209. Thioalkylation of *Meldrum*'s Acid: Protected Alkylidene Derivatives of Isopropylidene Malonate

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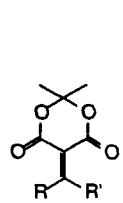
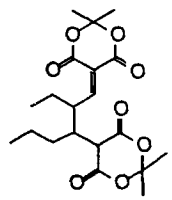
(6.IX.88)

Thioalkylated *Meldrum*'s acid is easily available by treatment of *Meldrum*'s acid with an aldehyde and thiophenol in the presence of catalytical amounts of piperidinium acetate (→**1–6**, *Table 1*). The adducts **1–6** are crystalline, stable compounds and they can be caused to react directly with nucleophiles and dienes (see **3**→**7–12**, *Scheme 1*). The regeneration of the parent olefin is effected thereby by simply dissolving the adduct under neutral or basic conditions. Extension of this method to thiocarboxylic acids allowed the preparation of the corresponding formaldehyde derivatives **13** and **15** *(Table 3)*.

Introduction. – Isopropylidene alkylidenemalonates **i** [1] have achieved considerable interest as highly reactive *Michael* acceptors [2], electron-deficient dienophiles [3], strongly polarized heterodienes [4], and as precursors of the corresponding saturated compounds [5] as well as of methylene ketenes [6].



i



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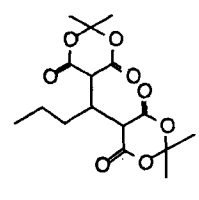

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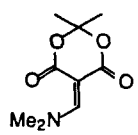

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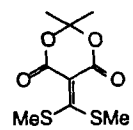


v

Our own interest in these structures stems from their potential as unique alkylating bioprobes [7]. Besides, their reactivity provides special insight into the dynamic character of vinylogous nucleophilic additions.

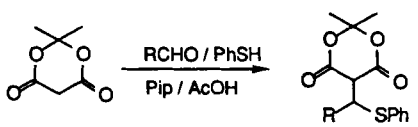
A simple synthetic approach to alkylidenemalonates **i**, the *Knoevenagel* condensation with *Meldrum*'s acid (= 2,2-dimethyl-1,3-dioxane-4,6-dione), has been shown to be efficient in the case of aromatic and α-branched aldehydes [8] as well as for certain ketones [8] [9] or imines [10] [11]. In the reaction of simple aldehydes, however, the olefins tend to be trapped by *Meldrum*'s acid [12], or, as in the case of butyraldehyde, to undergo

a further *Knoevenagel* reaction followed by the *Michael* addition[1]). Several methods have been developed to overcome this problem. Thus, the olefins have been trapped *in situ* with dienes [3a,b], olefins [4], reducing agents [5a,b], indole [2b,d], methoxide [13], and secondary amines [14]. For heteronucleophiles, the addition is reversible, and the olefin can be regenerated by treatment with acid, thus providing an easy access to the alkylidene derivatives **i**. More recently, compounds of type **i** have also been prepared by addition of metallorganic reagents to olefins **iv** and **v** [15] [16].

A limitation, however, of these methods is the use of fairly strong bases combined with the requirement of anhydrous reaction conditions. We have found thio derivatives to be the intermediates of choice for many of these trapping reactions.

Results. – Good yields of the crystalline adducts **1**–**6** were obtained by simply mixing *Meldrum's* acid, aldehyde, and thiophenol in the presence of piperidinium acetate in MeCN, quenching the reaction with an excess of aq. citric-acid solution, and filtering the product *(Table 1)*. Similar results could be obtained by using a variety of different solvents and bases[2]). Due to its high volatility combined with the discrete melting points and crystalline character of the adducts, thiophenol seemed to be the most appropriate thiol. The method seems to be generally applicable to any aldehyde, except formaldehyde.

Table 1. *Synthesis of [1-(Phenylthio)alkyl]malonates* **1**–**6**



	R	M.p. [°]	Yield [%]
1	Me	102	91
2	Et	103–104	88
3	Pr	83–84	92
4	i-Pr	81–82	90
5	$CH_3(CH_2)_5$	96–97	88
6	Ph	98	88

Compounds **1**–**6** were stored at room temperature for several months without decomposition. In solution, partial dissociation occurred as shown in the ^{1}H-NMR spectra[3]). Depending on purity and solvent, characteristic equilibrium ratios of adduct and olefin/thiophenol were observed by ^{1}H-NMR *(Table 2)*.

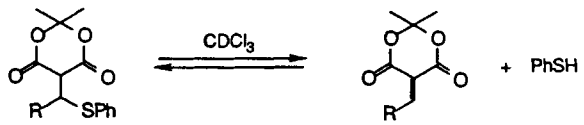
The versatility of compounds **1**–**6** is demonstrated in the case of the butyraldehyde adduct **3** *(Scheme 1)*. Due to the tendency to eliminate thiophenol, adduct **3** showed the same reactivity as the free olefin **7** yielding *e.g.* the epoxide **8** with H_2O_2. In addition, adduct **3** was observed to undergo an oxidative cyclization with *Meldrum's* acid: On trying to eliminate the thiophenol moiety by oxidation with sodium metaperiodate, we obtained cyclopropane derivative **9** as a by-product; the yield of **9** was strongly improved by adding 1 equiv. of *Meldrum's* acid. This suggests that in the formation of **9** from **7**, olefin **7** undergoes addition of H_2O, followed by a *retro*-aldol reaction to generate

[1]) On reacting *Meldrum's* acid with butyraldehyde in MeCN in the presence of catalytical amounts of piperidine, we obtained a 52% yield of the dimer **ii** (m.p. 117–118°), probably the same compound that was believed to be the *Michael* adduct **iii** [13]. Reduction of dimer **ii** with $NaBH_4$ [5c] gave the corresponding alkane (m.p. 65–67°; dec.).

[2]) *E.g.*, with THF or CH_2Cl_2 as solvent and proline or hydrazine as catalyst.

[3]) The same phenomenon has been observed in the case of adducts of cyclic tertiary amines [17].

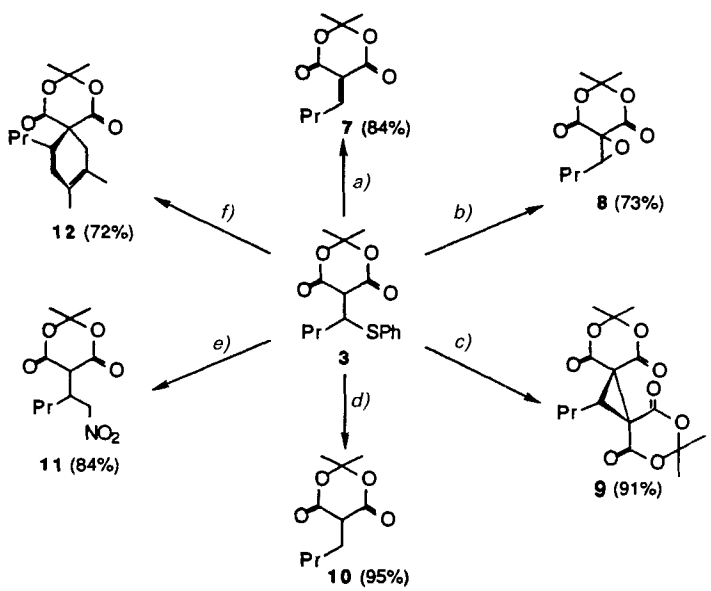
Table 2. *Ratios Adduct/Olefin + Thiophenol*



Adduct	1	2	3	4	5	6
R	Me	Et	Pr	i-Pr	$CH_3(CH_2)_5$	Ph
Adduct/olefin + thiophenol[a])	5.5:1	2.5:1	1:1	1:0	1:0	15:1

[a]) The ratios were determined by integration of the olefin peak (7.9–8.1 ppm) and the methine protons 3.7–4.1 ((H–C(1)) and 3.9–5.2 (H–C(2)) ppm).

Scheme 1



a) $K_3[Fe(CN)_6]$, KOH; *b)* H_2O_2, MeCN; *c) Meldrum's* acid, $NaIO_4$, MeCN/H_2O; *d)* $NaBH_4$, THF/EtOH; *e)* $MeNO_2$, Bu_4NOH, MeOH/THF; *f)* 2,3-dimethyl-1,3-butadiene, CH_2Cl_2.

unsubstituted *Meldrum's* acid. This then adds to olefin **7** as a radical[4]), generated by H-transfer to a phenylthio radical. The radical produced by this addition might then undergo a further H-abstraction followed by a ring closure, to give **9**. The structure is in agreement with elementary analysis as well as spectral data. In addition, we have saponified **9** to the corresponding known tetraacid [18].

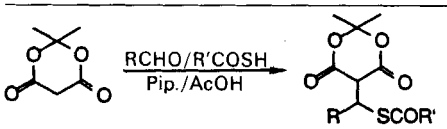
Reaction of **3** with $NaBH_4$, $MeNO_2$, or 2,3-dimethyl-1,3-butadiene gave the alkyl derivative **10**, the nitro compound **11**, and the *Diels-Alder* adduct **12**, respectively.

As mentioned above, probably the most valuable compound, the formaldehyde/thiophenol adduct, was not stable enough to be isolated in pure form. On trying to diversify

[4]) The *Michael* adduct of *Meldrum's* acid to olefin **7** could not be cyclized with sodium metaperiodate in the presence of thiophenol.

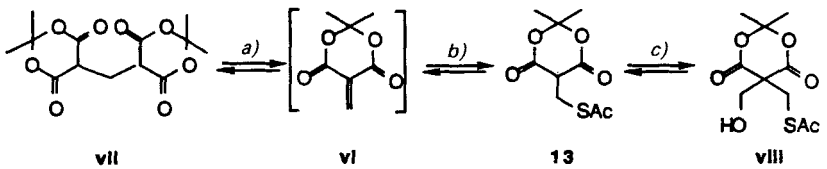
our method, we found, to our astonishment, that the stability of thiocarboxylic-acid adducts was even higher then the one of the corresponding thiophenol adducts. Using thioacetic acid, up to 75% of formaldehyde derivative **13** were obtained *(Table 3)*. Adducts **14** and **15** were prepared similarly. The intermediate on the way to **13**, the methylidene-substituted *Meldrum*'s acid **vi**, is initially not only trapped by the thioacid,

Table 3. *Synthesis of [1-(Thiocarboxy)alkyl]malonates* **13–15**



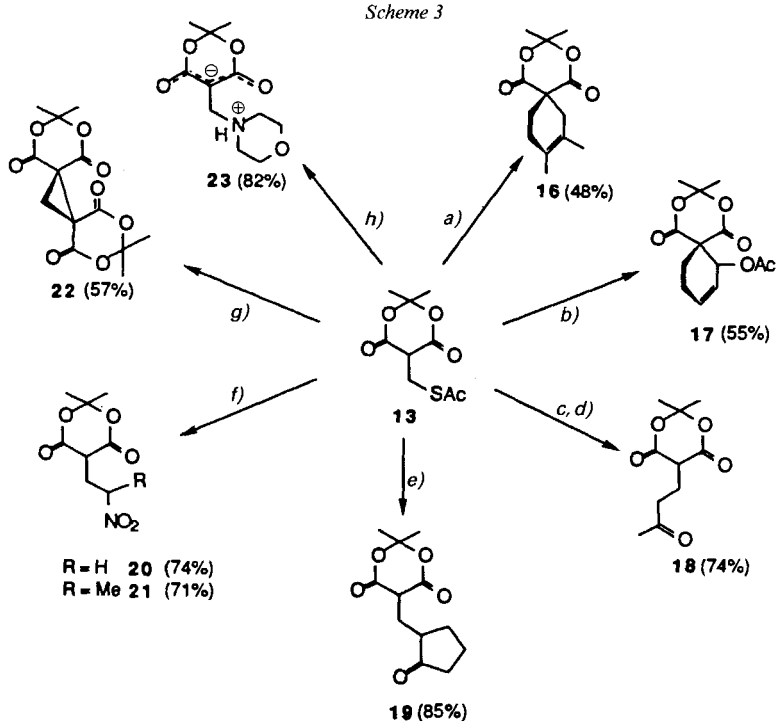
	R, R'	M.p. [°]	Yield [%]
13	H, Me	108–109 (dec.)	75
14	Me, Me	105	94
15	H, Ph	110–111 (dec.)	68

Scheme 2



a) Meldrum's acid; *b)* AcSH; *c)* HCHO.

Scheme 3



a) 2,3-Dimethyl-1,3-butadiene, DMSO; *b)* 1,3-butadienyl acetate, DMSO; *c)* 2-methoxypropene, K_2CO_3, MeCN; *d)* H^+; *e)* morpholinocyclopentanone enamine, MeCN; *f)* RCH_2NO_2, Bu_4NOH, THF; *g) Meldrum*'s acid, $NaIO_4$, MeCN, H_2O; *h)* morpholine, MeCN.

but also by *Meldrum*'s acid to give the known diisopropylidene methylenedimalonate (**vii**) [12a]. Thus, on quenching the reaction at an early stage, different mixtures of *Michael* adduct **vii**, thioacetic-acid adduct **13**, and formaldehyde adduct **viii** *(Scheme 2)* were obtained. On longer reaction times using 1.3 equiv. of formaldehyde, only **13** was isolated[5]).

In addition to the well known reaction of methylidene-substituted *Meldrum*'s acid with dienes (→**16**, **17**) [3a, b] [15], **13** reacted with enol ethers [4c] and nucleophiles such as nitronates and enamines under mild conditions (→**18**–**21**; *Scheme 3*). The parent olefin could, thereby, be generated under neutral or basic conditions. In analogy to the transformation **3**→**9** (see *Scheme 1*), **13** gave **22**. Reaction of **13** with morpholine, finally, gave a good yield of the *Mannich* adduct **23**, as stable compound that should also allow the generation of the methylidene-substituted *Meldrum*'s acid under acidic conditions [14].

We acknowledge and appreciate the support of the *National Science Foundation*, Synthetic Organic and Natural Products Division, grant CHE8421137 AO2, and the *NSF* Instrumentation Program.

Experimental Part

1. *General.* H_2O-sensitive reactions were carried out in oven-dried flasks (120°) under N_2. THF was distilled over Na/benzophenone just prior to use. MeCN was stored over 4-Å molecular sieves. Solns. were dried ($MgSO_4$) and evaporated < 40° in a *Büchi* rotary evaporator. TLC: *Merck* precoated silica gel *60 F-254* plates, detection by UV and phosphomolybdic acid. M.p. (of recrystallized products, uncorrected): *Thomas-Hoover-Uni-Melt* apparatus. IR: *Nicolet 60-SX;* KBr pellets. ^{1}H- and ^{13}C-NMR: *Bruker AM-300* or *Bruker WM-360;* chemical shifts δ in ppm rel. to TMS as internal standard, coupling constants J in Hz; the solvent used for ^{13}C-NMR and ^{1}H-NMR was always the same. MS: *Finnigan 4021 GCMS/DS* by direct probe sample introduction; chemical ionization (CI) was accomplished with NH_3. Elemental analyses were performed by *Spang Microanalytical Laboratories*, Eagle Harbor, Mi.

2. *Synthesis of* **1**–**6**. 2.1. *General Procedure.* Crystalline piperidinium acetate (0.1 equiv.) was added with stirring to a cooled soln. (5°) of *Meldrum*'s acid (= isopropylidene malonate; 1 equiv.), aldehyde, and thiophenol (1.05 equiv. each) in MeCN. After 1 h, the cooling bath was removed and stirring was continued for 2–4 h (TLC). The reaction was quenched by slowly adding an excess of aq. 10% citric-acid soln. The product was filtered, washed sequentially with H_2O and Et_2O/pentane 1:5 and finally dried under high vacuum. Care should be taken in drying and recrystallizing of the products since heating over 40° can cause decomposition!

2.2. *Isopropylidene 2-(Phenylthio)propane-1,1-dicarboxylate (= 2,2-Dimethyl-5-[1-(phenylthio)ethyl]-1,3-dioxane-4,6-dione;* **1**). *Meldrum*'s acid (2.00 g, 13.9 mmol), thiophenol, and acetaldehyde in 30 ml of MeCN at 5° in a closed flask: 3.54 g (91%) of **1**. M.p. (AcOEt/hexane) 102°. IR: 1779*m*, 1747*s*, 1386*s*, 1328*s*, 1317*s*, 1270*m*, 1233*m*, 1205*m*, 1188*m*, 1055*m*, 1026*m*, 985*m*, 876*m*, 752*m*. ^{1}H-NMR ($CDCl_3$): 7.55–7.21 (*m*, 5 arom. H); 4.10 (*dq*, J = 2.6, 7.1, H–C(2)); 3.84 (*d*, J = 2.6, H–C(1)); 1.77 (*s*, Me); 1.75 (*s*, Me); 1.60 (*d*, J = 7.1, 3 H–C(3)); olefin (+ thiophenol): 8.03 (*q*, J = 7.5, H–C(2)); 2.49 (*d*, J = 7.5, 3 H–C(3)); 1.74 (*s*, 2 Me); ratio 5.5:1. ^{13}C-NMR: 163.8; 163.4; 135.3; 132.1; 129.2; 127.7; 105.2; 52.0; 42.9; 28.4; 27.2; 19.2. MS: 280 (14, M^+), 113 (18), 112 (19), 110 (50), 109 (19), 84 (15), 69 (100), 68 (37). Anal. calc. for $C_{14}H_{16}O_4S$ (280.34): C 59.98, H 5.75, S 11.44; found: C 59.89, H 5.73, S 11.48.

2.3. *Isopropylidene 2-(Phenylthio)butane-1,1-dicarboxylate (= 2,2-Dimethyl-5-[1-(phenylthio)propyl]-1,3-dioxane-4,6-dione;* **2**). *Meldrum*'s acid (2.00 g, 13.9 mmol), thiophenol, and propionaldehyde in 20 ml of MeCN: 3.61 g (88%) of **2**. M.p. (AcOEt/hexane) 103–104°. IR: 1778*m*, 1748*s*, 1386*m*, 1322*m*, 1292*m*, 1209*m*, 1181*m*, 1067*m*, 882*m*, 751*m*. ^{1}H-NMR ($CDCl_3$): 7.55–7.15 (*m*, 5 arom. H); 3.88 (*ddd*, J = 2.3, 5.8, 8.2, H–C(2)); 3.84 (*d*, J = 2.3, H–C(1)); 2.18–2.08 (*m*, 1 H); 1.97–1.87 (*m*, 1 H); 1.78 (*s*, Me); 1.75 (*s*, Me); 1.08 (*t*, J = 7.3, 3 H–C(4)); olefin (+thiophenol): 7.91 (*t*, J = 7.5, H–C(2)); 2.95 (*dq*, J = 7.5, 7.5, 2 H–C(3)); 1.75 (*s*, Me); 1.21 (*t*, J = 7.5, 3 H–C(4)); ratio 2.5:1. ^{13}C-NMR: 164.1; 164.0; 135.8; 131.8; 129.2; 127.5; 105.3; 51.1; 50.3; 28.4; 27.6; 27.4; 12.9. MS: 294 (18, M^+), 127 (15), 110 (54), 109 (29), 108 (28), 83 (100), 66 (20). Anal. calc. for $C_{15}H_{18}O_4S$ (294.37): C 61.20, H 6.16, S 10.89; found: C 61.09, H 6.16, S 10.83.

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[5]) An excess of formaldehyde was required to assure complete conversion of **vii** to **13** (and **viii**).

2.4. *Isopropylidene 2-(Phenylthio)pentane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-[1-(phenylthio)butyl]-1,3-dioxane-4,6-dione*; **3**). *Meldrum's* acid (10.00 g, 69.4 mmol), thiophenol, and butyraldehyde in 20 ml of MeCN: 1970 g (92%) of **3**. M.p. (AcOEt/hexane) 83–84°. IR: 1784*s*, 1745*s*, 1580*m*, 1481*s*, 1462*m*, 1438*s*, 1339*m*, 1330*s*, 1306*s*, 1272*s*, 1215*s*, 1210*s*, 1055*s*, 1004*m*, 983*m*, 738*m*, 728*m*, 690*m*. ^{1}H-NMR ($CDCl_3$): 7.53–7.13 (*m*, 5 arom. H); 3.98 (*ddd*, *J* = 2.3, 5.4, 7.8, H–C(2)); 3.83 (*d*, *J* = 2.3, H–C(1)); 2.17–2.03 (*m*, 1 H); 1.87–1.73 (*m*, 1 H); 1.78 (*s*, Me); 1.74 (*s*, Me); 1.79–1.60 (*m*, 1 H); 1.48–1.36 (*m*, 1 H); 0.91 (*t*, *J* = 7.4, 3 H–C(5)); olefin **7** (+thiophenol): see *3.1*; ratio 1:1. ^{13}C-NMR: 163.9 (2); 135.7; 131.7; 129.1; 127.4; 105.2; 51.3; 48.1; 36.3; 28.3; 27.3; 21.2; 13.6. MS: 308 (4, M^+), 141 (22), 140 (16), 123 (15), 122 (62), 110 (100), 109 (28), 97 (23), 94 (34), 84 (21), 68 (48), 66 (54). Anal. calc. for $C_{16}H_{20}O_4S$ (380.40): C 62.31, H 6.54, S 10.40; found: C 62.23, H 6.62, S 10.45.

2.5. *Isopropylidene 3-Methyl-2-(phenylthio)butane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-[2-methyl-1-(phenylthio)propyl]-1,3-dioxane-4,6-dione*; **4**). *Meldrum's* acid (2.00 g, 13.9 mmol), thiophenol, and isobutyraldehyde in 5 ml of MeCN: 1.93 g (90%) of **4**. M.p. (AcOEt/hexane) 81–82°. IR: 2974*m*, 1783*s*, 1742*s*, 1483*m*, 1440*m*, 1392*m*, 1384*m*, 1371*m*, 1324*s*, 1289*s*, 1219*m*, 1203*s*, 1064*m*, 886*m*, 741*m*. ^{1}H-NMR ($CDCl_3$): 7.51–7.22 (*m*, 5 arom. H); 3.95 (*dd*, *J* = 1.7, 10.6, H–C(2)); 3.73 (*d*, *J* = 1.7, H–C(1)); 2.62–2.46 (*m*, H–C(3)); 1.80 (*s*, Me); 1.74 (*s*, Me); 1.18 (*d*, *J* = 6.6, Me–C(3)); 1.02 (*d*, *J* = 6.7, Me–C(3)). ^{13}C-NMR: 164.8; 164.1; 136.3; 131.1; 129.1; 127.2; 105.3; 55.6; 49.7; 32.6; 28.4; 27.7; 22.0; 21.3. MS: 308 (3, M^+), 123 (18), 122 (32), 110 (47), 109 (67), 97 (67), 69 (22), 66 (35), 43 (100). Anal. calc. for $C_{16}H_{20}O_4S$ (308.40): C 62.31, H 6.54, S 10.40; found: C 62.35, H 6.61, S 10.32.

2.6. *Isopropylidene 2-(Phenylthio)octane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-[1-(phenylthio)heptyl]-1,3-dioxane-4,6-dione*; **5**). *Meldrum's* acid (1.00 g, 6.9 mmol), thiophenol, and heptanal in 10 ml of MeCN: 2.14 g (88%) of **5**. M.p. (AcOEt/hexane) 96–97°. IR: 2925*s*, 1785*m*, 1747*s*, 1482*m*, 1397*m*, 1388*m*, 1338*s*, 1330*s*, 1310*m*, 1272*m*, 1219*m*, 1203*s*, 1066*m*, 996*m*, 982*m*. ^{1}H-NMR ($CDCl_3$): 7.50–7.21 (*m*, 5 arom H); 3.96 (*ddd*, *J* = 2.4, 5.6, 9.5, H–C(2)); 3.82 (*d*, *J* = 2.4, H–C(1)); 2.15–2.05 (*m*, 1 H); 1.88–1.78 (*m*, 1 H); 1.78 (*s*, Me); 1.74 (*s*, Me); 1.67–1.55 (*m*, 1 H); 1.43–1.18 (*m*, 7 H); 0.87 (*t*, *J* = 7.5, 3 H–C(8)). ^{13}C-NMR: 164.0 (2); 135.7; 131.8; 129.2; 127.4; 105.2; 51.3; 48.4; 34.2; 31.6; 28.8; 28.3; 28.0; 27.4; 22.5; 14.0. MS: 350 (2, M^+), 194 (9), 164 (19), 139 (37), 110 (80), 109 (46), 108 (37), 69 (40), 68 (54), 67 (18), 66 (37), 55 (100). Anal. calc. for $C_{19}H_{26}O_4S$ (350.48): C 65.11, H 7.48, S 9.15; found: C 65.23, H 7.42, S 9.22.

2.7. *Isopropylidene 2-Phenyl-2-(phenylthio)ethane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-[α-(phenylthio)-benzyl]-1,3-dioxane-4,6-dione*; **6**). *Meldrum's* acid (1.00 g, 6.9 mmol), thiophenol, and benzaldehyde in 10 ml of MeCN: 2.10 g (88%) of **6**. M.p. (AcOEt/hexane) 98°. IR: 3060*w*, 1789*s*, 1740*s*, 1583*m*, 1496*m*, 1438*m*, 1393*s*, 1386*s*, 1345*s*, 1332*s*, 1231*s*, 1207*s*, 1069*s*, 738*s*, 709*s*. ^{1}H-NMR ($CDCl_3$): 7.62-7.20 (*m*, 2 Ph); 5.21 (*d*, *J* = 2.7, H–C(2)); 4.13 (*d*, *J* = 2.7, H–C(1)); 1.67 (*s*, Me); 1.43 (*s*, Me). ^{13}C-NMR: 163.6; 163.5; 138.4; 135.4; 131.7; 129.1 (2); 128.6; 128.2; 127.7; 105.5; 53.2; 51.9; 28.2; 27.7. MS: 342 (0.3, M^+), 175 (19), 174 (55), 146 (17), 110 (100), 109 (25), 102 (28), 84 (18), 66 (38). Anal. calc. for $C_{19}H_{18}O_4S$ (342.41): C 66.65, H 5.30, S 9.36; found: C 66.69, H 5.21, S 9.43.

3. *Transformations of* **3**. 3.1. *Isopropylidene 1-Penten-1,1-dicarboxylate* (= *5-Butylidene-2,2-dimethyl-1,3-dioxane-4,6-dione*; **7**). A soln. of **3** (6.00 g, 19.5 mmol) in MeCN (15 ml) was shaken with an aq. KOH soln. (2M, 80 ml) in a separatory funnel. A cooled, aq. soln. of $K_3[Fe(CN)_6]$ (7.20 g, 21.9 mmol, in 80 ml) was added with shaking. After 2 washings with Et_2O (100 ml), the aq. phase was added dropwise to a 10% HCl soln. (150 ml) at 5°. Extraction with Et_2O (60 ml), drying, and bulb-to-bulb distillation (100°/0.1 Torr) yielded 3.24 g (84%) of pure **7** as a colorless oil ([13]: m.p. 33–36°). ^{1}H-NMR ($CDCl_3$): 7.89 (*t*, *J* = 7.5, H–C(2)); 2.88 (*'q'*, *J* = 7.5, 2 H–C(3)); 1.70 (*s*, 2 Me); 1.66–1.52 (*m*, 2 H–C(4)); 0.97 (*t*, *J* = 7.5, 3 H–C(5)).

3.2. *Isopropylidene 1,2-Epoxypentane-1,1-dicarboxylate* (= *2,2-Dimethyl-3'-propylspiro[1,3-dioxane-5,2'-oxirane]-4,6-dione*; **8**). H_2O_2 (30%, 6 ml) was added at r.t. to a soln. of **3** (3.00 g, 9.7 mmol) in MeCN (30 ml). After 30 min, Et_2O (50 ml) was added. The org. phase was separated and washed with brine (30 ml). Drying, concentration under vacuum, and recrystallization from Et_2O/hexane yielded 1.52 g (73%) of **8** as colorless needles. M.p. 60–61°. IR: 2957*w*, 1791*s*, 1766*s*, 1394*m*, 1378*m*, 1348*m*, 1278*m*, 1229*m*, 1219*m*, 1205*m*, 1166*m*, 937*m*, 920*m*. ^{1}H-NMR ($CDCl_3$): 3.65 (*t*, *J* = 6.1, H–C(1)); 1.83 (*s*, 2 Me); 1.81–1.76 (*m*, 2 H); 1.70–1.52 (*m*, 2 H); 1.02 (*t*, *J* = 7.2, 3 H–C(5)). ^{13}C-NMR: 163.7; 161.8; 105.8; 68.4; 55.2; 28.7; 28.0; 27.7; 19.5; 13.7. CI-MS: 233 (13, $M^+ + 19$), 232 (100, $M^+ + 18$), 136 (4), 94 (6), 76 (10). Anal. calc. for $C_{10}H_{14}O_5$ (214.22): C 56.07, H 6.59; found: C 56.03, H 6.55.

3.3. *1,1:2,2-Diisopropylidene 3-Propylcyclopropane-1,1,2,2-tetracarboxylate* (= *2,2,2'',2''-Tetramethyl-3'-propyldispiro[1,3-dioxane-5,1'-cyclopropane-2',5''-1'',3''-dioxane]-4,4'',6,6''-tetrone*; **9**). A soln. of $NaIO_4$ (3.00 g, 14.0 mmol) in H_2O (40 ml) was added dropwise at 5° within 10 min to a stirred soln. of **3** (4.0 g, 13.0 mmol) and *Meldrum's* acid (1.90 g, 13.2 mmol) in MeCN (40 ml). The mixture turned red and a precipitate formed. After a further 15 min, H_2O was added, and the solid was filtered and washed carefully with H_2O (100 ml) and Et_2O (100 ml). Drying under high vacuum yielded 4.01 g (91%) of **9**. The diphenyl disulfide was easily recovered out of the

org. washings. The recrystallized (AcOEt/hexane) product decomposed on heating at *ca.* 191°. IR: 1801*m*, 1764*s*, 1398*m*, 1386*m*, 1282*s*, 1269*s*, 1251*m*, 1232*m*, 1205*s*. ^{1}H-NMR ($CDCl_3$): 3.23 (*t*, *J* = 7.8, H–C(3)); 2.05 (*'q'*, *J* = 7.6 (the 2 center peaks show up as *t*'s, *J* = 2.1), $CH_3CH_2CH_2$); 1.84 (*s*, 2 Me); 1.77 (*s*, 2 Me); 1.63 (*'sext.'*, *J* = 7.5 (the 2 center peaks show up as *t*'s, *J* = 2.1), $CH_3CH_2CH_2$); 1.03 (*t*, *J* = 7.5, $CH_3CH_2CH_2$). ^{13}C-NMR: 161.7; 159.2; 106.1; 42.3; 40.7; 28.1; 26.9; 25.2; 21.3; 13.6. CI-MS: 359 (18, $M^+ + 19$), 358 (100, $M^+ + 18$), 136 (4), 93 (6). Anal. calc. for $C_{16}H_{20}O_8$ (340.33): C 56.47, H 5.92; found: C 56.26, H 5.92.

3.4. *Isopropylidene Pentane-1,1-dicarboxylate* (= *5-Butyl-2,2-dimethyl-1,3-dioxane-4,6-dione;* **10**). $NaBH_4$ (1.00 g, 26.4 mmol) was added in 3 portions to a soln. at 5° of **3** (2.00 g, 6.5 mmol) in THF/EtOH 10:1 (20 ml). Upon adding the 1st portion of $NaBH_4$, the mixture turned deeply yellow. Then, the color faded. After 1 h stirring, the suspension was acidified with 10% HCl soln. and extracted with Et_2O (50 ml). The org. phase was washed with brine (50 ml), dried, and evaporated (drying under high vacuum) to yield 1.24 g (95%) of **10**. M.p. 59–61° ([5b]: 58–60°).

3.5. *Isopropylidene 2-(Nitromethyl)pentane-1,1-dicarboxylate* (= *1-(Nitromethyl)butyl-2,2-dimethyl-1,3-dioxane-2,6-dione;* **11**). Bu_4NOH (*Aldrich*, 1M in MeOH; 14 ml) was added dropwise at 5° to a soln. of **3** (2.00 g, 6.5 mmol) and nitromethane (1.00 g, 16.4 mmol) in THF (10 ml). After 2 h at r.t., 10% HCl soln. (50 ml) was added. Extraction with Et_2O (50 ml), washing of the org. phase with brine (50 ml), drying, concentration, and recrystallization from Et_2O/hexane yielded 1.41 g (84%) of **11**. M.p. 98–99°. IR: 2883*m*, 1778*s*, 1743v*s*, 1735v*s*, 1545v*s*, 1398*m*, 1387*m*, 1358*m*, 1328*s*, 1293*m*, 1241*m*, 1206*m*, 1065*m*, 1011*m*, 874*m*. ^{1}H-NMR ($CDCl_3$): 4.95 (*dd*, *J* = 8.3, 11.2, 1 H–C(3)); 4.56 (*dd*, *J* = 3.8, 11.2, 1 H–C(3)); 3.90 (*d*, *J* = 2.1, H–C(1)); 3.32–3.22 (*m*, 14 lines, H–C(2)); 1.81 (*s*, Me); 1.78 (*s*, Me); 1.62–1.30 (*m*, 4 H); 0.94 (*t*, *J* = 7.2, 3 H–C(5)). ^{13}C-NMR: 164.1 (2); 105.5; 76.0; 47.0; 36.2; 31.5; 28.2; 26.8; 20.6; 13.7. CI-MS: 278 (15, $M^+ + 19$), 277 (100, $M^+ + 18$), 219 (4), 192 (6). Anal. calc. for $C_{11}H_{17}NO_6$ (259.26): C 50.96, H 6.61, N 5.40; found: C 51.05, H 6.82, N 5.43.

3.6. *Isopropylidene 3,4-Dimethyl-6-propylcyclohex-3-ene-1,1-dicarboxylate* (= *2',2',3,4-Tetramethyl-6-propylspiro[3-cyclohexene-1,5'-1',3'-dioxane]-4',6'-dione;* **12**). A soln. of 2,3-dimethyl-1,3-butadiene (1.50 g, 18.3 mmol) in CH_2Cl_2 (5 ml) was added, at 5°, to a soln. of **3** (2.00 g, 6.5 mmol) in CH_2Cl_2 (30 ml). After 6 h at r.t., the mixture was evaporated and recrystallized from Et_2O/hexane (−15°): 1.31 g (72%) of **12**. M.p. 97–99°. IR: 2959*w*, 2874*w*, 1783*s*, 1744*s*, 1396*m*, 1388*m*, 1340*m*, 1330*s*, 1305*m*, 1272*m*, 1214*m*, 1202*m*. ^{1}H-NMR ($CDCl_3$): 2.70 (*d*, *J* = 17.2, H–C(2)); 2.35–2.22 (*m*, 1 H); 2.17 (*d*, *J* = 17.2, H–C(2)); 2.12–1.91 (*m*, 2 H); 1.67 (*s*, 2 Me); 1.62 (*s*, Me); 1.57 (*s*, Me); 1.46–1.34 (*m*, 1 H); 1.27–1.02 (*m*, 2 H); 0.85–0.77 (*m*, 4 H). ^{13}C-NMR: 171.9; 167.0; 125.4; 119.4; 104.2; 52.9; 40.8; 38.9; 34.2; 33.7; 29.9; 28.1; 19.9; 18.8; 18.1; 13.6. MS: 280 (8, M^+), 222 (14), 152 (13), 151 (100), 150 (37), 149 (40), 107 (91), 91 (39). Anal. calc. for $C_{16}H_{24}O_4$ (280.36): C 68.55, H 8.63; found: C 68.68, H 8.55.

4. *Synthesis of* **3**–**15**. 4.1. *General Procedure*. A soln. of *Meldrum's* acid (1 equiv.), aldehyde (1.0–1.3 equiv.), thiocarboxylic acid (1.05 equiv.), and piperidinium acetate (0.1 equiv.) in MeCN was stirred for *ca.* 20 h at r.t. The mixture was worked up as described for **1**–**6**. In the case of **13** and **14**, a precipitate, mainly diisopropylidene methylenedimalonate, formed after *ca.* 2 h.

4.1. *Isopropylidene 2-(Acetylthio)ethane-1,1-dicarboxylate* (= *5-[(Acetylthio)methyl]-2,2-dimethyl-1,3-dioxane-4,6-dione;* **13**). *Meldrum's* acid (10.00 g, 69.4 mmol), thioacetic acid (*Aldrich*, 90%; 6.0 ml, 75.6 mmol) and formalin (*Aldrich*, 37%; 6.9 ml, 92.1 mmol) in 10 ml of MeCN: 12.05 g (75%) of **13**. M.p. (AcOEt/hexane): 108–109° (dec.). IR: 1785*m*, 1743*s*, 1679*s*, 1398*m*, 1389*m*, 1362*m*, 1341*s*, 1291*s*, 1275*m*, 1205*m*, 1096*m*, 1065*m*. ^{1}H-NMR ($CDCl_3$): 3.95 (*t*, *J* = 5.5, H–C(1)); 3.51 (*d*, *J* = 5.5, 2 H–C(2)); 2.32 (*s*, AcS); 1.82 (*s*, Me); 1.75 (*s*, Me). ^{13}C-NMR: 194.5; 163.8 (2); 105.4; 47.1; 30.1; 28.3; 26.2; 24.4. CI-MS: 174 (40, $M^+ + 18 -$ AcSH), 133 (7), 116 (6), 76 (100). Anal. calc. for $C_9H_{12}O_5S$ (232.25): C 46.54, H 5.21, S 13.81; found: C 46.48, H 5.26, S 13.86.

4.2. *Isopropylidene 2-(Acetylthio)propane-1,1-dicarboxylate* (= *5-[1-(Acetylthio)ethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione;* **14**). *Meldrum's* acid (2.00 g, 13.9 mmol), thioacetic acid (1.2 ml, 15.1 mmol), and acetaldehyde (0.9 ml, 16.1 mmol) at 5° in 10 ml of MeCN in a tightly stoppered flask: 3.21 g (94%) of **14**. M.p. (AcOEt/hexane) 105°. IR: 1777*m*, 1737*s*, 1684*m*, 1389*m*, 1338*m*, 1320*m*, 1067*m*, 987*m*, 882*m*. ^{1}H-NMR ($CDCl_3$): 4.50 (*dq*, *J* = 2.9, 7.1, H–C(2)); 3.94 (*d*, *J* = 2.9, H–C(1)); 2.29 (*s*, AcS); 1.78 (*s*, Me); 1.73 (*s*, Me); 1.39 (*d*, *J* = 7.1, 3 H–C(3)). ^{13}C-NMR: 195.1; 163.3; 163.0; 105.2; 51.4; 35.3; 30.1; 28.3; 26.4; 17.2. CI-MS: 232 (7), 189 (9), 188 (100, $M^+ + 18 -$ AcSH), 147 (11), 76 (82). Anal. calc. for $C_{10}H_{14}O_5S$ (246.28): C 48.77, H 5.73, S 13.02; found: C 48.84, H 5.87, S 13.00.

4.3. *Isopropylidene 2-(Benzoylthio)ethane-1,1-dicarboxylate* (= *5-[(Benzoylthio)methyl]-2,2-dimethyl-1,3-dioxane-4,6-dione;* **15**). *Meldrum's* acid (3.00 g, 20.8 mmol), thiobenzoic acid (2.5 ml, 21.2 mmol), and formalin (*Aldrich*, 37%; 1.50 ml, 20.0 mmol): 4.16 g (68%) of **15**, after recrystallization from EtOAc/hexane[6]). M.p. 110–111° (dec.). IR: 1790*m*, 1751*s*, 1671*m*, 1665*m*, 1385*m*, 1332*m*, 1271*m*, 1207*m*, 1177*m*, 1066*m*, 928*m*. ^{1}H-NMR

[6]) The crude product contained diisopropylidene methylenedimalonate.

($CDCl_3$): 7.96 (*d*, *J* = 7.9, 2 arom. H); 7.58 (*t*, *J* = 7.9, 1 arom. H); 7.45 (*t*, *J* = 7.9, 2 arom. H); 3.99 (*t*, *J* = 5.6, H–C(1)); 3.75 (*d*, *J* = 5.6, 2 H–C(2)); 1.83 (*s*, Me); 1.78 (*s*, Me). CI-MS: 312 (6, $M^+ + 18$), 228 (13), 191 (27), 174 (100), 173 (23), 156 (45), 139 (64), 136 (20), 76 (21). Anal. calc. for $C_{14}H_{14}O_5S$ (294.33): C 57.13, H 4.79, S 10.89; found: C 57.17, H 4.83, S 10.91.

5. *Transformations of* **13**. 5.1. *Isopropylidene 3,4-Dimethylcyclohex-3-ene-1,1-dicarboxylate* (= *2',2',3,4-Tetramethylspiro[3-cyclohexene-1,5'-1',3'-dioxane]-4',6'-dione;* **16**). At r.t., 2,3-dimethyl-1,3-butadiene (2.00 g, 24.4 mmol) was added to a soln. of **13** (2.00 g, 8.6 mmol) in DMSO (3 ml). After 16 h, the mixture was diluted with CH_2Cl_2 (20 ml) and washed with H_2O. Drying and recrystallization from Et_2O/hexane gave 0.99 g (48%) of **16**. M.p. 88° ([3a]: 87–88°).

5.2. *Isopropylidene 2-Acetoxycyclohex-3-ene-1,1-dicarboxylate* (= *2-Acetoxy-2',2'-dimethylspiro[3-cyclohexene-1,5'-1',3'-dioxane]-4',6'-dione;* **17**). A mixture of **13** (2.0 g, 8.6 mmol) and 1,3-butadienyl acetate [20] (1.90 g, 17.1 mmol) in DMSO (3 ml) was stirred overnight. The mixture was diluted with CH_2Cl_2 (30 ml) and twice washed with brine (40 ml). Drying, evaporation of the solvent, trituration of the resulting oil with Et_2O, and filtering yielded 1.28 g (55%) of **17** as a single isomer. M.p. (AcOEt/hexane; premelted sample) 156–157°. IR: 1787*m*, 1751*s*, 1396*m*, 1385*m*, 1321*m*, 1302*m*, 1274*m*, 1237*s*, 1200*s*, 1031*m*, 937*m*. ^{1}H-NMR ($CDCl_3$): 5.92–5.83 (*m*, H–C(2), H–C(3)); 5.60–5.53 (*m*, H–C(4)); 2.32–2.08 (*m*, 4 H); 1.93 (*s*, AcO); 1.65 (*s*, 2 Me). ^{13}C-NMR: 169.3; 169.1; 163.8; 129.4; 123.4; 104.9; 71.9; 51.3; 30.9; 28.8; 28.5; 21.7; 20.5. CI-MS: 287 (14, $M^+ + 19$), 286 (100, $M^+ + 18$), 228 (15), 184 (40), 141 (54), 124 (47), 107 (69). Anal. calc. for $C_{13}H_{16}O_6$ (268.27): C 58.20, H 6.01; found: C 58.02, H 6.06.

5.3. *Isopropylidene 4-Oxopentane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-(3-oxobutyl)-1,3-dioxane-4,6-dione;* **18**). To a soln. of **13** (2.00 g, 8.6 mmol) in MeCN (20 ml), 2-methoxypropene (2.0 g, 27.7 mmol) and finely powdered anh. K_2CO_3 (1.50 g, 10.7 mmol) were simultaneously added. After efficient stirring for *ca.* 1 h (TLC), the excess enol ether was removed under vacuum and the suspension acidified by dropwise addition of 10% aq. HCl soln. (10 ml). The product was extracted with CH_2Cl_2 (30 ml), the org. phase dried, filtered, and evaporated. Trituration of the resulting oil with Et_2O/hexane 1:2 and filtering gave 1.37 g (74%) of **18** as colorless leaflets. M.p. (AcOEt/hexane) 118°. IR: 1787*s*, 1749*s*, 1709*s*, 1384*s*, 1354*m*, 1300*s*, 1227*m*, 1204*m*, 1165*m*, 1050*m*, 1011*m*, 987*m*. ^{1}H-NMR ($CDCl_3$): 3.84 (*t*, *J* = 5.6, H–C(1)); 2.70 (*t*, *J* = 7.1, 2 H–C(3)); 2.23 ('*q*', *J* = 6.7, 2 H–C(2)); 2.10 (*s*, 3 H–C(5)); 1.76 (*s*, Me); 1.71 (*s*, Me). ^{13}C-NMR: 207.7; 165.1; 104.9; 44.6; 39.2; 29.8; 28.4; 26.2; 20.0. CI-MS: 233 (12, $M^+ + 19$), 232 (100, $M^+ + 18$), 147 (5). Anal. calc. for $C_{10}H_{14}O_5$ (214.22): C 56.07, H 6.59; found: C 55.98, H 6.75.

5.4. *Isopropylidene 2-(2-Oxocyclopentyl)ethane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-[(2-oxocyclopentyl)-methyl]-1,3-dioxane-4,6-dione;* **19**). To a soln. of **13** (2.00 g, 8.6 mmol) at 5° in MeCN (20 ml), morpholinocyclopentanone enamine (3.00 g, 20.1 mmol) was added within 15 min. The mixture turned yellow and a precipitate formed. After stirring for further 15 min at 5° 10% aq. HCl soln. (20 ml) was added. The colorless clear soln. was stirred for 1 h at r.t. The product was extracted with CH_2Cl_2 (3 × 20 ml). On standing, a further amount of product crystallized out of the aq. soln. Drying ($MgSO_4$), evaporation of the solvent, drying under high vacuum, and trituration with pentane yielded 1.75 g (85%) of **19** as colorless crystals. M.p. 143° (AcOEt/hexane, dec.). IR: 1791*m*, 1745*s*, 1731*s*, 1384*m*, 1366*m*, 1343*m*, 1324*m*, 1305*m*, 1284*m*, 1208*m*, 1198*m*. ^{1}H-NMR ($CDCl_3$): 4.42 (*dd*, *J* = 3.4, 7.8, H–C(1)); 2.65–2.52 (*m*, 1 H); 2.35–1.94 (*m*, 7 H); 1.81 (*s*, Me); 1.73 (*s*, Me); 1.63–1.48 (*m*, 1 H). ^{13}C-NMR: 214.0; 165.7; 165.4; 104.9; 44.2; 43.3; 38.4; 30.5; 28.5; 26.2 (2); 20.5. CI-MS: 259 (13, $M^+ + 19$), 258 (100, $M^+ + 18$), 200 (9), 173 (8), 156 (10). Anal. calc. for $C_{12}H_{16}O_5$ (240.26): C 59.99, H 6.71; found: C 59.79, H 6.83.

5.5. *Isopropylidene 3-Nitropropane-1,1-dicarboxylate* (= *5-(2-Nitroethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione;* **20**). Bu_4NOH (*Aldrich*, 1M in MeOH; 20 ml) was added dropwise within 15 min at 5° to a soln. of **13** (2.00 g, 8.6 mmol) and nitromethane (1.50 g, 24.6 mmol) in MeCN (10 ml). After stirring for 15 min at 5°, the mixture was acidified with 10% HCl soln. (50 ml). The mixture was extracted with CH_2Cl_2 (40 ml), the org. phase concentrated and triturated with H_2O, and the resulting crystalline slurry filtered, washed sequentially with H_2O and Et_2O/pentane 1:1, and dried under high vacuum to yield 1.39 g (74%) of **20** as a colorless powder. M.p. 135–136° (dec.). IR: 1785*m*, 1734*s*, 1555*s*, 1388*m*, 1375*m*, 1359*m*, 1302*m*, 1201*m*, 1071*m*, 979*m*, 878*m*. ^{1}H-NMR ((D_6)DMSO): 4.71 (*t*, *J* = 7.1, 2 H–C(3)); 4.52 (*t*, *J* = 5.0, H–C(1)); 2.53 ('*q*', *J* = 6.3, 2 H–C(2)); 1.80 (*s*, Me); 1.67 (*s*, Me). ^{13}C-NMR: 165.3; 105.2; 72.7; 43.5; 28.0; 25.6; 22.8. CI-MS: 236 (10, $M^+ + 19$), 235 (100, $M^+ + 18$). Anal. calc. for $C_8H_{11}NO_6$ (217.18): C 44.24, H 5.11, N 6.45; found: C 44.36, H 5.25, N 6.43.

5.6. *Isopropylidene 3-Nitrobutane-1,1-dicarboxylate* (= *5-(2-Nitropropyl)-2,2-dimethyl-1,3-dioxane-4,6-dione;* **21**). As described for **20** using nitroethane (1.65 g, 22.0 mmol): 1.42 g (71%) of **21**. M.p. 132° (dec.). IR: 1776*m*, 1740*s*, 1542*s*, 1397*m*, 1388*m*, 1203*m*, 1063*m*, 991*m*. ^{1}H-NMR (CD_3CN): 4.92–4.80 (*m*, 14 lines, H–C(3)); 3.73 (*dd*, *J* = 4.5, 6.9, H–C(1)); 2.59 (*ddd*, *J* = 4.5, 9.0, 15.0, 1 H–C(2)); 2.18 (*ddd*, *J* = 4.5, 6.9, 15.0, 1 H–C(2));

1.63 (*s*, Me); 1.56 (*s*, Me); 1.42 (*d*, $J = 6.7$, 3 H–C(4)). ^{13}C-NMR: 166.1; 165.9; 106.5; 81.4; 44.3; 31.6; 28.6; 26.4; 19.8. CI-MS: 250 (12, $M^+ + 19$), 249 (100, $M^+ + 18$). Anal. calc. for $C_9H_{13}NO_6$ (231.20): C 46.75, H 5.67, N 6.06; found: C 46.75, H 5.77, N 6.08.

5.7. *1,1:2,2-Diisopropylidene Cyclopropane-1,1,2,2-tetracarboxylate* (= *2,2,2″,2″-Tetramethyldispiro[1,3-dioxane-5,1′-cyclopropane-2′,5″-1″,3″-dioxane]-4,4″,6,6″-tetrone* ; **22**). Treatment of **13** (3.02 g, 13.0 mmol) in the presence of *Meldrum's* acid (1.90 g, 13.2 mmol) with $NaIO_4$ (2.90 g, 13.6 mmol) as described for **9** yielded 2.21 g (57%) of **22**, after washing with CH_2Cl_2 (100 ml). The recrystallized (MeCN) **22** decomposed on heating at 206°. IR: 1804*m*, 1758*s*, 1398*m*, 1284*s*, 1253*m*, 1209*m*, 1197*m*, 1058*m*, 971*m*. ^{1}H-NMR (CD_3CN): 2.75 (*s*, 2 H–C(3)); 1.67 (*s*, 2 Me); 1.60 (*s*, 2 Me). ^{13}C-NMR: 161.8; 108.0; 40.5; 27.8; 27.4; 27.1. MS: 317 (15, $M^+ + 19$), 316 (100, $M^+ + 18$), 93 (7). Anal. calc. for $C_{13}H_{14}O_8$ (298.25): C 52.35, H 4.73; found: C 52.24, H 4.87.

5.8. *Isopropylidene 2-Morpholinoethane-1,1-dicarboxylate* (= *2,2-Dimethyl-5-(morpholinomethyl)-1,3-dioxan-4,6-dione*; **23**). Morpholine (1.74 g, 20.0 mmol) was added to a soln. of **13** (2.00 g, 8.6 mmol) at 5° in MeCN (10 ml). After 30 min, the crystals were filtered and washed sequentially with MeCN, Et_2O, and pentane to yield 1.72 g (82%) of **23**. M.p. 132–133° (dec.). IR: 1691*w*, 1593*s*, 1525*w*, 1456*w*, 1408*m*, 1388*m*, 1374*m*, 1259*m*, 1123*m*, 935*m*, 909*m*. ^{1}H-NMR ($CDCl_3$): 10.16 (br. *s*, NH); 4.08–3.94 (*m*, 4 H); 3.87 (*'d'*, $J = 3.6$, 2 H); 3.37 (*'d'*, $J = 12.5$, 2 H); 3.05–2.91 (*m*, 2 H); 1.60 (*s*, 2 Me). ^{13}C-NMR: 167.6; 102.1; 66.8; 63.6; 55.4; 51.3; 26.1. CI-MS: 244 (0.3, $M^+ + 1$), 105 (31), 88 (100). Anal. calc. for $C_{11}H_{17}NO_5$ (243.26): C 54.31, H 7.04, N 5.76; found: C 54.16, H 7.08, N 5.77.

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