Chromatography (60 g, 0–2% EtOH/$CHCl_3$) of the product mixture, followed by recrystallization from acetonitrile, gave pure **15a** (0.32 g, 71%).

Acknowledgment. We acknowledge Dr. Scott R. Wilson and Dr. Eileen N. Duesler for their work in performing the X-ray crystallography, using equipment purchased through a National Science Foundation Major Equipment Chemistry Department grant (MPS 75-05911). The mass spectral data processing equipment was provided by Research Grants No. CA 11388 and GM 16846, from the National Cancer Institute and National Institute of General Medical Sciences, respectively, National Institutes of Health, U.S. Public Health Service. Mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by Grant No. GM 27029 from the National Institutes of Health.

Registry No. **1**, 5918-93-4; **3**, 930-33-6; **4**, 16421-52-6; **9**, 80049-39-4; **10a**, 67908-99-0; **10b**, 67908-94-5; **12**, 80049-40-7; **13**, 80049-41-8; **14a**, 80049-42-9; **14b**, 80049-43-0; **15a**, 80049-44-1; **15b**, 80049-45-2; **16a**, 80049-46-3; **16b**, 80049-47-4; **17a**, 80049-48-5; **17b**, 80049-49-6; **18a**, 80049-50-9; **18b**, 80049-51-0; **19**, 21823-89-2; **20**, 645-36-3; **21**, 80063-08-7; **22**, 71397-61-0; **23**, 80049-52-1; potassium cyanate, 590-28-3; α-ureidoacetaldehyde diethyl acetal, 80049-53-2; β-D-1-*O*-acetyl-2,3,5-tri-*O*-benzoylribofuranose, 6974-32-9; semicarbazide hydrochloride, 18396-65-1; triethyl orthoformate, 122-51-0; aminotetrazole, 4418-61-5; 1-(trimethylsilyl)-5-[(trimethylsilyl)oxy]tetrazole, 34907-74-9; 1-carbamoyl-4-β-D-ribofuranosyl-2-tetrazene, 80049-54-3; β-D-2,3,5-tri-*O*-benzoylribofuranosyl chloride, 29706-90-9; silver isocyanate, 3315-16-0; hydrazine, 302-01-2; formic acid hydrazide, 624-84-0.

Supplementary Material Available: Tables listing positional and thermal parameters, bond lengths, bond angles, and torsion angles from the X-ray structure solutions for compounds **15b** and **16b** (10 pages). Ordering information is given on any current masthead page.

Intramolecular Photoarylations of *N*-(Haloaryl)ethyl β-Enaminones

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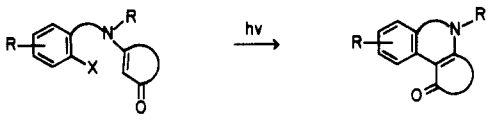
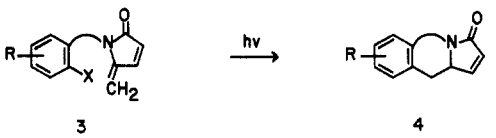
The photochemistry of several *N*-(haloaryl)ethyl β-enaminones was investigated in order to develop methods for preparation of tricyclic enaminone systems. The efficiencies of intramolecular photoarylations of the haloaryl systems were found to be dependent upon the wavelength of irradiation. Accordingly, irradiations of the haloaryl β-enaminones **9a,c,d,f** with Pyrex-filtered light leads to formation of the reduced N-cyclized and C-cyclized products **9b** or **9e**, **8a** or **8b**, and **10a** or **10b**, respectively. The major products in these processes are the reduced materials. In contrast, irradiations of the bromoaryl enaminones **9c** or **9f** with Vycor-filtered light results in high yielding conversions to the C-cyclized tricyclic enaminones **10a** and **10b** in synthetically useful yields ranging from 50% to 85%. A discussion of reasons for these wavelength dependencies is given in terms of excited-state discrimination in these bichromophoric systems. Possible reaction mechanisms are considered. The origin of another major product, **11**, generated by irradiation of **9f** with Vycor-filtered light, is also discussed.

Photocyclizations of *N*-haloaryl-substituted enaminones (**1** → **2**) and related enamides (**3** → **4**) have been employed

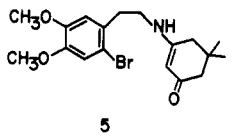


1 **2**



3 **4**

in the synthesis of a variety of heterocyclic compounds.[2,3] The reactions, in most cases, are efficient and thus useful in the preparation of complex structures found in natural products or their precursors. In recent studies,[4] we required simple methods for synthesis of the tricyclic β-enaminones **10a** and **10b**. Reports by Kibayashi and his co-workers[2] suggested that intramolecular photoarylations of appropriately substituted *N*-(haloaryl)ethyl enaminones **9** might be of use in this regard.[5] However, the reported variability of the yields of these processes left some doubt about the success of this adventure. For example, although irradiation of dioxane solutions of **5** with Pyrex-filtered



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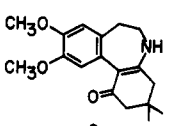

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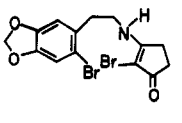

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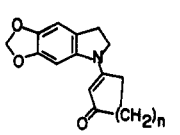


8a n=2
8b n=1

light for 125 h leads to generation of the cyclized product **6** in 91% yield, photolysis of the cyanopentenone analogue **9f** formed the dibromide **7** (4%) and hydroindole **8a** (29%) as the sole photoproducts. Equally inconsistent behavior

(1) To whom inquiries should be addressed at the University of Maryland.

(2) (a) Iida, H.; Aoyagi, S.; Kibayashi, C., *J. Chem. Soc. Perkin Trans. 1* **1977**, 120–122. (b) Iida, H.; Yuasa, Y., Kibayashi, C. *J. Chem. Soc., Chem. Commun.* **1978**, 766–767. (c) Iida, H.; Yuasa, Y., Kibayashi, C. *J. Org. Chem.* **1979**, *44*, 1236–1241.

(3) Bernhard, H. O.; Sniekus, V., *Tetrahedron Lett.* **1971**, 4867–4870. Ise, I. Sniekus, V., *J. Chem. Soc., Chem. Commun.* **1976**, 505–506.

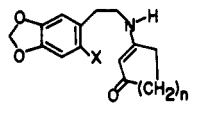
(4) Preliminary results of this work have been reported at the Southeast–Southwest Regional Meeting of the American Chemical Society New Orleans, 1980; abstract ORGN 364.

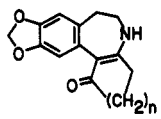
(5) (a) Other approaches involving intramolecular additions to benzynes appear possible.[5b] (b) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* **1979**, *44*, 1074–1080.

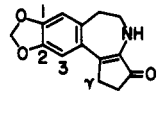
0022-3263/82/1947-0482$01.25/0

was reported for related systems.

On the basis of these observations, we initiated exploratory efforts aimed at developing reaction conditions to facilitate photocyclization of the N-(haloaryl)ethyl β-enaminones **9**. Irradiation of **9a** in 50:1 *p*-dioxane–ace-







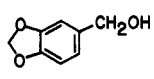
9a n=2; x=I
9b n=2; x=H
9c n=2; x=Br
9d n=1; x=I
9e n=1; x=H
9f n=1; x=Br

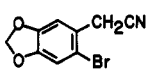
10a n=2
10b n=1

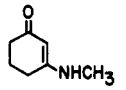
11

tonitrile solution containing triethylamine with Pyrex-filtered light led to formation of three products identified as the reduced (**9b**), N-cyclized (**8a**), and C-cyclized (**10a**) materials in respective yields of 42%, 22%, and 21%.[6] Similarly, **9d** gave the photoreduced product **9e**[6] exclusively when irradiated through Pyrex. Photolysis of the bromo aromatic enaminone **9c** under these conditions proceeded in an identical fashion, furnishing the reduced and cyclized products **9b**, **8a**, and **10a**.[6]

These results, which are comparable to those described by Kibayashi, demonstrate that irradiation of the enaminone systems with >300-nm light can result in the formation of a variety of products. In cases we have explored, photoreductions predominate, and the desired tricyclic enaminones are formed as only minor products. A search for more favorable reaction conditions prompted an inspection of the UV absorption spectral characteristics of haloaryl enaminones **9c** and **12–19** (Figure 1). This







17 **18** **19**

analysis demonstrates that the Pyrex-filtered light used in these experiments results in selective excitation of the enaminone chromophore. Although photoreaction in theory could occur from a species having excitation localized in this grouping, it seemed more reasonable to expect that photoarylation would take place through an excited aryl halide moiety populated by direct irradiation with higher energy light (vide infra). In addition, we felt that the inordinately long reaction times required when Pyrex is employed could be shortened considerably by the use of Vycor-filtered light (>220 nm). Accordingly, when *p*-dioxane solutions of the bromo enaminone **9c** containing triethylamine were irradiated through Vycor, the desired tricyclic enaminone **10a** was formed. Isolation of **10a** was accomplished by crystallization from the concentrated photolysate in yields ranging from 60% to 85%.[7] Furthermore, the previously unattainable tricyclic cyclopentenone derivative **10b** is furnished in a 47% isolated yield from **9f** by use of these conditions. Interestingly, a second photoproduct, the β-enaminone **11**, is isolated from the photolysate arising by irradiation of **9f** in a yield of 43%.

Structural assignments of the photocyclization products **10b** and **11** formed upon irradiation of **9f** are made on the

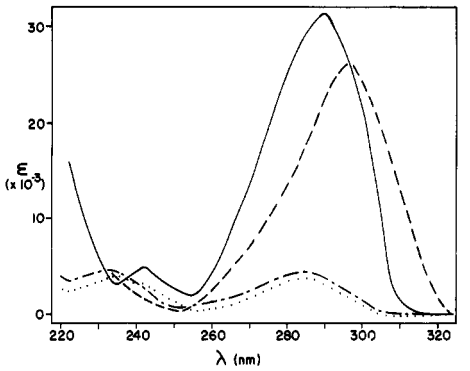


Figure 1. UV spectra (CH_3CN) of piperonyl alcohol (**17**, ···), bromo nitrile **18** (–·–), enaminone **19** (– – –), and haloaryl enaminone **9c** (—).

Table I. Spectroscopic Properties for the Tricyclic Enones 10a,b and 11

enone	^{1}H NMR (Me_2SO) δ aromatic H-3	enone γ-H	UV (MeOH) λ_{max}, nm (ε)
10a	6.79	2.76	301 (13 400)
10b	7.79	2.84	302 (13 900)
11	6.94	3.96	345 (29 700)

basis of characteristic spectroscopic data and comparisons with those obtained for the six-membered β-enaminone analogue **10a**, as summarized in Table I. Particularly useful are the chemical shifts of the aromatic H-3 and enone γ-protons which reflect the magnetic anisotropic effects of both the aromatic and carbonyl groupings. Model inspection indicates that the H-3 aromatic proton in **10b** is unique in that it is rigidly held in the deshielding regions of the carbonyl grouping. Similarly, the linearly phenyl-conjugted cyclopentenone chromophore present in **11** is expected to give rise to the longer wavelength $\pi-\pi^*$ maximum at 345 nm as compared to 302 nm for the cross-conjugated system in **10b**.[8]

A minor alteration in reaction conditions has effected a pronounced improvement of the efficiency, and thus the synthetic utility, of these intramolecular photoarylation reactions. Speculation about the source of this effect in terms of mechanisms for these processes appears warranted. One pathway for production of **10** involves photohomolysis of the carbon–halogen bond, generating aryl radicals **12**. Intramolecular capture by the enaminone α-carbon would give the C-cyclized products **10**. This route, most probably requiring direct light absorption by the aromatic nucleus,[9] finds precedent in biphenyl-forming photoarylation reactions.[10] Alternatively, electron transfer mechanisms via the diradical ions **13a** (a* and b* = + or –) could be initiated by excitation of either the aryl or enaminone chromophore and electron transfer in either direction.[11] These mechanisms are analogous to the $S_{RN}1$ pathways followed by related nucleophile arylations[12] and

(6) These materials were identified by comparison of their spectroscopic data with those of related compounds.[2c,5]

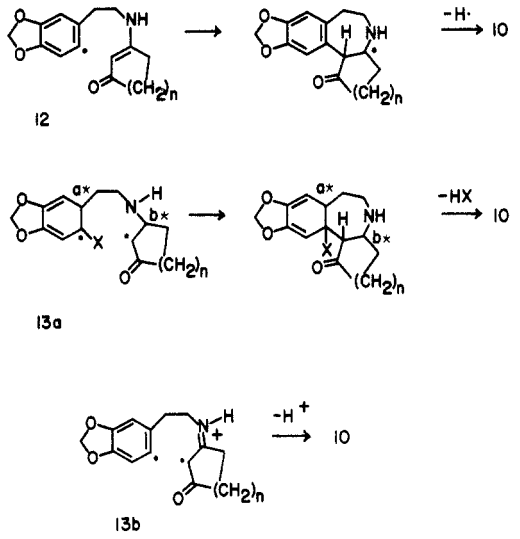
(7) When purification is accomplished by preparative thin-layer chromatography, N-cyclized material (**8a**) is isolated as well in approximately 20% yield.

(8) Identification of **11** is strongly based on comparison of its UV spectrum with those of similar compounds summarized in: Scott, A. I. "Interpretation of the Spectra of Natural Products"; Pergamon Press: Oxford, England, 1964; pp 107–108.

(9) Energy transfer from the enone to aromatic chromophores does not seem likely on the basis of the expected triplet and observed singlet energies of these systems.

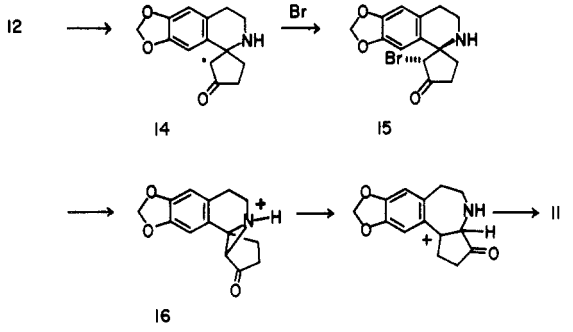
(10) Kupchan, S. M.; Kanojia, R. *Tetrahedron Lett.* **1966**, 5353–5356. Kupchan, S. M.; Miniot, J. L.; Kanojia, R. M.; O'Brien, J. B. *J. Org. Chem.* **1971**, *36*, 2413–2418.

(11) (a) Electronic excited states of organic compounds are both more easily reduced and oxidized by one electron transfer processes.[11b] (b) Gordon, M.; Ware, W. R. "The Exciplex"; Academic Press: New York, 1975.



employed in several approaches to natural product synthesis.[13] Thus, the dependence of the nature and composition of products on excitation wavelength might be due to differences in the nature of pathways available to the discriminatively excited haloaryl and enaminone groupings. Accordingly, the diradical ions or cationic diradicals **13a** and **13b** might choose hydrogen abstraction or N-cyclization as a major pathway for deactivation while C-cyclization might be an efficient route only when the aryl radical **12** is initially produced. Searches for a more detailed understanding of this intriguing phenomenon should provide data which relate directly to the synthetic versatility of this interesting photocyclization method.

The origin of the α-enaminone **11** appears intriguing. The initially formed aryl radical **12** might undergo competitive addition at the enaminone β-carbon in the five-membered-ring system (n = 2), producing the spirocyclic enonyl radical **14**. Indeed, in the absence of steric con-



straints, this is predicted to be the more favorable mode of addition of electron-rich alkoxy-substituted phenyl radicals to olefins possessing vicinally disposed electron-donating and -withdrawing substituents.[14] Thus, the enone ring size could have an effect upon the regiochemistry of intramolecular radical addition through compensatory electronic and steric controls. Several alternative sequences exist for conversion of the spirocyclic radical intermediate **14** to α-enaminone product **11**. The absence of examples of 1,2-shifts in radical systems of atoms lacking a vacant or latent atomic orbital of accessible energy[15] suggests that a simple pathway involving amine group migration is unreasonable. Another route involves recombination of a bromine atom with **14**, producing the α-halo-β-amino ketone **15**. Rearrangement of **15** to form **11** through the aziridinium ion intermediate **16** appears favorable. A more precise analysis of the mechanistic details of this unusual process must await further in-depth studies.

Experimental Section[16]

***N*-(3-Oxo-1-cyclohexenyl)-2-(2-iodo- and 2-bromo-4,5-methylenedioxyphenyl)ethanamine (9a and 9c).** These materials were prepared from the known[2c] arylethylamines by using procedures previously described for preparation of related substances.[2c] The enaminone **9a** [^{1}H NMR ($CDCl_3$) δ 7.20 (s, 1 H), 6.71 (s, 1 H), 5.97 (s, 2 H), 5.20 (s, 1 H), 5.10 (br s, 1 H); 3.20 (m, 2 H), 2.85 (m, 2 H), 1.8–2.4 (m, 6 H)] is yellow crystalline material (mp 180–181 °C) which was irradiated without further purification.

The enaminone **9c** is a white crystalline material: mp 218–220 °C; ^{1}H NMR (Me_4SO-d_6) δ 7.20 (s, 1 H), 7.13 (br s, 1 H), 6.99 (s, 1 H), 6.05 (s, 2 H), 4.90 (s, 1 H), 3.15 (m, 2 H), 2.82 (t, 2 H), 2.24 (t, 2 H), 2.16 (t, 2 H), 1.80 (m, 2 H); UV (MeOH) 290 nm (ϵ 36900), 206 (31700).

Anal. Calcd for $C_{15}H_{16}BrNO_3$: C, 53.23; H, 4.73; N, 4.14; Br, 23.67. Found: C, 53.42; H, 4.86; N, 4.09; Br, 23.57.

***N*-(3-Oxo-1-cyclopentenyl)-2-(2-iodo- and 2-bromo-4,5-methylenedioxyphenyl)ethanamine (9d and 9f).** The procedures analogous to those used for preparation of **9a** and **9c** were followed substituting 1,3-cyclopentanedione for 1,3-cyclohexanedione in the final condensation reactions. The enaminone **9d** [^{1}H NMR ($CDCl_3$/Me_4SO-d_6) δ 7.20 (s, 1 H), 6.81 (s, 1 H), 5.98 (s, 2 H), 5.00 (s, 1 H), 3.38 (m, 2 H), 2.98 (m, 4 H), 2.50 (m, 2 H)] is a tan solid (mp 177–179 °C) which was irradiated without further purification. The enaminone **9f** is a crystalline material: mp 203–205 °C; ^{1}H NMR (Me_4SO-d_6) δ 7.67 (br s, 1 H), 7.18 (s, 1 H), 6.99 (s, 1 H), 6.03 (s, 2 H), 4.89 (s, 1 H), 3.20 (m, 2 H), 2.81 (m, 2 H), 2.45 (m, 2 H), 2.12 (m, 2 H); UV (MeOH) λ_{max} 272 nm (ϵ 34300), 205 (31100).

Anal. Calcd for $C_{14}H_{14}BrNO_3$: C, 51.85; H, 4.32; N, 4.32; Br, 24.69. Found: C, 51.91; H, 4.39; N, 4.28; Br, 24.97.

Pyrex-Filtered Irradiation of 9a,cd. A solution of **9a** (0.210 g, 0.54 mmol) in 200 mL of 50:1 *p*-dioxane–acetonitrile containing 0.5 mL of triethylamine was irradiated with Pyrex filtered-light for 4 h with a 450-W Hanovia medium-pressure lamp under a nitrogen atmosphere. The crude photolysate was filtered and concentrated in vacuo, giving a residue which was subjected to preparative layer chromatography on silica gel (10% MeOH–$CHCl_3$). This yielded two major bands. Band 1 (R_f ca. 0.6) contained 30 mg of **8b** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.83 (s, 1 H), 6.78 (s, 1 H), 6.00 (s, 2 H), 5.50 (s, 1 H), 3.65–4.15 (m, 2 H), 3.15 (t, 2 H), 2.85 (t, 2 H), 2.40 (m, 2 H), 2.15 (m, 2 H). Band 2 (R_f ca. 0.4) contained 85 mg of a 2:1 (by NMR) mixture of **9b** (42%g) and **10a** (21%).

Pyrex Irradiation of **9c** yielded identical results.

A solution of **9d** (0.100 g, 0.3 mmol) in 250 mL of *p*-dioxane containing 0.5 mL of triethylamine was irradiated by using Pyrex-filtered light for 3.5 h under the conditions described above for **9a**. Similar workup conditions yielded a crude oil which was subjected to preparative layer chromatography on silica gel (20% MeOH–$CHCl_3$) to yield 50 mg (78%) of a brown oil whose ^{1}H NMR spectrum ($CDCl_3$) is consistent with that of photoreduced material **9e**:[2c] δ 6.85 (m, 3 H), 5.95 (s, 2 H).

(12) Bunnett, J. *Acc. Chem. Res.* **1978**, *11*, 413–420.

(13) Semmelhack, M. F.; Bargar, T. M. *J. Org. Chem.* **1977**, *42*, 1481–1482. Semmelhack, M. F.; Cheng, B. P.; Stauffer, P. D.; Rogerson, T. D.; Cheng, A.; Jones, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 2507–2516. Semmelhack, M. F.; Bargar, T. *Ibid.* **1980**, *102*, 7765–7774.

(14) (a) Frontier MO analysis[14b] suggests that electron-rich radicals should add to the position β to the electron-withdrawing group rather than the donating substituent due to the more favorable LUMO–singly occupied orbital interaction and greater LUMO coefficient β to the withdrawing group. (b) Fleming, I.; "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; Chapter 5, pp 182–227. (c) A more qualitative view of this feature has been discussed.[13d] (d) Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980**, *36*, 601–707.

(15) Friedlina, R. K. "Advances in Free Radical Chemistry"; Williams, G. H., Ed.; Academic Press: New York, **1965**; Vol. 1, pp 211–278.

(16) NMR spectra were recorded on Varian XL-200, EM-390, or T-60 instruments with $(CH_3)_4Si$ as an internal standard. UV spectra were measured with Perkin-Elmer 552 and GCA McPherson EV-700-56 instruments, and IR spectra were recorded by using Pye Unicara 3-200 and Perkin-Elmer 237 spectrometers. Mass spectra were obtained by use of a CEC-21-110 double-focusing mass spectrometer. Melting points taken on a Kratos (AEI)MS 902 apparatus are recorded uncorrected.

Vycor-Filtered Irradiation of 9c. Preparation of the Tricyclic Enaminone 10a. A solution of **9c** (1.00 g, 3 mmol) in 500 mL of *p*-dioxane containing 5.0 mL of triethylamine was irridiated for 2 h under a nitrogen atmosphere in the apparatus described above. The crude photolysate was filtered and concentrated in vacuo, giving a residue. A methylene chloride solution of the residue was washed with 5% $NaHCO_3$, dried, and concentrated in vacuo, giving a brown oil which crystallized when treated with $CHCl_3$–hexane solution. Recrystallization gave 0.815 g (85%) of pure tricyclic β-enaminone: mp 222 °C; IR (KBr) 3400, 3300, 3100, 2950, 15500 m^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.12 (br s, 1 H), 6.79 (s, 1 H), 6.62 (s, 1 H), 5.92 (s, 2 H), 3.44 (m, 2 H), 2.76 (m, 2 H), 2.48 (m, 2 H), 2.25 (m, 2 H), 1.76 (m, 2 H); UV (MeOH) λ_{max} 301 nm (ε 13400), 203 (18100); mass spectrum, *m/e* 257.1043 ($C_{15}H_{15}NO_3$ requires 257.1052).

Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.04; H, 5.84; N, 5.46. Found: C, 69.63; H, 5.81; N, 5.37.

Vycor-Filtered Irradiation of 9f. Preparation of the Tricyclic β- and α-Enaminones 10b and 11. A solution of **9f** (0.1 g, 0.3 mmol) in 250 mL of *p*-dioxane containing 0.5 mL of triethylamine was irradiated as described above for 1 h. A workup in a fashion described above yielded 31 mg (43%) of the β-enaminone **10b** as a tan crystalline solid: mp 250 °C dec; IR (KBr) 3250, 3080, 2950, 1550 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.15 (br s, 1 H), 7.79 (s, 1 H), 6.66 (s, 1 H), 5.91 (s, 2 H), 3.40 (m, 2 H), 2.84 (m, 2 H), 2.50 (m, 2 H), 2.31 (m, 2 H); UV (MeOH) λ_{max} 302 nm (ε 13900); mass spectrum, *m/e* 243.0892 ($C_{14}H_{13}NO_3$ requires 243.0893).

Alternate purification of the crude photolysate by preparative layer chromatography on silica gel (10% MeOH–$CHCl_3$) led to the isolation of **10b** (35 mg, 47%) from a band with an R_f of ca. 0.6 and 32 mg (43%, R_f ca. 0.7) of the α-enaminone **11** as a crystalline solid: mp 250 °C dec; IR (KBr) 3400, 3040, 2900, 1650, 1540 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 6.94 (s, 1 H), 6.85 (s, 1 H), 5.97 (s, 2 H), 5.20 (br s, H), 3.96 (m, 2 H), 3.02 (m, 4 H), 2.23 (m, 2 H); UV (MeOH) λ_{max} 345 nm (ε 29700); mass spectrum *m/e* 243.0905 ($C_{14}H_{13}NO_3$ requires 243.0893).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.35; N, 5.76. Found: C, 68.95; H, 5.41; N, 5.69.

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Nucleosides. 121. Improved and General Synthesis of 2′-Deoxy *C*-Nucleosides. Synthesis of 5-(2-Deoxy-β-D-*erythro*-pentofuranosyl)uracil, -1-methyluracil, -1,3-dimethyluracil, and -isocytosine[1]

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5-(2-Deoxy-β-D-*erythro*-pentofuranosyl)-1,3-dimethyluracil (**6a**), -1-methyluracil (**6b**), -uracil (**6c**), and -isocytosine (**6d**) were synthesized. Compounds **6b–d** are *C*-nucleoside isosteres of thymidine, 2′-deoxyuridine, and 2′-deoxycytidine, respectively. 1,3-Dimethylpseudouridine (**1a**), 1-methylpseudouridine (**1b**), pseudouridine (**1c**), and pseudoisocytidine (**1d**) were treated with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine to afford the corresponding 3′,5′-tetraisopropyldisiloxanyl derivatives **2** which were converted into the respective 2′-*O*-[(imidazol-1-yl)thiocarbonyl] *C*-nucleosides **3**. Compounds **3a,b** were converted directly into the corresponding 2′-deoxy β-*C*-nucleosides **5a,b** exclusively by reduction with *n*-Bu_3SnH. For the synthesis of 2′-deoxy β-*C*-nucleosides **5c,d**, the intermediates **3c,d** were trimethylsilylated prior to *n*-Bu_3SnH treatment. Deprotection of **5a–d** was effected by treatment with *n*-Bu_4NF, and the corresponding free 2′-deoxy β-*C*-nucleosides **6a–d** were obtained in good yields.

2′-Deoxypseudoisocytidine,[3] a *C*-nucleoside isostere of deoxycytidine, was first synthesized in small amounts by exploitation of several new reactions developed in our laboratory in the following manner: pseudouridine (**1c**) was converted into the 2′-chloro derivative[4] which was reductively dechlorinated to 2′-deoxypseudouridine (**6c**). Conversion of the latter into 1,3-dimethylpseudouridine (**1a**), followed by guanidine treatment,[5] afforded the 2′-deoxypseudoisocytidine (**6d**). This original procedure, however, requires careful chromatographic separation of the products in almost every step, resulting in a low yield of **6d**.

Recently, we developed an improved procedure[6] in which the proton at N-1 of **1c** was replaced by a methyl group to prevent undesirable α,β-isomerization. Thus, the 2′,3′-O-cyclic thiocarbonate of 1-methyl-5′-*O*-trityl-

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