quinoline}} (CH_3)_2CHC{\equiv}CH$$

usefulness of this preparation lies in the ready availability of the precursor ketones and the simplicity of the procedure. We believe this procedure to be general, limited only by the availability of starting ketones, and hence provides another manifold into allene chemistry.

Experimental Section

Boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard; infrared spectra were obtained on a Beckman IR-5 spectrophotometer and mass spectra were obtained on an AEI MS-30 spectrometer. Gas–liquid chromatography was performed on a Varian Aerograph Model 90-P unit using a 15 ft × 0.375 in. column with 15% SF-96 on Chromosorb W.

General Procedure for the Preparation of Vinyl Triflates. Vinyl triflates were prepared from the appropriate ketones and triflic anhydride on a 10–50 mmol scale using pyridine as base and anhydrous CCl_4 as solvent by standard procedures.[5] Triflates **3, 5,** and **7** have been previously prepared[7] as have **11** and **13**.[8] Triflate **9** was prepared from commercial 3-methyl-2-pentanone: bp 54–55° (13 mm); ir (thin film) 2967 (CH), 1692 (C=C), 1412 (S=O), and 1211 cm^{-1} (CF); nmr (CCl_4) δ 2.06 (q, 2 H, J = 7.0 Hz, $-CH_2-$), 1.98 (br s, 3 H, α-CH_3), 1.70 (br s, 3 H, β-CH_3), 1.02 (t, 3 H, J = 7.0 Hz, CH_3CH_2).

General Procedure for the Preparation of Allenes. To a 10-ml round-bottom flask, equipped with a magnetic stirrer and containing 3–6 ml of dry freshly distilled quinoline, was added 1–10 mmol of the appropriate vinyl triflate. The flask was connected to a bulb-to-bulb distillation apparatus and a receiver flask. The reaction flask and cross arm were heated to 100° for 2–6 days and the product collected with the receiver cooled to −78°. Yields of *isolated* products are reported in the table. The products so obtained usually contained small amounts of unreacted triflate and ketone as impurities. Final purification was achieved by means of preparative glc. For **4:** nmr (CCl_4) δ 4.43 (sept, 2 H, J = 3.2 Hz, $C{=}CH_2$), 1.64 [t, J = 3.2 Hz, $(CH_3)_2C{=}$] [lit.[9] δ 4.43, J = 3.0 Hz, and δ 1.65, J = 3.0 Hz]; ir (thin film) 1960 (C=C=C) and 847 cm^{-1}; mass spectrum 68 (M^+, 100), 67 (54), 65 (18), 53 (52), 51 (21), 50 (20), 41 (40), 40 (22), 39 (40). For **6:** ir (CCl_4) 2941 (CH), 2288 (CD), and 1949 cm^{-1} (C=C=C); mass spectrum 70 (M^+, 61). For **8:** mass spectrum 74 (M^+, 13). For **10:** nmr (CCl_4) δ 4.50 (sext., 2 H, J = 3.0 Hz, $C{=}CH_2$), 1.90 (m, 2 H, $-CH_2-$), 1.65 (t, 3 H, J = 3.0 Hz, $CH_3C{=}C$), 0.99 (t, 3 H, J = 7.0 Hz, CH_3CH_2) [lit.[9] nmr (CCl_4) δ 4.55 (m, 2 H, $C{=}CH_2$)]; ir (thin film) 1961 cm^{-1} (C=C=C) [lit.[10] 1960 cm^{-1}]. For **12:** nmr (CCl_4) δ 4.88 (m 1 H, C=CH), 1.63 (m 6 H, $(CH_3)_2C$), 1.58 (m 3 H, $CH_3CH{=}$); ir 1965 cm^{-1} (C=C=C) [lit.[9] nmr δ 4.80 (m 1 H), 1.63 (m, 6 H), 1.57 (m 3 H); ir 1959 cm^{-1}]. For **14:** nmr (CCl_4) δ 1.75 (s, 12 H, CH_3); ir (CCl_4) 2940, 1629, 1447, 1379, 1186, and 1074 cm^{-1}; mass spectrum 96 (M^+, 87), 81 (100), 79 (38), 57 (19), 56 (25), 55 (15), 54 (50), 48 (10), 42 (75).

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Registry No.—**3,** 28143-80-8; **4,** 598-25-4; **5,** 53730-65-7; **6,** 53730-66-8; **7,** 52847-16-2; **8,** 53730-67-9; **9,** 53730-68-0; **10,** 7417-48-3; **11,** 52149-34-5; **12,** 3043-33-2; **13,** 52149-35-6; **14,** 1000-87-9; 3-methyl-2-pentanone, 565-61-7.

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Synthesis and Reactions of 6-Methylsulfonyl-9-β-D-ribofuranosylpurine

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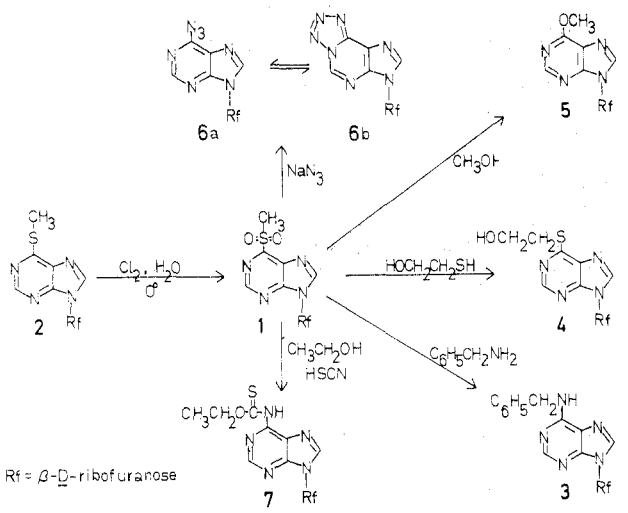
Although sulfones are generally quite stable, methyl sulfonyl substituents at low electron density positions of a pyrimidine or purine can be excellent leaving groups, and this fact has been employed in the past in nucleoside synthesis[1-4]. Early attempts to prepare 6-methylsulfonyl-9-β-D-ribofuranosylpurine (1) gave only its hydrolysis product inosine;[3] a similar sulfone was recently proposed as an intermediate but no attempt to characterize it was described.[1] We wish to report the isolation of pure 1 in good yield and

Scheme I



some of the physical and chemical properties of this compound.

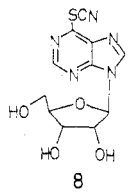
Chlorine oxidation of 6-methylthio-9-β-D-ribofuranosylpurine (**2**) in aqueous ethanol at 0° gives, after neutralization with $NaHCO_3$ and crystallization, the sulfone nucleoside **1** in 50% yield. This compound is stable as a solid and in neutral solution, but decomposes slowly in acidic media to form inosine. Decomposition in base, on the other hand, occurs with some cleavage of the glycosidic bond to give 6-methylsulfonylpurine, which can subsequently hydrolyze to hypoxanthine. In various pH 8 buffer systems at 37°, **1** decomposes slowly (about 20% decomposition after 2 hr) to a mixture of inosine, hypoxanthine, and 6-methylsulfonylpurine.

Compound **1** reacts readily with amines, mercaptans, and, to a lesser extent, alcohols, to give 6-substituted purine nucleosides by displacement of methylsulfinate (see Scheme I). Thus, a slight excess of benzylamine in methanol at 0° gives N^6-benzyladenosine (**3**)[5] in 25% yield after chromatographic separation. Mercaptoethanol in an aqueous solution of **1** reacts in a short time at 25° to give 6-(2-hydroxyethylmercapto)-9-β-D-ribofuranosylpurine (**4**). Methanolic ammonia at 0° converts *2* readily into 6-methoxy-9-β-D-ribofuranosylpurine (**5**)[6] after purification by column chromatography; this compound can also be formed in a solution of **1** in methanol after a few weeks at 25°. More basic nucleophiles tend to give hypoxanthine (see above) rather than direct displacement of methylsulfinate. Both ammonia and cyanide in water give only hypoxanthine in reactions with **1**.

The reaction of **1** with sodium azide in methanol at 25° proceeds readily to give high yields of 6-azido-9-β-D-ribofuranosylpurine (**6**). This nucleoside, which exists predominantly in the tetrazole form **6b**,[6,7] has been previously prepared by another approach.[6] It cannot be prepared by azide displacement on a more commonly used intermediate, 6-chloro-9-β-D-ribofuranosylpurine, presumably because compound **6** is unstable at the temperatures required to effect displacement of chloride.

Compound **6** readily undergoes photodecomposition. Irradiation of a 2 m*M* aqueous solution of **6** at wavelengths higher than 280 nm[8] gives after 3 hr a compound with the UV and TLC properties of adenosine. Similar tetrazoles are known to undergo photoreactions, giving intermediate nitrenes derived from the azide tautomer of the ground-state molecule.[9]

We initially prepared **1** as a potential intermediate in the synthesis of 6-isothiocyanato-9-β-D-ribofuranosylpurine, but this approach, as with all others we attempted, failed to give any isolated isothiocyanate. Refluxing **1** in an ethanolic solution of KSCN yields a mixture consisting in part of inosine, *O*-ethyl 9-β-D-ribofuranosylpurine-6-thiocarbamate (**7**), and compound **7**'s decomposition product adenosine, but *no reaction* occurs between **1** and KSCN or AgSCN in aprotic DMSO. Compound **7** is more easily prepared by reaction of **1** in ethanolic HSCN; again, *no reaction* occurs between **1** and HSCN in aprotic solvents. Attempts to obtain the isothiocyanate by rearrangement of 6-thiocyanato-9-β-D-ribofuranosylpurine (**8**)[10] also failed. Compound **8** when refluxed in an ethanolic solution of



8

KSCN gives only the thiocarbamate **7**; in other solvents, no reaction is observed. Reaction of KSCN with 6-chloro-9-β-D-ribofuranosylpurine gives, in aprotic solvent, compound **8**, and in ethanol (via **8**), thiocarbamate **7**.

Not only is compound **1** itself a useful synthetic intermediate, but the mild conditions of its formation and subsequent reactions make it readily applicable to nucleotide work. Phosphate derivatives of compound **2** can be oxidized to the corresponding 6-methylsulfonylpurine nucleotides and these further reacted to yield other nucleotides, without hydrolytic decomposition.[11] The stability of nucleotide derivatives of **1** in neutral solution plus their high reactivities with the common nucleophilic groups on enzymes suggest their potential use as affinity labels. The photolability of nucleotides of **6** at wavelengths above 280 nm indicates a potential use of these compounds as photoaffinity labels. We are currently exploring these possibilities in our laboratory.

Experimental

Materials and Methods. 6-Chloro-, 6-thio-, and 6-methylthio-9-β-D-ribofuranosylpurines were purchased from Papierwerke Waldhof-Aschaffenburg (Mannheim, Germany). Thin layer chromatographic R_f values were determined on DC-Microcards SI F, purchased from Riedel-De Haen Aktiengesellschaft (Seelze-Hannover, Germany). Elemental analyses were performed by Mikroanalytisches Labor Beller, Göttingen (Germany). The NMR spectra were obtained on a Bruker-Physics HFX 60 spectrometer, and the UV spectra on a CARY 16.

Synthesis of 6-Methylsulfonyl-9-β-D-ribofuranosylpurine (1). A solution of 390 mg (1.3 mmol) of 6-methylthio-9-β-D-ribofuranosylpurine in 20 ml of 90% ethanol was cooled to 0° and chlorine gas was bubbled slowly through this solution until the reaction was complete, as indicated by rough UV analysis of the reaction mixture and by the yellow tint of excess chlorine, about 10 min. At this point, nitrogen gas was bubbled through for a few minutes; then 550 mg (0.65 mmol) of $NaHCO_3$ was added. After 10–15 min of stirring at 0° with continued nitrogen bubbling, the reaction mixture was filtered to remove inorganic salts and cooled overnight to give 179 mg (0.54 mmol, 42%) of needles, melting range 97–100°. A second crop of crystals was obtained from the concentrated filtrate, giving a total yield of 50%. λ_{max}, nm ($\epsilon \times 10^{-3}$): pH 1, 278 (8.2); pH 7, 278 (8.7); pH 12, unstable. PMR (D_2O): δ 9.31 (s, 1 H), 9.16 (s, 1 H), 6.42 (d, J = 5 Hz, 1 H), 4.95 (q, J = 5 Hz, 1 H), 4.30–4.68 (m, 2 H), 4.02 (d, J = 3 Hz, 2 H), 3.62 (s, 3 H). TLC, silica gel, 9:1 EtAc–EtOH, R_f 0.18.

Anal. Calcd for $C_{11}H_{14}N_4SO_6$: C, 40.00; H, 4.24; N, 16.96; S, 9.70. Found: C, 39.83; H, 4.69; N, 17.00; S, 9.67.

Higher yields of the sulfone, with a purity sufficient for synthetic purposes, can be obtained by the following simple procedure. A solution of 1.013 g (3.37 mmol) of 6-methylthio-9-β-D-ribofuranosylpurine in 40 ml of 85% ethanol was cooled to −10° in a NaCl–ice water bath. Chlorine gas was slowly bubbled through as before, with the reaction going to completion after 15 min. Nitro-

gen gas was bubbled through for 5 min, during which time the sulfone dropped out of the concentrated solution as clusters of small needles. The reaction mixture was allowed to stand an additional 3–5 min at −10°, then filtered. The filtrate was washed with 10 ml of cold 85% ethanol and dried, giving 838 mg (2.54 mmol, 75% yield) of crystals melting in the range 90–96°, but chromatographically pure and giving an R_f value and UV spectrum identical with those of the material obtained by the first procedure.

Synthesis of 6-(2-Hydroxyethylmercapto)9-β-D-ribofuranosylpurine (4). To a solution of 125 mg (0.38 mmol) of sulfone 1 in 25 ml of water at 25° was added 0.1 ml of mercaptoethanol, and the solution was stirred for 4 hr. The solvent was removed under vacuum and the oil was pumped on for 0.5 hr to remove mercaptoethanol. Absolute ethanol was added and evaporated off, and the oil obtained was dissolved with warming in absolute ethanol and refrigerated. Crystals began to appear after 1 day and were collected after 4 days to give 55 mg (0.168 mmol, 44% yield) of 6-(2-hydroxyethylmercapto)-9-β-D-ribofuranosylpurine (4) as hydroscopic crystals, melting range 105–115°. λ_{max}, nm ($\epsilon \times 10^{-3}$): pH 7, 287 (16.9), 290 (16.9). PMR (DMSO-d_6): δ 8.89 (s, 1 H), 8.86 (s, 1 H), 6.11 (d, J = 5 Hz, 1 H), 5.60 (d, J = 5 Hz, 1 H), 5.00–5.35 (m, 3 H), 4.68 (q, J = 5 Hz, 1 H), 3.92–4.41 (m, 2 H), 3.47–3.84 (m, 6 H). TLC, silica gel, 9:1 EtAc–EtOH, R_f 0.18.

Anal. Calcd for $C_{12}H_{16}N_4SO_5 \cdot \frac{1}{4}H_2O$: C, 43.37; H, 4.97; N, 16.87; S, 9.64. Found: C, 43.33; H, 5.09; N, 16.67; S, 9.44.

Synthesis of 6-Azido-9-β-D-ribofuranosylpurine (6). To 700 mg (2.12 mmol) of sulfone 1 in 100 ml of anhydrous methanol was added 191 mg (2.94 mmol) of sodium azide, and the solution was stirred for 2 hr at 25°, then cooled overnight at 5°. The white amorphous solid was collected and the filtrate reduced in volume and cooled to give more solid material with the correct UV spectrum, a total of 559 mg (1.91 mmol, 90% yield). The product had a UV spectrum identical with that reported for 6-azido-9-β-D-ribofuranosylpurine (6) prepared by another route.[6] Its melting range is 212–214° (lit. 222°). PMR (DMSO-d_6): δ 10.15 (s, 1 H), 8.95 (s, 1 H), 6.18 (d, J = 5 Hz, 1 H), 5.64 (d, J = 6 Hz, 1 H), 5.00–5.37 (m, 2 H), 4.61 (q, J = 5 Hz, 1 H), 3.92–4.40 (m, 2 H), 3.50–3.83 (m, 2 H). TLC, silica gel, 9:1 EtAc–EtOH, R_f 0.25.

Synthesis of *O*-Ethyl 9-β-D-Ribofuranosylpurine-6-thiocarbamate (7). To 763 mg (2.67 mmol) of 6-chloro-9-β-D-ribofuranosylpurine in 30 ml of absolute ethanol was added 895 mg (9.2 mmol) of potassium thiocyanate, and the solution was refluxed 25 hr. The solvent was removed under vacuum and the crude mixture chromatographed on silica gel using an 8–12% linear gradient of methanol in chloroform. The product fractions were collected and the residue after removal of solvents was crystallized from hot ethanol, giving 207 mg (0.52 mmol, 19% yield) of the thiocarbamate, with ¾ ethanols of crystallization, melting range 103–106°. λ_{max}, nm ($\epsilon \times 10^{-3}$): pH 1, 305 (22.8); pH 7, 297 (20.1). PMR after exchange with D_2O and removal of ethanol of crystallization under vacuum): δ 11.94 (s, 1 H), 8.92 (s, 1 H), 8.88 (s, 1 H), 6.13 (d, J = 5 Hz, 1 H), 3.87–4.83 (m, 5 H), 3.53–3.86 (m, 2 H), 1.27 (6, J = 7 Hz, 3 H). TLC, silica gel, 9:1 EtAc–EtOH, R_f 0.32.

Anal. Calcd for $C_{13}H_{17}N_5O_5S \cdot \frac{3}{4}\ CH_3CH_2OH$: C, 44.70; H, 5.51; N, 17.98; S, 8.22. Found: C, 44.70; H, 5.46; N, 18.15; S, 8.24.

Reaction of 6-Methylsulfonyl-9-β-D-ribofuranosylpurine (1) with Thiocyanic Acid Generated in Situ. To a solution of 17.5 mg (0.053 mmol) of sulfone (1) in 20 ml of ethanol were added 0.25 ml of a 1.0 *N* HCl solution and 13 mg (0.135 mmol) of potassium thiocyanate. The mixture was stirred at 25° for 9 hr, at which point a UV spectrum showed only the desired product. Thick layer chromatographic separation (silica gel, 3:1 EtAc–EtOH) gave one main nucleoside product, which was eluted and shown to be *O*-ethyl 9-β-D-ribofuranosylpurine-6-thiocarbamate (7) (0.14 mmol, 27% yield) by its TLC and UV properties.

Acknowledgment. We thank B. Seeger for the NMR spectra. Partial support for this project by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We also wish to thank Professor D. Shugar for helpful discussions.

Registry No.—1, 53821-41-3; 2, 342-69-8; 4, 53821-42-4; 6, 53821-43-5; 7, 53821-44-6; mercaptoethanol, 60-24-2; 6-chloro-9-β-D-ribofuranosylpurine, 5399-87-1; potassium thiocyanate, 333-20-0.

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Chlorination of 6-Methyl-1,6-naphthyridin-5(6*H*)-one

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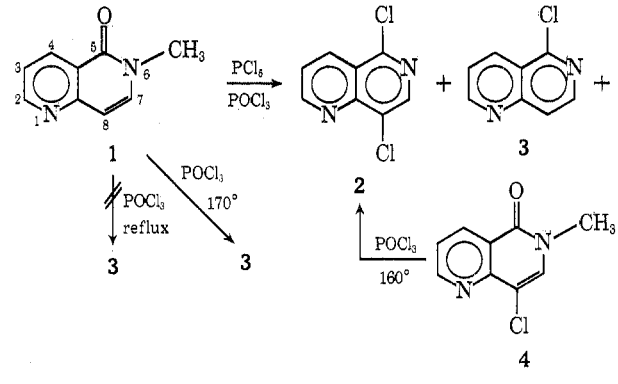
The reaction of 2-methyl-1-isoquinolone using $POCl_3$ and PCl_5 has been reported to yield 1-chloroisoquinoline.[1,2] An investigation by Haworth and Robinson[3] of this reaction found not only the major product but some 1,4-dichloroisoquinoline.

We subjected 6-methyl-1,6-naphthyridin-5(6*H*)-one (1) to the same reaction conditions as above and isolated 5,8-dichloro- (2) and 5-chloro-1,6-naphthyridine (3), 8-chloro-6-methyl-1,6-naphthyridin-5(6*H*)-one (4), and some starting material.



The structure of the major component (2) was established by spectroscopic measurement and chemical derivation. The mass spectrum indicated that the molecule contains two chlorine atoms. It was found by inspection of the nmr spectrum that the 2, 3, and 4 positions did not contain a chloro substituent since its line pattern was similar to that of the starting material and the parent ring compound.[4] The singlet absorption peak at 8.60 was assigned to the 7 proton on the following basis: (a) no cross ring coupling ($J_{4,8}$) was observed, and (b) the chemical shift of analogous protons in the isoquinoline series, 3-H (8.28) of 1,4-dichloroisoquinoline[5] and 4-H (7.80) of 1,3-dichloroisoquinoline.[6]

Since it is known that α and γ halogen substituents in quinoline[7] and isoquinoline[8] undergo nucleophilic displacement, 5,8-dichloro-1,6-naphthyridine was refluxed in a large excess of sodium methoxide in methanol for 4 hr. The mass spectrum of the product showed that the molecule now contains one methoxyl and one chloro group. The nmr spectral line pattern of the 2, 3, and 4 positions was unchanged from the starting material. The singlet proton at