(KBr) 1690 cm^{-1}; λ_{max} (MeOH) 303 nm (ϵ 11 000) and 256 (16 000); *m/e* 319.09549 (calcd for $C_{18}H_{13}N_3O_3$, 319.09568).

Anal. Calcd: C, 67.30; H, 4.06; N, 13.08. Found: C, 67.68; H, 3.99; N, 12.91.

Methanolysis of **1b** ($NaOCH_3$, MeOH) afforded benzalaniline and methyl 4-nitropyrrole-2-carboxylate.

Repetition of the above experiment with *p*-methoxybenzalaniline afforded **1a** (Ar = $CH_3OC_6H_4$): mp 143–145 °C; NMR δ 3.72 (3 H, s), 6.41 (1 H, dd, J = 5, 3 Hz), 6.63 (1 H, d, J = 5 Hz), and 6.80–7.93 (10 H, m); ν_{max} ($CHCl_3$) 1705 cm^{-1}; λ_{max} (MeOH) 230 nm (ϵ 1300) and 282 (12 000).

Anal. Calcd: C, 74.97; H, 5.31; N, 9.21. Found: C, 75.02; H, 5.24; N, 9.15.

Dimer of Pyrrole-2-carbonyl Chloride (3a). To a stirred solution of 0.21 g (1.6 mmol) of the above acid chloride in 2.0 ml of chloroform was added, with stirring, 0.5 ml of triethylamine. The resulting dark green solution was stirred for 30 min, the solvent evaporated, and the residue triturated with 10 ml of water. Recrystallization from a mixture of Me_2SoMe_2SO and CCl_4 (1:1 v/v) afforded 11 mg (4.7%) of the dimer **3a** (sublimes without melting above 250 °C): NMR (Me_2SO-d_6) δ 6.63 (2 H, dd, J = 4.2, 4.0 Hz), 7.43 (2 H, dd, J = 4.2, 2.0 Hz), and 7.85 (2 H, dd, J = 4.0, 2.0 Hz); ir ν_{max} (KBr) 1700, 1555, and 1460 cm^{-1}; uv λ_{max} (MeOH) 315 nm (ϵ 13 000), 303 (12 500), 273 (14 000), and 235 (22 000); mass spectrum *m/e* (rel intensity) 186 (32) and 86 (100); found, *m/e* 186.04291 (calcd for $C_{10}H_6N_2O_2$, 186.04293.)

Anal. Calcd: C, 64.52; H, 3.26; N, 15.05. Found: C, 63.19; H, 3.02; N, 14.82.

In a similar manner was prepared the dimer of 4-nitropyrrole-2-carbonyl chloride (**3b**) in 85% yield as light pink needles (from Me_2SO): mp > 340 °C; NMR (Me_2SO-d_6) δ 8.03 (2 H, d, J = 2 Hz) and 8.89 (2 H, d, J = 2 Hz); ν_{max} (KBr) 1735, 1560, and 1510 cm^{-1}; λ_{max} ($CHCl_3$) 288 nm (ϵ 28 300) and 266 (34 500); *m/e* 276.01297 (calcd for $C_{10}H_4N_4O_6$, 276.01308).

Anal. Calcd: C, 43.48; H, 1.46; N, 20.29. Found: C, 42.91; H, 1.78; N, 18.97.

Repetition of the above with indole-2-carbonyl chloride yielded the dimer, **2**, as an extremely insoluble orange solid: mp > 340 °C; ν_{max} (KBr) 1695 and 1560 cm^{-1}; λ_{max} ($CHCl_3$) 380 nm (ϵ 20 000), 263 (22 000), 308 (18 000), and 276 (35 000); *m/e* 286.07531 (calcd for $C_{18}H_{10}N_2O_2$, 286.07422).

Pyrrole-2-carbonyl Chloride and *N,N*-Dimethylisobutenylamine. Adduct 4. To a stirred solution of 0.43 g (3.2 mmol) of the above acid chloride in 2 ml of dry acetone was added a solution of 0.66 g (6.6 mmol) of the above enamine in 2 ml of acetone. The resulting solution was stirred for 30 min and solvent was evaporated, and the oily residue was subjected to thick layer chromatography (silica gel PF-254, 1.5 mm thick, 6% methanol in chloroform) to afford three fractions. (a) Pyrrole dimer **3a:** 11 mg. (b) Adduct **4:** 330 mg (58%), mp 79–81 °C (carbon tetrachloride); NMR (CCl_4) δ 0.62 (3 H, d, J = 7 Hz), 1.08 (3 H, d, J = 7 Hz), 2.25 (1 H, m), 2.95 (3 H, s), 5.08 (1 H, d, J = 1.5 Hz), 6.27 (1 H, m), 6.39 (1 H, m), and 6.76 (1 H, m); ν_{max} ($CHCl_3$) 1690 cm^{-1}; λ_{max} (MeOH) 278 nm (ϵ 8900), 242 (5500), and 235 (5800); *m/e* 178.11061 (calcd for $C_{10}H_{14}N_2O$, 178.11061).

Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 71.01; H, 8.36; N, 16.57. Found: C, 70.92; H, 8.21; N, 16.51.

(c) *N,N*-Dimethylpyrrole-2-carboxamide (**5**): 32 mg (8%) (sublimed at 55 °C 0.08 mm); mp 96–98 °C (lit.[7] 100–101 °C); NMR δ 3.18 (6 H, s), 6.13 (1 H, m), 6.58 (1 H, m), 6.93 (1 H, m), and 10.7 (1 H, bs); ν_{max} ($CHCl_3$)3450 and 1685 cm^{-1}; λ_{max} (MeOH) 263 nm (ϵ 12 000); *m/e* 138.07919 (calcd for $C_7H_{10}N_2$, 138.07931).

Repetition of the above experiment using 1 equiv each of the enamine and triethylamine afforded a 55% yield of the dimer (**3a**) and 18% yield of the dimethylamide (**5**).

If this experiment is repeated using the pyrrolidine enamine of cyclohexanone one obtains a 32% yield of the dimer and 24% yield of pyrrolidinopyrrole-2-carboxamide: mp 109–112 °C; δ NMR 1.97 (4 H, bs), 3.72 (4 H, bs), 6.28 (1 H, m), 6.62 (1 H, m), 6.97 (1 H, m), 6.97 (1 H, m), and 10.25 (1 H, bs); ν_{max} ($CHCl_3$) 3450 and 1590 cm^{-1}; λ_{max} (MeOH) 266 nm (ϵ 15 500) and 227 (7000).

Indole-2-carbonyl Chloride and *N,N*-Dimethylisobutenylamine. Adduct 6. To a stirred solution of 0.427 g (2.39 mmol) of the acid chloride in 2 ml of dry acetone was added a solution of 0.506 g (5.06 mmol) of *N,N*-dimethylisobutenylamine in 2 ml of acetone. The resulting solution was stirred for 4 h and evaporated, and the residue triturated with 25 ml of chloroform to afford 64 mg of the indole dimer (**2**) as an insoluble orange solid. The soluble material was subjected to thick layer chromatography (silica gel G, 6% MeOH in chloroform) to afford two components. (a) Adduct **6:** 399 mg, mp 139–131.5 °C (after sublimation); NMR ($CDCl_3$) δ 0.80 (3 H, d, J = 8 Hz), 0.70 (3 H, d, J = 8 Hz), 2.6 (1 H, m), 3.14 (3 H, s), 3.38 (1 H, d, J = 1.5 Hz), and 6.8–7.8 (5 H, m); ν_{max} ($CHCl_3$) 1695 cm^{-1}; λ_{max} (MeOH) 312 nm (ϵ 9700), 298 (13 000), 290 (11 500), and 236 (11 700); *m/e* 228.1262 (calcd for $C_{14}H_{16}N_2O$, 228.1262).

Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 73.65; H, 7.08; N, 12.28. Found: C, 73.64; H, 7.04; N, 12.21.

(b) *N,N*-Dimethylindole-2-carboxamide (**7**): 12 mg (3% yield); mp 183–185 °C (lit.[8] 180–182 °C); NMR (acetone-d_6) δ 3.32 (6 H, s), 6.80–7.70 (5 H, m), and 10.5 (1 H, bs); ν_{max} ($CHCl_3$) 3450 and 1610 cm^{-1}; λ_{max} (MeOH) 293 nm (ϵ 17 500); *m/e* 188.09480 (calcd for $C_{11}H_{12}N_2O$, 188.09496).

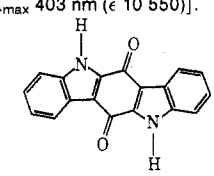
Repetition of the above experiment using 1 equiv each of the enamine and triethylamine afforded a 5% yield of the dimer (**2**) and a 9% yield of the amide (**7**).

If this experiment is repeated using the pyrrolidine enamine of cyclohexanone one obtains a 13% yield of the dimer (**2**) and a 15% yield of pyrrolidinopyrrole-2-carboxamide: mp 193–197 °C; NMR (Me_2SO-d_6) δ 1.98 (4 H, m), 3.67 (2 H, m), 3.87 (2 H, m), 7.0–7.8 (5 H, m), and 11.6 (1 H, bs); ν_{max} (KBr) 3240 and 1590 cm^{-1}; λ_{max} (MeOH) 293 nm (ϵ 17 000) and 225 (16 500).

Registry No.—**1a** (Ar = C_6H_5), 58881-38-2; **1a** (Ar = $CH_3OC_6H_4$), 58881-39-3; **1b** (Ar = C_6H_5), 58881-40-6; **2**, 58881-41-7; **3a**, 484-73-1; **3b**, 58881-42-8; **4**, 58881-43-9; **5**, 7126-47-8; **6**, 58881-44-0; **7**, 7511-14-0; pyrrole-2-carbonyl chloride, 5427-82-7; pyrrole-2-carboxylic acid, 634-97-9; indole-2-carbonyl chloride, 58881-45-1; 4-nitropyrrole-2-carbonyl chloride, 28494-49-7; benzalaniline, 538-51-2; *p*-methoxybenzalaniline, 836-41-9; *N,N*-dimethylisobutenylamine, 692-31-9; pyrrolidine enamine of cyclohexanone, 1125-99-1; pyrrolidinopyrrole-2-carboxamide, 58904-52-2.

References and Notes

(1) J. D. Roberts and C. M. Sharts, *Org. React.*, **12** (1962).
(2) J. C. Martin et al., *J. Org. Chem.*, **36**, 2211 (1971).
(3) P. W. Hickmott, *Chem. Ind. (London)*, 731 (1974), and references cited therein.
(4) M. Nicolas et al., *Bull. Soc. Chim. Fr.*, **5**, 44 (1938).
(5) W. L. Kermack, W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, **119**, 1602 (1921).
(6) Where not quoted, the spectral properties of compounds were those expected for the structures given.
(7) C. W. N. Cumper and J. W. M. Wood, *J. Chem. Soc. B*, 1811 (1971).
(8) W. Chindler, *Helv. Chim. Acta*, **40**, 2156 (1957).
(9) This type of tertiary amine cleavage reaction has been documented: J. D. Hobson and J. G. McCluskey, *J. Chem. Soc. C*, 2015 (1967).
(10) A somewhat similar indole dimer has been prepared: J. Szmuskovicz, *J. Org. Chem.*, **28**, 2930 (1963). This structure for **2** was ruled out by comparison of uv data [**8**, λ_{max} 403 nm (ϵ 10 550)].



8

(11) Support of this work by NIH is acknowledged.

---

^{15}N–^{13}C Coupling for Determination of the Site of N-Alkylation of Nitrogen Heterocycles. *linear*-Benzopurines

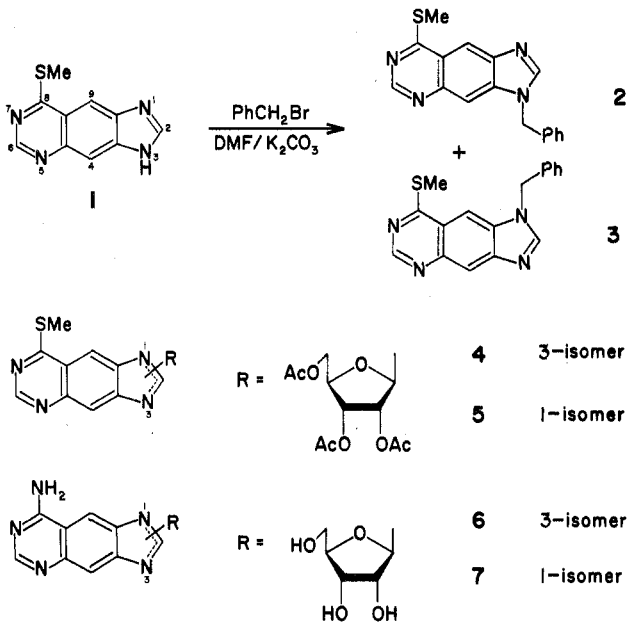
David F. Wiemer, David I. C. Scopes, and Nelson J. Leonard*

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received April 6, 1976

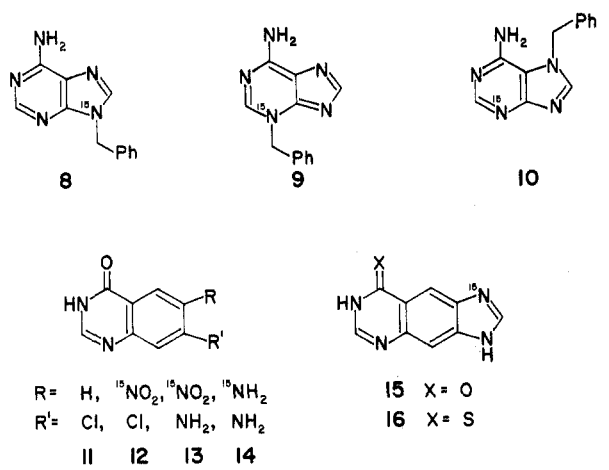
Observation of spin–spin coupling between ^{15}N and ^{13}C nuclei in ^{13}C NMR spectroscopy can be of considerable assistance in solving structural problems. For example, this technique has been used to advantage in the structure elucidation of the metabolites tenellin and bassianin,[1] and ^{13}C assignments have been determined from the magnitude of ^{15}N–^{13}C coupling constants.[2] In this paper we report the use of such coupling for determining the site of alkylation in a nitrogen heterocycle.

The benzylation products of 8-methylthioimidazo[4,5-*g*]quinazoline (1) have recently been assigned as 3-benzyl-



8-methylthioimidazo[4,5-*g*]quinazoline (**2**) and 1-benzyl-8-methylthioimidazo[4,5-*g*]quinazoline (**3**).[3] Since the 3-benzyl derivative **2** was prepared by an alternative unambiguous route its structure is certain, but that of the other isomer **3** was based on uv and NMR arguments[3,4] which, although compelling, were not definitive. The uv spectra of both **2** and **3** have been used as comparison models for the assignments of **4** and **5** as the products of ribosidation of 8-methylthioimidazo[4,5-*g*]quinazoline (**1**).[4] The ribosides **4** and **5** were subsequently converted to *linear*-benzoadenosine (**6**) and the 1 isomer **7**, respectively. In order to confirm the structure of the latter nucleoside isomer it becomes necessary to demonstrate that **3** is indeed the other product of benzylation of **1** and not an isomer derived from reaction at the 5 or 7 position.

NMR spectral studies of the benzylated products of 8-methylthioimidazo[4,5-*g*]quinazoline-*1*-^{15}N could lead to verification of the fact that benzylation of **1** occurs at the 1 position as well as the 3 position. Observation of ^{15}N–Cα–H coupling in the ^1H NMR spectrum would be indicative of the benzyl group being located at the 1 position, although ^{15}N–C–H couplings across an sp^3 carbon atom are generally small (0–1 Hz) and may not necessarily be detected.[5] In the ^{13}C NMR spectrum, observation of an ^{15}N–^{13}C coupling between $^{15}N^1$ and the benzylic carbon would unequivocally confirm the structural assignment **3** and thus place the earlier uv correlations on a firm basis. As suitable models for ^{15}N–^{13}C coupling between aromatic nitrogen and benzylic carbon we examined the proton-decoupled ^{13}C NMR spectra of the ^{15}N-labeled benzyladenine derivatives **8**,[6] **9**,[7b] and **10**[7a] which were



available to us. ^{15}N–^{13}C coupling was observed for **8** (doublet at 48.2 ppm, $^1J_{(^{15}NC)}$ = 9.3 Hz) and for **9** (doublet at 54.0 ppm, $^1J_{(^{15}NC)}$ = 7.2 Hz). No long-range coupling between the benzylic carbon and $^{15}N^3$ of 7-benzyladenine-*3*-^{15}N was observed.

8-Methylthioimidazo[4,5-*g*]quinazoline-*1*-^{15}N was readily synthesized using the route previously described starting from 7-chloro-4-quinazolone (**11**).[3] The ^{15}N label was incorporated by nitration of **11** with nitric acid-^{15}N to give **12** under conditions somewhat modified from the earlier procedure (see Experimental Section). The remainder of the synthesis followed the sequence described in the earlier work through intermediates **13**, **14**, **15**, and **16**. Benzylation of **1**, using benzyl bromide and potassium carbonate in dimethylformamide, provided the two *N*-benzyl isomers, **2** and **3**, which were separated by column chromatography.

Definitive evidence for the sites of benzylation was obtained from the proton-decoupled ^{13}C NMR spectra of the two isomers. The benzylic carbon of 3-benzyl-8-methylthioimidazo[4,5-*g*]quinazoline-*1*-^{15}N (**2**) resonates as a singlet at δ 52.3 ppm. That of the other isomer appears as a doublet ($^1J_{(^{15}NC)}$ = 8.6 Hz), due to ^{15}N–^{13}C coupling, at δ 50.6 ppm, thereby indicating direct attachment of the benzyl moiety to N-1. The magnitude of the ^{15}N–^{13}C coupling for this isomer is very similar to the values observed for the model systems 9-benzyladenine-*9*-^{15}N and 3-benzyladenine-*3*-^{15}N, **8** and **9**, respectively. The spectral data conclusively demonstrate the earlier structural assignment **3** to be correct for the second benzylation product of **1**. The ^1H NMR spectrum of each of the isomers was also examined, with irradiation at δ 7.30 to eliminate small long-range coupling with the protons on the phenyl ring. The signal for the benzylic protons of 3-benzyl-8-methylthioimidazo[4,5-*g*]quinazoline-*1*-^{15}N was a singlet while the corresponding resonance for the other benzylation product appeared as a doublet ($^2J_{(^{15}NH)}$ = 1.2 Hz) due to ^{15}N–Cα–H coupling. This serves as further confirmation of our structural assignments although this approach may not be as widely useful because of the smaller $^2J_{(^{15}NH)}$ values across an sp^3 carbon atom. The positive assignment of structure **3** also confirms the assignment of N-1 as the site of ribosidation of compound **1**, along with the N-3 product.[4]

This method for determining the site of alkylation or ribosidation may well prove applicable in other heterocyclic systems where ^{15}N can be specifically incorporated. The variety of ^{15}N sources commercially available makes this possible in numerous systems.

Experimental Section

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Varian Associates HA-100 spectrometer using tetramethylsilane as an internal standard. The proton-decoupled ^{13}C NMR spectra were recorded on a Varian Associates XL-100-15A spectrometer interfaced with a Digilab NMR-3 data system (256 K disk) operating at 25.2 MHz. The ^{13}C NMR samples were run in $(CD_3)_2SO$/TFA solution (1:1 ratio) at a probe temperature of 35°C with an internal ^2H lock [$(CD_3)_2SO$]. Chemical shifts are given in parts per million downfield from internal tetramethylsilane as zero. Spectra were obtained in 24 h using the following typical conditions: bandwidth 5882 Hz, pulse width 10–20 μs, acquisition time 1–1.5 s, spin decoupler offset 45 800 Hz (corresponding to 5 ppm downfield from Me_4Si at 100 MHz), noise bandwidth 2.5 kHz, and a sampling of 16K data points. At 16K data points the system provides a frequency resolution of 0.7 Hz. Low-resolution mass spectra were obtained on a Varian MAT CH-5 spectrometer coupled with a 620i computer and STATOS recorder.

7-Chloro-6-nitro-4-quinazolone-*6*-^{15}N (12). 7-Chloro-4-quinazolone (1.0 g, 5.55 mmol) was added to an ice-cold solution of nitric acid-^{15}N (ICN, 1.0 g of 99 atom % nitric acid-^{15}N, purchased, as a 10 N solution) in concentrated sulfuric acid (8.5 ml). The mixture was allowed to warm to room temperature and was then heated at 100 °C for 2.0 h. The resulting solution was poured into ice water (150 ml) and the product was collected by filtration and air dried. Crystalli-

zation from acetic acid gave **12** (0.71 g, 57%) as yellow prisms, identical by TLC with an authentic sample: mp 300–302 °C (lit.[3] 300–303 °C); mass spectrum (70 eV) *m/e* (rel intensity) 228 (33, M^+), 226 (100, M^+), 225 (0.6, $C_8H_4ClN_3O_3$).

3- and 1-Benzyl-8-methylthioimidazo[4,5-*g*]quinazoline-*1*-^{15}N (2 and 3). These compounds were prepared from **12** via the sequence described in the text, using the experimental procedures which were reported previously.[3] Intermediates were characterized at each step by melting point, uv, and TLC comparison with authentic samples. The overall yield for the six-step sequence was ~19% for each isomer: **2**, ^1H NMR [$(CD_3)_2SO$/TFA] δ 5.84 (s, 2, CH_2), 9.66 d, 1, J = 6.5 Hz, 2-H); **3**, ^1H NMR [$(CD_3)_2SO$/TFA] δ 5.92 (d, 2, J = 1.2 Hz, CH_2), 9.69 (d, 1, J = 6.5 Hz, 2-H).

3-Benzyladenine-*3*-^{15}N (9) and 7-Benzyladenine-*3*-^{15}N (10). The ^{15}N label was incorporated via nitration of 4-bromoimidazole with nitric acid-^{15}N in the sequence previously described for the preparation of (unlabeled) 7-benzyladenine.[7a] Debenzylation of 7-benzyladenine-*3*-^{15}N with sodium/liquid ammonia[7b] provided adenine-*3*-^{15}N which was converted to **9** by the conventional procedure.[8] **10**: ^1H NMR [$(CD_3)_2SO$] δ 8.18 (d, 1, J = 15 Hz, 2-H).

Acknowledgments. This work was supported by Research Grant MPS 74-05911 (current no. CHE 74-05911) from the National Science Foundation. One of us (D.F.W.) held a fellowship from the Lubrizol Foundation. We wish to thank Mr. S. Silber for his assistance in providing nuclear magnetic resonance spectra.

Registry No.—**1** ($^{15}N^1$), 59710-62-2; **2**, 59710-63-3; **3**, 59710-64-4; **9**, 59710-65-5; **10**, 59710-66-6; **11**, 31374-18-2; **12**, 59710-67-7; nitric acid-^{15}N, 43625-06-5; 4-bromoimidazole, 2302-25-2; benzyl bromide, 100-39-0.

References and Notes

(1) A. G. McInnes, D. G. Smith, C-K. Wat, L. C. Vining, and J. L. C. Wright, *J. Chem. Soc., Chem. Commun.*, **281** (1974).
(2) A. M. Nadzan and K. L. Rinehart, manuscript in press.
(3) N. J. Leonard, A. G. Morrice, and M. A. Sprecker, *J. Org. Chem.*, **40**, 356 (1975).
(4) N. J. Leonard, M. A. Sprecker, and A. G. Morrice, *J. Am. Chem. Soc.*, **98**, 3987 (1976).
(5) For a recent review containing ^{15}N–^{13}C and ^{15}N–C–H coupling data see T. Axenrod in "Nitrogen NMR", M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, N.Y., 1973, pp 286 and 292; M. Witanowski, *Pure Appl. Chem.*, **37**, 225 (1974).
(6) N. J. Leonard and T. R. Henderson, *J. Am. Chem. Soc.*, **97**, 4990 (1975).
(7) (a) N. J. Leonard, K. L. Carraway and J. P. Helgeson, *J. Heterocycl. Chem.*, **2**, 291 (1965); (b) K. L. Carraway, Ph.D. Thesis, University of Illinois, 1966.
(8) (a) J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **84**, 1914 (1962); (b) N. J. Leonard and T. Fujii, *ibid.*, **85**, 3719 (1963); (c) B. C. Pal, *Biochemistry*, **1**, 558 (1962).

Dihydro-1,4-dithiin Annelation

C. H. Chen* and B. A. Donatelli

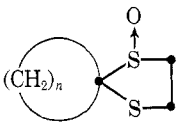
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received April 20, 1976

Synthetic methods available for the construction of rings fused to heterocyclic molecules are limited owing to the vulnerability of the heteroatom to the well-established conditions often employed in carbocyclic chemistry.[1] As part of our studies on the reactivity and synthetic uses of monosulfoxides of 1,3-dithiolane,[2] we now report a method for constructing carbocyclic fused dihydro-1,4-dithiins under mild conditions. This new heterocyclic annelation reaction is outlined in the following starting from the corresponding cyclic ketones **1**.

Dithiolation of **1** was accomplished in the usual manner.[3] Selective oxidation of the spiro-1,3-dithiolane **2** using *m*-chloroperbenzoic acid (MCPBA) in cold methylene chloride afforded the desired monosulfoxide **3** in good yields (Table I). Azeotropic distillation of the latter in benzene in the presence of a catalytic amount (ca. 10%) of *p*-toluenesulfonic acid (PTSA) smoothly transformed the spiro-1,3-dithiolane 1-oxide **3** by loss of H_2O to the dithiin **4** in essentially quantitative yield.

Table I[5]



Registry no.	*n*	Bp (mp), °C	% yield
59796-89-3	3	59–60 (10–12 μ)	64[a]
59796-90-5	4	53.5 (8 μ)	64[b,c]
59796-91-7	5	(82.8)	75[a]
59796-92-8	6	(59.2)	64[a]
59796-93-9	11	(107.2)	88[a]
59796-94-0	14	(88.9)	87[b]

[a] Based on the corresponding ketone **1**. [b] Based on pure spiro-1,3-dithiolane **2**. [c] Prepared by $NaIO_4$ oxidation in methanol and water.

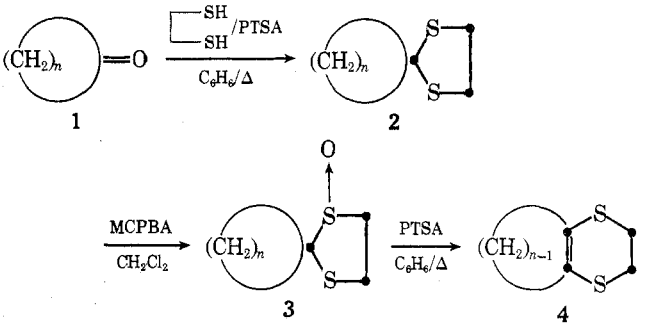
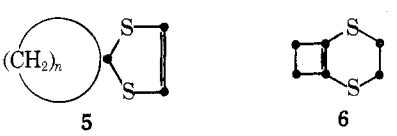
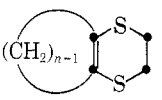


Table II lists yields of these ring expansion reaction products **4**. The absence of absorptions in the olefinic region of the NMR spectra of **4** and the appearance of a singlet at around δ 3.0 ppm for the ring protons of the dihydro-1,4-dithiin system[2] excludes the presence of isomeric 1,3-dithiole **5**, which would be expected to form under the normal Pummerer rearrangement conditions.[4] Attempts to prepare the cyclobutene derivative **6** were unsuccessful. While under the normal



experimental conditions (10% PTSA, PhH reflux, 30 h), the starting monosulfoxide **3** (n = 3) was found to be unreactive, under more strenuous conditions (e.g., 50% PTSA, PhH, re-

Table II[5]



Registry no.	*n*	Bp, °C (mm)	% yield[a]
35756-14-0	4	71–72 (0.4)	96
23285-17-8	5	109–110 (1.4)[b]	93
59796-95-1	6	88–89 (0.3)	95
59796-96-2	11	169–170 (1.1)	96
59796-97-3	14	186–189 (0.8–0.9)	85

[a] Yield of pure product based on **3**. [b] Lit. bp 90–98 °C (1.0 mm): L. Levine and L. Jackson, U. S. Patent 3 439 051 (1969).