180°). In each case *ca.* 2% isomerization to the cis isomer of the cyclopropane had occurred. Optical density changes of each solution as a result of irradiation were negligible.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also grateful to Professors Gary Griffin and Stanley Cristol for helpful discussions.

Photosensitized Cycloadditions to 1,3-Dimethyl-6-azauracil and 1,3-Dimethyl-6-azathymine. An Imine Linkage Unusually Reactive toward Photocycloaddition

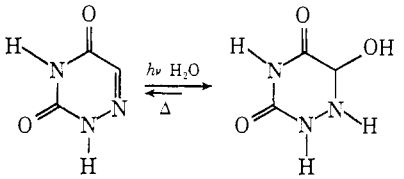
John S. Swenton*[1a] and John A. Hyatt[1b,c]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 14, 1974*

Abstract: The acetone-sensitized cycloaddition of 1,3-dimethyl-6-azathymine (**1b**) and 1,3-dimethyl-6-azauracil (**2b**) to olefins has been studied. For **2b** high yield cycloadducts were formed with ethylene, tetramethylethylene, isobutylene, ethyl vinyl ether, vinyl acetate, and isopropenyl acetate. In the case of the oxygen-substituted olefins, epimeric 8-substituted 1,2,4-triazabicyclo[4.2.0]octane-3,5-diones were formed with greater than 95% regioselectivity. Photosensitized cycloaddition studies of **1b** with tetramethylethylene and vinyl acetate indicate that the photochemical reactivity of **1b** and **2b** is qualitatively similar. These results are discussed with reference to the general low photochemical reactivity of imines in cycloaddition reactions.

The photochemical reactivity of excited pyrimidine bases[2] and their aza analogs[3] has attracted much attention in recent years. In particular 6-azathymine (**1a**) and 6-azauracil (**2a**) derivatives, which theoretically[4] should show photochemical behavior similar to thymine and uracil, have shown photochemical reactivity much to the contrary. Thus, Prusoff[3a,b] has reported that 6-azathymine and its ribonucleoside were essentially resistant to the effects of uv irradiation. In addition, the presence of **1a** in bacterial DNA and the incorporation of **1a** in *Enterococcus stei* increased the resistance of these materials toward uv irradiation. While facile photodimerization of neither **1a** nor **2a** has been observed, photohydration of **2a** has been recently reported to afford 5-hydroxy-5,6-dihydro-6-azauracil (**3**).[3f,g] This hydration product results from the opposite mode of water addition than that observed in uracil derivatives.

The low reactivity of these 6-aza analogs toward photodimerization may be viewed in a much larger context, namely the reluctance of >C=N– systems to undergo bimolecular 2 + 2 additions. Thus, while



2 **3**

photocycloadditions of olefins to other olefins,[5] to ketones,[6] and to thioketones[7] to yield the expected four-membered ring compounds are well characterized, until recently we knew of only two formal examples of >C=N– additions to carbon–carbon double bonds.[8] These processes involved the photoaddition of 2,5-diphenyl-2,3,4-oxadiazole to indene and furan.[8] Our preliminary report of the photoaddition of ethyl vinyl ether to 6-azauracil[1c] and that of Koch's work with 3-ethoxyisoindolone[9a] and 2-phenyl-2-oxazolin-4-one[9b] serve as the only simple examples of these cycloaddition processes.

Our interest in 6-azauracil and 6-azathymine photochemistry initially evolved from our studies of uracil photoaddition reactions.[2] However, in view of the rare occurrence of cycloadditions to the >C=N– linkage we have investigated the generality of this process. We wish to report here the high yield acetone photosensitized cycloadditions of 1,3-dimethyl-6-aza-

(1) (a) Alfred P. Sloan Fellow, 1971–1973, Camille and Henry Dreyfus Teacher–Scholar, 1972–1977. (b) Ohio State University Fellow, 1971, 1973. (c) For a preliminary report, see J. A. Hyatt and J. S. Swenton, *J. Chem. Soc., Chem. Commun.*, 1145 (1972).

(2) For leading references, see J. S. Swenton, J. A. Hyatt, J. M. Lesy, and J. Clardy, *J. Amer. Chem. Soc.*, **96**, 4885 (1974).

(3) (a) W. Prusoff, *Biochim. Biophys. Acta*, **58**, 588 (1962); (b) H. Gunther and W. Prusoff, *ibid.*, **49**, 361 (1967); (c) A. Wacker, H. Dellweg, L. Trager, A. Kornhauser, E. Lodeman, G. Turch, R. Selzer, P. Chandra, and K. Ishimoto, *Photochem. Photobiol.*, **3**, 369 (1964); (d) R. Kleopfer and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 255 (1972); (e) L. Kittler and H. Berg, *Photochem. Photobiol.*, **6**, 199 (1967); (f) L. Kittler and G. Lober, *Monatsber. Deut. Akad. Wiss. Berlin*, **13**, 216 (1971); (g) L. Kittler and G. Lober, *Photochem. Photobiol.*, **10**, 35 (1969).

(4) (a) M. Mentione and B. Pullman, *Biochim. Biophys. Acta*, **91**, 387 (1964); (b) B. Bullman, *Photochem. Photobiol.*,-7, 525 (1968); (c) V. Danilov, Y. Kruglyak, V. Kuprievich, and V. Ogloblin, *Theor. Chim. Acta*, **14**, 242 (1969).

(5) (a) R. Warrener and J. Brenner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966); (b) W. Dilling, *Chem. Rev.*, **66**, 373 (1966); (c) "Photochemistry," Vol. 4, D. Bryce Smith, Ed., The Chemical Society, Burlington House, London, 1960.

(6) D. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

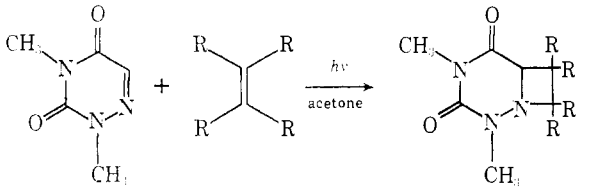
(7) (a) E. T. Kaiser and T. Wulfers, *J. Amer. Chem. Soc.*, **86**, 1897 (1964); (b) A. Ohno, *Int. J. Sulfur Chem., Part B*, **6**, 183 (1971).

(8) (a) O. Tsuge, M. Tashiro, and K. Oe, *Tetrahedron Lett.*, 3971 (1968); (b) O. Tsuge, K. Oe, and M. Tashiro, *Tetrahedron*, **29**, 41 (1973).

(9) (a) T. Koch and K. Howard, *Tetrahedron Lett.*, 4035 (1972); (b) T. Koch and R. Rodenhorst, *ibid.*, 4039 (1972).

uracil (**2b**) and 1,3-dimethyl-6-azathymine (**1b**) to a variety of unsaturated linkages.

Photosensitized Addition of 1,3-Dimethyl-6-azauracil (2b) to Simple Olefins. Due to the low solubility of 6-azauracil and 6-azathymine in most common organic solvents, the easily prepared, soluble, and volatile 1,3-dimethyl derivatives were employed in this work. Acetone sensitized cycloaddition of **2b** to the symmetrical olefins ethylene and tetramethylethylene proceeded smoothly with the production of the corresponding cycloadducts **4a** and **4b** in isolated yields of 91 and



2b 4a, R = H; 4b, R = CH_3

88%, respectively. The structures for these compounds were supported by combustion and mass spectral analyses as well as their spectroscopic properties (see Experimental Section).

The success of these photoadditions of **2b** to symmetrical olefins prompted us to examine reactions with disubstituted olefins. Acetone sensitized cycloadditions of **2b** to cyclohexene, *cis*-cyclooctene, and *trans*-cyclooctene afforded mixtures of cycloadducts in high yield (see Table I). The isomeric adducts were not separated but characterized as mixtures. The combustion analyses, ir, nmr, and mass spectra of these purified adduct isomers supported their assignment as 1:1 adducts of **2b** and olefin.

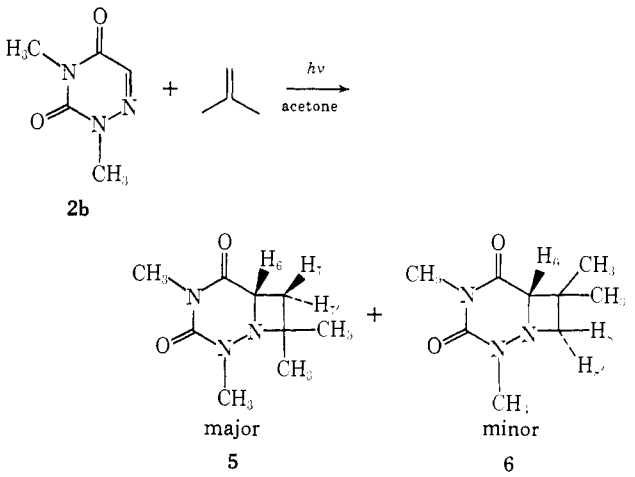
Table I. Isolated Product Yields from Cycloaddition Reactions of 1,3-Dimethyl-6-azauracil

Olefin	Yield of cycloadduct, %
Ethylene	91.0
Tetramethylethylene	87.8
Isobutylene	78.0
	3.0–5.0[b]
Cyclohexene	74.5
cis- and *trans*-cyclooctene	92.6
Ethyl vinyl ether	90.0[a]
Vinyl acetate	95.6[a]
Isopropenyl acetate	65.0[a]

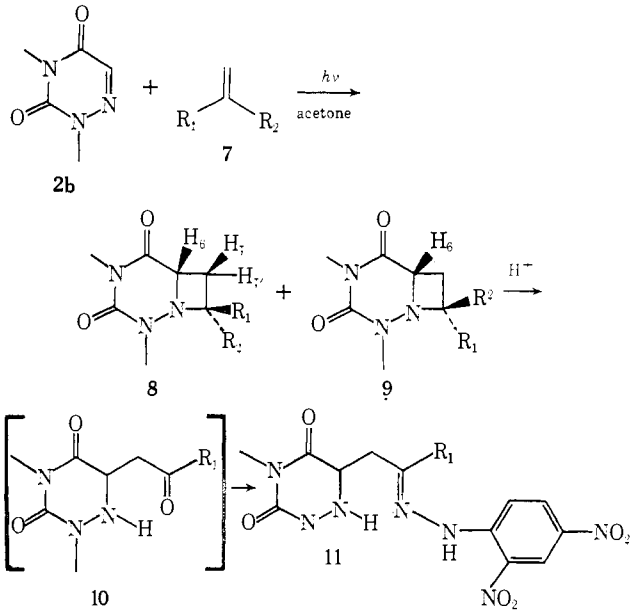
[a] Yield of both epimers. [b] The yield of minor regioisomer.

To explore the regioselectivity of the **2b** cycloaddition to 1,1-disubstituted olefins, the photosensitized reaction of **2b** with isobutylene was studied. Acetone-sensitized photoaddition of **2b** to isobutylene at −78° afforded two products in the ratio of 92:8 (vpc and nmr analysis). The major product was isolated in 78% yield by column chromatography while the minor adduct was obtained pure by preparative vpc. The usual analytical and spectroscopic data indicated these compounds to be 1:1 adducts and their orientation was readily established by nmr. Thus, the major product, **5**, showed H_6 as a doublet of doublets centered at δ 4.40 (J = 8 Hz and J = 4 Hz) while **6** showed H_6 as a singlet centered at δ 4.08.

Photosensitized Addition of 1,3-Dimethyl-6-azauracil (2b) to Vinyl Ethers and Vinyl Esters. The high yields in the photoadditions of **2b** to simple olefins prompted an examination of additions to functionalized olefins. Acetone-sensitized irradiation of **2b** in acetonitrile containing ethyl vinyl ether led to the formation of four products in the ratio of 44:51:3:2 (vpc analysis). The products were found to be quite unstable and attempted separation of the major products by column or preparative gas chromatography under a variety of conditions led to partial decomposition. Florisil chromatography did afford the 51% product in pure form, mp 58–61°. This material analyzed for a 1:1 adduct of **2b** and **7a** and nmr analysis indicated the orientation as shown below, either **8a** or **9a** (see Figure 1). Thus, ir-



major **5** minor **6**



2b **7** **8** **9** **10** **11**

a, R_1 = H; R_2 = OEt
b, R_1 = H; R_2 = $OC(O)CH_3$
c, R_1 = CH_3; R_2 = $OC(O)CH_3$

radiation of the δ 2.4 signal attributable to the methylene group (H_7, $H_{7'}$) caused the resonances at C_6 and C_8 to collapse to singlets. This result is only consistent with orientation **8a** or **9a**. The 44% product could not be obtained in pure form; however, an nmr sample of it contaminated with 25% of major isomer showed behavior analogous to the 51% product in double irradiation experiments. In addition, the mass spectra of the 44 and 51% products were identical when obtained by the vpc–mass spectrum technique.

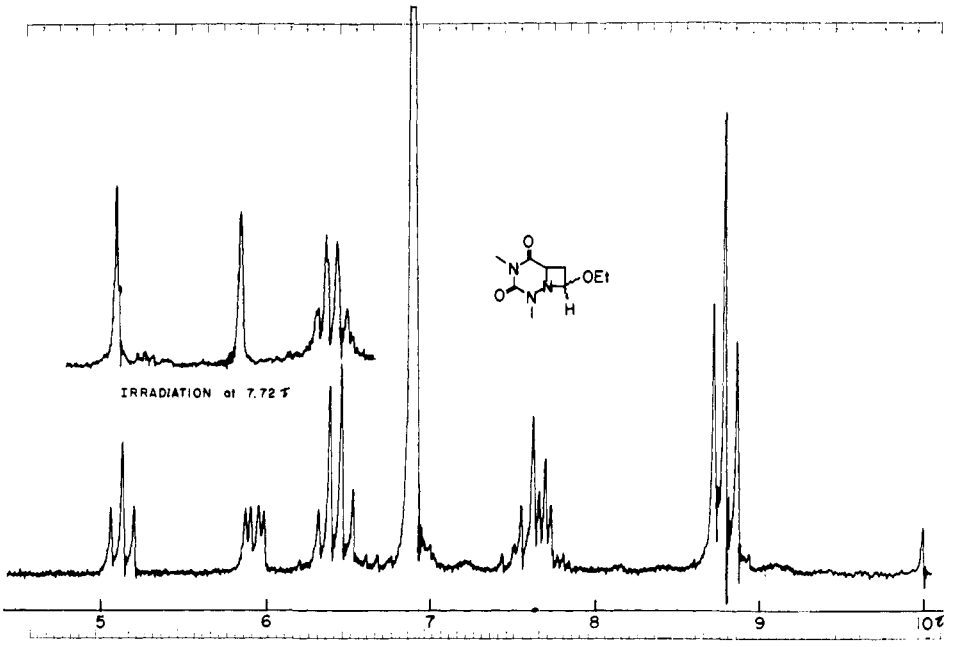
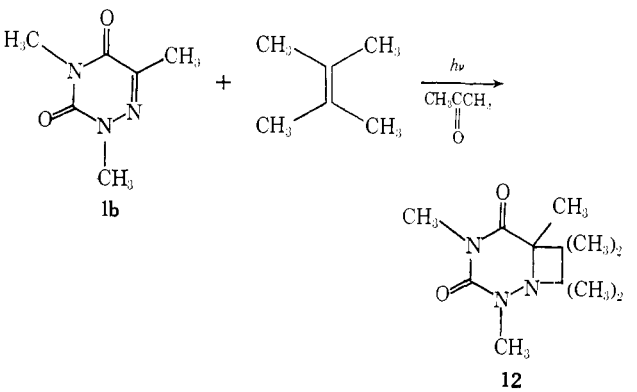


Figure 1. Decoupling results of 1,3-dimethyl-6-azauracilethyl vinyl ether photoadduct, **8a**.

To firmly establish the epimeric nature of the major products, **8a** and **9a**, the hydrolysis of crystalline epimer and of the crude product mixture was performed in the presence of 2,4-dinitrophenylhydrazine. From the crystalline epimer the 2,4-DNP derivative **11a** was obtained in 84% yield while from the crude product mixture **11a** was isolated in 74% yield. Thus, the high regioselectivity of the cycloaddition process is rigorously established. Unfortunately, no evidence is available to establish which isomer is **8a** and which is **9a**.

The generality of this type of photoaddition was demonstrated by the reactions of **2b** with vinyl acetate and isopropenyl acetate. In each case good yields of the C_8 epimeric products were obtained. The regioselectivity was established by the acid-catalyzed hydrolyses of these photoadducts and the 2,4-DNP trapping of the resultant amino carbonyl compounds. In each case the only products observed were those of the indicated orientation; exo–endo stereochemistry was not established.

Photosensitized Cycloaddition Reactions of 1,3-Dimethyl-6-azathymine (1b). Since much of the earlier photochemical and photobiological studies were concerned with 6-azathymine rather than 6-azauracil derivatives, it was imperative to establish photoreactivity for 6-azathymine derivatives. Acetone-sensitized addition of **1b** to tetramethylethylene led to the formation of the 1:1 adduct, **12**, in 70% yield. The structure assignment followed unequivocally from analytical and spectroscopic data.



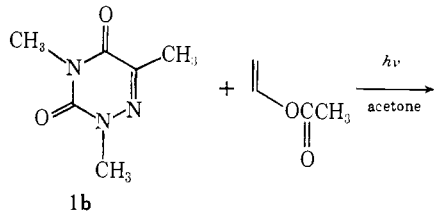
The high regioselectivity for the cycloadditions of **1b** was demonstrated by its reaction with vinyl acetate. In this case two adducts, which could be separated by column chromatography, were obtained in 70% yield. The epimeric nature and orientation of the adducts were established by hydrolysis to and *in situ* trapping of **14** by 2,4-DNP reagent. Full spectroscopic data on these compounds are presented in the Experimental Section.

Discussion

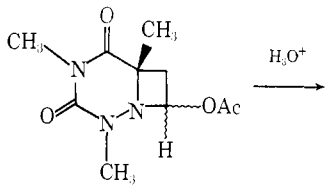
Several proposals have been made concerning the low dimerization reactivity of these 6-aza analogs. Theoretically, it has been suggested that 6-aza systems of this type possess unreactive n–π^* transitions at lower energy than the C_5–N_6 localized π–π^* level.[4e] This would then explain why correlations of the unpaired electron density at the C_5–N_6[4a,b] linkage would lead to erroneous conclusions concerning dimerization reactivity. Morrison and Kloepfer[3d] proposed that for 1,3-dimethyl-6-azathymine, the lack of ground state stacking in aqueous solution could account for the low dimerization efficiency. Finally, the failure to isolate dimers could be related to the lability of the dimeric 1,2- or 1,3-diazetidines. This latter suggestion has some support from work on the irradiation of imine **16**.[10] The two isolated products from the reaction were *cis*-stilbene **17** and azobenzene (**18**). These products could reasonably arise *via* decomposition of an initially formed 1,2-diazetidine (**19**).

We feel that the strong similarity regarding cycloaddition facility and regioselectivity between 1,3-dimethyluracil and 1,3-dimethyl-6-azauracil rules out any pronounced difference in the excited state configuration

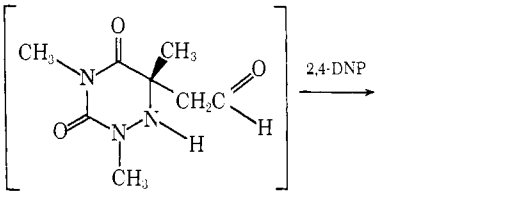
(10) S. Searles and R. A. Closen, *Tetrahedron Lett.*, 1627 (1965).



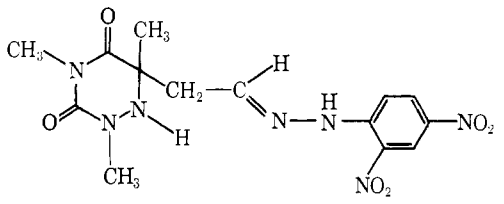
1b



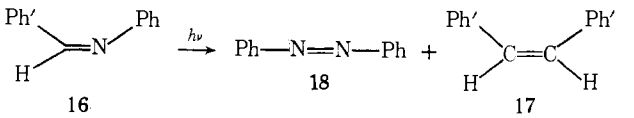
12,13



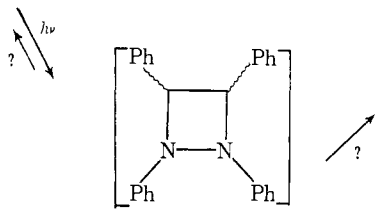
14



15



16 18 17

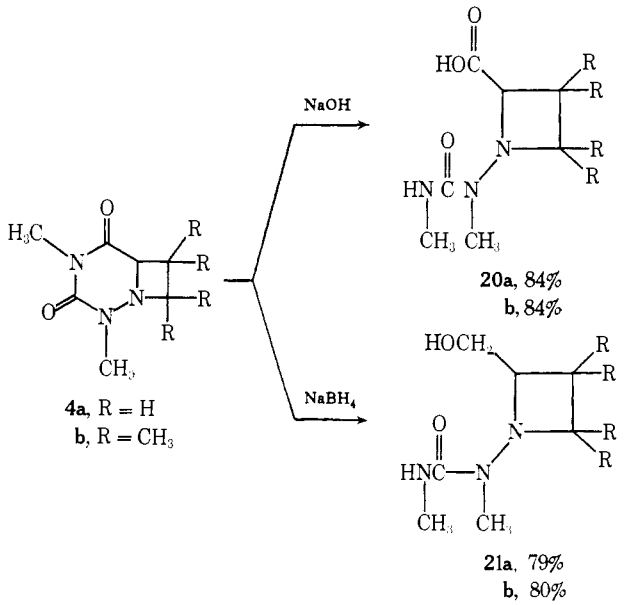


19

of the two molecules. Thus, the proposal attributing the low dimerization reactivity to a lowest n–π^* configuration seems less probable. While the lack of stacking may be important in aqueous solution, it does not seem to account for the general lack of dimerization reactivity of these systems. Obviously, further work on the dimerization reaction is needed to reconcile it with these high yield cycloaddition processes.

A second point concerns the structural feature(s) which permit facile cycloaddition to the generally unreactive imine linkage. One possibility is the presence of the imine linkage of **1b** and **2b** in a six-membered ring. This lessens deactivation processes arising from bond rotations and nitrogen inversion mechanisms.[11,12] However, this condition may not be sufficient for imine photoreactivity, since attempted cycloadditions to cyclic imines lacking the carbonyl group have not been successful thus far.[13] It may be necessary for a conjugated electron-withdrawing group to be present for maximum reactivity. In future publications we hope to amplify on these points in structurally altered systems.

Finally, we wish to note that these 6-azauracil adducts may serve as attractive intermediates in the synthesis of aminoazetidine derivatives. Thus, either hydrolytic or reductive cleavage of the urea function readily affords high yields of substituted derivatives of *N*-aminoazetidines.



4a, R = H
b, R = CH_3

20a, 84%
b, 84%

21a, 79%
b, 80%

Experimental Section

General Procedures. Melting points were taken in capillaries in a Thomas-Hoover "Unimelt" apparatus and are corrected. Infrared spectra were taken in the indicated phase on either a Perkin-Elmer Model 137 or 467 spectrophotometer. Nuclear magnetic resonance spectra were recorded at 60 MHz on Varian A-60 and A-60A instruments and at 100 MHz on Varian HA-100 or Jeolco MH-100 instruments; spectra were recorded in the indicated solvent and are reported in δ units downfield from internal tetramethylsilane standard. Mass spectra were obtained with an AEI MS-902 instrument at an ionizing potential of 70 eV. Unless otherwise noted, irradiations were performed with Pyrex-filtered light from a 450-W Hanovia medium-pressure source, in a nitrogen atmosphere. Low-temperature irradiations were performed utilizing the apparatus of Onsley and Bloomfield.[14] Gas chromatographic analyses were effected using a 5 ft × $^1/_8$ in. column of 3% SE-30 on 100–120 mesh Varaport 30 in a Varian Aerograph Model 1400 flame ionization gas chromatograph; column temperatures in the 110–180° range were used. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by Heterocyclic Chemical Co., Harrisonville, Mo., on sublimed or molecularly distilled pure samples.

Acetone Sensitized Additions of 1,3-Dimethyl-6-azathymine (1b). Tetramethylethylene. A solution of 1.50 g (0.01 mol) of **1b**,[15] 7.5 g (0.09 mol) of tetramethylethylene, and 15 ml of purified acetone in 150 ml of acetonitrile was irradiated for 20 hr. At this time gas chromatographic analysis showed about 20% of **1b** remaining and a single product peak at longer retention time. The solvent from the reaction mixture was removed *in vacuo* to afford a yellow oil which was chromatographed on 75 g of silica gel (2.5 × 60 cm column). Elution proceeded as follows: 10% ether in hexane, 1000 ml, nil; 20% ether–hexane, 500 ml, nil; 25% ether–hexane, 500 ml, nil; 33% ether–hexane, 50 ml, nil; 33% ether–hexane, 350

(11) J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *J. Amer. Chem. Soc.*, **93**, 4808 (1971).
(12) J. S. Swenton, T. J. Ikeler, and G. L. Smyser, *J. Org. Chem.*, **38**, 1157 (1973).
(13) Unpublished results of R. Blankenship.
(14) D. Onsley and J. Bloomfield, *Org. Prep. Proced. Int.*, **3**, 61 (1971).
(15) J. Gut, M. Prystas, J. Jonas, and F. Sorm, *Collect. Czech. Chem. Commun.*, **26**, 974 (1961).

ml, *ca.* 1.50 g of photoproduct as a clear oil; 33% ether–hexane, 200 ml, 0.30 g of unreacted **1b**; 33% ether–hexane, 250 ml, nil.

The chromatographed product crystallized upon trituration with pentane, and was recrystallized from ether–pentane to afford 1.25 g (67.5%) of 2,4,6,7,7,8,8-heptamethyl-1,2,4-triazabicyclo[4.2.0]octane-3,5-dione (**12**) as fine needles: mp 74–75°; ir (KBr) 5.87, 6.00, 7.61, 9.52, 13.58, and 19.0 μ; nmr ($CDCl_3$, 60 MHz) 3.20 (s, 1 H), 3.15 (s, 3 H), 1.31 (s, 3 H), 1.25 (s, 3 H), 1.20 (s, 3 H), 1.12 (s, 3 H), and 1.03 (s, 3 H); mass spectrum (70 eV) *m/e* 239 (P, 58), 224 (P − 15, 8.0), 155 (P − 84, 100).

Anal. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.84; N, 17.56. Found: C, 60.25; H, 8.90; N, 17.69.

Vinyl Acetate. A solution of 1.55 g (0.01 mol) of **1b**, 10 g of vinyl acetate, and 20 g of acetone in 250 ml of acetonitrile was purged with nitrogen and irradiated through a Corex filter for 18 hr, at which time gas chromatographic analysis showed total loss of **1b** and formation of two products in the ratio of 55:45. The reaction mixture was concentrated *in vacuo* to afford a light yellow oil which was chromatographed on Florisil (100 g, 3 × 40 cm column). Elution proceeded as follows: 25% ether in hexane, 500 ml, nil; 50% ether–hexane, 100 ml, 0.94-g mixture (*ca.* 50:50 by vpc) of the epimeric adducts; 50% ether–hexane, 300 ml of a pure component, 0.75 g; 50% ether–hexane, 100 ml, nil. Total yield of adduct was 1.69 g (70.8%). The mixed fraction was rechromatographed with 35% ether–hexane elution to afford a pure sample of the second epimer.

The more slowly eluting epimer was obtained as a white crystalline material, mp 104–105.5° after recrystallization from ether–hexane, and was unstable with respect to storage: ir (KBr) 5.71, 5.87, 5.98, 7.55, 8.27, and 13.50 μ; nmr ($CDCl_3$, 60 MHz) δ 6.00 (m, 1 H), 3.21 (s, 3 H), 3.06 (s, 3 H), 2.51 (m, 2 H), 2.02 (s, 3 H), and 1.52 (s, 3 H); mass spectrum (70 eV) *m/e* 241, (P, 10.5), 198 (Ac, 28), 182 (P − OAc, 8.7), and 155 (P − CH_2=CHOAc, 100%). The unstable nature of this material precluded combustion analysis; exact mass 241.1062 (calcd, 241.1066).

The more rapidly eluting epimer was obtained as a clear oil from the Florisil column: ir (neat) 5.73, 5.84, 5.95, 8.19, 9.43, and 13.5 μ; nmr ($CDCl_3$, 60 MHz) δ (5.87 (t, J = 7 Hz, 1 H), 3.23 (s, 3 H), 3.17 (s, 3 H), 2.0–3.1 (m, 2 H), 2.13 (s, 3 H), and 1.56 (s, 3 H); mass spectrum (70 eV) 241 (P, 3.0), 198 (P − Ac, 11.0), 182 (P − OAc, 6.5), 155 [P − (CH_2=CHOAc), 100]. The unstable nature of this compound precluded elemental analysis; exact mass 241.1067 (calcd, 241.1062).

Trapping of the Amino Aldehyde from Hydrolysis of the 1,3-Dimethyl-6-azathymine–Vinyl Acetate Cycloadduct. A solution of 0.38 g of a 1:1 mixture of the two epimeric 2,4,6-trimethyl-7-acetoxy-1,2,4-triazacyclo[4.2.0]octane-3,5-diones (**12** and **13**) in 10 ml of 95% ethanol was added to a solution of 350 mg of 2,4-dinitrophenylhydrazine in 10 ml of ethanol containing 5 ml of 50% H_2SO_4. The cloudy reaction mixture was let stand at room temperature overnight and the crude product filtered off. Recrystallization from ethanol gave 0.53 g (89%) of **15** as yellow crystals: mp 211–212°; ir (Nujol null) 5.87, 6.00, and 8.80 μ; mass spectrum (70 eV) *m/e* 379 (P, 1.0), 224 (11.5), 206 (11.5), and 155 (100).

Anal. Calcd for $C_{14}H_{17}N_7O_6$: C, 44.32; H, 4.50; N, 25.85. Found: C, 44.19; H, 4.54; N, 25.94.

Acetone-Sensitized Additions of 1,3-Dimethyl-6-azauracil (2b). Ethylene. A solution of 5.0 g (0.035 mol) of **2b** in 650 ml of acetone was cooled to −78° and irradiated while a rapid stream of ethylene was admitted for 40 hr; vpc analysis at this time showed loss of **2b** and formation of a single photoproduct at longer retention time. The reaction mixture was then concentrated *in vacuo* to afford a light yellow oil which was distilled *in vacuo* through a short-path still. The photoadduct, **4a**, was obtained as a clear liquid, 5.46 g (91%): bp 73–75° (0.15 mm); ir (neat) 5.83, 5.99, 6.90 (br), 7.54, 8.84, and 13.50 μ; nmr ($CDCl_3$, 100 MHz) δ 4.35 (structured doublet, J = 8.2 and 2.4 Hz, 1 H), 3.72 (m, 2 H), 3.23 (s, 3 H), 3.06 (s, 3 H), 2.53 (m, 1 H), and 2.17 (m, 1 H); mass spectrum (70 eV) *m/e* 169 (P, 21), 141 [retro (2 + 2), 100], and 117.5 (metastable).

Anal. Calcd for $C_7H_{11}N_3O_2$: C, 49.70; H, 6.55; N, 24.84. Found: C, 49.66; H, 6.75; N, 24.87.

Isobutylene. A solution of 2.0 g (0.014 mol) of **2b** in 500 ml of acetone was cooled to −78° and 30 ml of isobutylene was added. The mixture was stirred by nitrogen purging and irradiated for 23 hr, at which time vpc analysis showed approximately 10% of **2b** remaining and formation of two photoproducts in the ratio 92:8. The oil obtained by evaporation of the solvent was chromatographed on a 2 × 40 cm column of silica gel. Elution proceeded as follows: 15% ether in hexane, 1000 ml, nil; 25% ether–hexane, 500 ml, nil; 33% ether–hexane, 100 ml, nil; 33% ether–hexane, 250 ml, 214 mg of unreacted **2b**; 33% ether–hexane, 200 ml, *ca.* 1:1 mixture of the photoproducts **5** and **6** as a clear oil; 33% ether–hexane, 350 ml, major photoproduct **5** as a clear oil. The fraction containing the mixture of **5** and **6** was then rechromatographed under the same conditions to afford pure **5**, and **6** containing about 10% **5**.

The major photoproduct, **5**, 1.96 g (78%), was purified for analysis by molecular distillation at 65° (0.01 mm): ir (neat) 5.86, 5.99, 6.92, 7.57, 7.92, and 13.61 μ; nmr ($CDCl_3$, 60 MHz) δ 4.40 (doublet of doublets, J = 8.1 and 3.9 Hz, 1 H), 3.23 (s, 3 H), 3.13 (s, 3 H), 2.6–1.9 (m, 2 H), 1.37 (s, 3 H), 1.27 (s, 3 H); mass spectrum (70 eV) *m/e* 197 (P, 28) and 141 [retro (2 + 2), 100].

Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.80; H, 7.67; N, 21.30. Found: C, 54.48; H, 7.56; N, 21.33.

The minor product, **6**, was isolated from the 90:10 chromatographic fraction by preparative vapor phase chromatography (10 ft × 0.25 in. 5% SE-30 on Chrom W, 140°) and further purified by molecular distillation at 65° (0.01 mm): ir (neat) 5.86, 5.96, 6.92 (br), 7.66, 8.77, and 13.47 μ; nmr ($CDCl_3$, 60 MHz) δ 4.08 (s, 1 H), partially obscured AB system centered at 3.45 (J = 7 Hz, with addition splitting of ~1.5 Hz, 3 H), 3.22 (s, 3 H), 3.05 (s, 3 H), 1.50 (s, 3 H), and 1.07 (s, 3 H); mass spectrum (70 eV) *m/e* 197 (P, 12), 142 [retro (2 × 2), 100].

Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.81; H, 7.67; N, 21.30. Found: C, 54.62; H, 7.81; N, 21.41.

A subsequent irradiation using 5.0 g of **2b** afforded 6.58 g (94%) of a 92:8 mixture of **5** and **6** as a clear oil after distillation.

Tetramethylethylene. A solution of 10.0 g (0.071 mol) of **2b**, 25 g (0.30 mol) of tetramethylethylene, and 50 ml of pure acetone in 1 l. of acetonitrile was nitrogen-purged and irradiated for 30 hr, at which time vpc analysis showed less than 5% of **2b** remaining and formation of a single photoproduct. The light yellow reaction mixture was stripped *in vacuo* to afford an oil which yielded 9.05 g of crystalline **4b** upon cooling. The mother liquors from this crystallization were then chromatographed on 200 g of silica gel (5 × 50 cm) using 25% ether–hexane as eluent and an additional 4.86 g of pure adduct was obtained. The two crops of **4b** were combined and recrystallized from ether–pentane to afford a total yield of 13.9 g (88%) of **4b**: mp 61–63°; ir (KBr) 5.86, 5.99, 6.88 (br structured band), 7.59, 8.77, and 13.58 μ; nmr ($CDCl_3$, 100 MHz) δ 3.82 (s, 1 H), 3.03 (s, 3 H), 2.99 (s, 3 H), 1.39 (s, 3 H), 1.18 (s, 3 H), 1.09 (s, 3 H), and 0.91 (s, 3 H); mass spectrum (70 eV) *m/e* 225 (P, 6.2), 141 (P − C_6H_2, 17), and 84 (C_6H_{12}, 100).

Anal. Calcd for $C_{11}H_{19}N_3O_2$: C, 58.64; H, 8.50; N, 18.65. Found: C, 58.91; H, 8.65; N, 18.39.

Cyclohexene. A solution of 2.3 g (0.016 mol) of **2b**, 25 ml of purified acetone, and 15 ml of cyclohexene in 200 ml of acetonitrile was purged with dry nitrogen and irradiated for 6.0 hr, at which time gas chromatographic analysis disclosed nearly total loss of **2b** and formation of at least three products (peaks overlap) which appeared at longer retention time. The solvent was removed *in vacuo* to give a yellow oil which was chromatographed on a 5 × 30 cm column of silica gel. Elution proceeded as follows: 10% ether–hexane, 500 ml, nil; 25% ether–hexane, 500 ml, nil; 35% ether–hexane, 500 ml, nil; 50% ether–hexane, 600 ml, an oil which crystallized on standing, 2.71 g (74.5%). The solid was recrystallized from ether–pentane and had constant mp 47–50°; however, vpc and tlc analysis demonstrated that this material is a mixture of two isomers: ir (KBr) 5.83, 5.99, 6.90, 7.61, 8.80, and 13.41 μ; nmr ($CDCl_3$, 60 MHz) δ 4.4 (broad d, J = 9.0 Hz, 1 H), 4.0 (m, 1 H), 3.20 [m (3 peaks), 6 H], and 2.5–1.0 (m, 9 H); exact mass 223.1323 (calcd, 223.1321).

Anal. Calcd for $C_{11}H_{17}N_3O_2$: C, 59.17; H, 7.67; N, 18.82. Found: C, 58.89; H, 7.45; N, 18.78.

***cis*- and *trans*-Cyclooctene.** A solution of 3.0 g (0.021 mol) of **2b**, 30 ml of acetone, and 20 g of *cis*-cyclooctene in 200 ml of acetonitrile was nitrogen purged and irradiated until vpc analysis showed complete loss of **2b** and formation of two product peaks in the ratio 1.5:1 (*ca.* 12 hr). Evaporation of solvent left a yellow oil which was chromatographed on a 5 × 40 cm column of silica gel. Elution proceeded as follows: 20% ether–hexane, 1000 ml, nil; 30% ether–hexane, 100 ml, nil; 30% ether–hexane, 1500 ml, mixture of epimeric products as a clear oil, 4.94 g (92.6%). An analogous reaction between **2b** and *trans*-cyclooctene gave the same products in approximately the same ratio.

The product was further purified for analysis by molecular distillation (110° (0.01 mm): ir (neat) 5.86, 5.98, and 13.50 μ; nmr ($CDCl_3$, 60 MHz) δ 4.3–3.3 (broad m, 2 H), 2.9–3.2 [m (3 peaks), 6 H], and 2.6–0.8 (broad m, 13 H); mass spectrum (70 eV) *m/e* 251 (P, 14), 141 [retro (2 + 2), 100].

Anal. Calcd for $C_{13}H_{21}N_3O_2$: C, 62.13; H, 8.42; N, 16.72. Found: C, 62.14; H, 8.39; N, 16.60.

Ethyl Vinyl Ether. A solution of 1.38 g (0.0097 mol) of **2b**, 20 ml of ethyl vinyl ether, and 15 ml of pure acetone in 250 ml of acetonitrile was irradiated in a base-washed apparatus. After 3.5 hr, vpc analysis showed complete consumption of **2b** and formation of two products in the ratio 0.85:1.00. Evaporation of the reaction mixture left 2.03 g (98%) of a clear oil. Either vpc or adsorption chromatography on a variety of adsorbants led to partial decomposition of the products, and only the major epimer could be isolated in the pure form. Elution chromatography on 150 g of Florisil gave the following results: 30% ether in hexane, 150 ml, nil; 30% ether–hexane, 375 ml, 0.803 g (42%) of the major photoproduct; 30% ether–hexane, 100 ml, mixture of the two products; 30% ether–hexane, 200 ml, nil. The *major product* gave white plates from cold pentane: mp 58–61°; ir (KBr) 5.81, 6.91, and 7.51 μ; nmr ($CDCl_3$, 100 MHz) δ 4.90 (t, J = 7.0 Hz, 1 H), 4.20 (doublet of doublet, J = 4.0 and 8.0 Hz, 1 H), 3.68 (q, J = 7.0 Hz, 2 H), 3.21 (s, 6 H), 2.36 (m, 2 H), 1.22 [(t, J = 7 Hz, 3 H); irradiation of the 3.68 signals gave 2.36 (m, 2 H) and 4.20 (s, 1 H)]; mass spectrum (70 eV) m/e 213.111 (P; calcd 213.1113, 2.68), 185 (P − C_2H_5, 2.60), 167 (P − OC_2H_5, 1.18), 142 (1,3-dimethyl-6-azauracil, 34.5), and 72 (CH_2=$CHOC_2H_5$, 100).

Anal. Calcd for $C_9H_{15}N_3O_3$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.62; H, 7.13; N, 19.41.

The minor product could not be isolated in pure form; the nmr spectrum was obtained with a sample contaminated with *ca.* 10% of the major product, and the mass spectrum was obtained by gc–mass spectroscopy: nmr ($CDCl_3$, 100 MHz) δ 4.91 (m, 1 H), 4.29 (broad d, 1 H), 3.62 (q, J = 7 Hz, 2 H), 2.99 (s, 6 H), 2.75 (m, 2 H), and 1.25 (t, J = 7 Hz, 3 H).

Vinyl Acetate. A solution of 3.0 g (0.021 mol) of **2b**, 20 g of vinyl acetate, and 20 ml of acetone in 200 ml of acetonitrile was irradiated (Corex filter) for 40 hr, by which time vpc analysis showed complete consumption of **2b** and formation of two products in the ratio 60:40. The reaction mixture was concentrated *in vacuo* to afford a yellow, viscous oil which was immediately chromatographed on a Florisil column (5 × 40 cm). Elution proceeded as follows: 25% ether in hexane, 500 ml, nil; 50% ether in hexane, 250 ml, nil; 50% ether–hexane, 175 ml, 1.77 g of the 60% product as white crystals; 50% ether–hexane, 200 ml, 2.02 g of a 1:1 mixture of the two photoproducts as an oil; 50% ether–hexane, 300 ml, 0.83 g of the 40% photoproduct as white crystals; 50% ether–hexane, 250 ml, nil. Total yield of products, 4.62 g (95.6%). The fraction of a 1:1 mixture of epimers was reserved for acid hydrolysis and trapping experiments.

The major (60%) isomer, which decomposed slowly on standing, was recrystallized from ether–pentane and had: mp 78.5–80°; ir (KBr) 5.73, 5.88, 6.00, 7.54, 8.28, 9.87, and 13.52 μ; nmr ($CDCl_3$, 60 MHz) δ 6.08 (broad d, J = 5.0 Hz, 1 H), 4.50 (broad d, J = 7.2 Hz, 1 H), 3.27 (s, 3 H), 3.03 (s, 3 H), 2.9–2.1 (m, 2 H), and 2.03 (s, 3 H); exact mass 227.0909 (calcd, 227.0906).

The second photoproduct (40% component) gave plates, mp 82–83°, after recrystallization from ether–pentane; ir (KBr) 5.73, 5.90–6.03 (br), 7.51, 8.19, 9.60, 10.53, 11.18, 13.32, and 13.63 μ; nmr ($CDCl_3$, 60 MHz) δ 6.08 (t, J = 7.3 Hz, 1 H), 4.36 (t, J = 6.0 Hz, 1 H), 3.26 (s, 3 H), 3.14 (s, 3 H), 2.60 (m, 2 H), and 2.14 (s, 3 H); exact mass 227.0909 (calcd, 227.0906).

Isopropenyl Acetate. Irradiation through Corex of a solution of 2.0 g (0.014 mol) of **2b**, 20 ml of acetone, and 20 ml of isopropenyl acetate in 250 ml of acetonitrile under nitrogen for 4.5 hr led to loss of the starting material and formation of two products in the ratio 13.5:1, by vpc analysis. Removal of solvent *in vacuo* gave a clear oil which crystallized upon standing at −10° for 12 hr. Recrystallization of this product from ether gave 2.23 g (65.0%) of the pure major photoproduct, mp 99–102°. The solid compound decomposed rapidly at room temperature with liberation of acetic acid; a freshly recrystallized sample was characterized: ir (KBr) 5.73, 5.84, and 5.98 μ; nmr ($CDCl_3$, 60 MHz) δ 4.28 (doublet of doublets, J = 6.5 and 3.0 Hz, 1 H), 3.18 (s, 3 H), 3.13 (s, 3 H), 2.8–2.5 (m, 2 H), 1.94 (s, 3 H), and 1.71 (s, 3 H). A combination analysis was not undertaken due to the unstable nature of the compound.

Acid-Catalyzed Hydrolysis of 1,3-Dimethyl-6-azauracil Adducts of Ethyl Vinyl Ether and Vinyl Acetate, and Trapping of the Amino Carbonyl Compound with 2,4-Dinitrophenylhydrazone. Ethyl Vinyl Ether Cycloadducts. A freshly prepared 0.42-g sample of a 40:60 mixture of epimeric ethers was dissolved in 10 ml of 95% ethanol, added to a solution of 0.80 g of 2,4-dinitrophenylhydrazine in 30 ml of 10% ethanolic H_2SO_4, and allowed to stand at room temperature for 1.0 hr. Filtration of the crude product and recrystallization from ethanol gave 0.58 g (74%) of **11a** as yellow plates, mp 160–164° dec. This 2,4-dinitrophenylhydrazone was found to be identical in all respects with a sample prepared in 84% yield from the pure crystalline major photoproduct: ir (Nujol null) 2.85, 2.98, 5.8, 6.0, 6.19, 6.30, 7.60, and 13.50 μ.

Anal. Calcd for $C_{13}H_{16}N_7O_6$: C, 42.74; H, 4.14; N, 26.84. Found: C, 42.73; H, 4.35; N, 26.64.

Vinyl Acetate Cycloadducts. A solution of 0.5 g of a 1:1 mixture of the epimeric acetates in 15 ml of ethanol was added to 15 ml of a solution of 2,4-dinitrophenylhydrazine reagent. After standing at room temperature for 17 hr, the product was filtered and recrystallized from ethanol to give 0.66 g (82.0%) of **11b**, mp 159–162°. This compound was found to be identical in all respects (mixture melting point, ir, tlc) to the 2,4-dinitrophenylhydrazone derived from decomposition of the epimeric ethyl vinyl ether cycloadducts.

Acid-Catalyzed Hydrolysis of 1,3-Dimethyl-6-azauracil and Isopropenyl Acetate Cycloadduct. A solution of 300 mg of the crystalline acetate from cycloaddition in 5 ml of ethanol was added to 5 ml of 2,4-DNP reagent and allowed to stand at room temperature overnight. The solid product was recrystallized from ethanol to afford 0.428 g (91%) of **11c** as yellow needles: mp 157–158°; ir (Nujol 3.02, 3.07, 5.82, 5.88, and 6.00 μ; mass spectrum (70 eV) m/e 279 (P, 1.2), 238 (7.5), and 141 (100).

Anal. Calcd for $C_{14}H_{17}N_7O_6$: C, 44.32; H, 4.52. Found: C, 43.92; H, 4.58.

1-(1,3-Dimethylureido)-3,3,4,4-tetramethylazetidine-2-carboxylic Acid (20b). A solution of 0.50 g (2.2 mmol) of **4b** in 20 ml of 10% aqueous sodium hydroxide was stirred at room temperature for 10 hr, and then heated at reflux for 2.0 hr. The cooled reaction mixture was acidified to litmus with aqueous HCl and extracted with methylene chloride (5 × 25 ml). The dried extract was stripped *in vacuo* to afford 0.50 g of white solid product; recrystallization from acetone–methylene chloride gave 0.483 g (90.0%) of pure urea acid, **20b**: mp 228–228.5°; ir (KBr) 2.88, 3.3–4.3 (br), 5.79, 6.11, 6.47, 8.10, and 13.19 μ; nmr (DMSO-d_6, 60 MHz) δ 12.2 (broad s, 1 H), 6.8 (broad s, 1 H), 4.14 (s, 1 H), 2.80 (s, 3 H), 2.58 (s, d, J = 4.5 Hz, 3 H), and 1.06 (m, 12 H); mass spectrum (70 eV) m/e 243 (P, 8.9), 228 (P − CH_3, 0.8), 198 (P − CO_2H), 185 (P − $CONHCH_3$, 10.3), 156 (P − $N(CH_3)CONHCH_3$, 85), and 84 [$(CH_3)_2$-C=$C(CH_3)_2$, 100].

Anal. Calcd for $C_{11}H_{21}N_3O_3$: C, 54.30; H, 8.70; N, 17.27. Found: C, 54.59; H, 8.71; N, 17.12.

1-(1,3-Dimethylureido)-2-hydroxymethyl-3,3,4,4-tetramethylazetidine (21b). A solution of 450 mg (2.0 mmol) of **4b** in 35 ml of 85% ethanol was treated with 1.0 g of sodium borohydride in small portions, and stirred at room temperature for 17 hr. The reaction mixture was filtered and the filtrate neutralized by addition of Ag50W cation exchange resin (H^+ form), refiltered, and stripped *in vacuo*. The residue was then dissolved in 50 ml of methanol and reevaporated; three repetitions served to remove all boron compounds. The oily residue was stored at −10° under 1:1 ether–hexane for 1 week and the resultant white needles recrystallized from ether–hexane to afford 77% of **21b**: mp 125–127°; ir (KBr) 2.90, 6.15, 6.60, 7.11, 9.56, and 10.60 μ; nmr ($CDCl_3$, 60 MHz) δ (6.40 (broad s, 1 H), 3.70 (m, 3 H), 3.30 (broad s, 1 H), 3.02 (s, 3 H), 2.81 (d, J = 5 Hz, 3 H), 1.18 (s, 6 H), and 1.09 (s, 6 H); mass spectrum (70 eV) m/e 229 (P), 211 (P − H_2O), and 198 (P − CH_2OH).

Anal. Calcd for $C_{11}H_{23}N_3O_2$: C, 57.61; H, 10.11; N, 18.32. Found: C, 57.43; H, 10.12; N, 18.31.

1-(*sym*-Dimethylureido)azetidine-2-carboxylic Acid (20a). A solution of 63.0 mg (0.45 mmol) of **4a** in 0.5 ml of ethanol was added to 5 ml of 10% aqueous sodium hydroxide and stirred at room temperature overnight. The reaction mixture was then acidified with aqueous hydrochloric acid and extracted with methylene chloride (4 × 20 ml). The dried extract was evaporated *in vacuo* to yield an oil which solidified in ethyl acetate to afford 58.0 mg (83.5%) of **20a**: mp 181–183° dec; ir (Nujol null) 2.95, 3.3–4.2 (br), 5.83, 6.17, 8.30 (br), 10.52, and 13.15 μ; nmr (DMSO-d_6, 100 MHz) δ 6.90 (br, 1 H), 4.32 (t, J = 8.5 Hz, 1 H), 3.6–3.0 (m, 2 H), 2.76 (s, 3 H), 2.57 (d, J = 5 Hz, 3 H), and 2.4–1.8 (m, 2 H); mass spectrum (70 eV) m/e 187.0959 (calcd, 187.0957) (P, 11), 130 (P − Me − NCO, 25%), 115 (P − Me − NCO, −Me, 12), and 58 (MeHNCO, 100).

1-(*sym*-Dimethylureido)-2-hydroxymethylazetidine (21a). A solution of 0.470 g (2.8 mmol) of 2,4-dimethyl-1,2,4-triazabicyclo[4.2.0]-octane-3,5-dione (**4a**) in 35 ml of 90% methanol was treated with 0.60 g of sodium borohydride portionwise over 1 hr and stirred at room temperature for 12 hr. The reaction mixture was then rendered slightly acidic with AG50W ion exchange resin and filtered, and the solvent was removed *in vacuo*. The residue was

azeotroped three times with 30 ml of methanol and the orange residue obtained was extracted with chloroform. The chloroform extract was stripped *in vacuo* to afford 0.372 g (79%) of the product as a clear syrup. A sample of this material was further purified by molecular distillation at 130° (0.10 mm); a clear syrup identical with the above crude product was obtained: ir (neat) 2.95 (b), 6.10, 6.51, 7.07, and 13.2 μ; nmr ($CDCl_3$, 100 MHz) δ 6.62 (s, 1 H), 4.0–3.0 (m, 6 H), 2.96 (s, 3 H), 2.79 (s, 3 H), and 1.90 (m, 2 H); mass spectrum (70 eV) *m/e* 173.1167 (calcd, 173.1164) (P, 12), 155 (P − H_2O, 8), 142 (P − H, − $NHCH_3$, 7), 115 (P − $CONHCH_3$, 47), and 56 (CH_3NHCO, 100). This compound was characterized more fully as its acetate. The acetate prepared from the alcohol and acetic anhydride in 96% yield was a clear liquid: ir (neat) 2.93, 5.74, 6.02, 6.56, 8.07, and 9.65 μ; nmr ($CDCl_3$, 60 MHz) δ 6.23 (br s, 1 H), 4.14 (d, J = 2.5 Hz, 2 H), 4.14–3.20 (m, 3 H), 2.96 (s, 3 H), 2.78 (d, J = 5.0 Hz, 3 H), 2.06 (s, 3 H), and 2.1–1.7 (m, 2 H); mass spectrum (70 eV) *m/e* 215.1273 (calcd, 215.1269) (P, 17, 156 (P − OAc, 30), 128 (P − $N(CH_3)CONHCH_3$, 55), and 97 (100).

Anal. Calcd for $C_9H_{17}N_3O_3$: C, 50.22; H, 7.96; N, 19.52. Found: C, 50.23; H, 7.95; N, 19.62.

Photochemical Cycloadditions of Triplet 1,3-Dimethyluracil to Olefins. Structural Studies on the Adducts

John S. Swenton,*[1a] John A. Hyatt,[1b,c] James M. Lisy,[1d] and Jon Clardy[1d,e]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Ames Laboratory—USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received February 14, 1974*

Abstract: The acetone-sensitized additions of 1,3-dimethyluracil (**1**) to ketene diethyl acetal (**2a**), *tert*-butyl vinyl ether (**2b**), and vinyl acetate (**2c**) have been studied. From excited **1** and **2a** an 85% yield of cis- and trans-fused 8,8-diethoxy-2,4-diazabicyclo[4.2.0]octane-3,5-diones in a ratio of 84:16 were produced. From cycloaddition of excited **1** to **2b** and **2c** good yields of cis-fused 8-substituted 2,4-diazabicyclo[4.2.0]octa-3,5-diones were formed. The orientation and stereochemistry of all these adducts were rigorously established by a combination of chemical, labeling, and X-ray crystallographic studies.

While the photochemistry of both uracil and thymine derivatives has been extensively studied, most of the emphasis has been placed on the hydration and dimerization reaction of these moieties.[2] In view of the considerable interest in relating chemical reactivity and excited state electron distribution in these systems,[3] we felt it would be valuable to develop reactions which could probe the electronic character of the excited state. A reasonable choice for such a study was cycloaddition reactions of these excited bases to olefins. Thus, the rates and efficiencies of these cycloadditions as a function of olefin structure would possibly contribute to a basic understanding of the electronic character of the nucleic acid excited states. Since at the time this work was begun little was known of the photochemical processes of excited uracil[4–6] or thymine[7] with olefins, by necessity detailed structural studies of the products from these systems were required. We wish to report here chemical, labeling, kinetic, and X-ray studies which establish the orientation and stereochemistry of the major cycloadducts from 1,3-dimethyluracil (**1**), with ketene diethyl acetal (**2a**), *tert*-butyl vinyl ether (**2b**), and vinyl acetate (**2c**).

Orientation of the Cycloadducts from 1. The importance of the triplet state of uracil in its dimerization reactions,[8] together with the possible complicating factor of products being derived from both singlet and triplet excited state on direct irradiation,[9] led us to investigate the triplet sensitized reactions of **1**. Photosensitized addition of **1** to **2a**, **2b**, and **2c** produced in each case two major products in good overall yield (Table I). There are numerous possible structures for these compounds. In addition to the two regioisomers i and ii, there are epimeric centers at either C_7 or C_8 and the possibility of either cis- or trans-ring fusions at C_1 and C_6. Thus, we first sought to establish the regiospecificity of these reactions.

The reaction of triplet 1,3-dimethyluracil (**1**) with ketene diethyl acetal, (**2a**) will be discussed first. Irradiation of a 4% solution of **1** and a fivefold molar excess of **2a** in acetonitrile–acetone with Corex-filtered light resulted in the formation of two products in a ratio of *ca.* 86:14 (vpc). Both compounds were obtained as crystalline solids after silica gel chromatography, and their combustion analyses and mass spectra

(1) (a) Alfred P. Sloan Fellow (1970–1972); Camille and Henry Dreyfus Teacher–Scholar (1971–1976); (b) Ohio State University Graduate Fellow (1970–1971 and 1972–1973); (c) For a preliminary report, see J. A. Hyatt and J. S. Swenton, *J. Amer. Chem. Soc.*, **94**, 7605 (1972); (d) Iowa State University; (e) Camille and Henry Dreyfus Teacher–Scholar (1972–1977); Alfred P. Sloan Fellow (1973–1975).

(2) For reviews in this area, see (a) J. R. Burr, *Advan. Photochem.*, **6**, 193 (1968); (b) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Macmillan, New York, N. Y., 1961, pp 162–220; (c) E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **8**, 578 (1969); (d) *Photochem. Photobiol.*, **7**, 511 (1968).

(3) For leading references, see (a) Z. Neiman, *Isr. J. Chem.*, **9**, 119 (1971); (b) V. I. Danelov, Y. A. Kruglyak, V. A. Kuprievich, and V. V. Ogloblin, *Theor. Chim. Acta*, **14**, 242 (1969); (c) B. Pullman, *Photochem. Photobiol.*, **7**, 525 (1968); (d) V. Klunwashter, J. Drobnik, and L. Augenstein, *ibid.*, **5**, 579 (1966); (e) A. Imamura, H. Fuyita, and C. Nagata, *Bull. Chem. Soc. Jap.*, **40**, 21 (1967).

(4) (a) E. Krajewska and D. Shugar, *Acta Biochim. Polon.*, **19**, 207 (1972); (b) R. Beugelmans, J. Fourney, S. Gero, M. LeGoff, D. Mereur, V. Ratovelomana, and M. Janot, *C. R. Acad. Sci.*, **274**, 882 (1972).

(5) C. Helene and F. Brun, *Photochem. Photobiol.*, **11**, 77 (1970).

(6) The orientation of the adduct between thymine and acrylonitrile, while not rigorously established, was proposed to be 7-cyano-6-methyl-2,4-diazabicyclo[4.2.0]octa-3,5-dione.[5] The orientation differs from that established here for adducts of 1,3-dimethyluracil with olefins.

(7) R. Malewski and H. Morrison, *Mol. Photochem.*, **4**, 507 (1972).

(8) For leading references, see E. Hayan, *J. Amer. Chem. Soc.*, **91**, 5397 (1969).

(9) (a) H. Morrison and R. Kleopfer, *J. Amer. Chem. Soc.*, **90**, 5037 (1968); (b) H. Morrison, A. Feeley, and R. Kleopfer, *J. Chem. Soc., Chem. Commun.*, 358 (1972); (c) R. Kleopfer and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 255 (1972).