bon disulfide (1.00 g, 13.2 mmol) and heated at 100° as described above for **1a**. The thiazole **2b** crystallized from dichloromethane–ether as pale yellow needles (0.324 g, 39%): mp 223–224°; ir ν_{max} (Nujol) 3120, 1605, 1505, 1090, 1075, 710 cm^{-1}; ^1H NMR δ_{Me_4Si} (DMSO-d_6) 2.23 (s, 3 H), 7.36 (s, br, 5 H), 13.09 (s, br, 1 H, exchanges with D_2O); ^{13}C NMR δ_{Me_4Si} (DMSO-d_6) 12.46, 122.50, 127.95, 128.60, 128.97, 134.10, 186.21; mass spectrum (70 eV) *m/e* 207 (M^+), 175 ($M^+ - S$), 148 [Ph-(c-C_2S)-CH_3], 121 (PhCS), 116 ($PhC{\equiv}CCH_3$), 91, 77.

Anal. Calcd for $C_{10}H_9NS_2$: C, 57.94; H, 4.38; N, 6.75. Found: C, 58.00; H, 4.81; N, 6.64.

Methylation of Thiazole 2b. The thiazole **2b** (0.238 g, 1.2 mmol) was methylated with methyl iodide (0.200 g, 1.4 mmol) in 15 ml of 1 *M* NaOH as described above for **2a**. The thiazole thioether **4b** was obtained as a pale yellow oil (0.220 g, 87%); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 2.42 (s, 3 H), 2.64 (s, 3 H), 7.31 (s, br, 5 H); mass spectrum (70 eV) *m/e* 221 (M^+).

Anal. Calcd for $C_{11}H_{11}NS_2$: C, 59.69; H, 5.01; N, 6.33. Found: C, 59.33; H, 4.95; N, 6.16.

Acknowledgment. Partial support of this research came from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are indebted to the National Science Foundation for providing funds towards the purchase of a pulse Fourier transform NMR spectrometer.

Registry No.—**1a,** 7654-06-0; **1b,** 16205-14-4; **2a,** 25445-02-7; **2b,** 7725-94-2; **4a,** 25445-03-8; **4b,** 54410-38-7; **5,** 1826-13-7; carbon disulfide, 75-15-0.

References and Notes

(1) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(2) V. Nair, *J. Org. Chem.*, **37**, 802, 2508 (1972).
(3) A. Hassner and D. J. Anderson, *J. Am. Chem. Soc.*, **93**, 4339 (1971).
(4) A. Hassner and D. J. Anderson, *J. Chem. Soc., Chem. Commun.*, 45 (1974).
(5) V. Nair and K. H. Kim, *Tetrahedron Lett.*, 1487 (1974); *J. Org. Chem.*, **39**, 3763 (1974).
(6) V. Nair, *Tetrahedron Lett.*, 4831 (1971).
(7) V. Nair, *J. Org. Chem.*, **33**, 2121 (1968).
(8) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. IV, Chemical Publishing Co., New York, N.Y., 1963, p 422.
(9) W. O. Faye, *J. Chem. Educ.*, 841 (1969).
(10) M. Komatsu, Y. Ohshiro, K. Yasuda, S. Ichijima, and T. Agawa, *J. Org. Chem.*, **39**, 957 (1974).
(11) T. A. Foglia, L. M. Gregory, G. Maerker, and S. F. Osman, *J. Org. Chem.*, **36**, 1068 (1971).
(12) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).
(13) K. B. Sukumaran, C. S. Angadiyavar, and M. V. George, *Tetrahedron*, **28**, 3987 (1972).
(14) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972.
(15) R. B. Johns, *J. Am. Chem. Soc.*, **71**, 383 (1949).
(16) M. Bachstez, *Ber.*, **47**, 3163 (1914).

Pyrolysis of 2-Alkoxy-1-azetines

Donald H. Aue* and Darryl Thomas

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

Received July 23, 1974

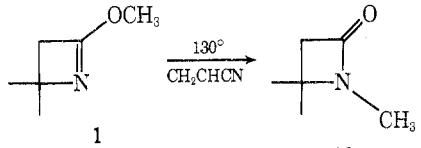
In studies of addition reactions of imino ethers,[1] we were concerned about the conditions necessary for thermal ring opening of 2-alkoxy-1-azetines.[2] We find that complete rearrangement occurs within 8 hr at 200° for 2-methoxy-1-azetines. For azetine **1**, vacuum pyrolysis at 200° for 8 hr results in complete conversion to the unsaturated imino ether **3**. Azetine **4** at 200° for 8 hr gives complete conversion to the analogous unsaturated imino ether **6**. These products can be rationalized by 1,5-hydrogen shifts of the expected intermediates **2** and **5**. Vacuum pyrolysis of azetine **8** under identical conditions gives a 40:60 mixture of isomers **10** and **11** separated by VPC. The compound with the greater retention time was assigned structure **10** by comparison with **3** and **6**. Compound **11** is the product of the alternative 1,5-hydrogen transfer process from **9**. Although **8** readily gives **11**, the analogous product **7** is not formed from azetine **4**. Apparently the *E* isomer of **5**, which would be required for a 1,5-hydrogen shift to produce **7**, is not formed from **4** because of methyl group repulsions.[3] This observation is in good accord with a mechanism involving ring opening of 1-azetines to vinyl imines like **5**, and it eliminates the possibility of a 1,4-diradical intermediate,[2] which would not be expected to specifically give **6** and no **7**.

Paquette and coworkers[2] have reported that ring opening of both (*Z*)- and (*E*)-3,4-diethyl-2-methoxy-1-azetines **12** at 600° give the same mixture of unsaturated imino ethers **14** and **15**. (*Z*)-**12** should open to the *E*, anti vinyl imine **13**, but it should not be capable of 1,5-hydrogen shifts by analogy with our results on pyrolysis of **4**. The

rearrangement of (*E*)-**12** to the same mixture of 1,5-hydrogen shift products as from (*Z*)-**12** can be explained by assuming that **14** and **15** interconvert by equilibration of each with (*Z*)-**12**. These products could be formed from (*E*)-**12** via *Z*, *anti*-**13**, which could rearrange to the *Z*, syn vinyl imine **13** by inversion at the imine nitrogen. A 1,5-hydrogen shift would then provide **15** [in equilibrium via (*Z*)-**12** with **14**]. Inversion at nitrogen would be expected to occur readily at these temperatures.[4] Furthermore, in the pyrolysis of 1-azirines, Wendling and Bergman have shown such an azetine to vinyl imine reaction to be reversible at 500° as required for equilibration of **14** and **15**,[5] and we have observed that **10** and **11** slowly equilibrate at 200° to give mainly **10** (with less than 5% **11**).

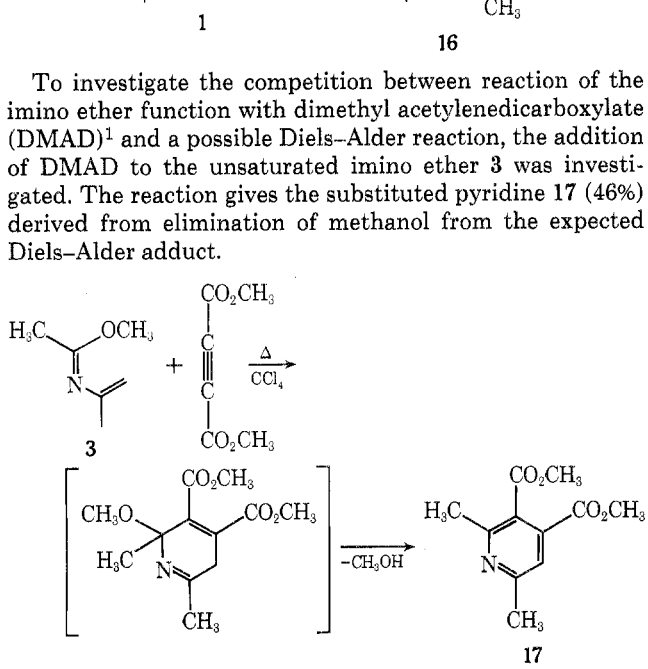
Rates of thermal ring opening of azetines **1**, **4**, and **8** were determined approximately by pyrolysis in the gas phase at 160°. Under these conditions, the dimethylazetine **1** opened to **3** with a rate constant of 0.75×10^{-5} sec^{-1}, while the opening of **4** to **6** was somewhat faster ($k \simeq 2.2 \times 10^{-5}$ sec^{-1}). Relief of the cis-methyl repulsion on opening from **4** to **5** can account for the increased rate for the trimethylazetine **4**. The tetramethylazetine **8** shows the slowest rate at 160° ($k = 0.27 \times 10^{-5}$ sec^{-1}), presumably because of the strong methyl group repulsions on opening to **9**.[3] The rates of these reactions are nearly the same as the rates of ring opening of analogous cyclobutenes to butadienes.[6] This is in contrast to the effect of oxygen and nitrogen on the rates of rearrangement of 2-oxetenes[7] and other heterocycles,[8,9] which rearrange more rapidly than analogous hydrocarbons. The rates of ring opening of 2-azetines appear to be variable. Some 2-azetines[10-13] have been reported to be stable up to 140°, while another rearranges at 25°.[12]

In contrast to the thermal ring opening of 2-alkoxy-1-azetines in the vapor phase, 2-alkoxy-1-azetines rearrange to a Chapman product at high concentration in the liquid phase. Thus, heating a concentrated solution of **1** in acrylonitrile to 130° for 4 days results in an intermolecular[14] Chapman rearrangement to the *N*-methyl-β-lactam **16** and no acrylonitrile addition to **1**.[15]



1 16

To investigate the competition between reaction of the imino ether function with dimethyl acetylenedicarboxylate (DMAD)[1] and a possible Diels–Alder reaction, the addition of DMAD to the unsaturated imino ether **3** was investigated. The reaction gives the substituted pyridine **17** (46%) derived from elimination of methanol from the expected Diels–Alder adduct.



17

Experimental Section

General Procedure for Pyrolyses of Azetines. Approximately 40 mg (0.35 mmol) of azetine was freeze degassed and vacuum transferred into a 200-ml reaction vessel. The vessel was sealed and placed in an oven set at either 162.6 ± 0.2 or 198.2 ± 0.2° for 8 hr with a sample pressure of ca. 50 mm. The end of the sample tube was cooled to −196° and opened. The NMR spectrum (in CCl_4) was integrated or the sample was analyzed by VPC to give the percentage composition of the reaction mixture. Approximate first-order rate constants were obtained from two kinetic points within the first 2 half-lives. The pyrolyses gave no nonvolatile material or side products.

Pyrolysis of 2-Methoxy-4,4-dimethylazetine (1). A. When 46 mg of **1**[1a] was heated to 200° for 8 hr according to the general procedure above, it gave compound **3** cleanly by bulb-to-bulb distillation: ir (CCl_4) 3080, 2960, 1680, 1625, 1440, 1370 cm^{-1}; NMR (CCl_4) δ 1.75 (m, 3 H), 1.87 (s, 3 H), 3.60 (s, 3 H), 3.90 (m, 1 H); 4.17 (m, 1 H); mass spectrum (70 eV) *m/e* 113.0839 (calcd for $C_6H_{11}NO$, 113.0841); *m/e* (rel intensity) 113 (M^+, 38), 98 (10), 83 (13), 82 (8), 81 (5), 72 (7), 71 (5), 70 (5), 58 (10), 57 (8), 56 (10), 43 (24), 42 (100), 41 (32), 40 (8), 39 (18), 29 (5, 28 (18), 27 (8), 15 (12).

B. When **1** was heated to 162.6° according to the general procedure above, it gave a first-order rate constant of $0.75 \pm 0.1 \times 10^{-5}$ sec^{-1} based on NMR analysis of the products. When compound **3** was heated to 160° for 24 hr, no **1** was observed by NMR.

Pyrolysis of 2-Methoxy-3,4,4-trimethylazetine (4). A. When 40 mg of **4**[1a] was heated to 200° for 8 hr according to the general procedure above, it gave compound **6** cleanly by bulb-to-bulb distillation: ir (CCl_4) 3090, 2975, 2940, 1680, 1625, 1465, 1440, 1330, 1270, 1230 cm^{-1}; NMR (CCl_4) δ 1.08 (t, J = 7.7 Hz, 3 H), 1.73 (m, 3 H), 2.26 (q, J = 7.7 Hz, 2 H), 3.58 (s, 3 H), 3.88 (m, 1 H), 4.14 (m, 1 H); mass spectrum (70 eV) *m/e* 127.0993 (calcd for $C_7H_{13}NO$, 127.0997); *m/e* (rel intensity) 127 (M^+, 41) 112 (31), 97 (13), 84 (19), 71 (11), 70 (9), 58 (38), 57 (19), 56 (100), 55 (16), 42 (20), 41 (31), 39 (21), 28 (31), 27 (17), 15 (16).

B. When **4** was heated to 162.6° according to the general procedure above, it gave a first-order rate constant of $2.2 \pm 0.3 \times 10^{-5}$ sec^{-1}.

Pyrolysis of 2-Methoxy-3,3,4,4-tetramethylazetine (8). A. When **8**[1a] was heated to 200° for 20 hr according to the general procedure above, it gave a mixture composed of 40% compound **10** and 60% compound **11** cleanly by bulb-to-bulb distillation. The compounds were separated on a 0.25 in. × 10 ft column of 10% SE-30 on 60/80 Chromosorb W, giving pure **10** and pure **11**. Pure **10**: retention time (79°) 9.7 min; ir (CCl_4) 3090, 2970, 2935, 1675, 1630, 1470, 1290, 1260, 1100 cm^{-1}; NMR (CCl_4) δ 1.07 (d, J = 6.9 Hz, 6 H), 1.73 (m, 3 H), 2.94 (heptet, J = 6.9 Hz, 1 H), 3.58 (s, 3 H), 3.87 (m, 1 H), 4.12 (m, 1 H); mass spectrum (70 eV) *m/e* 141.1154 (calcd for $C_8H_{15}NO$, 141.1154); *m/e* (rel intensity) 141 (M^+, 11), 126 (10), 98 (2.5), 96 (2.5), 84 (8), 70 (10), 69 (12), 68 (6), 58 (14), 56 (25), 55 (3), 43 (13), 42 (8), 41 (17), 39 (8), 32 (4), 29 (3), 28 (29), 27 (6), 18 (100), 17 (19), 15 (5). Pure **11**: retention time (79°) 8.2 min; ir (CCl_4) 3080, 2960, 1675, 1640, 1295, 1205, 1160 cm^{-1}; NMR (CCl_4) δ 1.01 (d, J = 6.2 Hz, 3 H), 1.82 (m, 3 H), 3.54 (s, 3 H), 3.54 (heptet, J = 6.2 Hz, 1 H), 4.80 (m, 1 H), 5.05 (m, 1 H); mass spectrum (70 eV) *m/e* 141.1155 (calcd for $C_8H_{15}NO$, 141.1154); *m/e* (rel intensity) 141 (M^+, 32) 140 (15), 126 (56), 98 (10), 85 (10), 70 (12), 69 (34), 68 (59), 59 (17), 58 (24), 56 (32), 55 (12), 43 (24), 42 (22), 41 (85), 40 (10), 39 (34), 28 (44), 27 (20), 18 (100), 17 (20), 15 (22). Uv spectra of **10** and **11** showed only end absorption with a shoulder at 240 nm (ε ~800).

B. When **8** was heated according to the general procedure above, it gave a first-order rate constant of $0.21 \pm 0.03 \times 10^{-5}$ sec^{-1} at 162.8° and 9×10^{-5} sec^{-1} at 198.2°. Using a log A of 14.0, these rate constants are consistent with $E_a \cong 39.0$ kcal/mol. Heating **8** at 198.2° for 100 hr gave a mixture containing 90% of **10** and 10% of **11** by VPC analysis. Heating **10** at 198.2° for 100 hr gave less than 5% of **11**. Thus **10** and **11** equilibrate at 198.2° to give mainly **10**.

Liquid-Phase Thermolysis of 2-Methoxy-4,4-dimethylazetine (1). A mixture of 176 mg of **1** and 183 mg of acrylonitrile was freeze degassed and vacuum sealed in an NMR tube. The tube was placed in an oil bath at 130° with the solution level at the oil level. The solution was heated in this manner for 3 days. Following the course of the reaction by NMR showed the buildup of 1,4,4-trimethyl-1-azacyclobutan-2-one (**16**) at the expense of azetine **1**. The tube was heated for 3 days longer to ensure complete conversion to the β-lactam **16**. The tube was opened and the β-lactam **16** was isolated by bulb-to-bulb distillation: ir (CCl_4) 1750 cm^{-1};

NMR (CCl_4) δ 1.37 (s, 6 H) and 2.65 (s, 5 H) [lit. NMR ($CDCl_3$) δ 1.35 (s, 6 H) and 2.65 (s, 5 H)].[16]

Reaction of 3 with DMAD. A mixture of 40 mg (0.354 mmol) of **3** and 47 mg (0.331 mmol) of DMAD in 4 ml of carbon tetrachloride was refluxed for 2 days and the solvent was removed in vacuo. Vacuum distillation gave 34 mg (46% yield) of dimethyl 2,6-dimethylpyridine-3,4-dicarboxylate (**17**): bp ca. 100° (10^{-3} mm); ir (CCl_4) 3000, 1745, 1600, 1580, 1445, 1380, 1325, 1270, 1220, 1160, 1085 cm^{-1}; NMR (CCl_4) δ 2.53 (s, 3 H), 2.57 (s, 3 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 7.33 (s, 1 H); mass spectrum (70 eV) *m/e* 223.0848 (calcd for $C_{11}H_{13}NO_4$; 223.0844); *m/e* (rel intensity) 223 (M^+, 2), 192 (10), 191(12), 159 (6), 133 (6), 128 (8), 101 (3), 100 (7), 85 (2), 68 (9), 59 (4), 58 (4), 44 (5), 43 (21), 42 (4), 41 (5), 40 (2), 39 (3), 32 (5), 31 (5), 29 (5), 28 (21), 27 (2), 18 (100), 17 (18), 15 (15).

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No.—**1**, 23974-38-1; **3**, 54384-93-9; **4**, 52856-04-9; **6**, 54384-94-0; **8**, 49680-46-8; **10**, 54384-95-1; **11**, 54384-96-2; **16**, 23974-51-8; **17**, 54384-97-3; DMAD, 762-42-5.

References and Notes

(1) (a) D. H. Aue and D. Thomas, *J. Org. Chem.*, **39**, 3855 (1974); (b and c) ibid., submitted for publication.
(2) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **92**, 1763 (1970), report opening of 2-alkoxyazetines at 600°.
(3) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965). Equilibration of **14** and **15** via (*E*), *syn*-**13** is unlikely, since no **7** was formed from **5** via (*E*)-**5**.
(4) D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 36 (1967).
(5) L. A. Wendling and R. G. Bergman, *J. Am. Chem. Soc.*, **96**, 308 (1974).
(6) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", National Standard Reference Data Series, U.S. National Bureau of Standards, 1970, pp 285–293. The activation energy for ring opening of *cis*-1,2,3,4-tetramethylcyclobutene is 37.4 kcal/mol (log A = 14.1). The calculated activation energy for ring opening of **1** is ca. 38 kcal/mol assuming log $A \cong 14$.
(7) L. E. Friedrich and G. B. Schuster, *J. Am. Chem. Soc.*, **93**, 4603 (1971).
(8) D. H. Aue, R. B. Lorens, and G. S. Helwig, *Tetrahedron Lett.*, 4795 (1973).
(9) D. H. Aue, M. J. Meshishnek, and D. F. Shellhamer, *Tetrahedron Lett.*, 4799 (1973).
(10) Union Carbide Corp., Netherlands Appl. 6,507,886 (1965); *Chem. Abstr.*, **64**, 19631*a* (1966).
(11) E. Winterfeldt and W. Krohn, *Chem. Ber.*, **102**, 2336 (1969).
(12) J. L. Derocque, W. J. Theuer, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968); E. J. Volker, M. G. Pleiss, and J. A. Moore, ibid., **35**, 3615 (1970).
(13) L. de Vries, *J. Org. Chem.*, **39**, 1707 (1974).
(14) J. Schulenberg and S. Archer, *Org. React.*, **14**, 1 (1965).
(15) Activated double bonds require a Lewis acid catalyst in order to add to imines. See (a) A. V. Gomez, J. Barluenga, and V. Gotor, *Tetrahedron Lett.*, 2819 (1973); (b) D. F. Worth, E. F. Elslager, and S. C. Pericone, *J. Heterocycl. Chem.*, **11**, 69 (1974); (c) R. Fuks, R. Buijle, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **5**, 585 (1966); and ref 10.
(16) D. Bormann, *Justus Liebigs Ann. Chem.*, **725**, 124 (1969).

Photolysis of Azido-1,3,5-triazine. Photocycloaddition of Singlet Nitrene to Nitriles

Hideo Yamada, Haruo Shizuka,* and Kohji Matsui

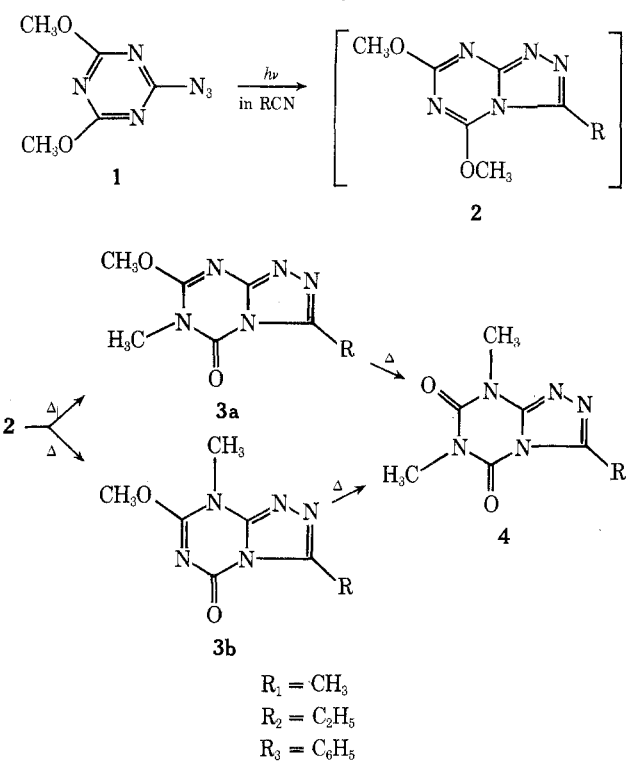
Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Received November 19, 1974

There has been considerable interest recently in the field of nitrene chemistry, and many nitrene reactions (addition to olefins, insertion into the C–H bond, ylide formation with Lewis bases, and other reactions) have been reported.[1] As for the reaction of nitrenes with nitriles, carbethoxynitrene[2,3] and acetylnitrene[4] add to the nitrile group to yield 1,3,4-oxadiazoles. However, little mechanistic work has been reported and photolysis of azido-1,3,5-triazine has not been studied. The reactivity of the triazinyl nitrene is unknown. Triazine derivatives give rise photochemically to interesting reactions: the photo-Smiles rearrangement,[5] the photo-Fries rearrangement,[6] and the phototriazinylation.[7] During the course of our studies on triazine photochemistry, we have carried out the photolysis of azidotriazine in nitriles, and observed the photocycloaddition of singlet triazinyl nitrene to the CN group.

The photolysis of 2-azido-2,4-dimethoxy-1,3,5-triazine (**1**) in degassed and aerated nitriles at 254 nm is shown in Scheme I. The photoproducts which could be isolated are listed in Table I.

Scheme I



$R_1 = CH_3$
$R_2 = C_2H_5$
$R_3 = C_6H_5$

The uv spectral change of **1**, for example, in acetonitrile (R_1CN) showed a great decrease in the λ_{max} (238 nm) of the starting material[8] and a slight increase in the 260–310-nm range during the photolysis. This change indicates that both **3a**R_1 (7-methoxy-3,6-dimethyl-*s*-triazolo[4,3-*a*]-1,3,5-triazin-5-one) and **3b**R_1 (7-methoxy-3,8-dimethyl-*s*-triazolo[4,3-*a*]-1,3,5-triazin-5-one) were not primary photoproducts, but were formed thermally from **2**R_1 (5,7-dimethoxy-3-methyl-*s*-triazolo[4,3-*a*]-1,3,5-triazine), because the absorption maxima of **2a**R_1 and **3b**R_1 are at 240 and at 255 nm, respectively. This result was confirmed by a change in the NMR spectra of the photolyzed solution[9] that occurred after standing at room temperature, and the appearance of only weak ir absorption at the characteristic 1735-cm^{-1} absorption of **3a** and **3b** immediately after irradiation.

Similarly, the photoadducts **3a**R_2 and **3b**R_2 (trace) were detected in the photolyzed solution of **1** in propionitrile (R_2CN). In the case of benzonitrile (R_3CN), the final product **4**R_3 (6,8-dimethyl-3-phenyl-*s*-triazolo[4,3-*a*]-1,3,5-triazine-5(6*H*),7(8*H*)-dione) was the only one isolated:[10] the analytical and spectral data agreed with those reported by Kobe et al.[11] The O → N shifts of methyl groups[12] in the photoproducts **2** took place easily even at room temperature. The lack of aromaticity in the compounds **2** and **3** may facilitate the O → N shifts of methyl groups, as has been suggested by Reynolds et al.[13] The O → N shift of