Table I. Electronegativities[a,b]

	Li	Be								B	C	N	O	F
H	1.00	1.48								1.84	2.35	3.16	3.52	4.00
P	0.98	1.57								2.04	2.55	3.04	3.44	3.98
A	0.97	1.47								2.01	2.50	3.07	3.50	4.10
S	0.99	1.50								2.00	2.50	3.00	3.50	4.00
	Na	Mg								Al	Si	P	S	Cl
H	0.89	1.24								1.40	1.64	2.11	2.52	2.84
P	0.93	1.31								1.61	1.90	2.19	2.58	3.16
A	1.01	1.23								1.47	1.74	2.06	2.44	2.83
S	0.91	1.18								1.43	1.66	1.90	2.12	2.35
	K	Ca	Sc	Ti	V	Cr	Mn	Cu	Zn	Ga	Ge	As	Se	Br
H	0.73	0.96	1.14	1.27	1.42	1.72	1.88	1.10	1.40	1.54	1.69	1.99	2.40	2.52
P	0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.90	1.65	1.81	2.01	2.18	2.55	2.96
A	0.91	1.04	1.20	1.32	1.45	1.56	1.60	1.75	1.66	1.82	2.02	2.20	2.48	2.74
S	0.79	1.10							1.40	1.50	1.66	1.81	1.96	

[a] FSGO values are based on hydride scale: $\epsilon_{Li} = 1.00$; $\epsilon_F = 4.00$. On this scale $\epsilon_H = 2.79$ as compared with 2.20 on Pauling and Allred–Rochow scales. [b] H denotes FSGO hydride scale; P denotes Pauling scale, values from A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961); A denotes Allred–Rochow scale, values from ref 3; S denotes St. John–Bloch scale, values from ref 6.

sharing of the bonding electrons. In short, the deviation of f_{AB} from 0.5 measures the degree of electron transfer within a bond, and this is, presumably, the most conceptually attractive and most direct measure of differences in electron attracting power, or electronegativity.[11]

The simplest definition of electronegativity difference in terms of f_{AB} is a direct proportionality:[12]

$$(\epsilon_B - \epsilon_A) = K(f_{AB} - 0.5) \quad (2)$$

the constant in eq 2 may be eliminated by taking a ratio,

$$(\epsilon_B - \epsilon_A)/(\epsilon_B - \epsilon_C) = (f_{AB} - 0.5)/(f_{CB} - 0.5) \quad (3)$$

from which we note that if reference electronegativities are selected for two elements to set a standard point and scale expansion factor, then electronegativities can be generated for other atoms using only the f_{AB} values taken from ab initio quantum mechanical calculations. Alternatively, eq 2 could be rewritten as

$$(\epsilon_B - \epsilon_A) = K(R_A - R_B)/(2R_A + 2R_B) \quad (4)$$

Equation 4 emphasizes the fundamental symmetry of our definition. Further, since the classical bond contribution to the molecular dipole moment would be $\delta = 2e(R_A - R_B)/2$, eq 4 displays the anticipated relationship between electronegativity and dipole moment.

Since many hydrides have been studied by the FSGO method,[13] hydrides have been used to generate a nonempirical electronegativity scale. Li and F (in LiH and HF) were assigned the electronegativities 1.00 and 4.00, respectively, and electronegativities were subsequently calculated for H and the other atoms[14] listed in Table I. One observes that the predicted electronegativities are in remarkable agreement with widely used empirical values. The small lowering of the electronegativities of most third-row elements, in comparison to the Pauling or Allred–Rochow values, is consistent with the trends suggested by Phillips[5] and St. John and Bloch.[6] With the exception of H (which is unique in the FSGO framework in that there is no nuclear shielding) and Cu (the bond length of CuH is grossly overestimated by FSGO[13d]), the agreement with the Allred–Rochow scale is particularly striking. However, in contrast to the Allred–Rochow scale, note that sulfur is predicted to be more electronegative than carbon, in agreement with chemical behavior.

We find that the proposed electronegativity scale is usually consistent with electronegativity differences (computed from f_{AB} by eq 2 or 3) for nonhydride compounds. For example (hydride scale in parenthesis): $\epsilon_{Cl} - \epsilon_{Li} = 1.80$ (1.84) in LiCl, $\epsilon_O - \epsilon_{Be} = 1.87$ (1.69) in BeO, $\epsilon_O - \epsilon_{Si} = 1.86$ (1.88) in SiO, $\epsilon_O - \epsilon_C = 1.28$ (1.17) in methanol, $\epsilon_O - \epsilon_H = 0.70$ (0.74) in methanol, and $\epsilon_{Li} - \epsilon_{Na} = 0.13$ (0.11) in NaLi. However, electronegativities vary, as one might expect, with number of lone pairs and formal charge. For example, $\epsilon_O = 3.84$, 3.74, 3.52, and 3.23 in the respective species H_4O^{2+}, H_3O^+, H_2O, and OH^-; $\epsilon_{Sc} = 1.14$ and 1.04 in ScH_3 and ScH; and $\epsilon_O - \epsilon_C = 1.54$ (1.17) in the triply bonded carbon monoxide.

In conclusion we suggest that the above results constitute prima facie evidence for both the validity of the generally accepted interpretation of electronegativity and for the conceptual utility of the FSGO method.

References and Notes

(1) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, pp 88–93.
(2) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).
(3) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
(4) R. T. Sanderson, *J. Chem. Educ.*, **29**, 539 (1952); **31**, 2, 238 (1954).
(5) J. C. Phillips, "Covalent Bonding in Crystals, Molecules, and Polymers", University of Chicago Press, Chicago, Ill., 1969, p 230.
(6) J. St. John and A. N. Bloch, *Phys. Rev. Lett.*, **33**, 1095 (1974).
(7) A. A. Frost, *J. Chem. Phys.*, **47**, 3707 (1967).
(8) See, for example, E. R. Talaty, A. K. Schwartz, and G. Simons, *J. Am. Chem. Soc.*, **97**, 972 (1975) and references cited therein.
(9) P. H. Blustin and J. W. Linnett, *J. Chem. Soc., Faraday Trans. 2*, **70**, 274 (1974).
(10) This is an interpretation, as the location of the center of a bonding orbital is being considered instead of the molecular electron density.
(11) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(12) This definition requires a well-defined bonding orbital and may not apply to extremely ionic bonding such as in alkali fluorides.
(13) (a) First-row hydrides, A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968); (b) second-row hydrides, S. Y. Chu and A. A. Frost, *J. Chem. Phys.*, **54**, 760 (1971); (c) K–Mn hydrides, E. R. Talaty, A. J. Feary, and G. Simons, *Theor. Chim. Acta*, **41**, 133 (1976); (d) Cu–Br hydrides, G. Simons and E. R. Talaty, unpublished.
(14) Using the calculated multipliers $f_{LiH} = 0.893$ and $f_{FH} = 0.233$ in eq 3, and setting $\epsilon_{Li} = 1.000$ and $\epsilon_F = 4.000$, yields $\epsilon_H = 2.786$ and $K = 4.546$. In methane, for example, $f_{CH} = 0.595$; hence, $\epsilon_C = -4.546(f_{CH} - 0.5) + 2.786 = 2.354$.

Gary Simons,* Melvin E. Zandler, Erach R. Talaty
Department of Chemistry, Wichita State University
Wichita, Kansas 67208

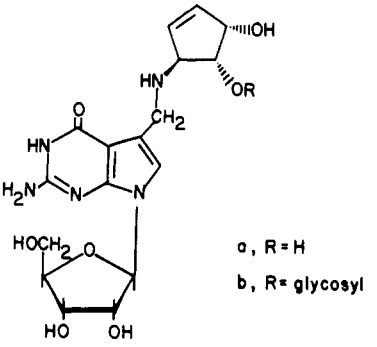
Received August 25, 1976

Synthesis of 2-Amino-5-cyano-7-(β-D-ribofuranosyl)-pyrrolo[2,3-*d*]pyrimidin-4-one. An Important Precursor for the Synthesis of Nucleoside Q and Q*

Sir:

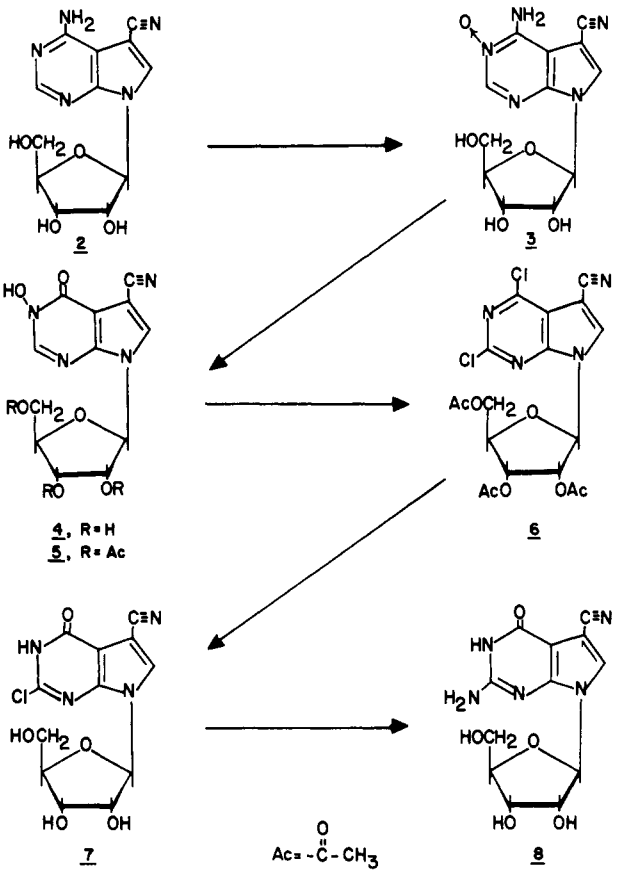
The structure of nucleoside Q was recently elucidated and reported[1] to be 2-amino-5-(4,5-*cis*-dihydroxy-1-cyclopenten-3-yl-*trans*-aminomethyl)-7-(β-D-ribofuranosyl)pyrrolo-[2,3-*d*]pyrimidin-4-one (**1a**). This modified nucleoside oc-

cupies the first position of the anticodon[2] of *E. coli* $tRNA^{Tyr}$, $tRNA^{His}$, $tRNA^{Asn}$, and $tRNA^{Asp}$ and has now been shown[3] to be widely distributed in tRNA from animal as well as plant sources. A biosynthetic study[4] has revealed that nucleoside Q arises from a guanine residue. During the course of modification (G → Q), the C8 carbon and N7 nitrogen of the guanine precursor are expelled, which suggests that the biosynthesis of nucleoside Q may be similar to the biosynthesis of toyocamycin from adenosine[5] with the precursor for the aglycon of nucleoside Q presumably being guanosine. Prompted by these reports and the fact that we have been involved in pyrrolo[2,3-*d*]pyrimidine nucleoside research for several years,[6] we explored several synthetic routes which were designed to furnish the nucleoside moiety of nucleosides Q and Q*.[7] We now wish to report the synthesis of 2-amino-5-cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one (**8**, reaction scheme), a potential precursor of nucleosides Q (**1a**) and Q* (**1b**).



1

We elected to use toyocamycin[6b] (**2**), a nucleoside antibiotic[5] with established chemotherapeutic and biological properties,[8] as the starting material for our synthesis. Toyocamycin was oxidized with *m*-chloroperbenzoic acid in glacial acetic acid at 65 °C for 2 h. This furnished a white crystalline compound (75% yield) which was assumed to be toyocamycin 3-*N*-oxide (**3**) (mp 269 °C dec). Deamination of **3** with nitrous acid in dimethylformamide furnished 5-cyano-3-*N*-hydroxy-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one (**4**, 55%) (mp 230–232 °C; uv λ_{max}^{MeOH} 274 nm (ε, 8040), 302 sh (4640); ir (KBr) 2240 cm^{-1} (C≡N)). Acetylation of **4** with acetic anhydride/pyridine at room temperature for 5 h provided a near-quantitative yield of **5** which was then treated with phosphorus oxychloride at reflux in the presence of 2,6-lutidine. The latter procedure[9] conveniently chlorinated the positions ortho (C2 and C4) to the N3 position of the heterocyclic aglycon. After removal of the excess phosphorus oxychloride and column chromatography (Mallinckrodt CC-7; chloroform–ethyl acetate, 4:1, v/v), we obtained crystalline 5-cyano-2,4-dichloro-7-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidine (**6**) in 38% yield (mp 125 °C, uv λ_{max}^{MeOH} 285 nm (ε, 6130); ir (KBr) 2240 cm^{-1} (C≡N)). A saturated aqueous barium hydroxide solution containing the dichloro nucleoside **6** was stirred at room temperature for 30 h. The resulting suspension was carefully adjusted to pH 2 with 20% aqueous sulfuric acid and filtered, and the filtrate readjusted to pH 7. The neutralized filtrate was then taken to dryness in vacuo. The solid residue was purified by column chromatography (CC-7; ethyl acetate–methanol, 9:1, v/v) to afford 2-chloro-5-cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one (**7**) in 40% yield (mp >165 °C dec; uv $\lambda_{max}^{pH\ 1}$ 257 nm (ε, 5200), $\lambda_{max}^{pH\ 11}$ 277 sh (ε, 3500), 265 (5900); ir (KBr) 2230 cm^{-1} (C≡N)). ^1H NMR spectroscopy and elemental analysis[10] established that a displacement of the 4-chloro group was concomitant with deacetylation. Furthermore, proof that the chloro group in the C4 position had been displaced rather than the C2 chloro group was established by a removal of the C2 chloro group of **7** with hydrogen and Pd/C to afford the known 5-cyano-7-(β-D-ribofuranosyl) pyrrolo[2,3-*d*]pyrimidin-4-one.[11]



2 **3** **4** **5** **6** **7** **8**

Conversion of **7** to the desired guanosine analogue **8** was first attempted using methanolic ammonia in a steel reaction vessel at 120 °C. The use of methanolic ammonia was found to be unsuitable[12] and furnished only a limited amount of **8** which was accompanied by several undesired side products. We then changed our reaction conditions and used liquid ammonia in a steel reaction vessel at 100 °C to obtain the desired 2-amino-5-cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one (**8**) in 76% yield (mp 267 °C dec; mass spectrum (EI, 5-Me_3Si, 70 eV) *m/e* 667 (M); ^1H NMR (Me_2SO-d_6) δ 7.98 (s, 1, H6), 6.82 (bs, 2, NH_2), 5.92 (d, 1, H1′, $J_{1',2'}$ = 2.8 Hz); uv $\lambda_{max}^{pH\ 1}$ 288 nm (ε, 6850), 267.5 (8450), 227 (17 350), $\lambda_{max}^{pH\ 11}$ 285.5 nm (ε, 7000), 267.5 (6500), 225.5 (20 000); ir (KBr) 2240 cm^{-1} (C≡N). The successful synthesis of **8** has provided a pathway to nucleosides Q and Q* as well as a general method for the synthesis of other guanosine analogues in the pyrrolopyrimidine area.

Acknowledgment. The authors are indebted to Mr. Steven J. Manning for the large scale synthesis of certain intermediates used in this study and to Mrs. Suzanne Mason for technical assistance. This research program is supported by research contract N01-CM-43806 from the Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, Department of Health, Education and Welfare. C.-S. C. acknowledges support from Training Grant CA-05209 from the National Cancer Institute.

References and Notes

(1) (a) H. Kasai, Z. Ohashi, F. Harada, S. Nishimura, N. J. Oppenheimer, P. F. Crain, J. G. Liehr, D. L. von Minden, and J. A. McCloskey, *Biochemistry*, **14**, 4198 (1975). (b) T. Ohgi, T. Goto, H. Kasai, and S. Nishimura, *Tetrahedron Lett.*, 367 (1976). (c) It should be pointed out that the stereo-

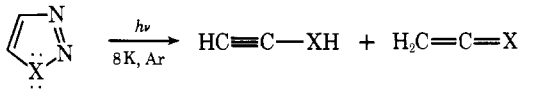
chemistry of the side chain (the three chiral centers) is still under investigation and the total synthesis of nucleoside Q should corroborate the tentative assignments reported in ref 1a and 1b.
(2) F. Harada and S. Nishimura, *Biochemistry*, **11**, 301 (1972).
(3) H. Kasai, Y. Kuchino, K. Nihei, and S. Nishimura, *Nucleic Acid Res.*, **2**, 1931 (1975).
(4) Y. Kuchino, H. Kasai, K. Nihei, and S. Nishimura, *Nucleic Acid Res.*, **3**, 393 (1976).
(5) R. J. Suhaldolnik, "Nucleoside Antibiotics", Wiley-Interscience, New York, N.Y. 1970, Chapter 8.
(6) (a) K. H. Schram and L. B. Townsend, *J. Chem. Soc., Perkin Trans. 1*, 1253 (1975); (b) R. L. Tolman, R. K. Robins, and L. B. Townsend, *J. Am. Chem. Soc.*, **91**, 2102 (1969), and references cited therein.
(7) Professor K. Nakanishi recently reported (presented at the Centennial American Chemical Society Meeting, New York, N.Y., April 1976, CARB 31) the structure of Q*. He indicated that Q* possessed a mixture of *O*-glycosides on the 4-position of the cyclopentenyl moiety. His data strongly suggested that the *O*-glycoside portion was a mixture of the following hexoses: β-D-mannosyl (~75%)/β-D-galactosyl (~25%); for complete details see H. Kasai, K. Nakanishi, R. D. MacFarlane, D. F. Torgerson, Z. Ohashi, J. A. McCloskey, H. J. Gross, and S. Nishimura, *J. Am. Chem. Soc.*, **98**, 5044 (1976).
(8) L. B. Townsend in "Handbook of Biochemistry and Molecular Biology", 3d ed, Nucleic Acids Vol. 1, G. D. Fasman, Ed., Chemical Rubber Co. Press, Cleveland, Ohio, 1975, p 390.
(9) H. Kawashima and I. Kumashiro, *Bull. Chem. Soc. Jpn.*, **40**, 639 (1967).
(10) Satisfactory analytical data (C, H, and N) were obtained for all compounds reported in this communication. A chlorine analysis was also obtained for compound **7**.
(11) B. C. Hinshaw, J. F. Gerster, R. K. Robins, and L. B. Townsend, *J. Org. Chem.*, **35**, 236 (1970).
(12) G. R. Revankar and R. K. Robins, *Ann. N.Y. Acad. Sci.*, **255**, 166 (1975).

Chin Shu Cheng, Barbara C. Hinshaw
Raymond P. Panzica, Leroy B. Townsend*
Department of Biopharmaceutical Sciences and Department of Chemistry
University of Utah, Salt Lake City, Utah 84112
Received April 19, 1976

Photolysis of Isotopically Labeled 1,2,3-Selenadiazole and 1,2,3-Thiadiazole. Symmetry Properties of the Paths Leading to Ethynyl Mercaptan and Selenol. Evidence for Thiirene[1]

Sir:

We recently reported[2] on the irradiation with Pyrex-filtered mercury lamp light of matrix-isolated 1,2,3-thiadiazole (**1a**), whose photodecomposition appears to involve the potentially antiaromatic molecule, thiirene (**2**), as a transient species.[3,4]



1a, X = S
b, X = Se
3 **4**

In this communication we describe the photochemistry of matrix-isolated 1,2,3-selenadiazole[5] (**1b**), (which exhibits, in its details, behavior quite distinct from its sulfur analogue)[2] and further experiments with isotopically labeled **1a.** Irradiation with Pyrex-filtered mercury lamp light of argon or nitrogen matrix-isolated **1b** at 8 K ($M/R \sim 500$) gave ethynyl selenol **3b,** selenoketene **4b,** and acetylene (**5**) (a product not observed in the photolysis of **1a**).[6] It is noteworthy that **1b** is not interconverting with the more photostable 1,3,4-selenadiazole[7,8] (**6b**), since neither **6b** nor its major photoproduct, hydrogen cyanide, are observed during the photolysis of **1b.**

Selenol **3b** possesses key bands at 3318 (≡CH str), 2050 (C≡C str), and 581 cm^{-1} (≡CH in-plane bend), virtually identical with those observed for the corresponding modes in **3a**[2] and ethynyl selenoethers.[9] The assignment of an extremely intense band at 1695 cm^{-1} in the spectrum of photolysate to the C=C stretch of **4b** is reasonable, in light of the value of the corresponding mode in thioketene (1755 cm^{-1}). This band

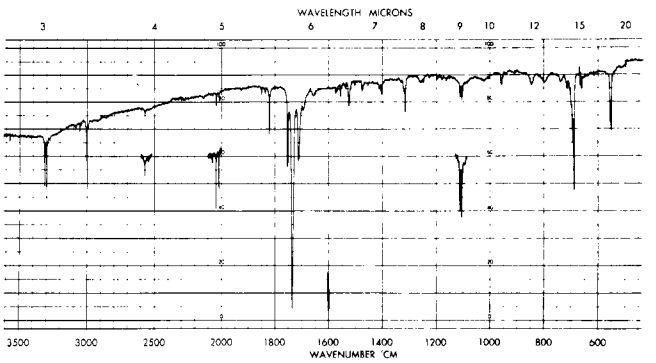


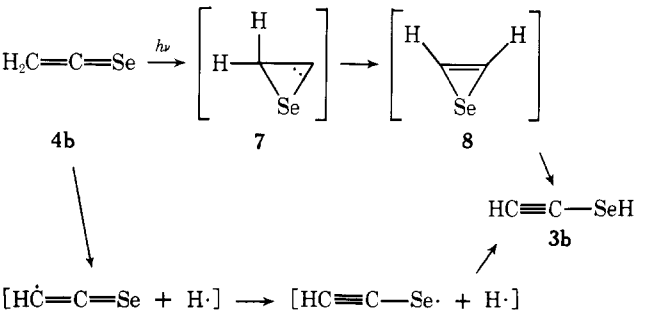
Figure 1. Spectrum of argon matrix-isolated 1,2,3-thiadiazole-*4*-^{13}C (90% isotopically pure) (M/R = 500) photolyzed at 8 K for 105 min with Pyrex-filtered light. Starting thiadiazole has been destroyed. Pairs of bands due to isomeric ^{13}C ethynyl mercaptans are seen at 3307 and 3325 (CH str), 2025 and 2045 (C≡C str), and 552 and 555 cm^{-1}. There is a 10% contribution from the carbon-12 spectrum.

displays, on substitution of **1b** with deuterium, behavior typical of parent cumulenes:[10] ν_{d_0} = 1699, ν_{d_1} = 1698, ν_{d_2} = 1681 cm^{-1}. Detection of selenoketene represents one of the few documented examples of a species possessing a C=Se double bond.[11-13]

Photolysis with Pyrex-filtered light of argon matrix-isolated 4-deuterio-1,2,3-selenadiazole[5] ($M/R \sim 400$) gives product spectra containing absorption characteristic of ≡C-H (3318 cm^{-1}) and ≡C-D (2580 cm^{-1}) stretches in the ratio of ca. 0.2; under identical conditions the 5-deuterio isomer gives these bands in an approximately inverse ratio of 3.5! Whereas the hydrogens of the thiadiazole framework become equilibrated through a symmetrical species en route to ethynyl mercaptan **3a,** it is clear from the foregoing labeling experiments that the major portion of ethynyl selenol **3b** is not formed via a pathway which equilibrates the hydrogens.

If the Pyrex filter is removed after monodeuterated selenadiazole has been fully photodecomposed, and the "Pyrex" photolysate is then irradiated with a bare lamp (λ > 200 nm), the selenol increases at the expense of both acetylene **5** and selenoketene **4b,** with the ratio ≡CH/≡C-D(str) of the selenols converging to 1.0.

A possible mechanism for the loss of acetylene could involve the addition of photochemically excited selenium atoms to neighboring acetylene molecules.[15] Plausible explanations for the trade-off of selenoketene **4b** for selenol **3b** include (1) conversion of **4b** to the carbene **7,** which could, in turn, isom-



erize to predominantly the selenol through selenirene **8,** or (2) a reaction mediated by a hydrogen radical cleaved from the carbon end of **4b,** which then readds to the selenium terminus. Support for the latter alternative is derived from the observation that irradiation (λ > 200 nm) of the photolysate from **1b** isolated in a carbon monoxide host at 8 K produces absorptions [ν = 1865 (s), 1093 cm^{-1} (m)] in the infrared, indicative of the formyl radical.[16,17]

The results of irradiating 1,2,3-thiadiazole-*4*-^{13}C (**9**) (90% isotopically pure) in solid argon are pictured in Figure 1. Pairs