Photocycloaddition of 2-Oxopyran-3-carbonitriles to 2,3-Dimethylbut-2-ene

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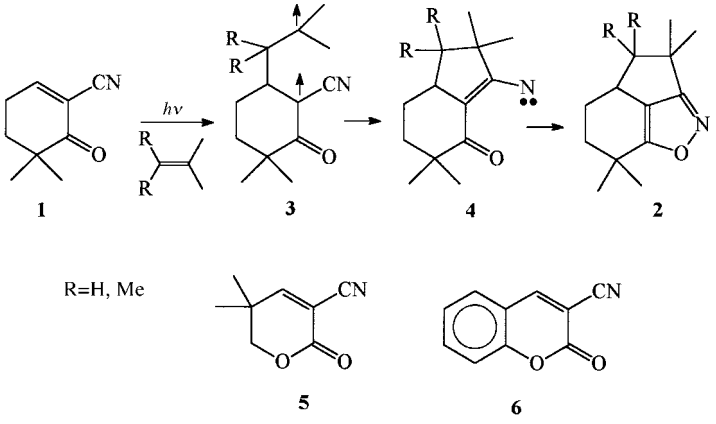
On acetone-sensitized irradiation in the presence of 2,3-dimethylbut-2-ene, α-cyano-α,β-unsaturated δ-lactone **5** is converted both to cyclopentapyrans resulting from stepwise addition of the alkene to the olefinic C(β)- and the nitrile C-atom of triplet excited **5**, and cyclobutapyranes, *i.e.*, [2 + 2] cycloadducts. Similarly, direct irradiation of 1-benzopyran-3-carbonitrile **6** in the presence of the same alkene affords cyclobutabenzopyran **13** and cyclopentabenzopyran **14**, the latter resulting from an upper excited triplet state of **6**.

1. Introduction. – Irradiation of oxo-cyclohexene-carbonitrile **1** in the presence of alkenes affords tricyclic isoxazoles **2** [1] [2] *via* 1,5-cyclization [3] of triplet biradical **3** and subsequent electrocyclic ring closure of β-acylvinylnitrene **4**. Here, we report results on the photochemical behavior of α-cyano lactones **5** and **6** in the presence of 2,3-dimethylbut-2-ene (*Scheme 1*).

Scheme 1



2. Results. – On direct irradiation of α-cyano lactone **5** in the presence of tenfold molar excess of 2,3-dimethylbut-2-ene in MeCN with light of either 300-nm or 254-nm wavelength, no formation of photoproducts occurs, as these undergo immediate

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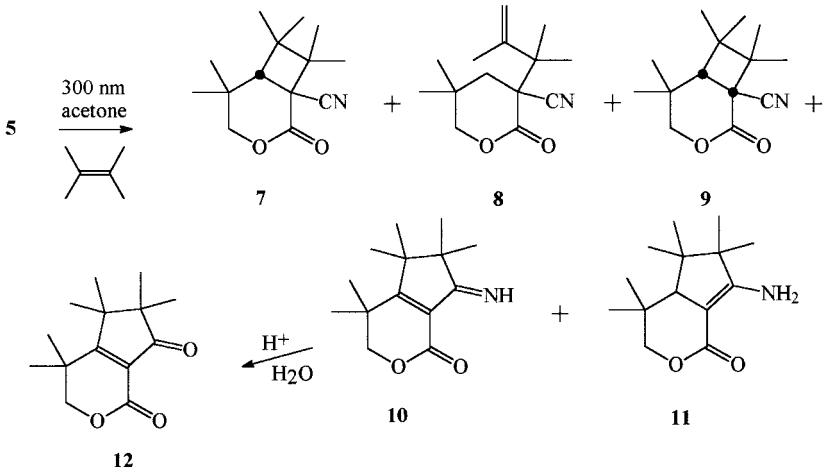
photodegradation. In contrast, acetone-sensitized irradiation (300 nm) of **5** and the same alkene allows conversions of up to 65–70% of **5** before the onset of consecutive photodecomposition of products. Monitoring the reaction by GC/MS indicates the formation of five products, **7**–**11**, numbered according to their increasing retention times, in 2:1:5:4:6 ratio. Products **7**–**10** all exhibit M^+ at m/z 235, *i.e.*, they are [pyranone + alkene] adducts, while the major product **11** has M^+ at m/z 237. Products **7** and **9** have very similar mass spectra with an intensive peak at m/z 84, typical for 1,1,2,2-tetramethylcyclobutane radical-cation fragmentation. The photoproducts were separated and isolated by liquid chromatography, their structural assignments stemming from spectroscopic evidences. Finally, compound **10** is easily converted to **12** (M^+ 236) by acid hydrolysis (*Scheme 2*).

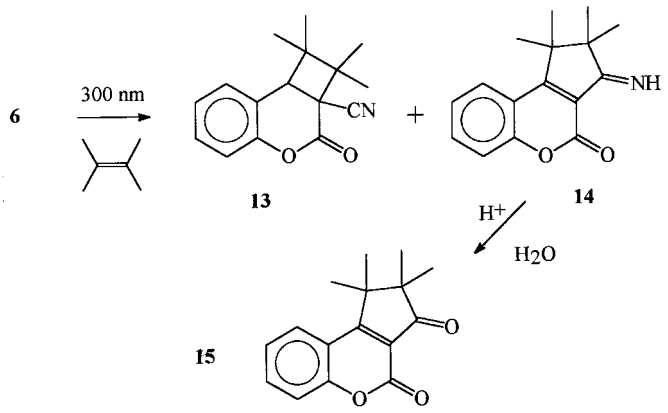
Scheme 2



Irradiation (300 nm) of 1-benzopyran-3-carbonitrile **6** in MeCN in the presence of the same alkene affords products **13** and **14** in a 6:1 ratio. Both compounds are [coumarin + alkene] adducts with M^+ at m/z 255, their formation being quenched by added naphthalene. On acetone-sensitized irradiation, the same ratio **13**/**14** is observed, but by using thioxanthone as sensitizer (irradiation with $\lambda = 395$ nm), **13** is formed exclusively. Separation and isolation of the photoproducts is again achieved by liquid chromatography, compound **14** being easily converted by acid hydrolysis to **15**, whose structure was established by X-ray analysis (*Scheme 3*).

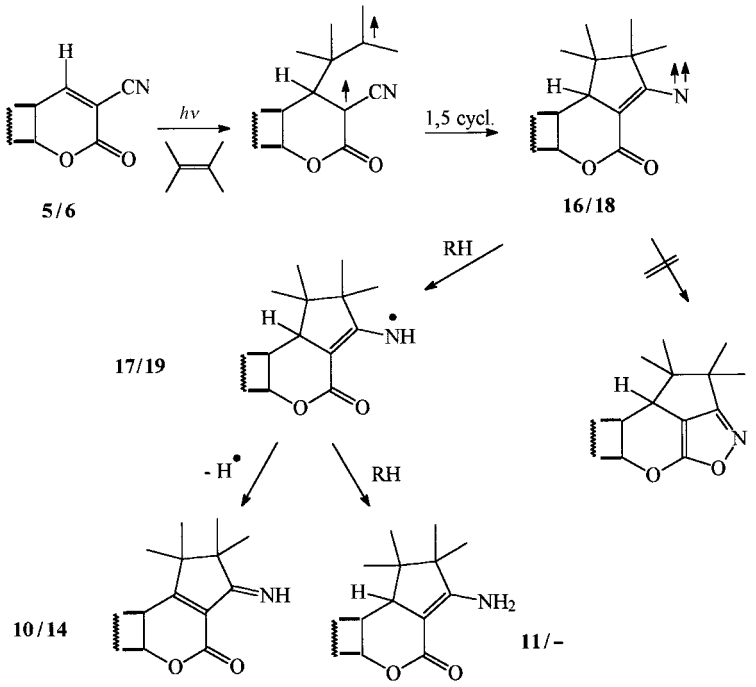
3. Discussion. – At first sight, the behavior of the triplet lactone **5** towards 2,3-dimethylbut-2-ene parallels that of triplet ketone **1** inasmuch as [3 + 2] cycloadducts are formed preferentially to cyclobutanes (60:40 for **5** and >95:5 for **1**). Nevertheless, it is of interest that, in contrast to **4**, β-acylvinylnitrene **16**, formed by 1,5-cyclization from the triplet biradical precursor, does *not* undergo intersystem crossing and subsequent electrocyclic ring closure to a 1,2-oxazole. Instead, **16** reacts further *via* H-abstraction [4] to iminyl radical **17** which can either afford imino lactone **10** by loss of a H-atom [5], or abstract a second H-atom to give enamino lactone **11**. Similarly, triplet

Scheme 3



18, formed from **6**, gives radical **19** which now reacts exclusively to imino lactone **14**, as the eliminated H-atom is a benzylic one (*Scheme 4*).

Scheme 4



The easy access to tricyclic ketone **15** is remarkable, as it represents a partial structure of *Aflatoxin B* [6], but unfortunately the yield of **14** from **6** is very low. As **14** is formed from an upper triplet state, accessible both from S_1 and by using acetone ($E_T = 80$ kcal/mol) but not thioxanthone ($E_T = 62$ kcal/mol) as sensitizer, it seems

worthwile to introduce substituents, *e.g.*, MeO groups, on the aromatic ring. This could reduce the energy gap between the two reactive triplet states and thus increase the ratio of cyclopentacoumarin *vs.* cyclobutacoumarin formation. Synthetic and photochemical studies in this direction are now in progress.

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Experimental Part

1. *General*. Cyano lactones **5** [7] and **6** [8] were synthesized according to the literature procedures. Photolyses were performed with a *Rayonet RPR-100* photoreactor equipped with 300-nm or 254-nm lamps, and with a 250-W high pressure Hg lamp in combination with a liquid filter solution of 75 g of $NaNO_2$/l H_2O ($\lambda >$ 390 nm). GC: 30-m *SE 30* capillary column. ^{1}H- and ^{13}C-NMR Spectra: at 500 and 125.77 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %). X-Ray analysis: *Enraf-Nonius CAD-4* four circle diffractometer with CuK_α radiation ($\lambda = 1.54178$ Å) at 173 K.

*Acetone-Sensitized Photoaddition of 5,5-Dimethyl-2-oxo-5,6-dihydro-2*H*-pyran-3-carbonitrile (**5**) to 2,3-Dimethylbut-2-ene.* An Ar-degassed soln. of 3.02 g (20 mmol) **5** and 16.8 g (0.2 mol) of 2,3-dimethylbut-2-ene in 100 ml of acetone was irradiated (300 nm) for 40 h with up to 35% conversion of **5** as monitored by GC. After evaporation of the solvent, chromatography (SiO_2; pentane/Et_2O/acetone 4:2:1) afforded first 50 mg (3%) of *(1α,6β)-5,5,7,7,8,8-hexamethyl-2-oxo-3-oxabicyclo[4.2.0]octane-1-carbonitrile* (**7**). M.p. 78–84°. ^{1}H-NMR ($CDCl_3$): 4.40, 3.98 (*AB*, *J* = 10, 2 H); 2.10 (*s*); 1.50, 1.38, 1.25, 1.22, 1.14, 0.98 (6*s*, 6 Me). ^{13}C-NMR ($CDCl_3$): 80 (CH_2); 53 (CH). MS: 220 (0.1, $[M-Me]^+$), *97*.

The second fraction consisted of 300 mg (18%) of *(1α,6α)-5,5,7,7,8,8-hexamethyl-2-oxo-3-oxabicyclo[4.2.0]octane-1-carbonitrile* (**9**). M.p. 96–97°. ^{1}H-NMR ($CDCl_3$): 4.53 (*d*, *J* = 10); 4.04 (*dd*, *J* = 1.5, 10); 2.41 (*d*, *J* = 1.5); 1.49, 1.35, 1.15, 1.13, 1.08, 0.97 (6*s*, 6 Me). ^{13}C-NMR ($CDCl_3$): 79 (CH_2); 54 (CH). MS: 220 (0.1, $[M-Me]^+$), *97*.

The third fraction consisted of 35 mg (2%) of *5,5-dimethyl-2-oxo-3-(1,1,2-trimethylprop-2-enyl)-3,4,5,6-tetrahydro-2*H*-pyran-3-carbonitrile* (**8**). M.p. 46–51°. ^{1}H-NMR ($CDCl_3$): 5.09 (*s*); 4.96 (*s*); 3.98 (*s*, 2 H); 1.87, 1.47, 1.34, 1.27, 1.00 (5 *s*, 5 Me). ^{13}C-NMR ($CDCl_3$): 165 (*s*); 147 (*s*); 121 (*s*); 116 (*t*); 79 (*t*); 48 (*s*); 47 (*s*); 43 (*t*); 30 (*s*); 26, 25, 23, 21, 19 (CH_3). MS: 235 (0.1, M^+), *83*.

The fourth fraction consists of 1.2 g of **5**. The fifth fraction consisted of 460 mg (28%) of *7-amino-4,4,5,5,6,6-hexamethyl-4,4a,5,6-tetrahydrocyclopenta[*c*]pyran-1-one* (**11**). M.p. 175–176°. ^{1}H-NMR ($CDCl_3$): 3.76, 3.50 (*AB*, *J* = 10.7, 2 H); 2.48 (*s*); 1.03, 0.98, 0.97, 0.95, 0.84, 0.78 (6 Me). ^{13}C-NMR ($CDCl_3$): 170 (*s*); 168 (*s*); 89 (*s*); 83 (*t*); 56 (*d*); 50 (*s*); 48 (*s*); 34 (*s*); 25, 24, 23, 22, 21, 18 (6 Me). MS: 237 (20, M^+), *182*.

The final fraction consisted of 280 mg (17%) of *7-imino-4,4,5,5,6,6-hexamethyl-3,4,5,6-tetrahydrocyclopenta[*c*]pyran-1-one* (**10**), already contaminated with 10–15% of ketone **12**. ^{1}H-NMR ($CDCl_3$): 3.95 (*s*, 2 H); 1.29 (*s*, 6 H); 1.15 (*s*, 6 H); 1.04 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 188 (*s*); 160 (*s*); 130 (*s*); 120 (*s*); 78 (*t*); 40 (*s*); 35 (*s*); 30 (*s*); 25, 24, 23 (Me). MS: 235 (25, M^+), *220*.

Hydrolysis of the Imine **10**. To a soln. of 12 mg (0.05 mmol) of **10** in 5 ml of Et_2O, 5 ml 0.01N HCl were added, and the two layers stirred for 5 min. The org. phase was then separated, washed with aq. $NaHCO_3$ and aq. NaCl, and dried ($MgSO_4$). Evaporation of the solvent afforded 9 mg (75%) of *4,4,5,5,6,6-hexamethyl-3,4,5,6-tetrahydrocyclopenta[*c*]pyran-1,7-dione* (**12**). M.p. 102–105°. ^{1}H-NMR ($CDCl_3$): 3.96 (*s*, 2 H); 1.34 (*s*, 6 H); 1.21 (*s*, 6 H); 0.98 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 205 (*s*); 160 (*s*); 130 (*s*); 120 (*s*); 78 (*t*); 40 (*s*); 35 (*s*); 30 (*s*); 25, 24, 23 (Me). MS: *236* (100, M^+).

*Photoaddition of 2-Oxo-2*H*-benzopyran-3-carbonitrile (**6**) to 2,3-Dimethylbut-2-ene.* An Ar-degassed soln. of 860 mg (5 mmol) of **6** and 4.2 g (50 mmol) 2,3-dimethylbut-2-ene in 25 ml of MeCN was irradiated (300 nm) for 48 h up to 65% conversion of **6**. After evaporation of the solvent, chromatography (SiO_2; hexane/AcOEt 1:1) of the residue (35% **6**, 56% **13**, and 9% **14**) afforded first 580 mg (45%) of *3-oxo-1,1,2,2-tetramethyl-1,2,2a,3-tetrahydro-8b*H*-cyclobuta[*c*]benzopyran-2a-carbonitrile* (**13**). M.p. 124°. ^{1}H-NMR ($CDCl_3$): 7.32 (*ddd*, *J* = 1.5, 7.6, 8.1); 7.17 (*ddd*, *J* = 1, 7.6, 7.7); 7.08 (*dd*, *J* = 1, 8.1); 7.02 (*dd*, *J* = 1.5, 7.6); 3.74 (*s*); 1.53, 1.30, 1.15, 0.75 (4 *s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 161 (*s*); 151 (*s*); 129 (*d*), 128 (*d*); 125 (*d*); 118 (*s*); 117 (*d*); 117 (*s*); 50 (*s*); 47 (*d*); 45 (*s*); 44 (*s*); 26 (*q*); 25 (*q*); 22 (*q*); 21 (*q*). MS: 255 (0.1, M^+), *84*.

The second fraction consisted of **6** (200 mg). Finally, we obtained 90 mg (7%) of *3-imino-1,1,2,2-tetramethyl-1,2-dihydrocyclopenta[*c*]benzopyran-4-one* (**14**). M.p. 137–142°. ^{1}H-NMR ($CDCl_3$): 7.93 (*dd*, *J* = 1.5, 8.1); 7.56 (*ddd*, *J* = 1.5, 7.6, 8.1); 7.38 (*dd*, *J* = 1.0, 8.1); 7.28 (*ddd*, *J* = 1.0, 7.7, 8.1); 1.40 (*s*, 6 H); 1.15 (*s*, 6 H).

^{13}C-NMR ($CDCl_3$): 183 (*s*); 170 (*s*); 159 (*s*); 155 (*s*); 133 (*d*); 126 (*d*); 125 (*d*); 118 (*d*); 118 (*s*); 117 (*s*); 51 (*s*); 49 (*s*); 25 (*q*); 23 (*q*). MS: 255 (9, M^+), *240*.

Sensitized Photoaddition of **6** *to 2,3-Dimethylbut-2-ene.* Monitoring the irradiation (254 nm) in acetone as solvent indicated the formation of **13** and **14** in a 6:1 ratio. Similarly, on irradiation (400 nm) in MeCN using thioxanthone as sensitizer, only **13** was formed.

Quenching Experiment. Ar-degassed solns. containing 10 mg (0.06 mmol) **6** and 50 mg (0.6 mmol) of alkene, and increasing amounts (up to 0.3M) of naphthalene in 2 ml of MeCN were irradiated (350 nm) in a merry-go-round setup. The resulting experimental slope corresponds to $k_q\tau = 2\ \text{M}^{-1}$ indicating a minimal life time of 0.2 ns for the quenched triplet state.

Hydrolysis of the Imine **14**. To a soln. of 14 mg (0.05 mmol) of **14** in 5 ml of Et_2O, 5 ml of 0.1N HCl were added, and the two layers stirred for 15 m. The org. phase was then separated, washed with aq. $NaHCO_3$ and aq. NaCl, and dried ($MgSO_4$). Evaporation of the solvent afforded 13 mg (96%) *1,1,2,2-tetramethyl-1,2-dihydro-1*H,*4*H-*cyclopenta[*c*]benzopyran-3,4-dione* (**15**). M.p. 181° (from AcOEt). ^{1}H-NMR ($CDCl_3$): 8.05 (*dd*, $J = 1.5$, 8.1); 7.70 (*m*, 1 H); 7.46 (*dd*, $J = 1.0$, 8.1); 7.38 (*m*, 1 H); 1.53 (*s*, 6 H); 1.16 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 205 (*s*); 180 (*s*); 157 (*s*); 156 (*s*); 135 (*d*); 127 (*d*); 125 (*d*); 119 (*s*); 118 (*s*); 117 (*s*); 54 (*s*); 47 (*s*); 25 (*q*); 21 (*q*). MS: 256 (72, M^+), *241*.

X-Ray Analysis of **15**. Transparent blocks, $0.7 \times 0.4 \times 0.2$ mm, were obtained by recrystallization from AcOEt. M.p. 181°. Crystal data: $C_{16}H_{16}O_3$, M_r 256.3, monoclinic, space group $P2_1/c$, $a = 8.663(1)$, $b = 7.135(1)$, $c = 20.999(2)$ Å, $\beta = 101.59(1)°$, $V = 1271.5(3)$ Å^3, $Z = 4$, $D_x = 1.339\ \text{g}\cdot\text{cm}^{-3}$, $F(000) = 544$, $\mu = 0.743\ \text{cm}^{-1}$. The cell parameters were determined by least-squares refinement against the setting angle of 25 reflections $\Theta = 42.7 - 45.9°$. Of the 2650 independent reflections ($\Theta_{max} = 76.4°$), 2592 were considered to be observed [$I > 2\sigma(I)$]. Final R values for all reflections: $R = 0.0556$ ($wR2 = 0.1392$)[2]).

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