A study on the scope of the photochemical ring contraction of substituted 2-amino-3-cyano-4*H*-pyrans to cyclobutenes: crystal structure of 3-carbamoyl-3-cyano-1-ethoxycarbonyl-4-isopropyl-2-phenylcyclobutene

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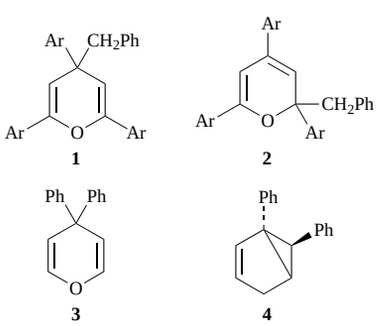
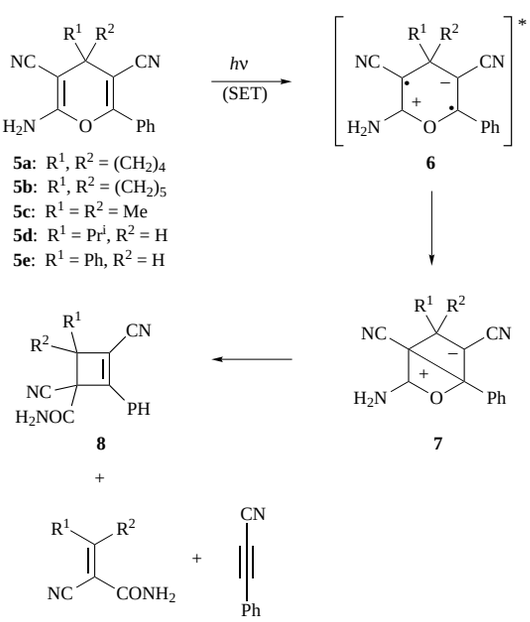
A study on the influence of substitution on the photochemical reactivity of a series of differently substituted 2-amino-4*H*-pyrans 10a–h has been carried out. All of the compounds undergo ring contraction to the corresponding cyclobutenes 11a–h on direct irradiation. Variable amounts of the enamides 12 and the alkynes 13 were also obtained, as secondary photoproducts. The results obtained show that the cyclization takes place in reasonable yields with alkyl, phenyl and hydrogen substitution at C-4 and at C-6. Cyano, ethoxycarbonyl and benzoyl substitution at C-5 also promotes the reaction. A high degree of stereochemical control was observed in most cases. The molecular geometry of cyclobutene 11a$_1$ has been established by X-ray diffraction analysis. This study also shows that the crystal packing is formed by a system of chains linked by strong hydrogen bonds.

Introduction

Although the photochemical reactivity of heterocyclic compounds has been extensively studied,[1] that of 4*H*-pyrans has received very little attention. For many years the only photochemical reactions reported for 4*H*-pyran derivatives were: (i) the 1,3-benzyl migration in compound **1** to give the isomeric 2*H*-pyran **2**[2] and (ii) the di-π-methane rearrangement in the 4,4-diphenylsubstituted 4*H*-pyran **3** to yield the bicyclic compound **4**.[3] We have contributed to this area of research report-



ing, some years ago, the novel photochemical ring contraction of some 2-amino-3,5-dicyano-6-phenyl-4*H*-pyrans **5a**–**d**, differently substituted on C-4, to the corresponding cyclobutenes **8**.[4,5] This rearrangement is accompanied by the formation of variable amounts of 3-phenylpropynenitrile and the corresponding enamides **9** (Scheme 1). The mechanism outlined in Scheme 1 was proposed to account for the formation of the cyclobutenes **8**. This involves intramolecular single-electron transfer (SET) from the enamino moiety to the cyano, phenyl substituted unit followed by transannular bond formation within the resulting zwitterion-biradical **6** to afford the stabilized zwitterion **7**. Ring opening of the oxetane ring within **7** yields the observed cyclobutene **8**. The formation of the enamides **9** and the 3-phenylpropynenitrile was proposed to result from the secondary photolysis of the cyclobutenes **8**.



Scheme 1

In order to determine further the scope of the reaction and to confirm our mechanistic postulates we have carried out a study aimed at determining the possible influence of changes in substitution at positions 4, 5 and 6 of the pyran ring on the outcome of the reaction. The compounds selected for this study were the 4*H*-pyrans **10a**–**h**.

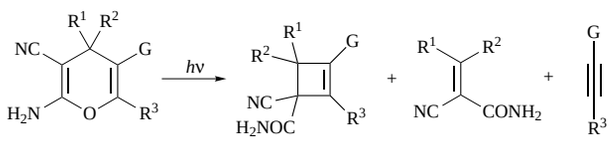
Results and discussion

The 2-amino-4*H*-pyrans **10** were prepared by a 6-*exo-dig* cyclization[6] of δ-oxo nitriles generated by Michael addition of malononitrile to the appropriately substituted α,β-unsaturated ketones, according to the methods previously described.[7] Direct

Table 1 Photochemical reactivity of 4*H*-pyrans

4*H*-Pyran	R^1	R^2	R^3	G	Cyclobutene (%)	**12** (%)	**13** (%)
10a	Pr^i	H	Ph	CO_2Et	**11a$_1$** (26)	—	16
		H			**11a$_2$** (26)		
10b	Pr^i	H	Me	CO_2Et	**11b** (49)	—	—
10c	Ph	H	Ph	CO_2Et	**11c** (29)	11	10
10d	Ph	H	Me	CO_2Et	**11d** (29)	20	8
10e	Ph	H	Ph	COPh	**11e** (21)	17	13
10f	Ph	H	H	CN	**11f** (23)	17	22
10g	Pr^i	H	Me	CN	**11g** (19)	13	12
10h	Ph	Me	Ph	CN	**11h** (39)	12	12

irradiation of compounds **10a**–**h**, for variable lengths of time, gave the corresponding cyclobutenes **11a**–**h** (Scheme 2) in yields



10 **11** **12** **13**

Scheme 2

in the range 49–19%, after column chromatography on silica gel (Table 1). The identity of the cyclobutenes **11a**–**h** was established by comparison of analytical and spectroscopic data. All of them showed a weak stretching cyano band at 2220–2240 cm^{-1} in their IR spectra. The cyclobutenes **11a$_1$**, **11a$_2$**, **11b** and **11g** having a 4-isopropyl group showed the cyclobutene hydrogen as a doublet at 3.0–3.4 ppm. The presence of a phenyl group in this position (C-4) in **11c**–**f** shifted the signal of this proton to 7.2–7.8 ppm.

The corresponding enamides **12** and the alkynes **13** were obtained in the irradiation of the pyrans **10**, as minor products. The identity of these compounds was determined by comparison with authentic samples. However, ethyl propynoate **13** was not isolated in the irradiation of **10b**. Similarly, the corresponding enamides **12** were not isolated in the irradiation of **10a** and **10b**. This is probably due to decomposition of these compounds during chromatography on silica gel, since the analyses of the crude reaction mixtures by TLC and ^{1}H NMR spectroscopy clearly indicated the presence of the corresponding enamides and the alkyne.

Compounds **10a**–**e** were chosen in order to determine whether the replacement of the 5-cyano group in compounds **5**, by an ethoxycarbonyl group in pyrans **10a**–**d** and by a benzoyl group in **10e** would affect the reaction adversely. These two functions have the capacity to act as electron acceptors. The results obtained in this study show that a decrease in the electron-accepting capacity of the functional group present at C-5 does not have a negative effect on the outcome of the reaction. In fact, the efficiency of the reaction for compounds **10a**–**d** is comparable, in qualitative terms, to that reported for the pyrans **5**.

In our previous report, the photochemistry of the pyran **5e** was studied.[4,5] In this instance the corresponding cyclobutene was not obtained, the only isolated product being 3-phenylpropynenitrile. However, the corresponding cyclobutene and the enamide were detected by thin-layer chromatography. The impossibility of isolating the cyclobutene in this case was considered to be due to thermal instability. Therefore, compounds **10c**–**f** and **10h**, with a 4-phenyl group, were selected in an attempt to determine whether changes in substitution at positions 5 and 6 of the pyran skeleton would confer enough stability to the cyclobutene to allow its isolation. The results obtained demonstrated that the replacement of the cyano group present in **5e** by an ethoxycarbonyl group, as in **10c**–**d**, and by a benzoyl group, as in **10e**, permits the isolation of the corresponding 4-phenyl substituted cyclobutenes **11c**–**e** in yields in the range 29–21%. The irradiation of the 5-cyanopyran **10h** affords the cyclobutene **11h** in 39% yield, showing that the replacement of the hydrogen atom at C-4 in **5e** by a methyl group, as in **10h**, increases the stability of the cyclobutene and making possible its isolation.

All the pyrans **5** previously described have a 6-phenyl group. The study of compounds **10b**, **10d**, **10f** and **10g** was aimed at extending the reaction to compounds with hydrogen or methyl substitution at C-6. The results obtained show that the change in substitution at C-6 from phenyl in compounds **5** to hydrogen, as in **10f**, or methyl, as in **10b**, **10d** and **10g**, does not adversely affect the reaction.

It is clear from these results that the photo-rearrangement of differently substituted 2-amino-4*H*-pyrans to cyclobutenes is very general indeed. The isolated yields obtained in this study are comparable to those previously reported by us, showing that the reaction can be extended to pyrans differently substituted at positions 4, 5 and 6 of the ring.

Interestingly, the highly substituted cyclobutenes obtained in the reaction present two stereogenic centres. However, it is worth mentioning that the stereoisomers ratio was determined only after column chromatography due to the complexity of the ^{1}H NMR spectra of the crude photolysate. Unfortunately, due to the high degree of substitution in all the positions of the cyclobutene ring it was impossible to assign the stereochemistry of the different diastereoisomers using ^{1}H NMR spectroscopy. The above considerations being taken into account, rearrangement of the pyrans **10b** and **10e**–**h** gives one of the two possible diastereoisomers of the corresponding cyclobutenes **11b** and **11e**–**h**, only. The rearrangement of pyran **10d** seems also to be stereoselective affording the cyclobutene **11d** as a mixture of diastereoisomers in a ratio of 10:1. The stereoselectivity decreases in the case of **10c**. In this instance the cyclobutene **11c** is obtained as a 2:1 mixture of stereoisomers. However, there is no stereochemical control in the case of the pyran **10a**. The irradiation of **10a** brings about the formation of **11a** as a 1:1 mixture of the two possible diastereoisomers (**11a$_1$** and **11a$_2$**) that were separated by column chromatography.

At this point in the study it was considered of interest to carry out an X-ray diffraction analysis of the cyclobutenes. Our intention was to obtain conclusive evidence on the proposed structure and, at the same time, to get information on the stereochemical outcome of the reaction. In our previous report the proposed structure for the cyclobutenes was based on conventional spectroscopy, mass spectroscopy and microanalysis. However, the absence in the literature of examples of highly substituted cyclobutenes that could be compared with those obtained in our studies, prompted us to find a definitive proof for the proposed structure. Among the cyclobutenes **11** obtained in this study the only one that was suitable for X-ray analysis was compound **11a$_1$**. The structural analysis of this compound proved it to be the proposed cyclobutene. The molecular structure obtained is shown in Fig. 1, together with

Table 2 Selected torsion angles for compound **11a$_1$**

Atomic distance (Å)	Angle (°) (esd)	Atomic distance (Å)	Angle (°) (esd)
C(2)–C(1)–C(4)–C(3)	4.1(1)	C(1)–C(4)–C(18)–C(19)	−180.0(2)
C(4)–C(1)–C(2)–C(3)	−3.6(1)	C(4)–C(1)–C(5)–O(6)	−150.2(2)
C(1)–C(2)–C(3)–C(4)	4.1(1)	C(3)–C(2)–C(10)–C(11)	70.4(3)
C(2)–C(3)–C(4)–C(1)	−4.3(2)	C(2)–C(3)–C(13)–O(14)	165.0(2)

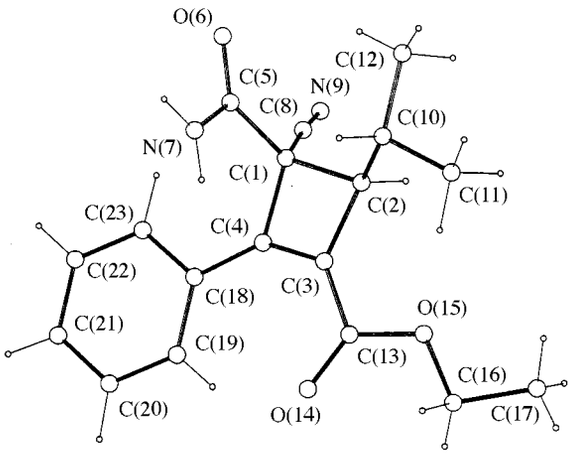


Fig. 1 Molecular structure of compound **11a$_1$** showing the atomic numbering

the atomic numbering scheme. This allowed us to assign the configuration *RS*,*SR* for this isomer (**11a$_1$**). The main geometrical features of the molecule are shown in Table 2.

Bond distances and angles involved in the cyclobutene ring of compound **11a$_1$** were compared with those previously published for related cyclobutenes;[8] the mean values, with the standard deviation for each distance or angle obtained for **11a$_1$**, are presented in Table 2 and are quite similar to the mean values of the related structures previously reported. The central ring is not planar, the atoms comprising the least squares plane [C(1), C(2), C(3), C(4)] deviating by 0.026(2), −0.028(2), 0.026(2) and −0.025(2) Å respectively. There are short intramolecular contacts between C(19) and O(14) [3.080(2) Å] and between O(15) and C(11) [3.030(5) Å] (see Fig. 1) attributed to C–H···O interactions. The crystal packing is shown in Fig. 2; it presents chains along the *b* axis formed by molecules of alternating *RS* and *SR* configurations linked by two sets of H-bonds between the amido protons of one molecule and the oxygen atoms of centrosymmetrically related neighbours [N(7)···O(14)^{i} and N(7)···O(6)^{ii}, see Fig. 2]. The methyl groups [C(11), C(12) and C(17)] point towards the *b*,*c* plane.

Unfortunately, the assignment of the stereochemistry of cyclobutene **11a$_1$** has not allowed us to determine the stereoselectivity observed in the other cases studied as has been explained above. The δ value of the hydrogen present in most of the cyclobutenes, **11a**–**g**, was very sensitive to the substitution on the cyclobutene ring, thus disallowing an accurate correlation between the δ values and absolute configuration in the C-3, C-4 atoms.

In summary, we have carried out a photochemical study of a series of differently substituted 2-amino-4*H*-pyrans. The results obtained show that the reaction takes place with alkyl, phenyl and hydrogen substitution at C-4 of the 4*H*-pyran ring. The rearrangement also takes place with cyano, ethoxycarbonyl and benzoyl substitution at C-5 and hydrogen, methyl or phenyl substitution at C-6. The molecular geometry of cyclobutene **11a$_1$** has been established by X-ray diffraction and a system of chains formed by strong hydrogen bonds has been shown to be present in the crystal packing. This general synthetic approach opens the possibility of preparing new optically active cyclobutenes starting from the readily available enantiomerically pure 4*H*-pyrans.[9]

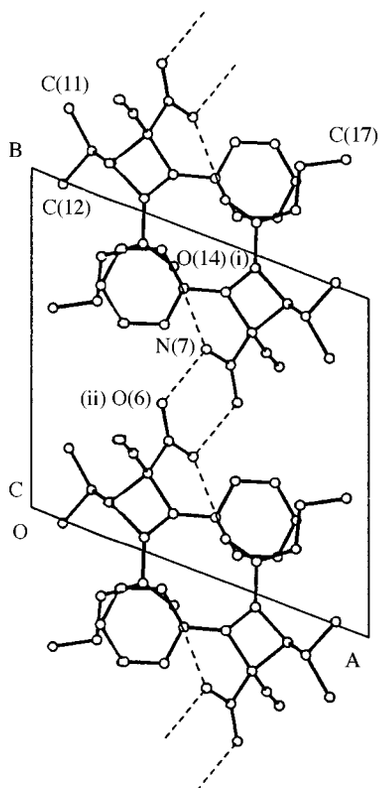


Fig. 2 Crystal packing of compound **11a$_1$**, as projected along the *c* axis,[19] showing the intermolecular H bonds in a chain. Hydrogen bonds X–H···Y (symmetry code; Å and °): N(7)–H(71) 0.91(3); N(7)···O(14)^{i} 2.905(3); H(71)···O(14)^{i} 2.04(3); N(7)–H(71)···O(14)^{i} 158(4); N(7)–H(72) 0.91(3); N(7)···O(6)^{ii} 2.897(3); H(72)···O(6)^{ii} 1.99(3); N(7)–H(72)···O(6)^{ii} 173(2). i and ii stand for $1-x$, $-y$, $-z$ and $1-x$, $1-y$, $-z$ respectively.

Experimental

Melting points were determined on a Buchi 530D apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Perkin–Elmer 781 spectrophotometer as liquid films, unless otherwise stated, and band positions are reported in wavenumbers (cm^{-1}). NMR spectra were run at the Servicio de RMN de la Universidad Complutense de Madrid in a Varian VXR-300S, using $CDCl_3$ as solvent and TMS as internal standard. Coupling constants *J* are given in Hz. Combustion analyses were carried out by the Servicio de Microanálisis de la Universidad Complutense de Madrid. Column chromatography was performed using silica gel 60 (40–63 mm) (Merck). Commercially available starting materials and reagents were purchased from the Aldrich Chemical Co. Ether refers to diethyl ether.

Synthesis of starting pyrans

The 4*H*-pyrans **10a**–**h** necessary for this study have been described previously.[10]

Preparative photolyses

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 dichloromethane

(400 cm^3) were purged with argon for 1 h and irradiated under a positive pressure of argon for the times shown. After completion of the irradiation the solvent was removed under reduced pressure and the products were separated by flash chromatography.

Irradiation of 2-amino-3-cyano-5-ethoxycarbonyl-4-isopropyl-6-phenyl-4*H*-pyran 10a

This compound (398 mg, 1.3 mmol) was irradiated for 30 min. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (8:2) gave ethyl phenylpropynoate (36 mg, 16%), starting material (73 mg, 18%) and the cyclobutene **11a$_1$** (103 mg, 26%). Further elution with hexane–ethyl acetate (7:3) gave the cyclobutene **11a$_2$** (104 mg, 26%). Finally, elution with hexane–ethyl acetate (1:1) afforded a complex mixture of compounds, the major component of which was identified by independent synthesis following the method described by Focaud.[11] Thus, a mixture of isobutyraldehyde (0.72 g, 0.01 mol), 2-cyanoacetamide (0.7 g, 0.01 mol), ammonium acetate (0.77 g, 0.01 mol) and acetic acid (0.2 g, 3.3 mmol) in toluene (100 cm^3) was refluxed for 20 h. The water generated during the reaction was removed azeotropically using a Dean–Stark trap. The mixture was then cooled, washed with aqueous Na_2CO_3 and water, dried ($MgSO_4$), filtered and concentrated to dryness. The crude product was purified by flash column chromatography using hexane–ethyl acetate (8:2) as eluent to yield the enamide **12a** as a solid (6.3 g, 46%), mp 77–79 °C (from hexane); ν_{max}(KBr)/cm^{-1} 3400, 3330, 3195 (NH_2), 2240 (CN) and 1700 and 1615 ($CONH_2$); δ_H($CDCl_3$) 1.16 (6 H, d, *J* 6.6, 2 Me), 2.96 (1 H, d, sep, *J* 10.6 and 6.6, CH), 6.20, 6.40 (2 H, 2 br s, NH_2) and 7.52 (1 H, d, *J* 10.6, vinyl H); δ_C($CDCl_3$) 21.5 (2 Me), 31.9 (CH), 107.7 (vinyl C), 115.1 (CN), 161.8 (vinyl C) and 167.9 ($CONH_2$); *m/z* 138 (M^+, 9) and 123 (19) (Found: C, 61.19; H, 7.71; N, 19.95. $C_7H_{10}N_2O$ requires C, 60.89; H, 7.32; N, 20.27%).

Cyclobutene 11a$_1$. Mp 105–107 °C (from ethanol); ν_{max}(KBr)/cm^{-1} 3390, 3320, 3170 (NH_2), 2240 (CN), 1710, 1695 and 1625 (CO_2Et and $CONH_2$); δ_H($CDCl_3$) 1.07 (3 H, d, Me), 1.09 (3 H, d, Me), 1.37 (3 H, t, Me), 2.13 (1 H, m, CH), 3.44 (1 H, d, CH), 4.33 (2 H, m, CH_2), 6.00, 6.20 (2 H, 2 br s, NH_2), 7.43 (3 H, m, aryl H) and 7.91 (2 H, m, aryl H); *m/z* 312 (M^+, 3), 269 (100), 241 (24) and 71 (11) (Found: C, 68.81; H, 6.84; N, 8.95. $C_{18}H_{20}N_2O_3$ requires C, 69.21; H, 6.45; N, 8.97%).

Cyclobutene 11a$_2$. Mp 146–147 °C (from hexane–ethyl acetate, 1:1); ν_{max}(KBr)/cm^{-1} 3325, 3300 and 3175 (NH_2), 2240 (CN), 1690, 1645 and 1615 (CO_2Et and $CONH_2$); δ_H($CDCl_3$) 1.15 (3 H, d, Me), 1.17 (3 H, d, Me), 1.37 (3 H, t, Me), 2.24 (1 H, m, CH), 3.18 (1 H, d, CH), 4.31 (2 H, m, CH_2), 6.20, 6.35 (2 H, 2 br s, NH_2), 7.45 (3 H, m, aryl H) and 7.93 (2 H, m, aryl H); *m/z* 312 (M^+, 3), 269 (100), 239 (37), 223 (19), 194 (12), 152 (9) and 77 (13) (Found: C, 68.85; H, 6.50; N, 8.96. $C_{18}H_{20}N_2O_3$ requires C, 69.21; H, 6.45; N, 8.97%).

Crystal data for **11a$_2$**.—$C_{18}H_{20}N_2O_3$, M_w = 312.37, Triclinic, *P*-1, a = 11.6134(3), b = 10.8259(3), c = 7.6326(1) Å, α = 95.808(2), β = 103.472(2), γ = 108.934(2)°, V = 866.26(4) Å^3, Z = 2, D_c = 1.15 g cm^{-3}, F(000) = 318, μ = 6.13 cm^{-1}. Refined cell parameters were obtained from setting angles of 72 reflections. A prismatic white crystal (0.47 × 0.43 × 0.20 mm) was used for the analysis.

Data collection.—Automatic Philips PW 1100 four circle diffractomer with graphite oriented monochromator and Cu-Kα radiation. The intensity data were collected using the $\omega/2\theta$ scan mode between $2 < \theta < 65°$; two standard reflections were measured every 90 min with no intensity variation. A total of 2919 reflections were measured and 2505 were considered as observed [$I < 3\sigma(I)$ criterion]. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement.—The structure was solved by direct methods using SIR88.[12] H atoms were located from Fourier difference maps, except those involved in methyl groups which were calculated; all of them were included in a mixed refinement. A convenient weighting scheme was applied to obtain flat dependence in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$.[13] Final R (Rw) value was 4.5 (5.4).

Atomic scattering factors for the compound were taken from International Tables for X-Ray Crystallography[14] and calculations were performed using XRAY80,[15] XTAL,[16] HSEARCH[17] and PARST.[18] Detailed crystallographic results for this work have been deposited with the Cambridge Crystallographic Data Centre and are available on request. Such a request should be accompanied by a full bibliographic citation together with the reference number 207/146.†

Irradiation of 2-amino-3-cyano-5-ethoxycarbonyl-4-isopropyl-6-methyl-4*H*-pyran 10b

This compound (321 mg, 1.5 mmol) was irradiated for 1 h. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (9:1) gave starting material (34 mg, 11%). Further elution using hexane–ethyl acetate (8:2) afforded cyclobutene **11b** (157 mg, 49%) and a complex mixture of compounds the major component of which was the enamide **12a**. Cyclobutene **11b** was obtained as a solid, mp 107–109 °C (from hexane–ethyl acetate 1:1) and as the only diastereoisomer; ν_{max}(KBr)/cm^{-1} 3400, 3320 and 3195 (NH_2), 2240 (CN), 1725, 1700 and 1625 (CO_2Et and $CONH_2$); δ_H($CDCl_3$) 1.09 (3 H, d, Me), 1.11 (3 H, d, Me), 1.32 (3 H, t, CH_3), 2.06 (1 H, d, sep, CH), 2.10 (3 H, d, *J* 2.4, Me), 3.10 (1 H, dc, *J* 8.7 and 2.4, CH), 4.24 (2 H, m, CH_2) and 6.30, 6.50 (2 H, 2 br s, NH_2); δ_C($CDCl_3$) 16.0 (Me), 22.4 (Me), 23.2 (Me), 32.2 (CH), 51.6 (quaternary C), 57.0 (CH), 61.2 (CH_2), 115.6 (CN), 136.6 (vinyl C), 148.0 (vinyl C), 158.6 (CO) and 162.4 ($CONH_2$); *m/z* 250 (M^+, 7), 234 (13), 207 (41), 205 (100), 204 (72) and 177 (31) (Found: C, 62.43; H, 7.12; N, 11.23. $C_{13}H_{18}N_2O_3$ requires C, 62.38; H, 7.25; N, 11.19%).

Irradiation of 2-amino-3-cyano-5-ethoxycarbonyl-4,6-diphenyl-4*H*-pyran 10c

This compound (590 mg, 1.7 mmol) was irradiated for 30 min. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (9:1) gave ethyl 3-phenylpropynoate (30 mg, 10%). Further elution using hexane–ethyl acetate afforded starting material (188 mg, 32%) and the cyclobutene **11c** (173 mg, 29%). Finally, elution with hexane–ethyl acetate (1:1) gave 2-cyano-3-phenylpropenamide **12c** (32 mg, 11%) as a solid, mp 123–125 °C. This was identical with an authentic sample.[11] The cyclobutene **11c** was obtained as a solid and as a mixture of diastereoisomers (**a** and **b**; ratio 2:1); ν_{max}(KBr)/cm^{-1} 3410 and 3190 (NH_2), 2220 (CN), 1715, 1690, 1680 and 1610 (CO_2Et and $CONH_2$); δ_H($CDCl_3$) 0.87 (isomer **a**) and 1.10 (isomer **b**) (3 H, t, Me), 3.96 (isomer **a**) and 4.15 (isomer **b**) (2 H, q, CH_2), 5.70–5.90 (2 H, m, NH_2 of both isomers), 7.18 (isomer **a**) and 7.95 (isomer **b**) (1 H, s, CH) and 7.20–7.50 (10 H, m, aryl H of both isomers); *m/z* 346 (M^+, 7), 273 (100) and 156 (19) (Found: C, 72.79; H, 5.25; N, 8.06. $C_{21}H_{18}N_2O_3$ requires C, 72.82; H, 5.24; N, 8.09%).

Irradiation of 2-amino-3-cyano-5-ethoxycarbonyl-6-methyl-4-phenyl-4*H*-pyran 10d

This compound (315 mg, 1.1 mmol) was irradiated for 30 min. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (8:2) gave ethyl but-2-ynoate (10 mg, 8%), starting material (184 mg, 59%) and the cyclobutene **11d** (94 mg, 29%). Further elution using hexane–ethyl acetate (7:3) afforded 2-cyano-3-phenylpropenamide (39 mg, 20%). The cyclobutene **11d** was obtained as a solid, mp 151–153 °C (from hexane–ethyl acetate, 1:1) and as a 10:1 mixture of diastereoisomers.

† For further details of this scheme, see Instructions for Authors (1997), *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, Issue 1.

Major isomer. ν_{max}(KBr)/cm^{-1} 3350 and 3160 (NH_2), 2210 (CN), 1710, 1660, 1630 and 1610 (CO_2Et and $CONH_2$); δ_H($CDCl_3$) 1.18 (3 H, t, Me), 2.41 (3 H, s, Me), 4.22 (2 H, q, CH_2), 5.90, 6.30 (2 H, 2 br s, NH_2), 7.16 (1 H, s, CH) and 7.38 (5 H, m, aryl H); *m*/*z* 284 (M^+, 4.4), 211 (100), 194 (6.6) and 166 (10) (Found: C, 67.21; H, 5.44; N, 9.39. $C_{16}H_{16}N_2O_3$ requires C, 67.59; H, 5.67; N, 9.85%).

Irradiation of 2-amino-5-benzoyl-3-cyano-4,6-diphenyl-4*H*-pyran 10e

This compound (507 mg, 1.3 mmol) was irradiated for 90 min. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (8:2) gave 1,3-diphenylprop-2-yn-1-one (37 mg, 13%), starting material (182 mg, 36%), a complex mixture of unidentified compounds (69 mg) and the cyclobutene **11e** (107 mg, 21%). Further elution using hexane–ethyl acetate (7:3) afforded 2-cyano-3-phenylpropenamide (39 mg, 17%) and polar material (70 mg). The cyclobutene **11e** was obtained as a solid, mp 87–89 °C (from ethanol) and as the only diastereoisomer; ν_{max}(KBr)/cm^{-1} 3380, 3330 and 3210 (NH_2), 2210 (CN), 1670, 1590 and 1570 (CO and $CONH_2$); δ_H($CDCl_3$) 5.70, 5.93 (2 H, 2 br s, NH_2) and 7.10–7.80 (16 H, m, aryl H and CH) (Found: C, 79.48; H, 4.74; N, 7.72. $C_{25}H_{18}N_2O_2$ requires C, 79.35; H, 4.79; N, 7.40%).

Irradiation of 2-amino-3,5-dicyano-4-phenyl-4*H*-pyran 10f

This compound (295 mg, 1.32 mmol) was irradiated for 1 h. After removal of the solvent, flash chromatography of the residue using hexane–ethyl acetate (9:1) gave propynenitrile (15 mg, 22%) and starting material (164 mg, 56%). Further elution using hexane–ethyl acetate (8:2) afforded the cyclobutene **11f** (67 mg, 23%) and, finally, elution with hexane–ethyl acetate (7:3) yielded 1-cyano-3-phenylpropenamide (38 mg, 17%). The cyclobutene **11f** was obtained as a solid, mp 142–144 °C (from ethanol) and as the only diastereoisomer; ν_{max}(KBr)/cm^{-1} 3370 and 3330 (NH_2), 2230 (CN) and 1705 ($CONH_2$); δ_H($CDCl_3$) 5.80 (1 H, s, NH), 6.45 (1 H, s, NH), 7.54 (3 H, m, aryl H), 7.70 (1 H, s, CH), 7.99 (1 H, s, vinyl H) and 8.00 (2 H, m, aryl H) (Found: C, 69.91; H, 4.11; N, 18.93. $C_{13}H_9N_3O$ requires C, 69.95; H, 4.06; N, 18.82%).

Irradiation of 2-amino-3,5-dicyano-4-isopropyl-6-methyl-4*H*-pyran 10g

This compound (544 mg, 2.68 mmol) was irradiated for 2.5 h. After removal of the solvent, flash chromatography using hexane–ethyl acetate (8:2) gave but-2-ynenitrile (20 mg, 12%), starting material (341 mg, 63%), and the cyclobutene **11g** (104 mg, 19%). Further elution using hexane–ethyl acetate (7:3) afforded 2-cyano-4-methylpent-2-enamide (48 mg, 13%) and unidentified polar material (29 mg). The cyclobutene **11g** was obtained as a solid, mp 151–152 °C (from hexane–ethyl acetate 1:1) and as the only isomer; ν_{max}(KBr)/cm^{-1} 3390, 3320 and 3180 (NH_2), 2250 and 2230 (CN), 1710, 1675 and 1640 ($CONH_2$); δ_H($CDCl_3$) 1.13 (3 H, d, Me), 1.15 (3 H, d, Me), 2.03 (1 H, m, CH), 2.06 (3 H, d, *J* 2.4, Me), 3.01 (1 H, dq, *J* 10.8, 2.4, CH) and 6.12 (2 H, br d, NH_2); δ_C($CDCl_3$) 14.2, 19.3, 20.3 (3 Me), 30.4 (CH), 51.4 (quaternary C), 57.0 (CH), 112.0, 115.7, 118.9 (2 CN and vinyl C), 157.3 (vinyl C) and 164.7 ($CONH_2$) (Found: C, 65.12; H, 6.19; N, 20.67. $C_{11}H_{13}N_3O$ requires C, 65.01; H, 6.45; N, 20.68%).

Irradiation of 2-amino-3,5-dicyano-4-methyl-4,6-diphenyl-4*H*-pyran 10h

This compound (600 mg, 1.9 mmol) was irradiated for 70 min. After removal of the solvent, flash chromatography of the residue using hexane gave 3-phenylpropynenitrile (20 mg, 12%). Further elution using hexane–ethyl acetate (9:1) afforded starting material (240 mg, 40%), the cyclobutene **11h** (230 mg, 39%) and 2-cyano-3-phenylbut-2-enamide (70 mg, 12%). The cyclobutene **11h** was obtained as a solid, mp 69–71 °C (from toluene–hexane, 1:1) and as the only diastereoisomer; ν_{max}(KBr)/cm^{-1} 3330 and 3200 (NH_2), 2220 (CN) and 1670 ($CONH_2$); δ_H($CDCl_3$) 1.8 (3 H, s, Me), 4.3 (2 H, br s, NH_2) and 7.3–7.6 (10 H, m, aryl H); *m*/*z* 313 (M^+, 76), 298 (39), 286 (20), 270 (24), 260 (36), 255 (45), 230 (21), 195 (20), 140 (18), 119 (63), 104 (100) and 77 (50) (Found: C, 77.00; H, 4.98. $C_{20}H_{15}N_3O$ requires C, 76.68; H, 4.79%). 2-Cyano-3-phenylbut-2-enamide obtained as a solid was identical with an authentic sample.[11]

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