was measured by HPLC analysis using anisole as an internal standard and 5% ethyl acetate in hexane as the solvent.

In the Stern–Volmer plots, the strength (A) of a chromatographic peak relative to the standard peak was taken to represent the percent formation or disappearance of a given compound. For the phenylalkanone disappearance and acetophenone–cyclobutanol appearance, ratios of the relative strength in the absence (A^0) and in the presence (A_x) of Ph_3P were taken as $\Phi^0/\Phi = A^0/A_x$ for the plotting of eq 13. The quantum yields of the formation of ethers **1** and **2**, Φ_e in eq 12, were calculated from the percent yields of the ethers, which were obtained from a predetermined calibration curve against the anisole internal standard.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, Ottawa, for generous financial support.

Registry No. **1a**, 81631-43-8; **1b**, 78522-84-6; **1c**, 86259-54-3; **2**, 4013-34-7; CBa, 935-64-8; CBb, 82245-43-0; CBc, 81759-40-2; butyrophenone, 495-40-9; valerophenone, 1009-14-9; γ-methylvalerophenone, 2050-07-9; acetophenone, 98-86-2; methanol, 67-56-1; triphenylphosphine, 603-35-0.

Formation and Reactions of Dewar 4-Pyrimidinones in the Photochemistry of 4-Pyrimidinones at Low Temperature. 2

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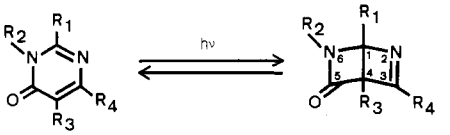
The photochemistry of the 4-pyrimidinones **1b–l** in liquid NH_3–ether solution at −40 °C or in methanol at −10 to −40 °C was studied. Irradiation of **1b–g** at low temperature gave the corresponding Dewar 4-pyrimidinones (**2b–g**), whose physical properties (IR, NMR, and UV) were determined. The photolysis of **1h–j** in methanol at −10 to −20 °C gave methanol adducts **5–7** which suggested the formation of the Dewar 4-pyrimidinones **2h–j**. However, the intermediate **2h** could not be detected in liquid NH_3–ether solution at −40 °C. The hydrogen of the imino group increases sharply the reactivity of **2h–j**. Irradiation of **1k** and **1l** in liquid NH_3–ether solution at −40 °C gave the crystalline product **3** and inseparable products, respectively, which did not suggest the formation of **2k** and **2l**. Presumably, the excited 4-pyrimidinone **1k** directly reacts with ammonia before electrocyclization. The 4-pyrimidinone **1l** may decompose by excitation. The reactions of the Dewar 4-pyrimidinones **2a–j** in methanol and in methanol containing sodium methoxide were studied. The products were the β-lactam **4**, imino ether **5**, and acetals **6–8**. The Dewar 4-pyrimidinones **2e–g** gave inseparable products and two unidentified products in methanol, respectively.

Recently, we have reported the photochemical reactions of 4-pyrimidinones in protic solvents.[1-3] The structures of the products suggested strongly that a Dewar 4-pyrimidinone is an intermediate. Low-temperature photolysis of 4-pyrimidinones was then undertaken in order to obtain the Dewar 4-pyrimidinones. 1,3,6-Trimethyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-ene (Dewar 4-pyrimidinone **2a**) was photochemically formed from 2,3,6-trimethyl-4-(3*H*)-pyrimidinone (**1a**) in liquid NH_3–ether solution at −40 °C, and the reaction of **2a** in protic solvents revealed that the Dewar 4-pyrimidinone **2a** is the intermediate (Scheme I).[3]

In the previous report,[1] several attempts to obtain β-lactams from some 4-pyrimidinones in methanol were unsuccessful. For example, 3,6-dimethyl-2-phenyl-4-(3*H*)-pyrimidinone (**1c**) was irradiated in methanol at 30–35 °C to give inseparable product(s). No corresponding β-lactam was obtained. The results suggested that either little or no photochemical reaction occurs or that the formed Dewar 4-pyrimidinone does not undergo a solvolysis reaction in methanol. The mechanistic question was resolved by application of the low-temperature method to 4-pyrimidinones **1b–l**. Experiments with the 4-pyrimidinones **1b-l** permitted examination of the generality of the photochemical electrocyclization of 4-pyrimidinones since replacement of the alkyl group with hydrogen, aryl, or thiomethyl provides insight into the solvolysis reactions of the Dewar 4-pyrimidinones in methanol.

Scheme I



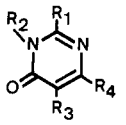
1a-g 2a-g

Results and Discussion

Photochemistry of 4-Pyrimidinones 1b–l at Low Temperature. Irradiation of 4-pyrimidinones **1b–l** has been carried out in liquid NH_3–ether solution at −40 °C or in methanol at −10 to −40 °C under a nitrogen atmosphere with a high-pressure mercury lamp through quartz or a Pyrex glass filter. The 4-pyrimidinones **1b–g** under irradiation gave mixtures of 5-oxo-2,6-diazabicyclo-

(1) Hirokami, S.; Hirai, Y.; Nagata, M.; Yamazaki, T.; Date, T. *J. Org. Chem.* **1979**, *44*, 2083–2087.
(2) Hirai, Y.; Yamazaki, T.; Hirokami, S.; Nagata, M. *Tetrahedron Lett.* **1980**, *21*, 3067–3070.
(3) Hirokami, S.; Takahashi, T.; Nagata, M.; Hirai, Y.; Yamazaki T. *J. Org. Chem.* **1981**, *46*, 1769–1777.

0022-3263/83/1948-2914$01.50/0



1

	R_1	R_2	R_3	R_4
a	CH_3	CH_3	H	CH_3
b	CH_3	CH_3	H	Ph
c	Ph	CH_3	H	CH_3
d	H	CH_3	H	CH_3
e	H	CH_3	CH_3	CH_3
f	CH_3	CH_3	CH_3	CH_3
g	SCH_3	CH_3	H	CH_3
h	CH_3	CH_3	H	H
i	$-(CH_2)_4-$		H	H
j	$-(CH_2)_5-$		H	H
k	CH_3	Ph	H	CH_3
l	CH_3	H	H	CH_3

[2.2.0]hex-2-enes (Dewar 4-pyrimidinones **2b–g**) and the starting materials (Scheme I). The physical properties and yields of the Dewar 4-pyrimidinones are listed in Tables I and II.

When the 4-pyrimidinones **1b–f** were irradiated through quartz at low temperature, the ratios of **1b–f** and **2b–f** reached constant values after 4–16 h. An analogous result was observed in the photochemistry of **1a** in liquid NH_3–ether solution at −40 °C.[3] The observation could be explained by an efficient photoreverse reaction of **2** to **1**. The Dewar 4-pyrimidinones **2b–g** were unstable in the inert solvent at room temperature and did not revert to **1** at 34 °C (C_6D_6). The half-life times of **2b–d** were 52, 3.3, and 5.4 h, respectively. The longer lifetime of **2b** compared to those of **2a**,[3] **2c**, and **2d** may be due to the stabilization of the imine bond of **2b** by the phenyl group.

The apparent wavelength and solvent effects on the yields of the Dewar 4-pyrimidinones were observed in the cases of **1b–d** are listed in Table II. When the solution containing **1c** was irradiated with a high-pressure mercury lamp through Pyrex glass ($\lambda > 290$ nm) and through quartz, the fractions of **2c** were 83% and 13%, respectively. For elucidation of the wavelength effect, the UV absorption spectra of the mixtures of **1c** (28%) and **2c** (72%) were measured in *n*-hexane. The calculated λ_{max} (ϵ) of **2c** and the observed λ_{max} (ϵ) of **1c** were 260 (1.1×10^3) and 292 nm (6.76×10^3), respectively. The extinction coefficient (ϵ) of **2c** at $\lambda > 300$ nm was extremely small, and that of **1c** was about 3.0×10^3 at 320 nm. This showed that the starting 4-pyrimidinone **1c** absorbs the light transmitted through the Pyrex filter but that the Dewar 4-pyrimidinone **2c** does not. Then, the reverse reaction of **2c** to **1c** by irradiation was suppressed and the fraction of **2c** increased. A similar wavelength effect was also observed in the photolysis of **1b**.

The UV absorption spectra of the mixture of **1d** (73%) and **2d** (27%) were measured in methanol and in *n*-pentane to elucidate the solvent effect on the yields of **2d** (Table II). The observed λ_{max} (ϵ) of **1d** were 272 nm (3.94×10^3) in methanol and 277 nm (3.22×10^3) in *n*-pentane. The calculated λ_{max} (ϵ) of the Dewar 4-pyrimidinone **2d** were 255 nm (1.9×10^3) in methanol and 252 nm (1.3×10^3) in *n*-pentane. The results indicated that the UV spectra of **1d** and **2d** were not remarkably influenced by solvent polarity. Presumably, the difference in the yields of **2d** between the reaction in liquid NH_3–ether and that in methanol was attributed to the changes in the quantum yield of **2d** from **1d** and that of **1d** from **2d** in the two solvents.[4a]

Irradiation of **1h** in liquid NH_3–ether solution at −40 °C gave no ^1H NMR and IR evidence for the formation of the corresponding Dewar 4-pyrimidinone **2h**, and the starting **1h** was quantitatively recovered. The Dewar 4-pyrimidinone **2h** could not be observed in methanol at −20 °C although two products (**5h** and **6h**), which were derived from **2h**, were isolated (Scheme III). The photochemical reaction of **1i** and **1j** was analogous to that of **1h**. No spectral evidence for the formation of **2i** and **2j** was found. The results suggest that 2h–j are unstable at room temperature and react with methanol to give the products even at low temperature. Presumably, the location of hydrogen on the imino group of the Dewar 4-pyrimidinone **2** substantially alters the stability and reactivity of **2**.

When 4-pyrimidinone **1k** was photolyzed in liquid NH_3–ether solution at −40 °C, a crystalline product, **3**, was isolated in 58% yield. The structure was assigned as *N*-phenyl-3[(2-aminoethylidene)amino]-2-butenamide from the spectral data. Further confirmation was achieved by conversion of **3** to the starting 4-pyrimidinone **1k** (59%) on alumina column (Scheme II). The photolysis of 2-methyl-d_3-3-phenyl-4-pyrimidinone (**1k(D)**) in liquid NH_3–ether solution gave the ethylidenic methyl-d_3-amidine **3(D)** (58%). The location of CD_3 group was determined by the ^1H NMR spectrum. The cyclization and separation of **3(D)** on alumina column gave **1k(D)** (74%). The results indicated clearly that ammonia adds to the C(2)–N(3) bond of **1k**. When **1k** was irradiated in methanol at −20 °C, the Dewar 4-pyrimidinone **2k** could not be detected by ^1H NMR or IR, and some inseparable products were obtained. Furthermore, irradiation of **1k** in acetonitrile at −30 °C gave no spectral evidence for the formation of **2k**. A plausible mechanism for the formation of the photoproduct **3** is shown in Scheme II. The excited 4-pyrimidinone **1k** is attacked at C(2) by ammonia to give A which leads to the formation of the product **3**. We cannot explain why the *N*-phenyl group markedly increases the reactivity of the excited **1k** (compared with the excited **1a–g**) toward the nucleophile.

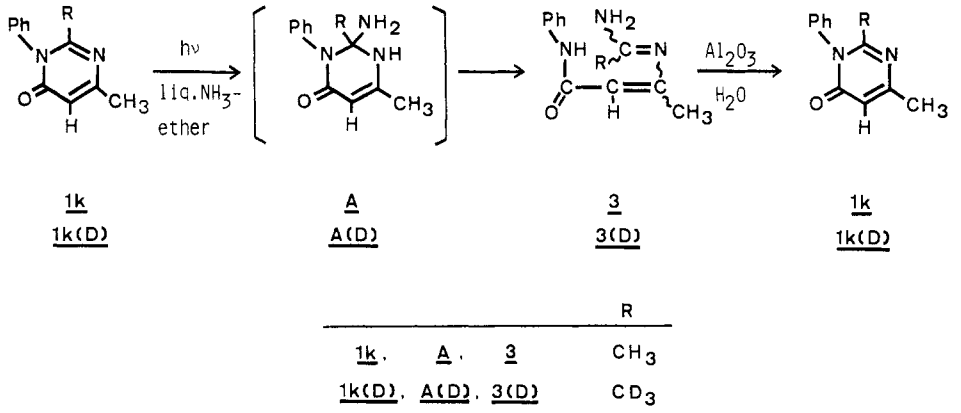
Irradiation of **1l** in liquid NH_3–ether solution at −40 °C gave inseparable product(s). Presumably, the excited **1l** decomposed before photoelectrocyclization.

Chemistry of the Dewar 4-Pyrimidinones. As mentioned above, irradiation of the 4-pyrimidinones **1h–j** in methanol and in methanol containing sodium methoxide at −20 to +20 °C gave the imino ether **5** and acetals **6** and **7** shown in Scheme III. The products indicated clearly that a new chemical bond is formed between positions 2 and 5 of **1h–j** by excitation; that is, the corresponding Dewar 4-pyrimidinones (**2h–j**) are formed. Therefore, the results of the photochemistry of **1h–j** are discussed together with the reactions of the Dewar 4-pyrimidinones **2b–g**. The reactions of the Dewar 4-pyrimidinones were carried out with the mixture of the Dewar 4-pyrimidinone and the starting material.

The reactions of the Dewar 4-pyrimidinones **2b–d** and the photolysis of **1h–j** in methanol and in basic methanol solution gave the β-lactam **4**, imino ether **5**, acetals **6–8**, and small amounts of the hydrolysates from the acetals. The photolysis of **1b–d** in the basic methanol solution at 0–20 °C gave the products **5–8** and the 4-pyrimidinone **9**. The reaction mechanism for the formation of the secondary photoproduct **9** will be discussed further below. The reaction products and their yields are shown in Scheme

(4) (a) We could not measure the quantum yields of **2d** from **1d** and of **1d** from **2d** due to the instability of **2d** at room temperature. (b) The reaction of **5h** with methanol in the presence of sodium methoxide gave **6h** (18%) and **1d** (58%).

Scheme II



	R
1k, A, 3	CH_3
1k(D), A(D), 3(D)	CD_3

Table I. IR and ^1H NMR Spectral Data for Dewar 4-Pyrimidinones[a]

compd	IR ($\nu_{C=O}$), cm^{-1} (in $CHCl_3$)	^1H NMR (C_6H_6), δ (proton type) R_1	R_2	R_3	R_4
2a[b]	1750	1.32 (CH_3)	2.48 (CH_3)	3.69 (CH)	1.75 (CH_3)
2b	1755	1.38 (CH_3)	2.43 (CH_3)	4.15 (CH)	7.00-7.93[c] (Ph)
2c	1750	7.70-7.60[c] (Ph)	2.48 (CH_3)	3.93 (CH)	1.78 (CH_3)
2d	1750	4.56[d] (CH)	2.52 (CH_3)	3.90[d] (CH)	1.74 (CH_3)
2e	1755	4.46 (CH)	2.50 (CH_3)	1.04 (CH_3)	1.67 (CH_3)
2f	1745	1.21 (CH_3)	2.44 (CH_3)	0.97 (CH_3)	1.66 (CH_3)
2g	1755	1.66[e] (SCH_3)	2.50 (CH_3)	3.97 (CH)	1.66[e] (CH_3)

[a] Unless otherwise stated, the ^1H NMR signals of the Dewar 4-pyrimidinones were singlets. [b] Reference 3. [c] The signals of the aromatic protons of 1 and 2 were multiplets and could not be distinguished. [d] The signals were doublets and the coupling constant was $J = 2$ Hz. [e] The corresponding signals in $CDCl_3$ were δ 2.15 (s) and 2.22 (s).

Table II. Yields of Dewar 4-Pyrimidinones

starting material	1, mmol	solvent[a]	irradn time, h	% yield[b] of 2
1a	16.70	A	9	33[c]
1b	1.64	A	6	9
1b	5.20	A	33[d]	22
1b	2.70	C	7	10
1c	2.64	A	7	13
1c	2.52	A	76[d]	83
1c	7.52	C	6	17
1d	16.20	A	16	6
1d	17.00	C	11	30
1e	11.00	C	10	12
1f	2.67	A	4	11
1g	8.93	B	2	10
1h	2.46	A	4	0[e]
1h	12.10	C	5	0[f]
1i	6.98	C	7	0[f]
1j	6.16	C	5	0[f]
1k	8.09	A	8	0[g]
1l	12.30	A	8	0[h]

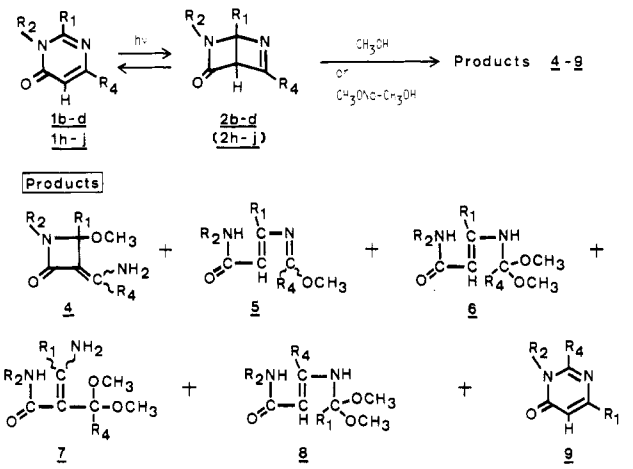
[a] A, liquid NH_3-ether (86:14 to 75:25 w/w %) at −40 °C; B, liquid NH_3-ether-CH_3CN (72:18:10 w/w %) at −40 °C; C, CH_3OH at −10 to −40 °C. The volume of the solvents was about 230 mL. [b] The yields were estimated by integration of the peak areas of the ^1H NMR spectra. [c] Reference 3. [d] Irradiation was carried out with a Pyrex glass filter. [e] The starting material 1h was quantitatively recovered. [f] The imino ether 5 and acetals 6 and 7 were obtained (Table III). [g] The amidine 3 was obtained (Scheme II). [h] Some inseparable product(s) was obtained.

III and Tables III–V and IX. The chemical names, melting points, and spectral and analytical data of the products are summarized in Tables VI–VIII (supplementary material).

The reaction of **2e–g** in methanol gave inseparable product(s) and two unidentified products, respectively.

The structures of the products were assigned from spectral data and confirmed by the chemical methods (see

Scheme III



Experimental Section). The stereochemistry about the double bond of the acetal **7d** was determined by comparison of the ^1H NMR data with those of amino vinyl ketones reported by Dudek and Volpp.[5]

The formation of the β-lactam **4b** from the Dewar 4-pyrimidinone **2b** in methanol could be explained by solvolysis to an intermediate carbocation, **10**, which reacts with methanol to give **4b** through the imine form **11** (Scheme IV).[1,3]

Two possible mechanisms for the formation of the imino ether **5a** from the Dewar 4-pyrimidinone **2a** in the presence of base are the addition of the nucleophile to the imino group of **2a** and the abstraction of the methine proton of **2a** by base.[3] In the present experiment, the imino ether **5** was isolated from the photolysate of **1h** in methanol and from the reaction of **2c** with methanol in the absence of a strong base. The addition mechanism therefore seems

(5) Dudek, G. O.; Volpp, G. P. *J. Am. Chem. Soc.* **1963**, *85*, 2697–2702.

Table III. Photolysis of 4-Pyrimidinones 1h-j in Methanol and in Methanol Containing Sodium Methoxide

starting material	1, mmol	solvent[a]	irradn time, h	temp, °C	recovered 1, %	products (yield, %)[b]
1h	12.10	C	5	−20	67	5h (76), 6h (11)
1h	9.77	D'	7	0	43	6h (47), 7h (6.8),[c] 9h = 1d (2.2)
1i	6.98	C	7	−10	54	7i (1.8)[c]
1i	3.39	D	4.5	20	10	7i (47)
1j	6.16	C	5	−10	50	7j (3.6)[c,d]
1j	3.21	D	1.5	20	28	7j (12)[c,e]

[a] C, CH_3OH (230 mL); D, CH_3ONa-CH_3OH (0.085 M, 350 mL); D', CH_3ONa-CH_3OH (0.085 M, 230 mL). [b] The yield was corrected for the recovered starting material. [c] Conversion yields of 7h-j were estimated from the amounts of the corresponding hydrolysates 20-22, respectively. [d] 3-Oxo-8-octanelactam (23, 4.0%) and ε-caprolactam (14%) were isolated from the reaction mixture. [e] 3-Oxo-8-octanelactam (23 29%) was isolated from the reaction mixture.

Table IV. Thermal Reactions of Dewar 4-Pyrimidinones 2b-d in Methanol and in Methanol Containing Sodium Methoxide

starting material	1, mmol	ratio of 1/2[a]	solvent[b]	recovered 1, %	product (yield,[c] %)
1b	10.40	83:17	C	83	4b (31)[f]
1b	2.70	90:10	D	78	5b (24)
1c	1.58	68:32	C	65	5c (34)
1c	7.52	83:17	D	81	5c (65)
1d	17.00	70:30	C	68	5d (18),[g] 7d (28)[g]
1d	16.70	70:30	D	60	(*E*)-7d (33), (*Z*)-7d (13), 8d = 6h (30)
1e	11.00	88:12	C	82	*d*, *h*
1f	2.67	89:11	C	84	*d*, *h*
1g	8.93	90:10	C	62	*e*, *h*

[a] The mixtures of 1 and 2 were used for the reactions. The ratios of 1 and 2 were estimated by integration of the peak areas of the ^1H NMR spectra. [b] C, CH_3OH; D, CH_3ONa-CH_3OH (0.05-0.1 M). The solution of 2 in 100-230 mL was stored at −20–0 °C for 1-7 days. [c] The yields were based on the calculated amounts of 2. [d] Some inseparable product(s) was obtained. [e] Two unidentified products were isolated. [f] The ratio of *E* and *Z* isomers was 32:68 by ^1H NMR analysis. The ratios remained unchanged in $CDCl_3$ and in CD_3OD. [g] The yields of 5d and 7d were estimated from the amounts of the hydrolysates 17 and 18, respectively. [h] Yield not determined.

Table V. Photolysis of 4-Pyrimidinones 1b-d in Methanol Containing Sodium Methoxide[a] at 20 °C

starting material	1, mmol	irradn, time, h	recovered 1, %	products (yield, %)[b]
1b	7.38	6	56	5b (34), 9b = 1c (28)
1c	5.47	3	39	5c (40), 9c = 1b (58)
1d	16.10	4	36	5d[c] (5.4), (*Z*)-7d (19), 8d = 6h (21)

[a] CH_3ONa-CH_3OH (0.053 M, 350 mL). [b] The yield was corrected for the recovered starting material. [c] Recrystallization of 5d from benzene-methanol gave 17 (68%).

Table IX. Hydrolysis of Imino Ether 5 and Acetals 6 and 7

starting material	amount, mmol	condition[a]	product(s)	yield, %
5d	0.562	E	*N*-methyl-3-(actylamino)-2-propenamide (17)	68
5h	2.43	F	*N*-methyl-3-(formylamino)-2-butenamide (19)	44
6h = 8d	0.203	G	3,6-dimethyl-4(3*H*)-pyrimidinone (1d)	41
			19	21
(*E*)-7d	0.271	G	*N*-methyl-2-acetyl-3-amino-2-propenamide (18)	52
(*Z*)-7d	0.149	G	18	39
7i	0.515	F	3-amino-2-formyl-2-heptene-7-lactam (21)	104

[a] E, recrystallization of 5d from benzene-methanol gave 17; F, the starting material was adsorbed on a column of alumina (20-25 g) at 20-25 °C for 31.5-37 h and eluted; G, the starting material was stirred in 2 mL of H_2O at 20-25 °C for 0.5 h.

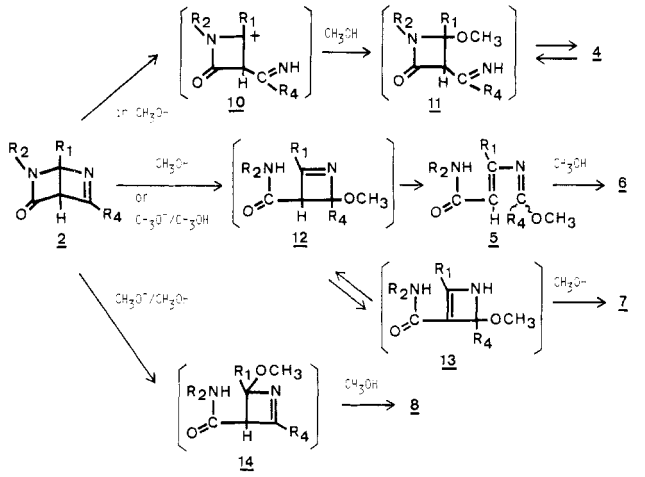
more reasonable, and we shall, for the time being, discuss our results in terms of this process.

The reactions of the Dewar 4-pyrimidinone **2** with methanol or methoxide anion, except for **2b**, gives the azetine **12**, which either isomerizes to **13** or undergoes β cleavage to give **5**. The addition of methanol to **5** gives the acetal **6**.[4b] The intermediate **13** reacts with methanol to give the acetal **7**.

The Dewar 4-pyrimidinone **2d** in methanol containing sodium methoxide gave the acetals **7d** and **8d**. The product **7d** is produced by the addition of the nucleophile to the imine bond of **2d**, but the acetal **8d** is not. Another initial reaction (S_N2) which competes with the addition reaction occurs by attack of methoxide anion on the bridgehead C(1) with concomitant cleavage of C(1)–N(6) bond to give **14**, which leads to the formation of the acetal **8** (Scheme IV).

The reaction of the Dewar 4-pyrimidinone **2b** in the presence of methoxide anion gave the imino ether **5b** and not the β-lactam product. Similar results were observed in the reaction of **2a** in basic methanol solution.[3] In the absence of a strong base, 1,3,6-trialkyl- and 3-aryl-1,6-dialkyl-substituted Dewar 4-pyrimidinones react only by the unimolecular S_N1[1,3] mechanism. In the presence of a strong base, the nucleophilic addition mechanism dominated, and the imino ether product was obtained. The results indicate clearly that the S_N1 and the nucleophilic addition reactions are competitive.

Scheme IV



Scheme V

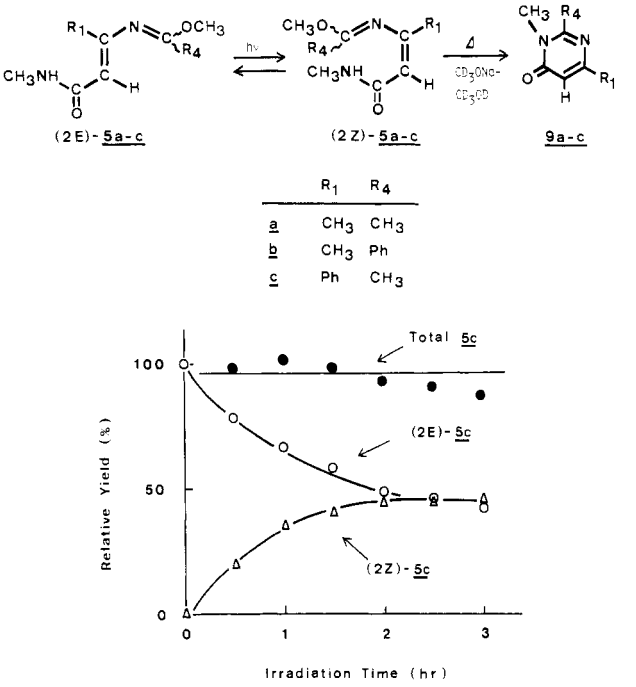


Figure 1. Effect of irradiation time on the isomerization of (2*E*)-**5c**. Relative yields were based on the initial amount of (2*E*)-**5c** (100%).

Nucleophilic addition takes place in methanol even in the absence of sodium methoxide for the Dewar 4-pyrimidinones having a hydrogen or an aryl group at position 1 or a hydrogen at position 3. The diminution of the S_N1 reaction may be due to the instability and difficult production of the secondary carbocation in methanol or the sharp increase of the reactivity of the imino group with methanol. However, we cannot explain why the 3,6-dimethyl-1-phenyl(Dewar 4-pyrimidinone) (**2c**) does not react by the S_N1 reaction.

In the experiment, all the *N*-alkyl-4-pyrimidinones undergo the photoelectrocyclization reaction (the formation of the Dewar 4-pyrimidinone). The reactions of the Dewar 4-pyrimidinones in methanol are strongly dependent on substituent groups.

Geometrical Photoisomerization of the Imino Ethers. It was of interest that the 4-pyrimidinone isomers **9b,c** were not formed in the reactions of the Dewar 4-pyrimidinones **2b,c** with methanol or methanol containing sodium methoxide but were obtained in the photolysis of 4-pyrimidinones **1b,c** in the presence of sodium methoxide. The imino ethers **5a–c** were the exclusive products in the reaction of the Dewar 4-pyrimidinones **2a–c** with methanol in the presence of methoxide anion.[3] Thus, the 4-pyrimidinones **9b,c** might be formed by a further photochemical reaction of the imino ethers **5b,c**. Moreover, no thermal reaction of **5a–c** was observed in CD_3ONa–CD_3OD at room temperature, indicating strongly that a geometrical isomer of **5a–c** underwent the cyclization reaction to give **9a–c** in the presence or absence of base.

In order to confirm the reaction mechanism, we studied the photochemistry of the imino ethers **5a–c** in CD_3O-Na–CD_3OD and in CD_3OD. When the imino ether **5c** [λ_{max} (MeOH) 266 nm (ϵ 1.22 × 10^4)] in methanol-d_4 containing sodium methoxide-d_3 (0.02 M) was irradiated through a Corning glass filter (λ > 220 nm) at 254 nm in a quartz NMR tube at 20–25 °C, new signals in ^{1}H NMR spectrum appeared at δ 3.55 (s, 3 H) and 6.37 (s, 1 H) which were assigned to the *N*-methyl and olefinic protons of the 4-pyrimidinone **9c** (=**1b**). The protons of the 2-methyl group were observed as a small signal due to the H/D exchange under the reaction conditions. After a 6.5-h irradiation, the starting **5c** was quantitatively converted to **9c** (=**1b**).

The photochemical reaction of the imino ethers (**5a** and **5b**) in basic methanol-d_4 paralleled closely that of **5c** (Scheme V).

The photolysis of **5c** in CD_3OD showed new signals at δ 1.77 (s, 3 H), 2.77 (s, 3 H), 3.89 (s, 3 H), and 5.84 (s, 1 H) in the ^{1}H NMR spectrum. The new signals could be assigned to those of the geometric isomer(s) of **5c**. In the ^{1}H NMR spectrum, the intensities of the new signals increased with irradiation time, whereas those of **5c** decreased (Figure 1). After a 2.5-h irradiation, the ^{1}H NMR signals exhibited the presence of an equilibrium mixture of the imino ether **5c** (50%) and the geometric isomer(s) (50%). When a catalytic amount of CD_3ONa–CD_3OD solution was added to the irradiated solution, the new signals of the geometric isomer(s) disappeared, and the signals of the 4-pyrimidinone **9c** (=**1b**) appeared in the ^{1}H NMR spectrum. The geometric isomer(s) was quantitatively converted to **9c**, and the signals of **5c** remained unchanged.

Analogous changes in the ^{1}H NMR spectra were observed in the photolysis of the imino ethers **5a,b**, and the formation of the 4-pyrimidinones **9a,b** was confirmed when a small amount of basic methanol-d_4 was added.

The mechanistic uncertainty concerns the configuration of **5a–c** and the corresponding photoisomers about the carbon–carbon (C–C) and nitrogen–carbon (N–C) double bonds. The configuration of **5a–c** about the C–C double bond could be deduced from the ^{1}H NMR spectra of **5d** and its hydrolysate **17**. The coupling constants of the olefinic protons of **5d** (J = 13 Hz at δ 5.71 and 7.69) and **17** (J = 14 Hz at δ 5.54 and 7.54) indicated an *E* (trans) configuration. The configuration of **5a–c** is then 2*E*.

The imino ethers **5a–c** appeared to be single geometric isomers about the N–C double bond by the ^{1}H and ^{13}C NMR spectra and by the measurement of the temperature dependence (−60 to +34 °C) of the ^{1}H NMR spectra. The configuration about the imine double bond could not be determined in view of the very limited knowledge[6] of the isomerism of the imino ethers.

Irradiation of **5a–c** at 254 nm gives an excited imino ether, which may undergo a geometrical isomerization about the C–C and/or the N–C double bonds. The ^{1}H NMR spectrum of the photoisomer showed the presence

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of a single geometrical isomer. The configuration of the photoisomer must be 2Z,4E or 2Z,4Z which readily cyclizes to give the corresponding 4-pyrimidinone when the amide hydrogen is abstracted by methoxide anion. Further work is needed to determine the configuration about the imine bond.

Experimental Section

Melting points were measured with a Yanako melting point apparatus and were uncorrected. The spectroscopic measurements were carried out with the following instruments: IR, JASCO IRA-1; UV, Hitachi Model 200-10; mass spectra, JEOL OISG-2 at 70 eV; NMR (^{1}H and ^{13}C), Varian EM-390 and Varian XL-200, chemical shifts were reported in parts per million on the δ scale relative to a Me_4Si internal standard.

The preparative irradiation of 4-pyrimidinone solution was carried out in methanol or in methanol containing sodium methoxide at −40 to +20 °C and in liquid NH_3–ether (86:14 to 75:25 w/w %) at −40 °C.[3] Column chromatography was conducted by utilizing Merck 70–230-mesh alumina (activity II–III) and Sephadex LH-20 (Pharmasia Fine Chemicals AB). Flash column chromatography was performed by using Merck silica gel 60 (230–400 mesh).

Materials. 2,3-Dimethyl-6-phenyl-4(3*H*)-pyrimidinone (**1b**),[7] 3,6-dimethyl-2-phenyl-4(3*H*)-pyrimidinone (**1c**),[8] 3,6-dimethyl-4(3*H*)-pyrimidinone (**1d**),[9] 3,6-dimethyl-2-(methylthio)-4(3*H*)-pyrimidinone (**1g**),[10] 2,3-dimethyl-4(3*H*)-pyrimidinone (**1h**),[11] and 2,6-dimethyl-4(3*H*)-pyrimidinone (**1l**)[12] were prepared as described in the literature. 3,5,6-Trimethyl-4(3*H*)-pyrimidinone (**1e**) and 2,3,5,6-tetramethyl-4(3*H*)-pyrimidinone (**1f**) were synthesized from the corresponding amidine hydrochlorides and β-keto esters according to the procedures previously described for the preparation of related compounds.[1] 6,7,8,9-Tetrahydro-4*H*-pyrido[1,2-*a*]pyrimidin-4-one (**1i**)[13] and 6,7,8,9,10-pentahydro-4*H*-pyrido[1,2-*a*]azepin-4-one (**1j**)[14] were prepared from the corresponding hydrochlorides[15,16] and sodium salt of ethyl formylacetate[17] as reported in the literature.[16] 2,6-Dimethyl-3-phenyl-4(3*H*)-pyrimidinone (**1k**)[18] was synthesized by cyclization of *N*-phenyl-β-(acetylamino)crotonamide as reported in the literature.[19] All compounds showed λ_{max} (MeOH) 278 ± 4 nm (ϵ 6 × 10^3) in UV spectra. The IR spectra ($CHCl_3$) in each case showed a peak at 1680–1645 cm^{-1}. The analytical data are shown in Table VIII (supplementary material).

The melting points of 4-pyrimidinones (**1e,f,i–k**) were 51–53, 105–105.5, 80–82, 59–60 (lit.[14] mp 66–67 °C), and 94–96 °C (lit.[18] mp 92–93 °C), respectively.

General Procedures for the Irradiation of 4-Pyrimidinones and for the Isolation of the Photoproducts. The 4-pyrimidinone (0.5–2 g) was dissolved in 230 mL of liquid NH_3–ether at −40 °C or methanol at −10 to −40 °C in a reaction cell. The solution was irradiated under dry nitrogen with a 100-W high-pressure mercury lamp. The reaction progress was routinely followed by the ^{1}H NMR spectra. The irradiation at 20 °C was carried out in a reaction cell of 350 mL. The photolysis of the 4-pyrimidinones and the reaction of the Dewar 4-pyrimidinones in methanol containing sodium methoxide were performed in the concentration range of 0.05–0.1 M. After irradiation or a dark reaction, the solution was neutralized by an ion-exchange resin (Amberlite IRC-50) when the solution contained sodium methoxide, and the solvent was evaporated. The reaction mixture was separated by column chromatography on alumina or on Sephadex LH-20.

The main experimental conditions, products, and yields are listed in Tables II–V.

***N*-Phenyl-3-[(aminoethylidene)amino]-2-butenamide (3).** A solution of **1k** (1.619 g, 8.09 mmol) in 230 mL of liquid NH_3–ether was irradiated at −40 °C for 8 h, and the solvent was evaporated. Separation of the residue by column chromatography (Sephadex LH-20) with acetone as an eluant gave unreacted **1k** (1.212 g, 75%) and the amidine **3** (0.256 g, 15%). Recrystallization of **3** from ethyl acetate–*n*-hexane gave colorless leaflets.

Cyclization of 3 on an Alumina Column. The amidine **3** (86 mg, 0.396 mmol) was dissolved in benzene–methanol (9:1) and adsorbed on a column of alumina (20 g) for 67.5 h. Elution with the same solvent as an eluant gave 47 mg (59%) of **1k** which was identical (spectra) with the starting 4-pyrimidinone **1k**.

Preparation of 6-Methyl-3-phenyl-2-(trideuteriomethyl)-4(3*H*)-pyrimidinone [1k(D)]. A solution of **1k** (2.023 g, 10.1 mmol) in 19.80 g of CH_3OD (99 D atom %; Merck) containing 0.75 mL of *tert*-butyl amine was stored under a nitrogen atmosphere at 35 °C for 75 h. Evaporation of the solvent gave a crystalline solid **1k(D)** (2.07 g, 100%; 86 D atom % by ^{1}H NMR), which was used without further purification: mp 91–91.5 °C; mass spectrum, *m/e* 203 (M$^+$).

***N*-Phenyl-3-[(1-aminotrideuterioethylidene)amino]-2-butenamide [3(D)].** A solution of **1k(D)** (2.027 g, 9.99 mmol) in 230 mL of liquid NH_3–ether was irradiated for 8 h, and the solvent was evaporated. Separation of the the residue by column chromatography (Sephadex LH-20) with acetone as an eluant gave unreacted **1k(D)** (1.659 g, 82%; 86 D atom % by ^{1}H NMR) and the deuterated amidine **3(D)** (0.230 g, 11%; 82 D atom % by ^{1}H NMR) as crystalline solid: mass spectrum, *m/e* 220 (M$^+$).

Cyclization of 3(D) on an Alumina Column. The amidine **3(D)** (0.230 g, 1.05 mmol) was dissolved in benzene–methanol (9:1) and adsorbed on a column of alumina (50 g) for 48 h. Elution with the same solvent as an eluant gave the deuterated 4-pyrimidinone (0.157 g, 74%; 64 D atom % by ^{1}H NMR) which was identical (spectra) with **1k(D)**: mass spectrum, *m/e* 203 (M$^+$).

Acetylation of the Mixture of (*E*)- and (*Z*)-*N*-Methyl-3-(α-aminobenzylidene)-4-methoxy-4-methyl-2-azetidinone (4b). A mixture of 1.339 g (5.77 mmol) of (*E*)- and (*Z*)-β-lactam isomers **4b** (68:32, by ^{1}H NMR), acetic anhydride (5mL), and pyridine (3 drops) was stirred under a nitrogen atmosphere at 50–55 °C for 90 min. After neutralization with aqueous 10% NaOH solution, the mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated NaCl aqueous solution, dried over K_2CO_3, and evaporated to give an oil. The crude mixture was separated by flash column chromatography (silica gel, 70 g) with benzene–ethyl acetate (1:2) as an eluant to give 5-acetyl-2,3-dimethyl-6-phenyl-4(3*H*)-pyrimidinone (**16**, 0.291 g) and *N*-methyl-3-[α-(acetylamino)benzylidene]-4-methoxy-4-methyl-2-azetidinone (**15**, 0.463 g). Recrystallization of **16** and **15** from benzene–*n*-hexane and from methanol-ether afforded 0.228 (16%) and 0.395 g (25%) of colorless prisms, respectively.

Structural Confirmation of the Products 5–7. The structures of the imino ethers **5** were assigned by the spectral data which were analogous to the imino ether **5a**.[3] Further confirmation of **5d** and **5h** was achieved by hydrolysis. The structures of the acetals **6** and **7** were deduced from the hydrolysates. The acetals **7h** and **7j** were not isolated, and their structures were deduced from their hydrolysates, *N*-methyl-3-amino-2-formyl-2-butenamide (**20**, 6.8% from **1h**) and 3-amino-2-formyl-2-octene-8-lactam (**22**, 12% from **1j**), which were isolated from the photolysate by column chromatography (Sephadex LH-20 and alumina, respectively) (Table III). The hydrolysates **19** and **20** were confirmed by synthesis.

The experimental conditions of the hydrolysis, products, and yields were summarized in Table IX.

Synthesis of *N*-Methyl-3-amino-2-formyl-2-butenamide (20) and *N*-Methyl-3-(formylamino)-2-butenamide (19). Formic acetic anhydride (1.18 g, 13.4 mmol) was added dropwise to a solution of *N*-methyl-3-amino-2-butenamide (1.50 g, 13.2 mmol) in 10 mL of $CHCl_3$ with stirring at 0 °C. After the mixture was stirred for 0.5 h at 20–25 °C, the solvent and the excess reagent were evaporated under reduced pressure to give an oily residue.

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Crystallization of the residual oil from ethyl acetate gave 1.08 g (58%) of **20** as colorless prisms. The liquid fraction was concentrated under reduced pressure to give 0.36 g (19%) of **19** as colorless prisms. The butenamides **19** and **20** were identical (by their spectra) with the hydrolysates from the imino ether **5h** and the acetal **7h**, respectively.

Chemical names, physical data, and analytical data for the compounds **1–7** and **15–23** are summarized in Tables VI–VIII (supplementary material).

General Procedure for the Geometrical Photoisomerization of Imino Ethers 5a–c in CD_3OD. Photochemical reaction was carried out with a low-pressure mercury lamp (30 W) through a Corning 9-54 color filter in a quartz NMR tube. CD_3OD was purged with dry nitrogen. The (2*E*)-imino ether (25–30 mg) was irradiated in CD_3OD (0.3–0.4 mL) at 20–25 °C. After irradiation, 20 μL of CD_3ONa–CD_3OD (0.05 M) was added to the reaction mixture. The 2*Z* isomers were quantitatively converted to **9a–c**.

General Procedure for the Irradiation of Imino Ethers (2*E*)-5a–c in CD_3ONa–CD_3OD. Photolysis of the (2*E*)-imino ethers was carried out in CD_3OD (0.3–0.4 mL) containing 0.022–0.029 M of CD_3ONa. The relative yields of the products were monitored by ^1H NMR analysis. After neutralization of the irradiated solution, the solvent was evaporated. The amounts of the products were analyzed by ^1H NMR spectra.

Irradiation of (2*E*)-5a in CD_3ONa–CD_3OD. From 27.8 mg (0.164 mmol) of (2*E*)-**5a** was obtained 24.3 mg (96%) of a mixture of (2*E*)-**5a** (52%) and **9a** (=**1a**) (48%) after a 16.5-h irradiation. The yields of (2*E*)-**5a** and **9a** (=**1a**) were 50% and 46%, respectively.

Irradiation of (2*E*)-5b in CD_3ONa–CD_3OD. From 29.8 mg (0.128 mmol) of (2*E*)-**5b** were obtained 27.5 mg (105%) of a mixture of (2*E*)-**5b** (16%), **9b** (=**1c**, 67%), and **1b** (17%) after a 36-h irradiation. The yields of (2*E*)-**5b**, **9b** (=**1c**), and **1b** were 17%, 70%, and 18%, respectively.

Irradiation of (2*E*)-5c in CD_3ONa–CD_3OD. From 29.8 mg (0.128 mmol) of (2*E*)-**5c** was obtained 27.5 mg (107%) of **9c** (=**1b**) after a 3-h irradiation.

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Registry No. **1b**, 86421-66-1; **1c**, 20959-22-2; **1d**, 17758-19-9; **1e**, 86421-67-2; **1f**, 86421-68-3; **1g**, 3240-60-6; **1h**, 17758-38-2; **1i**, 65754-05-4; **1j**, 52090-53-6; **1k**, 32363-53-4; **1k**(D), 86421-75-2; **1l**, 6622-92-0; **2b**, 86421-69-4; **2c**, 86421-70-7; **2d**, 86421-71-8; **2e**, 86421-72-9; **2f**, 86421-73-0; **2g**, 86436-06-8; **3**, 86421-74-1; **3**(D), 86436-07-9; (*E*)-**4b**, 86421-76-3; (*Z*)-**4b**, 86421-77-4; (*E*)-**5a**, 86421-78-5; (*Z*)-**5a**, 86421-79-6; (*E*)-**5b**, 86421-80-9; (*Z*)-**5b**, 86421-81-0; (*E*)-**5c**, 86421-82-1; (*Z*)-**5c**, 86421-83-2; **5d**, 86421-84-3; **5h**, 86421-85-4; **6h**, 86421-86-5; (*E*)-**7d**, 86421-87-6; (*Z*)-**7d**, 86421-88-7; **7h**, 86421-89-8; **7i**, 86421-90-1; **7j**, 86421-91-2; **15**, 86421-92-3; **16**, 86421-93-4; **17**, 73645-41-7; **18**, 73645-38-2; **19**, 73645-40-6; **20**, 73645-39-3; **21**, 86421-94-5; **22**, 86436-08-0; **23**, 86421-95-6; ε-caprolactam, 105-60-2; *N*-methyl-3-amino-2-butenamide, 24392-27-6.

Supplementary Material Available: Chemical names, melting points, spectral data (IR, UV, ^1H NMR, and MS), and analytical data for the compounds **1–7** and **15–23** (Tables VI–VIII) (6 pages). Ordering information is given on any current masthead page.

New General Synthesis of Diaryl Tellurides from Aromatic Amines

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A number of substituted diaryl tellurides were obtained from aryldiazonium tetrafluoroborates and potassium tellurocyanide in dimethyl sulfoxide at ambient temperature. Aryl tellurocyanides were isolated as byproducts in some experiments and postulated as intermediates in the reactions.

Although many methods are available for the preparation of diaryl tellurides,[1] only very few of them are general enough to allow the introduction of a broad variety of substituents. The reaction of diarylmercury and elemental tellurium[2,3] is perhaps the most general method at hand, but it requires the synthesis and high-temperature pyrolysis of hazardous organic mercury compounds, which are serious drawbacks. The complex reaction of aromatic Grignard reagents with tellurium tetrachloride[4] has been used for the synthesis of many diaryl tellurides, but isolation is often difficult due to formation of several byproducts such as diaryl ditellurides, aromatic hydrocarbons, and elemental tellurium. The condensation of $TeCl_4$ with 2 equiv of an aromatic compound, followed by reduction, is a good route to diaryl tellurides containing electron-donating substituents.[5]

We report herein a general synthesis of diaryl tellurides from diazotized aromatic amines and potassium tellurocyanide, KTeCN. Aryldiazonium salts (1) have been frequently used for the synthesis of organotellurium compounds.[6] Renson[7] treated diazotized anthranilic acid with a number of sodium arenetellurolates, $ArTe^-Na^+$, to obtain unsymmetrical tellurides of the general formula **2**. Sadekov[8] similarly prepared a number of unsymmetric diaryl tellurides from aryldiazonium tetrafluoroborates and so-

2, R = phenyl, *p*-tolyl, 3-thienyl

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