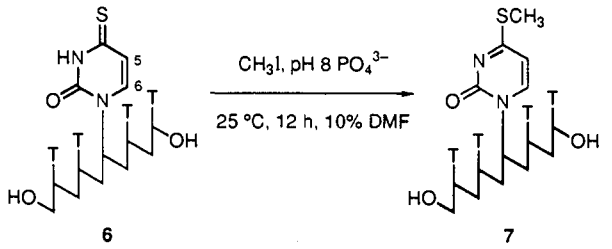
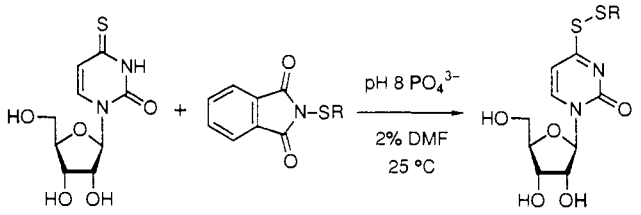
The thiocarbonyl group of **5** and **6** proved suitable for attachment of pendant groups. In studies utilizing 4-thiouridine, we observed that significant rates of S-alkylation[13] under aqueous conditions (50 mM pH 8 PO_4^{3-}, 10–30% DMF) required reactive electrophiles such as allylic or benzylic bromides. This methodology was applied by treatment of pentamer **6** with iodomethane (≈1 equiv) in 0.1 M pH 8 phosphate buffer (10% DMF) and afforded *S*-methyl thioimidate **7** in quantitative yield, as evidenced by the complete disappearance of the C5-H and C6-H signals of **6** in the ^1H NMR, which were replaced by two new signals corresponding to **7**.[14] Although S-alkylation of the thiocarbonyl group of **6** occurred quantitatively, it is not apparent whether this protocol for attachment of tethers will prove selective with oligonucleotides containing nucleophilic residues (e.g., G or A).



6 **7**

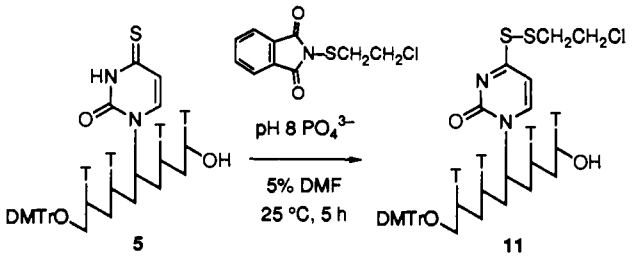
We developed a simple method for tether attachment that relied on selective mixed disulfide formation. Reaction of 4-thiouridine (**8**) with *N*-mercaptophthalimides **9a–d**[15,16] (1 equiv) in aqueous buffer containing 2% DMF (25 °C, 1 h) effected thiol-group transfer to afford mixed imino disulfides **10a–d** in ≥90% yields.



8

9a	R = CH_3	10a
9b	R = CH_2CH_2Cl	10b
9c	R = CH_2CH_2Br	10c
9d	R = $CH_2CH_2CH_2Cl$	10d

Similarly, treatment of pentanucleotide **5** with the thiol-transfer reagent *N*-((2-chloroethyl)thio)phthalimide (**9b**)[16] in phosphate buffer (pH 8) containing 5% DMF effected quantitative conversion to disulfide **11**. Effective conversion of **5** to **11** was evident in the ^1H NMR (500 MHz, D_2O) by the complete disappearance of the C5-H and C6-H signals of **5**, which were replaced by two new signals corresponding to **11**.[17] The transformation of **5** to **11** is anticipated to be selective for thioalkyl transfer to thiocarbonyl groups and, therefore, potentially more appropriate for tether attachment than S-alkylation.



5 **11**

We have demonstrated a convenient and effective protocol for the incorporation of 4-thio-2′-deoxyuridine into simple oligonucleotides. This procedure used an *S*-(2-cyanoethyl) ether[9] as a thiocarbonyl protecting group, which was shown to be completely stable to the reaction conditions used during solid-phase oligonucleotide synthesis. Quantitative S-deprotection was effected by treatment of the support-linked oligonucleotide with DBU in CH_3CN. Further studies illustrated that the thiocarbonyl group provides a convenient point of attachment of alkyl tethers by postsynthetic S-alkylation or mixed disulfide formation. This methodology will be of potentially general value in appending a variety of reactive or reporter groups to 4-thio-2′-deoxyuridine-containing oligonucleotides.

Acknowledgment. We thank the American Cancer Society (IRG-107P), the Camille and Henry Dreyfus Foundation (NF-89-18), and the Carolina Venture Fund for their generous support of this work. NMR spectra were obtained on instruments purchased with funds from the National Science Foundation (CHE-8411172 and CHE-8904942) and the National Institutes of Health (S10-RR02425).

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(14) Characteristic chemical shift values (500 MHz, D_2O): δ 6.54 (1 H, C5-H), 7.68 (1 H, obscured by thymidine, C6-H) for **6**; δ 6.58 (1 H, C5-H), 8.01 (1 H, C6-H) for **7**.
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(16) Reagent **9b** was prepared from phthalimide and 2-chloroethanethiol by the method of Behforouz and Kerwood (ref 15a). 2-Chloroethanethiol was prepared from ethylene sulfide by the method of Meade and Woodward (*J. Chem. Soc.* **1948**, 1894). Reagents **9a–c** were prepared in an analogous manner.
(17) Characteristic chemical shift values (500 MHz, D_2O): δ 6.46 (1 H, C5-H), 7.66 (1 H, partially obscured by thymidine, C6-H) for **5**; δ 7.05 (1 H, C5-H), 8.24 (1 H, C6-H) for **11**.

Hydrogen Trajectories in Alkene to Carbene Rearrangements. Unequal Deuterium Isotope Effects for the Axial and Equatorial Paths

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The rearrangement of a singlet carbene to an alkene is well-known, and its stereochemical aspects have been probed experimentally[1] and theoretically[2] for migration of H (**1** → **2**). The

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(1) (a) Nickon, A.; Huang, F. C.; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264–5265. (b) Kyba, E. P.; Hudson, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 5696–5697. (c) Kyba, E. P.; Hudson, C. W. *J. Org. Chem.* **1977**, *42*, 1935–1939. (d) Freeman, P. K.; Hardy, T. A.; Balyeat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* **1977**, *42*, 3356–3359. (e) Seghers, L.; Shechter, H. *Tetrahedron Lett.* **1976**, *23*, 1943–1946. (f) Kyba, E. P.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8329–8330. (g) Kirmse, W.; Ritzer, J. *Chem. Ber.* **1985**, *118*, 4987–4996.

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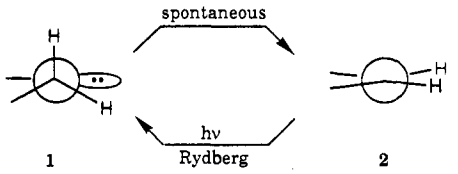
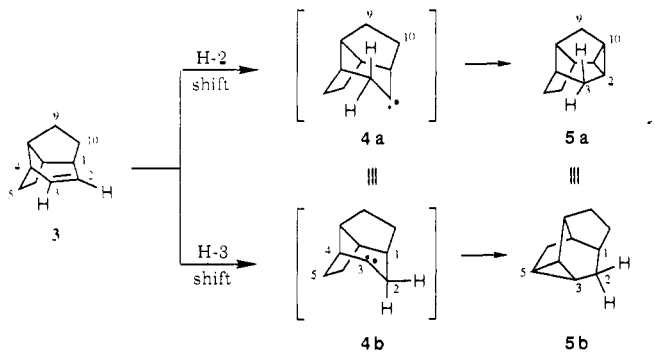
reverse process, namely, rearrangement of an alkene to a carbene (**2** → **1**), is also amply documented and can often be induced by appropriate irradiation.[3] In such irradiations, the carbene is believed to arise from a Rydberg excited state of the alkene, e.g., R(3s), which has radical cation character and can undergo a 1,2-shift of a substituent. No information (experiment or theory) is currently available on any geometric aspects of a Rydberg-induced alkene → carbene rearrangement. We now report a stereochemical study of H and D shifts in a cyclohexenic ring by use of double labeling (^{13}C, D). Our findings indicate a migration trajectory that favors development of an axial CH, and this ax/eq preference is appreciably greater for D shift than for H shift.

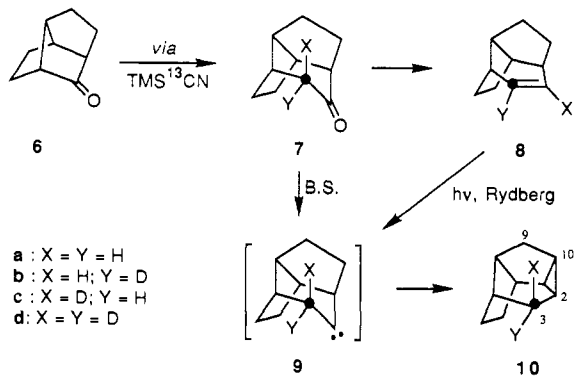


Our study involves homobrexene (**3**), in which the double bond resists relocation and is incapable of $Z \rightleftharpoons E$ isomerization. Also, the two vinyl H's are equivalent, and shift of either one produces the same carbene (i.e., **4a** ≡ **4b** in the absence of labeling). Carbene **4**, which is precluded from adopting a boat form, can partly revert to **3**, but much of it undergoes 1,3-insertion to the tetracycle **5**. (Note that **5a** ≡ **5b** in the absence of labeling.) Any ax vs eq stereoselectivity in the **3** → **4** migration of vinyl H would be preserved in tetracycle **5**. To remove the symmetry in the parent alkene **3** we synthesized two doubly-labeled analogs. Each labeled alkene has a full ^{13}C at C-3; additionally, one analog has a single D at C-2 whereas the other has a single D at C-3.



In tetracycle **5a** the two methylene H's at C-3 differ in chemical shift, and a molecule with a single D at this site, by virtue of D one-bond coupling with ^{13}C (ca. 20 Hz), is readily distinguished by D NMR from an isotopomer in which deuterium and ^{13}C are not directly connected (as would be the case for the ~50% of the molecules that begin with ^{13}C at C-3 and follow the path **3** → **4b** → **5b**). We synthesized the doubly-labeled substrates **8b** and **8c** (● ≡ ^{13}C) as well as authentic samples of the expected D epimeric tetracycles **10b** and **10c** as follows.

Ring expansion of brexan-2-one[4] (**6**) by a Tiffeneau–Demjanov sequence that utilized TMS^{13}CN provided [3-^{13}C]homobrexan-2-one (**7a**). Brief, mild (NaOMe/MeOD) treatment selectively exchanged the axial H in **7a** to produce **7c**, and prolonged exchange provided the d_2 analog **7d**. Also, a mild treatment selectively washed out the axial D from ketone **7d** to provide **7b**.[5] Each of the ketones **7a–d** was converted to its corresponding (arylsulfonyl)hydrazone (without loss of stereochemical integrity for the D compounds). A Shapiro reaction[6] on the derivative from **7d** with an H_2O quench gave **8b**, and a similar sequence on the derivative from **7a** with a D_2O quench provided **8c**.



Tetracycles **10a–c** were obtained from the respective (arylsulfonyl)hydrazones (of **7a–c**) by conventional, aprotic thermal Bamford–Stevens reactions,[7] which proceed via carbene **9**. This carbene produces a mixture of tetracycle **10** and alkene **8** (ratio ~3:1), readily separated and purified. Deuterium NMR of **10b** and **10c** confirmed that the stereochemical integrity of D was fully preserved in the **7** → **9** → **10** sequence. The chemical shift for D in **10c** is 1.98 (J_{DC} = 19.9 Hz) and that in **10b** is 1.43 (J_{DC} = 19.7 Hz), and mixtures of these epimers are readily assayed.

We irradiated **8b** in pentane (185 nm, 4 h, 25 °C, 38.6% conversion).[8a] The derived mixture[9] was diluted with natural abundance **5** to facilitate isolation and purification of labeled tetracycle. The **10b**/**10c** ratio in this diluted, purified tetracycle was assayed to be 2.3 by means of heteronuclear multiple quantum coherence (HMQC) ^{1}H NMR,[10] and this ratio reflects the ax/eq selectivity in the Rydberg-induced H shift. Remaining alkene **8** was also isolated, and its NMR revealed that **8b** had undergone a small amount (8.4%) of scrambling to **8c**.

Our second substrate **8c** was likewise irradiated (6 h, 24.3% conversion),[8b] and the same protocol revealed for deuterium shift a trajectory preference D_{ax}/D_{eq} = 10.2. Recovered alkene **8c** had undergone 10.8% conversion to the scrambled isomer **8b**. Since any scrambling diminishes isotopic integrity, its overall consequence would be to *lower* slightly the experimental ax/eq selectivity. Consequently, our H_{ax}/H_{eq} and D_{ax}/D_{eq} ratios of 2.3 and 10.2, respectively, represent minimum values.

That the extent of ax/eq preference differs for H and D migration indicates that the primary isotope effect (k_H/k_D) for the equatorial pathway is greater than that for the axial pathway by a factor of 4.4 (see eq 1).[11] In this connection we note that

$$\frac{H_{eq}/D_{eq}}{H_{ax}/D_{ax}} = \frac{10.2}{2.3} = 4.4 \qquad (1)$$

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(8) Suprasil-type low-pressure Hg lamp. (a) Initial concentration, 2.9 × 10^{-2} M; ^{13}C = 100.0 ± 0.6%; d_0 = 1.1%; d_1 = 91.8%; d_2 = 7.2%. (b) Initial concentration, 2.9 × 10^{-2} M; ^{13}C = 100.0 ± 0.6%; d_0 = 2.9%; d_1 = 97.1%; d_2 = 0.16%.

(9) 2-Methylenebrexane (from ring contraction) is a substantial component. Controls showed that this alkene is stable to our irradiation and undergoes no positional carbon scrambling.

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workers who used D labeling to study the stereochemistry of H shifts when carbenes rearrange to alkenes (**1** → **2**) have had to presume that k_H/k_D values for axial and equatorial pathways are equal.[1a-f] To our knowledge, the validity of this presumption has not been tested but perhaps deserves reconsideration in view of our present findings on the **2** → **1** process.

The factors responsible for the dissimilarity in isotope effects for the ax and eq trajectories in the photic **2** → **1** process are not clear. The extent of bond breaking, bond making, etc., for the two transition states could differ, in which case zero-point energy considerations would be relevant. Alternatively, H tunneling[12] might play a significant role, and if so, our isotope effects imply greater H tunneling for the equatorial trajectory. Inasmuch as D is far less subject to tunneling than H,[12,13] our D_{ax}/D_{eq} ratio may be the more genuine indicator of any inherent stereoelectronic factor in the alkene → carbene rearrangement.

Tunneling and isotope effect considerations may also be relevant in discussions of experimental H_{ax}/H_{eq} ratios[1f,14] in carbene → alkene (i.e., **1** → **2**) rearrangements.[1,2,15]

Acknowledgment. Supported by the National Science Foundation (CHE-9005952). We thank Professors E. R. Thornton, J. R. Knowles, and A. G. M. Barrett for helpful discussions.

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(14) Nickon, A. *Acc. Chem. Res.*, submitted for publication. (b) Nickon, A.; Stern, A. G.; Ilao, M. C., submitted for publication.

(15) For comments on H tunneling in rearrangements of carbenes, see ref 2e and Osamura, Y.; Shaeffer, H. F., III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904-1907. Gray, S. K.; Miller, W. H.; Yamaguchi, Y.; Shaeffer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 1900-1904.

X-ray Structure of Thiolatocopper(II) Complexes Bearing Close Spectroscopic Similarities to Blue Copper Proteins

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The synthesis and structural characterization of a thiolatocopper(II) complex which closely mimics the spectroscopic characteristics of blue copper proteins have been longtime goals in bioinorganic chemistry.[1-3] We recently reported the preparation of Cu(S*t*Bu)(HB(3,5-*i*Pr$_2$pz)$_3$) (**1**) which bears a close resemblance in its spectroscopic properties to blue copper proteins.[4] In this communication, we describe the crystal structure of an analogous thiolato complex Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**). The preliminary structure of Cu(SCPh$_3$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**3**) is also presented.

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(2) Recent reviews on the chemistry of blue copper proteins: (a) Adman, E. T. In *Metalloproteins Part 1*; Harrison, P., Ed.; Verlag Chemie: Weinheim, FRG, 1985; p 1. (b) Sykes, A. G. *Struct. Bonding* **1990**, *75*, 175. (c) Sykes, A. G. *Adv. Inorg. Chem.* **1991**, *36*, 377.

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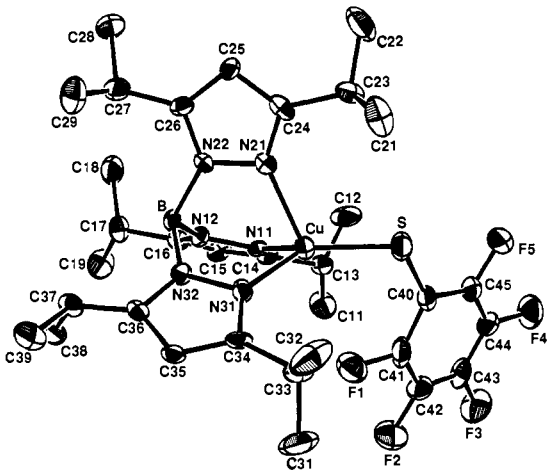

Figure 1. ORTEP view of Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**). The octane molecule of crystallization is omitted for clarity. Selected bond distances (Å) and angles (deg): Cu-S, 2.176 (4); Cu-N11, 2.037 (9), Cu-N21, 2.119 (8), Cu-N31, 1.930 (9); S-Cu-N11, 122.7 (3); S-Cu-N21, 112.7 (2); S-Cu-N31, 134.6 (3); N11-Cu-N21, 90.9 (3); N11-Cu-N31, 93.9 (4); N21-Cu-N31, 90.2 (3); Cu-S-C40, 111.7 (4).

Reactions of a bis(μ-hydroxo) complex [Cu(HB(3,5-*i*Pr$_2$pz)$_3$)]$_2$(OH)$_2$ with a variety of thiols were surveyed to ascertain whether they could afford a stable thiolatocopper(II) complex. Thus 1-4 equiv of the thiol was added into a solution of the bis(μ-hydroxo) complex in CH_2Cl_2 at -78 °C. This reaction method effected the preparation of **1** as we reported previously.[4] The thiols surveyed include almost all of the aliphatic and aromatic thiols commercially available. With most of the thiols, the addition caused instantaneous decoloration of the solution, presumably due to the facile reduction to form a copper(I) complex. With C_6F_5SH and Ph_3CSH, however, moderately stable complexes Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**) and Cu(SCPh$_3$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**3**) were successfully obtained, and both of the complexes were isolated and crystallized.[5] The absorption and EPR spectra of **2** and **3** are comparable to those of **1**, and the close spectroscopic resemblance between **1-3** and blue copper proteins, azurin (Az) and plastocyanin (Pc), is evident.[6]

Figure 1 indicates the molecular structure of **2**, which definitely establishes the monomeric structure of **2**.[7] The coordination structure of **2** is described as distorted tetrahedral, or more precisely trigonal pyramidal, with a N_3S ligand donor set. Accordingly, the copper positions close to the basal trigonal plane consisting of N11, N31, and S; the distance between the copper and the basal plane is 0.34 Å, whereas a ca. 0.70-Å separation is expected for a regular tetrahedron. The copper(II)-thiolate sulfur distance of 2.18 Å is distincly shorter than those of the synthetic copper(II) thiolato complexes reported so far (2.23-2.94 Å)[8] and comparable to those found in blue copper proteins (see

(5) Complex **2** was isolated as crystalline solids from a mixture of CH_2Cl_2/pentane/octane at -20 °C. Anal. Calcd for $C_{33}H_{46}N_6BCuF_5S$: C, 54.43; H, 6.37; N, 11.54. Found: C, 55.14; H, 6.28; N, 10.71. UV-vis (CH_2Cl_2, at 20 °C, nm, ϵ/cm^{-1} M^{-1}): 420 (630), 665 (5960), 1020 (1200). EPR (toluene, at -160 °C): $g_\parallel$, 2.30; $g_\perp$, 2.10; $A_\parallel$, 54 × 10^{-4} cm^{-1}. Complex **3** was isolated in a similar manner. Satisfactory elemental analysis was obtained. UV-vis (CH_2Cl_2, at 20 °C, nm, ϵ/cm^{-1} M^{-1}): 440 (340), 625 (6600), 910 (1230). EPR (toluene, at -160 °C): $g_\parallel$, 2.23; $g_\perp$, 2.07; $A_\parallel$, 74 × 10^{-4} cm^{-1}.

(6) Pc (spinach) UV-vis: 460 (590), 597 (4900), 770 (1670) nm. EPR: $g_\parallel$, 2.23; $g_\perp$, 2.06; $A_\parallel$, 63 × 10^{-4} cm^{-1}. Az (*A. denitrificans*) UV-vis: 460 (580), 619 (5100), 780 (1040) nm. EPR: $g_\parallel$, 2.26; $g_\perp$, 2.06; $A_\parallel$, 60 × 10^{-4} cm^{-1}. Aniscough, E. W.; Bingham, A. G.; Brodie, A. M.; Ellis, W. R.; Gray, H. B.; Loehr, T. M.; Plowman, J. E.; Norris, G. E.; Baker, E. N. *Biochemistry* **1987**, *26*, 71.

(7) **2**·0.5(*n*-C$_8$H$_{18}$) crystallized in the monoclinic space group P_{21}/a with a = 25.364 (7) Å, b = 16.166 (3) Å, c = 9.924 (3) Å, β = 90.52 (3)°, V = 4069 (3) Å^3, and Z = 4. The structure was solved by the direct method and refined anisotropically for all non-hydrogen atoms by block-diagonal least-squares techniques (TEXSAN). All hydrogen atoms except those on the octane molecule were calculated and fixed in the final refinement cycles. The current $R(R_w)$ factor is 7.28(6.29)% for 2573 reflections collected at -45 °C ($3° \le 2\theta \le 45°$, $|F_o| \ge 3\sigma|F_o|$).

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