Cycloadditions, 43[1]

Cyclobutanones via Photoreactions of Chromium-Carbene Complexes with Olefins and Dienes – A Comparison with the Traditional Ketene Method

Stephan Köbbing[2][a], Jochen Mattay*[a] and Gerhard Raabe[b]

Organisch-Chemisches Institut der Universität Münster[a],
Orléansring 23, D-48149 Münster

Institut für Organische Chemie der Technischen Hochschule Aachen[b],
Prof.-Pirlet-Straße 1, D-52074 Aachen

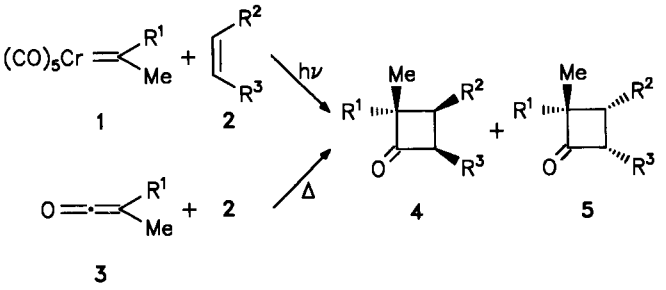
Received February 15, 1993

Key Words: Cyclobutanones / Chromium-carbene complexes / Ketenes / [2 + 2] Cycloadditions

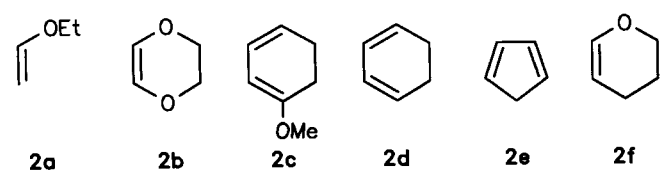
Photolysis of chromium-carbene complexes **1** in the presence of olefins and dienes yields cyclobutanones **4** and **5** with varying stereoselectivity. Under oxidative conditions lactones **6**, **7**, **8**, and **10** are obtained as byproducts. Thermal reactions of ketenes **3** with olefins and dienes yield the same cyclobutanones with usually equal selectivities. In the case of 2,3-dihydro-1,4-dioxin as olefin, diene **9** is obtained as a byproduct. Cycloaddition reactions of **1a** or **3a** with 1,2-dimethylenecyclopentane (**11**) yield the spirocyclic cyclobutanones **12** and **13**. The symmetric ketone **16** and the ketene dimer **17** are formed as additional products upon cycloaddition of ketene **3b** to tetraethoxyethylene. Novel α-(butylthio)cyclobutanones **4j**, **k**, **l**, **m** and **5k**, **l** are formed by cycloaddition reactions of the newly prepared compounds **1c** and **3c**. The ketene dimer **20** is formed by thermal reactions of **3a** with olefins. Unusually low stereoselectivities are observed in the case of photolytic reactions of **1c** with dienes.

Cyclobutanones, important precursors of many natural products and complex organic molecules[3], are often prepared by thermal cycloadditions of ketenes to olefins[4] as well as by photolytic reactions of chromium-carbene complexes with electron-rich olefins and dienes[5] (Scheme 1). Mechanistic studies indicate that the photolysis of chromium-carbene complexes generates a metal-coordinated ketene[6].

Scheme 1



Scheme 2. Olefins and dienes employed



Preliminary studies have shown that methoxy(methyl)ketene (**3a**) is easily accessible[7]. A new approach to α-(phenylthio)cyclobutanones is also given. In addition to our previous report α-(butylthio)cyclobutanones are prepared for the first time by cyclization of the new compounds **1c** and **3c**. In this paper the full details and a comparison of both methods are reported.

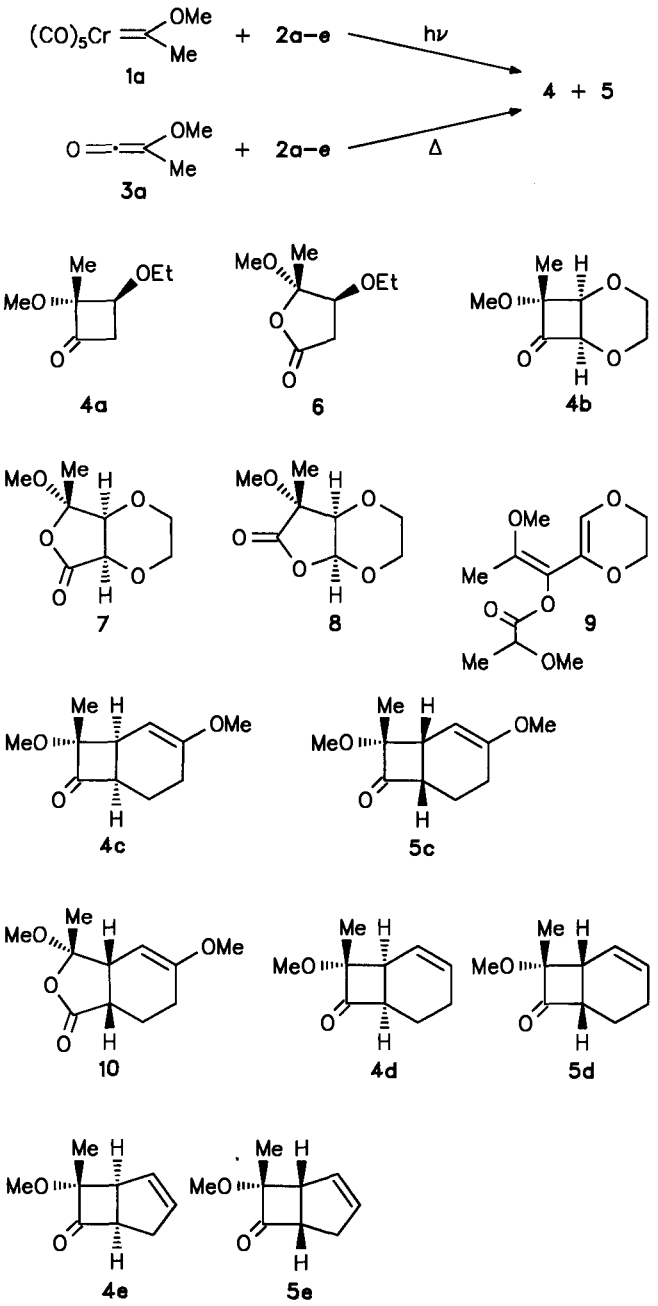
1. Photochemical and Thermal Reactions of Methoxy-Methyl-Substituted Carbene Complexes and Ketenes

Photolytic reactions of the methoxycarbene complex **1a** are well-known, and two different methods are described[5]. For example, irradiation of **1a** and ethyl vinyl ether (**2a**) in acetonitrile followed by air oxidation of the chromium residue yields the cyclobutanone **4a**[5a]. In the presence of carbon monoxide the cyclobutanones **4a** and **5a** are obtained (Table 1)[5b]. An additional advantage of this method is that $Cr(CO)_6$ can be recovered in 60–70% yield and reused. Both photolytic methods are employed to compare the methoxycarbene complex **1a** with the ketene **3a** (Scheme 3).

In contrast to the above mentioned results, irradiation of **1a** and **2a** in acetonitrile under similar conditions yields **4a** and the lactone **6** as a byproduct. The structure of **6** is confirmed by a Baeyer-Villiger oxidation of the cyclobutanone **4a** (Chapter 4). Lactone formation can be due to the sensitivity of cyclobutanones to the air-oxidation conditions, since it is also observed in the case of irradiation of **1a** with **2b** or **2c**. The structures of the obtained lactones **7** and **8**

are confirmed by a Baeyer-Villiger oxidation of **4b** (Chapter 4) and, in addition, by X-ray analysis of **7** (cf. Chapter 5). The stereochemistry of **10** is assigned by NOE measurements. Irradiation of **1a** and **2b–e** in the presence of CO yields the expected cyclobutanones.

Scheme 3



In contrast to photolytic reactions the thermal cycloaddition of ketene **3a** fails at room temperature. This low reactivity is known from other alkoxyketenes[8]. The desired cyclobutanones are obtained by conducting the reaction at higher temperature. Therefore, triethylamine in cyclohexane is added to a solution of 2-methoxypropanoyl chloride[9] and the olefin in refluxing cyclohexane. In the case of 2,3-dihydro-1,4-dioxin as olefin, diene **9** is obtained as a byproduct.

Table 1. Comparison of the methoxycarbene complex **1a** with the related ketene **3a**

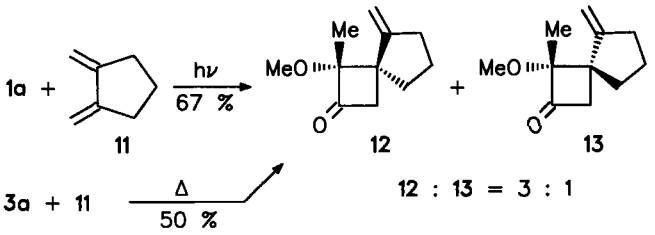
Starting Material	Olefin	Conditions	Yield[a]	Ratio[b]
1a	**2a**	hν/ether/CO[c]	87 %[c]	**4a** : **5a** = 6 : 1[c]
1a	**2a**	1) hν/CH_3CN, 2) ox.[d]	85 %[d]	only **4a**[d]
1a	**2a**	1) hν/CH_3CN, 2) ox.	48 %	**4a** : **6** = 4 : 1
3a	**2a**	cyclohexane/reflux	47 %	only **4a**
1a	**2b**	hν/ether/CO	47 %	only **4b**
1a	**2b**	1) hν/CH_3CN, 2) ox.	47 %	**4b** : **7** : **8** = 4.5 : 1.4 : 1
3a	**2b**	cyclohexane/reflux	44 %	**4b** : **9** = 4.2 : 1
1a	**2c**	hν/ether/CO	73 %	**4c** : **5c** = 15 : 1
1a	**2c**	1) hν/CH_3CN, 2) ox.	62 %	**4c** : **5c** : **10** = 14 : 1 : 3
3a	**2c**	cyclohexane/reflux	66 %	**4c** : **5c** = 14 : 1
1a	**2d**	hν/ether/CO[c]	52 %[c]	**4d** : **5d** = 14 : 1[c]
3a	**2d**	cyclohexane/reflux	43 %	**4d** : **5d** = 13 : 1
1a	**2e**	hν/ether/CO[c]	67 %[c]	**4e** : **5e** = 10 : 1[c]
3a	**2e**	cyclohexane/reflux	40 %	**4e** : **5e** = 9 : 1

[a] Yields for isolated, and purified products. — [b] Determined by ^{1}H-NMR spectroscopy and confirmed by GLC. — [c] Ref.[5b]. — [d] Ref.[5a].

This can be explained by a base-catalyzed enolization of the cyclobutanone **4b**, followed by ring opening of the cyclobutene and trapping of the dienol by a second equiv. of 2-methoxypropanoyl chloride or vice versa.

Novel spirocyclic cyclobutanones **12** and **13** are obtained in good yields after cycloaddition of **1a** or **3a** to 1,2-dimethylenecyclopentane (**11**) as olefin (Scheme 4).

Scheme 4



The different reactivites of the intermediates indicate that the generation of free ketenes during photolysis can be ruled out. However, the stereoselectivities of both reactions are nearly identical. The activation of the ketene moiety during photolysis is only affected by the metal. Whereas alkenes and dienes give cyclobutanones with chromium-carbene complexes the corresponding reactions with alkynes fail. For example, **1a** and 1-ethoxy-1-propyne do not form any isolable product upon photolysis. This behavior has also been observed for other alkynes by Hegedus and coworkers[5b]. In contrast, the ketene **3a** and 1-ethoxy-1-propyne form the corresponding cyclobutenone in 48% yield[4b].

2. Photochemical and Thermal Reactions of Methyl-Phenylthio-Substituted Carbene Complexes and Ketenes

In contrast to methoxy(methyl)ketene (**3a**) cycloaddition reactions of methyl(phenylthio)ketene (**3b**) are well-

known[10,11]. After the reaction of **3b** with **2a**, **2e**, and **2f** at room temperature the diastereomeric pure cyclobutanones **4f**, **4h**, and **4i** are obtained (Scheme 5). The proposed *endo*-configuration[10] of the phenylthio substituent has been disproved by Ghosez and van Meerssche[11].

The cycloaddition of **3b** to 1-methoxy-1,3-cyclohexadiene in boiling cyclohexane yields **4g** and small amounts of the *endo*-diastereomer **5g** (Table 2).

Scheme 5

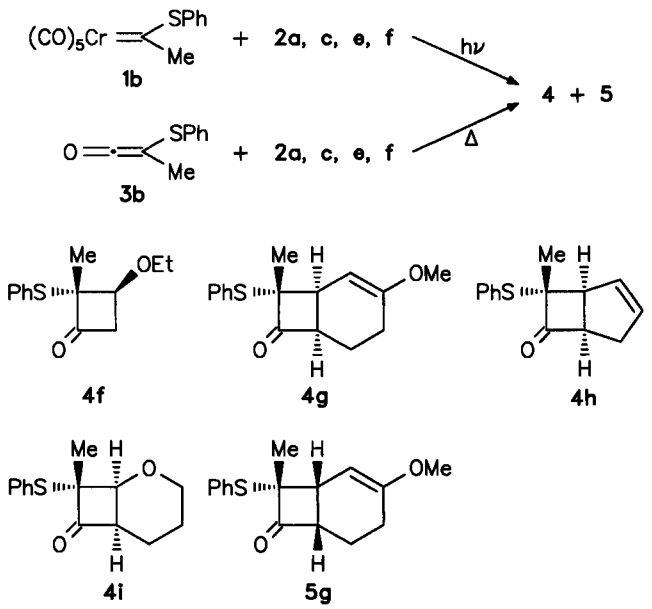


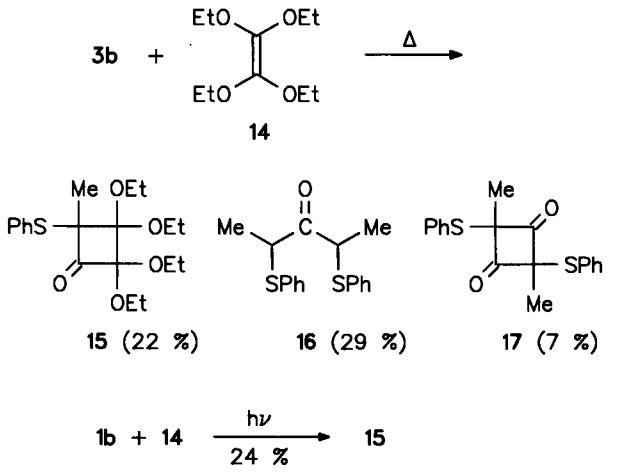
Table 2. Comparison of the (phenylthio)carbene complex **1b** with the related ketene **3b**

Starting Material	Olefin	Conditions	Yield[a]	Ratio[b]
1b	**2a**	hν/ether/CO	64 %	only **4f**
3b	**2a**	*n*-hexane/25 °C[c]	26 %[c]	only **4f**[c]
1b	**2c**	hν/ether/CO	50 %	only **4g**
3b	**2c**	cyclohexane/reflux	85 %	**4g** : **5g** = 75 : 1
1b	**2e**	hν/ether/CO	83 %	only **4h**
3b	**2e**	ether/25 °C[d]	86 %[d]	only **4h**[d]
3b	**2e**	*n*-hexane/25 °C[c]	83 %[c]	only **4h**[c]
1b	**2f**	hν/ether/CO	50 %	only **4i**
3b	**2f**	benzene/25 °C[c]	64 %[c]	only **4i**[c]

[a] Yields are for isolated and purified products. — [b] Determined by ^{1}H-NMR spectroscopy and confirmed by GLC. — [c] Ref.[10]. — [d] Ref.[11].

The thiocarbene complex **1b** can be easily synthesized according to a new method reported by Aumann and Schröder[12]. Irradiation of **1b** and the olefin, using the conditions described for the methoxycarbene complex **1a**[5a], is not successful. However, after photolysis at $\lambda > 400$ nm (Chapter 4) diastereomeric pure cyclobutanones **4f–i** are obtained in good to excellent yields.

Scheme 6



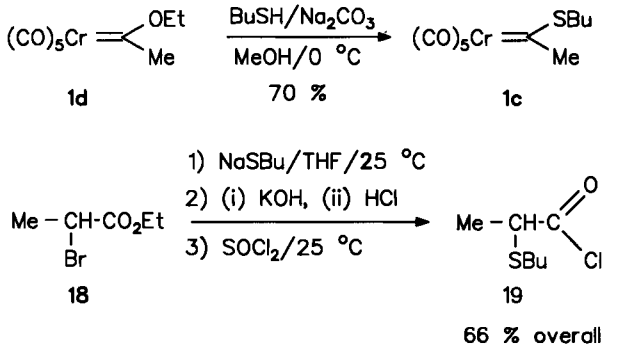
The stereoselectivities of both reactions are identical and the reactivities of **1b** and **3b** are similar (note that the thermal reaction of **3b** with **2c** is conducted in boiling cyclohexane). According to results reported by Hoffmann and coworkers[13] doubly substituted ketenes should not form cyclobutanes with tetraalkoxyethylenes[14]. Nevertheless, the photolysis of **1b** and **14** yields the highly functionalized cyclobutanone **15** (Scheme 6).

Moreover, the thermal reaction of **3b** with **14** also leads to the cyclobutanone **15** but the main product is the symmetric ketone **16**. As an additional product small amounts of the ketene dimer **17** are formed.

3. Photochemical and Thermal Reactions of Butylthio-Methyl-Substituted Carbene Complexes and Ketenes

For the third comparison we have selected the (butylthio)carbene complex **1c** and the related ketene **3c**. Analyzing the reactivity and stereoselectivity of **1c** and **3c** in comparison with the phenylthio-substituted compounds **1b** and **3b** should be of interest. Moreover, **1c** and **3c** are easily accessible in analogy to the phenylthio-substituted compounds **1b** and **3b** (Scheme 7).

Scheme 7. Synthesis of the butylthio-substituted compounds **1c** and **19**, precursor for **3c**

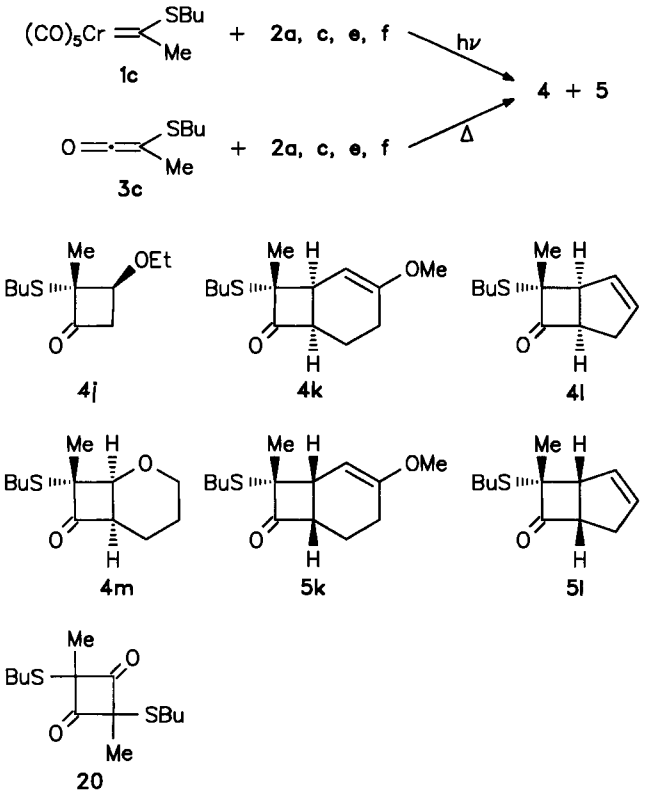


In contrast to the ketene **3b**, the butylthio derivative **3c** dimerizes even at room temperature with formation of the

1,3-cyclobutanedione **20**. Hence, cycloadditions of **3c** are conducted in boiling cyclohexane to suppress the formation of **20**. Nevertheless, **20** is formed by the reaction of **3c** with the enol ethers **2a** and **2f**. In the case of the reaction with the cyclic enol ether **2f** the reactivity of **3c** is very low, and the ketene dimer **20** is obtained as the main product. Depending on the reactivity of **3c** towards dienes, yields are remarkably high (Table 3), and no formation of **20** is observed.

The comparison of **1b** with the (butylthio)carbene complex **1c** shows that **1c** is less reactive. Similar to the thermal reactions of the ketene **3c** the yield is low in the case of the photolysis of **1c** and **2f**. The reactivity of **1c** towards dienes is much higher. With the exception of **20** the same products are observed as in the case of the cycloaddition reactions of **3c** (Scheme 8). In view of the high diastereoselectivity observed for **1b** that of the reaction of **1c** with dienes is unusual (Table 3). The reason for this behavior is not clear, since a secondary isomerization can be excluded because irradiation of the pure *exo*-compounds **4k** and **4l** yields no *endo*-cyclobutanones.

Scheme 8



4. Solid-State Structure of Lactone 7

The six-membered ring has a chair conformation (Figure 1), and carbon atoms C6, C8, C9, and C11 lie almost in a plane with the oxygen atoms O1 and O5 0.61(3) and 0.55(3) Å above and below, respectively. Bond lengths in the five-membered ring are those of a typical γ-lactone[15]. While the C2–C6 bond adopts an equatorial position, the C7–C11 bond is axial yielding a *cis*-2,3-disubstituted 1,4-dioxane. As a result, the five-membered ring is distinctively non-planar with a significant mean deviation of the ring atoms from their best plane (0.14 Å). Shortening of the C8–C9 bond relative to the expected value indicates disorder of this molecular fragment.

Table 3. Comparison of the (butylthio)carbene complex **1b** with the related ketene **3b**

Starting Material	Olefin	Conditions	Yield[a]	Ratio[b]
1c	**2a**	hν/ether/CO	44 %	only **4j**
3c	**2a**	cyclohexane/reflux	70 %	**4j** : **20** = 1 : 2
1c	**2c**	hν/ether/CO	65 %	**4k** : **5k** = 5 : 1
3c	**2c**	cyclohexane/reflux	82 %	**4k** : **5k** = 12 : 1
1c	**2e**	hν/ether/CO	70 %	**4l** : **5l** = 2 : 1
3c	**2e**	cyclohexane/reflux	69 %	**4l** : **5l** = 11 : 1
1c	**2f**	hν/ether/CO	24 %	only **4m**
3c	**2f**	cyclohexane/reflux	60 %	**4m** : **20** = 1 : 1.4

[a] Yields are for isolated purified products. – [b] Determined by ^{1}H-NMR spectroscopy and confirmed by GLC.

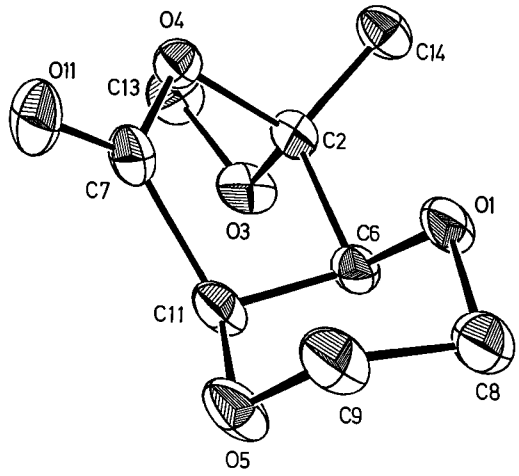


Figure 1. Displacement ellipsoids of 7 at room temperature (plotted at 30% probability)[23] and numbering of atoms. Selected bond distances [Å] and bond angles [°]: O1–C6 1.419(3), O1–C8 1.437(3), C2–O3 1.404(3), C2–O4 1.468(3), C2–C6 1.529(3), O3–C13 1.426(3), O4–C7 1.357(3), O5–C11 1.411(3), O5–C9 1.436(3), C6–C11 1.518(3), C7–O11 1.198(3), C7–C11 1.515(4), C8–C9 1.487(3); C6–O1–C8 111.5(2), O3–C2–O4 108.7(1), O3–C2–C14 114.7(2), O3–C2–C6 104.6(2), O4–C2–C14 107.6(2), O4–C2–C6 103.7(2), C14–C2–C6 116.7(2), C2–O3–C13 116.8(2), C7–O4–C2 110.2(2), C11–O5–C9 111.5(2), O1–C6–C11 110.6(2), O1–C6–C2 107.2(2), C11–C6–C2 101.4(2), O11–C7–O4 121.8(2), C11–C7–O11 129.3(2), O4–C7–C11 109.0(2), O1–C8–C9 110.2(2), O5–C9–C8 110.6(2), O5–C11–C7 113.9(2), O5–C11–C6 116.5(2), C7–C11–C6 102.1(2)

Financial support by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, the *Gesellschaft zur Förderung der Universität Münster* and the *Land Nordrhein-Westfalen* is gratefully acknowledged. We also thank *Bayer AG*, *BASF AG*, *Heraeus Noblelight GmbH*, and *Philips Bildröhrenwerke AG* for generous gifts of chemicals and equipments. We further thank *A. Karwe* for some

preparations of starting materials and cyclobutanones as well as *S. Ullmann* for typing parts of the manuscript.

Experimental

IR: Shimadzu IR-408 or Perkin Elmer 298 Infrared Spectrophotometer. – ^{1}H NMR: Bruker WM 300 (300 MHz). – ^{13}C NMR: Bruker WM 300 (75 MHz), Bruker AM 360 (90 MHz). – MS: Varian MAT CH 7A (GLC-MS coupling) or Finnigan MAT 312. – HPLC: Kontron pump 420, RI detector Bischoff RI 8110, column 250 × 20 mm, LiChrosorb Si 60-5 (Fa. Merck). – Column chromatography: Merck Kieselgel 60, Art. 7734. – GLC: Siemens Sichromat 3 with FID detector and Spectra Physics integrator SP 4290 or Siemens Sichromat 4 with FID detector and Spectra Physics integrator SP 4400, capillary column Hewlett Packard Ultra 2. – Elemental analyses: Heraeus CHN-O-Rapid or Perkin-Elmer 240 Elemental Analyser. – Melting points: Büchi 510 melting point apparatus, all melting points are uncorrected.

Solvents: THF and diethyl ether are dried with KOH and distilled. Chloromethane, cyclohexane, ethyl acetate, *n*-hexane, pentane, and petroleum ether are distilled at atmospheric pressure. Acetonitrile (Baker grade), dichloromethane (Baker grade), and methanol (Baker grade) are used without further purifications.

Photolytic reactions of the (phenylthio)carbene complex **1b** and the (butylthio)carbene complex **1c** are conducted in a reaction vessel surrounded by a filter solution for $\lambda > 400$ nm. This solution is prepared by the addition of 54 ml of 30% aqueous ammonia to a solution of 4.5 g of copper sulfate in 6 ml of water. The solution is added to a second solution containing 22.5 g of sodium nitrite and 30 ml of water. Finally, the mixture is diluted with water to 1000 ml.

The following chemicals were prepared according to literature procedures: pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (**1a**)[16], pentacarbonyl[(methyl)(phenylthio)carbene]chromium(0) (**1b**)[12], 2-methoxypropanoyl chloride[9], 2-(phenylthio)propanoyl chloride[10a], 2,3-dihydro-1,4-dioxin (**2b**)[17], 1-methoxy-1,3-cyclohexadiene (**2c**)[18], 1,2-dimethylenecyclopentane (**11**)[19], tetraethoxyethylene (**14**)[14].

Photolytic Reactions of Carbene Complexes with Olefins – General Procedure. Method A: 5 mmol of olefin is added with a syringe to a solution of 1 mmol of the carbene complex in 20 ml of diethyl ether in a 50-ml Duran pressure tube. The solution is saturated with CO (3 cycles to 5 bar of CO) and irradiated (Philips HPK 125-W high-pressure mercury lamp, Duran immersion well) under CO overnight. The colorless solution is removed by a pipet from precipitated $Cr(CO)_6$, and the solvent is evaporated. Afterwards, the mixture is triturated with 20 ml of methanol to separate the remainder of $Cr(CO)_6$. The solvent is evaporated, the residue is put on a 15 × 2-cm silica gel column and eluted with cyclohexane/ethyl acetate or petroleum ether/ether to give pure cyclobutanones. The isomer ratio is determined by ^{1}H-NMR spectroscopy and confirmed by GLC. For the isolation and characterization of the single diastereomers a second column chromatography is necessary.

Method B: 1 mmol of **1a** and 5 mmol of the olefin are placed in a Duran test tube and dissolved in 10 ml of acetonitrile. The tube is then sealed with a rubber septum, evacuated and purged with argon (three times). The resulting orange solution is irradiated overnight in a merry-go-round apparatus (Fa. Mangels), which is fitted with a Duran immersion well containing a Philips HPK 125-W high-pressure mercury lamp. During the irradiation the color of the solution changes to pale yellow. After complete consumption of **1a** (controlled by TLC) the solvent is evaporated, the yellow residue is dissolved in ethyl acetate, the obtained solution diluted with one volume of *n*-hexane and air-oxidized [75-W Linodym lamp (Fa. Lindner) or sunlight]. Filtration and evaporation of the solvent from the filtrate give almost pure products. The ratio is determined by ^{1}H-NMR analysis and confirmed by GLC. For the isolation and characterization of the single compounds a second column chromatography or HPLC is necessary.

Thermal Reaction of Ketenes with Olefins – Genral Procedure: A solution of triethylamine (1.1 equiv.) in 15 ml of cyclohexane is added dropwise for a period of 15 min to a boiling solution of 1 g of acyl chloride (precursors for **3**) and 5 equiv. of the olefin in 25 ml of cyclohexane. The mixture is refluxed for 4 h and stirred at room temp. overnight. After filtration the precipitate is washed with 30 ml of diethyl ether, and the solvent is evaporated in vacuo. The residue is put on a 35 × 2.5 cm silica gel column and eluted with cyclohexane/ethyl acetate or petroleum ether/ether to give pure cyclobutanones.

Photochemical Reaction of **1a** *with* **2a** *(Method B):* From 580 mg (2.32 mmol) of pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (**1a**) and 840 mg (11.67 mmol) of ethyl vinyl ether (**2a**) in 25 ml of acetonitrile after irradiation for 16 h and purification (cyclohexane/ethyl acetate, 9:1) 183 mg (48%) of **4a** and **6** (ratio 4:1) is obtained as a colorless oil. The pure compounds are separated by HPLC.

anti-3-Ethoxy-2-methoxy-2-methylcyclobutanone (**4a**): The ^{1}H- and ^{13}C-NMR data of compound **4a** are in accordance with literature data[5b].

anti-4-Ethoxy-4,5-dihydro-5-methoxy-5-methyl-2(3H)-furanone (**6**): IR (neat): $\tilde{\nu} = 2965$ cm^{-1} (CH); 1730 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 1.12$ (t, $J = 7.0$ Hz, 3H, CH_2CH_3), 1.50 (s, 3H, CH_3), 2.42 (dd, $J = 17.6/1.8$ Hz, 1H, CH_2), 2.81 (dd, $J = 17.6/5.9$ Hz, 1H, CH_2), 3.40 (s, 3H, OCH_3), 3.45 (m$_c$, 2H, CH_2CH_3), 3.75 (dd, $J = 5.9/1.8$ Hz, 1H, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 14.97$ (CH_3), 15.70 (CH_3), 35.33 (C-3), 50.05 (OCH_3), 65.48 (C-6), 79.93 (C-4), 111.3 (C-5), 174.7 (C-2). – MS (70 eV), *m/z* (%): 143 (6) [$M^+ - OCH_3$], 115 (6), 72 (56). – $C_8H_{14}O_4$ (174.2): calcd. C 55.16, H 8.10; found C 54.94, H 8.25.

Thermal Reaction of **3a** *with* **2a**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 5.9 g (81.60 mmol) of ethyl vinyl ether (**2a**), and 1.25 ml (8.98 mmol) of triethylamine after heating for 6 h and purification (cyclohexane/ethyl acetate, 8:2) 600 mg (47%) of **4a** is obtained as a pale yellow oil.

Baeyer-Villiger Oxidation of **4a**: 159 mg (1.89 mmol) of $NaHCO_3$ and 164 mg (0.95 mmol) of dry MCPBA are added to a solution of 100 mg (0.63 mmol) of **4a** in 10 ml of dichloromethane. The mixture is stirred for 6 h at room temp. (TLC, cyclohexane/ethyl acetate, 8:2). After dilution with 20 ml of dichloromethane 10 ml of 10% aqueous sodium carbonate is added. The organic layer is separated, washed with 10% aqueous sodium carbonate, satd. aqueous sodium chloride, and dried with magnesium sulfate. Evaporation of the solvent and column chromatography of the residue (eluent cyclohexane/ethyl acetate, 8:2) yield 80 mg (73%) of lactone **6** as a colorless oil.

Photochemical Reaction of **1a** *with* **2b** *(Method A):* From 250 mg (1.0 mmol) of **1a** and 430 mg (5 mmol) of 2,3-dihydro-1,4-dioxin (**2b**) after irradiation for 11 h and purification (cyclohexane/ethyl acetate, 8:2) 80 mg (47%) of **4b** is obtained as a colorless oil.

exo-8-Methoxy-8-methyl-2,5-dioxabicyclo[4.2.0]octan-7-one (**4b**): IR (neat): $\tilde{\nu} = 1786$ cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 1.25$ (s, 3H, CH_3), 3.25 (s, 3H, OCH_3), 3.62 (m$_c$, 4H, $[CH_2]_2$), 3.98 (d, $J = 8.0$ Hz, 1H, CH), 5.09 (d, $J = 8.0$ Hz, 1H, COCH). – ^{13}C NMR

($CDCl_3$): δ = 8.70 (CH_3), 53.46 (OCH_3), 63.00 (CH_2), 63.61 (CH_2), 68.57 (C-1), 83.13 (C-6), 91.91 (C-8), 205.3 (C-7). – MS (70 eV), *m/z* (%): 144 (29) [M^+ – CO], 129 (37), 86 (26). – $C_8H_{12}O_4$ (172.2): calcd. C 55.81, H 7.02; found C 55.71, H 7.05.

Photochemical Reaction of **1a** *with* **2b** *(Method B):* From 1.04 g (4.16 mmol) of **1a** and 1.79 g (20.8 mmol) of **2b** in 40 ml of acetonitrile after irradiation for 24 h and purification (cyclohexane/ethyl acetate, 85:15) 378 mg (47%) of **4b**, 7, and **8** (ratio 4.5:1.4:1) is obtained as a colorless oil. The pure compounds are separated by HPLC.

exo-9-Methoxy-9-methyl-2,5,8-trioxabicyclo[4.3.0]nonan-7-one (7): m.p. 77°C. – IR ($CDCl_3$): $\tilde{\nu}$ = 1788 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.58 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.72 (m_c, 4H, $[CH_2]_2$), 3.92 (d, *J* = 4.0 Hz, 1H, CH), 4.71 (d, *J* = 4.0 Hz, 1H, COCH). – ^{13}C NMR ($CDCl_3$): δ = 15.34 (CH_3), 50.25 (OCH_3), 62.62 (CH_2), 64.19 (CH_2), 71.95 (C-1), 74.28 (C-6), 107.6 (C-9), 172.8 (C-8). – MS (70 eV), *m/z* (%): 157 (1) [M^+ – OCH_3], 144 (22) [M^+ – CO_2], 86 (25). – $C_8H_{12}O_5$ (188.2): calcd. C 51.06, H 6.43; found C 51.25, H 6.44.

exo-9-Methoxy-9-methyl-2,5,7-trioxabicyclo[4.3.0]nonan-8-one (**8**): m.p. 89°C. – IR (KBr): $\tilde{\nu}$ = 1775 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 1.40 (s, 3H, CH_3), 3.30 (s, 3H, OCH_3), 3.62 (m_c, 1H, $[CH_2]_2$), 3.78 (m_c, 3H, $[CH_2]_2$), 4.04 (m_c, 1H, CH); 5.81 (d, *J* = 2 Hz, 1H, COCH). – ^{13}C NMR ($CDCl_3$): δ = 11.04 (CH_3), 51.85 (OCH_3), 59.59 (CH_2), 63.75 (CH_2), 75.63 (C-1), 82.55 (C-9), 97.04 (C-6), 171.8 (C-8). – MS (70 eV), *m/z* (%): 144 (24) [M^+ – CO_2], 86 (6). – $C_8H_{12}O_5$ (188.2): calcd. C 51.06, H 6.43; found C 50.94, H 6.52.

Thermal Reaction of **3a** *with* **2b**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 3.5 g (40.60 mmol) of 2,3-dihydro-1,4-dioxin (**2b**), and 1.25 ml (8.98 mmol) of triethylamine after heating for 4 h and purification (cyclohexane/ethyl acetate, 8:2) 570 mg (44%) of **4b** and **9** (ratio 4.2:1) is obtained as a yellow oil. The compounds are separated by a second column chromatography.

2,3-Dihydro-6-[2-methoxy-1-(2-methoxypropanoyloxy)-1-propenyl]-1,4-dioxin (**9**): IR (neat): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1625 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.48 (d, *J* = 6.7 Hz, 3H, $CHCH_3$), 2.10 (s, 3H, CH_3), 3.44 (s, 3H, $CHOCH_3$), 3.60 (s, 3H, OCH_3), 4.00 (q, *J* = 6.7 Hz, 1H, $CHCH_3$), 4.09 (m_c, 4H, $[CH_2]_2$), 6.20 (s, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 13.11 ($CHCH_3$), 18.17 (CH_3), 55.11 ($CHOCH_3$), 57.23 (OCH_3), 64.04 (CH_2), 64.11 (CH_2), 76.01 (CH); 123.6 (H_3CC=), 127.6 (=CH), 130.8 (C=CH), 145.2 (OCOC=), 170.9 (C=O). – MS (70 eV), *m/z* (%): 258 (20) [M^+], 172 (100), 157 (77), 143 (10). – $C_{12}H_{18}O_6$ (258.3): calcd. C 55.81, H 7.02; found C 54.32, H 7.04.

Baeyer-Villiger Oxidation of **4b**: 160 mg (1.92 mmol) of $NaHCO_3$ and 164 mg (0.95 mmol) of dry MCPBA are added to a solution of 110 mg (0.64 mmol) of **4b** in 10 ml of dichloromethane. The mixture is stirred for 6 h at room temp. (TLC, cyclohexane/ethyl acetate, 8:2). After dilution with 20 ml of dichloromethane 10 ml of 10% aqueous sodium carbonate is added. The organic layer is separated, washed with 10% aqueous sodium carbonate, satd. aqueous sodium chloride, and dried with magnesium sulfate. Evaporation of the solvent and column chromatography of the residue (eluent cyclohexane/ethyl acetate 8:2) yield 110 mg (91%) of 7 and **8** (ratio 4.8:1) as a colorless oil.

Photochemical Reaction of **1a** *with* **2c** *(Method A):* From 250 mg (1.0 mmol) of **1a** and 550 mg (5 mmol) of 1-methoxy-1,3-cyclohexadiene (**2c**) after irradiation for 10 h and purification (cyclohexane/ethyl acetate, 85:15) 143 mg (73%) of **4c** and **5c** (ratio 15:1) is obtained as a colorless oil. The pure compounds are isolated by a second column chromatography.

3,exo-8-Dimethoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (**4c**): IR (neat): $\tilde{\nu}$ = 1772 cm^{-1} (C=O), 1660 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.20 (s, 3H, CH_3), 1.70 (m_c, 1H, $[CH_2]_2$), 2.05 (m_c, 3H, $[CH_2]_2$), 2.98 (ddt, *J* = 10.7/4.7/1.0 Hz, 1H, CH), 3.35 (s, 3H, OCH_3), 3.58 (s, 3H, =OCH_3), 3.76 (ddd, *J* = 10.7/6.3/4.2 Hz, 1H, COCH), 4.68 (dd, *J* = 4.7/1.1 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 12.80 (CH_3), 19.79 (C-5), 24.78 (C-4), 36.40 (C-1), 52.84 (OCH_3), 53.37 (C-6), 53.69 (OCH_3), 90.17 (C-2), 95.31 (C-8), 157.8 (C-3), 211.1 (C-7). – MS (70 eV), *m/z* (%): 196 (24) [M^+], 168 (2) [M^+ – CO], 110 (100). – $C_{11}H_{16}O_3$ (196.2): calcd. C 67.32, H 8.22; found C 67.12, H 8.27.

3,endo-8-Dimethoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (**5c**): m.p. 47°C. – IR (neat): $\tilde{\nu}$ = 1776 cm^{-1} (C=O), 1705 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.50 (s, 3H, CH_3), 1.70 (m_c, 1H, $[CH_2]_2$), 1.95 (m_c, 1H, $[CH_2]_2$), 2.15 (m_c, 1H, $[CH_2]_2$), 2.91 (ddt, *J* = 9.8/4.6/1.2 Hz, 1H, CH), 3.39 (m_c, 1H, COCH) overlapped by 3.41 (s, 3H, OCH_3), 3.55 (s, 3H, =OCH_3), 4.72 (dd, *J* = 4.6/1.7 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 18.84 (C-5), 19.84 (CH_3), 24.25 (C-4), 37.34 (C-1), 48.84 (C-6), 52.98 (OCH_3), 53.89 (OCH_3), 89.75 (C-2), 91.25 (C-8), 157.0 (C-3), 211.5 (C-7). – MS (70 eV), *m/z* (%): 196 (29) [M^+], 110 (100). – $C_{11}H_{16}O_3$ (196.2): calcd. C 67.32, H 8.22; found C 67.27, H 8.34.

Photochemical Reaction of **1a** *with* **2c** *(Method B):* From 2.25 g (9 mmol) of **1a** and 4.95 g (45 mmol) of **2c** in 90 ml of acetonitrile after irradiation for 21 h and purification (cyclohexane/ethyl acetate, 9:1) 1.09 g (62%) of **4c**, **5c**, and **10** (ratio 14:1:3) is obtained as a colorless oil. The pure compounds are separated by HPLC.

3,endo-9-Dimethoxy-9-methyl-8-oxabicyclo[4.3.0]non-2-en-7-one (**10**): m.p. 93–94°C. – IR (neat): $\tilde{\nu}$ = 1770 cm^{-1} (C=O), 1660 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.55 (s, 3H, CH_3), 1.75 (m_c, 1H, $[CH_2]_2$), 1.92 (m_c, 1H, $[CH_2]_2$), 2.10 (m_c, 1H, $[CH_2]_2$), 2.22 (m, 1H, $[CH_2]_2$), 3.02 (dm, *J* = 9.7 Hz, 1H, CH), 3.20 (dm, *J* = 9.7 Hz, 1H, COCH), 3.40 (s, 3H, OCH_3), 3.60 (s, 3H, =OCH_3), 4.50 (dd, *J* = 3.4/2.0 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 17.56 (CH_3), 20.31 (C-5), 23.72 (C-4), 38.18 (C-1), 44.90 (C-6), 50.25 (OCH_3), 53.97 (=$COCH_3$), 89.39 (C-2), 110.2 (C-9), 158.0 (C-3), 178.0 (C-7). – MS (70 eV), *m/z* (%): 212 (4) [M^+], 181 (17) [M^+ – OCH_3], 110 (100). – $C_{11}H_{16}O_4$ (212.2): calcd. C 62.25, H 7.60; found C 62.16, H 7.80.

Thermal Reaction of **3a** *with* **2c**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 2.7 g (24.5 mmol) of **2c**, and 1.25 ml (8.98 mmol) of triethylamine after heating for 4 h and purification (cyclohexane/ethyl acetate, 85:15) 1.07 g (67%) of **4c** and **5c** (ratio 14:1) is obtained as a colorless oil. The compounds are separated by a second column chromatography.

Photochemical Reaction of **1a** *with* **11** *(Method A):* From 250 mg (1.0 mmol) of **1a** and 490 mg (5 mmol) of 1,2-dimethylenecyclopentane (**11**) after irradiation for 10 h and purification (cyclohexane/ethyl acetate, 95:5), 120 mg (67%) of **12** and **13** (ratio 3:1) is obtained as a colorless oil. The pure compounds are isolated by a second column chromatography.

exo-3-Methoxy-3-methyl-5-methylenespiro[3.4]octan-2-one (**12**): IR (neat): $\tilde{\nu}$ = 3060 cm^{-1} (=CH), 1771 (C=O), 1681 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.25 (s, 3H, CH_3), 1.65 (m_c, 3H, $[CH_2]_3$), 2.40 (m_c, 3H, $[CH_2]_3$), 2.80 (d, *J* = 17.3 Hz, 1H, CH_2), 3.00 (d, *J* = 17.3 Hz, 1H, CH_2), 3.40 (s, 3H, OCH_3), 4.79 (dd, *J* = 4.2/2.3 Hz, 1H, =CH), 5.09 (dd, *J* = 4.2/2.0 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 13.70 (CH_3), 22.44 (C-8), 33.00 (CH_2), 33.85 (CH_2), 49.45 (C-4), 50.59 (C-6), 53.28 (OCH_3), 93.40 (C-3), 106.7 (=CH_2), 153.2 (C-5), 207.9 (C-2). – MS (70 eV), *m/z* (%): 180 (20) [M^+], 165 (21) [M^+ – CH_3], 152 (25) [M^+ – CO]. – $C_{11}H_{16}O_2$ (180.2): calcd. C 73.30, H 8.95; found C 73.37, H 9.17.

endo-3-Methoxy-3-methyl-5-methylenespiro[3.4]octan-2-one (**13**): IR (neat): $\tilde{\nu} = 3060\ cm^{-1}$ (=CH), 1776 (C=O), 1640 (C=C). – ^1H NMR ($CDCl_3$): $\delta = 1.42$ (s, 3H, CH_3), 1.70 (m_c, 3H, $[CH_2]_3$), 2.10 (m_c, 1H, $[CH_2]_3$), 2.50 (m_c, 2H, $[CH_2]_3$), 2.84 (d, $J = 19.2$ Hz, 1H, CH_2), 2.91 (d, $J_{1,1} = 19.2$ Hz, 1H, CH_2), 3.30 (s, 3H, OCH_3), 4.88 (dd, $J = 4.3/2.3$ Hz, 1H, $=CH_2$), 5.06 (dd, $J = 4.3/2.0$ Hz, 1H, $=CH_2$). – ^{13}C NMR ($CDCl_3$): $\delta = 14.99$ (CH_3), 23.46 (C-8), 34.02 (CH_2), 35.95 (CH_2), 48.37 (C-4), 52.57 (OCH_3), 53.25 (C-6), 93.09 (C-3), 107.3 ($=CH_2$), 153.4 (C-5), 208.0 (C-2). – MS (70 eV), *m/z* (%): 180 (21) [M^+], 165 (19) [$M^+ - CH_3$], 152 (22) [$M^+ - CO$]. – $C_{11}H_{16}O_2$ (180.2): calcd. C 73.30, H 8.95; found C 72.55, H 8.93.

Thermal Reaction of **3a** *with* **11**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 2.4 g (24.5 mmol) of 1,2-dimethylenecyclopentane (**11**), and 1.25 ml (8.98 mmol) of triethylamine after heating for 6 h and purification (cyclohexane/ethyl acetate, 95:5) 730 mg (50%) of **12** and **13** (ratio 3:1) is obtained as a yellow oil. The compounds are separated by a second column chromatography.

Thermal Reaction of **3a** *with* **2d**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 1.96 g (24.4 mmol) of 1,3-cyclohexadiene (**2d**), and 1.25 ml (8.98 mmol) of triethylamine after heating for 4 h and purification (cyclohexane/ethyl acetate, 95:5) 570 mg (43%) of **4d** and **5d** (ratio 13:1) is obtained as a pale yellow oil. The compounds are separated by a second column chromatography.

exo-8-Methoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (**4d**) *and endo-8-Methoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one* (**5d**): The ^1H-NMR data of **4d** and **5d** are in accordance with literature values[5b].

Thermal Reaction of **3a** *with* **2e**: From 1.0 g (8.16 mmol) of 2-methoxypropanoyl chloride, 1.62 g (24.5 mmol) of cyclopentadiene (**2e**), and 1.25 ml (8.98 mmol) of triethylamine after heating for 4 h and purification (cyclohexane/ethyl acetate, 95:5) 500 mg (40%) of **4e** and **5e** (ratio 9:1) is obtained as a pale yellow oil. The compounds are separated by a second column chromatography.

exo-7-Methoxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (**4e**) *and endo-7-Methoxy-7-methylbicyclo[3.2.0]hept-2-en-6-one* (**5e**): The ^1H-NMR data of **4e** and **5e** are in accordance with literature values[5b].

Photochemical Reaction of **1b** *with* **2a** *(Method A)*: From 350 mg (1.07 mmol) of pentacarbonyl[(methyl)(phenylthio)carbene]-chromium(0) (**1b**) and 770 mg (10.69 mmol) of ethyl vinyl ether (**2a**) after irradiation for 15 h ($\lambda > 400$ nm) and purification (petroleum ether/diethyl ether, 4:1) 160 mg (63%) of **4f** is obtained as a colorless oil.

anti-3-Ethoxy-2-methyl-2-(phenylthio)cyclobutanone (**4f**): IR (neat): $\tilde{\nu} = 3050\ cm^{-1}$ (=CH), 2965 (CH), 1774 (C=O), 1710 (C=C). – ^1H NMR ($CDCl_3$): $\delta = 1.21$ (t, $J = 7.0$ Hz, 3H, CH_2CH_3), 1.45 (s, 3H, CH_3), 2.96 (dd, $J = 18.2/5.1$ Hz, 1H, CH_2), 3.20 (dd, $J = 18.2/7.6$ Hz, 1H, CH_2), 3.52 (dq, $J = 7.0/2.0$ Hz, 2H, CH_2CH_3), 4.05 (dd, $J = 7.6/5.1$ Hz, 1H, CH), 7.34 (m_c, 3H, SPh), 7.64 (m_c, 2H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 14.97$ (CH_3), 15.00 (CH_3), 50.05 (C-4), 68.03 (CH_2CH_3), 69.71 (C-2), 72.37 (C-3), 128.8 (2 CH, SPh), 128.9 (1 CH, SPh), 130.4 (C_q, SPh), 135.8 (2 CH, SPh), 208.0 (C-1). – MS (70 eV), *m/z* (%): 236 (16.2) [M^+], 164 (80), 136 (24), 109 (51) [SPh], 77 (57) [Ph], 72 (30). – $C_{13}H_{16}O_2S$ (236.3): calcd. C 66.07, H 6.82; found C 66.18, H 6.99.

Photochemical Reaction of **1b** *with* **2c** *(Method A)*: From 360 mg (1.1 mmol) of **1b** and 610 mg (5.5 mmol) of 1-methoxy-1,3-cyclohexadiene (**2c**) after irradiation for 15 h ($\lambda > 400$ nm) and purification (petroleum ether/diethyl ether, 9:1) 140 mg (50%) of **4g** is obtained as a colorless oil.

3-Methoxy-8-methyl-exo-8-(phenylthio)bicyclo[4.2.0]oct-2-en-7-one (**4g**): IR (neat): $\tilde{\nu} = 3043\ cm^{-1}$ (=CH), 1761 (C=C), 1650 (C=C). – ^1H NMR ($CDCl_3$): $\delta = 1.21$ (s, 3H, CH_3), 1.62 (m_c, 1H, $[CH_2]_2$), 2.04 (m_c, 3H, $[CH_2]_2$), 2.96 (dd, $J = 9.7$, 5.1 Hz, 1H, CH), 3.53 (s, 3H, OCH_3), 3.99 (dm, $J = 9.7$ Hz, 1H, COCH), 4.68 (dd, $J = 5.1/1.5$ Hz, 1H, =CH), 7.31 (m_c, 3H, SPh), 7.48 (m_c, 2H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 16.12$ (CH_3), 19.71 (C-5), 24.76 (C-4), 35.76 (C-1), 53.57 (C-6), 53.97 (OCH_3), 68.07 (C-8), 90.47 (C-2), 128.6 (1 CH, SPh), 128.7 (2 CH, SPh), 131.7 (C_q, SPh), 134.9 (2 CH, SPh), 158.2 (C-3), 209.5 (C-7). – MS (70 eV), *m/z* (%): 274 (20) [M^+], 164 (44), 136 (22), 110 (71), 109 (96) [SPh], 77 (77) [Ph]. – $C_{16}H_{18}O_2S$ (274.4): calcd. C 70.04, H 6.61; found C 69.91, H 6.83.

Thermal Reaction of **3b** *with* **2c**: From 1.0 g (4.98 mmol) of 2-(phenylthio)propanoyl chloride, 2.74 g (24.91 mmol) of 1-methoxy-1,3-cyclohexadiene (**2c**), and 0.77 ml (5.48 mmol) of triethylamine after heating for 4 h and purification (petroleum ether/diethyl ether, 9:1) 1.16 g (85%) of **4g** and **5g** (ratio 75:1) is obtained as a colorless oil. After a second column chromatography small amounts of a mixture of **4g** and **5g** (ratio 1.22:1) are obtained. An ^1H-NMR analysis of this mixture gives the following data of **5g**:

3-Methoxy-8-methyl-endo-8-(phenylthio)bicyclo[4.2.0]oct-2-en-7-one: ^1H NMR ($CDCl_3$): $\delta = 1.45$ (s, 3H, CH_3), 1.62 (m_c, 1H, $[CH_2]_2$), 1.78 (m_c, 1H, $[CH_2]_2$), 2.23 (m_c, 2H, $[CH_2]_2$), 3.06 (dd, $J = 9.8/5.0$ Hz, 1H, CH), 3.60 (s, 3H, OCH_3), 3.65 (dm, $J = 9.8$ Hz, 1H, COCH), 4.85 (dd, $J = 5.0/1.0$ Hz, 1H, =CH), 7.30 (m_c, 3H, SPh), 7.60 (m_c, 2H, SPh).

Photochemical Reaction of **1b** *with* **2e** *(Method A)*: From 330 mg (1.0 mmol) of **1b** and 330 mg (5.0 mmol) of cyclopentadiene (**2e**) after irradiation for 19 h ($\lambda > 400$ nm) and purification (petroleum ether/diethyl ether, 9:1) 190 mg (83%) of **4h** is obtained as a colorless oil, which crystallizes upon standing.

7-Methyl-exo-7-(phenylthio)bicyclo[3.2.0]hept-2-en-6-one (**4h**): m.p. 49 °C (ref.[10] 52.5 – 54 °C). – IR (neat): $\tilde{\nu} = 3045\ cm^{-1}$ (=CH), 1765 (C=O). – ^1H NMR ($CDCl_3$): $\delta = 1.25$ (s, 3H, CH_3), 2.42 (dddd, $J = 17.3/9.3/4.2/2.0$ Hz, 1H, CH_2), 2.65 (dm, $J = 17.3$ Hz, 1H, CH_2), 3.36 (ddd, $J = 9.3/5.0/2.3$ Hz, 1H, CH), 4.08 (ddd, $J = 9.3/7.4/1.4$ Hz, 1H, COCH), 5.75 (ddd, $J = 5.8/4.5/2.3$ Hz, 1H, $CHCH=$), 5.91 (ddd, $J = 5.8/3.9/2.0$ Hz, 1H, $CH=CHCH_2$), 7.33 (m_c, 3H, SPh), 7.50 (m_c, 2H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 15.86$ (CH_3), 34.01 (C-4), 50.07 (C-1), 59.25 (C-5), 70.71 (C-7), 128.8 (2 CH, SPh), 128.9 (CH), 129.0 (CH), 131.2 (C_q, SPh), 135.3 (1 CH, C-2), 135.33 (2 CH, SPh), 209.6 (C-6). – MS (70 eV), *m/z* (%): 230 (15) [M^+], 202 (8) [$M^+ - CO$], 164 (70), 109 (45) [SPh], 77 (96) [Ph], 66 (60). – $C_{14}H_{14}OS$ (230.3): calcd. C 73.01, H 6.13; found C 72.59, H 6.17.

Photochemical Reaction of **1b** *with* **2f** *(Method A)*: From 340 mg (1.03 mmol) of **1b** and 430 mg (5.12 mmol) of 3,4-dihydro-2*H*-pyran (**2f**) after irradiation for 19 h ($\lambda > 400$ nm) and purification (petroleum ether/diethyl ether, 9:1) 120 mg (50%) of **4i** is obtained as a colorless oil, which crystallizes upon standing.

8-Methyl-exo-8-(phenylthio)-2-oxabicyclo[4.2.0]octan-7-one (**4i**): m.p. 81 °C (ref.[10] 85 – 85.5 °C). – IR (neat): $\tilde{\nu} = 3047\ cm^{-1}$ (=CH), 1770 (C=O), 1731 (C=C). – ^1H NMR ($CDCl_3$): $\delta = 1.40$ (s, 3H, CH_3), 1.50 (m_c, 2H, CH_2), 1.63 (m_c, 1H, CH_2), 2.11 (m_c, 1H, CH_2), 3.30 (dm, $J = 8.0$ Hz, 1H, COCH), 3.86 (m_c, 2H, OCH_2), 4.18 (d, $J = 8.0$ Hz, 1H, CH), 7.32 (m_c, 3H, SPh), 7.47 (m_c, 2H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 14.15$ (CH_3), 16.59 (C-5), 21.99 (C-4), 53.74 (C-6), 64.91 (C-3), 69.53 (C-8), 70.63 (C-1), 128.7 (1 CH, SPh), 128.9 (2 CH, SPh), 130.6 (C_q, SPh), 134.8 (2 CH, SPh), 206.9 (C-7). – MS (70 eV), *m/z* (%): 248 (9) [M^+], 220 (5) [$M^+ - CO$], 164 (74), 109 (45) [SPh], 84 (13), 77 (44) [Ph]. – $C_{14}H_{16}O_2S$ (248.3): calcd. C 67.71, H 6.49; found C 68.02, H 6.80.

Photochemical Reaction of **1b** *with* **14** *(Method A):* From 330 mg (1.0 mmol) of **1b** and 1.02 g (5.0 mmol) of tetraethoxyethylene (**14**) after irradiation for 37 h ($\lambda > 400$ nm) and purification (petroleum ether/diethyl ether, 9:1) 90 mg (24%) of **15** is obtained as a colorless oil.

2,2,3,3-Tetraethoxy-4-methyl-4-(phenylthio)cyclobutanone (**15**): IR (neat): $\tilde{\nu} = 3049$ cm^{-1} (=CH), 1763 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (m_c, 12H, CH_2CH_3), 1.39 (s, 3H, CH_3), 3.59–3.94 (m_c, 8H, CH_2), 7.30 (m_c, 3H, SPh), 7.54 (m_c, 2H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 14.77$ (CH_3), 14.91 (CH_3), 15.00 (CH_3), 15.15 (CH_3), 15.22 (CH_3), 59.97 (CH_2), 60.70 (CH_2), 61.05 (CH_2), 62.26 (CH_2), 67.61 (C-4), 103.6 (C-3), 110.6 (C-2), 128.9 (2 CH, SPh), 129.0 (1 CH, SPh), 129.2 (C_q, SPh), 136.4 (2 CH, SPh), 203.0 (C-1). – MS (70 eV), *m/z* (%): 368 (12) [M^+], 340 (11) [M^+ – CO], 204 (17), 164 (25), 109 (100) [SPh], 77 (70) [Ph]. – $C_{19}H_{28}O_5S$ (368.5): calcd. C 61.93, H 7.66; found C 62.32, H 7.61.

Thermal Reaction of **3b** *with* **14**: From 1.0 g (4.98 mmol) of 2-(phenylthio)propanoyl chloride, 3.05 g (14.95 mmol) of tetraethoxyethylene (**14**), and 0.77 ml (5.48 mmol) of triethylamine after heating for 7 h and purification (petroleum ether/diethyl ether, 20:1) 380 mg (22%) of **15** is obtained as a colorless oil. Subsequently, a yellow oil is eluted. This oil is purified by a second column chromatography (eluent chloromethane) to yield 280 mg (36%) of a yellow solid consisting of the symmetric ketone **16** and the ketene dimer **17** (ratio 4.1:1). The pure compounds are obtained after crystallization from *n*-hexane.

2,4-Bis(phenylthio)-3-pentanone (**16**): m.p. 114°C. – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1} (=CH), 3038 (=CH), 2980 (CH), 1685 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 1.39$ (d, $J = 7.8$ Hz, 6H, CH_3), 4.11 (q, $J = 7.8$ Hz, 2H, CH), 7.30 (m_c, 10H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 15.08$ (CH_3), 48.72 (CH), 128.6 (2 CH, SPh), 129.0 (4 CH, SPh), 131.6 (2 C_q, SPh), 134.1 (4 CH, SPh), 200.6 (C-3). – MS (70 eV), *m/z* (%): 302 (11) [M^+], 137 (100), 109 (28) [SPh], 77 (8) [Ph]. – $C_{17}H_{18}OS_2$ (302.5): calcd. C 67.51, H 6.00; found C 67.53, H 6.15.

2,4-Dimethyl-2,4-bis(phenylthio)-1,3-cyclobutanedione (**17**): m.p. *116–117°C.* – IR (KBr): $\tilde{\nu} = 3040$ cm^{-1} (=CH), 2960 (CH), 1738 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 1.20$ (s, 6H, CH_3), 7.35 (m_c, 6H, SPh), 7.47 (m_c, 4H, SPh). – ^{13}C NMR ($CDCl_3$): $\delta = 16.22$ (CH_3), 76.79 (C-2 and C-4), 128.4 (2 C_q, SPh), 129.2 (4 CH, SPh), 130.2 (2 CH, SPh), 136.7 (4 CH, SPh), 201.3 (C-1 and C-3). – MS (70 eV), *m/z* (%): 328 (6) [M^+], 300 (14) [M^+ – CO], 272 (8) [M^+ – 2 CO], 164 (44), 109 (65) [SPh], 77 (52) [Ph]. – $C_{18}H_{16}O_2S_2$ (328.5): calcd. C 65.82, H 4.91, found C 65.55, H 5.03.

Pentacarbonyl[(butylthio)(methyl)carbene]chromium(0) (**1c**): To a solution of 6.14 g (23 mmol) of pentacarbonyl[(ethoxy)(methyl)-carbene]chromium(0) (**1d**) in 115 ml of methanol 2.44 g (23 mmol) of sodium carbonate and 4.20 g (46 mmol) of 1-butanethiol are added at 0°C. The brown solution is stirred for 15 min, then 25 ml of water and 25 ml of petroleum ether are added. The organic layer is separated and the aqueous layer extracted with petroleum ether. The combined organic layers are dried with sodium carbonate, and the solvent is evaporated. Column chromatography of the residue (eluent petroleum ether) yields 5.0 g (70%) of **1c** as a dark red oil. – IR (neat): $\tilde{\nu} = 2955$ cm^{-1} (CH), 2045 (*trans*-C=O), 1900–1980 (*cis*-C=O). – ^{1}H NMR (C_6D_6/CS_2): $\delta = 0.87$ (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.29 (sept, $J = 7.2$ Hz, 2H, CH_2CH_3), 1.42 (dt, $J = 7.4/7.2$ Hz, 2H, SCH_2CH_2), 2.53 (t, $J = 7.4$ Hz, 2H, SCH_2), 3.26 (s, 3H, CH_3). – ^{13}C NMR (C_6D_6/CS_2): $\delta = 13.79$ (CH_2CH_3), 22.29 (CH_2CH_3), 29.19 (SCH_2CH_2), 42.36 (SCH_2), 45.60 (CH_3), 216.6 (4 C_q, *cis*-CO), 227.2 (*trans*-CO), 366.06 (carbene C). – MS (70 eV), *m/z* (%): 308 (8) [M^+], 280 (4) [M^+ – CO], 252 (5) [M^+ – 2 CO], 224 (11) [M^+ – 3 CO], 196 (16) [M^+ – 4 CO], 168 (28) [M^+ – 5 CO]. – $C_{11}H_{12}CrO_5S$ (308.3): calcd. C 42.86, H 3.92; found C 43.29, H 4.07.

Synthesis of 2-(Butylthio)propanoyl Chloride (**19**)

2-(Butylthio)propanoic Acid: 45.1 g (0.5 mol) of 1-butanethiol is added dropwise to 9.2 g (0.4 mol) of sodium. The heterogeneous mixture gets warm and the thiol is boiling. After the addition of the thiol the mixture is stirred at room temp. for 2 h. The white solid is suspended in 150 ml of dry THF, then a solution of 36.2 g (0.2 mol) of ethyl 2-bromopropionate (**18**) in 75 ml of dry THF is added dropwise, and the mixture is stirred at room temp. overnight. It is subsequently diluted dropwise with water to dissolve precipitated sodium bromide. The solution is extracted five times with dichloromethane, and the organic layers are combined. After evaporation of the solvent 100 ml of ethanol and a solution of 33.6 g (0.6 mol) of KOH in 50 ml of water are added to the residue. The mixture is heated to reflux for 4 h, and the ethanol is evaporated after cooling. The resulting salt of the acid is dissolved in a minimum amount of water, the solution is acidified (pH = 1) with concd. aqueous HCl at 0°C, extracted with diethyl ether, and the extract is dried with magnesium sulfate. Evaporation of the diethyl ether and distillation of the residue in vacuo yield 22.78 g (70%) of 2-(butylthio)propanoic acid as a colorless liquid, b.p. 163–165°C/3 Torr. – IR (neat): $\tilde{\nu} = 2945$ cm^{-1} (CH), 1700 (C=O), 1280, 930. – ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.42 (sept, $J = 7.2$ Hz, 2H, CH_2CH_3) overlapped by 1.45 (d, $J = 7.0$ Hz, 3H, $CHCH_3$), 1.60 (m_c, 2H, SCH_2CH_2), 2.68 (m_c, 2H, SCH_2), 3.40 (q, $J = 7.0$ Hz, 1H, CH), 10.5–11.0 (s, 1H, OH). – ^{13}C NMR ($CDCl_3$): $\delta = 13.38$ (CH_2CH_3), 16.57 (C-3), 21.71 (CH_2CH_3), 31.01 (CH_2), 31.07 (CH_2), 40.59 (C-2), 179.8 (C-1). – MS (70 eV), *m/z* (%): 162 (58) [M^+], 144 (7) [M^+ – CO], 89 (100) [SBu]. – $C_7H_{14}O_2S$ (162.3): calcd. C 51.82, H 8.70; found C 52.04, H 8.94.

19: 13.85 g (190 mmol) of $SOCl_2$ is added dropwise to 22.0 g (136 mmol) of 2-(butylthio)propanoic acid at –20°C. The mixture is stirred overnight, $SOCl_2$ is evaporated, and the residue is distilled to yield 23.1 g (94%) of **19** as a colorless liquid, b.p. 29°C/Torr. – IR (neat): $\tilde{\nu} = 2950$ cm^{-1} (CH), 1755 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (t, $J = 7.3$ Hz, 3H, CH_2CH_3), 1.41 (sept, $J = 7.3$ Hz, 2H, CH_2CH_3), 1.43 (d, $J = 7.0$ Hz, 3H, $CHCH_3$), 1.59 (m_c, 2H, SCH_2CH_2), 2.62 (t, $J = 7.4$ Hz, 2H, SCH_2), 3.70 (q, $J = 7.0$ Hz, 1H, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 13.39$ (CH_2CH_3), 17.28 (C-3), 21.70 (CH_2CH_3), 31.83 (CH_2), 31.94 (CH_2), 51.93 (C-2), 173.1 (C-1). – MS (70 eV), *m/z* (%): 182 (6) [M^+, ^{37}Cl], 180 (14) [M^+, ^{35}Cl], 144 (8) [M^+ – HCl], 89 (7) [SBu]. – $C_7H_{13}ClOS$ (180.7): calcd. C 46.53, H 7.25; found C 46.62, H 7.52.

2,4-Bis(butylthio)-2,4-dimethyl-1,3-cyclobutanedione (**20**): A solution of 0.62 g (6.09 mmol) of triethylamine in 15 ml of cyclohexane is added dropwise to a solution of 1.0 g (55.3 mmol) of **19** in 25 ml of cyclohexane. The mixture is stirred at room temp. overnight, and the solvent is evaporated. Column chromatography (petroleum ether/diethyl ether 9:1) of the residue yields 400 mg (50%) of **20** as a yellow oil. – IR (neat): $\tilde{\nu} = 2945$ cm^{-1} (CH), 1732 (C=O). – ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 7.3$ Hz, 6H, CH_2CH_3), 1.41 (m_c, 4H, CH_2CH_3), 1.58 (m_c, 4H, SCH_2CH_2), 1.66 (s, 6H, CH_3), 2.75 (t, $J = 7.4$ Hz, 4H, SCH_2). – ^{13}C NMR ($CDCl_3$): $\delta = 13.43$ (2 CH_2CH_3), 18.61 (2 CH_3), 21.83 (2 CH_2CH_3), 30.23 (2 CH_2), 31.24 (2 CH_2), 71.60 (C-2 and C-4), 201.56 (C-1 and C-3). – MS (70 eV), *m/z* (%): 288 (10) [M^+], 260 (17.9) [M^+ – CO], 232 (10) [M^+ – 2 CO], 144 (61). – $C_{14}H_{24}O_2S_2$ (288.5): calcd. C 58.29, H 8.39; found C 58.43, H 8.44.

Photochemical Reaction of **1c** *with* **2a** *(Method A):* From 320 mg (1.04 mmol) of **1c** and 380 mg (5.28 mmol) of ethyl vinyl ether (**2a**) after irradiation for 15 h ($\lambda > 400$ nm) and purification (pe-

troleum ether/diethyl ether, 4:1) 100 mg (44%) of **4j** is obtained as a colorless oil.

anti-2-(Butylthio)-3-ethoxy-2-methylcyclobutanone (**4j**): IR (neat): $\tilde{\nu}$ = 2945 cm^{-1} (CH), 1773 (C=O), 1438, 1290, 1110, 902 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.23 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 1.40 (m_c, 2H, CH_2CH_3), 1.48 (s, 3H, CH_3), 1.54 (m_c, 2H, SCH_2CH_2), 2.65 (m_c, 2H, SCH_2), 2.94 (dd, *J* = 18.1/4.2 Hz, 1H, CH_2), 3.54 (q, *J* = 7.0 Hz, 2H, OCH_2) overlapped by 3.58 (dd, *J* = 18.1/7.2 Hz, 1H, CH_2), 3.92 (dd, *J* = 7.2/4.2 Hz, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 13.50 (CH_2CH_3), 14.63 (CH_3), 14.98 (OCH_2CH_3), 21.93 (CH_2CH_3), 28.31 (SCH_2CH_2), 31.42 (SCH_2), 50.23 (C-4), 65.95 (OCH_2), 66.91 (C-2), 73.17 (C-3), 205.4 (C-1). – MS (70 eV), *m/z* (%): 216 (3) [M^+], 144 (100), 89 (9) [SBu], 72 (11). – $C_{11}H_{20}O_2S$ (216.3): calcd. C 61.07, H 9.32; found C 61.08, H 9.66.

Thermal Reaction of **3c** *with* **2a**: From 1.0 g (5.53 mmol) of 2-(butylthio)propanoyl chloride (**19**), 2.0 g (27.70 mmol) of **2a**, and 0.85 ml (6.09 mmol) of triethylamine after heating for 4 h and purification (petroleum ether/diethyl ether, 9:1) 240 mg (30%) of **20** is obtained as a yellow oil. Subsequently 480 mg (40%) of the cyclobutanone **4j** is eluted as a colorless oil.

Photochemical Reaction of **1c** *with* **2c** *(Method A)*: From 300 mg (0.97 mmol) of **1c** and 540 mg (4.91 mmol) of **2c** after irradiation for 10 h (λ > 400 nm) and purification (petroleum ether/diethyl ether, 9:1) 160 mg (65%) of **4k** and **5k** (ratio 5:1) is obtained as colorless oil.

exo-8-(Butylthio)-3-methoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (**4k**): IR (neat): $\tilde{\nu}$ = 2945 cm^{-1} (CH), 1762 (C=O), 1653 (C=C). – ^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.30 (s, 3H, CH_3), 1.39 (m_c, 2H, CH_2CH_3), 1.53 (m_c, 2H, SCH_2CH_2), 1.65 (m_c, 1H, $[CH_2]_2$), 1.97 (m_c, 1H, $[CH_2]_2$), 2.08 (m_c, 2H, $[CH_2]_2$), 2.60 (dt, *J* = 7.5/1.6 Hz, 2H, SCH_2), 2.80 (dd, *J* = 9.4/5.1 Hz, 1H, CH), 3.56 (s, 3H, OCH_3), 4.20 (dm, *J* = 9.4 Hz, 1H, COCH), 4.66 (dd, *J* = 5.1/1.4 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 13.49 (CH_2CH_3), 15.92 (CH_3), 19.81 (C-5), 21.91 (CH_2CH_3), 24.74 (C-4), 29.27 (SCH_2CH_2), 31.42 (SCH_2), 35.95 (C-1), 53.02 (C-6), 53.89 (OCH_3), 65.03 (C-8), 90.71 (C-2), 158.0 (C-3), 209.3 (C-7). – MS (70 eV), *m/z* (%): 254 (20) [M^+], 197 (11) [M^+ – Bu], 144 (21), 110 (98), 57 (100). – $C_{14}H_{22}O_2S$ (254.4): calcd. C 66.10, H 8.72; found C 66.22, H 9.02.

endo-8-(Butylthio)-3-methoxy-8-methylbicyclo[4.2.0]oct-2-en-7-one (**5k**): IR (neat): $\tilde{\nu}$ = 2945 cm^{-1} (CH), 1770 (C=O), 1705 (C=C). – ^1H NMR ($CDCl_3$): δ = 0.82 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.32 (m_c, 2H, CH_2CH_3), 1.45 (m_c, 2H, SCH_2CH_2), 1.53 (s, 3H, CH_3), 1.73 (m_c, 1H, $[CH_2]_2$), 1.94 (m_c, 1H, $[CH_2]_2$), 2.11 (m_c, 2H, $[CH_2]_2$), 2.55 (m_c, 2H, SCH_2), 2.86 (ddt, *J* = 9.8/4.9/1.1 Hz, 1H, CH), 3.47 (dm, *J* = 9.8 Hz, 1H, COCH) overlapped by 3.50 (s, 3H, OCH_3), 4.69 (dd, *J* = 4.9/1.1 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 13.56 (CH_2CH_3), 21.61 (C-5), 21.90 (CH_2CH_3), 22.88 (CH_3), 25.50 (C-4), 28.48 (SCH_2CH_2), 31.25 (SCH_2), 37.65 (C-1), 52.54 (C-6), 54.06 (OCH_3), 66.35 (C-8), 90.40 (C-2), 158.40 (C-3), 211.52 (C-7). – MS (70 eV), *m/z* (%): 254 (11) [M^+], 197 (16) [M^+ – Bu], 144 (12), 110 (38), 57 (43). – $C_{14}H_{22}O_2S$ (254.4): calcd. C 66.10, H 8.72; found C 65.80, H 8.80.

Thermal Reaction of **3c** *with* **2c**: From 1.0 g (5.53 mmol) of **19** 3.04 g (27.65 mmol) of **2c** and 0.85 ml (6.09 mmol) of triethylamine after heating for 4 h and purification (petroleum ether/diethyl ether, 9:1) 1.14 g (82%) of **4k** and **5k** (ratio 12:1) is obtained as a colorless oil.

Photochemical Reaction of **1c** *with* **2e** *(Method A)*: From 330 mg (1.07 mmol) of **1c** and 350 mg (5.30 mmol) of **2e** after irradiation for 12 h (λ > 400 nm) and purification (petroleum ether/diethyl ether, 9:1), 160 mg (70%) of **4l** and **5l** (ratio 2:1) is obtained as a colorless oil.

exo-7-(Butylthio)-7-methylbicyclo[3.2.0]hept-2-en-6-one (**4l**): IR (neat): $\tilde{\nu}$ = 3045 cm^{-1} (=CH), 2950 (CH), 1764 (C=O), 1690 (C=C). – ^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.33 (s, 3H, CH_3), 1.40 (m_c, 2H, CH_2CH_3), 1.53 (m_c, 2H, SCH_2CH_2), 2.44 (dddd, *J* = 17.3/9.4/4.2/2.0 Hz, 1H, CH_2), 2.5 (m_c, 3H, CH_2 and SCH_2), 3.19 (ddd, *J* = 9.2/5.0/2.3 Hz, 1H, CH), 4.30 (ddd, *J* = 9.2/7.1/1.6 Hz, 1H, COCH), 5.73 (ddd, *J* = 5.7/4.5/2.3 Hz, 1H, CHCH=), 5.92 (ddd, *J* = 5.7/4.0/2.0 Hz, 1H, CH=CHCH$_2$). – ^{13}C NMR ($CDCl_3$): δ = 13.45 (CH_2CH_3), 15.60 (CH_3), 21.88 (CH_2CH_3), 28.97 (SCH_2CH_2), 31.31 (SCH_2), 33.86 (C-4), 50.17 (C-1), 58.67 (C-5), 67.65 (C-7), 129.2 (C-3), 135.0 (C-2), 208.5 (C-6). – MS (70 eV), *m/z* (%): 210 (7) [M^+], 182 (3) [M^+ – CO], 144 (21), 125 (22) [M^+ – SBu], 66 (42), 57 (31). – $C_{12}H_{18}OS$ (210.3): calcd. C 68.53, H 8.63; found C 68.46, H 9.01.

endo-7-(Butylthio)-7-methylbicyclo[3.2.0]hept-2-en-6-one (**5l**): IR (neat): $\tilde{\nu}$ = 3043 cm^{-1} (=CH), 2964 (CH), 1769 (C=O). – ^1H NMR ($CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.40 (m_c, 2H, CH_2CH_3), 1.52 (m_c, 2H, SCH_2CH_2), 1.66 (s, 3H, CH_3), 2.47 (dddd, *J* = 17.2/9.7/3.7/1.8 Hz, 1H, CH_2), 2.62 (m_c, 1H, CH_2), 2.73 (m_c, 2H, SCH_2), 3.38 (ddd, *J* = 9.4/7.8/2.3 Hz, 1H, CH), 3.96 (ddd, *J* = 9.4/8.0/1.5 Hz, 1H, COCH), 5.84 (ddd, *J* = 4.6/4.1/2.3 Hz, 1H, CHCH=), 5.90 (ddd, *J* = 4.6/3.7/1.8 Hz, 1H, CH=CHCH$_2$). – ^{13}C NMR ($CDCl_3$): δ = 13.58 (CH_2CH_3), 22.01 (CH_2CH_3), 23.31 (CH_3), 28.79 (SCH_2CH_2), 31.92 (SCH_2), 34.44 (C-4), 52.27 (C-1), 57.71 (C-5), 68.52 (C-7), 130.1 (C-3), 134.4 (C-2), 212.7 (C-6). – MS (70 eV), *m/z* (%): 210 (6) [M^+], 182 (5) [M^+ – CO], 144 (46), 125 (36) [M^+ – SBu], 66 (36), 57 (74). – $C_{12}H_{18}OS$ (210.3): calcd. C 68.53, H 8.63; found C 68.82, H 8.99.

Thermal Reaction of **3c** *with* **2e**: From 1.0 g (5.53 mmol) of **19**, 1.83 g (27.65 mmol) of **2e**, and 0.85 ml (6.09 mmol) of triethylamine after heating for 4 h and purification (petroleum ether/diethyl ether, 9:1) 800 mg (69%) of **4l** and **5l** (ratio 11:1) is obtained as a colorless oil.

Photochemical Reaction of **1c** *with* **2f** *(Method A)*: From 340 mg (1.1 mmol) of **1c** and 460 mg (5.48 mmol) of 3,4-dihydro-2*H*-pyrane (**2f**) after irradiation for 12 h (λ > 400 nm) and purification (petroleum ether/diethyl ether, 9:1) 60 mg (24%) of **4m** is obtained as a colorless oil.

exo-8-(Butylthio)-8-methyl-2-oxabicyclo[4.2.0]octan-7-one (**4m**): IR (neat): $\tilde{\nu}$ = 2945 cm^{-1} (CH), 1770 (C=O). – ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.37 (m_c, 2H, CH_2CH_3), 1.44 (s, 3H, CH_3), 1.52 (m_c, 5H, $[CH_2]_2$ and SCH_2CH_2), 2.10 (dm, *J* = 13.4 Hz, 1H, $CHCH_2$), 2.61 (m_c, 2H, SCH_2), 3.31 (ddm, *J* = 13.4/11.4 Hz, 1H, COCH), 3.85 (dm, *J* = 11.4 Hz, 1H, CH), 4.02 (m_c, 2H, OCH_2). – ^{13}C NMR ($CDCl_3$): δ = 13.34 (CH_2CH_3), 13.88 (CH_3), 18.59 (C-5), 21.76 (CH_2), 21.93 (CH_2), 28.78 (SCH_2CH_2), 31.37 (SCH_2), 52.97 (C-6), 64.84 (C-3), 66.35 (C-8), 70.32 (C-1), 207.1 (C-7). – MS (70 eV), *m/z* (%): 228 (13) [M^+], 200 (4) [M^+ – CO], 171 (19) [M^+ – Bu], 144 (80), 84 (37), 57 (82). – $C_{12}H_{20}O_2S$ (228.4): calcd. C 63.12, H 8.83; found C 63.47, H 9.01.

Thermal Reaction of **3c** *with* **2f**: From 1.0 g (5.53 mmol) of **19**, 2.32 g (27.62 mmol) of **2f**, and 0.85 ml (6.09 mmol) of triethylamine after heating for 4 h and purification (petroleum ethcr/diethyl ether, 9:1) 250 mg (31%) of **20** is obtained as a yellow oil. Subsequently, 360 mg (29%) of the cyclobutanone **4m** is eluted as a colorless oil.

X-Ray Structure Analysis of Lactone **7**: Single crystals of sufficient quality were obtained from *n*-hexane. Lactone **7** crystallizes in the triclinic space group $P\bar{1}(2)$ with *a* = 6.509(1), *b* = 6.798(2),

$c = 11.249(3)$ Å, $\alpha = 100.31(2)$, $\beta = 89.77(2)$, and $\gamma = 114.55(1)°$. 25 reflections in the range $6.5 \leq \Theta \leq 14.1°$ for the determination of cell constants. $Z = 2$, $M_r = 188.18$, and $V = 444.02$ Å^3 result in $D_{cal} = 1.407$ g · cm^{-3}. $F(000) = 200$. Graphite-monochromated Mo-K_α radiation, $\mu = 1.27$ cm^{-1}. Data collection at room temp. with an Enraf-Nonius CAD4 diffractometer. 2242 reflections were collected in the range $-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $0 \leq l \leq 14$ merged to give 2029 data ($R_w = 0.005$). Lorentz and polarization but no absorption correction. $\sin\Theta/\lambda_{max} = 0.6$ for the solution and refinement of the structure. The structure was solved by direct methods as implemented in the XTAL2.6 program package[20] employing GENSIN[21] to generate structure-invariant relationships and GENTAN[22] for the general tangent-phasing procedure. The positions of all atoms were identified in the initial E map. 1378 reflections with $I > 2\sigma(I)$ were included in the final full-matrix least-squares refinement of 119 variables terminating at $R = 0.044$ [$R_w = 0.046$, $w = 1/\sigma^2(F)$]. Final shift/error smaller than 0.0002, maximum residual electron density 0.2 eÅ^{-3}, and $r^* = 2170$. The coordinates of all hydrogen atoms were calculated in idealized positions and were held fixed in the final refinement ($U_H = 0.038$ Å^2).

[1] Part 42: F. Müller, J. Mattay, S. Steenken, *J. Org. Chem.*, in press.
[2] Taken in part from St. Köbbing, Dissertation, Universität Münster, **1992**.
[3] D. Bellus, B. Ernst, *Angew. Chem.* **1988**, *100*, 820–850; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 797–839.
[4] [4a] L. Ghosez, J. M. O'Donnell in *Pericyclic Reactions* (Eds.: A. Marchand, R. E. Lehr), Academic Press, New York, **1977**, vol. II, p. 79–140. – [4b] W. T. Brady in *The Chemistry of Ketenes, Allenes and Related Compounds* (Ed.: S. Patai), Interscience Publications, New York, **1980**, p. 278–308. – [4c] W. T. Brady, *Tetrahedron* **1981**, *37*, 2949–2966.
[5] [5a] M. A. Sierra, L. S. Hegedus, *J. Am. Chem. Soc.* **1989**, *111*, 2335–2336. – [5b] B. C. Söderberg, L. S. Hegedus, M. A. Sierra, *J. Am. Chem. Soc.* **1990**, *112*, 4364–4374.
[6] L. S. Hegedus, G. de Weck, S. D'Andrea, *J. Am. Chem. Soc.* **1988**, *110*, 2122–2126.
[7] S. Köbbing, J. Mattay, *Tetrahedron Lett.* **1992**, *33*, 927–930.
[8] [8a] D. Bellus, *J. Org. Chem.* **1979**, *44*, 1208–1211. – [8b] T. DoMinh, O. P. Strausz, *J. Am. Chem. Soc.* **1970**, *92*, 1766–1768.
[9] A. M. Likhosherstov, V. N. Kulakov, N. K. Kochetkov, *Zh. Obshch. Khim.* **1969**, *39*, 1405–1439.
[10] [10a] T. Minami, M. Ishida, T. Agawa, *J. Chem. Soc., Chem. Commun.* **1978**, 12–13. – [10b] M. Ishida, T. Minami, T. Agawa, *J. Org. Chem.* **1979**, *44*, 2067–2073.
[11] P. Michel, M. O'Donnell, R. Biname, A. M. Hesbain-Frisque, L. Ghosez, J. P. Declercq, G. Germain, E. Arte, M. van Meerssche, *Tetrahedron Lett.* **1980**, *21*, 2577–2580.
[12] R. Aumann, J. Schröder, *Chem. Ber.* **1990**, *123*, 2053–2058.
[13] R. W. Hoffmann, K. Bressel, J. Gehlhaus, H. Häuser, *Chem. Ber.* **1971**, *104*, 873–885.
[14] D. Bellus, H. Fischer, H. Greuter, P. Martin, *Helv. Chim. Acta* **1978**, *61*, 1784–1813.
[15] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1–S19.
[16] E. O. Fischer, R. Aumann, *Chem. Ber.* **1968**, *101*, 954–962.
[17] M. Fétizon, P. Goulaouic, I. Hanna, *Heterocycles* **1989**, *28*, 521–527.
[18] G. M. Trampe, Dissertation, Technische Hochschule Aachen, **1988**.
[19] R. Sustmann, P. Daute, R. Sauer, A. Sommer, W. S. Rahanovsky, *Chem. Ber.* **1989**, *122*, 1551–1558.
[20] S. R. Hall, J. M. Stewart Eds., *XTAL2.6 User's Manual*, Universities of Western Australia and Maryland, **1989**.
[21] S. R. Hall, *GENSIN. XTAL2.6 User's Manual* (Eds.: S. R. Hall, J. M. Stewart), Universities of Western Australia and Maryland, **1989**.
[22] S. R. Hall, *GENTAN. XTAL2.6 User's Manual* (Eds.: S. R. Hall, J. M. Stewart), Universities of Western Australia and Maryland, **1989**.
[23] C. K. Johnson, *ORTEP: Report ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, **1965**.
[24] Further details of the crystal structure determination of **7** are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57047, the names of the authors, and the bibliographical data.

[56/93]