On the Most Powerful Chemical Traps for Bis(methoxycarbonyl)carbene (= 2-Methoxy-1-(methoxycarbonyl)-2-oxoethylidene)

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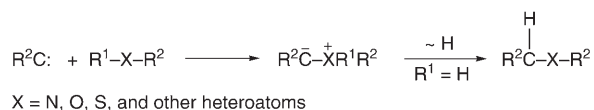
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The efficiency and validity of different chemical substrates for trapping bis(methoxycarbonyl)carbene (= 2-methoxy-1-(methoxycarbonyl)-2-oxoethylidene; **1**) is dependent on the conditions of carbene generation. On conventional photolysis of dimethyldiazomalonate (= 2-diazopropanedioic acid dimethyl ester; **2**) by long-wave UV light (through a *Pyrex* filter, $\lambda > 290$ nm), the most powerful trap for carbene **1** in the series of substrates Me$_2$S, MeOH, cyclohexane, and pyridine is Me$_2$S (with an efficiency ratio of *ca.* 6:4:2:1, resp.). When short-wave decomposition of diazomalonate **2** is employed (through a quartz filter, $\lambda > 210$ nm), more reliable and useful chemical traps for bis(methoxycarbonyl)carbene (**1**) are pyridine and cyclohexane, whose adducts with **1** are rather stable under short-wave-irradiation conditions. Application of alcohols for the trapping of **1** proves to be preferential when simultaneous monitoring of carbene and oxoketene formation during photolysis is necessary.
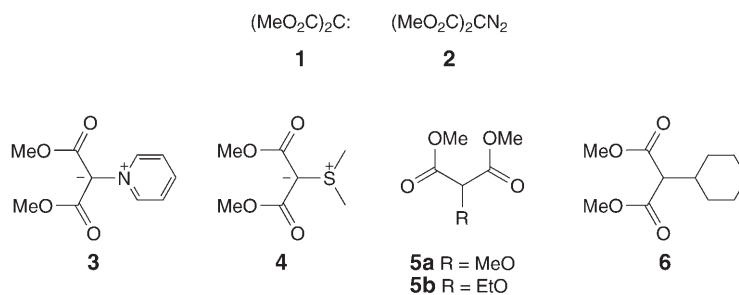
1. Introduction. – Chemical identification of carbenes and quantitative determination of carbene products in reaction mixtures are typically realized by using so-called 'carbene traps' [1]. Besides traditional alkenes [1][2], compounds bearing heteroatoms with unshared electron pairs in their structure are also generally used [1][3–6] (*Scheme 1*). The most frequently employed compounds for this purpose, especially upon laser-flash photolysis of diazo compounds and other precursors of carbenes, are pyridine [3], sulfides [4], alcohols [5], and some other substrates [6]. But, to the best of our knowledge [1], the direct experimental comparison of the efficiency of these chemical traps in reactions of carbenes generated by photochemical decomposition of diazo compounds was not carried out yet.

Scheme 1

$$R^2C: \;+\; R^1{-}X{-}R^2 \;\longrightarrow\; R^2\bar{C}{-}\overset{+}{X}R^1R^2 \;\xrightarrow[R^1\,=\,H]{\sim\,H}\; R^2\overset{H}{\underset{\mid}{C}}{-}X{-}R^2$$

X = N, O, S, and other heteroatoms

2. Results and Discussion. – We represent herein the results of a comparative study of the efficiency of pyridine (Py), dimethyl sulfide (Me$_2$S), methanol (MeOH), and cyclohexane (C$_6$H$_{12}$) as traps of bis(methoxycarbonyl)carbene = (2-methoxy-1-(methoxycarbonyl)-2-oxoethylidene; **1**), generated by conventional (steady) photolysis of

dimethyl 2-diazomalonate (**2**). The tentative evaluation of the photochemical stability of the carbene adducts **3** – **6** with the substrates listed above under conditions of the photolysis will be considered as well.

For a more reliable identification and quantitative determination of the reaction products formed during photochemical decomposition of diazomalonate **2**, the assumed adducts of photochemical reactions, namely pyridinium ylide **3**, sulfonium ylide **4**, 2-alkoxymalonates **5a,b**, and 2-cyclohexylmalonate **6**, were prepared by independent synthesis.

2.1. *Preparation of Adducts.* Two methods were used to synthesize pyridinium ylide **3** (*Scheme 2*), *i.e.*, reaction of 2-bromomalonate **7** with pyridine in the presence of Et₃N [7][8a], and long-wave¹) irradiation (through *Pyrex* filter, $\lambda > 290$ nm) of diazomalonate **2** in pyridine solution. Both ways gave rise to good yields of ylide **3** (65 – 87%), but in terms of the availability of starting material and the ease of scaling the synthesis, the reaction of bromomalonate **7** with pyridine was favored over the photolysis of diazomalonate **2**. The structure of pyridinium ylide **3** was confirmed by the preparation of the cycloadduct **8**, which is formed by reaction of ylide **3** with dimethyl acetylenedicarboxylate (DMAD) followed by spontaneous elimination of methyl formate from the intermediate tetrahydro-1*H* pyrrole derivative **9** [3a][8b] (*Scheme 2*).

The sulfonium ylide **4** was prepared by long-wave irradiation of diazomalonate **2** in Me₂S solution during 16 h [4a][9], and substituted malonates **5a,b** and **6** were synthesized by catalytic decomposition of **2** in the presence of the corresponding substrate MeOH, EtOH, or cyclohexane by analogy with the known procedures [10] (*Scheme 3*). Relevant spectroscopic data of **5** and **6** are given in the *Exper. Part*.

2.2. *Comparison Study of the Efficiency of Pyridine, Me₂S, MeOH, and Cyclohexane as Traps of Carbene* **1**. The generation of bis(methoxycarbonyl)carbene (**1**) was accomplished by long-wave or short-wave irradiation of solutions of diazomalonate **2** containing the carbene traps pyridine, Me₂S, MeOH, and cyclohexane. After completion of diazomalonate photolysis (14 – 23 h; TLC monitoring of the reaction), the composition of the product mixture was determined by ¹H-NMR spectroscopy (*Fig.*). Then the mixture was separated by column chromatography (silica gel). The assignment of the ¹H-NMR signals of the product mixture was achieved by comparison

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¹) In the following, 'long-wave' means *Pyrex*-filtered light with $\lambda > 290$ nm, and 'short-wave' means quartz-filtered light with $\lambda > 210$ nm.

Scheme 2
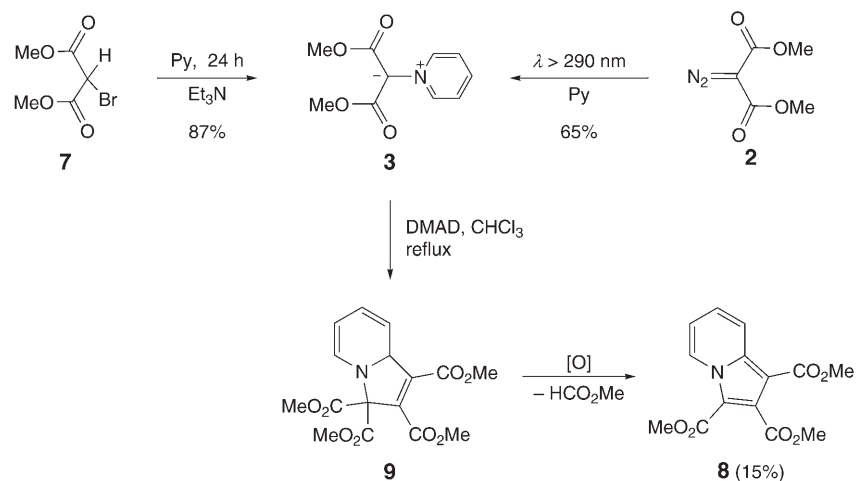
Scheme 3
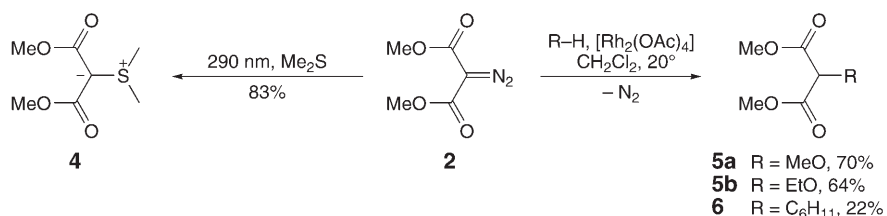
with the ^{1}H-NMR data of the compounds **3**–**6** obtained by independent synthesis. All adducts **3**–**6** exhibited well-defined signals in the ^{1}H-NMR spectrum, which enabled a reliable quantitative analysis of the product mixture. The relative yields of **3**–**6** were determined by the ratio of the integrals of the following ^{1}H-NMR signals (*Fig.*): δ 7.74 (*t*, 2 arom. H), 8.16 (*t*, 1 arom. H), and 8.60 (*d*, 2 arom. H) of pyridinium ylide **3**, δ 2.89 (*s*, 6 H, 2 Me) of sulfonium ylide **4**; δ 4.45 (*s*, 1 H, C*H*OMe) of 2-methoxymalonate **5a**, and δ 3.19 (characteristic *d*, C*H*C$_6$H$_{11}$) of 2-cyclohexylmalonate **6**. The results are shown in *Scheme 4*.

Initially, generation of bis(methoxycarbonyl)carbene (**1**) was accomplished by long-wave irradiation of diazomalonate **2** in cyclohexane containing equimolar amounts of pyridine, Me$_2$S, and MeOH with the molar ratio 1:10 of diazomalonate **2** to each trap. In doing so, it was assumed that in the presence of pyridine, Me$_2$S, and MeOH, cyclohexane will operate only as an inert solvent, since one would expect that the above-mentioned nucleophilic reagents are much more reactive with respect to the
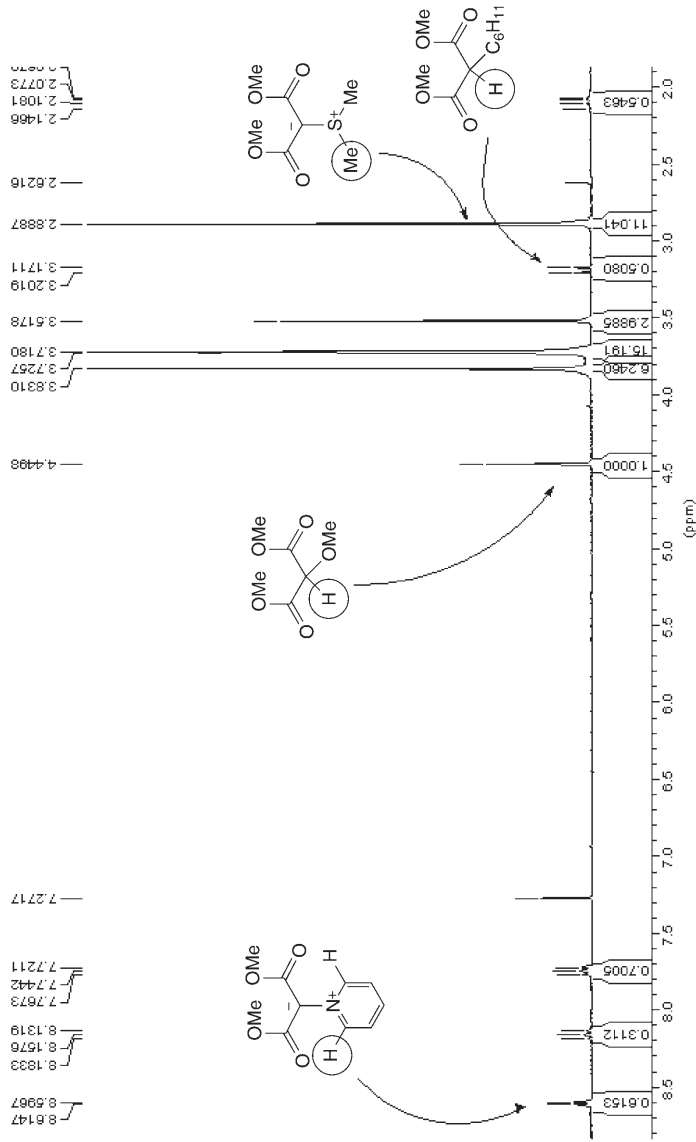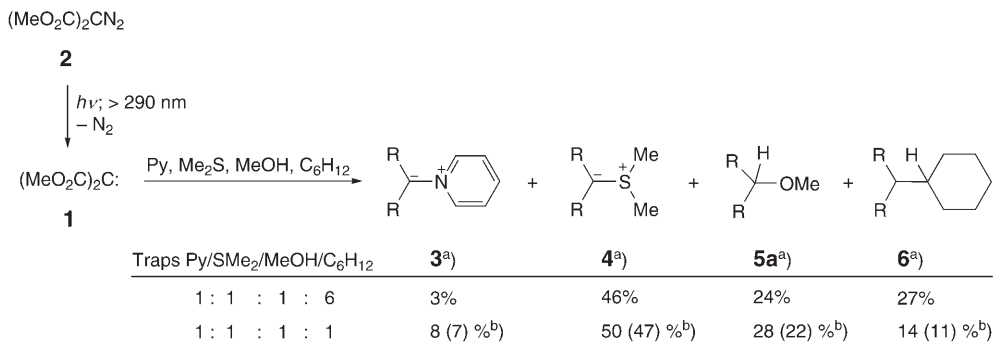
Figure. *¹H-NMR Spectrum of the 'crude' product mixture obtained by long-wave photolysis of diazomalonate 2 in solution of an equimolar mixture of pyridine, Me₂S, MeOH, and cyclohexane. The CH₂ signals of adduct 6 are not displayed.*

Scheme 4

Traps Py/SMe₂/MeOH/C₆H₁₂	3[a]	4[a]	5a[a]	6[a]
1 : 1 : 1 : 6	3%	46%	24%	27%
1 : 1 : 1 : 1	8 (7) %[b]	50 (47) %[b]	28 (22) %[b]	14 (11) %[b]

[a]) R = MeO₂C. [b]) Preparative yields in parentheses.

electrophilic singlet (MeO₂C)₂C: (**1**) than the hydrocarbon cyclohexane [1][2]). However, as shown by the data listed in *Scheme 4*, photolysis of diazo compound **2** in cyclohexane solution, in the presence of pyridine, Me₂S, and MeOH with the molar ratio diazomalonate **2**/nucleophile/cyclohexane 1:10:60, gives rise to the formation of the four reaction products **3**, **4**, **5a**, and **6**. That is, besides the anticipated pyridinium ylide **3** and sulfonium ylide **4**, as well as the insertion product **5a** of carbene **1** into the O−H bond of MeOH, a substantial amount (27%) of 2-cyclohexylmalonate **6** was identified in the reaction mixture – the insertion product of carbene **1** into the C−H bond of cyclohexane. The highest yield under these reaction conditions was observed for sulfonium ylide **4** (46%), and the lowest for pyridinium ylide **3** (3%). Thus the relative efficiency of carbene traps under the above-mentioned conditions (**2**/nucleophile/cyclohexane 1:10:60) decreases in the series Me₂S > cyclohexane > MeOH > pyridine with the ratio 15.3:9:8:1, neglecting a statistical factor for cyclohexane.

Generation of carbene **1** by photolysis of diazomalonate **2** with long-wave light in the presence of equimolar amounts of all four reagents and a 10-fold excess of each of them relative to diazomalonate **2** also gives the four products **3–6**. But under these conditions (**2**/nucleophile/cyclohexane 1:10:10), the relative efficiency of the traps is slightly different and decreases in the series Me₂S > MeOH > cyclohexane > pyridine with the ratio 6.3:3.5:1.8:1.

It was also established by a reference experiment, that on long-wave irradiation, the resulting adducts **3–6** of carbene **1** with the traps are photochemically rather stable, and their ratio during photolysis remains essentially unchanged (*ca.* 6:4:2:1).

Hence, on generation of carbene **1** by long-wave photolysis of diazomalonate **2**, the most powerful traps for (MeO₂C)₂C: (**1**) are Me₂S and MeOH, and the efficiency of pyridine, which is normally used in laser-flash photolysis of diazo compounds and other precursors of carbenes [3], is 6 and 4 times lower under the same reaction conditions.

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[2]) The mechanism of the formation of ylides **3** and **4** and insertion products **5** and **6**, as well as the feasible involvement in these processes of the excited states of diazo compound **2** and the corresponding dimethyl 3*H*-diazirine-3,3-dicarboxylate are not considered in this paper.

2.3. *Stability of the Adducts.* To ascertain the validity of the investigated reagents as carbene traps in the steady photolysis of diazomalonate **2** by short-wave light, the stability of the obtained adducts **3–6** was estimated under short-wave irradiation in solution of anhydrous MeOH during 2–12 h. Analysis of the resulting reaction mixture as described above established that pyridinium ylide **3** and C–H insertion adduct **6** of carbene **1** with cyclohexane are quite stable and remain essentially unchanged over a few hours irradiation under these conditions. However, sulfonium ylide **4** rapidly decomposes on short-wave irradiation giving rise predominantly to the product of a *Stevens* rearrangement [4a][11] (for a few examples of a thermal *Stevens* rearrangement, see [11a, b]) (*Scheme 5*).

Scheme 5

4　　　　　　　36%
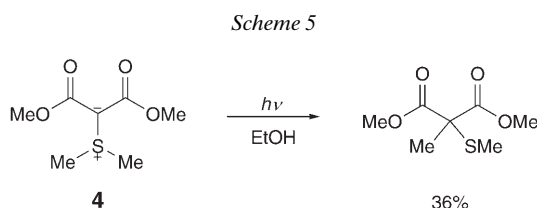
Also the insertion product **5** of bis(methoxycarbonyl)carbene (**1**) in the O–H bond of MeOH or EtOH, *i.e.*, the 2-alkoxymalonates **5a** and **5b**, undergoes partial photochemical decomposition to dimethyl malonate (**10**; 21 and 13% yield, resp.), after 2 h of short-wave irradiation in absolute EtOH (*Scheme 6*). Presumably, dimethyl malonate (**10**) is formed by photochemical cleavage of the 2-alkoxymalonate **5** through the *Norish-II*-type mechanism [12].

Scheme 6

5a R' = H
5b R' = Me　　　　　　　　　　　　　　　　　　**10**
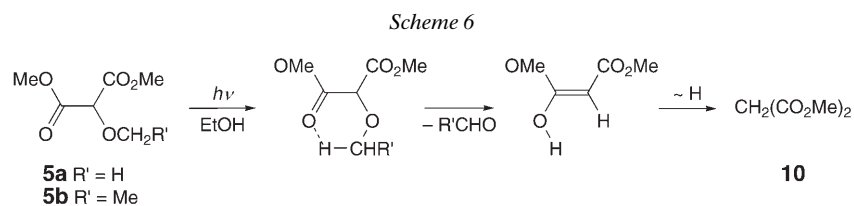
3. Conclusions. – Thus, it was established that in the series of substrates Me₂S, MeOH, cyclohexane, and pyridine, the most powerful trap for bis(methoxycarbonyl)-carbene (**1**) generated by conventional long-wave photolysis of dimethyl diazomalonate (**2**) is Me₂S. On steady short-wave irradiation of **2**, in spite of the lower efficiency, pyridine and cyclohexane are by far more reliable and useful traps of **1** since the resulting adducts are photochemically stable and remain essentially intact during short-wave photochemical runs. However, it is appropriate to mention that the formed pyridinium ylide **3** has a very strong absorption band in the same UV region as diazomalonate **2** (244 and 251 nm, resp.), which causes an increase of the decomposition time of the diazo compound. This seems to be the reason why the use of pyridine for trapping of carbene **1** during conventional short-wave photolysis of diazomalonates seems to be inexpedient.

In comparison with Me₂S, alcohols have an almost two times lower efficiency as traps for carbene **1** and, in addition, their adducts **5** experience partial photochemical decomposition during short-wave irradiation. Nevertheless, in some cases, application of MeOH or EtOH as carbene trap during short-time photolysis of diazocarbonyl compounds proves to be the method of choice, since an alcohol could simultaneously serve as the trap for highly reactive ketenes, which are usually produced by *Wolff* rearrangement of actually all diazocarbonyl compounds [13].

Experimental Part

1. *General.* Reactions were carried out in dry abs. solvents which were purified according to the standard procedures. Irradiation of dimethyl diazomalonate (= 2-diazopropanedioic acid dimethyl ester; **2**), ylide **3**, and 2-substituted malonates **5** and **6** was carried out at $18 – 20°$ by means of a Hg lamp *Hanau S-81* (100 – 130 Wt) in 80 ml or 25 ml vessels through a quartz or *Pyrex* filter ($\lambda > 210$ or 290 nm, resp.). The photolysis progress was usually monitored by TLC, apart from reactions of **2** when the amount of evolved N_2 was measured. Column chromatography (CC) and flash chromatography (FC): silica gel *L 40* (100 μm). Anal. TLC: *Silufol-UV-254* plates, benzene or petroleum ether/Et₂O as eluents. UV/VIS Spectra: *Specord-M-40* instrument; region 200 – 500 nm; 0.3 – 6 mM MeOH solns.; 0.05 – 1.0 cm cuvette; λ_{max} in (log ε). IR Spectra: *Specord-IR-75* instrument; 0.002 – 0.030M CHCl₃ solns. NMR Spectra: *Bruker-AM-300* spectrometer; 300 MHz for ¹H, 75.5 MHz for ¹³C; Me₄Si as internal reference; acid-free CDCl₃ solvent, stored over dry K₂CO₃; δ in ppm, J in Hz.

2. *Preparations of Adducts.* 2.1. *2-Pyridinium Bis(methoxycarbonyl)methylide (= 1-[2-Methoxy-2-(methoxycarbonyl)-2-oxoethyl]pyridinium Inner Salt*; **3**). *Method A.* A soln. of **2** (1.01 g, 6.4 mmol) in freshly distilled pyridine (75 ml) was irradiated by long-wave UV light during 12 h. Then the pyridine was evaporated at $18 – 20°/10 – 15$ Torr, then 1 – 2 Torr. The crystalline yellowish residue was washed with hot Et₂O (50 ml) on a *Hirsch* funnel: 0.79 g (65%) of **3**. M.p. 185 – 186°. UV: 244 (4.89), 390 (3.59). ¹H-NMR: 8.60 ($d, J = 5.82$, 2 arom. H); 8.17 ($t, J = 7.26$, 1 arom. H); 7.75 ($t, J = 7.26$, 2 arom. H); 3.72 (s, 2 Me). ¹³C-NMR: 51.0 (Me); 77.7 (C–COOMe); 126.2 (2 arom. C); 141.7 (3 arom. C); 150.4 (2 arom. C); 165.7 (COOMe). EI-MS: 209 (27, M^+), 178 (38), 151 (53), 148 (38), 120 (26), 93 (100), 79 (30), 78 (20), 65 (29), 63 (23), 59 (14), 52 (27), 51 (18). Anal. calc. for C₁₀H₁₁NO₄ (209.20): C 56.75, H 5.29, N 6.55; found: C 56.41, H 5.30, N 6.70.

Method B. The 2-bromomalonate **7** (20 g, 95 mmol) was added dropwise during 10 min to stirred pyridine (118.7 g, 1.5 mol), and the mixture was stirred for 24 h. Then Et₃N (14.1 g, 0.14 mol) was added, and the mixture was stirred for 5 h. The solvent was evaporated at $18 – 20°/10 – 15$ Torr, then 1 – 2 Torr. The residue was extracted with a mixture of hot benzene (350 ml) and CHCl₃ (7 ml), and the obtained soln. was concentrated: 17.2 g (87%) of **3**. M.p. 184 – 185°.

2.2. *Indolizine-1,2,3-tricarboxylic Acid Trimethyl Ester* (**8**). To a soln. of **3** (1.05 g, 5 mmol) in CHCl₃ (20 ml), but-2-ynedioic acid dimethyl ester (DMAD; 0.71 g, 5 mmol, 0.61 ml) was added, and the mixture was refluxed for 5 h (TLC: full conversion of **3**). The solvent was evaporated at 10 – 15 Torr, and the crude dark-red oil was subjected to CC (aluminium oxide (17 g), benzene). After concentration of the main fraction at 10 – 15 Torr, the residue was purified again by CC (Et₂O/petroleum ether 1:1). The combined fraction of the product was dried (MgSO₄) and concentrated: 0.218 g (15%) of **8**. M.p. 146 – 147° (MeOH) [8b]. ¹H-NMR: 3.91 (s, 2 MeO); 4.01 (s, 1 MeO); 7.06 ($dd, J = 6.5, 6.5$, 1 arom. H); 7.39 ($dd, J = 6.4, 9.4$, 1 arom. H); 8.35 ($d, J = 9.4$, 1 arom. H); 9.53 ($d, J = 6.5$, 1 arom. H). EI-MS: 291 (96, M^+), 260 (100), 233 (6), 230 (9), 202 (22), 188 (15), 143 (19), 130 (9), 115 (13).

2.3. *Dimethylsulfonium Bis(methoxycarbonyl)methylide (= [2-Methoxy-1-(methoxycarbonyl)-2-oxo-ethyl]dimethylsulfonium Inner Salt*; **4**). A soln. of **2** (3.01 g, 19 mmol) in freshly distilled Me₂S (70 ml) was irradiated by long-wave UV light during 17 h. The Me₂S was removed at $40 – 45°/1$ atm, then 1 – 2 Torr. The crystalline yellowish residue was washed with hot Et₂O (50 ml) on a *Hirsch* funnel: 2.99 g (83%) of **4**. M.p. 168 – 169° (MeOH/Et₂O 1:4) [4a]. UV: 237 (4.76), 293 (2.18). ¹H-NMR: 2.89 (s, 2 Me); 3.71 (s, 2 Me). ¹³C-NMR: 28.2 (MeS); 51.2 (MeO); 59.0 (C–COOMe); 167.2 (COOMe).

2.4. *2-Substituted Methyl Esters* **5** *and* **6**. *General Procedure A* (*G.P. A*). [Rh$_2$(OAc)$_4$] (13 mg, 0.0316 mmol) was added to the soln. of 10 equiv. of EtOH, MeOH, or cyclohexane in CH$_2$Cl$_2$ (5 ml) under Ar. Then, 1 equiv. of diazomalonate **2** (0.5 g, 3.16 mmol) was added dropwise under Ar during 30 min. The mixture was stirred for 48 h (TLC monitoring). After filtration of the mixture through silica gel (2 g) and washing with CH$_2$Cl$_2$ (10 ml), the solvents were evaporated at 15–20 Torr, and the residue was purified by CC (Et$_2$O/petroleum ether gradient). The desired product was distilled at 1–2 Torr.

2.4.1. *2-Methoxypropanedioic Acid Dimethyl Ester* (**5a**). According to the *G.P. A*, with MeOH (1.01 g, 1.27 ml, 31.6 mmol) and **2** (0.5 g, 3.16 mmol): 0.36 g (70%) of **5a**. B.p. 75–80°/1–2 Torr [5a]. ^{1}H-NMR: 3.51 (*s*, 1 MeO); 3.83 (*s*, 2 MeO); 4.45 (*s*, CH). ^{13}C-NMR: 53.3 (MeO); 59.1 (MeO); 80.6 (C(2)); 167.1 (C(1)).

2.4.2. *2-Ethoxypropanedioic Acid Dimethyl Ester* (**5b**). According to the *G.P. A*, with EtOH (0.89 g, 1.13 ml, 19.4 mmol) and **2** (0.31 g, 1.94 mmol): 0.22 g (64%) of **5b**. B.p. 75–80°/1–2 Torr [5a]. ^{1}H-NMR: 1.30 (*t*, *J* = 6.9, *Me*CH$_2$O); 3.66 (*q*, *J* = 6.9, Me*CH*$_2$O); 3.82 (*s*, 2 MeO); 4.54 (*s*, CH). ^{13}C-NMR: 15.3 (*Me*CH$_2$O); 53.2 (MeO); 67.4 (Me*CH*$_2$O); 79.2 (C(2)); 167.4 (C(1)).

2.4.3. *2-Cyclohexylpropanedioic Acid Dimethyl Ester* (**6**). According to the *G.P. A*, with cyclohexane (2.66 g, 3.42 ml, 31.6 mmol) and **2** (0.5 g, 3.16 mmol): 0.15 g (22%) of **6**. B.p. 90–92°/1–2 Torr. ^{1}H-NMR: 0.85–1.31 (*m*, 5 H); 1.62–1.77 (*m*, 5 H); 2.01–2.16 (*m*, 1 H); 3.19 (*d*, *J* = 9.42, *CH*COOMe); 3.73 (*s*, 2 MeO). ^{13}C-NMR: 26.3, 26.5, 31.1, 38.4 (4 cyclohexyl C); 52.6 (MeO); 58.5 (*CH*COOMe); 169.6 (*C*OOMe). EI-MS: 214 (12, *M*$^+$), 183 (17), 155 (2), 133 (39), 132 (100), 101 (28), 100 (39), 95 (62), 81 (11), 74 (8), 67 (12), 59 (9), 55 (15), 41 (19), 39 (12).

3. *Photochemical Experiments*. 3.1. *Photolysis of Dimethyl Diazomalonate* (**2**) *in Cyclohexane Solution in the Presence of Pyridine/Me$_2$S/MeOH*. A mixture of **2** (0.5 g, 3.1 mmol), Me$_2$S (1.86 g, 30 mmol), MeOH (0.96 g, 30 mmol), and pyridine (2.37 g, 30 mmol) in cyclohexane (18 ml, 0.1665 mol) in a 25 ml photolysis reactor with a *Pyrex* filter was irradiated for 14.5 h (TLC monitoring). The solvent and nucleophilic reagents were removed at 18–20°/10–15 Torr, then 1–2 Torr. The residue was diluted with CHCl$_3$ (10 ml), and a 0.5 ml sample of the soln. was subjected to ^{1}H-NMR analysis of the product mixture. The rest of the soln. was treated with Et$_2$O (20 ml), and the crystalline ylides **3** and **4** were separated by decantation. The solvents were evaporated at r.t./10–15 Torr, and the residue was separated by CC (petroleum ether/Et$_2$O/EtOH gradient). The individual fractions after CC were dried (MgSO$_4$) and concentrated. The isolated compounds were microdistilled or recrystallized: 0.166 g (25%; 27%[3])) of **6**, 0.095 g (19%; 24%[3])) of **5a**, 0.244 g (44%; 46%[3])) of **4**, and 0.013 g (2%; 3%[3])) of **3**.

3.2. *Photolysis of Dimethyl Diazomalonate* (**2**) *in Cyclohexane/Me$_2$S/MeOH/Pyridine 1:1:1:1*. A mixture of **2** (0.5 g, 3.1 mmol), Me$_2$S (4.65 g, 75 mmol), MeOH (2.4 g, 75 mmol), pyridine (5.93 g, 75 mmol), and cyclohexane (6.3 g, 75 mmol) in a 25 ml photolysis reactor with a *Pyrex* filter was irradiated for 23 h (TLC monitoring). Workup was performed as described in *Exper. 3.1*: 0.073 g (11%; 14%[3])) of **6**, 0.111 g (22%; 28%[3])) of **5a**, 0.280 g (47%; 50%[3])) of **4**, and 0.045 g (7%; 8%[3])) of **3**.

3.3. *Photochemical Stability of Pyridinium Ylide* **3**. Pyridinium ylide **3** was irradiated by long- and short-wave light during 12 h in MeOH or Me$_2$S soln. (60 ml), with addition of cyclohexane or MeOH (10 mol-equiv.), resp. Workup was performed as described in *Exper. 3.1*. Only starting **3** was isolated after irradiation, in 91 and 95% yield, resp.

3.4. *Photochemical Stability of 2-Alkoxymalonates* **5** *and 2-Cyclohexylmalonate* **6**. *General Procedure B* (*G.P. B*). Compound **5** or **6** was irradiated by short-wave light in abs. EtOH in a 25 ml photolysis reactor during 2 h. Then EtOH was removed at 18–20°/10–15 Torr. The residue was analyzed by ^{1}H-NMR spectroscopy and the product yields were determined by the internal normalization method based on the comparison of the intensity of the H–C(2) signals of **5** or **6** and dimethyl malonate (**10**).

According to the *G.P. B*, 0.235 g (1.46 mmol) of 2-methoxymalonate **5a** yielded, after photolysis, **5a** (79%) and **10** (21%).

According to the *G.P. B*, 0.6 g (3.42 mmol) of 2-ethoxymalonate **5b**, yielded after photolysis, **5b** (87%) and **10** (13%).

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[3])   Yield by ^{1}H-NMR analysis of the crude product mixture, determined by means of the method of internal normalization.

According to the *G.P. B*, 0.19 g (0.87 mmol) of 2-cyclohexylmalonate **6** yielded, after photolysis, only **6** (87%).

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