Photocycloaddition of 2*H*-1-Benzopyran-3-carbonitriles and 2*H*-1-Benzothiopyran-3-carbonitriles to Alkenes and Alkenynes

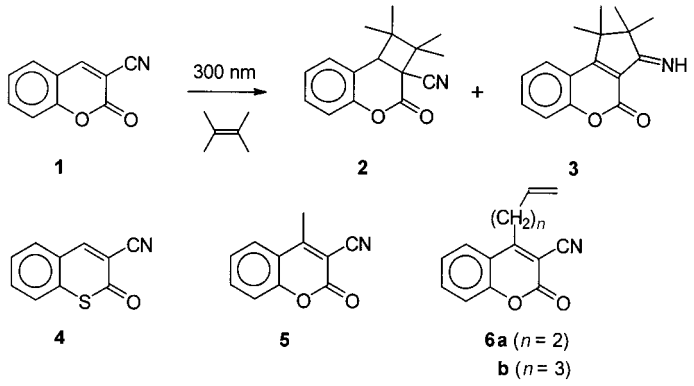
by **Dirk Schwebel** and **Paul Margaretha***

Institute of Organic Chemistry, University of Hamburg, D-20146 Hamburg

Both (intermolecular) photocycloadditions of 2*H*-1-benzopyran- and 2*H*-1-benzothiopyran-3-carbonitriles to 2,3-dimethylbut-2-ene and 2-methylbut-1-en-3-yne, and (intramolecular) photoisomerization of 4-(alkenyl)benzopyran-3-carbonitriles were investigated. In contrast to 2*H*-1-benzopyran-3-carbonitrile (**1**), its thia analog **4** reacts with 2,3-dimethylbut-2-ene selectively, to afford only cyclobuta derivative **7**. In the presence of 2-methylbut-1-en-3-yne, both **1** and **4** behave alike to afford the all-*cis*-cyclobuta diastereoisomers, **15** and **8**, respectively, as main products, as well as minor amounts of cyclobutenes **17** and **10**, respectively, which result from the addition of the terminal C-atom of the acetylenic bond to C(3) of the heterocycle. 4-Methyl-2*H*-1-benzopyran-3-carbonitrile (**5**) does not undergo photoaddition to the alkene or the alkenyne mentioned above, whereas the corresponding intramolecular [2 + 2] photocycloaddition of 4-(pent-4-enyl)benzopyran-3-carbonitrile (**6b**) to tetracycle **20** proceeds quantitatively.

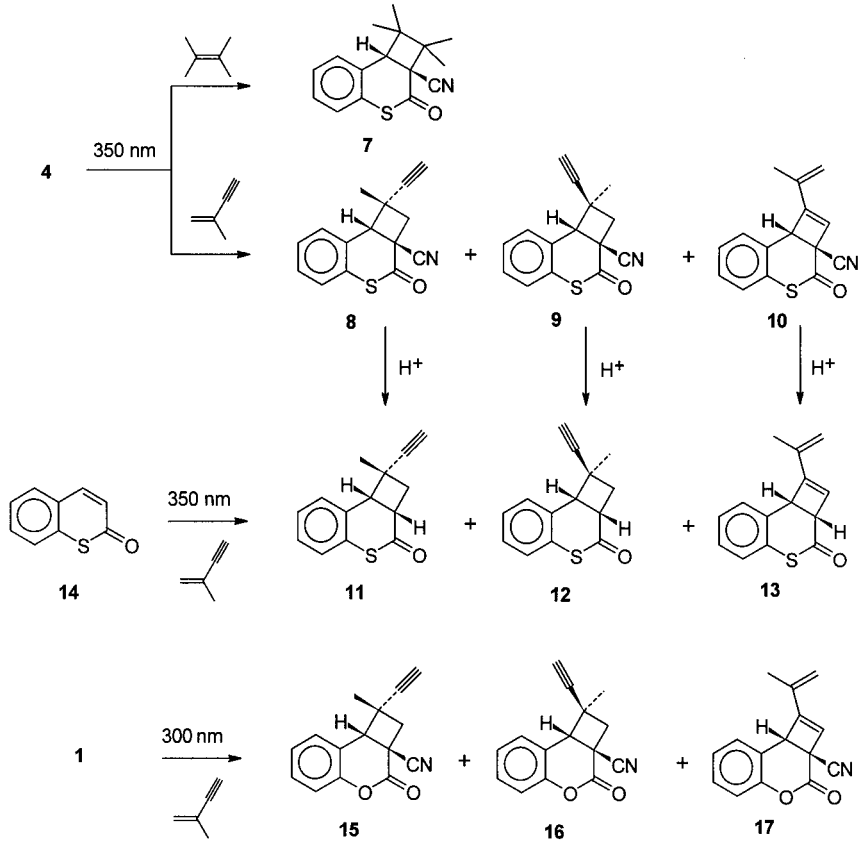
Introduction. – We have recently reported [1] that irradiation of 2*H*-1-benzopyran-3-carbonitrile (**1**) in the presence of 2,3-dimethylbut-2-ene affords a cyclobutabenzopyran **2** as major and cyclopenta-benzopyran **3** as minor product. The imino compound **3** is readily hydrolyzed to a tricyclic keto lactone representing a partial structure of *aflatoxin B*. Here, we report on the photocycloaddition of 2*H*-1-benzothiopyran-3-carbonitrile **4** to the same alkene, on the photoreactions of **1** and **4** with 2-methylbut-1-en-3-yne, on the irradiation of 4-methyl-2*H*-1-benzopyran-3-carbonitrile (**5**) in the presence of alkenes, and finally on the photoisomerization (intramolecular photocycloaddition) of 4-(alkenyl)-2*H*-1-benzopyran-3-carbonitriles **6** (*Scheme 1*).

Scheme 1



Results. – Irradiation (350 nm) of 2*H*-1-benzothiopyran-3-carbonitrile (**4**) in the presence of a tenfold molar excess of 2,3-dimethylbut-2-ene affords exclusively the *cis*-fused cyclobuta-benzothiopyran **7**. Irradiation of **4** in the presence of a tenfold molar excess of 2-methylbut-1-en-3-yne affords a 83 : 14 : 3 mixture (GC) of cycloadducts **8**, **9** and **10**, which, on chromatographic (SiO_2) workup, are already partially converted into three novel products **11**, **12**, and **13**, respectively. Quantitative conversion of **8**–**10** to **11**–**13** is achieved by stirring the cycloadducts for 12 h at room temperature in EtOH containing traces of HCl. These same products **11**–**13** are formed on irradiation (350 nm) of 2*H*-1-benzothiopyran-2-one (**14**) in the presence of the same enyne, but in a slightly different (80 : 13 : 7) ratio. Irradiation (300 nm) of **1** in the presence of 2-methylbut-1-en-3-yne affords a 89 : 9 : 2 mixture (GC) of cycloadducts **15**–**17** (*Scheme 2*).

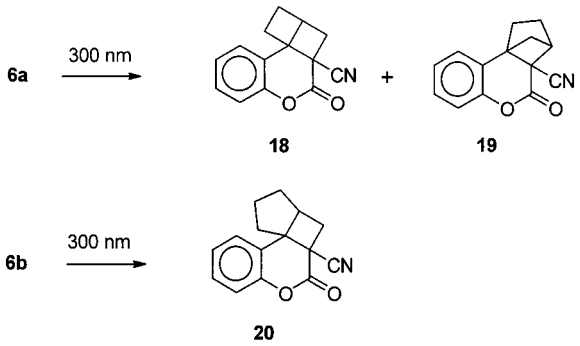
Scheme 2



4-Methyl-2*H*-1-benzopyran-3-carbonitrile (**5**) turns out to be photostable in the presence of 2,3-dimethylbut-2-ene, 2-methylbut-1-en-3-yne, or isobutene. On irradiation in CD_3OD as solvent, slow degradation occurs, but no incorporation of D into the starting material is observed. In contrast, 4-(alkenyl)-2*H*-1-benzopyran-3-carbonitriles

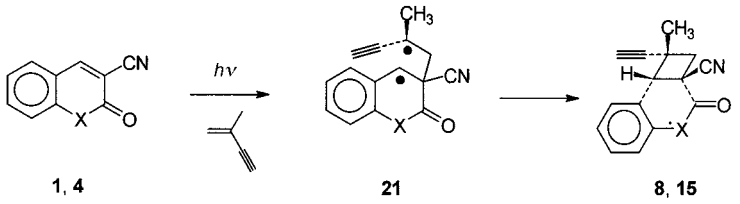
6a and **6b** undergo photoisomerization (300 nm), **6a** affording a 1:6 mixture (GC) of **18** and **19** up to 50% conversion of starting material, while **6b** is quantitatively and selectively converted to **20** (*Scheme 3*). All new photoproducts were fully characterized by ^{1}H- and ^{13}C-NMR, including ^{1}H,^{1}H-, ^{1}H,^{13}C-COSY and NOE spectra, and, in addition, the structures of **16** and **20** were established by X-ray crystal-structure analyses.

Scheme 3



Discussion. – On comparing the results of the photoaddition of the title compounds **1** and **4** to 2,3-dimethylbut-2-ene or 2-methylbut-1-en-3-yne, respectively, both differences and similarities are observed. On the one side, irradiation of **1** in the presence of the above-mentioned alkene gives both cyclobuta-benzopyran **2** and cyclopenta-benzopyran **3** (*Scheme 1*), while **4** affords selectively cyclobuta-benzothiopyran **7** under these conditions. We had proposed [1] that **3** results from an upper excited triplet state of **1**, and it is conceivable that no such state is populated by intersystem crossing from singlet excited **4**. On the other side, both **1** and **4** give very similar product mixtures on irradiation in the presence of the alkenyne mentioned above, and even **14**, which does not have a CN group on C(3), behaves alike, affording roughly 90% of that diastereoisomeric cyclobuta compound, in which the ethynyl group and benzo moiety are located on the same side (*i.e.*, *cis*) of the four-membered ring, besides traces of the other diastereoisomer, and of a cyclobutene. Apparently, biradical **21**, the precursor for both cyclobutanes, seems to be stabilized by π-π stacking in the conformation, which leads preferentially to **8**, **11**, and **15** (*Scheme 4*). It is also noteworthy that, in the photoaddition of **1**, **4**, or **14** to 2-methylbut-1-en-3-yne, no 1,6-cyclization products of **21** are formed, in contrast to the reaction of excited cyclohex-2-enones with the same enyne [2][3]. We had correlated the formation of 6-acyl-3-

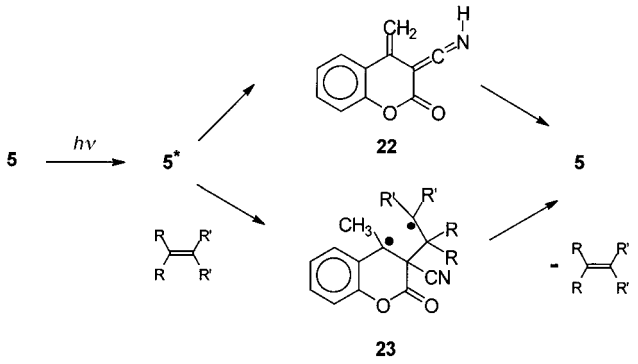
Scheme 4



methylidenecyclohexenes in such reactions with conformational preferences of the intermediate (oxocyclohexyl)propargyl biradical [2][3], whereby 1,6-cyclization is kinetically favored over 1,4-cyclization. Most probably benzo-fused biradicals **21** are not conformationally flexible enough to undergo such a cyclohexa annelation.

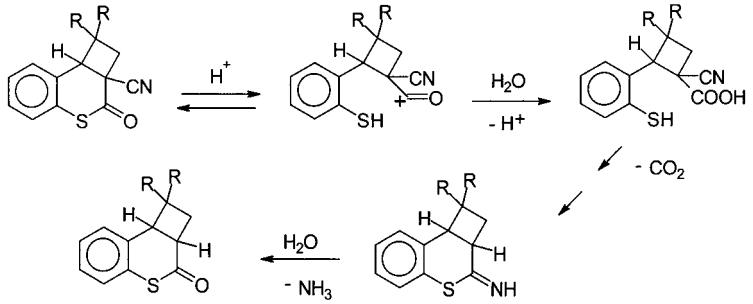
The observation that 4-methyl derivative **5** does not undergo photoaddition to 2,3-dimethylbut-2-ene, isobutene, or 2-methylbut-1-en-3-yne could be due to efficient intramolecular H-transfer from the Me group to the CN N-atom in the excited benzopyran-carbonitrile to give the unsaturated ketene-imine **22**, which would tautomerize back to **5**. Alternatively, biradical **23** resulting from addition of an alkene (or enyne) to C(3) of excited **5** could possibly be reverted quantitatively to starting materials, to the exclusion of any ring closure (*Scheme 5*). The experimental result that, on prolonged irradiation in CD_3OD, no incorporation of D into the Me group of **5** is detected by ^{1}H-NMR, renders this second deactivation sequence more plausible. The regioselectivity observed in the photocyclization of 4-alkenyl derivatives **6**, *i.e.*, preferential formation of 'cross' adduct **19** from **6a** and exclusive conversion of **6b** to 'straight' adduct **20**, correlates to the well-established trend of formation of a five-membered ring in the initial bonding step in such reactions [4].

Scheme 5



Finally, the ease of conversion of cycloadducts **8**–**10** to **11**–**13** is remarkable. As observed, these cyclobuta-benzothiopyran-carbonitriles undergo partial conversion to the (hydrodecyanated) benzothiopyrans already on attempted chromatography on SiO_2 and quantitative transformation on stirring in ethanolic HCl at room temperature, in contrast to their benzopyran counterparts **15**–**17**, which are not affected by chromatographic workup. The much higher rate of CN/H exchange for the thiacycle than for the oxacycle is probably not due to an anchimeric assistance, *i.e.*, a direct neighboring-group participation, but rather to the more efficient protonation and ring-opening sequence of a thiolactone as compared to a lactone (*Scheme 6*). The ensuing steps, *i.e.*, spontaneous decarboxylation of a dialkylcyanacetic acid, cyclization *via* nucleophilic addition of the thiol S-atom to the electrophilic C-atom of the C≡N bond, and subsequent hydrolysis are trivial. This assumption is corroborated by the stability on (acidic) workup of cycloadduct **7**, wherein the additional gem-dimethyl group in the cyclobutane ring should rather slow down *inter*- than *intramolecular* interactions.

Scheme 6



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Experimental Part

1. *General*. Photolyses: *Rayonet RPR-100* photoreactor equipped with either 300-nm or 350-nm lamps. GC: 30-m *SE-30* cap. column. UV Spectra: in nm ($\log \varepsilon$). ^{1}H- and ^{13}C-NMR spectra: at 500 and 125.8 MHz, resp.; chemical shifts in ppm rel. to TMS (=0 ppm). MS: at 70 eV; in *m/z* (rel. intensity in %). X-Ray crystal-structure analyses: *Enraf-Nonius-CAD-4* four-circle diffractometer at 293 K with CuK_α radiation ($\lambda = 1.54178$ Å).

2. *Starting Materials.* Compounds **1** [5], **4** [6], **5** [7], **6a** [8] and **14** [9] were synthesized according to the mentioned literature.

Synthesis of **6b**. Oxidation of 2-(1-hydroxycyclohex-5-enyl)phenol [10] with MnO_2 in pentane [11] affords *1-(2-hydroxyphenyl)hex-5-en-1-one* (43%, yellow oil), which, on reaction with malonodinitrile according to [7], followed by chromatography (SiO_2, hexane/AcOEt 1:4), gives *2-oxo-4-(pent-4-enyl)-2*H*-1-benzopyran-3-carbonitrile* (**6b**) in 57% yield. M.p. 85°. UV (MeCN): 340 (3.175), 297 (3.883). ^{1}H-NMR ($CDCl_3$): 7.75–7.68 (*m*, 2 H); 7.45–7.40 (*m*, 2 H); 5.85 (*ddt*, *J* = 10.7, 17.3, 6.6, 1 H); 5.16 (*d*, *J* = 17.3, 1 H); 5.11 (*d*, *J* = 10.7, 1 H); 3.11 (*t*, *J* = 6.8, 2 H); 2.30 (*dt*, *J* = 6.6, 6.8, 2 H); 1.85 (*quint.*, *J* = 6.8, 2 H). ^{13}C-NMR ($CDCl_3$): 166.5 (*s*); 156.8 (*s*); 153.8 (*s*); 136.6 (*d*); 135.1 (*d*); 125.8 (*d*); 125.4 (*d*); 118.0 (*d*); 117.4 (*s*); 116.6 (*t*); 113.3 (*s*); 101.9 (*s*); 33.6 (*t*); 31.3 (*t*); 28.9 (*t*). MS: 239 (36, M^+), *185*.

3. *Photolyses.* 3.1. *General Procedure.* Ar-Degassed solns. of 1 mmol of coumarin and, in intermolecular cycloadditions, 10 mmol of alkene in 5 ml of MeCN are irradiated with light of the wavelength given for the time indicated (monitoring by GC, increasing retention times), followed by evaporation of the solvent and excess alkene, and by the workup as described.

3.2. *Photoaddition of 2-Oxo-2*H*-1-benzothiopyran-3-carbonitrile* (**4**) *to 2,3-Dimethylbut-2-ene:* 300 nm; 30 h; total conversion to **7** (100%); chromatography (SiO_2; hexane/AcOEt 1:1) affords 175 mg (64%) of cis-*3-oxo-1,1,2,2-tetramethyl-1,2-dihydro-3*H,*8b*H-*cyclobuta[c]benzothiopyran-2a-carbonitrile* (**7**). M.p. 89°. ^{1}H-NMR ($CDCl_3$): 7.30 (*dt*, *J* = 1.5, 7.1, 1 H); 7.25 (*dt*, *J* = 1.5, 7.1, 1 H); 7.12 (*dd*, *J* = 1.5, 7.1, 1 H); 7.09 (*dd*, *J* = 1.5, 7.1, 1 H); 4.03 (*s*); 1.57, 1.18, 1.12, 0.90 (4*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 190.8 (*s*); 130.4 (*s*); 129.5 (*d*); 128.3 (*d*); 127.6 (*d*); 126.2 (*d*); 125.6 (*s*); 117.6 (*s*); 53.9 (*d*); 51.1 (*s*); 50.9 (*s*); 46.4 (*s*); 25.9, 24.9, 21.3, 20.8 (4*q*, 4 Me). MS: 271 (2, M^+), *84*.

3.3. *Photoaddition of 2-Oxo-2*H*-1-benzothiopyran-3-carbonitrile* (**4**) *to 2-Methylbut-1-en-3-yne:* 350 nm; 24 h; total conversion to **8**/**9**/**10** (83:14:3). As chromatography on SiO_2 leads to conversion to **11**/**12**/**13**, resp., the spectral data are from the product mixture.

*1α,2aα,8bα-1-Ethynyl-1-methyl-3-oxo-1,2-dihydro-3*H,*8b*H-*cyclobuta[c]benzothiopyran-2a-carbonitrile* (**8**): ^{1}H-NMR ($CDCl_3$): 7.35 (*dt*, *J* = 1.5, 7.6, 1 H); 7.29 (*dt*, *J* = 1.5, 7.6, 1 H); 7.15 (*m*, 2 H); 4.11 (*s*); 3.17, 2.88 (*AB*, *J* = 12.0, 2 H); 2.21 (*s*); 1.58 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 194.9 (*s*); 131.5 (*s*); 129.2 (*d*); 129.1 (*d*); 127.2 (*d*); 126.3 (*d*); 124.8 (*s*); 117.6 (*s*); 83.7 (*s*); 75.9 (*d*); 57.9 (*d*); 46.3 (*d*); 40.9 (*s*); 39.4 (*s*); 28.5 (*q*). MS: 253 (3, M^+), *159*.

*1α,2aβ,8bβ-1-Ethynyl-1-methyl-3-oxo-1,2-dihydro-3*H,*8b*H-*cyclobuta[c]benzothiopyran-2a-carbonitrile* (**9**): ^{1}H-NMR ($CDCl_3$): 7.37 (*m*, 2 H); 7.12 (*m*, 2 H); 4.64 (*s*); 3.29, 2.90 (*AB*, *J* = 12.0, 2 H); 2.52 (*s*); 1.23 (*s*, 3 H). MS: 253 (4, M^+), *159*.

cis-*1-(Methylethenyl)-3-oxo-3*H,*8b*H-*cyclobuta[c]benzothiopyran-2a-carbonitrile* (**10**): ^{1}H-NMR ($CDCl_3$): 7.35 (*m*, 2 H); 7.15 (*m*, 2 H); 6.12 (*s*); 5.18 (*s*); 5.13 (*s*); 4.85 (*s*); 2.38 (*s*, 3 H). MS: 253 (2, M^+), *159*.

3.4. *Photoaddition of* 2H-*1-Benzothiopyran-2-one* (**14**) *to 2-Methylbut-1-en-3-yne.* 350 nm; 24 h; total conversion to **11**/**12**/**13** (80:13:7); chromatography (SiO_2; hexane/AcOEt 1:2) affords 160 mg (70%) of *1α,2aα,8bα-1-ethynyl-1-methyl-1,2,2a,3-tetrahydro-8b*H-*cyclobuta[*c*]benzothiopyran-3-one* (**11**): M.p. 113°. ^{1}H-NMR ($CDCl_3$): 7.23 (*dt*, *J* = 1.5, 7.6, 1 H); 7.19 (*dt*, *J* = 1.5, 7.6, 1 H); 7.10 (*dd*, *J* = 1.5, 7.6, 1 H); 7.08 (*dd*, *J* = 1.5, 7.6, 1 H); 3.84 (*d*, *J* = 9.5, 1 H); 3.43 (*ddd*, *J* = 3.5, 9.5, 10.0, 1 H); 2.76 (*dd*, *J* = 3.5, 12.0, 1 H); 2.57 (*dd*, *J* = 10.0, 12.0, 1 H); 2.14 (*s*); 1.58 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 200.3 (*s*); 132.7 (*s*); 129.1 (*d*); 127.9 (*d*); 126.6 (*d*); 125.9 (*d*); 124.1 (*s*); 86.2 (*s*); 74.2 (*d*); 52.7 (*d*); 42.2 (*d*); 41.7 (*s*); 40.8 (*t*); 28.3 (*q*). MS: 228 (6, M^+), *134*. The spectral data of the two minor products stem from the original product mixture.

*1α,2aβ,8bβ-1-Ethynyl-1-methyl-1,2,2a,3-tetrahydro-8b*H-*cyclobuta[*c*]benzothiopyran-3-one* (**12**): ^{1}H-NMR ($CDCl_3$): 7.34 (*dt*, *J* = 1.5, 7.6, 1 H); 7.29 (*dt*, *J* = 1.5, 7.6, 1 H); 7.15 (*dd*, *J* = 1.5, 7.6, 1 H); 7.14 (*dd*, *J* = 1.5, 7.6, 1 H); 4.37 (*d*, *J* = 10.0, 1 H); 3.49 (*ddd*, *J* = 3.5, 10.0, 10.5, 1 H); 2.97 (*dd*, *J* = 10.5, 12.0, 1 H); 2.44 (*dd*, *J* = 3.5, 12.0, 1 H); 2.41 (*s*); 1.19 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 200.4 (*s*); 130.7 (*s*); 129.3 (*d*); 128.2 (*d*); 127.1 (*d*); 126.1 (*d*); 124.6 (*s*); 90.2 (*s*); 70.3 (*d*); 51.6 (*d*); 41.7 (*t*); 40.7 (*d*); 37.7 (*s*); 22.7 (*q*). MS: 228 (2, M^+), *134*.

cis-*1-(Methylethenyl)-2a,3-dihydro-8b*H-*cyclobuta[*c*]benzothiopyran-3-one* (**13**): ^{1}H-NMR ($CDCl_3$): 7.45 (*m*, 2 H); 7.25 (*m*, 2 H); 6.07 (*s*); 5.15 (*s*); 4.99 (*s*); 4.59 (*d*, *J* = 4.6, 1 H); 3.94 (*d*, *J* = 4.6, 1 H); 1.80 (*s*, 3 H). MS: 228 (17, M^+), *134*.

3.5. *Photoaddition of 2-Oxo-*2H-*1-benzopyran-3-carbonitrile* (**1**) *to 2-Methylbut-1-en-3-yne:* 300 nm; 12 h; total conversion to **15**/**16**/**17** (89:9:2); chromatography (SiO_2; hexane/AcOEt 2:1) affords 166 mg (70%) of *1α,2aα,8bα-1-ethynyl-1-methyl-3-oxo-1,2-dihydro-3*H,*8b*H-*cyclobuta[*c*]benzopyran-2a-carbonitrile* (**15**): M.p. 167°. ^{1}H-NMR ($CDCl_3$): 7.39 (*dd*, *J* = 1.5, 7.6, 8.1, 1 H); 7.21 (*ddd*, *J* = 1.0, 7.6, 8.1, 1 H); 7.13 (*dd*, *J* = 1.0, 8.1, 1 H); 7.11 (*dd*, *J* = 1.5, 7.6, 1 H); 3.90 (*s*); 3.16, 2.96 (*AB*, *J* = 12.2, 2 H); 2.20 (*s*); 1.62 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 162.3 (*s*); 151.7 (*s*); 130.3 (*d*); 128.2 (*d*); 125.4 (*d*); 117.4 (*d*); 117.3 (*s*); 116.7 (*s*); 83.3 (*s*); 75.7 (*d*); 51.9 (*d*); 46.0 (*d*); 39.0 (*s*); 33.2 (*t*); 28.0 (*q*). MS: 237 (7, M^+), *171*.

X-Ray Crystal-Structure Determination of **15**: pale yellow, transparent blocks (0.60 × 0.70 × 0.30 mm) from CH_2Cl_2, $C_{15}H_{11}NO_2$, M_r 237.257, monoclinic, space group *P*2/*c*, *Z* = 4, *a* = 6.278(5), *b* = 13.753(18), *c* = 14.696(14) Å, *β* = 100.85(2)°, *V* = 1246.1(2) Å^3, D_x = 1.2646(2) g·cm^{-3}.

The spectral data of the two minor products, **16** and **17**, stem from the original product mixture.

*1α,2aβ,8bβ-1-Ethynyl-1-methyl-3-oxo-1,2-dihydro-3*H,*8b*H-*cyclobuta[*c*]benzopyran-2a-carbonitrile* (**16**): ^{1}H-NMR ($CDCl_3$): 7.39 (*dt*, *J* = 1.5, 7.6, 1 H); 7.21 (*dt*, *J* = 1.5, 7.6, 1 H); 7.13 (*dd*, *J* = 1.5, 7.6, 1 H); 7.11 (*dd*, *J* = 1.5, 7.6, 1 H); 4.39 (*s*); 3.37, 2.88 (*AB*, *J* = 12.7, 2 H); 2.54 (*s*); 1.10 (*s*, 3 H). MS: 237 (6, M^+), *171*.

cis-*1-(Methylethenyl)-3-oxo-3*H,*8b*H-*cyclobuta[*c*]benzopyran-2a-carbonitrile* (**17**): ^{1}H-NMR ($CDCl_3$): 7.42 (*m*, 2 H); 7.25 (*m*, 2 H); 6.12 (*s*); 5.34 (*s*); 5.23 (*s*); 4.69 (*d*); 1.62 (*s*, 3 H). MS: 237 (24, M^+), *171*.

3.6. *Photoaddition of 4-Methyl-3-oxo-2*H-*benzopyran-3-carbonitrile to Alkenes* (*2,3-Dimethylbut-2-ene, 2-Methylprop-1-ene, 2-Methylbut-1-en-3-yne*): 300 nm; 72 h; no conversion of starting material as monitored by GC against an internal standard. On irradiation (300 nm) of 8.5 mg (0.1 mmol) of **5** in 2 ml of a mixture MeCN/CD_3OD 1:1 for 24 h, no incorporation of D in the starting material is observed (^{1}H-NMR).

3.7. *Irradiation of 4-(But-3-enyl)-3-oxo-2*H-*benzopyran-3-carbonitrile* (**6a**): 300 nm; 72 h; 50% conversion to a mixture **18**/**19**/**6a** (6:44:50); chromatography (SiO_2; hexane/AcOEt 2:1) affords 70 mg (32%) of *3-oxo-4-oxatetracyclo[9.2.1.0^{2,11}.0^{5,10}]tetradeca-5,7,9-triene-2-carbonitrile* (**19**). Colorless oil. ^{1}H-NMR (C_6D_6): 6.81–6.71 (*m*, 3 H); 6.66 (*dd*, *J* = 1.5, 7.6, 1 H); 2.68 (*dd*, *J* = 1.0, 2.5, 1 H); 1.82 (*dddd*, *J* = 2.5, 3.5, 8.6, 11.7, 1 H); 1.70 (*dddd*, *J* = 3.0, 3.5, 8.6, 11.2, 1 H); 1.62 (*dddd*, *J* = 2.4, 2.5, 3.0, 8.6, 1 H); 1.55 (*ddd*, *J* = 3.5, 9.6, 11.2, 1 H); 1.23 (*dddd*, *J* = 1.0, 3.5, 9.6, 11.7, 1 H); 0.53 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR ((D$_6$)Acetone): 163.3 (*s*); 153.4 (*s*); 130.9 (*d*); 127.3 (*d*); 126.4 (*d*); 122.7 (*s*); 117.6 (*d*); 114.3 (*s*); 56.1 (*s*); 48.1 (*s*); 47.7 (*d*); 41.8 (*t*); 26.9 (*t*); 25.6 (*t*). MS: 225 (100, M^+).

The spectral data of the minor product **18** stems from the original product mixture.

2-Oxo-3-oxatetracyclo[8.4.0.0^{4,9}.0^{10,13}]tetradeca-4,6,10-triene-1-carbonitrile (**18**). MS: 225 (100, M^+).

3.8. *Irradiation of* **6b**: 300 nm; 2 h; total conversion to **20** (100%); chromatography (SiO_2; hexane/AcOEt 2:1) affords 143 mg (60%) of *4-oxo-5-oxatetracyclo[10.3.0.0^{3,12}.0^{6,11}]pentadeca-6,8,10-triene-3-carbonitrile* (**20**). M.p. 32–34°. ^{1}H-NMR ($CDCl_3$): 7.30–7.21 (*m*, 3 H); 7.09 (*dd*, *J* = 1.5, 7.6, 1 H); 3.01 (*dd*, *J* = 9.6, 13.7, 1 H); 2.81 (*m*, 1 H); 2.54 (*dd*, *J* = 6.1, 13.7, 1 H); 2.48 (*m*, 1 H); 2.34 (*m*, 1 H); 2.32 (*m*, 1 H); 2.23 (*m*, 1 H); 1.88 (*m*, 1 H); 1.74 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 163.6 (*s*); 149.8 (*s*); 129.3 (*d*); 125.9 (*d*); 125.3 (*d*); 124.0 (*s*); 117.8 (*d*); 116.5 (*s*); 51.7 (*s*); 46.8 (*d*); 39.9 (*s*); 37.3 (*t*); 35.9 (*t*); 32.5 (*t*); 26.0 (*t*). MS: 239 (43, M^+), *185*.

X-Ray Crystal-Structure Determination of **20**: pale yellow transparent blocks (0.60 × 0.50 × 0.35 mm) from CH_2Cl_2, $C_{15}H_{13}NO_2$, M_r 239.273, monoclinic, space group, *P*21/*c*, *Z* = 4, *a* = 10.6097(10), *b* = 10.692(3), *c* = 11.4805(19) Å, *β* = 113.794(11)°, *V* = 1191.6(4) Å^3, D_x = 1.3338(4) g·cm^{-3}.

4. *Acid-Catalyzed Hydrodecyanation of* **8**–**10** *to* **11**–**13**, *Respectively.* A soln. of 25.3 mg (0.1 mmol) of the mixture **8**/**9**/**10** (*cf. 3.3*) and 1 µl of HCl in 10 ml of EtOH is stirred at r.t. for 12 h. After addition of H_2O (10 ml) and Et_2O (10 ml), the org. layer is separated, washed with sat. aq. NaCl, and dried ($MgSO_4$). Evaporation of the solvent affords 20.5 mg (90%) of a mixture **11**/**12**/**13** (83 : 14 : 3). M.p. 89–91°.

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