Synthesis of Cyclobutenes by the Novel Photochemical Ring Contraction of 4-Substituted 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyrans

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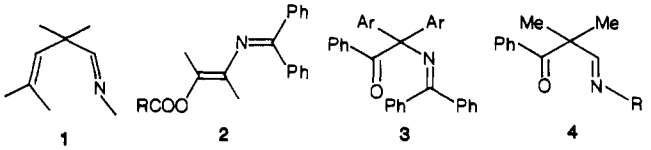
4-Substituted 2-amino-3,5-dicyano-6-phenyl-4*H*-pyrans undergo a novel photochemical ring contraction to cyclobutenes from the triplet state. For example, irradiation of a solution of 2-amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclopentane (**9a**) in methylene chloride gives 3-(aminocarbonyl)-1,3-dicyano-2-phenylspiro-[3.4]oct-1-ene (**18a**) in good yield. This transformation is accompanied by 3-phenylpropiolonitrile and enamide **15a**, which are the products of secondary photochemical fission of **18a**. An electron-transfer mechanism is proposed for the reaction.

In recent years we have been interested in the photochemical reactivity of organic molecules in which there can be intramolecular interaction between an imino moiety and another functional group. As a result, we have observed the novel photoreactions of imines **1**, **2**, **3**, and **4** into the photoproducts **5**,[1] **6**,[2] **7**,[3] and **8**,[4] respectively. It is clear from these results that the incorporation of a nitrogen into the system has a profound effect on the course of the reaction. The behavior of these molecules is substantially different from the reactions of β,γ-unsaturated enones to which the imines are structurally related.[5]



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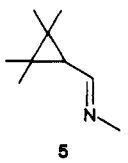

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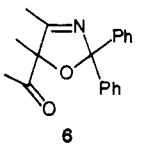

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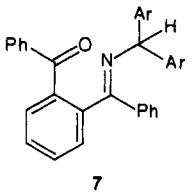

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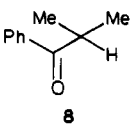

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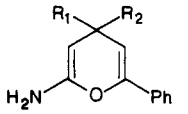
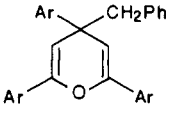
Many of the new reactions described by us can be interpreted as a consequence of an electron-transfer process from the nitrogen lone pair to the C–O or the C–C double bonds.

A consideration of the structural features in one of the systems (the conversion of **2** into **6** mentioned above) shows the presence of an electron-rich double bond substituted by both an oxygen and a nitrogen. The photochemical outcome of this reaction is apparently dominated by the presence of both this electron-rich moiety and the electron-deficient ester group. We have sought molecules that have similar structural features, i.e., an electron-rich alkene and an electron-accepting group, in the hope of uncovering other examples of intramolecular electron transfer which could lead to novel reactivity. Such molecules are represented by the 4*H*-pyrans **9**, which have the necessary features.

The pyrans **9** might not be considered as good contenders for unexpected reactivity if predictions are based on previous results. It is known that 4*H*-pyrans are photochemically reactive and will undergo either a 1,3-benzyl migration in the triaryl substituted derivatives **10** to afford the 2*H* isomers **11**[6,7] or a 1,2-aryl migration in the 4*H*-pyrans **12** yielding the bicyclic product **13** by a di-π-methane process.[8]

In this paper we report the details of the photochemical behavior of the 4*H*-pyran derivatives **9**.[9]





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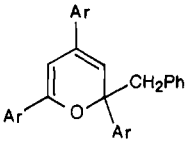

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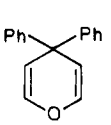
9a: R^1, $R^2 = (CH_2)_4$
b: R^1, $R^2 = (CH_2)_5$
c: $R^1 = R^2 = CH_3$
d: $R^1 = (CH_3)_2CH$, $R^2 = H$
e: $R^1 = C_6H_5$, $R^2 = H$
f: $R^1 = p\text{-}CNC_6H_4$, $R^2 = H$
g: R^1, $R^2 = (CH_2)_3$
h: $R^1 = R^2 = CN$



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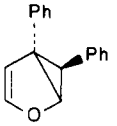

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Results and Discussion

The 4*H*-pyrans **9a–g** were synthesized by condensation of ω-cyanoacetophenone with an aldehyde or ketone followed by reaction of this intermediate with malononitrile by the procedure described previously.[10] The 4*H*-pyran **9h** was prepared by a variation of this procedure involving addition of ω-cyanoacetophenone to tetracyanoethylene as described in the Experimental Section.

The 4*H*-pyrans **9a–g** are all photochemically reactive. Irradiation of solutions of the pyrans **9** in methylene

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(1) (a) Armesto, D.; Horspool, W. M.; Fernandez-Martin, J.; Perez-Ossorio, R. *J. Chem. Res., Synop.* **1986**, 46; *J. Chem. Res., Miniprint* **1986**, 0631. (b) Armesto, D.; Langa, F.; Fernandez-Martin, J.; Perez-Ossorio, R.; Horspool, W. M. *J. Chem. Soc., Perkin, Trans. 1* **1987**, 743. (c) Armesto, D.; Horspool, W. M.; Langa, F.; Perez-Ossorio, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1039. (d) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1874.
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chloride for varying times under conventional conditions through a Pyrex filter brought about conversion into several products. The workup and product identification for the irradiation of **9a** is typical for all of the others. Thus, after removal of the solvent, the oily residue was flash chromatographed[11] on silica gel to afford the following in order of elution: 3-phenylpropiolonitrile (**14**, 40%), recovered starting material (10%), an unknown compound (27%), which was shown by mass spectroscopy to be isomeric with the starting material, and the enamide **15a** (46%).

PhC≡CCN

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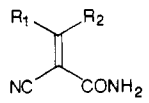
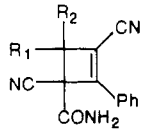
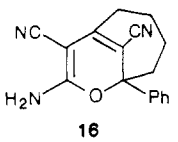


15a: $R^1, R^2 = (CH_2)_4$ (46%)
b: $R^1, R^2 = (CH_2)_5$ (38%)
c: $R^1 = R^2 = CH_3$ (47%)



18a: $R^1, R^2 = (CH_2)_4$ (27%)
b: $R^1, R^2 = (CH_2)_5$ (45%)
c: $R^1 = R^2 = CH_3$ (47%)
d: $R^1 = (CH_3)_2CH$, $R^2 = H$ (47%)

The identity of the nitrile **14** was readily established by its spectroscopic properties.[12] The identification of enamide **15a** was also readily carried out by spectroscopic methods and by comparison with data for the authentic material.[13] On the basis of the photochemistry of 4*H*-pyrans[6-8] previously reported, there seemed to be only two possibilities for the structure of the product of photoisomerization. The di-π-methane reactivity, if it were to occur in **9a**, could only involve a cross-ring interaction. Such reactivity can be excluded since there is no precedent in the 4*H*-pyran system. The 1,3-migration path, if followed, would yield either the bicyclic compound **16** or the enamide **17**, which could arise by secondary photolysis of **16**.



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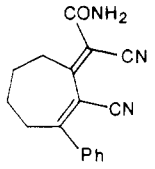

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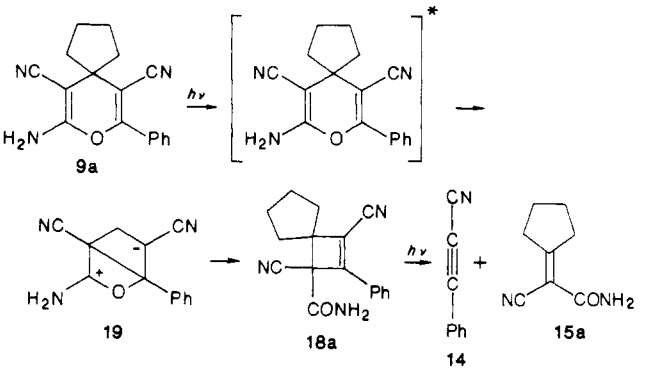
The data obtained for the unknown compound are not compatible with either **16** or **17**. The ^{13}C NMR spectrum is particularly helpful in an assignment of structure since it shows four high-field saturated carbon atoms (23.5, 23.7, 31.0, and 34.7 ppm), two deshielded saturated carbon atoms (55.0 and 60.7 ppm), and two alkene carbons (113.0 and 150.8 ppm), as well as signals for two cyano groups, one amide, and one phenyl ring. Such a spectrum is compatible with the spiro[3.4]oct-1-ene **18a** although other possibilities cannot be excluded. The formation of a cyclobutene ring must be due to a novel mode of reactivity. A possible path to such a compound could involve an intramolecular electron transfer from the electron-rich oxygen, nitrogen substituted double bond to the cyano, phenyl substituted unit. Transannular bonding within this radical cation/radical anion would afford the stabilized zwitterion **19**, which could collapse to the observed product **18a** (Scheme I). Further proof that the cyclobutene is the correct structure is obtained from secondary photolysis

Scheme I



where irradiation of **18a** for 1 h affords the enamide **15a** (54%), the nitrile **14** (64%), and recovered starting material **18a** (23%). The photochemical fission of cyclobutenes is not without literature precedent.[14] Thus, the enamide **15a** and the nitrile **14** arise by this path although this might not be exclusive since we observed the formation of these and the cyclobutene even at short irradiation times. Thus, an alternative reaction mode to account for the formation of **14** and **15a** could be fission of the C4–C5 and the C6–O bonds in the excited state prior to cyclization to intermediate **19**.

All the other pyrans **9b–g** are photochemically reactive. However, the corresponding cyclobutenes **18b–d** are obtained only with **9b–d**. In the irradiation of pyrans **9e–g**, only phenylpropiolonitrile is isolated from the crude reaction mixture. However, the thin-layer chromatography of the reaction mixtures in each of these cases shows the formation of two new products in addition to the propiolonitrile. The R_f values of these two products were those expected for the corresponding cyclobutenes and enamides. All the attempts to isolate these two photoproducts were unsuccessful (probably due to thermal instability). Nevertheless, the isolation of phenylpropiolonitrile could be regarded as indirect evidence for the formation of the cyclobutene since it has been demonstrated that it can arise by a secondary photolysis of the initially formed cyclobutene.

In general, the photochemical reactivity of the 4*H*-pyrans **9a–g** is independent of the nature of the substituent at position 4 of the pyran ring. There is not evidence from our results that a 1,3-hydrogen migration takes place in the derivatives **9d–f** since these compounds follow the cyclobutene path with reasonable efficiency. The derivatives **9e,f**, in which there is an aryl group in position 4 of the pyran ring, were selected to examine the possibility of a competing di-π-methane process leading to 1,2-phenyl migration of the type reported by Gravel et al.[8] No evidence for the participation of this path was uncovered.

The transformation of pyran **9a** into the cyclobutene **15a** was demonstrated to arise from the triplet state by the use of acetone- or acetophenone-sensitized irradiation. An attempt to quench the photoreaction with oxygen failed, and again the cyclobutene **15a** was obtained. The failure of the quencher to inhibit the reaction could be construed as evidence for the involvement of an electron-transfer process. Substantiation of this comes from the fact that previous studies on the photochemistry of ketones[15] and esters[16] have clearly demonstrated that intramolecular electron transfer processes cannot be quenched. In order

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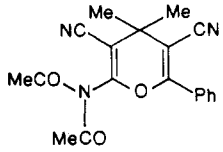
to obtain additional evidence for the proposed electron-transfer mechanism for the cyclization, the 4*H*-pyran **20** was irradiated for 4 h. In this case, the electron density of the enamine double bond should be considerably lower than in the other pyrans **9a–g** due to the conjugation of the nitrogen lone pair with the two acetyl groups. Consequently, the efficiency of an electron transfer should be considerably lower or simply might not take place in this case. The lack of reactivity of the 4*H*-pyran **20** is in agreement with this hypothesis and supports the proposed mechanism.

The dicyano-substituted 4*H*-pyran **9h** is photochemically stable under the conditions for the conversion of **9a–g**, and even on longer irradiation **9h** is recovered unchanged. The failure of this compound to undergo rearrangement is not clear although it could be due to an alternative electron-transfer mode such as involvement of the 4,4-dicyano groups.



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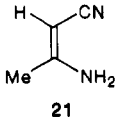

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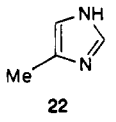

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The behavior of the 4*H*-pyrans leading to ring contraction is new. The photochemical reactivity observed for these molecules must be due to the type of substitution on the double bonds of the pyran. The presence of amino and cyano substituents could permit intramolecular electron transfer as suggested by us. Furthermore, the resultant zwitterion **19** is stabilized by the same substituents. It is also worth noting that the observed reactivity is in complete contrast to the photochemistry of related systems such as the enaminonitriles **21** that undergo cyclization to imidazoles **22**.[17]

Experimental Section

Melting points were determined on a Büchi 510D apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and band positions are reported in wavenumbers. Ultraviolet spectra were recorded on a Perkin-Elmer I24 spectrophotometer in methylene chloride solutions. Proton NMR spectra were recorded on a Varian T60A spectrometer with chemical shifts (δ) expressed in parts per million downfield from internal Me_4Si. ^{13}C NMR spectra were recorded on a Varian FT 80A at 20 MHz. The mass spectra were determined on a Varian MAT-711 spectrometer. Elemental analyses were performed by the Consejo Superior de Investigaciones Cientificas, Madrid.

Synthesis of Pyrans 9a–h. The pyrans **9a–e** and **9g** were synthesized by the method previously described.[10,18] Pyrans **9f** and **9h** were synthesized as indicated below.

Synthesis of 2-Amino-3,5-dicyano-4-(*p*-cyanophenyl)-6-phenyl-4*H*-pyran (9f). Synthesis of α-Benzoyl-*p*-cyanocinnamonitrile. *p*-Cyanobenzaldehyde (1.31 %, 10 mmol) and ω-cyanoacetophenone (1.45 g, 10 mmol) were dissolved in ca. 30 mL of dry ethanol, and a few drops of piperidine were added. The reaction mixture was stirred at room temperature. After 3–4 min, a white solid precipitated. This was filtered and crystallized in ethanol, yielding α-benzoyl-*p*-cyanocinnamonitrile (1.54 g, 60%): mp 132–134 °C; IR (KBr) 3010, 2230, 2215, 1670, 1600, 1270, 840, 700 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.4–8.2 (m, 10 H, Ar and CH). Anal. Calcd for $C_{17}H_{10}N_2O$: C, 79.06; H, 3.87; N, 10.85. Found: C, 78.76; H,4.05; N, 10.90.

α-Benzoyl-*p*-cyanocinnamonitrile (1 g, 3.9 mmol) and malononitrile (256 mg, 3.9 mmol) were dissolved in ca. 20 mL of dry ethanol, and a few drops of piperidine were added. The reaction mixture was stirred for 30 min at room temperature. After this time, a white solid had precipitated. The solid was filtered and recrystallized from ethanol to yield pyran **9f** (1.04 g, 83%): mp 206–208 °C; IR (KBr) 3410, 3300, 3180, 2230, 2205, 2109, 1670, 1600, 1400, 1330, 1250, 1140, 770, 760, 680 cm^{-1}; UV (CH_2Cl_2) λ_{max} 234 nm (ϵ 24 000), 264 (20 000); ^1H NMR (DMSO-d_6) δ 4.6 (s, 1 H, CH), 7.2–7.9 (m, 11 H, Ar and NH_2). Anal. Calcd for $C_{20}H_{12}N_4O$: C, 74.07; H, 3.70; N, 17.28. Found: C, 73.77; H, 3.86; N, 17.40.

Synthesis of 2-Amino-3,4,4,5-tetracyano-6-phenyl-4*H*-pyran (9h). A solution of tetracyanoethylene (2.56 g, 20 mmol) and ω-cyanoacetophenone (2.90 g, 20 mmol) in acetonitrile (20 mL) was kept at room temperature for 4 days. The solution was then evaporated under vacuum until only one third of the original volume remained. To this solution was added carbon tetrachloride (ca. 15 mL). The copious precipitate formed was collected by filtration and purified by crystallization from acetonitrile/carbon tetrachloride to yield pyran **9h** (3.71 g, 68%): mp 245–247 °C; IR (KBr) 3220, 2230, 2220, 1615, 1590, 1480, 1450, 1440, 1360, 1200, 1110, 1000, 1030, 690 cm^{-1}; UV (CH_2Cl_2) λ_{max} nm (ϵ 13 000), 405 (7000); ^1H NMR (DMSO-d_6) δ 7.6–7.2 (m, 5 H, Ar), 8.2 (br s, 1 H, NH_2), 11.5 (br s, 1H, NH_2); ^{13}C NMR (DMSO-d_6) δ 51.15, 96.0, 109.5, 110.6, 112.7, 113.6, 118.9, 126.2, 129.0, 130.0, 133.9, 141.9, 158.7; MS, *m/e* (relative intensity) 273 (M^+, 7), 257 (36), 246 (89), 219 (100), 203 (34), 191 (55), 164 (40), 117 (56), 105 (41), 77 (62). Anal. Calcd for $C_{15}H_7N_6O$: C, 65.93; H, 2.56; N, 25.64. Found: C, 65.64; H, 2.27; N, 25.71.

Synthesis of *N*,*N*-Diacetyl-2-amino-3,5-dicyano-4,4-dimethyl-6-phenyl-4*H*-pyran (20). Acetyl chloride (1 mL, 14 mmol) was added to a solution of pyran **9c** (0.4 g, 1.6 mmol) and pyridine (1.1 mL, 14 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was stirred for 2 h at room temperature, then washed with water (3 × 50 mL), and dried over $MgSO_4$. The solvent was evaporated under vacuum, and the white solid residue was purified by column chromatography on silica gel using hexane/ethyl acetate, 8:2, as eluent, to yield pyran **20** (0.42 g, 79%): mp 108–109 °C (from ethanol); IR (KBr) 2980, 2220, 1740, 1680, 1620, 1370, 1310, 1230, 1200, 1130, 780, 700 cm^{-1}; UV (CH_2Cl_2) λ_{max} 246 nm (ϵ 18 000); ^1H NMR ($CDCl_3$) δ 1.6 (s, 6 H, 2 CH_3), 2.4 (s, 6 H, 2 CH_3CO), 7.2–7.6 (m, 5 H, Ar); MS, *m/e* 335 (M^+, 4), 320 (9), 278 (95), 236 (78), 105 (11), 77 (14), 43 (100). Anal. Calcd for $C_{19}H_{17}N_3O_3$: C, 68.06; H, 5.07; N, 12.53. Found: C, 68.22; H, 5.22; N, 12.80.

Preparative Photolysis of Pyrans 9a–h. The photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400-W medium-pressure Hg arc lamp. Solutions of the pyrans in anhydrous methylene chloride (generally 380 mL is used except where other volumes are mentioned) were purged for 1 h with nitrogen and irradiated under a positive pressure of nitrogen. After completion of the irradiation, the solvent was removed under reduced pressure, and the products were separated by flash chromatography on silica gel.

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclopentane (9a). Pyran **9a** (600 mg, 2.2 mmol) was irradiated for 1 h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (110 mg, 40%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (60 mg, 10%), cyclobutene **18a** (160 mg, 27%), and enamide **15a** (150 mg, 46%).

Cyclobutene **18a**: mp 148–149 °C (from ethanol); IR (KBr) 3380–3180 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1610 ($CONH_2$) cm^{-1}; UV (CH_2Cl_2) λ_{max} 290 nm (ϵ 19 000); ^1H NMR (DMSO-d_6) δ 1.7–2.1 (m, 8 H, 4 CH_2), 7.5 (s, 5 H, Ar), 7.8 (br s, 2 H, NH_2); ^{13}C NMR (DMSO-d_6) δ 23.5, 23.7,31.0, 34.7, 55.0, 60.7, 113.0, 116.2, 116.7, 126.4, 128.6, 129.5, 132.1, 150.8, 164.9; MS, *m/e* 277 (M^+, 76), 276 (100), 260 (12), 259 (15), 249 (41), 248 (47), 233 (44). Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.62; H, 5.45; N, 15.15. Found: C, 73.64; H, 5.50; N, 15.40.

Enamide **15a**: This compound was identified by independent synthesis following the method described by Foucaud.[13]

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclohexane (9b). Pyran **9b** (600 mg, 2.1 mmol) was irradiated for 1 h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (80 mg, 30%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (80 mg, 13%), cyclobutene **18b** (270 mg, 45%), and enamide **15b** (130 mg, 38%).

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Cyclobutene (**18b**): mp 155–156 °C (from ethanol); IR (KB) 3400–3200 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1620 ($CONH_2$) cm^{-1}; UV (CH_2Cl_2) λ_{max} 289 nm (ϵ 19000); ^1H NMR (DMSO-d_6) δ 1.4–2.1 (m, 10 H, 5 CH_2), 7.6 (s, 5 H, Ar), 7.9 (br s, 2 H, NH_2); ^{13}C NMR (DMSO-d_6) δ 22.5, 23.2, 24.5, 30.2, 34.6, 54.1, 55.1, 114.0, 116.2, 116.5, 126,4, 128.8, 129.4, 132.6, 151.7, 164.3; MS, *m/e* 291 (M^+, 100), 290 (94), 262 (39), 248 (76), 247 (48), 220 (33), 77 (12). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.20; H, 5.60; N, 14.37.

Enamide **15b**: This compound was identified by independent synthesis following the method described by Foucaud.[13]

Irradiation of 2-Amino-3,5-dicyano-4,4-dimethyl-6-phenyl-4*H*-pyran (9c). Pyran **9c** (600 mg, 2.4 mmol) was irradiated for 1 h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (80 mg, 26%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (30 mg, 5%), cyclobutene **18c** (280 mg, 47%), and enamide **15c** (140 mg, 47%).

Cyclobutene **18c**: mp 136–138 °C (from ethanol); IR (KBr) 3400–3200 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1610 ($CONH_2$) cm^{-1}; UV (CH_2Cl_2) λ_{max} 287 nm (ϵ 15000); ^1H NMR (CD_3OD) δ 1.5 (s, 3 H, CH_3), 1.7 (s, 3 H, CH_3), 4.7 (br s, 2 H, NH_2), 7.3–7.8 (m, 5 H, Ar); ^{13}C NMR (CD_3OD) δ 20.8, 24.7, 51.9, 56.1, 113.1, 117.4, 118.8, 127.9, 130.2, 133.1, 151.9, 167.6; MS, *m/e* 251 (M^+, 52), 250 (32), 236 (100), 219 (12), 207 (24), 204 (40), 180 (20), 127 (22). Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.71; H, 5.18; N, 16.73. Found: C, 71.55; H, 5.25; N, 16.80.

Enamide **15c**: mp 92–93 °C;[19] IR (KBr) 3420 and 3160 (NH_2), 2200 (CN), 1680 ($CONH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H, CH_3), 2.4 (s, 3 H, CH_3), 6.3 (br s, 2 H, NH_2). Anal. Calcd for $C_6H_8N_2O$: C, 58.06; H, 6.45; N, 22.58. Found: C, 58.00; H, 6.76; N, 22.66.

Irradiation of 2-Amino-3,5-dicyano-4-isopropyl-6-phenyl-4*H*-pyran (9d). Pyran **9d** (600 mg, 2.3 mmol) was irradiated for 2 h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (70 mg, 24%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (70 mg, 12%) and cyclobutene **18d** (280 mg, 47%). The formation of another photoproduct, probably the enamide **15d**, was observed by thin-layer chromatography of the crude reaction product, but all the attempts to isolate it were unsuccessful.

Cyclobutene **18d**: mp 150–152 °C (from ethanol); IR (KBr) 3400–3200 (NH_2), 2240 (CN), 2200 (CN), 1680 ($CONH_2$), 1620 ($CONH_2$) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.1 (t, 6 H, 2 CH_3), 2.0 (m, 1 H, CH), 3.2 (d, 1 H, CH), 7.6 (s, 5 H, Ar), 7.8 (br s, 2 H, NH_2); ^{13}C NMR (DMSO-d_6) δ 19.1, 20.2, 30.5, 51.6, 56.3, 112.6, 114.3, 116.2, 126.1, 128.5, 129.7, 132.4, 152.8, 165.3; MS, *m/e* 265 (M^+, 90), 264 (24), 248 (29), 222 (100). Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.45; H, 5.66; N, 15.85. Found: C, 72.78; H, 5.74; N, 15.52.

Irradiation of 2-Amino-3,5-dicyano-4,6-diphenyl-4*H*-pyran (9e). Pyran **9e** (600 mg, 2.0 mmol) was irradiated for $1^1/_2$ h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (50 mg, 20%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (320 mg, 53%) and a complex mixture of products (120 mg) that were not separated nor identified.

Irradiation of 2-Amino-3,5-dicyano-4-(*p*-cyanophenyl)-6-phenyl-4*H*-pyran (9f). Pyran **9f** (550 mg, 1.7 mmol) was irradiated for $2^1/_2$ h. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (30 mg, 14%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (180 mg, 33%) and a complex mixture of products (190 mg) that were not separated nor identified.

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclobutane (9g). Pyran **9g** (590 mg, 2.2 mmol) was irradiated for 35 min. Chromatography using toluene as eluent gave 3-phenylpropiolonitrile (10 mg, 4%). Further elution with toluene/ethyl acetate, 9:1, gave starting material (90 mg, 15%) and 190 mg of a highly unstable yellow solid that was not identified.

Irradiation of 2-Amino-3,4,4,5-tetracyano-6-phenyl-4*H*-pyran (9h). Pyran **9h** (550 mg, 2.0 mmol) was irradiated for 5 h. After this, unchanged starting material (550 mg) was recovered.

Irradiation of 3-(Aminocarbonyl)-1,3-dicyano-2-phenylspiro[3.4]oct-1-ene (18a). A solution of cyclobutene **18a** (170 mg, 0.6 mmol) in CH_2Cl_2 (270 mL) was irradiated for 1 h under the same general conditions used for the photolyses of pyrans **9**. The crude reaction product was flash chromatographed on silica gel with toluene as eluent to give 3-phenylpropiolonitrile (50 mg, 64%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (40 mg, 23%) and enamide **15a** (50 mg, 54%).

Irradiation of *N,N*-Diacetyl-2-amino-3,5-dicyano-4,4-dimethyl-6-phenyl-4*H*-pyran (20). A solution of pyran **20** (210 mg, 0.6 mmol) in CH_2Cl_2 (270 mL) was irradiated for 4 h under the same general conditions used for the photolyses of pyrans **9**. After this, unchanged starting material (210 mg) was recovered.

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclopentane (9a) in Acetone. A solution of the pyran **9a** (341 mg, 1.23 mmol) in acetone (320 mL) was irradiated for 2 h. The crude reaction product was chromatographed on silica gel with toluene as eluent. This gave 3-phenylpropiolonitrile (20 mg, 13%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (114 mg, 33%), cyclobutene **18a** (99 mg, 29%), and enamide **15a** (48 mg, 26%).

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclopentane (9a) in the Presence of Acetophenone. A solution of the pyran **9a** (117 mg, 0.42 mmol) and acetophenone (36 mL, 0.3 mol) in CH_2Cl_2 (320 mL) was irradiated for 2 h. The solvent and the acetophenone were removed by distillation under vacuum. TLC examination of the resultant mixture showed the presence of the three photoproducts and starting material.

Irradiation of 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran-4-spirocyclopentane (9a) in the Presence of Oxygen. A solution of the pyran **9a** (240 mg, 0.87 mmol) in CH_2Cl_2 (320 mL) was saturated with oxygen. The mixture was then irradiated for 15 min during which time oxygen was passed through the solution. The crude reaction product was chromatographed on silica gel with toluene as eluent as described above. This gave 3-phenylpropiolonitrile (22 mg, 20%). Further elution with toluene/ethyl acetate, 8:2, gave starting material (84 mg, 35%), cyclobutene **18a** (57 mg, 24%), and enamide **15a** (40 mg, 31%).

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Registry No. **9a**, 89809-98-3; **9b**, 89809-97-2; **9c**, 89809-95-0; **9d**, 89809-86-9; **9e**, 64646-31-7; **9f**, 120446-34-6; **9g**, 89809-99-4; **9h**, 120446-35-7; **14**, 935-02-4; **15a**, 875-61-6; **15b**, 704-16-5; **15c**, 93271-58-0; **18a**, 113555-38-7; **18b**, 120446-36-8; **18c**, 113555-39-8; **18d**, 120446-37-9; **20**, 120446-39-1; NC-*p*-C_6H_4CHO, 105-07-7; $PhCOCH_2CN$, 614-16-4; $PhCH{=}C(CN)COC_6H_4$-*p*-CN, 120446-38-0; $CH_2(CN)_2$, 109-77-3; $(CN)_2C{=}C(CN)_2$, 670-54-2.

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