Development of Reactions of 6- and 5-Substituted 1,3-Dimethyluracils with Dimethylsulfoxonium Methylide

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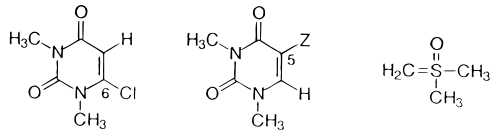
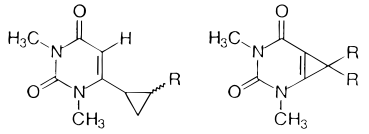
6-Chloro-1,3-dimethyluracil (**1**) reacts with dimethylsulfoxonium methylide (**3**, 2 equiv) to give sulfoxonium ylide **8** (51%). The structure of **8** is established spectroscopically and by its reactions with various electrophiles and electron-deficient olefins. Thus, **8** is converted by HCl to sulfoxonium chloride **7**, which then yields the 6-(chloromethyl)uracil **17** by heating in acetonitrile. Ylide **8** undergoes deuterium exchange at the 5-position, at its methine carbon, and into its methyl groups attached to sulfur. Reaction of **8** with benzoyl chloride gives the highly substituted ylide **19** or the nucleophilic substitution products **17** and **18** depending on reaction conditions. Treatment of **8** with electron-deficient olefins yields 6-cyclopropyluracils **20**−**31**. Many of the cyclopropyluracils have been converted to *trans*-1-(1,3-dimethyluracilyl)-2-vinylcyclopropanes and cycloheptenyluracils. Reactions of 5-substituted uracils **2** (Z = SOPh and SeOPh) with ylide **3** have been developed. 5-(Phenylsulfinyl)uracil **48** yields cyclothymine derivative **49**; 5-phenylseleninyluracil **52** gives methylide **8** as the major product.

Introduction

6-Chloro-1,3-dimethyluracil (**1**) undergoes many reactions with nucleophiles and is a useful intermediate for synthesis of 6-substituted derivatives via nucleophilic displacement.[2] Investigation has now been made of the behavior of **1** and 5-substituted 1,3-dimethyluracils (**2**) with dimethylsulfoxonium methylide (**3**) and determination of the products thereof. Further objectives of this study are synthesis of 6-cyclopropyluracils (**4**), their transformations, and various 5,6-uracilocyclopropenes (**5**).



1 **2** **3**

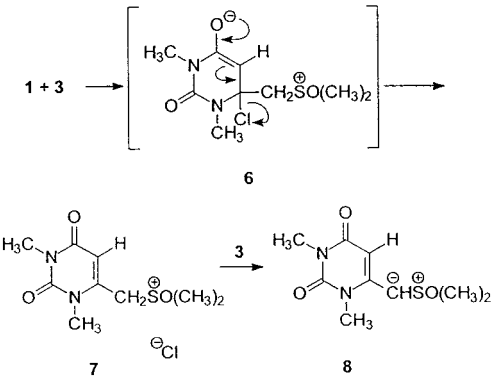


4 **5**

Results and Discussion

Reaction of **1** with **3** (2.2 equiv, prepared from trimethylsulfoxonium chloride and sodium hydride[3]) in THF at 20−25 °C gives crystalline dimethylsulfoxonium (1,3-dimethyl-6-uracilyl)methylide (**8**, Scheme 1) in 51% yield.[4] Ylide **8** is a stable solid (mp 193−195 °C) that is storable for months and whose structure is assigned from its elemental analysis, its mass, ^{1}H and ^{13}C NMR spectra, and its chemical behavior as will be described. A likely mechanism for formation of **8** involves attack of **3** at C-6 of **1**, loss of chloride ion from **6**, and then deprotonation of sulfoxonium chloride **7** by the second equivalent of **3** (Scheme 1).

Scheme 1



The ^{1}H NMR of **8** raises questions as to the exact structure of the ylide. The ^{1}H NMR signal for the proton attached at the methanide carbon of **8** is a sharp singlet at 4.25 ppm. Dimethylsulfoxonium 3-methylides **9** and **10**, however, exhibit broad signals for their methine protons on carbon adjacent to sulfur.[5] The broad singlets in **9** and **10** signal the possibility of exocyclic cis−trans geometrical isomerism at C-3 and interconversions as illustrated for **9** by **11** and **12** (eq 1). The proton NMR of **8** suggests that the ylide is a single geometric isomer, presumably **13**. A second geometric isomer, **14**, is less favorable because of steric interactions between the

(1) Present address: Department of Chemistry, Youngstown State University, 1 University Plaza, Youngstown, OH 44555-3663.

(2) (a) Pfleiderer, W.; Schündehütte, K.-H. *Liebigs Ann. Chem.* **1958**, 158. (b) Strauss, G. *Liebigs Ann. Chem.* **1960**, 205. (c) Pfleiderer, W.; Ram, V. J.; Knappe, W. R. *Liebigs Ann. Chem.* **1982**, 762.

(3) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(4) Similar methodology for functionalization of various heterocycles with diphenylsulfonium methylide and **32** has been employed by: (a) Taylor, E. C.; Martin, S. F. *J. Am. Chem. Soc.* **1972**, *94*, 2874. (b) Taylor, E. C.; Martin, S. F. *J. Am. Chem. Soc.* **1972**, *94*, 6218. (c) Taylor, E. C.; Martin, S. F. *Heterocycles* **1973**, 1, 59.

(5) Tamura, Y.; Miyamoto, T.; Nishamura, T.; Eiho, J.; Kita, Y. *J. Chem. Soc., Perkin Trans.* 1 **1974**, 102.

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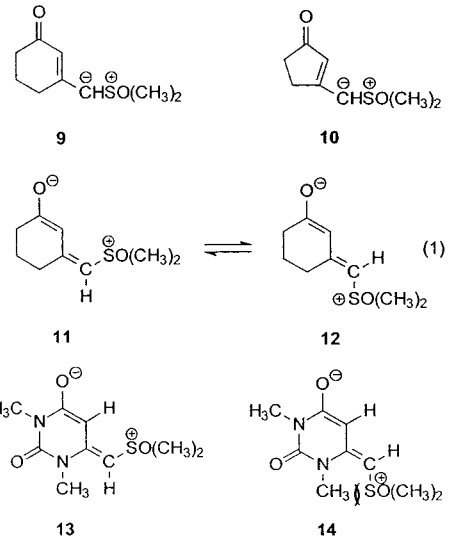
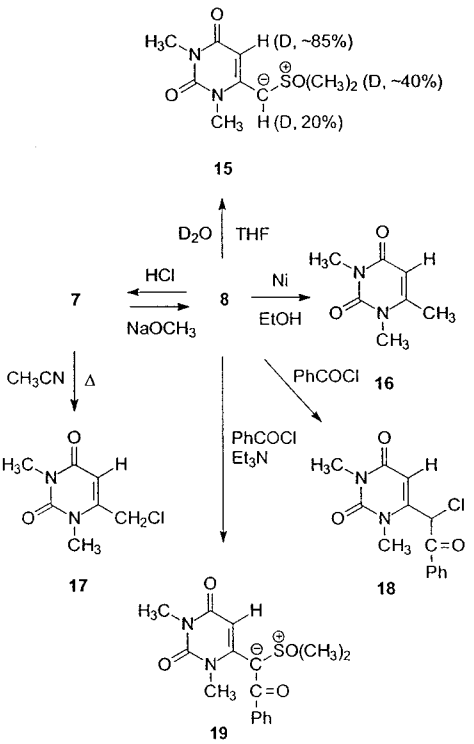
sulfoxonium moiety and the methyl group attached to N-1 of the uracil ring.



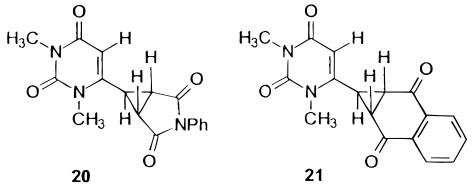
Ylide **8** undergoes many reactions (Scheme 2) that are consistent with its assigned structure. Hydrogen chloride in acetone or aqueous hydrochloric acid in acetonitrile at 0 °C converts **8** to sulfoxonium chloride **7** (72%), a readily handled solid. Sodium methoxide in methanol at room temperature effects deprotonation of **7** to **8**. Refluxing **8** in THF containing deuterium oxide resulted in **15** (Scheme 2) with ~85% deuterium at C-5 of the uracil ring, ~20% at the methanide carbon, and ~40% into the methyl groups attached to sulfur. As expected, deuterium was not exchanged into the N-1 or the N-3 methyl groups of **8**.

Scheme 2



Raney nickel in ethanol−water at 20−25 °C effects reductive elimination of the dimethylsulfoxonium moiety in **8** to yield 1,3,6-trimethyluracil[6] (**16**, 92%). Further, displacement of the dimethylsulfoxonium group by chloride ion to give 6-(chloromethyl)uracil **17** (72%) and dimethyl sulfoxide occurs upon heating **8** in acetonitrile. Of value in synthesis is that benzoyl ylide **19** (72%) is obtained from **8** and benzoyl chloride in acetonitrile in the presence of triethylamine. In the absence of triethylamine, benzoyl chloride and **8** in refluxing acetonitrile yield 6-(α-chlorophenacyl)uracil **18** (34%) along with **17** (42%). In the latter experiment, **18** is presumably formed by benzoylation of **8** and displacement of dimethyl sulfoxide by chloride ion. As previously described, **17** is readily formed by reaction of chloride ion with **7** as now generated in situ.

Sulfoxonium ylide **8** reacts with olefinic Michael acceptors with extrusion of dimethyl sulfoxide to give (6-uracilyl)cyclopropanes. Thus, **8** and *N*-phenylmaleimide (1.5 equiv) in refluxing acetonitrile yield *trans*-3-(6-uracilyl)-1,2-cyclopropanedicarboximide **20** (91%). The structural assignment of **20** is based on its elemental analysis, ^{1}H and ^{13}C NMR, and MS and on precedent.[7] The ^{1}H NMR triplet at δ 2.73 with $J = 2.9$ Hz and the doublet at δ 2.93 with $J = 3.3$ Hz support the assignment that the dimethyluracilyl and the phenylmaleimido groups are trans. Trans coupling constants in cyclopropanes generally fall within the range 3−5 Hz, whereas those for cis coupling usually lie in the 6−10 Hz range.[8]

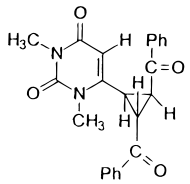


Further, 1,4-naphthoquinone undergoes addition of **8** in acetonitrile at ~82 °C followed by expulsion of dimethyl sulfoxide to yield *trans*-cyclopropane **21** (61%). The cyclopropyl hydrogens in the cycloadduct have coupling constants of ~5 Hz that are consistent with the assignment of **21** as trans. As in formation of **20**, avoidance of severe steric repulsion around the cyclopropyl ring explains exclusive formation of **21**.

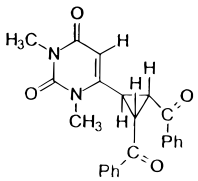
Ylide **8** also effects efficient cyclopropanations of electron-deficient, acyclic disubstituted olefins. For example, **8** reacts with *trans*-dibenzoylethylene in acetonitrile to give, after chromatography, isomers **22** and **23** in an 8:1 ratio and 71% overall yield. The first product to elute is **22**, the cyclopropane having one benzoyl group cis and the second trans to its dimethyluracil group. Stereochemical assignment of **22** is made from its ^{1}H and ^{13}C NMR spectra. Cycloadduct **22** exhibits distinct absorbances for three different cyclopropyl hydrogens and three different cyclopropyl carbons. The coupling constants for the hydrogen on the cyclopropyl carbon to which the uracil group is attached are 6.2 and 9.2 Hz and thus indicate that this proton is trans to a second proton and cis to a neighbor substituent. The second cycloadduct has a much simpler ^{1}H NMR spectrum than does **22**. ^{1}H NMR absorptions for all of its cyclopropyl protons occur between δ 3.4 and 3.5, and, since the ^{13}C NMR spectrum reveals resonances for only two types of

(6) Egg, H.; Volgger, I. *Synthesis* **1982**, *12*, 1071.
(7) Trost, B. M.; Melvin, L. S. In *Sulfur Ylides*; Academic Press: New York, 1975; and references therein.
(8) Morris, D. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 1987; p 116.

cyclopropyl carbons, this isomer is assigned as **23**. There is no evidence for formation of the relatively highly strained all cis isomer in these experiments.

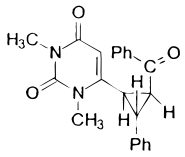


22

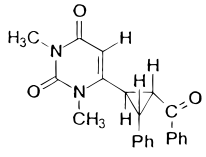


23

trans-Benzylideneacetophenone reacts readily with **8** to yield two separable cyclopropanes, **24** and **25**, in a 1:1 ratio in 63% total yield. Each product exhibits coupling constants of ~5.3 and 8.4 Hz for its cyclopropyl hydrogen adjacent to its uracil ring. A conclusion is that the hydrogen is cis to one hydrogen and trans to a second hydrogen in the cyclopropyl ring of each product. Choice as to which products are **24** and **25** cannot be made, however, on the basis of present NMR data. As will be indicated later, in all cases uracilylcyclopropanes containing cis highly polar substituents on C-2 (β positions) of their cyclopropyl rings elute more slowly on column chromatography and melt higher than do their corresponding trans isomers. On such bases the structures of the products of cyclopropanations of *trans*-benzylideneacetophenone with **8** are assigned provisionally as **24** and **25**, respectively.

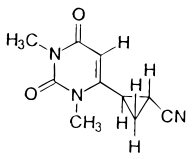


24

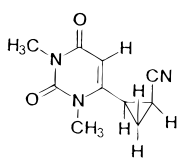


25

Monoactivated Michael acceptors are also effectively cyclopropanated by **8**. For example, acrylonitrile and **8** at 40 °C in acetonitrile give *trans*- and *cis*-cyclopropanes **26** and **27** in ~2:1 ratio in 67% yield. Isomers **26** and **27** are separable by chromatography on silica gel and crystallization from $CHCl_3/Et_2O$. Cyclopropane **26** is assigned as having its cyano and dimethyluracil groups trans on the basis of the ^{1}H NMR coupling constants for its cyclopropyl hydrogens. Values of 4.0 and 8.4 Hz from **26** for the proton on carbon attached to a cyano group indicate that this hydrogen is cis to only one other proton. The corresponding coupling constants for the hydrogen atom on the cyclopropyl carbon adjacent to the uracil group in **27** are 7.6 and 11.5 Hz, thus indicating that the proton is cis to two cyclopropyl hydrogen neighbors. In further support of the stereochemical assignments, the product designated as the cis isomer **27** is eluted on silica more slowly and has a higher melting point than does the trans product **26**.

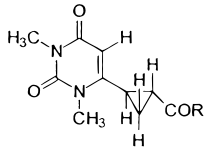


26

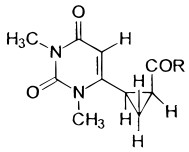


27

trans- and *cis*-cyclopropanes are also obtained in reactions of **8** with acrolein and with methyl vinyl ketone. Acrolein and **8** give **28** and **29** in a 4.25:1 ratio (94% yield), and methyl vinyl ketone and **8** form **30** and **31** in 6:1 ratio (91% yield). As in the previous examples, the stereochemistry of a present cycloadduct is assigned from the ^{1}H NMR coupling constants of its cyclopropyl hydrogens, its chromatographic properties, and the melting points of the members of the isomeric cyclopropane product pair. Thus, the NMR signal of the cyclopropyl hydrogen adjacent to the dimethyluracil group in **28** reveals coupling to two trans protons (J = 5.6, 4.8 Hz) and one cis proton (J = 10.1 Hz). In **29**, coupling constants of 6, 8, and 8 Hz for the methylene proton trans to the uracil ring and the aldehyde group indicate that the proton is cis to two vicinal neighbors. Coupling constants in **30** for the proton on carbon to which the acetyl group is attached are 5.1, 4.5, and 8.6 Hz, and thus, this proton is trans to two hydrogen neighbors and cis to another. The corresponding proton in isomer **31** is cis to two adjacent protons as evidenced by coupling constants of 8.1 and 14 Hz. In support of the stereochemical assignments of **28**−**31**, cis isomers **29** and **31** are eluted more slowly on silica gel and melt higher than their respective trans isomers **28** and **30**. Further, the trans/cis ratios of the cyclopropanes from reactions of **8** with acrylonitrile, acrolein, and methyl vinyl ketone show that as the alkene substituent becomes bulkier, the proportion of trans cycloadduct formed increases. Such effects are expected since substituents cis rather than trans to the dimethyluracil groups in the cyclopropanes result in steric repulsion.



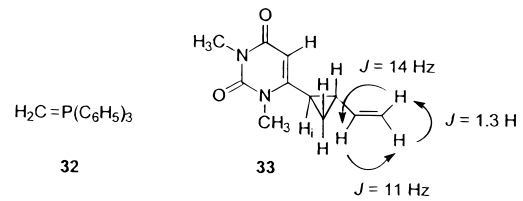
28, R = H
30, R = CH_3



29, R = H
31, R = CH_3

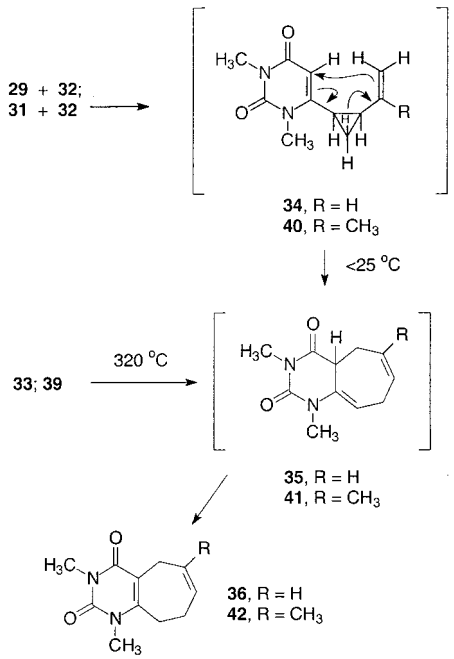
Reactions of carbonylcyclopropanes **28**−**31** with the Wittig ylide methylenetriphenylphosphorane (**32**)[9] were then investigated in order to prepare uracil derivatives. *trans*-Uracilylcyclopropanecarboxaldehyde **28** reacts with **32** at −78 to +25 °C to give *trans*-uracilyl(vinyl)cyclopropane **33** (91%). Assignment of **33** is made from DEPT ^{13}C multiplicities and from the ^{1}H NMR coupling constants of its terminal vinyl group. The ^{13}C NMR of **33** shows signals at 98.7 ppm for C-5 in the uracil ring (one proton attached), 115.5 ppm for the terminal vinyl carbon (two protons attached), and 137.7 ppm for the internal vinyl carbon (one proton attached). Further, the ^{1}H NMR of **33** reveals couplings of 1.3 Hz between the geminal protons and of 14 and 11 Hz between the trans- and the cis-vicinal protons of the vinyl group. Couplings of 5.5, 4.1, and 6.9 Hz for the methine ring proton (H_i in **33**) confirm that this hydrogen is cis to one neighbor. The corresponding proton in a *cis*-divinylcyclopropane will have two cis neighbors and therefore two large coupling constants.

(9) March, J. In *Advanced Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1992; p 956 and references therein.

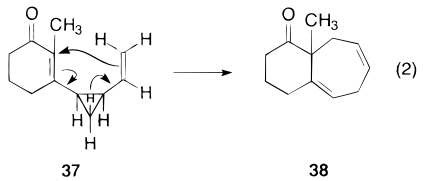


cis-Uracilylcyclopropanecarboxaldehydes **29** and **32** react while warming from −78 to +25 °C to yield cycloheptenouracil **35** (Scheme 3, 63%) as a crystalline

Scheme 3

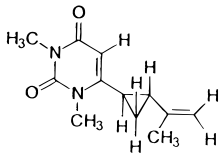


solid. Formation of *cis*-divinylcyclopropane **34**, the expected Wittig product, is likely the first step in the transformation to **35**. Intermediate **34** has its vinyl and uracilyl groups properly aligned for rapid [3,3] sigmatropic rearrangement[10] to **35**. Isomerization of **35**, possibly through its enol, then yields the more highly conjugated derivative **36** (Scheme 3). Conversion of **34** to **35** is similar to the spontaneous rearrangement of *cis*-vinylcyclopropylcyclohexenone **37** to cycloheptadienocyclohexane **38** (eq 2).[11] Further, heating **33** (Scheme 3) for 30 h



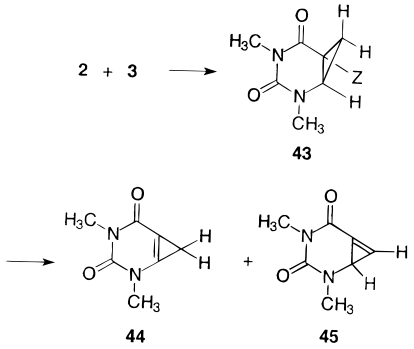
at 320 °C in *o*-dichlorobenzene yields **36** efficiently. Although rearrangement of **33** is not nearly as facile as for **34**, reorganization of the stereochemistry after breaking the three-membered ring in **33** allows proper orbital interaction for the thermal conversion to **35**, which then converts to **36**.

trans-2-Acetylcyclopropyluracil **30**, a methyl ketone homologue of **28**, is converted by phosphorane **32** at −70−25 °C to *trans*-divinylcyclopropane derivative **39** (91%). The behavior of **30** is therefore similar to that of **29** with **32**. Uracilylcyclopropane **39** is assigned from its analyses and its ^{1}H NMR signals at 4.8 ppm for its terminal olefin protons and at 5.5 ppm for its C-5 uracilyl proton as follows. The latter signal is a finely split doublet (J = 0.8 Hz) because of allylic coupling with the hydrogen on the cyclopropyl carbon attached to the uracilyl group. This cyclopropyl hydrogen is coupled to two trans neighbors (J = 6, 6.8 Hz) and one cis neighbor (J = 12.8 Hz), and thus, the stereochemistry of **39** as a *trans*-cyclopropane is established.



Reaction of *cis*-2-acetylcyclopropyluracil **31** with **32** (Scheme 3) occurs on warming above −70 °C to give cycloheptenyluracil **42** (75%) presumably upon formation and spontaneous rearrangement of *cis*-divinylcyclopropane **40** followed by tautomeric isomerization via **41**. Production of **42** so readily from **31** and **32** illustrates again vividly the importance of precise stereochemistry in divinylcyclopropane rearrangements. As to be expected, pyrolysis of *trans*-divinylcyclopropane **39** (Scheme 4) at 320 °C also produces **42** (70%). Of particular

Scheme 4



significance to the structural assignment of **42** is the ^{1}H NMR absorption for only one vinyl hydrogen at 5.3 ppm, which is coupled to the allylic methyl group (J = 1.4 Hz) and adjacent aliphatic protons (J = 4 Hz). As with **36**, there is no signal for a proton at C-5 in the uracil ring of **42**.

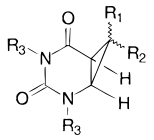
Investigation was then initiated of reactions of **3** with 5-substituted uracils **2** to form 5-substituted 5,6-methanouracils **43** (cyclothymines), which might eliminate to uracilocyclopropenes **44** and (or) **45** (Scheme 4). Uracils such as **44** and **45** are unknown and are of biochemical and medical interest as thymine mimics and for the great reactivities expected for their cyclopropene double bonds. Reaction of 1,3-dimethyluracil (**2**, Z = H) with **3** has been previously reported to give cyclothymine **46a**,[12] 1,3-

(10) Hudlicky, T.; Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org. React.* **1992**, *41*, 1.

(11) For example, see: (a) Marino, J. P.; Kanecko, T. *J. Org. Chem.* **1974**, *39*, 3175. (b) Bradbury, R. H.; Gilchrist, T. L.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3225.

(12) (a) Kunieda, T.; Witkop, B. *J. Am. Chem. Soc.* **1969**, *91*, 7751. (b) Kunieda, T.; Witkop, B. *J. Am. Chem. Soc.* **1971**, *93*, 3478. (c) Torrence, P. F.; Witkop, B. *Biochemistry* **1972**, *11*, 1731.

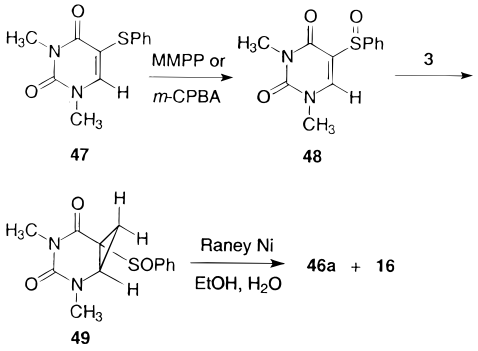
dibenzyluracil, and phenylmercuric bromodichloromethane yield cyclothymine **46b**,[13] and (*E*)- and (*Z*)-cyclothymines **46c** are obtained by addition−displacements of 5-bromo-1,3-dimethyluracil by sodium ethyl phenylacetate.[14]



46a, R_1, R_2 = H; R_3 = CH_3
46b, R_1, R_2 = Cl; R_3 = $CH_2C_6H_5$
46c, R_1 = C_6H_5; R_2 = CO_2Et; R_3 = $CH_2C_6H_5$

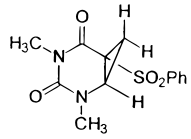
In present efforts to prepare 5-bromo-5,6-methanouracil **43** (Z = Br) for possible synthesis of **44** and/or **45**, reactions of **2** (Z = Br) with **3** (Scheme 4) or with **32** in THF at 0−25 °C are found to give inseparable polar products. However, 5-(phenylsulfinyl)uracil **48**, as obtained by oxidation of 5-(phenylsulfenyl)uracil **47**[15] with magnesium monoperoxyphthalate (MMPP, 59% yield) in ethanol/water or *meta*-chloroperoxybenzoic acid (*m*-CPBA, 80% yield) in methylene chloride, and **3** yield (phenylsulfinyl)cyclothymine **49** (68%, Scheme 5). Cyclothymine **49** is assigned from its analysis, its detailed NMR and MS properties, and its reduction by Raney nickel in water/ethanol to 1,3-dimethylcyclothymine (**46a**, 16%) and 1,3,6-trimethyluracil (**16**, 42%).

Scheme 5



47 **48** **49**

Since sulfoxides having cis β-hydrogens eliminate thermally to olefins and sulfenic acids (RSOH),[16] cyclothymine **49** was heated in various solvents for possible preparation of **44** and/or **45**. In refluxing THF for 12 h or in toluene in sealed tubes at 180 °C, **49** is stable. Pyrolyses of **49** in sealed tubes in xylenes at 270 °C, toluene at 240 °C, and acetonitrile at 200 and 280 °C give complex mixtures containing at least four compounds that could not be separated preparatively. Decomposition of **49** in the presence of anthracene at 275 °C in xylenes in efforts to trap **44** and/or **45** by Diels−Alder reactions gives a product mixture identical with that obtained in the absence of the trapping agent. 5-(Phenylsulfonyl)-uracil **50**, prepared by oxidation (88% yield) of **49** with MMPP in ethanol/water is more resistant to pyrolytic elimination than its precursor and does not serve as a preparative source of **44** or **45**.



50

Study was then directed to syntheses of 5-(phenylselenyl)uracil **51**, 1,3-dimethyl-5-phenylseleninyluracil **52**, and 5,6-methano-5-(phenylseleninyl)uracil **53** as in Scheme 6. Seleninylcyclothymine **53** is expected to eliminate at lower temperatures than does **49**. Selenyluracil **51** is readily prepared (80%, Scheme 6) by phenylselenation of **2** (Z = H) with diphenyl diselenide (1 equiv) and ammonium peroxydisulfate (2 equiv) in refluxing ethanol. Uracil **51** is assigned from its elemental, NMR, IR, and MS analyses. It has been previously established[17] that $(C_6H_5)_2Se_2/(NH_4)_2S_2O_8$ functions as an electrophilic phenylselenylating ($C_6H_5Se^+$) agent, and uracils undergo substitutions at their C-5 positions upon reactions with various electron-deficient reagents.[18] The assignment of **51** as the 5-isomer follows from the signal at 7.46 ppm in its proton NMR spectrum, which is typical for H-6 in 1,3-dimethyluracils. Synthesis of **51** has since been reported by a similar method in which [bis(trifluoroacetoxy)iodo]benzene was used to oxidize diphenyl diselenide in the presence of 1,3-dimethyluracil.[19] Oxidation of **51** with MMPP in ethanol/water then gives **52** (88%, Scheme 6).

Reaction of **52** with excess **3** (4 equiv) in THF at 20−25 °C followed by column chromatography using methanol/chloroform as eluents is of particular interest in that the principal product is **8** (34%, Scheme 6). Formation of **8** apparently arises from Michael-like addition of **3** to **52**, proton transfer in **54**, and elimination of PhSeOH in **55** (Scheme 6). Seleninyluracil **52** is as yet not usable for preparing **44** or **45**.

Study is now being made of the behavior of **52** with other methylene-transfer reagents and of syntheses of cyclothymines with appropriate leaving groups at C-6 and C-7 for use in preparing **44** and **45**.

Experimental Section

General Procedures. Melting points are uncorrected. Mass spectra were obtained in EI mode at 70 eV. ^{1}H NMR were recorded at either 200, 250, or 300 MHz; ^{13}C NMR were determined at 75 MHz. All NMR spectra were obtained for solutions in $CDCl_3$ or $(CD_3)_3SO$ as noted. Flash chromatography[20] was performed on silica gel 60 (230−400 mesh, E. Merck) and thin-layer chromatography (TLC) on aluminum-backed plates of silica gel 60 F254 (E. Merck). Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)dimethyloxosulfonium Methanide (8). Sodium hydride (2.52 g, 63.0 mmol as a 60% dispersion in mineral oil) was syringe-washed with Et_2O. The system was evacuated and purged with argon, and trimethylsulfoxonium chloride (8.09 g, 63.0 mmol) was added followed by anhydrous THF (200 mL). The resulting

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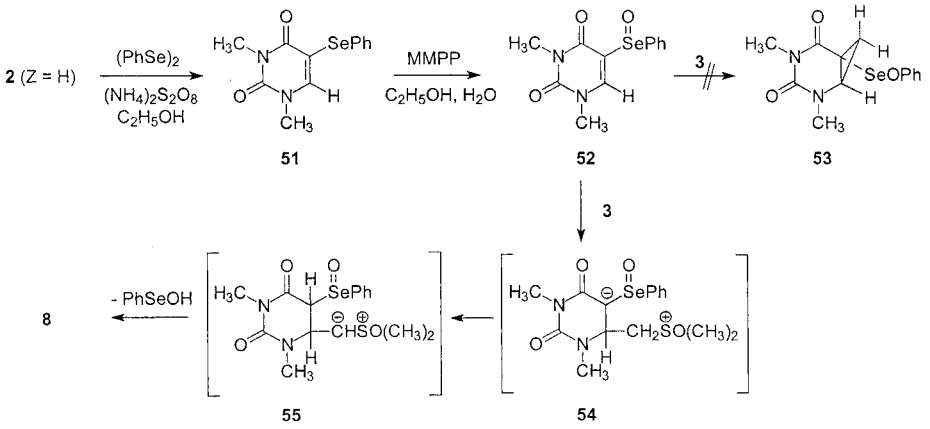
Scheme 6



suspension was stirred and vigorously refluxed for 3 h, after which time evolution of hydrogen ceased. The milky white mixture was cooled to 0 °C, and 6-chloro-1,3-dimethyluracil (**1**, 5.0 g, 28.6 mmol) in anhydrous THF (100 mL) was added over 30 min. The mixture was stirred at room temperature for 18 h, cooled to 0 °C, and filtered. The solid was washed with anhydrous THF and then extracted with boiling acetone. Removal of the acetone in vacuo gave a colorless solid (3.45 g) that was recrystallized from acetone to yield **8** (3.3 g, 51%) as colorless crystals: mp 193−195 °C; ν_{max} (KBr) 1690, 1630 cm^{-1}; ^{1}H NMR (DMSO-d_6) 3.07 (s, 3H), 3.17 (s, 3H), 3.51 (s, 6H), 4.25 (s, 1H), 5.06 (s, 1H); ^{13}C NMR (DMSO-d_6) 27.7, 38.8, 39.7, 40.0, 40.3, 57.7, 81.6, 153.3, 154.8, 163.4; found M$^+$ 230.0763, $C_9H_{14}N_2O_3S$ requires *m*/*z* 230.0735. Anal. Calcd for $C_9H_{14}N_2O_3S$: C, 46.94; H, 6.13. Found: C, 47.03; H, 6.12.

(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)dimethyloxosulfonium Chloride (7). Ylide **8** (230 mg, 1.0 mmol) was dissolved in refluxing acetone (100 mL). Hydrogen chloride was bubbled through the solution for 10 min, during which time a solid precipitated. The solution was cooled to 0 °C and filtered. Recrystallization of the solid from methanol−benzene yielded colorless crystals of sulfoxonium salt **7** (170 mg, 0.72 mmol, 72% yield): mp 133−135 °C; ν_{max} (KBr) 1690, 1670 cm^{-1}; ^{1}H NMR (DMSO-d_6) 2.53 (s, 6H), 3.14 (s, 3H), 3.35 (s, 3H), 4.75 (s, 2H), 5.96 (s, 1H); ^{13}C NMR (DMSO-d_6) 27.6, 31.1, 40.4, 41.4, 101.6, 126.9, 161.5; found M$^+$ 231.0735, $C_9H_{15}N_2O_3SCl$ requires *m*/*z* 231.0803. Anal. Calcd for $C_9H_{15}N_2O_3SCl$: C, 40.59; H, 5.68. Found: C, 40.34; H 5.69.

Alternatively, methanide **8** (100 mg, 0.43 mmol) was stirred with concentrated hydrochloric acid (0.5 mL) in dry acetonitrile (5 mL) at 0 °C for 30 min. The resulting solid was filtered and washed with dry acetone to leave colorless crystals of **7**, mp 134−135 °C. The ^{1}H and ^{13}C NMR of the product are identical with that of **7** prepared above.

Regeneration of Ylide 8. Sodium methoxide (17.0 mg, 0.3 mmol) was added to a solution of sulfoxonium salt **7** (50.0 mg, 0.2 mmol) in dry methanol (10 mL). After the mixture was stirred at room temperature for 2 h, the solvent was evaporated in vacuo to leave a colorless residue to which ethanol (15 mL) was added. The solution was filtered and evaporated to ~3 mL, and Et_2O was then added until the solution became cloudy. Filtration yielded colorless crystals of methanide **8** (35.0 mg, 73%), mp 190−193 °C. The ^{1}H NMR (DMSO-d_6) of the product agreed with that of **8** previously prepared.

1,3,6-Trimethyluracil (16). Ylide **8** (50 mg, 0.217 mmol) was dissolved in a 1:1 mixture of water and ethanol (10 mL), and Raney nickel (~100 mg, 50% slurry in water) was added. The mixture was stirred at room temperature for 30 min and filtered. The solvents were removed in vacuo, and the residue was dissolved in $CHCl_3$ and then washed with water. The organic layer was dried ($MgSO_4$), filtered, and evaporated to a colorless oil. Chromatography (silica gel, 2 g) using petroleum ether−EtOAc (1:3) as eluent afforded **16** as a colorless solid (34 mg, 0.2 mmol, 92%): mp 104−106 °C; ν_{max} ($CHCl_3$) 1702, 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.22 (s, 3H), 3.30, 3.38 (2 s, 6H), 5.59 (s, 1H); ^{13}C NMR ($CDCl_3$) 20.1, 27.9, 31.6, 101.2, 151.3, 152.5, 162.4; found M$^+$ 154.0740, $C_7H_{10}N_2O_2$ requires *m*/*z* 154.0740. The physical properties of **16** agree with those of an authentic sample.[6]

6-(Chloromethyl)-1,3-dimethyluracil (17). Sulfoxonium salt **7** (50.0 mg, 0.19 mmol) was suspended in dry acetonitrile (5 mL), and the solution was refluxed for 2 h. Evaporation of the solvent in vacuo left a colorless oil that, on chromatography on silica gel (5 g) using petroleum ether−EtOAc (2:1) as eluent, yielded colorless crystals of chloromethyl derivative **17**: mp 86−88 °C; ν_{max} ($CHCl_3$) 1705, 1667 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.31 (s, 3H), 3.49 (s, 3H), 4.29 (s, 2H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$) 28.1, 31.4, 41.3, 103.0, 148.7, 152.3, 162.1; found M$^+$ 188.0367, $C_7H_9N_2O_2Cl$ requires *m*/*z* 188.0353. Anal. Calcd for $C_7H_9N_2O_2Cl$: C, 44.67; H, 4.82. Found: C, 44.62; H, 4.80.

6-(Benzoyldimethylsulfoxonium)-1,3-dimethyluracil Methylide (19). Benzoyl chloride (0.15 g, 1.1 mmol) was added to a solution of methylide **8** (0.23 g, 1.0 mmol) and triethylamine (0.11 g, 1.0 mmol) in dry acetonitrile (50 mL), and the mixture was stirred at room temperature for 2 h. After removal of the solvent in vacuo, the residue was adsorbed onto silica gel and chromatographed using $CHCl_3$−methanol (20:1) as eluent. The residue obtained was triturated with Et_2O to give colorless crystals of methylide **19** (0.24 g, 0.72 mmol, 72% yield): mp 88−90 °C; ν_{max} ($CHCl_3$) 1698, 1652 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.30 (s, 3H), 3.41 (s, 3H), 3.60 (s, 3H), 3.71 (s, 3H), 5.69 (s, 1H), 7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) 27.9, 33.6, 42.1, 42.7, 45.6, 78.7, 110.0, 127.0, 128.3, 130.9, 138.5, 146.1, 152.5, 162.0, 183.2; found M$^+$ 334.0989, $C_{16}H_{18}N_2O_4S$ requires *m*/*z* 334.0987. Anal. Calcd for $C_{16}H_{18}N_2O_4S$: C, 54.47; H, 5.43. Found: C, 54.21; H, 5.52.

6-(α-Chlorophenacyl)-1,3-dimethyluracil (18) and 6-(Chloromethyl)-1,3-dimethyluracil (17). A solution of ylide **8** (0.23 g, 1.0 mmol) and benzoyl chloride (0.15 g, 1.1 mmol) in acetonitrile (50 mL) was refluxed for 1 h. The solvent was evaporated and the residue applied to a column of silica gel. Elution with petroleum ether−EtOAc (1:1) afforded two colorless solids. The first product eluted was identified as **18** (0.10 g, 0.34 mmol, 34%): mp 162−164 °C; ν_{max} ($CHCl_3$) 1707, 1662, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.32 (s, 3H), 3.43 (s, 3H), 5.97 (s, 1H), 6.09 (s, 1H), 7.48−7.97 (m, 5H); ^{13}C NMR ($CDCl_3$) 28.2, 32.1, 57.0, 104.0, 129.0, 129.3, 133.0, 135.0, 148.1, 152.2, 161.7, 188.0; found M$^+$ 292.0579, $C_{14}H_{13}N_2O_3Cl$ requires *m*/*z* 292.0615.

The second product eluted was identical with **17** produced above (0.08 g, 0.42 mmol, 42%): mp 86−88 °C.

***trans*-6-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)-3-phenyl-3-azabicyclo[3.1.0] hexane-2,4-dione (20).** A solution of uracil methanide **8** (230 mg, 1.0 mmol), *N*-phenylmaleimide (260 mg, 1.5 mmol), and dry acetonitrile (25 mL) was refluxed for 5 h. After removal of the acetonitrile in vacuo, the residue was taken up in water and extracted with $CHCl_3$. The combined organic extracts were washed with saturated brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel using petroleum ether−ethyl acetate (1:1) as eluent to give cyclo-

propane **20** as a colorless solid (295 mg, 91%, recrystallized from ethanol): mp 258−261 °C; ν_{max} ($CHCl_3$) 1785, 1724, 1666 cm^{-1}; ^1H NMR ($CDCl_3$) 2.73 (t, 1H, J = 3.0 Hz), 2.93 (d, 2H, J = 3.0 Hz), 3.34 (s, 3H), 3.59 (s, 3H), 5.64 (s, 1H), 7.23 (m, 5H); ^{13}C NMR ($CDCl_3$) 26.5, 28.1, 31.9, 32.0, 100.8, 126.2, 128.9, 128.3, 130.9, 147.6, 151.9, 161.8, 170.8; found M^+ 325.1074, $C_{17}H_{15}N_3O_4$ requires *m/z* 325.1062. Anal. Calcd for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65. Found: C, 62.86; H, 4.72.

***trans*-1-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)-1a,7a-dihydro-1*H*-cyclopropa[b]naphthalene-2,7-dione (21).** Ylide **8** (0.23 g, 1.0 mmol) and 1,4-naphthoquinone (0.24 g, 1.5 mmol) were refluxed in acetonitrile (10 mL) for 24 h. After the solvent had been evaporated under reduced pressure, the residue was dissolved in $CHCl_3$ and the solution washed with water. Drying ($MgSO_4$) and evaporation afforded a yellow oil that was then chromatographed (silica gel, petroleum ether−EtOAc 1:1) to afford **21** as an unstable yellow solid (0.19 g, 61%): mp >300 °C; ν_{max} ($CHCl_3$) 1710, 1690, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) 2.75 (t, 1H, J = 3.3 Hz), 2.97 (d, 2H, J = 3.5 Hz), 3.33 (s, 3H), 3.45 (s, 3H), 5.77 (s, 1H), 7.80−8.11 (m, 4H); ^{13}C NMR ($CDCl_3$) 26.9, 31.9, 32.4, 33.6, 100.6, 127.9, 130.7, 149.1, 151.9, 162.1, 165.9, 189.6; found M^+ 310.0973, $C_{17}H_{14}N_2O_4$ requires *m/z* 310.0953.

1-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)-2,3-dibenzoylcyclopropanes (22 and 23). A solution of **8** (230 mg, 1.0 mmol) and 1,2-*trans*-dibenzoylethylene (354 mg, 1.5 mmol) in dry acetonitrile (15 mL) was refluxed for 8 h. The solvent was removed, and the residue was chromatographed on silica gel (petroleum ether−EtOAc 1:1 as eluent) to give two isomeric cyclopropanes. The first product eluted was recrystallized from ethanol to yield colorless crystals of **22** (244 mg, 63%): mp 210−212 °C; ^1H NMR ($CDCl_3$) 3.11 (m, 1H), 3.32 (s, 3H), 3.34 (s, 3H), 3.80 (m, 1H), 3.99 (m, 1H), 5.86 (s, 1H), 7.50 (m, 6H); ^{13}C NMR ($CDCl_3$) 27.9, 30.7, 31.9, 32.7, 33.9, 103.2, 128.4, 128.5, 129.0, 134.2, 134.3, 136.0, 136.2, 148.2, 152.2, 162.1, 192.2, 195.0. The second product eluted was a colorless oil (31 mg, 8%) identified as **23**: ^1H NMR ($CDCl_3$) 3.36 (s, 3H), 3.40 (m, 3H), 3.60 (s, 3H), 5.74 (s, 1H), 7.41 (m, 10H). For a mixture of the two isomers: ν_{max} ($CHCl_3$) 3019, 1702, 1662, 1621, 1597 cm^{-1}; found M^+ 388.1423, $C_{23}H_{20}N_2O_4$ requires *m/z* 388.1457. Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 70.20; H, 5.36. Found: C, 69.72; H, 5.18.

1-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)-2-benzoyl-3-phenylcyclopropanes (24 and 25). A solution of ylide **8** (100 mg, 0.42 mmol) and *trans*-benzylideneacetophenone (265 mg, 1.30 mmol) in dry acetonitrile (15 mL) was refluxed for 36 h. After solvent removal, the residue was chromatographed (silica gel, petroleum ether−EtOAc, 2:1 as eluent) to yield two isomeric cyclopropanes **24** and **25**. The first product eluted was **24**, a colorless oil that crystallized from $CHCl_3$−Et_2O (50 mg, 32%): mp 145−147 °C; ν_{max} ($CHCl_3$) 3019, 1701, 1660, 1618, 1449 cm^{-1}; ^1H NMR ($CDCl_3$) 3.10 (m, 2H), 3.28 (s, 3H), 3.34 (s, 3H), 3.66 (m, 1H), 5.86 (s, 1H), 7.20 (m, 5H), 7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) 27.9, 29.9, 31.9, 32.5, 35.3, 102.3, 127.0, 127.9, 128.2, 128.9, 133.6, 133.9, 136.6, 149.6, 152.1, 162.3, 196.1; found M^+ 360.1522, $C_{23}H_{20}N_2O_4$ requires *m/z* 360.1570.

The second product eluted was **25**, an oil that upon trituration with Et_2O gave a colorless solid (48 mg, 31%) that was recrystallized from $CHCl_3$−Et_2O: mp 160−161 °C; ν_{max} ($CHCl_3$) 3020, 1699, 1660, 1620, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) 2.70 (m, 1H), 3.30 (s, 3H), 3.32 (m, 1H), 3.41 (s, 3H), 3.50 (m, 1H), 5.92 (s, 1H), 7.20 (m, 8H), 7.93 (m, 2H); ^{13}C NMR ($CDCl_3$) 27.9, 31.9, 32.6, 33.0, 33.7, 103.3, 126.6, 127.7, 128.2, 128.9, 129.0, 133.8, 136.9, 137.2, 149.9, 152.4, 162.4, 193.9; found M^+ 360.1505, $C_{23}H_{20}N_2O_4$ requires *m/z* 360.1570.

***trans*- and *cis*-2-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)cyclopropane-1-carbonitriles (26 and 27).** Ylide **8** (500 mg, 2.17 mmol) and freshly distilled acrylonitrile (2 mL) were refluxed in acetonitrile (50 mL) for 24 h. The solvent was removed and the residue chromatographed (silica gel, petroleum ether−EtOAc 1:2 as eluent) to give first trans isomer **26** as a colorless solid (210 mg, 44%) which was recrystallized from $CHCl_3$−Et_2O: mp 141−143 °C; ^1H NMR ($CDCl_3$) 1.50 (m, 1H), 1.70 (m, 2H), 2.35 (m, 1H), 3.35 (s, 3H), 3.60 (s, 3H), 5.50 (s, 1H); ^{13}C NMR ($CDCl_3$) 5.5, 13.5, 21.8, 27.8, 31.7, 99.8, 118.7, 150.4, 151.9, 161.9; found M^+ 205.0850, $C_{10}H_{11}N_3O_2$ requires *m/z* 205.0851.

The second compound eluted was collected as a colorless solid that was recrystallized from $CHCl_3$−Et_2O and identified as cis isomer **27** (110 mg, 23%): mp 190−192 °C; ^1H NMR ($CDCl_3$) 1.60 (m, 2H), 2.10 (m, 1H), 2.25 (m, 1H), 3.35 (s, 3H), 3.58 (s, 3H), 5.70 (s, 1H); ^{13}C NMR ($CDCl_3$) 6.0, 12.4, 20.7, 28.0, 31.6, 102.3, 117.2, 148.9, 152.1, 162.1; found M^+ 205.0852, $C_{10}H_{11}N_3O_2$ requires *m/z* 205.0851. For the mixture: ν_{max} ($CHCl_3$) 3019, 2400, 2246, 1704, 1666, 1625 cm^{-1}.

***trans*- and *cis*-2-(4,6-Diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)-cyclopropane carbaldehydes (28 and 29).** A solution of methanide **8** (500 mg, 2.15 mmol), dry acetonitrile (50 mL), and freshly distilled acrolein (0.43 mL, 6.45 mmol) was heated at 50 °C for 3 h. The volatiles were removed in vacuo, and the residue was dissolved in $CHCl_3$ and washed with water. The aqueous layers were washed with $CHCl_3$, and the combined organic extracts were dried ($MgSO_4$), filtered, and adsorbed onto silica gel. Chromatography (petroleum ether−EtOAc 1:2 as eluent) afforded *trans*-cyclopropane **28** (recrystallized from $CHCl_3$−Et_2O, mp 86−88 °C) followed by cis isomer **29** (recrystallized from $CHCl_3$−Et_2O, mp 116−120 °C). Overall, 430 mg of product was collected (94%). Integration of the ^1H NMR spectrum of the crude reaction product indicated the ratio of **28**:**29** to be 4.5:1.

For **28**: ν_{max} ($CHCl_3$) 2956, 1701, 1662 cm^{-1}; ^1H NMR ($CDCl_3$) 1.49 (m, 1H), 1.60 (m, 1H), 2.20 (m, 1H), 2.40 (m, 1H), 3.30 (s, 3H), 3.50 (s, 3H), 5.55 (s, 1H), 9.60 (d, 1H); ^{13}C NMR ($CDCl_3$) 14.5, 14.7, 22.1, 27.3, 29.5, 31.1, 98.9, 151.7, 151.9, 161.9, 198.0; found M^+ 208.0851, $C_{10}H_{12}N_2O_3$ requires *m/z* 208.0848. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.67; H, 5.81. Found: C, 57.65; H, 5.83.

For **29**: ν_{max} ($CHCl_3$) 2950, 1700, 1659 cm^{-1}; ^1H NMR ($CDCl_3$) 1.65 (m, 1H), 1.80 (m, 1H), 2.25 (m, 2H), 3.30 (s, 3H), 3.45 (s, 3H), 5.75 (s, 1H), 8.90 (d, 1H); ^{13}C NMR ($CDCl_3$) 11.9, 23.0, 27.8, 28.9, 31.5, 101.9, 146.6, 152.0, 162.0, 197.6; found M^+ 208.0850, $C_{10}H_{12}N_2O_3$ requires *m/z* 208.0857. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.67; H, 5.81. Found: C, 57.66; H, 5.85.

***trans*- and *cis*-1-Acetyl-2-(4,6-diaza-4,6-dimethyl-3,5-dioxocyclohex-1-enyl)cyclopropanes (30 and 31).** A solution of ylide **8** (500 mg, 2.17 mmol) and freshly distilled methyl vinyl ketone (2 mL) in dry acetonitrile (50 mL) was heated at 45 °C for 18 h and then concentrated in vacuo. Water was added, and the solution was extracted with $CHCl_3$. The combined organic layers were washed with water, dried ($MgSO_4$), filtered, and evaporated to a colorless oil. Chromatography (silica gel, petroleum ether−EtOAc 1:1 as eluent) gave *trans*-cyclopropane **30** (380 mg, 79%), mp 79−81 °C (recrystallized from $CHCl_3$−Et_2O) and cis isomer **31** (60 mg, 12%), mp 116−118 °C (recrystallized from $CHCl_3$−Et_2O).

For **30**: ν_{max} ($CHCl_3$) 1701, 1662, 1621 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (m, 1H), 1.46 (m, 1H), 2.20 (m, 1H), 2.25 (m, 1H), 2.28 (s, 3H), 3.19 (s, 3H), 3.37 (s, 3H), 5.41 (s, 1H); ^{13}C NMR ($CDCl_3$) 16.8, 23.8, 27.6, 28.9, 30.7, 31.4, 98.9, 152.1, 152.7, 162.2, 204.7; found M^+ 222.1001, $C_{11}H_{14}N_2O_3$ requires *m/z* 222.1004. Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.43; H, 6.35. Found: C, 59.53; H, 6.36.

For **31**: ν_{max} ($CHCl_3$) 1705, 1660, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) 1.45 (m, 1H), 1.59 (m, 1H), 2.18 (m, 1H), 2.22 (s, 3H), 2.50 (m, 1H), 3.24 (s, 3H), 3.35 (s, 3H), 5.65 (s, 1H); ^{13}C NMR ($CDCl_3$) 13.9, 24.9, 27.7, 27.8, 31.5, 31.6, 103.0, 149.9, 152.2, 162.3, 202.9; found M^+ 222.1022, $C_{11}H_{14}N_2O_3$ requires *m/z* 222.1004. Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.43; H, 6.35. Found: C, 59.40; H, 6.31.

***trans*-6-(2-Ethenylcyclopropyl)-1,3-dimethyluracil (33).** A solution of *n*-BuLi (1.37 mL, 2.19 M, 3.0 mmol) was added dropwise to a cold (−70 °C) suspension of methyltriphenylphosponium bromide (1.03 g, 2.9 mmol) in dry THF (30 mL). The mixture was stirred at −78 °C for 30 min. A solution of *trans*-cyclopropylcarboxaldehyde **28** (500 mg, 2.4 mmol) in THF (15 mL) was then added dropwise. After being allowed to warm to room temperature, the mixture was stirred for 18 h. The solvent was removed and the residue was chromatographed (silica gel, petroleum ether−EtOAc 1:2 as eluent) to

give alkene **33** as a colorless oil (450 mg, 91%): ^{1}H NMR ($CDCl_3$) 1.00 (m, 2H), 1.55 (m, 2H), 3.35 (s, 3H), 3.45 (s, 3H), 4.95 (dd, 1H), 5.10 (dd, 1H), 5.30 (m, 1H), 5.45 (s, 1H); ^{13}C NMR ($CDCl_3$) 13.8, 22.2, 25.2, 27.8, 31.8, 98.7, 115.5, 137.7, 152.4, 154.6, 162.8; found M^+ 206.1021, $C_{11}H_{14}N_2O_2$ requires *m*/*z* 206.1055.

2,4-Diaza-2,4-dimethyl-1,3-dioxobicyclo[5.4.0]undec-7-ene (36). A solution of methylenetriphenylphosphorane (**32**) was prepared as in the previous experiment from *n*-BuLi (0.59 mL, 2.19 M, 1.3 mmol) and methyltriphenylphosphonium bromide (445 mg, 1.25 mmol) in THF (10 mL). A solution of *cis*-carboxaldehyde **29** (216 mg, 1.04 mmol) in THF (7 mL) was added dropwise. After the mixture was warmed to room temperature and stirred for 18 h, the solvent was removed and the residue chromatographed (silica gel using petroleum ether−EtOAc 1:1 as eluent) to afford cycloheptadiene **36** as a pale yellow oil (135 mg, 63%): ν_{max} (neat) 2906, 1693, 1481, 1431 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.28 (m, 2H), 2.98 (m, 2H), 3.25 (m, 2H), 3.33 (s, 3H), 3.48 (s, 3H), 5.48 (m, 1H), 5.63 (m, 1H); ^{13}C NMR ($CDCl_3$) 22.1, 24.6, 27.3, 28.5, 31.8, 112.5, 127.0, 128.0, 151.6, 162.0; found M^+ 206.1039, $C_{11}H_{14}N_2O_2$ requires *m*/*z* 206.1055.

Alternatively, *trans*-divinylcyclopropane **33** was pyrolyzed at 320 °C in *o*-dichlorobenzene in a sealed tube for 30 h. Removal of solvent by vacuum distillation left a brown residue that was chromatographed (silica gel using petroleum ether−EtOAc 1:1 as eluent) to give cycloheptene **36**, identical in all respects to the sample prepared in the previous experiment.

***trans*-6-[2-(2-Propenyl)cyclopropyl]-1,3-dimethyluracil (39).** To a suspension of methyltriphenylphosphonium bromide (536 mg, 1.5 mmol) in dry THF (15 mL) at −70 °C under argon was added *n*-BuLi (1 M in hexane, 1.5 mL, 1.5 mmol) dropwise, and the resultant yellow solution was stirred at −70 °C for 30 min. *trans*-Cyclopropyl ketone **30** (222 mg, 1.0 mmol) was added dropwise in dry THF (10 mL) and the mixture then warmed to room temperature. After the mixture was stirred for 12 h, the solvent was removed in vacuo and the residue was dissolved in $CHCl_3$, washed with water, dried ($MgSO_4$), and evaporated to a colorless oil. Chromatography (silica gel using petroleum ether−EtOAc 1:1 as eluent) afforded divinylcyclopropane **39** (200 mg, 91%): mp 80−82 °C (recrystallized from $CHCl_3$−Et_2O); ν_{max} ($CHCl_3$) 1665, 1618, 1442, 1377 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.08 (m, 2H), 1.61 (m, 1H), 1.66 (s, 3H), 1.72 (m, 1H), 3.26 (s, 3H), 3.44 (s, 3H), 4.78 (m, 2H), 5.47 (s, 1H); ^{13}C NMR ($CDCl_3$) 12.5, 19.7, 20.4, 27.7, 27.9, 31.6, 98.6, 111.1, 142.2, 152.3, 155.1, 162.7; found M^+ 220.1206, $C_{12}H_{16}N_2O_2$ requires *m*/*z* 220.1212.

2,4-Diaza-2,4,8-trimethyl-1,3-dioxobicyclo[5.4.0]undec-7-ene (42). To a solution of methylenetriphenylphosphorane (**32**), prepared by adding *n*-BuLi (2.19 M, 0.14 mL, 0.30 mmol) to a suspension of methyltriphenylphosphonium bromide (96.4 mg, 0.27 mmol) in dry THF (5 mL) at −70 °C, was added *cis*-cyclopropyl ketone **31** (50 mg, 0.225 mmol). The solution was warmed to room temperature and stirred for 12 h. Removal of solvent in vacuo left a yellow residue that was dissolved in $CHCl_3$, washed with water, dried ($MgSO_4$), filtered, and evaporated to a colorless oil. Chromatography (silica gel using petroleum ether−EtOAc 1:1 as eluent) yielded a colorless oil that crystallized upon trituration with Et_2O (37 mg, 0.169 mmol, 75%): mp 101−103 °C; ν_{max} ($CHCl_3$) 1693, 1645, 1480, 1431 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.70 (s, 3H), 2.25 (m, 2H), 2.89 (m, 2H), 3.27 (m, 2H), 3.36 (s, 3H), 3.46 (s, 3H), 5.28 (m, 1H); ^{13}C NMR ($CDCl_3$) 24.5, 26.8, 27.0, 27.4, 28.5, 31.7, 98.0, 111.3, 121.7, 135.7, 151.3, 162.2; found M^+ 220.1216, $C_{12}H_{16}N_2O_2$ requires *m*/*z* 220.1212.

Alternatively, *trans*-divinylcyclopropane **39** (200 mg, 0.91 mmol) was pyrolyzed at 320 °C in *o*-dichlorobenzene in a sealed tube for 48 h. Removal of solvent by vacuum distillation left a brown residue that was chromatographed (silica gel, 10 g) using petroleum ether−EtOAc (1:1) as eluent to give cycloheptene **42** as a colorless solid (140 mg, 0.64 mmol, 70%), mp 100−103 °C. The ^{1}H, ^{13}C, and mass spectral properties of this product were identical to those of cycloheptene **42** prepared in the previous experiment.

5-Benzenesulfinyl-1,3-dimethyluracil (48). Sulfide **47** (2.48 g, 10.0 mmol)[16] was dissolved in dry CH_2Cl_2 (75 mL), and the solution was cooled to 0 °C. *m*-CPBA (2.16 g, 10.0 mmol, ∼80% assay) was added portionwise with stirring in 30 min. After being stirred for 3 h at room temperature, the mixture was washed with saturated Na_2CO_3 solution and water, dried ($MgSO_4$), filtered, and evaporated in vacuo to a colorless solid that was then recrystallized from benzene to yield colorless crystals of **48** (2.11 g, 8.0 mmol, 80% yield): mp 180−182 °C; ν_{max} ($CHCl_3$) 1713, 1665, 1478, 1445 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.28 (s, 3H), 3.52 (s, 3H), 7.46 (m, 3H), 7.78 (s, 1H), 7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) 27.8, 37.7, 117.3, 125.0, 129.1, 131.6, 141.6, 143.4, 151.1, 159.1; found M^+ 264.0549, $C_{12}H_{12}N_2O_3S$ requires *m*/*z* 264.0569. Anal. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.53; H, 4.58. Found: C, 54.43; H, 4.55.

2,4-Diaza-5-benzenesulfinyl-2,4-dimethyl-3,5-dioxobicyclo[4.1.0]heptane (49). Sodium hydride (0.17 g, 4.2 mmol, 60% suspension in mineral oil) was syringe-washed with anhydrous Et_2O. The system was evacuated and purged with argon, and trimethylsulfoxonium chloride (0.53 g, 4.2 mmol) was added followed by anhydrous THF (30 mL). The mixture was refluxed for 3 h and cooled to 0 °C, and **48** (1.0 g, 3.8 mmol) was added dropwise in dry THF (30 mL). After being at room temperature for 1 h, the mixture was filtered and the filtrate was evaporated in vacuo to a colorless oil that solidified upon trituration with Et_2O to **39** (0.71 g, 2.55 mmol, 67%): mp 134−137 °C (recrystallized from $CHCl_3$−Et_2O); ν_{max} ($CHCl_3$) 3442, 1703, 1665, 1479 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.26 (dd, 1H, J = 5.1, 6.2 Hz), 1.98 (dd, 1H, J = 6.3, 7.2 Hz), 3.06 (s, 3H), 3.10 (s, 3H), 3.31 (dd, 1H, J = 5.0, 7.8 Hz), 7.44 (m, 3H), 7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) 16.9, 27.7, 32.4, 35.4, 43.9, 124.7, 128.9, 132.1, 141.5, 150.3, 165.7; found M^+ − SOPh 153.0710, $C_7H_9N_2O_2$ (M − SOPh) requires *m*/*z* 153.0664.

Reduction of Cyclopropane 49; Preparation of 46a and 16. Cyclopropane **49** (278 mg, 1.0 mmol) was stirred at room temperature with Raney nickel (∼500 mg as an aqueous slurry) in ethanol (25 mL) for 1 h. The mixture was filtered, and the solvent was then removed. Chromatography of the residue (silica gel using petroleum ether−EtOAc 1:1 as eluent) afforded, first, 1,3-dimethylcyclothymine (**46a**) as a colorless oil (25 mg, 16%). The TLC mobility and ^{1}H and ^{13}C NMR spectra of **46a** matched that of an authentic sample.[12] The second product, collected as a colorless oil (65 mg, 42%), was identified as **16** by comparison of its ^{1}H and ^{13}C NMR spectra with an authentic sample.[6]

2,4-Diaza-5-benzenesulfonyl-2,4-dimethyl-3,5-dioxobicyclo[4.1.0]heptane (50). *m*-CPBA (450 mg, ∼2.1 mmol, ∼85% assay) was added portionwise to a solution of cyclopropane **49** (500 mg, 1.80 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The mixture was stirred at room temperature for 4 h and washed with water and saturated $NaHCO_3$. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated to afford a colorless oil that was chromatographed (silica gel using petroleum ether−EtOAc 1:1 as eluent) to give sulfone **50** as a colorless solid (360 mg, 68%): mp 196−198 °C; ν_{max} ($CHCl_3$) 1703, 1666, 1583, 1479, 1444 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.32 (dd, 1H, J = 5.4, 6.3 Hz), 2.07 (dd, 1H, J = 6.5, 7.4 Hz), 3.10 (s, 3H), 3.20 (s, 3H), 3.92 (dd, 1H, J = 5.3, 7.5 Hz), 7.51 (m, 3H), 8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) 19.3, 28.1, 35.5, 38.5, 44.2, 128.8, 129.7, 134.3, 138.3, 150.1, 162.8; found M^+ − SO_2-Ph 153.0644, $C_7H_9N_2O_2$ (M − SO_2Ph) requires *m*/*z* 153.0664. Anal. Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.80. Found: C, 52.96; H, 4.79.

1,3-Dimethyl-5-selenophenyluracil (51). A mixture of diphenyl diselenide (6.24 g, 20.0 mmol), ammonium persulfate (9.12 g, 40.0 mmol), and 1,3-dimethyluracil (2.8 g, 20.0 mmol) in absolute ethanol (300 mL) was refluxed 12 h and cooled, and the solvent was removed in vacuo to leave a yellow solid. Water was added, and the mixture was extracted with $CHCl_3$. The combined organic extracts were washed with water, dried ($MgSO_4$), filtered, and evaporated to a pale yellow solid. Trituration with Et_2O afforded selenide **51** (4.7 g, 16.0 mmol, 80%): mp 116−118 °C; ν_{max} ($CHCl_3$) 1706, 1652, 1617, 1578 cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.35 (s, 3H), 3.37 (s, 3H), 7.23 (m, 3H), 7.46 (s, 1H), 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) 28.6, 37.0, 102.9,

127.6, 129.3, 129.4, 132.4, 146.4, 151.5, 161.8; found M^+ 296.0040, $C_{12}H_{12}N_2O_2Se$ requires *m/z* 296.0063. Anal. Calcd for $C_{12}H_{12}N_2O_2Se$: C, 48.65; H, 4.09. Found: C, 48.47; H, 4.07.

1,3-Dimethyl-5-phenylseleninyluracil (52). 5-Selenophenyluracil **51** (2.95 g, 10.0 mmol) and MMPP (magnesium monoperoxyphthalate) (3.71 g, 6.0 mmol, 80% assay) were dissolved in a 1:1 mixture of ethanol and water (50 mL). The mixture was kept at 50 °C for 1 h, and the ethanol was removed in vacuo. The aqueous mixture was extracted with $CHCl_3$, and the combined organic extracts were washed with water, dried ($MgSO_4$), filtered, and evaporated to a pale yellow solid. Trituration with Et_2O afforded selenoxide **52** (2.74 g, 8.8 mmol, 88% yield): mp 182−185 °C (recrystallized from benzene); ν_{max} ($CHCl_3$) 1710, 1657, 1520, 1478 cm^{-1}; ^1H NMR ($CDCl_3$) 3.27 (s, 3H, NCH_3), 3.48 (s, 3H, NCH_3), 7.47 (m, 3H, aromatic), 7.81 (m, 2H, aromatic), 7.95 (s, 1H, H-6); ^{13}C NMR ($CDCl_3$) 27.9, 37.6, 113.8, 126.0, 129.5, 131.4, 141.4, 142.9, 151.2, 160.5; found M^+ 312.0018, $C_{12}H_{12}N_2O_3Se$ requires *m/z* 312.0013. Anal. Calcd for $C_{12}H_{12}N_2O_3Se$: C, 46.30; H, 3.88. Found: C, 46.70; H, 4.03.

Reaction of 52 and 3. Sodium hydride (0.312 g, 3.3 mmol) was syringe-washed with anhydrous Et_2O. The flask was purged with argon, and trimethylsulfoxonium chloride (0.416 g, 3.3 mmol) was added followed by dry THF (15 mL). The mixture was refluxed for 3 h and cooled to 0 °C, and 5-phenylseleninyluracil **52** (0.311 g, 1.0 mmol) was added dropwise in dry THF (15 mL) The mixture was stirred at room temperature for 12 h. Removal of solvent in vacuo produced a yellow oil that on chromatography (silica gel using methanol−$CHCl_3$ 1:2 as eluent) yielded sulfoxonium ylide **8** as a pale yellow solid (78 mg, 0.34 mmol, 34%), mp 192−195 °C. The spectral properties are identical to those given for **8** above.

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Supporting Information Available: Copies of the ^1H and ^{13}C NMR spectra for compounds **18**, **21**, **24**−**27**, **33**, **36**, **39**, **42**, and **49**. This material is available free of charge via the Internet at http://pubs.acs.org.

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