100. Octacarbonyldicobalt-Induced (1,3) H Shifts in 1-Methylallenecarboxylates and Allenic Lactones

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Dedicated to Professor Dr. *André S. Dreiding*

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The allenecarboxylates **1a, b** and allenic lactones **4a, b** undergo thermally induced (1,3) H shifts in the presence of $Co_2(CO)_8$. The non-isolated 1,3-dienes **2a, b** react further affording the *Diels-Alder* adducts **3a, b** *(Scheme 1)* in high yields. These adducts were not formed in the case of the 2-vinylbutenolides **5a, b** *(Scheme 2)*. On irradiation in the presence of $Co_2(CO)_8$ or $Mn_2(CO)_{10}$, the studied allenes reacted in a different manner, yielding either cyclization products **7** and **8** *(Scheme 3)* or products **9** and **10**, formed *via* H abstraction and solvent addition *(Schemes 4 and 5)*.

Introduction. – Allenes are known to take part in the *Diels-Alder* reaction as dienophiles [1] [2] or as dienes, provided they possess a conjugated vinylic substituent [3]. In continuation of previous work on the use of allenecarboxylates in the *Diels-Alder* reaction, we presently report the use of 1-methyl substituted allenecarboxylates in the *Diels-Alder* reaction in the presence of $Co_2(CO)_8$. The thermal behaviour of allenes when treated with $Co_2(CO)_8$ has been investigated earlier, but only polymerization [4], Co-complex formation [5], or inertness [6] have been observed. To our knowledge, there are no reports in the literature on C,C (1,3) H shifts in allenes induced by $Co_2(CO)_8$.

Thermal Behaviour of Allenes in the Presence of $Co_2(CO)_8$. – The allenecarboxylates **1a**, **1b** [7], and **1c** [1] as well as the allenic lactones **4a** and **4b** were found to be stable on heating in benzene at 90°. In the presence of 1 mol of $Co_2(CO)_8$ and under the same conditions, however, the esters **1a** and **1b** yielded the substituted mikanecic acid esters **3a** and **3b** in high yields *(Scheme 1)*, obviously *via* the primarily formed 1,3-dienes **2a** und **2b**, which spontaneously dimerized in a highly regioselective *Diels-Alder* fashion [8].

Scheme 1

1a-c   **2a, b**   **3a, b**

**a** $R = R' = CH_3$ **b** $R = CH_3, R' = C_2H_5$ **c** $R = Ph, R' = C_2H_5$

The structures **3a** and **3b** were established by the spectral data. Thus, the ^{1}H-NMR spectra showed one olefinic proton at about 6.5 ppm for H−C(1')^1), separate signals for two ester alkyl groups (Me or Et) and two *m*'s centered at about 2.4 and 2.1 ppm for two neighbouring CH$_2$ groups. The ^{13}C-NMR spectra also showed the presence of two ester-CO groups (one conjugated at about 167 ppm and the other non-conjugated at about 172 ppm), two CH$_2$ groups (*t*'s at about 29 and 22 ppm), and two quaternary C-atoms (*s*'s at about 60 and 54 ppm). Interestingly, the *retro-Diels-Alder* reaction was observed not to be a predominant fragmentation of these dimers under EI-MS conditions (see also [8]).

The allenic lactones **4a** and **4b** were found to undergo the same type of (1,3) H shift when heated in the presence of 1 mol-equiv. of Co$_2$(CO)$_8$. The 2-vinylbutenolides **5a** and **5b** formed, however, did not dimerize and could be isolated in high yields *(Scheme 2)*.

Scheme 2

4a,b　　　　　　　　　　　　　　**5a,b**
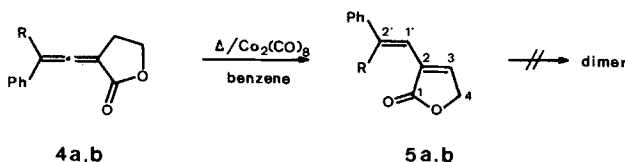
a R = CH$_3$　　**b** R = Ph

The structures of **5a** and **5b** were determined by the signals of H−C(3) (at 6.51 ppm for **5a** and 6.87 for **5b**) in the ^{1}H-NMR spectra and especially the ^{13}C-NMR signals of C(3) (*d* at 143.3 ppm for **5a** and 143.4 ppm for **5b**) and of C(2') (*s* at 144.1 ppm for **5a** and 148.2 ppm for **5b**). The (*E*)-configuration of the C(1')=C(2') bond of **5a** was established on the basis of the $^3J(CH_3,H)$ = 8.8 Hz [9].

An attempt to achieve the (1,3) H shift in the absence of Co$_2$(CO)$_8$ by heating a sample of **4b** under flow thermolysis conditions^2) failed to produce even traces of **5b**^{3}).

Treating dicyclohexylcarbodiimide under the same conditions as **1a,b** or **4a,b** with Co$_2$(CO)$_8$ afforded solely starting material.

Photochemical Behaviour of the Allenes. – The allenecarboxylates **1a**–**c** are known to rearrange photochemically affording cyclobutenones (*e.g.* **8**) and traces of 1,1,4,4-tetra-

Scheme 3

1b,c　　　　　　　　**6**　　　　　**7**　　　　　　　**8**

b R = CH$_3$　　**c** R = Ph
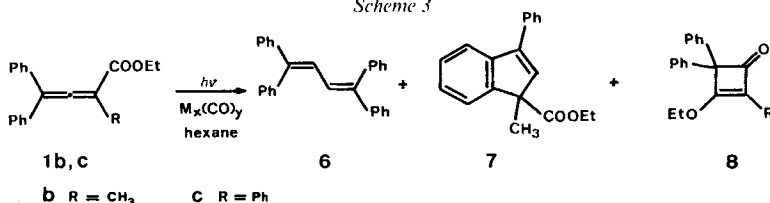
Starting material	M$_x$(CO)$_y$	Recovered 1 [%]	6 [%]	7 [%]	8 [%]
1b	Co$_2$(CO)$_8$	80	12	4	–
1b	Mn$_2$(CO)$_{10}$	60	4	4	–
1c	Co$_2$(CO)$_8$	80	trace	–	12

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^{1})　The absorption of the second olefinic proton H−C(2) was covered by the *m* of the aromatic protons.
^{2})　500°/0.5 Torr, N$_2$ flow of *ca.* 8 ml/min, 300-mm long quartz tube filled with quartz chips, and cold trap immersed in liquid N$_2$.
^{3})　Evidenced by GC, FID, 25-m *BP-5* glass capillary column, *Hewlett-Packard 5880A* instrument.

phenyl-1,3-butadiene (**6**) [10]. When the irradiation of **1b** was carried out in hexane in the presence of $Co_2(CO)_8$ or $Mn_2(CO)_{10}$, the yield of the 1,3-butadiene **6** increased *(Scheme 3)*, and a new product **7**[4]) was isolated in low yield, **8** being absent in the reaction mixture. On irradiation of **1c** in the presence of $Co_2(CO)_8$, however, the yield of **6** was not increased, and an indene derivative analogous to **7** was not observed. Instead, **8** was formed in lower yield as compared to the direct irradiation [10].

The structure of **6** was deduced from the comparison of the spectral data with those reported in [12] [13]. The structure of **7** was established by the MS (m/z 278 (M^+), 205 (M^+ – $COOC_2H_5$)), and the ^1H-NMR spectroscopy (1 $H–C=$, 2 diastereotopic CH_2 H-atoms, and CH_3 of an EtO group, and a CH_3 s (*cf.* [14])). The ^{13}C-NMR spectrum showed 3 s's for aromatic C-atoms and 1 s for an sp^3-C-atom.

Irradiation of the allenic lactone **4b** in hexane/Et_2O in the absence of $Co_2(CO)_8$ gave the 1,3-butadiene **6** in low yield and also two products **9** and **10**, whereas, in the presence of $Co_2(CO)_8$, **4b** decomposed *(Scheme 4)*.

Scheme 4

Reaction conditions	Recovered **4b** [%]	**6** [%]	**9** [%]	**10** [%][a])
hv[b])	15	3	18	21
$hv/Co_2(CO)_8$	[c])	2	–	–

[a])   Mixture of diastereoisomers.
[b])   Isolated non-optimized yields.
[c])   **4b** was only detected as an unseparable mixture.

The structure of **9**, having $M^+ = M(\mathbf{4b}) + 2$, was derived from the spectral data: the non-conjugated 5-membered lactone-CO group was evidenced from the absorption at 1770 cm^{-1} in the IR spectrum. The ^1H-NMR spectrum showed a d for H–C= at 5.88 ppm ($J = 5$) and m's for $–CH_2O$, $–CH–$, and $–CH_2–$. The ^{13}C-NMR spectrum exhibited a d at 40.9 ppm for C(2), a s at 147.1 ppm for C(2'), and a d at 129.9 ppm for C(1'). Compound **10** in the CI-MS showed m/z 337 ($M^+ + 1$) and 291 ($M^+ – CH_3CH_2O$) as dominant peaks, suggesting an addition product of **4b** and ether[5]). This structure was supported by NMR spectra. It is evident from the doubling of almost all signals that **10** is a mixture of two diastereoisomers.

Scheme 5

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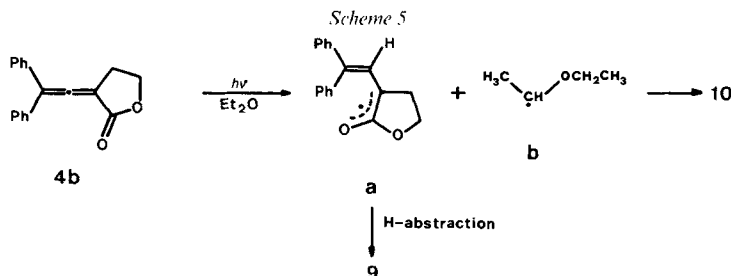
[4])   Formation of indene derivatives *via* isomerization of the Ph-substituted allenes in the presence of $Fe(CO)_5$ [6] or during irradiation [11] is known.

[5])   Photochemical addition of ethers onto C=C bonds of alkenes, enones, and quinones is known ([15], see also [16]).

The formation of **9** and **10** can be explained by proposing a radical pathway: the excited **4b** abstracts H from the ether-C(α) to give intermediates **a** and **b**. Recombination of **a** and **b** leads to **10**, whereas abstraction of another H from the solvent gives **9** *(Scheme 5)*.

Discussion. – The importance of $Co_2(CO)_8$ in carrying out (1,3) H shifts in the examined allenecarboxylates and allenic lactones is well demonstrated, since no reaction was found to take place in its absence. In the rearrangement of the H-atom, the electrophilicity of the central allene C-atom seems to play an important role. It is worth noting that only H-atoms in β-position with respect to a C=O function undergo a (1,3) shift, since **4a** afforded **5a** in high yield; no competing (1,3) H migration was detected taking place from the Me group at C(3) of the allene **4a** *(Scheme 2)*. It can be assumed that the C=O group takes part in the transient complexation facilitating in this way the H shift.

The 2-vinylbutenolides **5a** and **5b**, formed in high yields, unexpectedly failed to dimerize. An inspection of the transition states with the aid of *Dreiding* models indicates that the absence of this reaction can be ascribed to considerable interactions between the CH_2 H-atoms of the lactone of the diene with the C=O group of the dienophile.

The formation of the lactone **5a** and **5b** supports the postulated (1,3) H shift that affords the non-isolated dienes **2a,b** on the way to produce the *Diels-Alder* adducts **3a,b**. It can be concluded that in the presently observed cases the (1,3) H shifts proceed in a non-concerted manner as shown for other carbonyl-Co mediated (1,3) H shifts (*cf.* [17])[6].

Experimental Part

General. See [1].

1. **Methyl 2-Methyl-4,4-diphenyl-2,3-butadienoate (1a).** – A suspension of 2-methyl-4,4-diphenyl-2,3-butadienoic acid [7] (450 mg, 1.8 mmol) in Et_2O (5 ml) was treated with excess of CH_2N_2 soln. in Et_2O. After stirring for 10 min at r.t., the solvent was removed under vacuum, and the residue was recrystallized from MeOH at 0° to afford **1a** (390 mg) as colourless solid, m.p. 80.0–82.0°. A second fraction was obtained from the mother liquor (60 mg, total 95%), m.p. 79.5–82.0°. IR ($CHCl_3$): 1935m, 1705s, 1590m. ¹H-NMR (80 MHz, $CDCl_3$): 7.45–7.25 (m, arom. H); 3.78 (s, CH_3O); 2.08 (s, CH_3). ¹³C-NMR (50.4 MHz, $CDCl_3$): 212.5 (s, C(3)); 167.8 (s, C(1)); 135.4 (s, arom. C); 128.8, 128.6, 128.0 (3d, arom. CH); 112.5 (s, C(4)); 98.0 (s, C(2)); 52.3 (q, CH_3O); 15.3 (q, CH_3–C(2)). MS (70 eV): 265 (15), 264 (75, $M^{+\cdot}$), 250 (12), 249 (72), 221 (15), 205 (45), 203 (27), 202 (26), 189 (20), 178 (18), 165 (20), 105 (100), 77 (30). Anal. calc. for $C_{18}H_{16}O_2$ (264.33): C 81.79, H 6.10; found: C 81.29, H 6.08.

2. **2-(2-Phenyl-1-propenylidene)-4-butanolide (4a) and 2-(2,2-Diphenylvinylidene)-4-butanolide (4b).** – Lactones **4a** and **4b** were prepared following the procedure in [19] from diphenylacetyl chloride or 2-phenylpropionyl chloride and triphenyl(2-oxotetrahydrofuran-3-yliden)phosphorane [20] (*cf.* also [21]).

4a: 56%, m.p. 67.5–70.0° (Et_2O/hexane 2:1; [21]: viscous oil). UV (cyclohexane): 245 (9800). IR ($CHCl_3$): 3050w (sh), 2980w, 2915w, 1950m, 1745s, 1590w. ¹H-NMR (90 MHz, $CDCl_3$): 7.35 (br. s, arom. H); 4.41 (t, $J = 7.2$, CH_2O); 3.09 (t, $J = 7.2$, CH_2); 2.20 (s, CH_3). ¹³C-NMR (50.4 MHz, $CDCl_3$): 207.4 (s, C(1')); 169.8 (s, C(1)); 134.3 (s, arom. C); 128.6, 128.1, 126.3 (3d, arom. CH); 108.8 (s, C(2')); 94.7 (s, C(2)); 66.0 (t, CH_2O); 26.6 (t, CH_2); 16.5 (q, CH_3). MS (70 eV): 200 (94, $M^{+\cdot}$), 185 (6), 172 (40, $M^{+\cdot}$ – CO), 155 (63, $M^{+\cdot}$ – CHO_2), 141 (84), 129 (100), 115 (63), 77 (31). Anal. calc. for $C_{13}H_{12}O_2$ (200.24): C 77.98, H 6.04; found: C 78.10, H 5.77.

4b: 66%, m.p. 131–132° (dec., Et_2O/hexane; [21]: m.p. 132–133°). UV (cyclohexane): 234 (8100), 253 (5700). IR ($CHCl_3$): 2970m, 2910w, 2885w, 1945m, 1750s. ¹H-NMR (90 MHz, $CDCl_3$): 7.35 (m, arom. H); 4.42 (t, $J = 7.2$, CH_2O); 3.16 (t, $J = 7.2$, CH_2). ¹³C-NMR (50.4 MHz, $CDCl_3$): 208.2 (s, C(1')); 169.3 (s, C(1)); 134.2 (s, arom. C);

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[6]) A prototropic shift of the H-atom (*cf.* [18]) in the presently studied cases is unlikely, since the allenes **1b** and **4b** remained unchanged (as shown by TLC and GC), when refluxed for 3 h in benzene in the presence of 7.5 equiv. of weakly basic alumina *(Brockmann IV)*.

128.7, 128.5, 128.4 (3d, arom. CH); 117.3 (s, C(4)); 95.8 (s, C(2)); 65.9 (t, CH$_2$O); 26.8 (t, CH$_2$). MS (70 eV): 263 (20), 262 (100, $M^{+\cdot}$), 247 (9), 234 (13), 217 (28, $M^{+\cdot}$ – CHO$_2$), 215 (17), 202 (30), 179 (10), 105 (66).

3. Isomerization of 1a,b and 4a,b on Heating with Co$_2$(CO)$_8$. – A suspension of **1a,b** or **4a,b** (1 mmol) and Co$_2$(CO)$_8$ (1.2 mmol) in dry benzene (4 ml) was heated in a sealed tube for 24 h at 90° in the first case, and refluxed for 3 h in the latter case. The solvent was removed under vacuum and the residue was chromatographed on 5 prep. TLC plates with petroleum ether/Et$_2$O 9:1 (twice) in the case of **1a,b**, or with petroleum ether/Et$_2$O/AcOEt/butan-2-one 81:12:3.5:3.5 in the case of **4a,b**. The product was eluted with CHCl$_3$, the solvent removed under vacuum, and the residue recrystallized to give pure **3a,b** or **5a,b**.

Dimethyl 3,3-Diphenyl-4-(2,2-diphenylvinyl)cyclohex-1-ene-1,4-dicarboxylate (**3a**): 61%, m.p. 212.5–214.5° (heptane). IR (CHCl$_3$): 3050m (sh), 3000m, 2940m, 1720s (sh), 1705s, 1640m, 1590m. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.95 (d, $J = 8.0$, 2 H); 7.4–7.1 (m, 17 H, arom. H, H–C(2)); 6.95–6.80 (m, 2 H); 6.53 (s, H–C(1')); 3.77 (s, CH$_3$OOC–C(1)); 2.83 (s, CH$_3$OOC–C(4)); 2.7–2.4 (m, 2 H–C(6)); 2.2–2.0 (m, 2 H–C(5)). ^{13}C-NMR (62.9 MHz, CDCl$_3$): 172.9 (s, C(4)–COOCH$_3$); 167.3 (s, C(1)–COOCH$_3$); 145.2, 144.8, 143.1, 141.3, 138.8, 131.1 (6s, C(1), C(2'), 4 arom. C); 132.0, 130.4, 130.2, 128.2, 127.8, 127.4, 127.2, 127.1, 126.8, 126.2 (10d, arom. CH, C(2), C(1')); 60.1 (s, C(3)); 54.4 (s, C(4)); 51.8, 50.9 (2q, 2 COOCH$_3$); 29.3 (t, C(5)); 22.0 (t, C(6)). ^{13}C-NMR (coupled): 22.0 (td, ^1J(C,H) = 128.5, ^3J(C,H) = 7.0). MS (70 eV): 528 (10, $M^{+\cdot}$), 497 (12, $M^{+\cdot}$ – CH$_3$O), 496 (20, $M^{+\cdot}$ – CH$_4$O), 469 (3), 464 (22, $M^{+\cdot}$ – 2 CH$_4$O), 361 (10), 329 (11), 264 (25), 205 (100, Ph$_2$C$_4$H$_3^+$), 167 (18).

Diethyl 3,3-Diphenyl-4-(2,2-diphenylvinyl)cyclohex-1-ene-1,4-dicarboxylate (**3b**): 83%, m.p. 180.0–181.0° (hexane). IR (CHCl$_3$): 3050w (sh), 2970m, 2925w, 2890w, 1720s (sh), 1705s, 1640w, 1590w. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.98 (d, $J = 7.7$, 2 H); 7.4–7.0 (m, 17 H, arom. H, H–C(2)); 7.00–6.85 (m, 2 H); 6.53 (s, H–C(1')); 4.22 (q, $J = 7.0$, CH$_3$CH$_2$OOC–C(1)); 3.3–3.1 (m, CH$_3$CH$_2$OOC–C(4)); 2.6–2.3 (m, 2 H–C(6)); 2.2–2.0 (m, 2 H–C(5)); 1.31 (t, $J = 7.0$, CH$_3$CH$_2$OOC–C(1)); 0.65 (t, $J = 7.1$, CH$_3$CH$_2$OOC–C(4)). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 172.4 (s, C(4)–COOC$_2$H$_5$); 166.9 (s, C(1)–COOC$_2$H$_5$); 144.9 (d, C(2)); 144.8, 143.1, 141.0, 138.7, 131.3 (5s, arom. C, C(1), C(2')); 132.1, 130.6, 130.4, 130.3, 128.1, 127.7, 127.3, 127.1, 127.0, 126.7, 126.1 (11d, arom. CH, C(2), C(1')); 60.8, 60.2 (2t, 2 COOCH$_2$CH$_3$); 60.1, 54.2 (2s, C(3), C(4)); 29.2 (t, C(6)); 21.9 (t, C(5)). MS (70 eV): 557 (1), 556 (3, $M^{+\cdot}$), 511 (2), 510 (3, $M^{+\cdot}$ – C$_2$H$_6$O), 483 (1), 464 (4, $M^{+\cdot}$ – 2 C$_2$H$_6$O), 389 (11), 343 (9), 278 (18), 205 (100, Ph$_2$C$_4$H$_3^+$), 167 (12). Anal. calc. for C$_{38}$H$_{36}$O$_4$ (556.71): C 81.99, H 6.52; found: C 82.27, H 6.72.

2-(2-Phenyl-1-propenyl)-2-buten-4-olide (**5a**): 84%, m.p. 90.0–93.0° (hexane). UV (cyclohexane): 221 (11 100), 289 (26 200). IR (CHCl$_3$): 2930w, 2870w, 1755s, 1620m. ^{1}H-NMR (90 MHz, CDCl$_3$): 7.6–7.25 (m, arom. H, H–C(1')); 6.51 (s, H–C(3)); 4.90 (s, CH$_2$O); 2.30 (s, CH$_3$). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 173.9 (s, C(1)); 144.1 (s, C(2')); 142.5 (s, arom. C); 143.3 (d, C(3)); 128.9 (s, C(2)); 128.2, 127.8, 125.9 (3d, arom. CH); 114.7 (d, C(1')); 70.3 (t, CH$_2$O); 18.6 (q, CH$_3$). MS (70 eV): 200 (93, $M^{+\cdot}$), 172 (22, $M^{+\cdot}$ – CO), 171 (29, $M^{+\cdot}$ – CHO), 156 (50), 155 (100, $M^{+\cdot}$ – CHO$_2$), 143 (27), 141 (40), 129 (37), 128 (79), 115 (41), 91 (25), 77 (32). Anal. calc. for C$_{13}$H$_{12}$O$_2$ (200.24): C 77.98, H 6.04; found: C 77.71, H 6.03.

2-(2,2-Diphenylvinyl)-2-buten-4-olide (**5b**): 64%, m.p. 117.0–119.0° (hexane). UV (cyclohexane): 234 (39 400), 305 (49 200). IR (CHCl$_3$): 3050w, 3000w, 2925w, 2865w, 1760s, 1625w, 1607w. ^{1}H-NMR (90 MHz, CDCl$_3$): 7.7–7.1 (m, arom. H); 6.87 (s, H–C(1')); 6.08 (br. s, H–C(3)); 4.60 (s, CH$_2$O). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 174.0 (s, C(1)); 148.2 (s, C(2')); 143.4 (d, C(3)); 140.4, 139.7 (2s, arom. C); 129.3, 128.5, 128.3, 128.2, 128.0, 127.0 (6d, arom. CH); 128.1 (s, C(2)); 114.0 (d, C(1')); 70.3 (t, C(4)). MS (70 eV): 263 (14), 262 (78, $M^{+\cdot}$), 234 (12), 233 (100, $M^{+\cdot}$ – CHO), 218 (22), 217 (15, $M^{+\cdot}$ – CHO$_2$), 215 (17), 205 (48), 203 (30), 202 (30), 191 (12), 189 (13), 165 (12). Anal. calc. for C$_{18}$H$_{14}$O$_2$ (262.31): C 82.42, H 5.38; found: C 81.83, H 5.12.

4. Irradiation of 1b,c and 4b in the Presence of M$_x$(CO)$_y$. – 4.1. *Irradiation of* **1b,c**. A soln. of **1b** (1.0 g, 3.6 mmol) and Co$_2$(CO)$_8$ (1.05 g, 4.0 mmol) or Mn$_2$(CO)$_{10}$ (1.56 g, 4.0 mmol) in hexane (250 ml), or of **1c** (300 mg, 0.88 mmol) and Co$_2$(CO)$_8$ (390 mg, 1.14 mmol) in hexane (250 ml) was irradiated with 80-W *Hanovia* high-pressure Hg lamp through quartz at r.t. for 16 h, 12 h, and 10 h, respectively. The solvent was removed under vacuum, and the residue was chromatographed twice on prep. TLC plates with petroleum ether/Et$_2$O 5:1. The UV (254 nm)-detected zones were eluted with CHCl$_3$, the solvent was removed under vacuum, and the residue was recrystallized from hexane/Et$_2$O to give pure **1b,c**, **6**, **7**, or **8** (see *Scheme 3*).

1,1,4,4-Tetraphenyl-1,3-butadiene (**6**): m.p., UV and ^{1}H-NMR identical with those reported in [12] [13].

Ethyl 1-Methyl-3-phenylindene-1-carboxylate (**7**): m.p. 121.0–123.0°. IR (KBr): 1724s, 1600w, 1493m. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.4–7.05 (m, arom. H); 6.70 (s, H–C(2)); 3.85–3.45 (sym. m, AB of ABX_3, CH$_2$O); 1.31 (s, CH$_3$–C(1)); 1.09 (t, $J = 6$, CH$_3$CH$_2$O). ^{13}C-NMR (50.4 MHz): 173.1 (s, CO$_2$Et); 144.0, 141.8, 139.4 (3s, arom. C); 130.6, 130.1, 128.1, 127.8, 127.2 (5d, arom. CH); 60.7 (t, CH$_2$O); 54.8 (s, C(1)); 21.2 (q, CH$_3$–C(1)); 13.8 (q, CH$_3$CH$_2$O). MS (70 eV): 278 (25, $M^{+\cdot}$), 206 (20), 205 (100, $M^{+\cdot}$ – COOC$_2$H$_5$).

3-Ethoxy-2,4,4-triphenylcyclobut-2-enone (**8**): m.p. 119.0–120.5°. IR (CHCl$_3$): 1745s, 1625s, 1585s. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.74 (dd, $J = 8.3$, 1.5, 2 o-H in Ph–C(2)); 7.45–7.25 (m, 13 arom. H); 4.33 (q, $J = 7.1$, CH$_2$O);

1.23 (t, J = 7.1, CH$_3$). ^{13}C-NMR (62.9 MHz, CDCl$_3$): 185.0 (s, C(1)); 177.2 (s, C(3)); 138.6 (s, arom. $C-$C(3)); 129.1 (s, arom. $C-$C(4)); 128.7, 128.5, 127.9, 127.7, 127.6, 127.3 (6d, arom. CH); 122.0 (s, C(2)); 70.5 (t, CH$_2$O); 15.0 (q, CH$_3$). MS (70 eV): 341 (30), 340 (100, M^+), 312 (70), 311 (64), 294 (22), 267 (55), 265 (30), 255 (26), 253 (22), 252 (28), 178 (30), 165 (50), 105 (38). Anal. calc. for C$_{24}$H$_{20}$O$_2$ (340.42): C 84.68, H 5.92; found: C 84.75, H 5.87.

4.2. *Irradiation of* **4b**. A soln. of **4b** (262 mg, 1 mmol) in hexane/Et$_2$O 1:1 (250 ml) or of **4b** (524 mg, 2 mmol) and Co$_2$(CO)$_8$ (820 mg, 2.4 mmol) in hexane/Et$_2$O 1:1 (250 ml) was irradiated as described in *4.1* for 30 h or 16 h, respectively. The solvent was removed under vacuum, and the residue was chromatographed twice on prep. TLC plates with petroleum ether/Et$_2$O/AcOEt/butan-2-one 85:11:2:2. The UV (254 nm)-active zones were eluted with CHCl$_3$ and the solvent removed to afford the oily **9** and **10**, or the residue was recrystallized from hexane/Et$_2$O to give **4b** and **6** (see *Scheme 4*).

2-(2,2-Diphenylvinyl)-4-butanolide (**9**): 18%, colourless oil. IR (CHCl$_3$): 2960m, 2925m, 2860m, 1770s. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.6–7.0 (m, 10 arom. H); 5.98 (d, J = 9, H$-$C(1')); 4.5–4.25, 4.25–4.0 (2m, CH$_2$O); 3.5–3.3 (m, H$-$C(1)); 2.45–2.1 (m, 2 H$-$C(3)). ^{13}C-NMR (62.9 MHz, CDCl$_3$): 177.8 (s, C(1)); 147.1 (s, C(2')); 141.5, 139.1 (2s, arom. C); 129.9 (d, C(1')); 128.5, 128.3, 127.8, 127.6, 123.2 (5d, arom. CH); 66.5 (t, C(4)); 40.9 (d, C(2)); 30.9 (s, C(3)). MS (70 eV): 265 (21), 264 (100, M^+), 220 (20), 219 (36, $M^+ - $ CHO$_2$), 206 (21), 205 (90), 204 (28), 203 (26), 202 (22), 191 (28), 178 (20), 165 (27), 143 (21), 129 (37), 128 (20), 115 (19), 91 (27), 77 (13), 73 (11), 45 (12).

2-(1-Ethoxyethyl)-2-(2,2-diphenylvinyl)-4-butanolide (**10**): 21%, mixture of 2 diastereoisomers, colourless oil. IR (CCl$_4$): 2955m, 2925m, 2860m, 1760s, 1590w. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.45–7.1 (m, 10 arom. H); 6.46, 6.03 (2s, H$-$C(1') of 2 diastereoisomers); 4.2–3.8, 3.75–3.5, 3.5–3.2 (3m, 2 CH$_2$O, $-$CHO$-$); 2.35–2.1, 2.0–1.7 (2m, 2 H$-$C(3)); 1.32, 1.28 (2d, J = 6, CH$_3$CHO of 2 diastereoisomers); 1.13, 1.11 (2t, J = 7, CH$_3$CH$_2$O of 2 diastereoisomers). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 179.7, 178.6 (2s, C(1)); 144.2, 143.7, 142.6, 142.2, 139.2, 138.9 (6s, 2 arom. C, C(2')); 130.0–127.0 (arom. CH, C(1')); 82.7, 78.9 (2d, $-$CHO$-$); 66.8, 66.0, 65.0, 64.6 (4t, C(4), CH$_3$CH$_2$O); 54.6, 52.9 (2s, C(2)); 33.7, 26.6 (2t, C(3)); 15.2, 15.1, 14.7 (3q, 2 CH$_3$). CI-MS: 337 (100, $M^+ + 1$), 291 (80), 167 (30), 75 (24), 73 (32).

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