Light-Induced Cycloaddition of 2,3-Dihydro-2,2-dimethyl-4*H*-thiopyran-4-one (a 4-Thiacyclohex-2-enone) to Alkenes and Dienes

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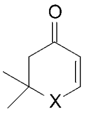
Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The reactivity of (thiacyclic)-2,3-dihydro-2,2-dimethyl-4*H*-thiopyran-4-one (**1a**) in light-induced cycloadditions to furan (**F**), acrylonitrile (**AN**), or 2,3-dimethylbut-2-ene (**TME**) is compared to that of (carbocyclic) 5,5-dimethylcyclohex-2-enone (**1b**). Whereas for the more-flexible thiacycle, the efficiency of [2+2]-photocycloadduct formation with **AN** or **TME** is generally much lower, the diastereoselectivity regarding the ring fusion in the bicyclo[4.2.0]octanes is quite similar for both enones. In contrast, **1a** affords exclusively *trans*-fused [4+2] cycloadducts with **F**, while **1b** gives predominantly the corresponding *cis*-fused products.

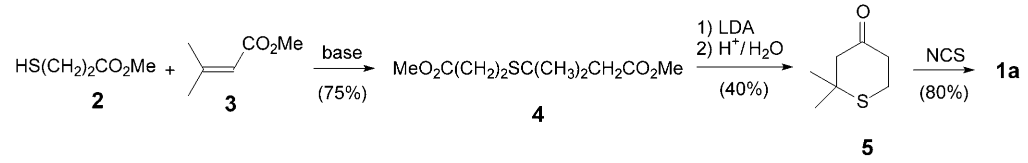
1. Introduction. – In the preparative application of photocycloadditions of cyclic enones to alkenes, two factors concerning product formation are of decisive relevance, namely the (overall) rate of conversion and the selectivity [1]. Unsaturated cyclic carbonyl compounds containing one S-atom in the ring represent attractive model compounds for such studies [2]. Some time ago, we have reported preliminary results on light-induced reactions of 2,3-dihydro-2,2-dimethyl-4*H*-thiopyran-4-one (=2,2-dimethyl-2,3-dihydrothiin-4-one; **1a**) [3]. On irradiation in MeOH, a mixture of 5- and 6-methoxy-substituted tetrahydro-2,2-dimethyl-4*H*-thiopyran-4-ones (=2,2-dimethylthian-4-ones) was obtained, while in the presence of furan (**F**), [4+2] cycloadducts were formed predominantly. Unfortunately at that time, the synthesis of the (saturated) precursor of **1a** required the use of large amounts of H_2S and therefore, we were unable to go more deeply into these investigations. In the meantime, we have developed a new H_2S-free synthetic approach to this same precursor **5**. In this paper, we supply a full account of the outcome of light-induced reactions of **1a** with furan (**F**), acrylonitrile (**AN**), and 2,3-dimethylbut-2-ene (**TME**) and also a comparative study of these same reactions for the corresponding carbocyclic enone **1b**.



1a X = S
b X = CH_2

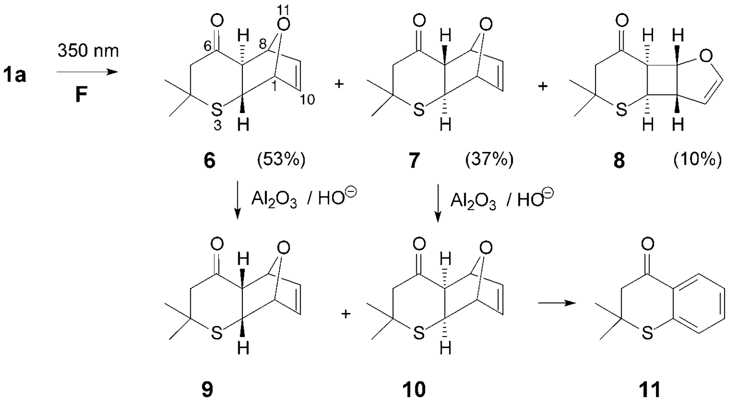
2. Results. – *Synthesis of* **1a**,**b**. The new synthetic approach to **1a** involves a *Michael* addition of methyl 3-mercaptopropanoate (**2**) to methyl 3-methylbut-2-enoate (**3**) affording diester **4**, followed by *Dieckmann* cyclization in the presence of lithium diisopropylamide (LDA) and subsequent saponification and decarboxylation to give tetrahydro-2,2-dimethyl-4*H*-thiopyran-4-one (**5**) (*Scheme 1*). The dehydrogenation of **5** to **1a** was performed with *N*-chlorosuccinimide (NCS) as already described [3]. The 5,5-dimethylcyclohex-2-enone (**1b**) was synthesized according to a published procedure [4].

Scheme 1



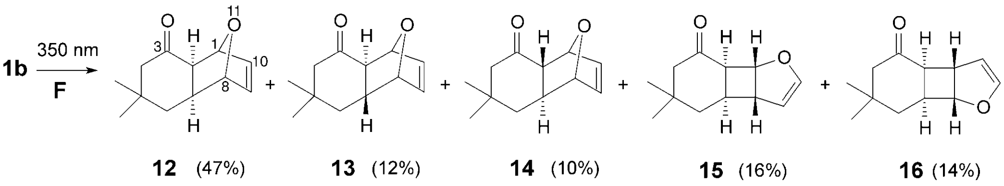
Photocycloadditions to Furan (**F**). Irradiation (λ 350 nm) of **1a** in a 1 : 1 mixture of **F** and MeCN afforded a 5 : 4 : 1 mixture (^{1}H-NMR) of cycloadducts **6**, **7**, and **8** (*Scheme 2*). Both the constitution and the configuration of the ring junction of the (minor) [2 + 2] photocycloadduct **8** were wrongly assigned in the preliminary communication [3]. Treatment of a mixture **6**/**7** with basic alumina for a short period leads to quantitative conversion to *cis*-fused cycloadducts **9** and **10**, respectively. On prolonged reaction, both compounds were converted to the formal dehydration product **11**. On heating (in the GC analyses) as well as in the presence of weak acids, *e.g.*, on contact with SiO_2 or in $CDCl_3$ solution, all these [4 + 2] cycloadducts undergo easily *retro-Diels–Alder* reactions.

Scheme 2



Similarly, irradiation of **1b** under these conditions gave the *cis*-fused [4 + 2] cycloadduct **12** as main product in addition to the *trans*-fused [4 + 2] cycloadducts **13** and **14**, and the [2 + 2] cycloadducts **15** and **16** (product distribution from ^{1}H-NMR) (*Scheme 3*). The overall rate of product formation was *ca.* 8 times faster for **1b** than for **1a**. Here again, the [4 + 2] cycloadducts **12**–**14** undergo both thermal and acid-catalyzed *retro-Diels–Alder* reactions.

Scheme 3



The differentiation between 11-oxa-3-thiatricyclo[6.2.1.0^{2,7}]undec-9-en-6-ones **6** and **7**, and **9** and **10**, respectively, as well as that between 11-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-ones **12**–**14** is straightforward from their ^{1}H-NMR spectra from the fact that in trinorbornene (or oxabicycloheptene) derivatives, *endo*-H-atoms resonate upfield by *ca.* 0.5 ppm compared to *exo*-H-atoms [5]. Selected NMR data of these [4 + 2] cycloadducts is summarized in *Tables 1* and *2*.

Table 1. *Selected NMR Data of [4 + 2] Photocycloadducts* **6**, **7**, **9** *and* **10**. Chemical shifts δ in ppm, coupling constants J in Hz. For numbering, see *Scheme 2*.

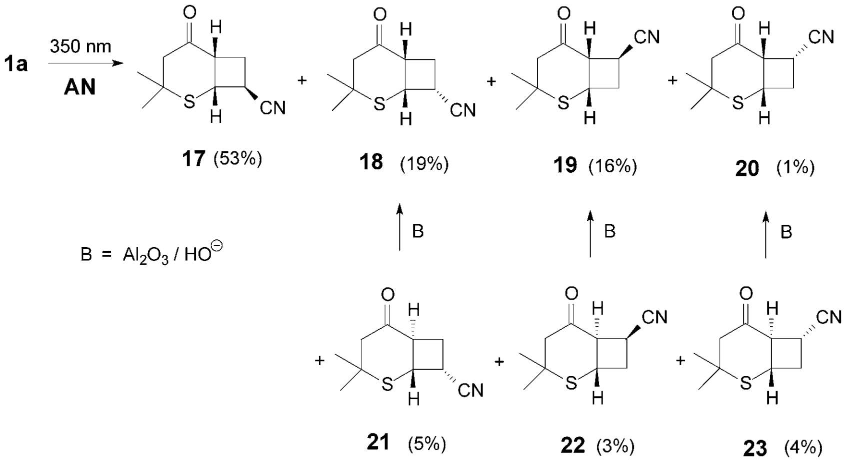
	6		**7**		**9**		**10**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	5.17 (J = 1.5, 3.5)	81.1	4.92 (br. *s*)	80.2	5.12 (J = 1.5, 4.3)	81.9	5.45 (br. *s*)	82.0
H–C(2)	3.28 (J = 3.5, 9.0)	45.1	2.77 (J = 8.9)	49.3	3.97 (J = 4.4, 8.8)	42.1	3.43 (J = 7.6)	43.1
C(4)		51.2		51.2		44.1		43.3
CH_2(5)	2.62, 2.52 (J = 14.2)	60.1	2.66, 2.42 (J = 14.2)	60.1	2.47, 2.35 (J = 17.5)	57.5	2.66, 2.47 (J = 16.4)	57.2
C(6)		205.3		205.9		210.1		209.3
H–C(7)	2.48 (J = 9.1)	63.1	3.20 (J = 2.7, 8.9)	61.2	3.01 (J = 4.9, 8.8)	50.2	2.33 (J = 7.6)	49.1
H–C(8)	5.12 (br. *s*)	75.2	5.11 (J = 1.5, 2.7)	80.0	5.33 (J = 1.5, 4.8)	81.1	4.81 (br. *s*)	83.9
H–C(9)	6.76 (J = 1.5, 5.6)	141.3	6.36 (J = 1.5, 5.6)	131.2	6.40 (J = 1.5, 5.6)	135.0	6.42 (J = 1.5, 5.6)	135.1
H–C(10)	6.22 (J = 1.5, 5.6)	130.2	6.61 (J = 1.5, 5.6)	140.1	6.40 (J = 1.5, 5.6)	135.1	6.48 (J = 1.5, 5.6)	135.0
Me	1.52, 1.45	31.9, 31.8	1.50, 1.41	31.9, 31.8	1.49, 1.29	32.0, 31.7	1.46, 1.39	31.7, 31.5

Photocycloadditions to Acrylonitrile (**AN**). On irradiation in benzene in the presence of a 20-fold molar excess of **AN**, **1a** afforded a mixture of seven [2 + 2] cycloadducts **17**–**23** of which **21**–**23** 'vanish' (established by ^{1}H-NMR) after treatment of the mixture with basic alumina (*Scheme 4*). The two main products **17** and **18** were isolated by chromatography, and their structure established by X-ray analysis (see *Exper. Part*). The other products were characterized after chromatography and isolation from the fractions where they show up in highest concentration, and in addition, by base-catalyzed interconversion of the *trans*- to the *cis*-fused cycloadducts.

Table 2. *Selected NMR Data* ($CDCl_3$) *of [4+2] Photocycloadducts* **12**–**14**. Chemical shifts δ in ppm, coupling constants *J* in Hz. For numbering, see *Scheme 3*.

	12		**13**		**14**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H−C(1)	4.86 (br. *s*)	83.1	5.00 (*J* = 1.5, 3.0)	75.1	4.98 (*J* = 1.5, 2.7)	79.1
H−C(2)	2.17 (*J* = 8.2)	45.1	1.92 (*J* = 2.9, 10.0)	59.9	2.55 (*J* = 2.7, 10.1)	58.1
C(3)		212.5		207.5		208.5
CH_2(4)	2.24, 2.07 (*J* = 17.5)	55.1	2.26, 2.16 (*J* = 14.3)	57.1	2.33, 2.08 (*J* = 14.3)	57.2
C(5)		32.1		39.5		39.1
H−C(6)	1.95, 1.31	42.2	1.80, 1.26	42.1	1.87, 1.83	43.0
H−C(7)	2.17 (*J* = 7.2, 8.2, 11.5)	36.1	2.15 (m)	50.1	1.65 (*J* = 3.3, 10.2, 12.0)	48.2
H−C(8)	5.16 (br. *s*)	82.2	4.97 (br. *s*)	81.1	4.68 (br. *s*)	80.3
H−C(9)	6.43 (*J* = 1.5, 5.6)	136.1	6.16 (*J* = 1.5, 5.6)	130.2	6.62 (*J* = 1.5, 5.6)	141.1
H−C(10)	6.36 (*J* = 1.5, 5.6)	135.0	6.68 (*J* = 1.5, 5.6)	141.1	6.28 (*J* = 1.5, 5.6)	130.3
Me	1.04, 0.97	31.2, 30.9	1.12, 0.98	31.9, 31.8	1.18, 1.11	32.0, 31.7

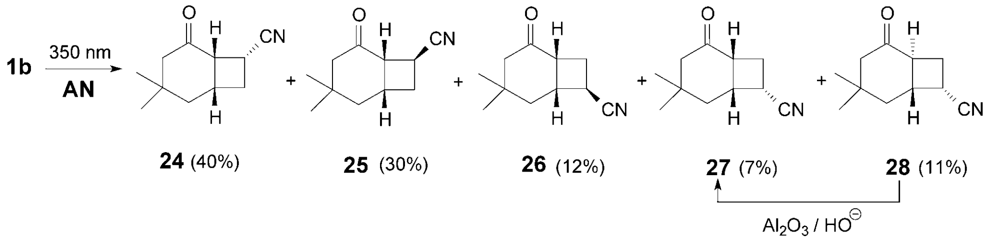
Scheme 4



As already described previously, **1b** under the same conditions gives **24** and **25** as main products and **26**–**28** as minor products, the two main products having been isolated by chromatography [6] (*Scheme 5*). As above, we have now identified the three minor components **26**–**28**, isolated from the corresponding fractions after chromatography and monitored the base-induced conversion of **28** to **27**. The overall rate of product formation is *ca.* 30 times faster for **1b** than for **1a**. The yield of the adduct formation in these reactions is slightly lower for **1a** (65–70%) than for **1b** (>95%).

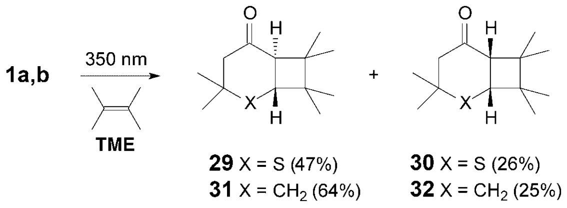
Photocycloadditions to 2,3-Dimethylbut-2-ene (**TME**). On irradiation in benzene in the presence of a 20-fold molar excess of **TME**, **1a** affords a 2:1 mixture of thiabicyclooctanones **29** and **30** (47% and 26% resp., by GC and ^{1}H-NMR) in addition to two minor (14% and 13%) not fully identified addition products originating *via* H-

Scheme 5



atom transfer from the intermediate diradical (*Scheme 6*). Similarly, **1b** gives a 2.5 : 1 mixture of bicyclooctanones **31** and **32** (64% and 25%), again in addition to two minor (6% and 4%) addition products [7]. In both reactions, the *trans*-fused [2 + 2] cycloadduct predominates. The overall rate of product formation here is *ca.* 120 times faster for **1b** than for **1a**. The yield of the adducts is much lower for **1a** (25 – 30%) than for **1b** (> 95%).

Scheme 6



3. Discussion. – Cyclooct-2-enone and cyclohept-2-enone undergo light-induced $(Z) \rightarrow (E)$ isomerization, this (intramolecular) reaction apparently occurring much faster than intermolecular processes, *e.g.*, [2 + 2] cycloaddition to alkenes [8]. In this context, oxathiinones and dihydrothiopyranones represent ideal model compounds for investigating the behavior of (photochemically generated) highly flexible cyclohex-2-enones due to the longer C–S bonds as compared to C–C bonds [9][10]. In this study, this fact is reflected by the results obtained from the determination of the relative rates of conversion of **1a** and **1b** to cycloadducts (*Table 3*), wherein the slowest reaction (**1a** + **TME**) is assigned $k_{\text{rel}} = 1$. As already mentioned, the product formation in all reactions of **1a** is much less efficient than that of **1b**.

Table 3. *Relative Rates of Conversion of* **1a** *and* **1b** (0.05M) *to Cycloadducts in the Presence of* **F**, **AN**, *or* **TME** (1M) *in Benzene* (λ 350 nm)

	F	**AN**	**TME**
1a	11	6	1
1b	90	180	120

The reactivity of triplet excited **1b** towards the alkenes/dienes studied parallels that of cyclohex-2-enone itself, for which again no significant differences in the overall rates of product formation had been observed, the addition to furan also proceeding at a slightly slower pace [11][12]. The triplet state of **1a** behaves more like that of cyclohept-2-enone in efficiently undergoing $(Z) \rightarrow (E)$ isomerization, as reflected on the one side by both much lower overall (bimolecular) rates of cycloadduct formation and total product yields, and on the other side by the (relative) increase in efficiency of furan-addition products. This would imply that cycloadducts from **1a** + **F** result from both the reaction of triplet **1a** + **F** and from (additional) trapping of (E)-**1a** by this diene, which again would explain, why **1a** and **F** give *trans*-fused [4 + 2] cycloadducts exclusively, in contrast to **1b** where the corresponding main adduct **12** has a *cis*-ring fusion.

Except for this difference in efficiency in product formation, **1a** and **1b** exhibit a similar behavior in [2 + 2] photocycloadditions towards alkenes. In the reaction with **TME**, the *trans*-fused cycloadduct represents the main product in each case. In the reaction with **AN**, small amounts (*ca.* 10%) of *trans*-fused cycloadducts are formed from both enones, but the major (*cis*-fused) products differ in the orientation of addition; whereas **1a** affords mainly (72%) so called head-to-tail adducts, *i.e.*, **17** and **18**, head-to-head adducts **24** and **25** represent the major (70%) products from **1b**. This result is easily explained by the fact that the S-atom in the triplet excited **1a** gives rise to a higher spin density on $C_{(\alpha)}$ of the enone (as compared to the situation in **1b**), thus favoring the primary addition step of this center to the methylene C-atom of ground-state **AN**.

The large amount of NMR data available for both [2 + 2] and [4 + 2] cycloadducts allows the setting up of some improved general rules for differentiating between *trans*- and *cis*-ring fusions in bi- and tricycles of the kind described in *Sect. 2*.

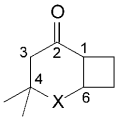
Regarding the ^{1}H-NMR data, it is well established that in *trans*-fused bicyclo[4.2.0]octan-2-ones such as the [2 + 2] cycloadducts, the H-atoms at the fusion site form a dihedral angle of 180° (axial, axial), and therefore, this vicinal coupling constant is larger than in *cis*-fused diastereoisomers (see $J(1,6)$ in *Table 4*). Furthermore, the size of the geminal coupling constant of the methylene H-atoms vicinal to the carbonyl group in cyclohexanones reflects the projected angle of CH_2 with the adjacent p orbital of the sp^2-hybridized C-atom [14]. Therefore, the magnitude of this coupling constant is significantly smaller in undistorted (chair-like) six-membered rings than in conformationally distorted compounds (see $J(3,3)$ of *trans*-fusion *vs.* *cis*-fusion in *Table 4*). Although these rules are quite generally valid, exceptions occur, as seen for compound **17**, where the corresponding geminal coupling constant ($J = 13.5$ Hz) suggests a *trans*-fused bicyclic structure, while from X-ray analysis the *cis*-fusion is evident. Thus, one of these parameters alone should never be used for configurational assignments. Fortunately, the ^{13}C-NMR chemical shifts also differ significantly between the *trans*- and *cis*-fused bicyclo[4.2.0]octanones, as all tetrahedral C-atoms of the six-membered ring in the *trans*-fused bicycles resonate at lower field than the corresponding C-atoms in *cis*-fused diastereoisomers (see C(1), C(3), C(4), and C(6) in *Table 4*), whereas the opposite is true for the carbonyl C-atoms (see C(2)).

Almost all these criteria can also be used to differentiate between the *trans*- and *cis*-fused [4 + 2] cycloadducts presented (*cf.* *Table 5*). Nevertheless, such a differentiation by using only the vicinal coupling constant for the H-atoms at the fusion sites (= bridgeheads) should be avoided, as these values are much more alike than those for the [2 + 2] cycloadducts discussed above.

Table 4. *Selected NMR Data for Bicyclo[4.2.0]octanones*[a]). Vicinal and geminal H,H-coupling constants in Hz, δ(C) in ppm.

	trans-Fusion		*cis*-Fusion	
	X = S	X = CH_2	X = S	X = CH_2
J(1,6)	11.3 – 12.0	12.5 – 13.3	7.3 – 9.0	8.2 – 10.1
J(3,3)	13.6 – 13.9	13.6 – 13.9	15.4 – 17.7	16.2 – 17.7
δ of C(1)	55 – 59	52 – 56	42 – 49	41 – 49
C(2)	201 – 205	205 – 208	206 – 208	208 – 214
C(3)	58 – 60	54 – 56	53 – 58	52 – 55
C(4)	52 – 54	40 – 41	43 – 49	30 – 36
C(6)	43 – 50	46 – 48	37 – 45	31 – 40

[a]) For convenience, the numbering of the six-membered-ring moiety is arbitrary (see **I**).

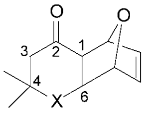


I

Table 5. *Selected NMR Data for [4+2]-Cycloadducts*[a]). Vicinal- and geminal H,H-coupling constants in Hz, δ(C) in ppm.

	trans-Fusion		*cis*-Fusion	
	X = S	X = CH_2	X = S	X = CH_2
J(1,6)	9.0	10.0 – 10.1	7.6 – 8.8	8.1 – 8.2
J(3,3)	14.1 – 14.2	14.2 – 14.3	16.4 – 17.5	17.4 – 17.5
δ of C(1)	61 – 63	58 – 60	49 – 50	45
C(2)	205 – 206	207 – 208	209 – 210	212
C(3)	60	57	57	55
C(4)	51	39	43 – 44	32
C(6)	45 – 49	48 – 50	42 – 43	36

[a]) For convenience, the numbering of the six-membered-ring moiety is arbitrary (see **II**).



II

Experimental Part

1. *General.* Photolyses were run in a *Rayonet RPR-100* photoreactor equipped with (16) 350-nm lamps and a merry-go-round setup, with solvents of spectrophotometric grade. Column chromatography (CC): silica gel *60* (*Merck*; 230 – 400 mesh). ^{1}H- (including two-dimensional) and ^{13}C-NMR Spectra (including ^{1}H,^{1}H plots): at 500.13 and 125.8 MHz, resp., δ in ppm, *J* in Hz. GC/EI-MS: at 70 eV; 30-m *SE-30* capillary column. X-Ray crystal-structure analyses: *Enraf-Nonius CAD-4* four circle diffractometer at 153 K with MoK_α radiation (λ 0.71973 Å).

2. *Tetrahydro-2,2-dimethyl-4*H*-thiopyran-4-one* (**5**). To a well-stirred ice-cooled mixture of methyl 3-methylbut-2-enoate (**3**; 57 g, 0.5 mol), 40% *Triton B* in MeOH (6 ml) and piperidine (5 ml) was added dropwise methyl 3-mercaptopropanoate (**2**; 60 g, 0.5 mol). After stirring for 24 h at 60°, Et_2O (200 ml) was added, the org.

phase washed thoroughly with 10% H_2SO_4, sat. $NaHCO_3$, and sat. NaCl soln., dried ($MgSO_4$), and evaporated, and the residue distilled under high vacuum: 87.8 g (75%) of *methyl 3-[3-methoxy-3-oxopropyl)thio]-3-methylbutanoate* (**4**). B.p. 113–114°/0.5 Torr. ^{1}H-NMR ($CDCl_3$): 3.70 (*s*, 3 H); 3.68 (*s*, 3 H); 2.88 (*t*, *J* = 7.1, 2 H); 2.61 (*s*, 2 H); 2.57 (*t*, *J* = 7.1, 2 H); 1.43 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 172.1 (*s*); 170.6 (*s*); 51.5 (*q*); 51.2 (*q*); 46.6 (*t*); 43.4 (*s*); 34.1 (*t*); 28.4 (*q*); 23.1 (*t*). MS: 234 (25, $M^{+\cdot}$), 73 (100). Anal. calc. for $C_{10}H_{18}O_4S$ (234.31): C 51.26, H 7.74; found: C 51.29, H 7.70.

To a freshly prepared LDA soln. (64 ml of $^iPr_2NH$, 250 ml of 15% BuLi in hexane) in THF (600 ml) at – 78° was added dropwise a soln. of **4** (36 g, 0.154 mol) in THF (300 ml). After stirring for 12 h, 10% aq. H_2SO_4 soln. (1.5 l) was added, and the mixture was extracted with Et_2O (3 ×). After evaporation, the residual keto ester was heated for 70 h in 10% aq. H_2SO_4 soln. (500 ml). Then, the mixture was extracted with pentane (3 ×), the combined org. phase washed with sat. $NaHCO_3$ and sat. NaCl soln. and dried ($MgSO_4$), and the residue distilled *in vacuo:* 8.8 g (40%) of **5** (b.p. 115–118°/12 Torr), which solidified on standing. M.p. and ^{1}H-NMR: as reported in [15]. ^{13}C-NMR ($CDCl_3$): 208.9 (*s*); 58.1 (*t*); 45.8 (*s*); 42.5 (*t*); 29.3 (*q*); 26.4 (*t*).

Conversion of **5** to **1a** with *N*-chlorosuccinimide/pyridine proceeded in 80% yield as reported in [3].

3. *Preparative Photolyses.* 3.1. *General Procedure.* Ar-Degassed 10^{-1} M solns. of **1a** or **1b** were irradiated in the presence of a 20-fold molar excess of 'alkene' in 10-ml *Pyrex* tubes for the time given, up to the degree of conversion indicated (GC monitoring). Workup of the crude product mixture was performed as described below.

3.2. *Photocycloaddition of* **1a** *to* **F**. A soln. of **1a** (142 mg) and **F** (3.4 g) in MeCN (10 ml overall) was irradiated for 70 h. GC Monitoring (increasing retention times) indicated the formation of **8/7/6** 1:4:5 besides 25% of residual **1a**, as already reported [3]. After evaporation, the residue was dissolved in CH_2Cl_2 (5 ml), and the soln. was stirred for 2 h over basic alumina (1 g) to give **9/10/8** 5:4:1. The composition of the mixture was established by ^{1}H-NMR in freshly prepared $CDCl_3$ solns. as **9** and **10** (even more than **7** and **8**) undergo *retro-Diels–Alder* reaction both thermally and on acid catalysis. Prolonged (24 h) stirring of the original product mixture afforded **11/8** 9:1, the spectral data of **11** matching those reported in [16]. ^{1}H- and ^{13}C-NMR of **6**, **7**, **9** and **10**: see *Table 1.*

3.3 *Photocycloaddition of* **1b** *to* **F**. A soln. of **1b** (124 mg) and **F** (3.4 g) in MeCN (10 ml overall) was irradiated for 10 h. GC Monitoring even at low degrees of conversion (< 20%) was inaccurate as the [4 + 2] cycloadducts **12**–**14** underwent *retro-Diels–Alder* reaction efficiently. Monitoring of the product distribution by ^{1}H-NMR in freshly prepared $CDCl_3$ soln. indicated the formation of **12/13/14/15/16** 47:12:10:16:14. NMR of **12**–**14** (taken from the product mixture): see *Table 2.*

3.4 *Photocycloaddition of* **1a** *to* **AN**. Three *Pyrex* tubes, each containing **1a** (142 mg) and **AN** (1.06 g) in benzene (10 ml overall) were irradiated for 21 h, up to total conversion. After evaporation, the residue (420 mg) containing **17**–**23** (*cf. Scheme 4*) was subjected to CC (2.5 × 40 cm column, Et_2O/pentane 6:1). The 1st fraction (20 mg) contained **23** contaminated with acrylonitrile dimers. The 2nd fraction (250 mg) consisted of **17/19** 4:1. Recrystallization of this mixture from hexane afforded 170 mg (29%) of **17**. The 3rd fraction (30 mg) contained **21/22** 2:1. The 4th fraction (90 mg) consisted of **18/20** 7:1. Careful washing of this mixture with hot hexane left behind 65 mg (11%) of **18**.

On treatment with basic alumina, **21** isomerized to **18**, **22** to **19**, and **23** to **20**.

Data of (1α,6α,8α)-3,3-Dimethyl-5-oxo-2-thiabicyclo[4.2.0]octane-8-carbonitrile (**17**): M.p. 101–102°. ^{1}H-NMR ((D_6)acetone): 4.54 (*dd*, *J* = 9.1, 9.2); 3.38 (*dddd*, *J* = 1.2, 3.5, 8.8, 9.1); 3.25 (*dddd*, *J* = 1.2, 8.8, 9.1, 9.2); 2.82 (*ddd*, *J* = 3.5, 9.1, 11.4); 2.77 (*d*, *J* = 13.5); 2.53 (*d*, *J* = 13.5); 2.48 (*dt*, *J* = 11.4, 8.8); 1.41 (*s*, 6 H). ^{13}C-NMR ((D_6)acetone): 207.5 (*s*); 120.5 (*s*); 55.5 (*t*); 49.0 (*s*); 47.0 (*d*); 44.8 (*d*); 30.8 (*d*); 30.7 (*q*); 30.5 (*q*); 26.5 (*t*).

Data of (1α,6α,8β)-3,3-Dimethyl-5-oxo-2-thiabicyclo[4.2.0]octane-8-carbonitrile (**18**): M.p. 108–110°. ^{1}H-NMR ((D_6)acetone): 4.38 (*ddd*, *J* = 2.9, 7.1, 7.4); 3.83 (*ddd*, *J* = 7.4, 8.8, 8.9); 3.33 (*ddd*, *J* = 7.1, 9.3, 9.4); 2.85 (*ddd*, *J* = 8.8, 9.3, 11.4); 2.73 (*ddd*, *J* = 8.9, 9.4, 11.4); 2.69 (*d*, *J* = 15.6); 2.50 (*d*, *J* = 15.6); 1.41 (*s*, 3 H); 1.35 (*s*, 3 H). ^{13}C-NMR ((D_6)acetone): 207.9 (*s*); 119.5 (*s*); 53.8 (*t*); 46.2 (*s*); 42.0 (*d*); 40.8 (*d*); 30.8 (*q*); 30.5 (*q*); 29.1 (*t*); 24.1 (*d*).

Data of (1α,6α,7α)-3,3-Dimethyl-5-oxo-2-thiabicyclo[4.2.0]octane-7-carbonitrile (**19**) *from* **17/19**: ^{1}H-NMR ((D_6)acetone): 4.25 (*dddd*, *J* = 1.2, 3.5, 7.5, 7.8); 3.78 (*dq*, *J* = 1.2, 8.3); 3.64 (*t*, *J* = 8.0); 2.85 (*ddd*, *J* = 7.5, 8.3, 12.3); 2.63, 2.58 (*AB*, *J* = 15.4, 2 H); 2.20 (*ddd*, *J* = 3.5, 8.3, 12.3); 1.39 (*s*, 3 H); 1.35 (*s*, 3 H). ^{13}C-NMR ((D_6)acetone): 206.5 (*s*); 121.1 (*s*); 53.1 (*t*); 48.5.0 (*d*); 46.8 (*s*); 38.5 (*d*); 30.7 (*q*); 30.6 (*q*); 30.5 (*t*); 23.5 (*d*).

Data of (1α,6α,7β)-3,3-Dimethyl-5-oxo-2-thiabicyclo[4.2.0]octane-7-carbonitrile (**20**) *from* **18/20**: ^{13}C-NMR ((D_6)acetone): 206.1 (*s*); 120.1 (*s*); 55.9 (*t*); 46.2 (*d*); 46.1 (*s*); 37.6 (*d*); 33.1 (*t*); 30.7 (q); 30.6 (q); 24.5 (*d*).

X-Ray Crystal-Structure Determination of **17**[1]. Pale colorless needles ($0.60 \times 0.20 \times 0.20$ mm) from hexane, $C_{10}H_{13}NOS$, M_r 195.28: orthorombic, space group $Pna2_1$, $Z=4$; $a=17.1992(17)$, $b=9.7287(10)$, $c=6.0749(6)$ Å; $V=1016.49(18)$ Å^3, $D_x = 1.276$ g cm^{-3}.

X-Ray Crystal-Structure Determination of **18**[1]. Pale colorless transparent blocks ($0.55 \times 0.74 \times 0.80$ mm) from acetone; $C_{10}H_{13}NOS$, M_r 195.28; orthorombic, space group $P2_12_12_1$, $Z=4$; $a=5.7170(2)$, $b=8.6358(4)$, $c=20.3293(8)$ Å; $V=1003.68(7)$ Å^3, $D_x=1.292$ g cm^{-3}.

3.5. *Photocycloaddition of* **1b** *to* **AN**. A soln. of **1b** (124 mg, 1 mmol) and **AN** (1.06 g, 20 mmol) in benzene (10 ml) was irradiated for 6 h, up to total conversion. The isolation of the two main products **24** and **25** has been reported in [6].

On treatment with basic alumina, **28** isomerized to **27**.

Data of (1α,6α,7α)-4,4-Dimethyl-2-oxobicyclo[4.2.0]octane-7-carbonitrile (**26**) *from Product Mixtures:* ^{13}C-NMR ($CDCl_3$): 212.1 (*s*); 120.5 (*s*); 53.2 (*t*); 41.5 (*d*); 40.7 (*d*); 40.2 (*t*); 36.1 (*s*); 30.7 (q); 30.6 (q); 28.1 (*t*); 27.5 (*d*).

3.6. *Photocycloaddition of* **1a** *to* **TME**. A soln. of **1a** (142 mg, 1 mmol) and **TME** (1.68 g, 20 mmol) in benzene (10 ml) was irradiated for 90 h up to 70% conversion of starting material. The residue (150 mg) was subjected to CC (pentane/Et_2O 4 : 1) which allowed the separation of **29/30** 2 : 1 (45 mg, 20%) from the minor open-chain adducts and from polymeric material. Prolonged stirring (12 h) of **29/30** over basic alumina led to almost quantitative isomerization of **29** to **30**.

Data of (1α,6α)-3,3,7,7,8,8-Hexamethyl-2-thiabicyclo[4.2.0]octan-5-one (**30**): Colorless oil. ^{1}H-NMR ($CDCl_3$): 3.56, 2.89 (*AB*, $J=7.3$, 2 H); 2.48, 2.43 (*AB*, $J=17.2$, 2 H); 6 Me signals. ^{13}C-NMR ($CDCl_3$): 208.9 (*s*); 58.5 (*t*); 49.1 (*d*); 45.5 (*d*); 43.1 (*s*); 40.2 (*s*); 40.1 (*s*); 6 Me signals.

Data of (1α,6β)-3,3,7,7,8,8-Hexamethyl-2-thiabicyclo[4.2.0]octan-5-one (**29**) *from Product Mixtures:* ^{1}H-NMR ($CDCl_3$): 3.50, 2.78 (*AB*, $J=12.0$, 2 H); 2.47, 2.27 (*AB*, $J=13.8$, 2 H); 6 Me signals. ^{13}C-NMR ($CDCl_3$): 206.5 (*s*); 59.2 (*t*); 59.1 (*d*); 52.1 (*s*); 50.5 (*d*); 40.4 (*s*); 40.2 (*s*); 6 Me signals.

3.7. *Relative Rate Measurements.* For comparative irradiations of **1a** and **1b** in the presence of the various alkenes, Ar-degassed solns. containing 0.1 mmol and 2.0 mmol of alkene in benzene (2 ml) were irradiated in a merry-go-round setup, the formation of products being monitored by GC, with dodecane as internal standard, after constant time intervals.

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Received March 16, 2005

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[1] CCDC-260927 and CCDC-260928 the supplementary crystallographic data for **17** and **18**, respectively. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.