236. A Note on Intramolecular Photochemical Cycloaddition of *N*-substituted Dimethacrylimides[1])

by **Alex Alder, Niklaus Bühler** and **Daniel Bellus**

Zentrale Forschungslaboratorien der *Ciba-Geigy AG*, CH-4002 Basel

Dedicated to Prof. Dr. *Oskar Jeger* on the occasion of his 65th birthday

(6.X.82)

Summary

The intramolecular photochemical [2+2]-cycloaddition of *N*-substituted dimethacrylimides **1a** and **1c**, respectively, proceeds under conditions of direct irradiation ($\lambda = 254$ nm) as well as triplet photosensitization highly regioselectively yielding predominantly the 'cross' bonding (head-to-tail) cycloadducts **3a** and **3c**, respectively, with a 3-azabicyclo[3.1.1]heptane ring system.

Introduction. – Recently we became aware of a communication describing an intramolecular [2+2]-photocycloaddition of *N*-substituted dimethacrylimides **1a** and **1b**. Thereby *Maruyama & Ishitoku* [3] claimed to have obtained the *N*-substituted *cis*-1,5-dimethyl-3-azabicyclo[3.2.0]heptane-2,4-diones **2a** and **2b** in yields up to 82%. This photochemical synthesis of **2** seemed amazingly simple, but questionable in view of a previous report that trimethacrylamide **1b** undergoes under similar conditions of unsensitized UV. irradiation an intramolecular 'cross' bonding (χ [2+2]-cycloaddition[2])) to form **3b** in 61% yield [5].

These conflicting reports and the fact that we were looking for an efficient synthesis of *cis*-*N*-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.2.0]heptane-2,4-dione (**2c**)[3]) provoked our effort to establish the nature of the products originating from the UV. irradiation of **1**. The available literature data on photochemical behaviour of molecules having two chromophores separated by three atoms allowed for **1** no sound judgment since both head-to-head (*e.g.* **1** → **2**) and head-to-tail (*e.g.* **1** → **3**) modes of intramolecular [2+2]-cycloadditions are well known [7][4]).

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[1]) Synthesis and Reactivity of Compounds with Cyclobutane Ring(s), Part 18. For Part 17, see [1]. For preliminary communication, see [2].

[2]) For an excellent introduction to the terminology of photochemical cycloaddition reactions, see *Turro* [4].

[3]) Compound **2c** is very active against the grey mould fungus, *Botrytis cinerea*, on grapes [6].

[4]) In addition, the results of γ-ray-initiated cyclopolymerization of dimethacrylimides indicate a considerable influence of the *N*-substituent on the proportion of the five-membered *vs.* six-membered cyclic structural units in the cyclopolymers [8].

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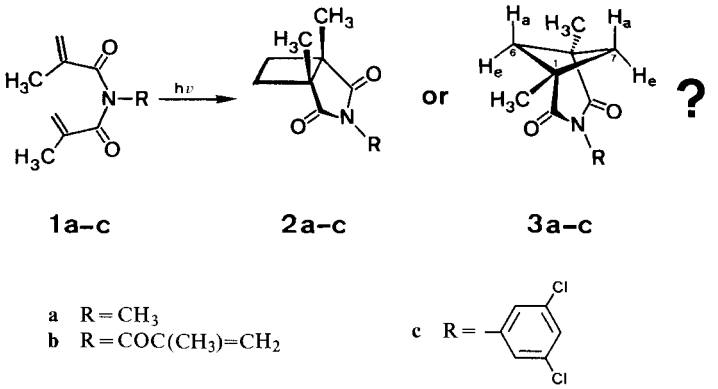
Scheme 1



We now report convincing chemical and spectroscopic evidence that both, the unsensitized as well as the triplet-sensitized intramolecular [2+2]-photocycloaddition of the *N*-substituted dimethacrylimides **1a** and **1c** proceed highly regioselectively yielding the head-to-tail 'cross' adducts **3a** and **3c**, respectively.

Direct irradiation. – *N*-Methyl-dimethacrylimide (**1a**) was irradiated in acetonitrile using a quartz-jacketed low-pressure mercury lamp ($\lambda = 254$ nm). After 3 h (conversion of **1a**: $\approx 90\%$)[5]), chromatography on silica gel gave 1,3,5-trimethyl-3-azabicyclo[3.1.1]heptane-2,4-dione (**3a**) as major product (66%) and 7% of the [3.2.0]bicyclic imide **2a**, which was erroneously reported [3] to be the *only* product (66%) formed in the photolysis of **1a** *(Table)*.

In order to examine the photostability of **2a** and **3a** (at $\lambda = 254$ nm), each of them was irradiated in (D_3)acetonitrile using a quartz NMR. tube. The course of the reaction was monitored by ^{1}H-NMR. spectroscopy. Whereas, even after 17 h, the minor product **2a** showed no change, slow formation of the N-formyl-amide **4** (12%) and the amide **5** (10%) was observed during irradiation (for 18 h) of the major isomer **3a**. Subsequently, both cyclobutenes **4** and **5**[6]) were isolated and characterized from a preparative photolysis of **3a** in acetonitrile.

Table. *Results of photochemical experiments with* **1a** *and* **1c**

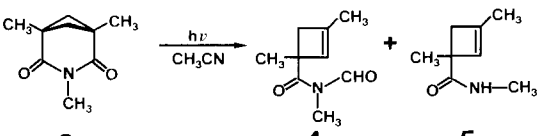
Compound	Irradiation conditions[a])	Conversion (%)	Yield (%) of **3**[b])	Yield (%) of **2**[b])
1a	$\lambda = 254$ nm, acetonitrile	90	66 (73)	7 (8)
1c	$\lambda = 254$ nm, acetonitrile	52	37 (73)	–[c])
1a	$\lambda \geq 290$ nm, CH_2Cl_2, benzophenone	98	71 (72)	10 (10)
1c	$\lambda \geq 290$ nm, CH_2Cl_2, benzophenone	100	60	–[c])

[a]) For details see *Exper. Part.* [b]) Absolute yield of isolated product, in parenthesis yield based on converted **1**. [c]) No **3c** could be detected in the reaction mixture by ^{1}H-NMR. spectroscopy.

[5]) Analogous reaction conditions as reported in the paper of *Maruyama & Ishitoku* [3].

[6]) The authors are grateful to Dr. *T. Winkler* for the measurement and interpretation of the NMR. spectra of compound **5** *(cf. Exper. Part)*.

Scheme 2



3a **4** **5**

In a complementary experiment, a (D_3)acetonitrile solution of *N*-methyl-dimethylacrylimide (**1a**) was irradiated in a NMR. tube using a *Pyrex*-jacketed high-pressure mercury lamp ($\lambda > 290$ nm). Fast conversion of **1a** to the [3.1.1]bicyclic imide **3a** occurred, and as expected[7]), no further reaction, *e.g.* to **4** or **5**, was observed.

Irradiation of *N*-(3,5-dichlorophenyl)dimethacrylimide (**1c**) in acetonitrile ($\lambda = 254$ nm) showed a much slower conversion of starting material than that observed in the case of the *N*-methyl-imide **1a**. The photolysis was discontinued after 5 h and the reaction mixture separated on silica gel. In addition to 48% of the starting material, *N*-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.1]heptane-2,4-dione (**3c**) was obtained in 37% yield as the only isolable regioisomer.

Triplet photosensitization. – A dichloromethane solution of **1a** was irradiated using a *Pyrex*-jacketed high-pressure mercury lamp ($\lambda > 290$ nm) and benzophenone (4 mol %) as a triplet sensitizer. After 98% conversion of starting material 71% of the [3.1.1]bicyclic imide **3a** and 10% of its [3.2.0]isomer **2a** were obtained. Analogous irradiation of *N*-(3,5-dichlorophenyl)dimethacrylimide **1c** gave 60% **3c** *(Table).*

Structure of photoproducts and discussion. – To elucidate the structures of the two bicyclic isomers **2a** and **3a**, as well as **2c** and **3c**, the spectroscopic evidence is discussed in terms of a comparison of the ^{1}H-NMR. spectra[8]) of **2c** and **3c**. Focusing on the hydrogen signals of the cyclobutane moiety, both compounds show an *AA'BB'*-system[9]) for the four H-atoms in question. The geminal and vicinal coupling constants in compound **2c** do not differ from the value expected for [n.2.0]bicyclic systems [10]. In the case of **3c**, the long-range coupling constants between both diaxial hydrogens H_a–C(6) and H_a–C(7) ($^4J(a,a) \approx 0$ Hz) as well as the diequatorial H-atoms H_e–C(6) and H_e–C(7) ($^4J(e,e) = 8$ Hz) are in agreement with the structure of a [3.1.1]bicyclic system containing a conformationally rigid puckered cyclobutane ring [11]. Further evidence for structural assignments was gained from the ^{13}C-NMR. spectra[8]) of **2c** and **3c**. Because of the considerable β-influence of the two angular methyl groups in compound **3c** the triplet of the two methylene C-atoms is shifted downfield to 45.4 ppm, whereas the corresponding signal for the [3.2.0]-isomer **2c** appears at 28.5 ppm.

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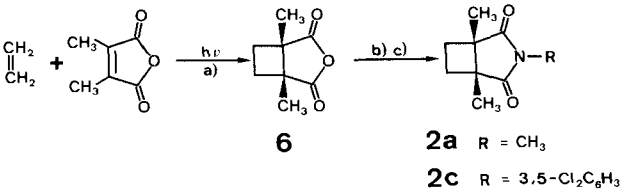
[7]) The UV. spectrum of bicyclic imide **3a** shows no absorption above $\lambda > 290$ nm.

[8]) The authors wish to thank Dr. *H. Sauter* for the measurement and interpretation of the NMR. spectra.

[9]) The ^{1}H-NMR. spectra of **2c** and **3c** were simulated by a computer-assisted analysis [9] and the calculated values of the coupling constants as well as the chemical shifts are in agreement with those obtained experimentally. We are grateful to Prof. *P. Diel* (University of Basel) for performing this spectral analysis.

Scheme 3



6 **2a** R = CH_3

2c R = 3,5-$Cl_2C_6H_3$

[a]) $(C_6H_5)_2CO$ (4.5 mol %)/CH_2Cl_2, −65°; light source: HPK-125 [6].
[b]) CH_3NH_2/hexane (for **2a**) or 3,5-dichloroaniline/Et_2O (for **2c**).
[c]) Acetic anhydride, reflux.

Unequivocal structural proof for the two isomeric cyclobutane structures in question, **2** *vs.* **3**, was furnished by simple chemical means. Thus, *cis*-1,2-dimethylcyclobutane-1,2-dicarboxylic anhydride (**6**) [12] was prepared by [2+2]-photocycloaddition of ethylene to dimethylmaleic anhydride in 52% yield [6] *(Scheme 3)*. The anhydride **6** was converted to the *N*-methyl-imide **2a**, which was identical (m.p., IR., ^{1}H- and ^{13}C-NMR.) with compound **2a**, isolated as the minor isomer from irradiation experiments with **1a**. On the other hand, **2a** and **2c** (prepared similarly from **6**, see *Scheme 3*) were in every respect different from the major products originating from the irradiation of **1a** and **1c**, *i.e.* **3a** and **3c**. Furthermore, alkaline hydrolysis of the [3.1.1]bicyclic imide **3c** yielded *cis*-1,3-dimethylcyclobutane-1,3-dicarboxylic acid **7**, m.p. 156–157° ([5]: m.p. 158–159.5°)[10]), which was converted to its anhydride **8**, m.p. 200–201° ([5]: m.p. 200–200.5°).

With these results in hand we believe to have accumulated conclusive evidence that the *N*-substituted dimethacrylimides **1a** and **1c** undergo preferentially[11]) head-to-tail intramolecular [2+2]-photocycloaddition[12]), as was correctly reported for **1b** [5]. Consequently, *Maruyama's & Ishitoku's* isolation [3] of *N*-substituted *cis*-1,5-dimethyl-3-azabicyclo[3.2.0]heptane-2,4-diones **2a** and **2b**, respectively, as the sole products from UV. irradiation of **1a** and **1b**, respectively, *must be in error*. Comparing the spectroscopic data published by these authors for the supposed compound **2a** with our spectra of **2a** and **3a**, we find perfect agreement of these data with those obtained for the [3.1.1]-bicyclic isomer **3a**. Furthermore, the recently reported photocleavage of the imide **2a** ($\lambda = 254$ nm) by the same authors [15] must seriously be questioned in view of the demonstrated photostability of **2a**[13]).

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[10]) This m.p. is different from the reported [13] m.p. of either of the two isomeric dicarboxylic acids considered to be *cis*- (m.p. 134–135°) and *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid (m.p. 237–238°).

[11]) We found, however, that the regiochemistry of this intramolecular [2+2]-photocycloaddition depends also on the substitution pattern of the acrylic double bonds [14].

[12]) Intramolecular *thermal* [2+2]-cycloaddition of **1c** also leads to the head-to-tail cycloadduct **3c**, but in a lower yield [14].

[13]) Considering the earlier reported confusion [3] of the said bicyclic isomers (**2a** and **3a**, resp.) we have reason to believe that the authors were actually describing the UV. irradiation of the imide **3a** and not of **2a**. Consequently, the structures reported for the two products from this photolysis [15] are doubtful and we presume that the cyclobutenes **4** and **5** we found upon irradiation of **3a** *(Scheme 2)* also represent the correct structures for the two photoproducts in question (our compound **5** possesses identical ^{1}H-NMR. data with one of the photoproducts reported in [15]).

On the basis of our results, we can conclude that in the case of *N*-substituted dimethacryl imides **1** the formation of intramolecular head-to-tail cycloadducts is the preferred reaction path regardless of irradiation conditions. Furthermore, the identical results of either triplet photosensitization of irradiation of **1a** with light of $\lambda > 290$ nm (n,π^*-excitation) indicates that the observed photocycloaddition involves the lowest-lying excited triplet state of the unsaturated imide chromophor of **1a**.

The authors are indebted to Mr. *E. Christen* for his skillful assistance in the laboratory and to our colleagues in the Physical and Analytical Departments for performing the spectral and elemental analyses.

Experimental Part

General remarks. Unless otherwise noted, materials and solvents were obtained from commercial suppliers and were used without further purification. UV. irradiations were performed at room temperature in a double wall immersion apparatus from either *Pyrex* or quartz using either a *Philips 125 HPK* high-pressure mercury lamp or a low-pressure *TNM 15/32* mercury lamp (*Quarzlampen GmbH*, Hanau). Thin layer chromatography (TLC.) was done with precoated silica gel plates (silica gel 60 F_{254}, *Merck*). For column chromatography *Merck silica gel 60* (70–230 mesh ASTM) was used and flash-chromatography (following the method described by *W. C. Still et al.* [16]) was performed with *Merck silica gel 60* (230–400 mesh ASTM). Physical constants and spectra were determined using the instrumentation indicated. UV. spectra (λ [nm]): *Varian Cary 118.* Melting points (m.p.): *Tottoli* capillary melting point apparatus (uncorrected). IR. spectra ($\tilde{\nu}$ [cm^{-1}]; in $CHCl_3$ unless otherwise noted): *Perkin-Elmer IR 157* or *IR 298*; absorptions were designed as strong (*s*), medium (*m*), weak (*w*), shoulder (*S*), or broad (br.). ^{1}H-NMR. and ^{13}C-NMR. spectra (δ [ppm] relative to internal TMS; in $CDCl_3$ unless otherwise noted; multiplicity: *s* = singlet, *d* = doublet, *d* × *d* = doublet of doublets, *t* = triplet, *qa* = quartet, *m* = multiplet, br. = broad; *J* [Hz] = apparent coupling constant); *Varian T 60, Varian HA 100* or *Varian HR 220* spectrometer (for ^{1}H-NMR.) and *Varian XL 100* (for ^{13}C-NMR.). Mass spectra (MS.) (tabulated as *m/z*, relative intensities in parentheses): *Varian CH-7 MAT* and *CEC 21/100*, at 70 eV.

1. Preparation of starting materials. – 1.1 *Preparation of* N-*methyldimethacrylimide* (**1a**) [17]. Following a procedure developed by *Butler & Myers* [8]. Yield: 11%; m.p. 89–90° (m.p. 90.5–91.5° [17]).

1.2. *Preparation of* N-*(3,5-dichlorophenyl)dimethacrylimide* (**1c**). In an analogous procedure described for the preparation of *N*-phenyl-dimethacrylimide [8]. To a stirred suspension of 5.0 g of a 50% dispersion of NaH in mineral oil and 35 ml dry THF a solution of 23.0 g (0.10 mol) of *N*-(3,5-dichlorophenyl)methacrylamide[14]) in 40 ml dry THF was added over a 3 h period. The resulting suspension of the sodium salt of the amide was transferred into an addition funnel and slowly added to a solution of 12.4 g (0.12 mol) of methacryloyl chloride in 50 ml of dry THF, keeping the temp. between 20 and 25°. The mixture was stirred for an additional hour, then 400 ml of hexane was added, the solid filtered off, and the solvent evaporated. The residue was recrystallized twice from hexane yielding 17.4 g (58%) of **1c**, m.p. 91.5–93.5°. – IR.: 3085*w*, 3020*w*, 2990*w*, 2960*w*, 2925*w*, 1715*m S*, 1695*m S*, 1680*s*, 1635*m*, 1590*m*, 1575*s*, 1450*m*, 1435*m*, 1415*w S*, 1380*w*, 1350*m*, 1325*w S*, 1305*m*, 1270*w*, 1165*s*, 1110*w*, 1095*w S*, 1045*w*, 1020*w*, 980*m*, 940*m*, 905*w*, 855*m*. – ^{1}H-NMR. (100 MHz): 1.94 (split *s*, 2 CH_3); 5.51 (br. *s*, 2 CH_2); 7.02 (*d*, *J* = 2, 2 arom. H); 7.31 (*t*, *J* = 2, 1 arom. H). – MS. (30°): 297 (2, M^+: ^{35}Cl), 212 (10), *69* (100), 41 (60).

$C_{14}H_{13}Cl_2NO_2$	Calc.	C 56.40	H 4.40	Cl 23.78	N 4.70%
(298.17)	Found	„ 56.42	„ 4.42	„ 24.06	„ 4.77%

2. Photolysis experiments. – 2.1. *Irradiation of* **1a** *in acetonitrile at* $\lambda = 254$ *nm.* A solution of 1.3 g (7.8 mmol) of **1a** in 130 ml acetonitrile was irradiated using a quartz-jacketed low-pressure Hg-lamp

[14]) This intermediate (m.p. 108–109°) was prepared from methacryloyl chloride and 3,5-dichloroaniline following a procedure described by *Butler & Myers* [8] for *N*-phenylmethacrylamide.

(90% conversion of **1a**). Chromatography (SiO_2, hexane/ether 4:1) gave pure fractions of 90 mg (7%) **2a** (distilled) and 860 mg (66%) **3a** (recrystallized from hexane/ether).

Data of 1,3,5-trimethyl-3-azabicyclo[3.1.1]heptane-2,4-dione (**3a**). M.p. 95–96°. – IR.: 3020*w*, 2975*w*, 2935*w*, 2875*w*, 1740*m*, 1680*s*, 1745*m*, 1450*w*, 1425*w*, 1370*m*, 1355*w*, 1345*m*, 1290*w*, 1270*w*, 1245*w*, 1055*m*, 1010*m*. – ^{1}H-NMR. (250 MHz): 1.34 (*s*, 6 H, H_3C–C(1) and H_3C–C(5)); 2.01–2.11 and 2.34–2.43 (*AA'BB'*-system, 4 H, 2 H–C(6) and 2 H–C(7)); 3.12 (*s*, 3 H, H_3C–N). – MS. (140°): 167 (66, M^+), 152 (12), 139 (45), 131 (15), 127 (13), 126 (45), 124 (23), 121 (15), *69* (100).

$C_9H_{13}NO_2$ (167.21) Calc. C 64.65 H 7.84 N 8.38% Found C 64.45 H 7.81 N 8.38%

Data of 1,3,5-trimethyl-3-azabicyclo[3.2.0]heptane-2,4-dione (**2a**). B.p. 60°/0.15 Torr. – IR.: 3030*w S*, 3020*w*, 2980*w*, 2960*w*, 2940*w S*, 2875*w*, 1775*w*, 1700*s*, 1465*m*, 1435*m*, 1390*m*, 1380*m*, 1335*m*, 1270*w*, 1105*w*, 1050*m*, 1015*w*. – ^{1}H-NMR. (250 MHz): 1.28 (*s*, 6 H, H_3C–C(1) and H_3C–C(5)); 2.04–2.25 (*AA'BB'*-system, 4 H, 2 H–C(6) and 2 H–C(7)); 3.03 (*s*, 3 H, H_3C–N). – MS. (70°): 168 (11), 167 (92, M^+), 139 (96), 111 (10), 110 (13), *82* (100), 69 (30), 67 (45).

$C_9H_{13}NO_2$ (167.21) Calc. C 64.65 H 7.84 N 8.38% Found C 64.29 H 7.85 N 8.21%

2.2. *Triplet sensitization of* **1a** *with benzophenone at* $\lambda \geq 290$ *nm.* A solution of 1.25 g (7.5 mmol) of **1a**, 54 mg (4 mol %) of benzophenone and 25 mg of 2,6-di(*t*-butyl)-4-methylphenol in 125 ml CH_2Cl_2 was irradiated using a *Pyrex*-jacketed high-pressure Hg-lamp (98% conversion of **1a**). Chromatography (SiO_2, hexane/ether 4:1) afforded 127 mg (10%) **2a** and 890 mg (71%) **3a**.

2.3. *Irradiation of* **1a** *at* $\lambda \geq 290$ *nm in (D$_3$)acetonitrile or (D$_6$)acetone, respectively.* The solution of 50 mg (0.3 mmol) of **1a** in 0.5 ml (D_3)acetonitrile or in 0.5 ml (D_6)acetone, respectively, were irradiated in a NMR. tube using a *Pyrex*-jacketed high-pressure Hg-lamp, and the course of the photolysis was monitored by ^{1}H-NMR. In both solvents, upon irradiation of 1 h complete conversion of **1a** to **3a** was observed.

2.4. *Irradiation of* **2a** *at* $\lambda = 254$ *nm.* The solution of 50 mg (0.3 mmol) of **2a** in 0.5 ml (D_3)acetonitrile were irradiated in a quartz NMR. tube using a quartz-jacketed low-pressure Hg-lamp, and the course of the photolysis was monitored by ^{1}H-NMR. No conversion of **2a** was found after 18 h of irradiation.

2.5. *Irradiation of* **3a** *at* $\lambda = 254$ *nm.* The solution of 1.0 g (6.0 mmol) of **3a** in 120 ml of acetonitrile was irradiated using a quartz-jacketed low-pressure Hg lamp (80% conversion of **3a**). Flash-chromatography (SiO_2, hexane/ether 2:1, then ether, and finally ether/CH_2Cl_2 4:1) afforded pure fractions of 131 mg (13%) **4** (distilled), 198 mg (20%) **3a** and 350 mg (42%) **5** (distilled).

*Data of 1,3-dimethyl-*N*-formyl-*N*-methyl-2-cyclobutenecarboxamide* (**4**). B.p. 65–70°/0.05 Torr. – IR. (liq.): 2980*w*, 2940*w S*, 1735*m*, 1680*s*, 1460*w*, 1420*w*, 1380*w*, 1345*m*, 1300*s*, 1280*m S*, 1250*w*, 1200*w*, 1115*w*, 1060*s*, 970*w*, 860*w*, 805*w*, 780*w*, 755*w*. – ^{1}H-NMR. (250 MHz): 1.37 (*s*, H_3C–C(1)); 1.74 (split *s*, H_3C–C(3)); 2.47 (split *AB*-system, *J(AB)* = 13, H–C(4)); 2.98 (br. *AB*-system, *J(AB)* = 13, H–C(4)); 3.11 (*s*, H_3C–N); 5.96 (*m*, H–C(2)); 9.14 (*s*, HCO–N). – MS. (20°): 167 (20, M^+), 139 (15), 138 (58), 126 (27), 124 (39), 110 (19), 109 (28), 108 (44), 96 (33), 82 (21), 81 (71), 80 (52), *79* (100), 77 (22), 67 (32), 65 (17), 60 (18), 58 (13), 55 (14), 53 (47).

$C_9H_{13}NO_2$ (167.21) Calc. C 64.65 H 7.84 N 8.38% Found C 64.81 H 7.82 N 8.04%

*Data of 1,3-dimethyl-*N*-methyl-2-cyclobutenecarboxamide* (**5**). B.p. 55–60°/0.005 Torr. – IR. (liq.): 3330*m*, 3035*w*, 2935*m*, 1655*s*, 1545*s*, 1450*m*, 1420*m*, 1375*w*, 1310*w* br., 1280*m*, 1250*w*, 1195*m*, 1160*m*, 1040*w*, 990*w*, 955*w*, 880*w* br., 815*m*. – ^{1}H-NMR. (250 MHz): 1.43 (*s*, H_3C–C(1)); 1.78 (*m*, H_3C–C(3)); 2.31 (split *AB*-system, *J* = 13, H–C(4)); 2.60 (br. *AB*-system, *J* = 13, H–C(4)); 2.79 (*d*, *J* = 5, 3 H, H_3C–N); 5.82 (*m*, H–C(2)); 5.8–5.95 (br., H–N). – ^{13}C-NMR.: 17.0 (*qa*, H_3C–C(3)); 21.7 (*qa*, H_3C–C(1)); 26.3 (*qa*, H_3C–N); 45.7 (*t*, split as *m*, ^3J(C(4),H(2)) = 11.5, C(4)); 132.0 (*d*, split as *m*, C(2)); 48.2 (*s*, C(1)); 149.3 (*s*, split as *qa*, C(3)); 177.0 (*s*, C=O). – MS. (20°): 139 (71, M^+), 138 (56), 124 (49), 122 (23), 110 (23), 109 (28), 108 (12), 97 (11), 96 (82), 82 (27), 81 (84), 80 (24), *79* (100), 77 (20), 71 (34), 67 (24), 66 (12), 65 (18), 58 (58), 56 (26), 55 (16), 53 (58).

2.6. *Irradiation of* **3a** *at* $\lambda \geq 290$ *nm.* Irradiation of a solution of 50 mg of **3a** in 0.5 ml CD_3CN in a NMR. tube using a *Pyrex*-jacketed high-pressure Hg-lamp showed no conversion of **3a**.

2.7. *Irradiation of* **1c** *in acetonitrile at* $\lambda = 254$ *nm.* The solution of 1.4 g (4.7 mmol) of **1c** in 135 ml acetonitrile was irradiated using a quartz-jacketed low-pressure Hg-lamp (5 h; 52% conversion of **1c**). Flash-chromatography (SiO_2, hexane/ether 4:1) afforded 0.67 g (48%) of **1c** and 0.52 g (37%) of

3-(3',5'-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.1]heptane-2,4-dione (**3c**), m.p. 173.5–175°. – IR.: 3080*w*, 3020*w*, 2975*w*, 2945*w S*, 2930*w*, 2870*w*, 1755*m*, 1730*w S*, 1710*s*, 1700*s S*, 1630*w*, 1590*m*, 1580*m*, 1470*w*, 1450*w*, 1435*m*, 1405*w*, 1385*w*, 1360*m*, 1330*w*, 1300*w*, 1170*s*, 1120*m*, 1100*w*, 1010*w*, 980*w*, 955*m*, 855*m*, 835*w*. – ^{1}H-NMR. (250 MHz): 1.40 (*s*, H_3C–C(1) and H_3C–C(5)); 2.16–2.25 (*AA'BB'*-system, J(a,e) = 9.5[9]), H_a–C(6), H_a–C(7)); 2.52–2.62 (*AA'BB'*-system, J(a,e) = 9.5, ^4J(e,e) = 8[9]), H_e–C(6), H_e–C(7)); 7.10 (*d*, J = 2, 2 arom. H); 7.40 (*t*, J = 2, 1 arom. H). – ^{13}C-NMR.: 19.4 (2 *qa*, H_3C–C(1), H_3C–C(5)); 45.4 (2 *t*, C(6) and C(7)); 127.5 (2 *d*, 2 arom. C); 128.7 (*d*, 1 arom. C); 43.3 (2 *s*, C(1) and C(6)); 135.0 (2 *s*, 2 arom. C); 135.6 (*s*, 1 arom. C); 177.0 (2 *s*, C(2) and C(4)). – MS. (55°): 301 (13), 300 (10), 299 (69), 298 (20), *297* (100, M^+: ^{35}Cl), 270 (16), 269 (13), 268 (19), 256 (18), 254 (18), 240 (12), 238 (13), 226 (14), 188 (13), 186 (20), 163 (13), 161 (17), 110 (13), 109 (55), 108 (40), 95 (20), 82 (81), 81 (82), 79 (20), 69 (47), 67 (84), 55 (12), 53 (17), 41 (80).

$C_{14}H_{13}Cl_2NO_2$	Calc.	C 56.40	H 4.40	Cl 23.78	N 4.70%
(298.17)	Found	„ 56.42	„ 4.41	„ 23.82	„ 4.75%

2.8. *Triplet sensitization of* **1c** *with benzophenone at* $\lambda \geq 290$ *nm.* The solution of 2.0 g (6.7 mmol) of **1c**, 0.1 g of benzophenone, 50 mg of 2,6-di(*t*-butyl)-4-methylphenol in 300 ml CH_2Cl_2 was irradiated using a *Pyrex*-jacketed high-pressure Hg-lamp (100% conversion of **1c**). After removal of solvent 1.2 g (60%) of **3c** was obtained by recrystallization (CH_2Cl_2/hexane). In the ^{1}H-NMR. spectrum of the crude reaction mixture no **2c** could be detected.

3. Additional experiments. – 3.1. *Preparation of* **2a** *from* cis-*1,2-dimethylcyclobutane-1,2-dicarboxylic anhydride* (**6**) [6] [12]. Into the solution of 1.0 g (6.5 mmol) of **6** in 50 ml hexane methylamine was introduced during ½ h. The precipitation formed was filtered off, washed with hexane and solved in 20 ml of acetic anhydride. The mixture was heated (reflux) for 4 h, then evaporated and chromatographed on silica gel (toluene/ethyl acetate 9:1). Distillation of the oil at 60°/0.15 Torr afforded 0.5 g (46%) of **2a**.

3.2. *Preparation of* **2c** *from* cis-*1,2-dimethylcyclobutane-1,2-dicarboxylic anhydride* (**6**). In an analogous manner as described in *3.1* a solution of 4.62 g (30 mmol) anhydride **6** and 4.86 g (30 mmol) 3,5-dichloroaniline in 100 ml dry ether (reflux) afforded 7.52 g (84%) of *3-(3',5'-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.2.0]heptane-2,4-dione* (**2c**), m.p. 153–155°. – IR.: 3090*w*, 3030*w*, 2980*w*, 2955*w*, 2940*w*, 2875*w*, 1780*w*, 1720*s S*, 1710*s*, 1590*m*, 1580*m*, 1460*w S*, 1445*m*, 1405*w*, 1385*m*, 1365*m*, 1320*w*, 1275*w*, 1170*m*, 1140*m*, 1105*m*, 1095*w S*, 970*w*, 955*w*, 900*w*, 885*w*, 860*m*. – ^{1}H-NMR. (250 MHz): 1.39 (*s*, H_3C–C(1), H_3C–C(5)); 2.13–2.43 (*AA'BB'*-system, J(gem) = 12.8, J(*trans*) = 6.6, J(*cis*) = 9.7 and 10.5, resp.[9]), 2 H–C(6) and 2 H–C(7)); 7.32 (*d*, J = 2, 2 arom. H); 7.40 (*t*, J = 2, 1 arom. H). – ^{13}C-NMR.: 15.8 (2 *qa*, H_3C–*C*(1) and H_3C–C(5)); 28.5 (2 *t*, C(6) and C(7)); 124.9 (2 *d*, 2 arom. C); 128.4 (*d*, 1 arom. C); 46.1 (2 *s*, C(1) and C(5)); 134.1 (*s*, 1 arom. C); 135.1 (2 *s*, 2 arom. C); 180.3 (2 *s*, C(2) and C(4)). – MS. (50°): 299 (27), 297 (43, M^+: ^{35}Cl), 271 (14), 269 (21), 124 (10), *82* (100), 69 (23), 67 (44), 54 (17), 53 (12), 41 (37).

$C_{14}H_{13}Cl_2NO_2$	Calc.	C 56.40	H 4.40	Cl 23.78	N 4.70%
(298.17)	Found	„ 56.50	„ 4.39	„ 23.87	„ 4.67%

3.3. *Alkaline hydrolysis of* **3a**. The solution of 1.0 g (3.35 mmol) of **3a** and 0.7 g KOH in 15 ml ethanol was heated under reflux during 24 h. After evaporation of the solvent the residue was dissolved in water and washed twice with ether. Addition of 2 N HCl, extraction with ether and evaporation gave 0.6 g (78%) of *cis*-1,3-dimethylcyclobutane-1,3-dicarboxylic acid [5] (recrystallized from ether/hexane, m.p. 156–157°). The diacid was dissolved in 10 ml acetylchlorid and stirred for 1 h at 60°. Evaporation of solvent and recrystallization of the residue from ether/hexane afforded 1,3-dimethylcyclobutane-*cis*-1,3-dicarboxylic anhydride, m.p. 200–201° ([5]: m.p. 200–200.5°).

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