

# Synthesis of Squaric Acid Derivatives by Lewis Acid-catalysed Reaction of its Dichloride, Methyl Ester Chloride, Diethylamide Chloride, and Ethyl Diester with Unsaturated Organosilanes: New Method for C–C Bond Formation on Cyclobutenedione

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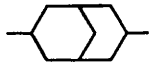
The squaric acid family of derivatives, *e.g.* dichloride **2**, methyl ester chloride **3**, diethyl amide chloride **4**, and ethyl diester **5**, reacted with a variety of unsaturated organosilanes **6** in the presence of a catalyst, typically titanium tetrachloride, at  $-78$  to  $0$  °C to give addition products (*e.g.*, **7**, **9**, **11**) and/or substitution products (*e.g.*, **8**, **10**, **12**, **13**) after dechlorosilylation either *via* 1,2- or 1,4-addition. The mode of addition depended on the nature of the acid family and on the substitution pattern of the organosilane. The former product predominated in the reaction of the chlorides **2–4** with all silyl ketene ketals used, and with some allylsilanes and silyl enol ethers unless the reactive site ( $\gamma$  to a silyl group) of these silanes was more crowded, whereas the diester **5** gave rise to the latter product **13** irrespective of the substitution pattern. In some cases, catalyst and reaction temperature also affected the mode of addition. The reactivity was found to be in the order **2** > **3** > **4**, being reflected in the reaction temperature.

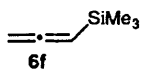
Squaric acid **1** is a four-membered oxocarbon compound,<sup>1</sup> which has potentially useful multifunctionality and ring strain in synthesis.<sup>2–5</sup> Based on the cyclobutenedione structure, acidic hydroxy groups are replaced by better leaving groups and then various nucleophiles can be introduced at the carbonyl or olefinic carbon. Thus modified cyclobutenone rings can be further transformed by thermolysis,<sup>6–13</sup> photolysis<sup>14</sup> and catalysis<sup>15–17</sup> with the aid of relief of ring strain. A variety of natural product syntheses were performed along these lines.<sup>18–22</sup> This strategy starts from carbon–carbon bond formation on the ring. Until now, additions to the ring enone moiety have been achieved mainly with organo-lithium,<sup>23</sup> -magnesium<sup>23,24</sup> and -copper<sup>25</sup> reagents with a transition metal as a catalyst.<sup>26,27</sup> An enamine has been reported to be a useful nucleophile.<sup>28</sup> Friedel–Crafts conditions were employed with aromatic compounds.<sup>29–31</sup>

Recently we have developed an alternative method for carbon–carbon bond formation on the ring: titanium tetrachloride-catalysed reaction of dichloride **2** with unsaturated organosilanes.<sup>32</sup> In this case, an allylsilane and a silyl enol ether underwent addition to the carbonyl group (1,2-addition) when the reactive site  $\gamma$  to a silyl group is unsubstituted. On the other hand, when the site was disubstituted the addition took place at the olefinic carbon (1,4-addition) to give substituted products after dechlorosilylation. We have now studied this type of addition reaction with the squaric acid family ranging from the dichloride **2** to the methyl ester chloride **3**, diethylamide chloride **4** and ethyl diester **5**. As for the unsaturated organosilanes **6** we employed not only allylsilanes **6a–f** and silyl enol ethers **6g–m** but also silyl ketene ketals **6n–p**. Full details are described, in this paper, of the relative reactivity and substituent effects under several different reaction conditions. The present Lewis acid-catalysed addition using organosilanes provides new methodology for carbon–carbon bond formation on the cyclobutenedione ring.

## Results and Discussion

The required squaric acid family **2–5** were prepared according to established procedures. The dichloride **2** was obtained in an

Squaric acid family			Unsaturated organosilanes			
Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	X
<b>1</b>	OH	OH	a; H	H	H	CH <sub>2</sub>
<b>2</b>	Cl	Cl	b; Me	H	H	CH <sub>2</sub>
<b>3</b>	Cl	OMe	c; H	H	Me	CH <sub>2</sub>
<b>4</b>	Cl	NEt <sub>2</sub>	d; H	(Me)	(H)	
<b>5</b>	OEt	OEt	e; H	Me	Me	CH <sub>2</sub>
			f; H	H	–[CH <sub>2</sub> ] <sub>2</sub> –	CH–
			g; Ph	H	H	O
			h; Ph	Me	H	O
			i; Ph	Me	Me	O
			j; Ad	H	H	O
			k; –[CH <sub>2</sub> ] <sub>4</sub> –		H	O
			l; 		H	O
			m; H	Me	Me	O
			n; OPh	H	H	O
			o; OEt	Me	H	O
			p; OMe	Me	Me	O

  
**6f**

acceptable yield by the reported SOCl<sub>2</sub>–dimethylformamide (DMF) method;<sup>2,33</sup> sublimation was applied for purification, because the sample obtained after only recrystallization (reported) was contaminated with tarry materials. The methyl ester chloride **3**<sup>24,34</sup> and the diethylamide chloride **4**<sup>31,34</sup> were synthesized from dichloride **2** by displacement with an appropriate alcohol and amine. The dichloride **2** was reported to be doubly substituted with simple alcohols.<sup>34</sup> In our hands, however, half-ester **3** was prepared by selective monosubstitution of dichloride **2** with methanol under reflux conditions in tetrahydrofuran (THF). This is in accord with the monohydroxylation of dichloride **2** with water under these conditions.<sup>35</sup> The diester **5** can be purchased or simply prepared with ethanol from acid **1** under azeotropic conditions.<sup>22</sup>

**Table 1** Addition reaction of the squaric acid family, *viz.* dichloride **2**, methyl ester chloride **3**, diethylamide chloride **4** and ethyl diester **5** with unsaturated organosilanes **6**

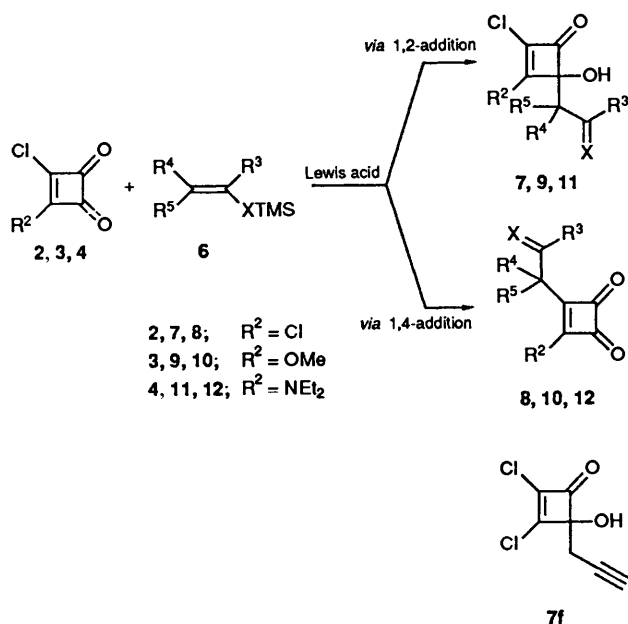
Entry	Acid family	Silane	Reaction conditions <sup>a</sup>			Products (% yield) <sup>b</sup> <i>via</i>	
			Time (t/min)	Temp. (T/°C)	Catalyst <sup>c</sup>	1,2-Addn.	1,4-Addn.
1	2	6a	5[10]	-78	T	7a(54)[66] <sup>d</sup>	
2	2	6a	5	-78	S	7a(34)	
3	2	6b	5	-78	T	7b(50)	
4	2	6c	5[10]	-78	T	7c(26)[55] <sup>d</sup>	
5	2	6d	5	-78	T	7d(8)	8d(68)
6	2	6e	5	-78	T	7e(32)	
7	2	6f	30	-50	T	7f(19)	
8	2	6g	1[10]	-78	T	7g(52)[74] <sup>d</sup>	
9	2	6g	5	-95	T		8g(32)
10	2	6g	1	r.t.	Tf		8g(28)
11	2	6h	1	-78	T	7h(38)	
12	2	6i	1	-78	T	7i(7)	8i(82)
13	2	6j	1	-78	T	7j(73)	8j(26) <sup>e</sup>
14	2	6k	1[10]	-78	T	7k(58)[70] <sup>d</sup>	
15	2	6k	5	-95	T		8k(40)
16	2	6l	1	-78	T	7l(32)	8l(40) <sup>e</sup>
17	2	6n	10	-78	T	7n(86)	
18	2	6n	60	r.t.	Z		8n(36)
19	2	6n	10	-95	T	7n(84)	
20	2	6o	10	-78	T	7o(22)	
21	2	6o	60	r.t.	Z		8o(56)
22	2	6p	10	-78	T	7p(46)	
23	2	6p	60	r.t.	Z		8p(50)
24	3	6a	10	-15	T	9a(82)	
25	3	6b	10	-15	T	9b(83)	
26	3	6c	10	-15	T	9c(37)	
27	3	6d	10	-15	T		10d(62)
28	3	6g	10	-15	T	9g(80)	
29	3	6h	10	-15	T	9h(49)	
30	3	6i	10	-15	T		10i(77)
31	3	6k	10	-15	T	9k(74)	
32	3	6m	10	-15	T		10m(69)
33	3	6p	10	-15	T	9p(76)	
34	4	6a	10	0	T	11a(83)	
35	4	6b	10	0	T	11b(66)	
36	4	6g	10	0	T	11g(83)	
37	4	6h	10	0	T	11h(67)	
38	4	6i	10	0	T		12i(14)
39	4	6k	10	0	T	11k(21)	
40	4	6m	10	0	T		12m(54)
41	4	6p	10	0	T	11p(61)	
42	5	6g	10	-15	T		13g(42)
43	5	6h	10	-15	T		13h(57)
44	5	6k	10	-15	T		13k(63)
45	5	6p	10	-15	T		13p(83)

<sup>a</sup> Proportions of each reagent (acid family:silane:catalyst) employed were 1:2:1. <sup>b</sup> Isolated yields are given. <sup>c</sup> Catalyst: T = TiCl<sub>4</sub>; Tf = CF<sub>3</sub>-SO<sub>2</sub>O-SiMe<sub>3</sub>; S = SnCl<sub>4</sub>; Z = ZnCl<sub>2</sub>. <sup>d</sup> The yield for the reaction time shown in square brackets. <sup>e</sup> The yields which were reported in the previous paper (ref. 32) should be exchanged as indicated in this Table.

First, the chloride **2**, which is expected to be the most reactive of the derivatives under investigation here, was chosen for the reaction with allylsilanes.<sup>36</sup> Typically, dichloride **2** and allyltrimethylsilane **6a** was treated with titanium tetrachloride at -78 °C in dichloromethane for 5 min, and the reaction mixture was quenched with ice-water. After the usual work-up, products were separated by silica gel chromatography to give 2,3-dichloro-4-hydroxy-4-(prop-2-enyl)cyclobut-2-enone **7a** in 54% yield; the product resulted from 1,2-addition (Table 1). The yield decreased rapidly at higher temperatures (0% at 0 °C) and more slowly at lower temperatures (34% at -95 °C) and increased slightly for prolonged reaction times (66% after 10 min). Among other Lewis acids examined, tin(IV) chloride was less effective (34%; entry 2), and both zinc chloride (at room temperature) and boron trifluoride-diethyl ether (at -78 °C) were ineffective. The structure was elucidated by spectral inspection; the key signals indicated the presence of hydroxy and strained carbonyl

groups (3319 and 1784 cm<sup>-1</sup> in the IR spectrum), and of a cyclobutenone ring involving three sp<sup>2</sup> and one sp<sup>3</sup> carbons ( $\delta_C$  187.7, 170.7, 133.7 and 93.2 in the <sup>13</sup>C NMR spectrum), and the presence of both chlorine atoms (*m/z* 192, 194, 196; M<sup>+</sup>, M<sup>+</sup> + 2, M<sup>+</sup> + 4; 9:6:1 in the mass spectrum). On going to a more substituted allylsilane, the addition mode changed as was demonstrated in the case of trimethylprenylsilane **6d**. The reaction with this silane under the same conditions afforded 3-chloro-4-(1,1-dimethylprop-2-enyl)cyclobut-3-ene-1,2-dione **8d** as the predominant product which resulted from 1,4-addition followed by dechlorosilylation. The structure was clearly confirmed by the spectral data; (1) No absorption due to a hydroxy group, but a couple of absorptions, at 1775 and 1809 cm<sup>-1</sup>, due to a 1,2-dione moiety (IR), (2) four signals, at  $\delta_C$  185.3, 193.0, 195.5 and 206.1, due to ring carbons (<sup>13</sup>C NMR), and (3) two 3:1 parent peaks at *m/z* 184 and 186 due to their being only one chlorine atom residing on the ring (MS). The

reactions using silanes **6b**, **6c** and **6e** resulted in the formation of 4-hydroxycyclobutenones **7b**, **7c** and **7e** respectively, and thus it was shown that  $\gamma$ -monosubstitution in the allylsilane did not change the mode of reactivity (1,2-addition), where a diastereoisomeric mixture was obtained (entries 4 and 6). Analogously, allenyltrimethylsilane **6f** added to the dichloride **2** to give the propargylated 1,2-addition product **7f** albeit in a low yield. On the other hand, propargyltrimethylsilane reacted but to give a complex mixture, and less nucleophilic ethenyl- and ethynyl-trimethylsilanes did not give any addition products.

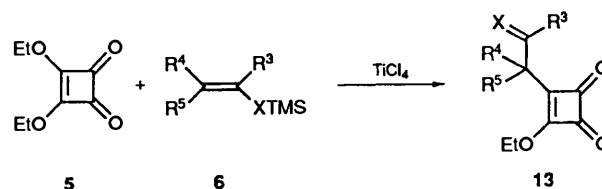


Next to be attempted was the reaction with silyl enol ethers **6g–m**<sup>37</sup> in the same way as with allylsilanes. In this case the reaction was carried out for 1 min; longer reaction times (10 min) raised the yield as seen in entries 8 and 14, but this is not always the case. As a catalyst, titanium tetrachloride was again better than tin(IV) chloride and zinc chloride with which a complex mixture was formed. A series of silyl enol ethers of phenyl ketones **6g–i** were examined for 1,2- vs. 1,4-addition reactivity. As a result, a similar tendency was observed for all three; with an increase in the number of methyl substituents on the enol ether (*i.e.* 0 to 2), the mode of addition changed from 1,2 to 1,4 (entries 8, 11 and 12). Although little, if any, 1,4-addition product arose from a silyl enol ether of cyclohexanone **6k**, those were considerably accompanied in the reaction with silyl enol ethers **6j** and **6l** involving a more bulky group such as an adamantane system in spite of this not being a doubly  $\gamma$ -substituted type. The 1,2- vs. 1,4-mode of addition was therefore influenced by the substitution pattern of the unsaturated organosilanes used (*vide supra*). These results could be explained by a steric factor. The Lewis acid-co-ordinated carbonyl carbon becomes more congested, compared with the olefinic carbon, making the 1,4-addition favourable, if the reactive site of the organosilanes is more crowded. Alternatively, this result may be considered in terms of thermodynamics, since the first formed 1,2-addition product possibly isomerizes to the 1,4-addition product.<sup>38</sup> Yet this seems unlikely because the control experiment (treatment of compound **7a** with titanium tetrachloride) did not show any evidence for isomerization. In the reactions of compound **6g**, interesting temperature and catalyst effects were observed. When lower temperatures such as at  $-95^\circ\text{C}$  or the presence of trimethylsilyl triflate as a catalyst was employed, 1,4-addition was rather favoured (entries 9 and

10). Such a temperature effect was observed also in compound **6k** (entry 15).

The reaction with a series of silyl ketene ketals **6n–p** was carried out similarly, and in this case titanium tetrachloride and zinc chloride were both found to be effective. However, these catalysts played a contrasting role. In the titanium tetrachloride-catalysed reaction, a disubstituted ketal **6p** no longer followed the previous mode of addition even if the reactive site is more crowded. All the ketals **6n–p** underwent the 1,2-addition at  $-78^\circ\text{C}$  to give acyloins **7n–p** (entries 17, 20 and 22). On the other hand, zinc chloride catalysed the 1,4-addition at room temperature to give product **8n–p** (entries 18, 21 and 23). The difference in catalytic action of the Lewis acids led to the formation of either addition products **7n–p** or substitution products **8n–p**.<sup>\*</sup> A related example of the dependence of products on a Lewis acid has been reported in silyl ketene ketal chemistry.<sup>40</sup> The temperature effect found for compounds **6g** and **6k** was also looked for in ketal **6n**, but no change in the mode of addition was observed (entry 19).

With these results in mind, we have applied the present method to the methyl ester chloride **3**, the diethyl amide chloride **4**, and the ethyl diester **5**. These compounds are expected to have relatively lower reactivity than the dichloride **2**, and in fact this was reflected in the higher reaction temperature and non-reactivity with some organosilanes. In particular, the reaction site was limited to the olefinic carbon in reactions with the diester **5**. As amino and alkoxy substituents on the ring attenuate one of the two carbonyl functionalities (namely, vinylogous ester and amide), the reaction occurred preferentially across the alternative chlorine-substituted enone moiety. First, the reaction of the ester chloride **3** was examined from  $-78$  to  $0^\circ\text{C}$  in the presence of titanium tetrachloride for 10 min, and the best yield was attained at  $-15^\circ\text{C}$ . The diethylamide chloride **4** was in turn less reactive than the ester chloride **3** and the products were obtained in satisfactory yields only at  $0^\circ\text{C}$ , although the yield decreased substantially for the more crowded organosilane **6i** and no product was obtained from compound **6d**. Notably, the mode of addition of substrates **3** and **4** with a series of unsaturated organosilanes resembled that of the dichloride **2**. Compared with the above chlorides **2–4**, diester **5** showed diverse reactivity. Under the catalysed conditions with titanium tetrachloride at  $-15^\circ\text{C}$ , diester **5** reacted with silyl enol ethers **6g**, **6h** and **6k** and a silyl ketene ketal **6p**, but not with the allylsilane **6a** or the more crowded silyl enol ether **6i**, because of its poor electrophilicity. In these cases, all the products, **13g**, **13h**, **13k** and **13p**, arose from 1,4-addition, irrespective of the substitution pattern of the organosilanes (entries 42–45). Hence, diester **5** has the advantage of selective synthesis for 3-substituted cyclobutene-1,2-diones.



The structural determination was based on IR, NMR and mass spectra, and whether the product formed *via* 1,2- or 1,4-

\* Competitive formation of a titanate intermediate, prior to addition, may change the course of reaction to the 1,2-addition mode. Indeed, when initial mixing of silyl ketene ketal **6p** and titanium tetrachloride to form a titanium enolate was followed by addition of compound **2**, the product **7p** could be produced also. Similarly, with the silyl enol ether **6i**, the product was **7i** rather than **8i** if the reagents were mixed in this way. The problem on the order of mixing these reagents is discussed in ref. 39.

addition could be clearly deduced by spectral analysis as exemplified first in the case of products **7a** and **8d**. The products from  $\gamma$ -monosubstituted silanes **6c**, **6e**, **6h**, **6k**, **6l** and **6o** each consisted of a diastereoisomeric mixture (ratio  $\sim$ 1:1 to 1:4) which was analysed without further separation.

In conclusion, the squaric acid family consisting of the dichloride **2**, methyl ester chloride **3**, diethylamide chloride **4**, and ethyl diester **5** were shown to be reactive with unsaturated organosilanes **6** in the presence of a Lewis acid, furnishing 1,2-addition products **7**, **9** and **11** and/or  $\beta$ -substitution products **8**, **10**, **12** and **13** via 1,4-addition followed by dechlorosilylation; (1) The reactivity is in the order  $2 > 3 > 4$ , corresponding to the reaction temperature of from  $-95$  to  $0^\circ\text{C}$ . The much lower reactivity of diester **5** is reflected in the limited reaction (*i.e.*, only with a silyl enol ether and silyl ketene ketal). (2) The 1,2- vs. 1,4-addition reactivity is controlled primarily by the presence of one substituent on both the squaric acid **1** and the organosilanes **6**; 1,2-addition occurs with the chlorides **2**, **3** and **4**, and 1,4-addition with the diester **5**. Instead, 1,4-addition prevails over 1,2-addition if allylsilanes and silyl enol ethers are doubly substituted at the reactive site  $\gamma$  to a silyl group. (3) This addition mode is changed in some cases by both change in reaction temperature and the presence of a catalyst, *e.g.* from 1,2- to 1,4-addition at  $-95^\circ\text{C}$  or by addition of zinc chloride. The products obtained above are good precursors for the ring transformation via a thermally allowed electrocyclic ring-opening,<sup>6-13</sup> and our work is now continuing with this in view.

## Experimental

**General.**—IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with a Varian GEMINI-200 spectrometer at 200 and 50 MHz, respectively, for samples in  $\text{CDCl}_3$  solution with  $\text{SiMe}_4$  as internal standard. *J*-Values are given in Hz. Mass spectra were recorded on a ESCO-EMD-05B spectrometer (EI at 20 or 70 eV). Flash chromatography was performed with a silica gel column (Fuji-Davison BW-300) eluted with mixed solvents [hexane (H), ethyl acetate (A)]. Microanalyses were performed with a Perkin-Elmer 2400 elemental analyser.

**Reagents and Solvents.**—Dichloromethane was dried over  $\text{CaCl}_2$ , distilled, and stored over 4 Å molecular sieves. Silyl enol ethers and silyl ketene ketals were obtained according to the standard methods developed by House and Ainsworth,<sup>41,42</sup> and allylsilanes were prepared by reactions of the corresponding organometallics with trimethylsilyl chloride;<sup>43</sup> Sakurai's modification<sup>44</sup> was used for crotylsilane **6c** (*E:Z* 36:64). Squaric acid **1** was supplied by Kyowa Hakko Kogyo Co. Ltd.

**Squaric Acid Family.**—Dichloride **2**, methyl ester chloride **3**, diethylamide chloride **4**, and ethyl diester **5** were prepared by following the reported procedures.

**Dichloride 2.** A mixture of acid **1** (1.14 g, 10 mmol), thionyl dichloride (1.8  $\text{cm}^3$ , 20 mmol) and DMF (5 drops) in dry benzene (10  $\text{cm}^3$ ) was refluxed for 6 h. The solvent was replaced with hexane (20  $\text{cm}^3$ ) and the soluble products were separated from gummy precipitates. Concentration and cooling, followed by filtration under nitrogen, gave yellow crystallines, which were further purified by sublimation ( $50^\circ\text{C}/20$  mmHg) to give chloride **2** (0.82 g, 54%).

**Ester chloride 3.** A solution of dichloride **2** (0.76 g, 5 mmol) in dry THF (10  $\text{cm}^3$ ) containing methanol (0.39  $\text{cm}^3$ , 10 mmol) was refluxed for 40 min. After evaporation of the solvent, addition and evaporation of dry diethyl ether (5  $\text{cm}^3$ ) were repeated until the residue solidified. Sublimation of the solid ( $120^\circ\text{C}/0.1$  mmHg) gave methyl ester chloride **3** (0.68 g, 94%) as yellow crystals; m.p.  $43.5$ – $47.1^\circ\text{C}$ ;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1811,

1767 and 1605 (cyclobutenedione);  $\delta_{\text{H}}$  4.53 (3 H, s, Me);  $\delta_{\text{C}}$  62.2, 167.0, 189.2, 192.1 and 197.4; *m/z* 148 and 146 ( $\text{M}^+ + 2$ ,  $\text{M}^+$ ; 1:3), 120 and 118 ( $\text{M}^+ + 2 - \text{CO}$ ,  $\text{M}^+ - \text{CO}$ ; 1:3) and 105 and 103 ( $\text{M}^+ + 2 - \text{CO} - \text{CH}_3$ ,  $\text{M}^+ - \text{CO} - \text{CH}_3$ ; 1:3, base).

**Amide chloride 4.** To a solution of dichloride **2** (0.91 g, 6 mmol) in dry dichloromethane (8  $\text{cm}^3$ ) at below  $10^\circ\text{C}$  was added diethylamino(trimethyl)silane (0.87 g, 6 mmol) dropwise, and the solution was refluxed for 30 min. After evaporation of the solvent, the residue was chromatographed on a silica gel column (elution H–A 2:1) to give diethylamide chloride **4** (0.99 g, 85%) as deep yellow crystals, m.p.  $49.2$ – $53.3^\circ\text{C}$ ;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1800, 1746 and 1622 (cyclobutenedione);  $\delta_{\text{H}}$  1.31 and 1.36 (each 3 H, t, *J* 7.2, Me) and 3.67 and 3.81 (each 2 H, q, *J* 7.2,  $\text{CH}_2$ );  $\delta_{\text{C}}$  14.3, 14.4, 44.5, 45.0, 150.7, 178.9, 185.5 and 191.5; *m/z* 189 and 187 ( $\text{M}^+ + 2$ ,  $\text{M}^+$ ; 1:3), 161 and 159 ( $\text{M}^+ + 2 - \text{CO}$ ,  $\text{M}^+ - \text{CO}$ , 1:3), 133 and 131 ( $\text{M}^+ + 2 - 2 \times \text{CO}$ ,  $\text{M}^+ - 2 \times \text{CO}$ ; 1:3), 118 and 116 ( $\text{M}^+ + 2 - 2 \times \text{CO} - \text{CH}_3$ ,  $\text{M}^+ - 2 \times \text{CO} - \text{CH}_3$ ; 1:3, base).

**Diester 5.** A suspension of acid **1** (1.14 g, 10 mmol) in ethanol (30  $\text{cm}^3$ )–benzene (10  $\text{cm}^3$ ) was refluxed for 10 h, using a Dean–Stark apparatus containing 3 Å molecular sieves as a dehydrant. Then the solvent was replaced with diethyl ether, and precipitates were removed by filtration. After evaporation of the solvent, the residual oil was subjected to bulb-to-bulb distillation [ $95^\circ\text{C}$  (oven temp.)/0.1 mmHg] to give diester **5** (1.51 g, 89%).

**Reaction of Squaric Acid Family with Unsaturated Organosilanes. General Procedure.**—To a solution of the acid family (0.5 mmol) and an organosilane (1 mmol) in dry dichloromethane (2  $\text{cm}^3$ ) was added titanium tetrachloride (0.06  $\text{cm}^3$ , 0.5 mmol) by syringe at the temperature depicted in Table 1 with exclusion of moisture. After an appropriate time, the reaction mixture was poured into cold water and extracted with dichloromethane. The extracts were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. Flash chromatography of the residue with the solvent specified gave the products. Unless otherwise noted, this procedure was applied to obtain the following products. Other catalysts employed were trimethylsilyl triflate (entry 10; catalytic amount, 5 mol%), tin(IV) chloride (entry 2) and zinc chloride (entries 18, 21 and 23), with which the reactions were carried out similarly at  $-78^\circ\text{C}$  or room temperature. See Table 1 for reaction conditions and isolated yields for each case.

**2,3-Dichloro-4-hydroxy-4-(prop-2-enyl)cyclobut-2-enone 7a.**—(Elution H–A 15:2), oil; TLC (H–A 15:2)  $R_f$  0.3; analytical data are cited in our previous paper.<sup>32</sup>

**2,3-Dichloro-4-hydroxy-4-(2-methylprop-2-enyl)cyclobut-2-enone 7b.**—(Elution: H–A 15:2), oil (Found: C, 46.2; H, 4.0.  $\text{C}_8\text{H}_8\text{Cl}_2\text{O}_2$  requires C, 46.4; H, 3.9%); TLC (H–A 15:2)  $R_f$  0.33;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3431 (OH), 1780 and 1580 (cyclobutenone) and 1647 (C=C);  $\delta_{\text{H}}$  1.85 (3 H, s, Me), 2.56 and 2.70 (each 1 H, dd, *J* 14 and 0.8,  $\text{CH}_2\text{C}=\text{C}$ ), 3.20 (1 H, br s, OH) and 5.01 (2 H, m, C=CH<sub>2</sub>);  $\delta_{\text{C}}$  23.3, 41.2, 92.5, 118.1, 139.4, 140.9, 170.4 and 187.6; *m/z* 210, 208 and 206 ( $\text{M}^+ + 4$ ,  $\text{M}^+ + 2$ ,  $\text{M}^+$ ; 1:6:9), 195, 193 and 191 ( $\text{M}^+ + 4 - \text{CH}_3$ ,  $\text{M}^+ + 2 - \text{CH}_3$ ,  $\text{M}^+ - \text{CH}_3$ ; 1:6:9), 182, 180 and 178 ( $\text{M}^+ + 4 - \text{CO}$ ,  $\text{M}^+ + 2 - \text{CO}$ ,  $\text{M}^+ - \text{CO}$ ; 1:6:9), 145 and 143 ( $\text{M}^+ + 2 - \text{CO} - \text{Cl}$ ,  $\text{M}^+ - \text{CO} - \text{Cl}$ ; 1:3) and 107 (base).

**2,3-Dichloro-4-hydroxy-4-(1-methylprop-2-enyl)cyclobut-2-enone 7c.**—Obtained as a  $\sim$ 1:1 diastereoisomeric mixture (elution H–A 15:2), oil (Found: C, 46.2; H, 4.0%); TLC (H–A 15:2)  $R_f$  0.33;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3451 (OH), 1782 and 1580 (cyclobutenone) and 1640 (C=C);  $\delta_{\text{H}}$  1.11 and 1.15 (each 1.5 H,

d,  $J$  7.0, Me), 2.78 (1 H, m, CHC=C), 2.80 (1 H, br s, OH), 5.28 (2 H, m, CH=CH<sub>2</sub>) and 5.85 (1 H, m, CH=CH<sub>2</sub>);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 15.0 and 15.4, 41.8 and 42.2, 95.8 and 95.7, 119.6 and 120.0, 133.8 and 134.1, 136.7 and 137.2, 169.2 and 170.3, and 187.4 and 187.5;  $m/z$  210, 208 and 206 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ , 1:6:9), 195, 193 and 191 ( $M^+ + 4 - CH_3$ ,  $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:6:9), 182, 180 and 178 ( $M^+ + 4 - CO$ ,  $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:6:9) and 107 (base).

**3-Chloro-4-(1,1-dimethylprop-2-enyl)cyclobut-3-ene-1,2-dione 8d.**—Isolated as the first fraction (elution H-A 15:2), oil (Found: C, 58.5; H, 4.9. C<sub>9</sub>H<sub>9</sub>ClO<sub>2</sub> requires C, 58.6; H, 4.9%); TLC (H-A 15:2)  $R_f$  0.58;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  1809, 1775 and 1561 (cyclobutenedione) and 1635 (C=C);  $\delta_H$  1.54 (6 H, s, Me), 5.18 and 5.23 (each 1 H, d,  $J$  17.3 and 10.5, respectively, C=CH<sub>2</sub>) and 6.07 (1 H, dd,  $J$  17.3 and 10.5, CH=C);  $\delta_C$  24.3, 41.5, 115.4, 140.1, 185.3, 193.0, 195.5 and 206.1;  $m/z$  186 and 184 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 171 and 169 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 158 and 156 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 121 ( $M^+ - CO - Cl$ ) and 91 (base).

The second fraction was the minor, oily product **7d**, which showed TLC (H-A 15:2)  $R_f$  0.48;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3461 (OH), 1782, 1582 (cyclobutenone) and 1635 (C=C);  $\delta_H$  1.25 and 1.26 (each 3 H, s, Me), 2.80 (1 H, br s, OH), 5.29 and 5.33 (each 1 H, dd,  $J$  17.4 and 1, and 10.8 and 1, respectively, C=CH<sub>2</sub>) and 6.06 (1 H, dd,  $J$  17.4 and 10.8, CH=C);  $\delta_C$  21.9, 22.7, 42.4, 97.9, 116.8, 134.4, 141.9, 169.5 and 187.6;  $m/z$  (no molecular ion) 208, 206 and 204 ( $M^+ + 4 - CH_4$ ,  $M^+ + 2 - CH_4$ ,  $M^+ - CH_4$ ; 1:6:9), 181, 179 and 177 ( $M^+ + 4 - CO - CH_3$ ,  $M^+ + 2 - CO - CH_3$ ,  $M^+ - CO - CH_3$ ; 1:6:9) and 92 (base) (Found: C, 48.9; H, 4.6. C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 48.9; H, 4.6%).

**2,3-Dichloro-4-(cyclopent-2-enyl)-4-hydroxycyclobut-2-enone 7e.**—Obtained as a ~1:2 diastereoisomeric mixture (elution H-A 15:2), oil (Found: C, 49.4; H, 3.7. C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 49.3; H, 3.7%); TLC (H-A 15:2)  $R_f$  0.34;  $\nu_{max}(\text{CHCl}_3)/\text{cm}^{-1}$  3470 (OH) and 1782 and 1580 (cyclobutenone);  $\delta_H$  2.00–2.20 (2 H, m, ring 5-H<sub>2</sub>), 2.30–2.60 (3 H, m, ring 4-H<sub>2</sub> + OH), 3.16–3.35 (1 H, m, ring 1-H), and 5.67 and 6.04 (each 1 H, m, ring 2- and 3-H);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 24.2 and 23.9, 32.3, 49.6 and 49.5, 95.4 and 95.2, 127.3 and 127.9, 136.2, 137.1 and 137.0, 171.5 and 170.1, and 187.9 and 189.7;  $m/z$  222, 220 and 218 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 194, 192 and 190 ( $M^+ + 4 - CO$ ,  $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:6:9), 157 and 155 ( $M^+ + 2 - CO - Cl$ ,  $M^+ - CO - Cl$ ; 1:3) and 119 (base).

**2,3-Dichloro-4-hydroxy-4-(prop-2-ynyl)cyclobut-2-enone 7f.**—(Elution H-A 15:2), oil (Found: C, 43.9; H, 2.1. C<sub>7</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 44.0; H, 2.1%); TLC (H-A 15:2)  $R_f$  0.34;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3426 (OH), 3302, 2120 (C≡C) and 1779 and 1580 (cyclobutenone);  $\delta_H$  2.19 (1 H, t,  $J$  2.7, C≡CH), 2.85 (2 H, d,  $J$  2.7, CH<sub>2</sub>) and 3.15 (1 H, br s, OH);  $\delta_C$  23.1, 74.0, 76.3, 92.6, 135.6, 169.8 and 186.4;  $m/z$  194, 192 and 190 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 166, 164 and 162 ( $M^+ + 4 - CO$ ,  $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:6:9), 129 and 127 ( $M^+ + 2 - CO - Cl$ ,  $M^+ - CO - Cl$ ; 1:3) and 91 (base).

**2,3-Dichloro-4-hydroxy-4-phenacylcyclobut-2-enone 7g.**—(Elution H-A 5:1), oil (Found: C, 53.0; H, 3.1. C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>3</sub> requires C, 53.2; H, 3.0%); TLC (H-A 5:1)  $R_f$  0.25;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3432 (OH), 1784 and 1582 (cyclobutenone) and 1684 (C=O);  $\delta_H$  3.49 and 3.63 (each 1 H, d,  $J$  17.8, CH<sub>2</sub>), 5.20 (1 H, br s, OH) and 7.48–7.98 (5 H, m, Ph);  $\delta_C$  39.0, 92.4, 128.8, 129.3, 134.5, 135.0, 136.0, 169.8, 185.5 and 199.1;  $m/z$  274, 272 and 270 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 236 and 234 ( $M^+ +$

$2 - HCl$ ,  $M^+ - HCl$ ; 1:3), 209 and 207 ( $M^+ + 2 - CO - Cl$ ,  $M^+ - CO - Cl$ ; 1:3) and 105 (base).

**3-Chloro-4-phenacylcyclobut-3-ene-1,2-dione 8g.**—Obtained as crystals when the reaction was conducted at  $-95^\circ\text{C}$  or with 5 mol% trimethylsilyl triflate as a catalyst (elution H-A 15:2), m.p. 138–141°C (Found: C, 61.3; H, 3.1. C<sub>12</sub>H<sub>7</sub>ClO<sub>3</sub> requires C, 61.4; H, 3.0%); TLC (H-A 15:2)  $R_f$  0.38;  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3432 (enol) and 1784, 1724 and 1564 (cyclobutenedione);  $\delta_H$  6.21 (1 H, s, C=CH), 7.45–7.59 (5 H, m, Ph) and 11.00 (1 H, s, OH);  $\delta_C$  88.7, 128.2, 129.3, 133.2, 133.3, 172.4, 175.1, 188.4, 187.0 and 202.7;  $m/z$  236 and 234 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 208 and 206 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ , 1:3), 199 ( $M^+ - Cl$ ) and 92 (base).

**4-(1-Benzoyl-ethyl)-2,3-dichloro-4-hydroxycyclobut-2-enone 7h.**—Obtained as a ~1:1 diastereoisomeric mixture (elution H-A 5:1), oil (Found: C, 54.9; H, 3.4. C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>3</sub> requires C, 54.8; H, 3.5%); TLC (H-A 5:1)  $R_f$  0.33;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3420 (OH), 1782 and 1580 (cyclobutenone) and 1678 (C=O);  $\delta_H$  1.65 and 1.72 (each 1.5 H, d,  $J$  7.2, Me), 4.06 and 4.14 (each 0.5 H, q,  $J$  7.2, CH), 5.35 and 5.60 (each 0.5 H, br s, OH), and 7.62–8.13 (5 H, m, Ph);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 13.8 and 14.8, 42.4 and 42.8, 95.0 and 95.1, 126.3 and 127.9, 128.7 and 128.8, 129.1 and 129.2, 129.4 and 129.5, 134.8 and 135.0, 168.8 and 171.3, 184.8 and 186.5, and 203.5 and 204.3;  $m/z$  288, 286 and 284 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 273, 271 and 269 ( $M^+ + 4 - CH_3$ ,  $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:6:9), 222 and 220 ( $M^+ + 2 - CO - HCl$ ,  $M^+ - CO - HCl$ ; 1:3) and 91 (base).

**3-Chloro-4-(1-benzoyl-1-methylethyl)cyclobut-3-ene-1,2-dione 8i.**—Isolated as the first fraction (elution H-A 15:2), oil (Found: C, 63.8; H, 4.3. C<sub>14</sub>H<sub>11</sub>ClO<sub>3</sub> requires C, 64.0; H, 4.2%); TLC (H-A 15:2)  $R_f$  0.35;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  1813, 1786, 1557 (cyclobutenedione) and 1687 (C=O);  $\delta_H$  1.81 (6 H, s, Me) and 7.39–7.77 (5 H, m, Ph);  $\delta_C$  24.0, 49.9, 128.8, 129.4, 133.9, 134.0, 135.2, 186.7, 192.0, 195.1, 197.8 and 204.1;  $m/z$  264 and 262 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 236 and 234 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 226 ( $M^+ - HCl$ ) and 107 (base).

The second fraction was a minor, oily product **7i**, which showed TLC (H-A 15:2)  $R_f$  0.2;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3447 (OH), 1782, 1575 (cyclobutenone) and 1684 (C=O);  $\delta_H$  1.48 and 1.61 (each 3 H, s, Me), 5.60 (1 H, br s, OH) and 7.43–7.76 (5 H, m, Ph);  $m/z$  302, 300 and 298 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 287, 285 and 283 ( $M^+ + 4 - CH_3$ ,  $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:6:9), 265 and 263 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3), 236 and 234 ( $M^+ + 2 - CO - Cl$ ,  $M^+ - CO - Cl$ ; 1:3) and 105 (base) (Found: C, 56.1; H, 4.2. C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>3</sub> requires C, 56.2; H, 4.0%).

**4-[(Adamant-1-yl)carbonylmethyl]-2,3-dichloro-4-hydroxycyclobut-2-enone 7j.**—Isolated as the second fraction (elution H-A 15:2), oil (Found: C, 58.6; H, 5.4. C<sub>16</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>3</sub> requires C, 58.4; H, 5.5%); TLC (H-A 15:2)  $R_f$  0.15;  $\nu_{max}(\text{CHCl}_3)/\text{cm}^{-1}$  3389 (OH), 1786, 1584 (cyclobutenone) and 1684 (C=O);  $\delta_H$  1.60–2.16 (15 H, m, adamantyl), 2.83 and 3.30 (each 1 H, d,  $J$  17.8, CH<sub>2</sub>) and 4.98 (1 H, br s, OH);  $\delta_C$  27.9, 36.5, 38.0, 38.4, 91.1, 135.1, 177.8, 187.8 and 196.0;  $m/z$  333, 331 and 329 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 295 and 293 ( $M^+ + 2 - HCl$ ,  $M^+ - HCl$ ; 1:3), 267 and 265 ( $M^+ + 2 - CO - HCl$ ,  $M^+ - CO - HCl$ ; 1:3) and 135 (base).

The first fraction was the minor product **8j**, m.p. 134–137°C, which showed TLC (H-A 15:2)  $R_f$  0.28;  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3449 (enol) and 1788, 1736 and 1559 (cyclobutenedione);  $\delta_H$  1.75–2.18 (15 H, m, adamantyl), 5.52 (1 H, d,  $J$  0.6, C=CH), 10.77 (1 H, d,  $J$  0.6, OH); a signal at  $\delta$  2.00 (s) may be ascribable to the keto form (<16% of the total compound);  $\delta_C$  28.0, 36.4, 39.8,

40.4, 87.2, 174.4, 184.6, 188.4 and 202.7; minor peaks appeared additionally due to the keto form;  $m/z$  294 and 292 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 266 and 264 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 257 ( $M^+ - Cl$ ), 238 and 236 ( $M^+ + 2 - 2 \times CO$ ,  $M^+ - 2 \times CO$ ; 1:3) and 135 (base) (Found: C, 65.5; H, 6.0.  $C_{16}H_{17}ClO_3$  requires C, 65.6; H, 5.9%).

**2-(2,3-Dichloro-1-hydroxy-4-oxocyclobut-2-enyl)cyclohexanone 7k.**—Obtained as a ~1:4 diastereoisomeric mixture (elution H-A 5:1), oil (Found: C, 48.2; H, 4.1.  $C_{10}H_{10}Cl_2O_3$  requires C, 48.2; H, 4.1%); TLC (H-A 5:1)  $R_f$  0.29;  $\nu_{max}(CHCl_3)/cm^{-1}$  3470 (OH), 1788 and 1578 (cyclobutenone) and 1700 (C=O);  $\delta_H$  1.25–3.10 (8 H, m, ring 3-, 4-, 5- and 6- $H_2$ ), 2.89 and 3.04 (0.2 H and 0.8 H respectively, ddd,  $J$  13, 5.6 and 1, ring 2-H) and 5.00 (1 H, br s, OH);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 24.3 and 24.4, 26.9 and 26.8, 29.7 and 29.5, 42.5 and 42.3, 51.0 and 51.5, 95.6 and 95.3, 134.9 and 134.8, 169.9 and 167.9, 184.9 and 185.3, and 213.6 and 213.1;  $m/z$  (no molecular ion) 215 and 213 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3) and 108 (base).

**3-Chloro-4-(2-oxocyclohexyl)cyclobut-3-ene-1,2-dione 8k.**—Obtained when the reaction was conducted at  $-95^\circ C$  (elution H-A 15:2), crystals, m.p. 78.5–80.2  $^\circ C$  (Found: C, 56.3; H, 4.5.  $C_{10}H_9ClO_3$  requires C, 56.5; H, 4.3%); TLC (H-A 15:2)  $R_f$  0.4;  $\nu_{max}(CHCl_3)/cm^{-1}$  3000 (enol) and 1786, 1734 and 1560 (cyclobutenedione);  $\delta_H$  1.40–2.70 (8 H, m, ring H) and 10.96 (1 H, s, OH);  $\delta_C$  21.2, 21.8, 24.3, 31.1, 102.0, 173.8, 176.1, 185.0, 187.4 and 202.0;  $m/z$  214 and 212 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 186 and 184 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 177 ( $M^+ - Cl$ ) and 113 (base).

**3-Chloro-4-(5-oxohomoadamant-4-yl)cyclobut-3-ene-1,2-dione 8l.**—Isolated as the first fraction (elution H-A 15:2), m.p. 133–136  $^\circ C$  (Found: C, 64.5; H, 5.6.  $C_{15}H_{15}ClO_3$  requires C, 64.6; H, 5.4%); TLC (H-A 15:2)  $R_f$  0.39;  $\nu_{max}(KBr)/cm^{-1}$  3410 (enol), 2918 (homoadamantyl) and 1780, 1718 and 1543 (cyclobutenedione);  $\delta_H$  1.78–3.37 (14 H, m, homoadamantyl) and 11.54 (1 H, s, OH); a signal at  $\delta$  4.01 may be ascribable to (<10% of the whole) keto form;  $\delta_C$  27.7, 32.1, 34.7, 35.0, 35.1, 39.7, 41.9, 49.1, 57.1, 112.2, 171.1, 183.9, 185.9, 189.9 and 203.1; minor peaks appeared additionally due to the keto form;  $m/z$  280 and 278 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 252 and 250 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 243 ( $M^+ - Cl$ ) and 92 (base).

The second fraction was the minor, oily product **7l** consisting of a ~1:1 diastereoisomeric mixture. This product was not stable enough for microanalysis (it partly decomposed during drying), and the structure was assigned only by spectral data; TLC (H-A 15:2)  $R_f$  0.28;  $\nu_{max}(neat)/cm^{-1}$  3389 (OH), 2916 (homoadamantyl), 1786 and 1580 (cyclobutenone) and 1670 (C=O);  $\delta_H$  1.60–2.90 (14 H, m, homoadamantyl), 3.03 and 3.25 (each 0.5 H, s, homoadamantane ring 4-H) and 5.20 (1 H, br s, OH);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 26.6 and 26.5, 29.0 and 29.3, 30.9 and 30.5, 32.0, 33.0 and 34.0, 35.0, 40.5 and 40.7, 49.3 and 49.2, 57.9, 97.1 and 96.8, 135.6 and 135.1, 167.7 and 169.9, 184.8 and 186.6, and 219.8 and 220.6;  $m/z$  (no molecular ion), 281 and 279 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3) and 210 (base).

**Phenyl (2,3-Dichloro-1-hydroxy-4-oxocyclobut-2-enyl)acetate 7n.**—(Elution H-A 15:2), oil (Found: C, 50.0; H, 2.9.  $C_{12}H_8Cl_2O_4$  requires C, 50.2; H, 2.8%); TLC (H-A 15:2)  $R_f$  0.21;  $\nu_{max}(neat)/cm^{-1}$  3449 (OH), 1788 and 1582 (cyclobutenone) and 1759 (C=O);  $\delta_H$  3.16 (2 H, s,  $CH_2$ ), 4.15 (1 H, br s, OH) and 7.09–7.46 (5 H, m, Ph);  $\delta_C$  36.6, 91.3, 121.6, 127.0, 130.0, 135.0, 150.3, 169.1, 169.4 and 185.1;  $m/z$  (no molecular ion) 252 and 250 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3) and 158 (base).

**Phenyl (2-Chloro-3,4-dioxocyclobut-1-enyl)acetate 8n.**—Obtained when the reaction was conducted with zinc chloride (elution H-A 15:2), oil (Found: C, 57.4; H, 2.9.  $C_{12}H_7ClO_4$  requires C, 57.5; H, 2.8%); TLC (H-A 15:2)  $R_f$  0.25;  $\nu_{max}(CHCl_3)/cm^{-1}$  1811, 1790 and 1589 (cyclobutenedione) and 1765 (C=O);  $\delta_H$  4.09 (2 H, s,  $CH_2$ ) and 7.12–7.46 (5 H, m, Ph);  $\delta_C$  31.5, 121.5, 127.0, 130.1, 150.5, 164.2, 190.2, 191.7, 193.5 and 194.5;  $m/z$  (no molecular ion) 224 and 222 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 187 ( $M^+ - CO - Cl$ ) and 92 (base).

**Ethyl 2-(2,3-Dichloro-1-hydroxy-4-oxocyclobut-2-enyl)propanoate 7o.**—Obtained as a ~1:2 diastereoisomeric mixture (elution H-A 15:2), oil (Found: C, 42.7; H, 4.0.  $C_9H_{10}Cl_2O_4$  requires C, 42.7; H, 4.0%); TLC (H-A 15:2)  $R_f$  0.21;  $\nu_{max}(neat)/cm^{-1}$  3430 (OH), 1794 and 1582 (cyclobutenone) and 1734 (C=O);  $\delta_H$  1.32 (3 H, t,  $J$  7.2,  $OCH_2Me$ ), 1.30 and 1.35 (each 2 H and 1 H, respectively, t,  $J$  7.2,  $COCH_2Me$ ), 2.96 and 3.05 (each 0.6' H and 0.3' H, respectively, q,  $J$  7.2, CH), 4.26 (2 H, q,  $J$  7.2,  $CH_2$ ) and 4.81 (1 H, br s, OH);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 12.9 and 12.4, 14.0 and 14.2, 41.8 and 41.5, 62.2, 94.6 and 94.7, 134.5 and 135.0, 169.2 and 168.6, 174.2 and 174.1, and 185.0 and 185.5;  $m/z$  (no molecular ion) 219 and 217 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3), 191 and 189 ( $M^+ + 2 - CO - Cl$ ,  $M^+ - CO - Cl$ ; 1:3) and 102 (base).

**Ethyl 2-(2-Chloro-3,4-dioxocyclobut-1-enyl)propanoate 8o.**—Obtained when the reaction was conducted with zinc chloride (elution H-A 15:2), oil (Found: C, 49.9; H, 4.2.  $C_9H_9ClO_4$  requires C, 49.9; H, 4.2%); TLC (H-A 15:2)  $R_f$  0.29;  $\nu_{max}(CHCl_3)/cm^{-1}$  1813, 1785 and 1578 (cyclobutenedione) and 1742 (C=O);  $\delta_H$  1.29 (3 H, t,  $J$  7,  $OCH_2Me$ ), 1.63 (3 H, d,  $J$  7.4,  $COCH_2Me$ ), 4.02 (1 H, q,  $J$  7.4, CH) and 4.25 (2 H, q,  $J$  7,  $CH_2$ );  $\delta_C$  13.8, 14.0, 38.2, 62.5, 169.0, 187.9, 192.2, 194.6 and 199.0;  $m/z$  218 and 216 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 189 and 187 ( $M^+ + 2 - CO - H$ ,  $M^+ - CO - H$ ; 1:2) and 161 and 159 ( $M^+ + 2 - CO - Et$ ,  $M^+ - CO - Et$ ; 1:3, base).

**Methyl 2-(2,3-Dichloro-1-hydroxy-4-oxocyclobut-2-enyl)-2-methylpropanoate 7p.**—(Elution H-A 5:1), oil (Found: C, 42.5; H, 4.1.  $C_9H_{10}Cl_2O_4$  requires C, 42.7; H, 4.0%); TLC (H-A 15:2)  $R_f$  0.21;  $\nu_{max}(neat)/cm^{-1}$  3436 (OH), 1794 and 1578 (cyclobutenone) and 1736 (C=O);  $\delta_H$  1.33 and 1.44 (each 3 H, s,  $CMe$ ), 3.80 (3 H, s,  $OMe$ ) and 5.14 (1 H, br s, OH);  $\delta_C$  21.5, 21.7, 45.0, 53.1, 97.6, 134.9, 168.5, 176.9 and 185.4;  $m/z$  256, 254 and 252 ( $M^+ + 4$ ,  $M^+ + 2$ ,  $M^+$ ; 1:6:9), 219 and 217 ( $M^+ + 2 - Cl$ ,  $M^+ - Cl$ ; 1:3) and 191 (base).

**Methyl 2-(2-Chloro-3,4-dioxocyclobut-1-enyl)-2-methylpropanoate 8p.**—Obtained when the reaction was conducted with zinc chloride (elution H-A 15:2), oil (Found: C, 49.9; H, 4.1.  $C_9H_9ClO_4$  requires C, 49.9; H, 4.2%); TLC (H-A 15:2)  $R_f$  0.28;  $\nu_{max}(CHCl_3)/cm^{-1}$  1815, 1785 and 1568 (cyclobutenedione) and 1744 (C=O);  $\delta_H$  1.68 (6 H, s,  $CMe_2$ ) and 3.79 (3 H, s,  $OMe$ );  $\delta_C$  22.8, 45.1, 53.3, 172.3, 186.1, 192.4, 194.4 and 202.1;  $m/z$  218 and 216 ( $M^+ + 2$ ,  $M^+$ ; 1:3) and 189 and 187 ( $M^+ + 2 - CO - H$ ,  $M^+ - CO - H$ ; 1:3, base).

**2-Chloro-4-hydroxy-3-methoxy-4-(prop-2-enyl)cyclobut-2-enone 9a.**—(Elution H-A 5:1), oil (Found: C, 51.0; H, 4.9.  $C_8H_9ClO_3$  requires C, 51.0; H, 4.8%);  $\nu_{max}(neat)/cm^{-1}$  3380 (OH) and 1779 and 1607 (cyclobutenone); TLC (H-A 3:1)  $R_f$  0.2;  $\delta_H$  2.61 and 2.68 (each 1 H, dd,  $J$  15.2 and 7.2,  $CH_2C=C$ ), 3.55 (1 H, br s, OH), 4.34 (3 H, s,  $OMe$ ), 5.16–5.31 (2 H, m,  $C=CH_2$ ) and 5.68–5.89 (1 H, m,  $CH=C$ );  $\delta_C$  37.5, 61.0, 89.3, 104.5, 120.8, 131.3, 183.8 and 188.1;  $m/z$  190 and 188 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 175 and 173 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 162 and 160 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 153 ( $M^+ - Cl$ ), and 103 (base).

**2-Chloro-4-hydroxy-3-methoxy-4-(2-methylprop-2-enyl)-cyclobut-2-enone 9b.**—(Elution H-A 5:1), *oil* (Found: C, 53.2; H, 5.6;  $C_9H_{11}ClO_3$  requires C, 53.4; H, 5.5%); TLC (H-A 3:1)  $R_f$  0.23;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3387 (OH) and 1779 and 1607 (cyclobutenone);  $\delta_H$  1.81 (3 H, dd,  $J$  0.8 and 0.6, Me), 2.57 and 2.66 (each 1 H, dd,  $J$  13.7 and 0.8,  $CH_2C=C$ ), 4.53 (3 H, s, OMe), 4.90 and 5.00 (each 1 H, m,  $C=CH_2$ );  $\delta_C$  23.1, 41.2, 61.0, 88.6, 104.6, 117.1, 140.1, 183.2 and 187.7;  $m/z$  204 and 202 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 189 and 187 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 176 and 174 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 166 ( $M^+ - HCl$ ) and 123 (base).

**2-Chloro-4-hydroxy-3-methoxy-4-(1-methylprop-2-enyl)-cyclobut-2-enone 9c.**—Obtained as a ~1:2 diastereoisomeric mixture (elution H-A 5:1), *oil* (Found: C, 53.4; H, 5.4.  $C_9H_{11}ClO_3$  requires C, 53.4; H, 5.5%); TLC (H-A 3:1)  $R_f$  0.23;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3412 (OH) and 1773 and 1605 (cyclobutenone);  $\delta_H$  1.12 and 1.13 (2 H and 1 H, respectively, d,  $J$  7, CMe), 2.64–2.82 (1 H, m,  $C=CCH$ ), 3.29 (1 H, br s, OH), 4.35 and 4.53 (2 H and 1 H, respectively, s, OMe), 5.16–5.27 (2 H, m,  $C=CH_2$ ) and 5.72–5.97 (1 H, m,  $CH=C$ );  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 15.1 and 15.3, 41.5 and 42.0, 61.1 and 61.0, 91.7 and 91.8, 104.5 and 104.7, 118.2 and 118.6, 137.9 and 137.8, 183.4 and 182.5, and 187.4 and 189.2;  $m/z$  204 and 202 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 189 and 187 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 176 and 174 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 166 ( $M^+ - HCl$ ) and 103 (base).

**3-(1,1-Dimethylprop-2-enyl)-4-methoxycyclobut-3-ene-1,2-dione 10d.**—(Elution H-A 5:1), *oil* (Found: C, 66.5; H, 6.8.  $C_{10}H_{12}O_3$  requires C, 66.7; H, 6.7%); TLC (H-A 3:1)  $R_f$  0.45;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  1792, 1765 and 1589 (cyclobutenedione);  $\delta_H$  1.43 (6 H, s,  $CMe_2$ ), 4.44 (3 H, s, OMe), 5.10 and 5.11 (each 1 H, dd,  $J$  17.5 and 0.6, and  $J$  10.3 and 0.6, respectively,  $C=CH_2$ ) and 6.05 (1 H, dd,  $J$  17.5 and 10.3,  $CH=C$ );  $\delta_C$  24.5, 40.4, 61.4, 133.8, 141.6, 188.6, 194.4, 195.2 and 197.6;  $m/z$  180 ( $M^+$ ), 165 ( $M^+ - CH_3$ ), 152 ( $M^+ - CO$ ), 137 ( $M^+ - CO - CH_3$ ) and 109 (base).

**2-Chloro-4-hydroxy-3-methoxy-4-phenacylcyclobut-2-enone 9g.**—(Elution H-A 3:1), *oil* (Found: C, 58.4; H, 4.3.  $C_{13}H_{11}ClO_4$  requires C, 58.6; H, 4.2%); TLC (H-A 3:1)  $R_f$  0.1;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3399 (OH), 1782 and 1611 (cyclobutenone) and 1684 ( $C=O$ );  $\delta_H$  3.38 and 3.59 (each 1 H, d,  $J$  17.5,  $CH_2$ ), 4.35 (3 H, s, OMe), 5.15 (1 H, br s, OH) and 7.45–7.69 (5 H, m, Ph);  $\delta_C$  39.3, 61.3, 88.1, 105.0, 128.8, 129.3, 134.8, 136.3, 182.7, 185.2 and 199.5;  $m/z$  268 and 266 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 230 ( $M^+ - HCl$ ), 203 ( $M^+ - CO - Cl$ ) and 105 (base).

**4-(1-Benzylethyl)-2-chloro-4-hydroxy-3-methoxycyclobut-2-enone 9h.**—Obtained as a ~1:2 diastereoisomeric mixture (elution H-A 3:1), *oil* (Found: C, 59.7; H, 4.8.  $C_{14}H_{13}ClO_4$  requires C, 59.9; H, 4.7%); TLC (H-A 3:1)  $R_f$  0.15;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3412 (OH), 1784 and 1615 (cyclobutenone) and 1680 ( $C=O$ );  $\delta_H$  1.43 and 1.56 (1 H and 2 H respectively, d,  $J$  7.2, CMe), 3.89 (1 H, q,  $J$  7.2, CH), 4.24 and 4.40 (2 H and 1 H, respectively, s, OMe), 5.02 and 5.09 (0.3' H and 0.6 H respectively, br s, OH) and 7.45–7.99 (5 H, m, Ph);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 14.4 and 14.2, 42.9 and 42.2, 61.3, 90.2 and 91.0, 104.4 and 105.2, 129.1 and 129.2, 129.4 and 129.3, 134.7 and 134.5, 135.2 and 135.5, 183.6 and 181.9, 184.7 and 186.3, and 204.5 and 204.1;  $m/z$  282 and 280 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 267 and 265 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 244 ( $M^+ - HCl$ ) and 105 (base).

**3-(1-Benzoyl-1-methylethyl)-4-methoxycyclobut-3-ene-1,2-dione 10i.**—(Elution H-A 3:1), *oil* (Found: C, 69.7; H, 5.5.  $C_{15}H_{14}O_4$  requires C, 69.8; H, 5.5%); TLC (H-A 3:1)  $R_f$  0.28;

$\nu_{max}(\text{neat})/\text{cm}^{-1}$  1792, 1761 and 1589 (cyclobutenedione) and 1682 ( $C=O$ );  $\delta_H$  1.71 (6 H, s, CMe), 4.33 (3 H, s, OMe) and 7.37–7.85 (5 H, m, Ph);  $\delta_C$  24.0, 48.9, 61.7, 128.8, 128.9, 133.4, 135.4, 185.8, 193.5, 194.3, 198.0 and 199.3;  $m/z$  258 ( $M^+$ ), 230 ( $M^+ - CO$ ), 215 ( $M^+ - CO - CH_3$ ) and 105 (base).

**2-(3-Chloro-1-hydroxy-2-methoxy-4-oxocyclobut-2-enyl)-cyclohexanone 9k.**—Obtained as a ~1:4 diastereoisomeric mixture (elution H-A 3:1), *oil* (Found: C, 54.0; H, 5.4.  $C_{11}H_{13}ClO_4$  requires C, 54.0; H, 5.3%); TLC (H-A 3:1)  $R_f$  0.1;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3414 (OH), 1784 and 1613 (cyclobutenone) and 1709 ( $C=O$ );  $\delta_H$  1.60–2.60 (8 H, m, ring  $[CH_2]_4$ ) 2.85 and 2.95 (0.2 H and 0.8 H respectively, ddd,  $J$  13, 5.8 and 1.2, ring 1-H), 4.34 and 4.36 (0.6 H and 2.4 H, respectively, s, OMe) and 4.92 (1 H, br s, OH);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 24.4, 27.0 and 26.8, 29.8 and 29.6, 42.5 and 42.4, 51.0 and 51.8, 61.3 and 61.1, 91.0, 105.4, 182.3 and 180.8, 184.4 and 184.9, and 214.1 and 213.3;  $m/z$  246 and 244 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 217 and 215 ( $M^+ + 2 - CO - H$ ,  $M^+ - CO - H$ ; 1:3), 209 ( $M^+ - Cl$ ), 181 ( $M^+ - CO - Cl$ ) and 105 (base).

**2-(2-Methoxy-3,4-dioxocyclobut-1-enyl)-2-methylpropanal 10m.**—(Elution H-A 3:1), *oil* (Found: C, 59.1; H, 5.6.  $C_9H_{10}O_4$  requires C, 59.3; H, 5.5%); TLC (H-A 3:1)  $R_f$  0.15;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  1794, 1765 and 1591 (cyclobutenedione) and 1734 ( $C=O$ );  $\delta_H$  1.50 (6 H, s,  $CMe_2$ ), 4.47 (3 H, s, OMe) and 9.61 (1 H, s, CHO);  $\delta_C$  19.6, 61.8, 103.8, 181.8, 193.7, 194.3, 198.1 and 199.1;  $m/z$  182 ( $M^+$ ), 153 ( $M^+ - CHO$ ) and 138 ( $M^+ - CHO - CH_3$ , base).

**Methyl 2-(3-Chloro-1-hydroxy-2-methoxy-4-oxocyclobut-2-enyl)-2-methylpropanoate 9p.**—(Elution H-A 3:1), *oil* (Found: C, 48.2; H, 5.4.  $C_{10}H_{13}ClO_5$  requires C, 48.3; H, 5.3%); TLC (H-A 3:1)  $R_f$  0.18;  $\nu_{max}(\text{neat})/\text{cm}^{-1}$  3437 (OH), 1784 and 1615 (cyclobutenone) and 1732 ( $C=O$ );  $\delta_H$  1.32 and 1.37 (each 3 H, s,  $CMe_2$ ), 3.77 (3 H, s,  $CO_2Me$ ), 4.36 (3 H, s, ring OMe) and 4.90 (1 H, s, OH);  $\delta_C$  21.7, 44.7, 52.9, 61.3, 93.3, 105.4, 177.4, 181.1 and 184.9;  $m/z$  250 and 248 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 235 and 233 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 213 ( $M^+ - Cl$ ) and 190 and 188 ( $M^+ + 2 - CO_2Me - H$ ,  $M^+ - CO_2Me - H$ ; 1:3, base).

**2-Chloro-3-diethylamino-4-hydroxy-4-(prop-2-enyl)cyclobut-2-enone 11a.**—(Elution H-A 2:1), *crystals*, m.p. 97–100 °C (Found: C, 57.6; H, 7.0; N, 6.0.  $C_{11}H_{16}ClNO_2$  requires C, 57.5; H, 7.0; N, 6.1%); TLC (H-A 1:1)  $R_f$  0.28;  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3316 (OH) and 1761 and 1595 (cyclobutenone);  $\delta_H$  1.30 (6 H, t,  $J$  7.2, 2 × Me), 2.56 and 2.85 (each 1 H, ddt,  $J$  14.4, 7.6 and 1, and  $J$  14.4, 7 and 1.2,  $C=CCH_2$ ), 3.40–3.76 (4 H, m,  $NCH_2$ ), 5.05–5.18 (2 H, m,  $C=CH_2$ ), 5.25 (1 H, br s, OH) and 5.58–5.79 (1 H, m,  $CH=C$ );  $\delta_C$  13.7, 14.4, 38.4, 43.4, 45.5, 88.6, 93.6, 119.2, 132.2, 171.0 and 185.9;  $m/z$  231 and 229 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 216 and 214 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 203 and 201 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3) and 142 (base).

**2-Chloro-3-diethylamino-4-hydroxy-4-(2-methylprop-2-enyl)-cyclobut-2-enone 11b.**—(Elution H-A 2:1), *crystals*, m.p. 90–93 °C (Found: C, 59.1; H, 7.4; N, 5.9.  $C_{12}H_{18}ClNO_2$  requires C, 59.1; H, 7.4; N, 5.8%); TLC (H-A 1:1)  $R_f$  0.3;  $\nu_{max}(\text{KBr})/\text{cm}^{-1}$  3218 (OH) and 1763 and 1589 (cyclobutenone);  $\delta_H$  1.29 and 1.32 (each 3 H, t,  $J$  7.2,  $NCH_2Me$ ), 1.75 (3 H, dd,  $J$  1.4 and 0.8,  $C=CMe$ ), 2.55 and 2.82 (each 1 H, dd,  $J$  13.8 and 0.6,  $C=CCH_2$ ), 3.37–3.83 (4 H, m,  $NCH_2$ ), 4.78 and 4.87 (each 1 H, m,  $C=CH_2$ ) and 4.97 (1 H, br s, OH);  $\delta_C$  13.4, 14.2, 23.4, 42.4, 43.2, 45.5, 88.6, 93.9, 115.8, 140.7, 170.6 and 185.7;  $m/z$  245 and 243 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 230 and 228 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 217 and 215 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3) and 188 and 186 ( $M^+ + 2 - CO - C_2H_5$ ,  $M^+ - CO - C_2H_5$ ; 1:3, base).

**2-Chloro-3-diethylamino-4-hydroxy-4-phenacylcyclobut-2-enone 11g.**—(Elution H–A 1:1), crystals, m.p. 135–138 °C (Found: C, 62.5; H, 5.9; N, 4.5.  $C_{16}H_{18}ClNO_3$  requires C, 62.4; H, 5.9; N, 4.6%); TLC (H–A 1:1)  $R_f$  0.2;  $\nu_{max}(KBr)/cm^{-1}$  3208 (OH), 1769 and 1597 (cyclobutenone) and 1676 (C=O);  $\delta_H$  1.27 and 1.35 (each 3 H, t,  $J$  7.2, Me), 3.41 and 3.71 (each 1 H, d,  $J$  16, COCH<sub>2</sub>), 3.50–3.72 (4 H, m, NCH<sub>2</sub>), 5.62 (1 H, br s, OH) and 7.42–7.99 (5 H, m, Ph);  $\delta_C$  13.4, 14.2, 41.1, 43.4, 45.7, 87.1, 94.6, 128.9, 129.0, 134.1, 136.9, 170.2, 183.7 and 198.6;  $m/z$  309 and 307 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 281 and 279 ( $M^+ + 2 - CO$ ,  $M^+ - CO$ ; 1:3), 204 and 202 ( $M^+ + 2 - PhCO$ ,  $M^+ - PhCO$ ; 1:3) and 104 (base).

**4-(1-Benzoyl-2-chloro-3-diethylamino-4-hydroxycyclobut-2-enone 11h.**—Obtained as a ~2:3 diastereoisomeric mixture (elution H–A 1:1), oil (Found: C, 63.6; H, 6.4; N, 4.3.  $C_{17}H_{20}ClNO_3$  requires C, 63.5; H, 6.3; N, 4.4%); TLC (H–A 1:1)  $R_f$  0.25;  $\nu_{max}(neat)/cm^{-1}$  3302 (OH), 1763 and 1593 (cyclobutenone) and 1680 (C=O);  $\delta_H$  1.18 and 1.21 (each 1.8 H, t,  $J$  7.2, NCH<sub>2</sub>Me), 1.29 and 1.31 (each 1.2 H, d,  $J$  7, NCH<sub>2</sub>Me), 1.27 and 1.39 (1.8 H and 1.2 H, respectively, d,  $J$  7.4, COCHMe), 3.21–3.78 (4 H, m, NCH<sub>2</sub>), 3.59 (1 H, br s, OH), 4.09 and 4.19 (0.6 H and 0.4 H, respectively, q,  $J$  7.4, COCH) and 7.41–8.03 (5 H, m, Ph);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 13.5 and 13.2, 14.2 and 14.1, 14.4 and 14.3, 43.4 and 43.1, 46.0 and 46.2, 90.4 and 90.5, 94.9 and 95.3, 128.9 and 129.0, 133.7 and 133.6, 137.0 and 137.8, 170.0 and 169.8, 182.6 and 184.1, and 202.7 and 202.6;  $m/z$  323 and 321 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 293 and 291 ( $M^+ + 2 - CO$ ; 1:3) and 104 (base).

**3-(1-Benzoyl-1-methylethyl)-4-(diethylamino)cyclobut-3-ene-1,2-dione 12i.**—(Elution H–A 1:1), crystals, m.p. 125–128 °C (Found: C, 72.0; H, 7.2; N, 4.8.  $C_{18}H_{21}NO_3$  requires C, 72.2; H, 7.1; N, 4.7%); TLC (H–A 1:1)  $R_f$  0.55;  $\nu_{max}(KBr)/cm^{-1}$  1777, 1732 and 1593 (cyclobutenedione) and 1676 (C=O);  $\delta_H$  0.87 and 1.03 (each 3 H, t,  $J$  7.4 and 7.2, respectively, NCH<sub>2</sub>Me), 1.80 (6 H, s, COCMe<sub>2</sub>), 3.09 and 3.70 (each 2 H, q,  $J$  7.2 and 7.4, respectively, NCH<sub>2</sub>) and 7.39–8.03 (5 H, m, Ph);  $\delta_C$  13.1, 14.4, 26.1, 42.9, 45.8, 49.4, 129.1, 129.7, 133.9, 134.7, 171.4, 181.0, 189.7, 194.2 and 201.4;  $m/z$  299 ( $M^+$ ), 271 ( $M^+ - CO$ ), 256 ( $M^+ - CO - CH_3$ ), 243 ( $M^+ - 2 \times CO$ ) and 138 (base).

**2-(3-Chloro-2-diethylamino-1-hydroxy-4-oxocyclobut-2-enyl)cyclohexanone 11k.**—Obtained as a ~1:2 diastereoisomeric mixture (elution H–A 1:1), crystals, m.p. 150–153 °C (Found: C, 58.9; H, 7.1; N, 4.8.  $C_{14}H_{20}ClNO_3$  requires C, 58.8; H, 7.1; N, 4.9%); TLC (H–A 1:1)  $R_f$  0.13;  $\nu_{max}(KBr)/cm^{-1}$  3254 (OH), 1759 and 1582 (cyclobutenone) and 1711 (C=O);  $\delta_H$  1.23 and 1.32 (each 3 H, t,  $J$  7.2, Me), 1.50–2.50 (8 H, m, ring [CH<sub>2</sub>]<sub>4</sub>), 2.73 and 3.03 (0.3 H and 0.6 H, respectively, dd,  $J$  10.4 and 6, ring 2-H), 3.30–3.78 (4 H, m, NCH<sub>2</sub>) and 5.38 (1 H, br s, OH);  $\delta_C$  pairing signals due to a diastereoisomeric mixture: 14.2 and 13.8, 14.8 and 14.6, 24.4 and 24.6, 25.6 and 26.9, 29.0 and 29.4, 42.1 and 42.9, 43.9, 45.6 and 46.2, 52.1 and 51.1, 91.6 and 90.8, 95.7 and 96.0, 166.8 and 171.2, 182.4 and 182.1, and 213.0 and 215.7;  $m/z$  287 and 285 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 258 and 256 ( $M^+ + 2 - CO - H$ ,  $M^+ - CO - H$ ; 1:3) and 116 (base).

**2-(2-Diethylamino-3,4-dioxocyclobut-1-enyl)-2-methylpropanal 12m.**—(Elution H–A 1:1), oil (Found: C, 64.4; H, 7.8; N, 6.2.  $C_{12}H_{17}NO_3$  requires C, 64.6; H, 7.7; N, 6.3%); TLC (H–A 1:1)  $R_f$  0.35;  $\nu_{max}(neat)/cm^{-1}$  1778, 1732 and 1595 (cyclobutenedione) and 1732 (C=O);  $\delta_H$  1.23 and 1.26 (each 3 H, t,  $J$  7.2, NCH<sub>2</sub>Me), 1.60 (6 H, s, OHCCMe<sub>2</sub>), 3.26 and 3.85 (each 2 H, q,  $J$  7.2, NCH<sub>2</sub>) and 9.58 (1 H, s, CHO);  $\delta_C$  13.0, 14.6, 21.4, 43.4, 46.1, 49.5, 165.7, 181.4, 190.5, 194.4 and 200.4;  $m/z$  223 ( $M^+$ ), 195 ( $M^+ - CO$ ), 167 ( $M^+ - 2 \times CO$ ) and 138 (base).

**Methyl 2-(3-Chloro-2-diethylamino-1-hydroxy-4-oxocyclobut-2-enyl)-2-methylpropanoate 11p.**—(Elution H–A 1:1), oil (Found: C, 53.7; H, 6.9; N, 4.9.  $C_{13}H_{20}ClNO_4$  requires C, 53.9; H, 6.9; N, 4.8%); TLC (H–A 1:1)  $R_f$  0.35;  $\nu_{max}(neat)/cm^{-1}$  3318 (OH), 1761 and 1597 (cyclobutenone) and 1730 (C=O);  $\delta_H$  1.24 and 1.31 (each 3 H, t,  $J$  7.2, NCH<sub>2</sub>Me), 1.34 and 1.42 (each 3 H, COCMe<sub>2</sub>), 3.29–3.74 (4 H, m, NCH<sub>2</sub>), 3.77 (3 H, s, OMe) and 5.15 (1 H, br s, OH);  $\delta_C$  13.4, 14.3, 22.2, 22.6, 43.2, 45.9, 46.3, 52.8, 93.2, 95.8, 168.8, 178.1 and 182.0;  $m/z$  291 and 289 ( $M^+ + 2$ ,  $M^+$ ; 1:3), 276 and 274 ( $M^+ + 2 - CH_3$ ,  $M^+ - CH_3$ ; 1:3), 254 ( $M^+ - Cl$ ), 232 and 230 ( $M^+ + 2 - CO_2Me$ ,  $M^+ - CO_2Me$ ; 1:3) and 124 (base).

**3-Ethoxy-4-phenacylcyclobut-3-ene-1,2-dione 13g.**—(Elution H–A 6:1), crystals m.p. 99–102 °C (Found: C, 69.0; H, 4.8.  $C_{14}H_{12}O_4$  requires C, 68.9; H, 4.9%); TLC (H–A 5:1)  $R_f$  0.15;  $\nu_{max}(KBr)/cm^{-1}$  3449 (enol) and 1782, 1717 and 1561 (cyclobutenedione);  $\delta_H$  1.54 (3 H, t,  $J$  7, Me), 4.90 (2 H, q,  $J$  7, OCH<sub>2</sub>), 5.98 (1 H, d,  $J$  0.6, C=CH), 7.39–7.88 (5 H, m, Ph) and 11.25 (1 H, d,  $J$  0.6, OH);  $\delta_C$  15.8, 71.5, 88.0, 127.4, 129.0, 131.9, 134.2, 168.7, 173.9, 184.4, 191.1 and 199.0;  $m/z$  244 ( $M^+$ ), 216 ( $M^+ - CO$ ), 187 ( $M^+ - CO - C_2H_5$ ) and 105 (base).

**3-(1-Benzoyl-1-methylethyl)-4-ethoxycyclobut-3-ene-1,2-dione 13h.**—(Elution H–A 6:1), oil (Found: C, 70.0; H, 5.4.  $C_{15}H_{14}O_4$  requires C, 69.8; H, 5.5%); TLC (H–A 5:1)  $R_f$  0.12;  $\nu_{max}(neat)/cm^{-1}$  1796, 1755 and 1597 (cyclobutenedione) and 1690 (C=O);  $\delta_H$  1.48 (3 H, t,  $J$  7.2, OCH<sub>2</sub>Me), 1.60 (3 H, d,  $J$  7, COCHMe), 4.74 (2 H, q,  $J$  7.2, OCH<sub>2</sub>), 4.77 (1 H, q,  $J$  7, COCH) and 7.41–8.01 (5 H, m, Ph);  $\delta_C$  14.0, 15.6, 39.5, 70.1, 128.9, 129.3, 134.3, 135.5, 180.7, 184.8, 189.8, 196.0 and 199.2;  $m/z$  258 ( $M^+$ ), 230 ( $M^+ - CO$ ) and 105 (base).

**3-Ethoxy-4-(2-oxocyclohexyl)cyclobut-3-ene-1,2-dione 13k.**—(Elution H–A 6:1), crystals, m.p. 128.5–130 °C (lit.,<sup>28</sup> 128 °C); TLC (H–A 5:1)  $R_f$  0.29;  $\nu_{max}(KBr)/cm^{-1}$  3449 (enol) and 1774, 1707 and 1580 (cyclobutenedione);  $\delta_H$  1.49 (3 H, t,  $J$  7.2, Me), 1.41–1.76 (8 H, m, ring [CH<sub>2</sub>]<sub>4</sub>), 4.85 (2 H, q,  $J$  7.2, OCH<sub>2</sub>) and 10.92 (1 H, s, OH).

**Methyl 2-(2-Ethoxy-3,4-dioxocyclobut-1-enyl)-2-methylpropanoate 13p.**—(Elution H–A 6:1), oil (Found: C, 58.3; H, 6.3.  $C_{11}H_{14}O_5$  requires C, 58.4; H, 6.2%); TLC (H–A 5:1)  $R_f$  0.22;  $\nu_{max}(neat)/cm^{-1}$  1796, 1755 and 1597 (cyclobutenedione) and 1740 (C=O);  $\delta_H$  1.48 (3 H, t,  $J$  7, OCH<sub>2</sub>Me), 1.59 (6 H, s, COCMe<sub>2</sub>), 3.75 (3 H, s, CO<sub>2</sub>Me) and 4.82 (2 H, q,  $J$  7, OCH<sub>2</sub>);  $\delta_C$  15.7, 23.0, 44.0, 52.9, 71.3, 173.5, 184.2, 193.4, 195.0 and 197.3;  $m/z$  226 ( $M^+$ ), 197 ( $M^+ - C_2H_5$ ) and 140 (base).

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