

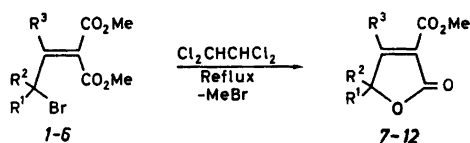
## $\alpha$ -Methoxycarbonyl- $\Delta^{\alpha,\beta}$ -butenolides from $\gamma$ -Bromoalkylidene Malonates

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When some  $\gamma$ -bromoalkylidene malonates were refluxed in tetrachloroethane,  $\alpha$ -methoxycarbonyl- $\Delta^{\alpha,\beta}$ -butenolides were formed by elimination of methyl bromide. The same transformation occurred on treatment of the bromides with a solution of silver perchlorate in ethyl acetate at room temperature. A reaction mechanism for this transformation is suggested, substantiated by kinetic measurements.

Table 1. Formation of lactones 7–12 from alkyl bromides 1–6.



Upon distillation of a mixture of alkyl *Z*- and *E*-2-aryl-3-bromomethyl-2-butenolate only the *E* isomer was obtained unchanged, whereas the *Z* isomer cyclized to an  $\alpha$ -aryl- $\beta$ -methyl- $\Delta^{\alpha,\beta}$ -butenolide (12–27 %) with the loss of alkyl bromide.<sup>1</sup> Iron powder seems to catalyze the lactonization of  $\alpha,\beta$ -unsaturated esters, facilitating both the elimination of methyl bromide and the isomerization of the carbon-carbon double bond.<sup>2,3</sup>

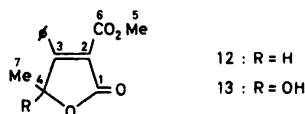
When dimethyl 2-bromo-2-methylpropylidenemalonate (3) was distilled at elevated temperature,  $\alpha$ -methoxycarbonyl- $\gamma,\gamma$ -dimethyl- $\Delta^{\alpha,\beta}$ -butenolide (9) was formed in good yield. In order to test if this pyrolytic reaction was general and of synthetic value, bromides 1–6 were heated under reflux in 1,1,2,2-tetrachloroethane.  $\alpha$ -Methoxycarbonyl- $\Delta^{\alpha,\beta}$ -butenolides 7–12 were formed in moderate to good yields (Table 1).

Lactones 7, 8 and 12 were difficult to purify. Lactone 8 decomposed on distillation or on prolonged storage at 5 °C. Lactones 7 and 12 both showed large melting point intervals although the elemental analysis agreed within 0.4 % units with the calculated values. On recrystallization of lactone 7 from methanol the solution rapidly turned yellow whereas

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Reaction time/h	No.	Yield %
1	H	H	H	1.3	7	48 <sup>b</sup>
2	H	Me	H	1	8	$\alpha$
3	Me	Me	H	1	9	72 <sup>b</sup>
4	Me	Et	H	1	10	43 <sup>b</sup>
5	H	H	Ø	16.5	11	63 <sup>b</sup>
6	H	Me	Ø	5	12	70 <sup>b</sup>

<sup>a</sup> The product decomposes on distillation at reduced pressure, but the NMR spectrum of the crude product shows that 8 is formed in good yield. The coupling constant  $J_{4,5} = 2$  Hz is characteristic for the  $\alpha,\beta$ -butenolides.<sup>8</sup> <sup>b</sup> Yield after recrystallization.

attempts to purify lactone 12 by preparative thin-layer chromatography resulted in oxidation of the allylic C–H bond to give lactone 13. If lactone 12 was kept in contact with air for several days, NMR spectrometry showed the appearance of 13 in the sample, the oxidation being faster at the melting point temperature.

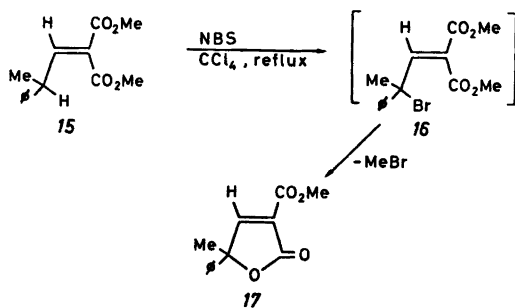


Among the butenolides the  $\Delta^{\alpha,\beta}$ -isomer is considered more stable than the  $\Delta^{\beta,\gamma}$ -isomer.<sup>4</sup> That the hydroxy lactone **13** in fact is the  $\Delta^{\alpha,\beta}$ -isomer, is indicated by the similarity to **12** as judged by the spectroscopic parameters (see Experimental). Similar allylic oxidation reactions are known to occur. After a few days in air  $\alpha$ -acetyl- $\beta,\gamma$ -diphenyl- $\Delta^{\alpha,\beta}$ -butenolide gave among other products a  $\gamma$ -hydroxylactone, probably arising from the decomposition of the hydroperoxide.<sup>5</sup> Autooxidation of  $\gamma$ -methyl- $\Delta^{\alpha,\beta}$ -butenolide and the corresponding  $\beta,\gamma$ -isomer both gave the  $\gamma$ -hydroperoxide besides polymeric compounds.<sup>6</sup>

The problems encountered in purifying **7** and **8** may besides oxidation at C-4, be caused by dimerization.<sup>7,8</sup>

When bromide **3** was heated at 110 °C in *N,N*-dimethylformamide the products were methyl 2-methoxycarbonyl-4-methyl-2,4-pentadienoate (**14**) (75 %) and **9** (25 %).

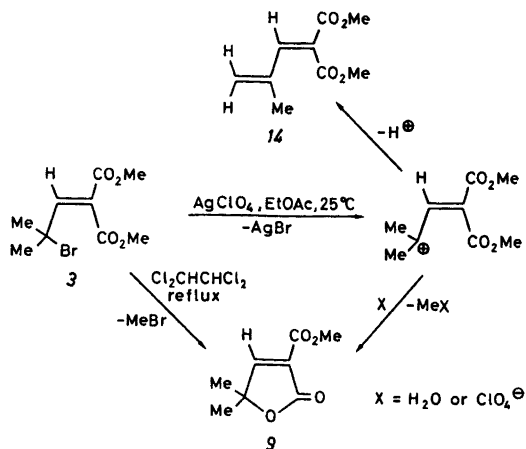
Treatment of dimethyl 2-phenylpropylidene-malonate (**15**) with *N*-bromosuccinimide (NBS) in boiling carbon tetrachloride gave butenolide **17** (73 %) (Scheme 1). Even when the bromination was done at 35 °C, catalyzed by UV light, **17** still was the main product, showing the great tendency of this system for lactone formation.



Scheme 1.

$\gamma$ -Bromoalkylidenemalonates can also be lactonized at room temperature. On treatment of **3** with silver perchlorate in ethyl acetate at 25 °C or at  $-40$  to  $-50$  °C, silver bromide precipitated immediately to give **9** in good yield, less **14** being formed at the lower temperature (Scheme 2). Treatment of **3** with anhydrous silver perchlorate<sup>9</sup> under the same conditions also gave **9**, showing that the perchlorate anion, the only nucleophile present, "picks up" the

methyl group. Butenolide **7** was obtained in better yield when **1** was treated with silver perchlorate compared to the yield obtained in refluxing tetrachloroethane (NMR of crude product).



Scheme 2.

Allylic bromination with NBS is considered to be a radical reaction.<sup>10</sup> As saturated esters with a radical site in the  $\gamma$ -position do not form lactones,<sup>11</sup> the transformation of **15** into **17** by a radical mechanism is less plausible.

When ethyl *cis*-2-bromocyclopentyl acetate was pyrolyzed, only a small amount of lactone was formed.<sup>12</sup> The *trans* isomer cyclized rapidly with inversion of configuration at the carbon atom originally carrying the bromo atom, indicating that the bromide did not dissociate into a free carbonium ion before lactonization occurred. In this case pyrolysis proceeds well provided that the oxygen of the ester can reach the rear of the carbon carrying the bromine atom.<sup>12</sup>

Allylic bromides dissociate easier than the corresponding saturated systems and the ionization is facilitated by  $\gamma$ -substituents which can stabilize a carbonium ion.<sup>13</sup> It therefore seemed reasonable that lactone **17** was formed by attack of the ester oxygen on the electron-deficient  $\gamma$ -carbon of a partly dissociated bromide **16**. Conditions favouring the release of the bromide ion accelerate the reaction as shown in the reaction of **3** with silver perchlorate.

The rate of lactonization of **3** in tetrachloroethane was unchanged upon addition of

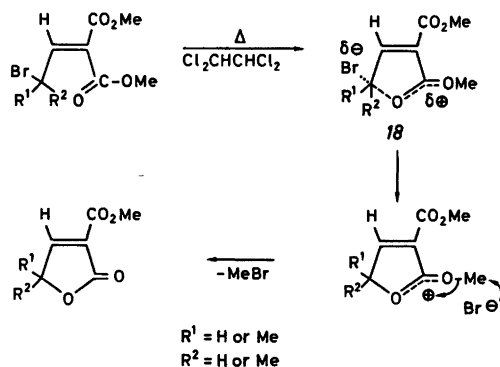
Table 2. Specific rate constants for the formation of butenolides 1–3.

Bromide	Solvent	Temp./°C	$\epsilon^{15}$	$E_T^{15}$	$k/10^{-4} \text{ s}^{-1}$
1	$\text{Cl}_2\text{CHCHCl}_2$	116	8.2 <sup>a</sup>	—	1.1
2	$\text{Cl}_2\text{CHCHCl}_2$	116			1.0
3	$\text{Cl}_2\text{CHCHCl}_2$	117			2.9
3	$\text{Cl}_2\text{CHCHCl}_2$	129			7.8
3	$\text{Cl}_2\text{CHCHCl}_2$	141			16.6
3	$\text{C}_6\text{H}_5\text{CN}$	116	25.2 <sup>b</sup>	42.0 <sup>b</sup>	1.5
3	$(\text{C}_6\text{H}_5)_2\text{O}$	116	3.7 <sup>c</sup>	35.3 <sup>b</sup>	0.23 <sup>d</sup>
3	$(\text{C}_6\text{H}_5)_2\text{O}$	141			0.92

<sup>a</sup> 20 °C. <sup>b</sup> 25 °C. <sup>c</sup> 30 °C. <sup>d</sup> The reaction is very slow and  $k$  is calculated by measuring the initial rate of lactonization.

hydroquinone (semiquantitative measurement) as expected with an ionic mechanism.

If the limiting stage of the lactonization is the ionization of the C–Br bond, the rate constant should increase with higher degree of alkyl substitution at the  $\gamma$ -carbon. The kinetics of the lactonization reaction were investigated by NMR spectrometry by measuring the rate of disappearance of the  $\gamma$ -methyl signal in bromides 2 and 3 (the methylene group in bromide 1). As expected the reaction was of first order. The rate constant for the lactonization of 3 in 1,1,2,2-tetrachloroethane is almost three times greater than the values found for 1 and 2 (Table 2), but this difference in reaction rate is small compared with the one found in solvolytic reactions (Table 3).<sup>14</sup> This may indicate that the ring closure of 1, 2 and 3 is best described by the cyclic transition state 18 (Scheme 3).



Scheme 3.

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Table 3. Relative rates of solvolysis of some chlorides and bromides in ethanol.<sup>14</sup>

Compound	Rate
Temperature 44.6 °C	
$\text{CH}_2 = \text{CHCH}_2\text{Cl}$	1.00
$\text{CH}_2 = \text{CHCHClCH}_3$	3.3
$\text{CH}_2 = \text{CHC}(\text{CH}_3)_2\text{Cl}$	2950
Temperature 55 °C	
$\text{CH}_3\text{CH}_2\text{Br}$	1.00
$(\text{CH}_3)_2\text{CHBr}$	0.725
$(\text{CH}_3)_3\text{CBr}$	831

In order to study the effect of the medium upon the reaction rate, bromide 3 was lactonized at 116–117 °C in tetrachloroethane, benzonitrile and phenyl ether. The use of the  $E_T$ -parameter as a measure of the polarity of the solvent is preferable to a purely electrostatic point of view (dielectric constant  $\epsilon$ ).<sup>15</sup> The rate of lactonization is six times greater in benzonitrile ( $E_T$  42.0) than in phenyl ether ( $E_T$  35.3). In tetrachloroethane the rate constant is almost two times greater than in benzonitrile although the  $E_T$ -value for tetrachloroethane probably is similar to the value given for benzonitrile.\* An acceleration of the reaction rate in polar solvents is in agreement with the transition state 18 in which charge is created upon passing from the initial to the transition state.

\* 1,2-dichloroethane ( $E_T$  41.9), dichloromethane ( $E_T$  41.1).<sup>15</sup>

The enthalpy of activation,  $\Delta H^\ddagger$ , for the lactonization of **3** in tetrachloroethane is calculated to be 97.2 kJ mol<sup>-1</sup> and the entropy of activation  $\Delta S^\ddagger$  - 66.6 J deg<sup>-1</sup> mol<sup>-1</sup>, the latter pointing to a more constrained transition state situation. This is consistent with a charged transition state requiring for the solvation a relatively large number of the weakly polar solvent molecules, and/or consistent with a transition state like **18** where the ring formation lies somewhat ahead of the breaking of the carbon-bromine bond.

Consequently, the experimental facts are probably best interpreted as follows:

(i) The lactonization of  $\gamma$ -bromoalkylidene malonates occurs by an ionic mechanism,

(ii) the reaction of bromide **3** with silver perchlorate at room temperature is probably best explained by the dissociation of **3** into a carbonium ion. Elimination of a proton from the neighbouring methyl group giving diene **14** (15 %) competes with the attack of the carbonyl oxygen at the positive centre to give lactone **9** (85 %),

(iii) in the highly polar solvent *N,N*-dimethylformamide (DMF) ionization of the C-Br bond is suggested to be fast. The high yield of **14** (75 %) in this case may be due to the action of DMF as a base, the elimination now being faster than the ring closure,

(iv) when **3** was refluxed in tetrachloroethane, no diene was detected, indicating that no carbonium ion was formed prior to the ring closure,

(v) the nucleophile is most probably the carbonyl oxygen and not the ether oxygen in the methoxy carbonyl group,<sup>18</sup>

(vi) the ester methyl group is "picked up" by the bromide ion in nonpolar solvents and by the perchlorate anion when the lactonization is carried out in the presence of anhydrous silver perchlorate.

As a rule tertiary bromides dissociate easier into carbonium ions than do primary and secondary ones. Bromide **3**, when heated in tetrachloroethane, has shown to give no carbonium ion, and a dissociation of **1** and **2** in the same solvent is not probable.

The kinetic measurements, (ii), (iii) and (iv) make structure **18** a plausible transition state when the ring closure reaction is done in non-polar solvents.

## EXPERIMENTAL

*General.* Melting points (uncorrected) were determined on a micro hot-stage. IR spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer, <sup>1</sup>H NMR spectra on a Varian A-60A spectrometer and on a Varian HA 100-15D spectrometer with Model V4333 variable temperature probe and Model V6040 temperature controller. <sup>13</sup>C NMR spectra were recorded on a FT NMR Spectrometer JEOL FX-60, the mass spectra on an AEI MS 902 instrument, and the UV spectra on a Cary 14 spectrophotometer. Elemental analysis were performed by I. Beetz, West-Germany.

The bromides **1-4** were made by condensation of the aldehydes with dimethyl malonate<sup>17-19</sup> followed by bromination with *N*-bromosuccinimide (NBS) in CCl<sub>4</sub> using 2,2'-azobis(2-methylpropionitrile) as a catalyst. The bromides **5** and **6** were made by condensation of the  $\alpha$ -bromoketone with dimethyl malonate.<sup>20</sup>

*Dimethyl 2-bromoethylidenemalonate (1)*, yield 51 %, m.p. 37 °C (ether/pentane). MS: *m/e* 157 (M-Br, 15). <sup>1</sup>H NMR (CCl<sub>4</sub>):  $\delta$  7.05 (1 H, t, *J* 8.5 Hz), 4.12 (2 H, d, *J* 8.5 Hz), 3.83 (3 H, s), 3.79 (3 H, s). IR (film): 1730 and 1640 cm<sup>-1</sup>. Found: C 35.97; H 4.03. Calc. for C<sub>7</sub>H<sub>9</sub>O<sub>4</sub>Br: C 35.44; H 3.80.

*Dimethyl 2-bromopropylidenemalonate (2)*, yield 75 %, b.p. 90-96 °C/0.5 mmHg. MS: *m/e* 171 (M-Br, 100). <sup>1</sup>H NMR (CCl<sub>4</sub>):  $\delta$  6.92 (1 H, d, *J* 10.5 Hz), 4.95 (1 H, m), 3.80 (3 H, s), 3.77 (3 H, s), 1.82 (3 H, d, *J* 6.5 Hz). IR (CHCl<sub>3</sub>): 1730 and 1635 cm<sup>-1</sup>. Found: C 38.52; H 4.83. Calc. for C<sub>8</sub>H<sub>11</sub>O<sub>4</sub>Br: C 38.25; H 4.38.

*Dimethyl 2-bromo-2-methylpropylidenemalonate (3)*, yield 70 %, m.p. 33.5 °C (ether/pentane). Anal. C<sub>9</sub>H<sub>13</sub>O<sub>4</sub>Br: C, H. MS: *m/e* 185 (M-Br, 43). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.12 (1 H, s), 3.83 (3 H, s), 3.80 (3 H, s), 1.93 (6 H, s). IR (KBr): 1735 and 1645 cm<sup>-1</sup>.

*Dimethyl 2-bromo-2-methylbutylidenemalonate (4)*, yield 57 %, b.p. 91-92 °C/0.02 mmHg. MS: *m/e* 199 (M-Br, 9). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.07 (1 H, s), 3.81 (3 H, s), 3.78 (3 H, s), 2.04 (2 H, q, *J* 6.5 Hz), 1.87 (3 H, s), 1.04 (3 H, t, *J* 6.5 Hz). IR (film): 1735 and 1640 cm<sup>-1</sup>.

*Dimethyl 2-bromo-1-phenylethylidenemalonate (5)*, yield 56 %, m.p. 46-47 °C (MeOH). Anal. C<sub>15</sub>H<sub>19</sub>O<sub>4</sub>Br: C, H. MS: *m/e* 312/314 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.34 (5 H, s), 4.68 (2 H, s), 3.83 (3 H, s), 3.48 (3 H, s). IR (CHCl<sub>3</sub>): 1725 and 1615 cm<sup>-1</sup>.

*Dimethyl 2-bromo-1-phenylpropylidenemalonate (6)*, yield 56 %, m.p. 65.5-66.5 °C (MeOH). Anal. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>Br: C, H. MS: *m/e* 247 (M-Br, 93). <sup>1</sup>H NMR (CCl<sub>4</sub>):  $\delta$  7.30 (5 H, s), 6.25 (1 H, q, *J* 7.0 Hz), 3.82 (3 H, s), 3.32 (3 H, s), 1.58 (3 H, d, *J* 7.0 Hz). IR (CHCl<sub>3</sub>): 1725 cm<sup>-1</sup>.

*Lactonization of bromides 1-6 in tetrachloroethane. General procedure.* A solution of the bromide in tetrachloroethane was refluxed for 1-16.5 h. After removal of the solvent, the products were recrystallized or distilled.

On lactonization of bromide 3, the methyl bromide evolved was collected at low temperature and identified by NMR and GLC.

*α*-Methoxycarbonyl-*Δ*<sup>α,β</sup>-butenolide (7), m.p. 85–99 °C (MeOH/ether) (On recrystallization from boiling methanol the solution turned yellow rapidly. As the elemental analysis is in agreement with the calculated values, this large melting point interval may be due to some thermal reaction during the melting process.) Anal. C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>: C, H. MS: *m/e* 142 (M<sup>+</sup>, 31). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.36 (1 H, t, *J* 2 Hz), 5.00 (2 H, d, *J* 2 Hz), 3.90 (3 H, s). IR (CHCl<sub>3</sub>): 1785, 1725 and 1635 cm<sup>-1</sup>.

*α*-Methoxycarbonyl-*γ*-methyl-*Δ*<sup>α,β</sup>-butenolide (8), <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.20 (1 H, d, *J* 2 Hz), 5.18 (1 H, m), 3.90 (3 H, s), 1.54 (3 H, d, *J* 7 Hz). IR (film): 1775, 1725 and 1635 cm<sup>-1</sup>.

*α*-Methoxycarbonyl-*γ,γ*-dimethyl-*Δ*<sup>α,β</sup>-butenolide (9), m.p. 81–82 °C (light petroleum 40–60 °C/MeOH). Anal. C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>: C, H. MS: *m/e* 170 (M<sup>+</sup>, 3). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.14 (1 H, s), 3.88 (3 H, s), 1.55 (6 H, s). IR (KBr): 1755, 1715 and 1615 cm<sup>-1</sup>.

*γ*-Ethyl-*α*-methoxycarbonyl-*γ*-methyl-*Δ*<sup>α,β</sup>-butenolide (10), m.p. 39 °C (ether/pentane). Anal. C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>: C, H. MS: *m/e* 184 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.17 (1 H, s), 3.90 (3 H, s), 1.90 (2 H, q, *J* 7.5 Hz), 1.53 (3 H, s), 0.92 (3 H, t, *J* 7.5 Hz). IR (CCl<sub>4</sub>): 1780, 1725 and 1620 cm<sup>-1</sup>.

*α*-Methoxycarbonyl-*β*-phenyl-*Δ*<sup>α,β</sup>-butenolide (11), m.p. 141–142 °C (MeOH). Anal. C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>: C, H. MS: *m/e* 218 (M<sup>+</sup>, 97). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.53 (5 H, s), 5.18 (2 H, s), 3.88 (3 H, s). IR (KBr): 1750, 1725 and 1635 cm<sup>-1</sup>.

*α*-Methoxycarbonyl-*γ*-methyl-*β*-phenyl-*Δ*<sup>α,β</sup>-butenolide (12), m.p. 87–100 °C (CHCl<sub>3</sub>/pentane). Anal. C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>: C, H. MS: *m/e* 232 (M<sup>+</sup>, 64). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.50 (5 H, s), 5.57 (1 H, q, *J* 7 Hz), 3.84 (3 H, s), 1.44 (3 H, d, *J* 7 Hz). <sup>13</sup>C NMR (15.0 MHz, CDCl<sub>3</sub>): δ 170.7 and 168.2 (C1 and C6), 162.5 (C3), 131.5, 129.0 and 128.0 (Ph), 119.3 (C2), 78.3 (C4), 52.5 (C5), 19.0 (C7). UV (MeOH): λ<sub>max</sub> 277 nm, ε 12 500. IR (KBr): 1740, 1720 and 1625 cm<sup>-1</sup>.

*γ*-Hydroxy-*α*-methoxycarbonyl-*γ*-methyl-*β*-phenyl-*Δ*<sup>α,β</sup>-butenolide (13). A solution of lactone 12 (0.5 g, 2.2 mmol) in methylene chloride was applied to a 20 cm × 40 cm plate covered with silica gel 60 PF<sub>254</sub> (1.5 mm thickness). After elution with ether/benzene 2:1 the product was extracted into methylene chloride to give 13, yield 0.1 g (19%), m.p. 101–102 °C (chloroform/pentane). Anal. C<sub>13</sub>H<sub>12</sub>O<sub>5</sub>: C, H. MS: *m/e* 248 (M<sup>+</sup>, 9), *m/e* 160 ((*φ*-C≡C-CO<sub>2</sub>Me)<sup>+</sup>, 96), *m/e* 129 (*φ*-C≡C-CO<sup>+</sup>, 100). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.2–7.9 (5 H, m), 4.94 (1 H, s), 3.78 (3 H, s), 1.64 (3 H, s). On addition of D<sub>2</sub>O the proton singlet at δ 4.94 disappeared. <sup>13</sup>C NMR (15.0 MHz, CDCl<sub>3</sub>): δ 166.7 (C1 and C6), 162.6 (C3), 131.4 and 128.6 (Ph), 119.9 (C2), 106.0 (C4), 52.7 (C5), 24.4 (C7). UV (MeOH): λ<sub>max</sub> 280 nm, ε 11 100. IR (KBr): 3300, 1755, 1725 and 1645 cm<sup>-1</sup>.

*Dimethyl 2-phenylpropylidenemalonate* (15),<sup>18</sup>

yield 60%, b.p. 102–103 °C/0.05 mmHg. Anal. C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>: C, H. MS: *m/e* 248 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.23 (5 H, s), 7.00 (1 H, d, *J* 11 Hz), 3.83 (3 H, s), 3.6–4.2 (1 H, m), 3.73 (3 H, s), 1.42 (3 H, d, *J* 7 Hz). IR (film): 1720 and 1635 cm<sup>-1</sup>.

*α*-Methoxycarbonyl-*γ*-methyl-*γ*-phenyl-*Δ*<sup>α,β</sup>-butenolide (17). To a solution of 15 (3.0 g, 12 mmol) in carbon tetrachloride (15 ml) NBS (2.1 g, 12 mmol) and benzoyl peroxide (20 mg) were added. The mixture was refluxed for 1 h, filtrated and washed with water to give 17, 1.9 g (68%), m.p. 113–114 °C (MeOH). MS: *m/e* 232 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.27 (1 H, s), 7.34 (5 H, s), 3.86 (3 H, s), 1.86 (3 H, s). IR (film): 1785 and 1720 cm<sup>-1</sup>. Found: C 66.80; H 5.22. Calc. for C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>: C 67.24; H 5.17.

In one experiment a solution of 15 in CCl<sub>4</sub> was kept at 35 °C, the reaction being catalyzed by UV-light. The main product was butenolide 17.

*Reaction of 3 in N,N-dimethylformamide*. A solution of 3 (1.0 g, 3.8 mmol) in *N,N*-dimethylformamide (9.5 ml) was kept at 110 °C for 105 min to give *methyl 2-methoxycarbonyl-4-methyl-2,4-pentadienoate* (14) (75%), <sup>1</sup>H NMR (DMF): δ 7.32 (1 H, s), 5.50–5.70 (2 H, m), 3.80 (3 H, s), 3.75 (3 H, s), 1.85 (3 H, broad s) and *butenolide 9*, (25%) (yields are estimated from the NMR spectrum).

*Reactions of bromides 1 and 3 with silver perchlorate. General procedure*. To a solution of the bromide in ethyl acetate was added a solution of silver perchlorate in ethyl acetate at room temperature. After silver bromide had precipitated, the mixture was filtrated and the solvent removed. Chloroform was added and the organic layer washed with water and dried over magnesium sulfate.

*α*-Methoxycarbonyl-*Δ*<sup>α,β</sup>-butenolide (7). To a solution of 1 (1.5 g, 6.3 mmol) in ethyl acetate (7 ml) was added a solution of silver perchlorate (1.6 g, 7.1 mmol) in ethyl acetate (8 ml). The mixture was stirred for 1 h to give mainly 7.

*α*-Methoxycarbonyl-*γ,γ*-dimethyl-*Δ*<sup>α,β</sup>-butenolide (9). To a solution of 3 (2.0 g, 7.5 mmol) in ethyl acetate (10 ml) was added a solution of silver perchlorate (2.0 g, 8.9 mmol) in ethyl acetate (10 ml) to give 9 (85%) and 14 (15%) (yields estimated from the NMR spectrum).

The same reaction was done at –40 to –50 °C to give 9 (92%) and 14 (8%) (yields estimated from the NMR spectrum).

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