Preparation and Selected Reactions of *t*-Butyl 2-Methylene-3-oxoalkanoates

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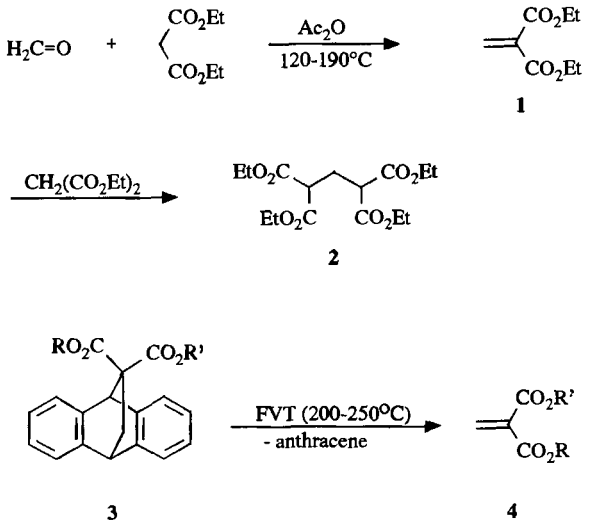
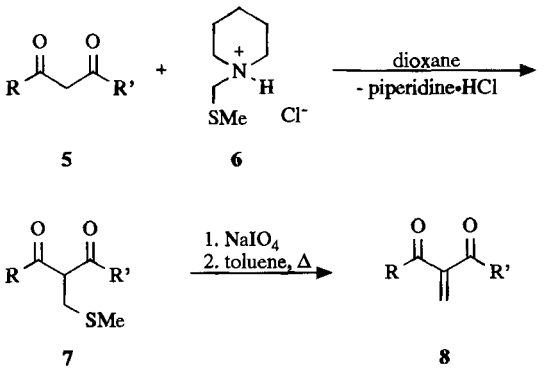
The title class of 1,1-diactivated ethylenes has been prepared in two steps from aldehydes and *t*-butyl acrylate by (i) DABCO-catalyzed coupling to give *t*-butyl 2-(hydroxyalkyl)-2-propenoates **11** and (ii) low-temperature Jones oxidation, followed by swift work up at low temperature. The resulting *t*-butyl 2-methylene-3-oxoalkanoates **12** are stabilized by sterically demanding and also by aromatic groups R. For primary unhindered alkyl groups, stability is low. The compounds enter into Michael reactions, hetero Diels-Alder additions with enol ethers, and self-dimerization.

2-Methylene-1,3-dicarbonyl compounds have been of interest for a long time. More than 100 years ago W. H. Perkin, Jr., suggested tentatively that he had obtained diethyl methylenemalonate (**1**) from a low-boiling fraction of the reaction of formaldehyde with malonic ester[1a,c]. Diester **1** is a plausible intermediate en route to the tetraester **2**, which was identified clearly[1b]. Later, the combination of formaldehyde with malonic esters was investigated by Bachman and Tanner[2] and also by Roberts[3a,b], who showed that the bulky di-*t*-butyl 2-methylenemalonate (**4**; R = R′ = *t*-butyl) can be handled more readily than simple ester analogs. Recently, a variety of α-methylenemalonic esters was obtained by retro Diels-Alder reaction (**3** → **4**)[4].



Another approach to 1,1-dicarbonyl-activated ethylenes (**5** → **7** → **8**) has been described by Yamauchi and his coworkers[5].

The related selenoxide elimination was investigated by Reich[6] and proceeded under milder conditions as usual. Again, the resulting 1,3-dicarbonyl compound can be handled relatively easily, if at least one R or R′ is aryl. The specific conversion of γ-butyrolactones into biologically active α-methylene-γ-butyrolactones poses similar experimental problems, because the product is a Michael acceptor, which is sensitive to nucleophiles[7].

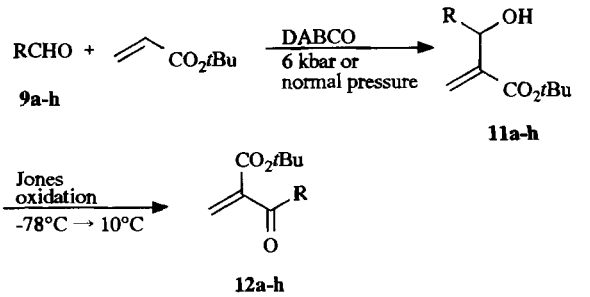


We here describe a simple route to β-keto-α-methylene carboxylic esters consisting of two stages:

(i) 1,4-Diazabicyclo[2.2.2]octane-(DABCO)-catalyzed coupling of various aldehydes with *t*-butyl acrylate to give α-(hydroxyalkyl)acrylic acid *t*-butyl esters (**9** → **11**).

(ii) Mild oxidation of the resulting functionalized allylic alcohols under Jones conditions to give the desired acceptor-substituted enones (**11** → **12**).

Scheme 1. Two-step route to **12a–h**



In previous work[8] on the coupling reaction of aldehydes with methyl acrylate[8-10] and also with other Michael acceptors[11] we have generally used an excess of methyl acrylate. This functions as solvent, especially for solid aldehydes, and can also be removed readily by distillative work up, without polymerization. However,

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t-butyl acrylate couples less readily than methyl acrylate, and is also a poorer solvent. In order to ensure that DABCO is dissolved in the reaction medium we added catalytic amounts of DABCO to an excess of *aldehyde* (30 mmol) and then added ca. 20 mmol of *t*-butyl acrylate. The coupling was carried out advantageously at high pressure (6 kbar)[12]. However, with propanal an attempted coupling with *t*-butyl acrylate at 6 kbar was not successful[13]. Therefore, the original procedure was adapted, using an excess of *t*-butyl acrylate, normal pressure and prolonged reaction times. 3-Phenylpropanal (**9d**), cyclohexanecarbaldehyde (**9e**), and 2-methylbutanal (**9f**) were coupled in the presence of 3-hydroxyquinuclidine, a catalyst introduced by Drewes and his coworkers[9].

Jones Oxidation of *t*-Butyl (2-Hydroxyalkyl)propenoates 11 at Low Temperature

Oxidation of allylic alcohols **11** with chromic acid was carried out by mixing reagents at −78°C. For secondary alkyl groups (**11e, f**) and also for aryl groups (**11g, h**), the reaction mixture was left for 15 min at −78°C, the bulk of acetone was distilled off quickly at ca. 10°C in a rotary evaporator, and the remaining sludge containing green Cr^{III} and the desired enone ester **12** was extracted with ether, washed with water, and dried. Flash chromatography afforded the enone esters **12e−h** which can be stored without decomposition in a refrigerator. The *p*-bromophenyl derivative **12h** which was used initially as a model, is crystalline (m.p. 62°C). It is important to work up the reaction mixture without delay, especially in the case of the most sensitive representatives containing unhindered primary alkyl groups (**12a−d**) to avoid polymerization or self-dimerization (see below). If the enone esters are stabilized kinetically by steric hindrance (**12e, f**) and by benzenoid conjugation (**12g, h**) isolated yields are improved (Table 1).

Table 1. Preparation of *t*-butyl 2-methylene-3-oxoalkanoates **12a−h** by oxidation of **11a−h**[a] (cf. Scheme 1)

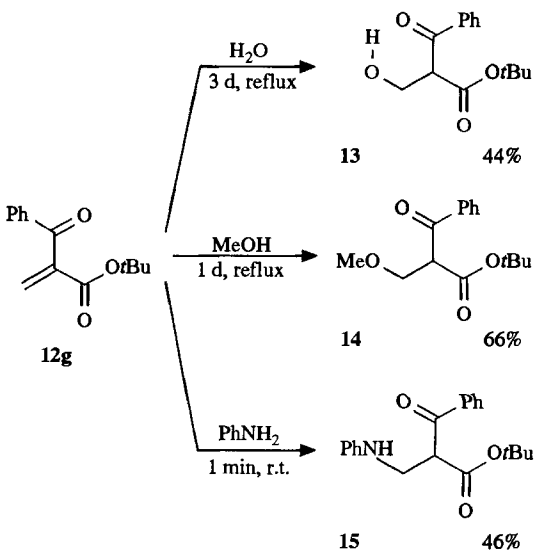
	R	Reaction time [min]	Isolated yield [%] of **12** (after chromatography)
a	Et	5	25−35
b	*n*-Pr	5	51
c	Me_2CHCH_2	5	48
d	$PhCH_2CH_2$	5	32−55
e	Cyclohexyl	15	63
f	EtCHMe	15	29
g	Ph	15	73−81[b]
h	*p*-BrC_6H_4	15	85−93

[a] All oxidations were run on a 2-mmol scale. − [b] Oxidation of **11g** to **12g** was also attempted with PCC on silica gel/CH_2Cl_2 at room temp. However, in this case the yield was only 7%.

In the ^{1}H-NMR spectrum the title compounds **12** displays a characteristic symmetric doublet of doublets ($^2J \approx 1.5$ Hz, $\delta \approx 6$) which appears downfield from the signal of the allylic alcohol precursor **11**. The purity of the liquid compounds was judged to be at least >90% on spectroscopic criteria. Crystalline **12h** gave a correct microanalysis.

Enone ester **12g** was investigated for nucleophilic additions with water, methanol, and aniline (Scheme 2). The uncatalyzed addition of water occurs slowly over a period of 3 d at reflux temperature, while aniline adds very rapidly.

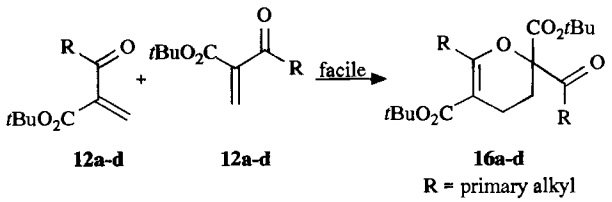
Scheme 2. Selected nucleophilic additions of **12g**[a]



[a] Cosolvent acetone. Yields are not optimized.

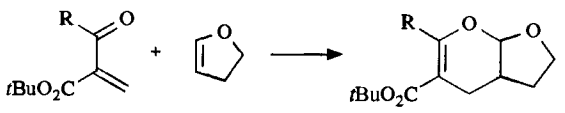
Sensitive 2-methylene-3-oxoalkanoates **12a−d** were also found to dimerize neat or in acetone, on standing at room temperature or after 30 d in a refrigerator at −20°C. The dimer is the "*para*-oriented" dihydropyran[14] of type **16a−d** (Scheme 3).

Scheme 3. Self-dimerization of 2-methylene-3-oxoalkanoates **12a−d**



The enone esters react with 2,3-dihydrofuran in an inverse electron-demand hetero Diels-Alder reaction[15] (Scheme 4, Table 2). The two rings are *cis*-fused (^3J = 3.5 Hz).

Scheme 4



Conclusion

A variety of *t*-butyl 2-methylene-3-oxoalkanoates **12** has been obtained[16] and fully identified by spectroscopy. The

compounds enter into Michael additions and hetero Diels-Alder reactions. The self-dimerization of **12a–d** to dihydropyrans occurs readily, as shown. The easy dimerization accounts for some of the previous difficulties in preparing and handling simple aliphatic 2-methylene-3-keto esters and 2-methylene-1,3-diketones, which behave as activated 1-oxabutadienes.

Table 2. Hetero Diels-Alder reactions with inverse electron demand

Enone ester	Reaction time [h]	Product	Isolated yield [%]
12a	10	**17a**	40
12d	15	**17d**	36
12e	20	**17e**	54
12g	17	**17g**	70
12h	3	**17h**	79

Note added in proof (September 4, 1991): After submission of this paper a series of α-methylene-β-keto sulfones has been described [A. Weichert, H. M. R. Hoffmann, *J. Org. Chem.* **56** (1991) 4098].

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Experimental

Melting points: Büchi apparatus. – Infrared spectra: Perkin-Elmer 1710 spectrometer. – ^{1}H NMR spectra: Bruker WH 90, WP 200 SY or AM 300 spectrometer. Chemical shifts are reported in δ values downfield from tetramethylsilane. – ^{13}C NMR spectra: Bruker WP 200 SY or a Bruker AM 300. Chemical shifts are reported in δ values downfield from tetramethylsilane. – Low- and high-resolution electron-impact mass spectra: Finnigan MAT 312 spectrometer with an ionization potential of 70 eV at room temperature, unless otherwise stated. – Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover. – Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30–60 μm). Analytical TLC was carried out on aluminium-backed 0.2-mm silica gel 60 F_{254} plates (E. Merck).

Three Procedures A–C for the Preparation of α-Hydroxyalkylated Acrylic Acid t-Butyl Esters. – A) *At Normal Pressure:* 1,4-Diazabicyclo[2.2.2]octane (DABCO) (3 mmol) and glacial acetic acid (0.6 mmol) were dissolved in a mixture of the aldehyde (20 mmol) and *t*-butyl acrylate (30 mmol). After the indicated reaction time at 35°C, the mixture was diluted with ether and washed with water (3 ×). The organic phase was dried ($MgSO_4$), the ether and the excess of *t*-butyl acrylate were distilled off under reduced pressure and the resulting crude product was purified by flash chromatography on silica gel (ether/light petroleum, 1:3).

B) *At 6 kbar:* In order to avoid precipitation of DABCO at high pressure, we mixed the excess of aldehyde (30 mmol) and *t*-butyl acrylate (22 mmol) with DABCO (2.2 mmol). After the indicated reaction time, the mixture was worked up as described for procedure A.

C) *With 3-Hydroxyquinuclidine:* As described for procedure A, but 3-hydroxyquinuclidine was used instead of DABCO. Normal pressure, reaction temp. 25°C (instead of 35°C).

1,1-Dimethylethyl 3-Hydroxy-2-methylenepentanoate (**11a**). – *Procedure A:* Propanal (9.31 g, 160 mmol), *t*-butyl acrylate (30.8 g, 240 mmol), DABCO (2.69 g, 24 mmol), glacial acetic acid (0.29 g, 4.8 mmol). Reaction time 14 d: crude yellow oil (13.5 g); 9.27 g (31%) of purified product **11a** was obtained as colorless oil. – IR (film): $\tilde{\nu}$ = 3441 cm^{-1}, 2976, 1708, 1630. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.94 [s, 9H, $C(CH_3)_3$], 1.53–1.82 (m, 2H, CH_2CH_3), 2.39 (br. s, 1H, OH), 4.28 (dd, J_{AX} = 6.5 Hz, J_{BX} = 7 Hz, 1H, $CH_XCH_AH_B$), 5.70 (dd, ^2J = 1.5 Hz, ^4J = 1 Hz, 1H, vinyl H), 6.14 (d, ^2J = 1.5 Hz, 1H, vinyl H). – MS (70 eV): *m/z* (%) = 186 (0) [M^+], 156 (11) [$M^+ - H_2O$], 129 (15), 57 (100).

1,1-Dimethylethyl 3-Hydroxy-2-methylenehexanoate (**11b**). – *Procedure A:* Butanal (9.00 g, 125 mmol), *t*-butyl acrylate (24.4 g, 190 mmol), DABCO (2.1 g, 19 mmol), glacial acetic acid (0.23 g, 3.8 mmol); reaction time 14 d; crude yellow oil (8.85 g), after purification colorless oil **11b** (4.89 g, 20%). Procedure B, after 7 d, gave **11b** (1.48 g, 34%). Spectroscopic data correspond with the literature[17].

1,1-Dimethylethyl 3-Hydroxy-5-methyl-2-methylenehexanoate (**11c**). – *Procedure A:* 3-Methylbutanal (10.7 g, 125 mmol), *t*-butyl acrylate (24.4 g, 190 mmol), DABCO (2.1 g, 19 mmol), glacial acetic acid (0.23 g, 3.8 mmol); reaction time 14 d: crude yellow oil (4.73 g), colorless oil after chromatography (4.11 g, 16%). Procedure B after 7 d, gave **11c** (2.46 g, 52%). Spectroscopic data correspond with the literature[17].

1,1-Dimethylethyl 3-Hydroxy-2-methylene-3-phenylpropanoate (**11g**). – *Procedure A:* Benzaldehyde (13.3 g, 125 mmol), *t*-butyl acrylate (25.4 g, 190 mmol), DABCO (2.1 g, 19 mmol), glacial acetic acid (0.23 g, 3.8 mmol); reaction time 21 d: crude yellow oil (25.3 g), colorless oil after chromatography (22.5 g, 77%). – IR ($CHCl_3$): $\tilde{\nu}$ = 3500 cm^{-1}, 2970, 1710, 1655, 1610 (w). – ^{1}H NMR ($CDCl_3$): δ = 1.34 [s, 9H, $C(CH_3)_3$], 3.17 (br. s, 1H, OH), 5.40 (s, 1H, C*H*OH), 5.67 (t, *J* = 3 Hz, 2H, vinyl H), 7.29 (s, 5H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 26.87 (q), 72.35 (d), 80.50 (s), 124.20 (t), 126.47 (d), 126.72 (d), 128.09 (d), 142.03 (s), 144.00 (s), 164.70 (s). – MS (70 eV): *m/z* (%) = 234 (0) [M^+], 177 (100) [M^+ – *t*-butyl], 77 (31).

1,1-Dimethylethyl 3-(4-Bromophenyl)-3-hydroxy-2-methylenepropanoate (**11h**). – *Procedure A: p*-Bromobenzaldehyde (0.93 g, 5 mmol), *t*-butyl acrylate (0.96 g, 7.5 mmol), DABCO (0.08 g, 0.75 mmol), glacial acetic acid (0.01 g, 0.15 mmol); reaction time 21 d: crude yellow oil (2.14 g), colorless crystals of **11h**, m.p. 62–63°C, after chromatography, yield 1.27 g (81%) of **11h**. – IR ($CHCl_3$): $\tilde{\nu}$ = 3602 cm^{-1}, 2981, 1698, 1630. – ^{1}H NMR (90 MHz, [D_6]acetone): δ = 1.37 [s, 9H, $C(CH_3)_3$], 2.85 (d, ^3J = 3.5 Hz, 1H, CHO*H*), 5.53 (d, ^3J = 3.5 Hz, 1H, C*H*OH), 5.97 (dd, ^2J = 2 Hz, ^4J = 1.5 Hz, 1H, vinyl H), 6.19 (dd, ^2J = 2 Hz, ^4J = 1.5 Hz, 1H, vinyl H), 7.22–7.60 (m, 4H, arom. H). – MS (70 eV): *m/z* (%) = 314/312 (0) [M^+], 257/255 (58) [M^+ – *t*-butyl], 77 (34), 57 (100).

1,1-Dimethylethyl 3-Hydroxy-2-methylene-5-phenylpentanoate (**11d**). – *Procedure C:* 3-Phenylpropanal (6.70 g, 50 mmol), *t*-butyl acrylate (9.61 g, 75 mmol), 3-hydroxyquinuclidine (0.95 g, 7.5 mmol): reaction time 18 d: crude brown oil (9.00 g), colorless oil after chromatography; yield 4.56 g (35%) of **11d**. Spectroscopic data correspond with the literature[17].

1,1-Dimethylethyl 3-Cyclohexyl-3-hydroxy-2-methylenepropanoate (**11e**). – *Procedure C:* Cyclohexanecarbaldehyde (2.24 g, 20 mmol), *t*-butyl acrylate (3.85 g, 30 mmol), 3-hydroxyquinuclidine (0.38 g, 3 mmol), reaction time 18 d: crude brown oil (3.15 g), colorless oil after chromatography; yield 1.43 g (30%) of **11e**. – IR (film): $\tilde{\nu}$ = 3462 cm^{-1}, 2928, 1709, 1628. – ^{1}H NMR (90 MHz, [D_6]acetone): δ = 0.78–1.89 (m, 11H, cyclohexyl H), 1.49 [s, 9H,

$C(CH_3)_3$], 2.82 (d, ^3J = 3.5 Hz, 1H, OH), 4.19–4.36 (m, 1H, CHOH), 5.74 (dd, ^2J = 2 Hz, ^4J = 1.5 Hz, 1H, vinyl H), 6.09 (dd, ^2J = 2 Hz, ^4J = 1 Hz, 1H, vinyl H). – MS (70 eV): *m/z* (%) = 240 (0) [M^+], 183 (17) [M^+ – *t*-butyl], 57 (100).

1,1-Dimethylethyl 3-Hydroxy-4-methyl-2-methylenehexanoate (**11f**). – *Procedure C:* 2-Methylbutanal (4.31 g, 50 mmol), *t*-butyl acrylate (9.61 g, 75 mmol), 3-hydroxyquinuclidine (0.95 g, 7.5 mmol); reaction time 18 d: crude brown oil (9.10 g), colorless oil after chromatography; yield 1.75 g (17%) of **11f**, diastereomeric mixture (1.6:1, cf. ^{1}H NMR). – IR (film): $\tilde{\nu}$ = 3465 cm^{-1}, 2966, 1708, 1628. – ^{1}H NMR (200 MHz, $CDCl_3$; major isomer): δ = 0.89 (d, ^3J = 7 Hz, 3H, $CHCH_3$), 0.92 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 1.02–1.83 (m, 3H, $CHCH_2$), 1.50 [s, 9H, $C(CH_3)_3$], 2.41 (br. d, ^3J = 6.5 Hz, 1H, OH), 4.24 (dd, J_{AX} = 6 Hz, J_{BX} = 6.5 Hz, 1H, $H_3CCH_ACH_XOH_B$), 5.68 (dd, ^2J = 1 Hz, ^4J = 0.5 Hz, 1H, vinyl H), 6.17 (dd, ^2J = 1 Hz, ^4J = 0.2 Hz, 1H, vinyl H); (minor isomer): δ = 0.81 (d, ^3J = 7 Hz, 3H, $CHCH_3$), 0.92 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 1.02–1.83 (m, 3H, $CHCH_2$), 1.51 [s, 9H, $C(CH_3)_3$], 2.73 (br. d, ^3J = 8 Hz, 1H, OH), 4.03 (dd, J_{AX} = 7.5 Hz, J_{BX} = 8 Hz, 1H, $H_3CCH_ACH_XOH_B$), 5.63 (dd, ^2J = 0.8 Hz, ^4J = 0.5 Hz, 1H, vinyl H), 6.13 (d, ^2J = 0.8 Hz, 1H, vinyl H). – MS (70 eV): *m/z* (%) = 214 (0) [M^+], 157 (8) [M^+ – *t*-butyl], 156 (8), 57 (100).

General Procedure for the Jones Oxidation of **11** *to* **12**: Jones' reagent was prepared from CrO_3 (26.7 g) and conc. H_2SO_4 (23 ml), which was made up to 100 ml with distilled water. A 100-ml flask equipped with a septum was charged with the functionalized allyl alcohol **11** (2 mmol) in acetone (26 ml) and cooled to –78°C. The solution was stirred vigorously and the Jones reagent (0.5 ml) was added in one portion. After the given reaction time, the bulk of the solvent was distilled off at ca. 10°C, the residue (ca. 2 ml plus solid Cr^{III} salts) was taken up in ether and dried ($MgSO_4$). The drying agent and Cr^{III} salts were filtered off, the filtrate was freed from solvent under reduced pressure (10°C), and the residue chromatographed without delay over flash-gel (ether/light petroleum, 1:3).

1,1-Dimethylethyl 2-Methylene-3-oxopentanoate (**12a**): The allylic alcohol **11a** (0.37 g) was allowed to react at –78°C for 5 min. Work up as described above gave **12a** as a light yellow oil (130 mg, 35%). – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1719, 1619, 1460, 1370, 1158, 850. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 7 Hz, 3H, CH_2CH_3), 1.42 [s, 9H, $C(CH_3)_3$], 2.46 (q, ^3J = 7 Hz, 2H, CH_2CH_3), 5.85, 5.97 (d, ^2J = 1.5 Hz, 2H, 2 vinyl H). – ^{13}C NMR ($CDCl_3$): δ = 7.88 (q, CH_2CH_3), 27.97 [q, 3C, $C(CH_3)_3$], 34.43 (t, CH_2CH_3), 82.11 [s, $C(CH_3)_3$], 130.52 (t, terminal vinyl C), 143.70 (s, C-2), 164.07 (s, C-1), 200.59 (s, C-3). – MS (70 eV): *m/z* (%) = 184 (0) [M^+], 128 (30), 57 (100).

Bis(1,1-dimethylethyl) 6-Ethyl-3,4-dihydro-2-(1-oxopropyl)-2H-pyran-2,5-dicarboxylate (**16a**): This compound was formed quantitatively from **12a** on standing at room temp. for 7 d. Flash chromatography (ether/light petroleum, 1:5) gave **16a** as a yellow oil. – IR (film): $\tilde{\nu}$ = 2977 cm^{-1}, 1733, 1707, 1631, 1369, 1090. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7 Hz, CH_3CH_2CO), 1.21 [s, 9H, $C(CH_3)_3$], 1.36 (t, ^3J = 7.5 Hz, CH_3CH_2C), 1.40 [s, 9H, $C(CH_3)_3$], 1.75–1.94 (m, 1H, $OCCH_AH_BCH_2$), 2.29–2.43 (m, 3H, $OCH_AH_BCH_2$), 2.51 (dq, ^2J = 12 Hz, ^3J = 7 Hz, 2H, CH_3CH_2CO), 2.74, 3.16 (dq, ^2J = 13 Hz, ^3J = 7.5 Hz, 2H, CH_3CH_2C). – ^{13}C NMR ($CDCl_3$): δ = 7.58 (q, CH_3CH_2CO), 11.93 (q, CH_3CH_2C), 19.15 (t, $EtCOCCH_2$), 25.21 (t, C=C–CH_2), 26.41 (t, CH_3CH_2C), 27.84 [q, $C(CH_3)_3$], 28.35 [q, $C(CH_3)_3$], 30.81 (t, CH_3CH_2CO), 79.95 [s, $OC(CH_3)_3$], 83.20 [s, $OC(CH_3)_3$], 86.29 (s, EtCOC), 103.26 (s, EtC=C), 165.35 (s, ester C=O), 166.64 (s, ester C=O), 167.11 (s, EtC=C), 205.03 (s, C=O). – MS (70 eV): *m/z* (%) = 368 (3) [M^+], 312 (7), 295 (12), 262 (13), 256 (45), 57 (100).

1,1-Dimethylethyl 2-Methylene-3-oxohexanoate (**12b**): The allylic alcohol **11b** (0.40 g) was allowed to react at –78°C for 5 min. Work up as described above gave **12b** as a light yellow oil (200 mg, 51%). – IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 2936, 1719, 1630, 1370, 1158, 850. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 1.50–1.82 (m, 2H, $CH_2CH_2CH_3$), 1.53 [s, 9H, $C(CH_3)_3$], 2.72 (t, ^3J = 7.5 Hz, 2H, $CH_2CH_2CH_3$), 6.20, 6.28 (d, ^2J = 1.5 Hz, 2H, 2 vinyl H). – MS (70 eV): *m/z* (%) = 198 (0) [M^+], 143 (9), 142 (25), 125 (33), 57 (100).

1,1-Dimethylethyl 5-Methyl-2-methylene-3-oxohexanoate (**12c**): Allylic alcohol **11c** (0.43 g) was allowed to react at –78°C for 5 min. Work up as described above gave **12c** as a light yellow oil (420 mg, 48%). – IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1719, 1620, 1370, 1159, 850. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.94 [d, ^3J = 6.5 Hz, 6H, $CH(CH_3)_2$], 1.53 [s, 9H, $C(CH_3)_3$], 1.98–2.33 [m, 1H, $CH(CH_3)_2$], 2.62 (d, ^3J = 6.5 Hz, 2H, CH_2CH), 6.17, 6.28 (d, ^2J = 1.5 Hz, 2H, 2 vinyl H). – MS (70 eV): *m/z* (%) = 212 (0) [M^+], 156 (23), 139 (25), 138 (26), 57 (100).

1,1-Dimethylethyl 2-Methylene-3-oxo-5-phenylpentanoate (**12d**): The allylic alcohol **11d** (0.43 g) was allowed to react at –78°C for 5 min. Work up as described above gave **12d** as a yellow oil (290 mg, 55%). – IR (film): $\tilde{\nu}$ = 2979 cm^{-1}, 1718, 1605, 1369, 1153, 848, 751, 700. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.5 [s, 9H, $C(CH_3)_3$], 2.80–2.11 (m, 4H, $PhCH_2CH_2$), 6.21, 6.30 (d, ^2J = 1 Hz, 2H, 2 vinyl H), 7.12–7.34 (m, 5H, arom. H). – MS (70 eV): *m/z* = 260 (0) [M^+], 204 (62), 186 (34), 185 (100), 57 (93).

1,1-Dimethylethyl 3-Cyclohexyl-2-methylene-3-oxopropanoate (**12e**): The allylic alcohol **11e** (0.48 g) was allowed to react at –78°C for 15 min. Work up as described above gave **12e** as a light yellow oil (300 mg, 63%). – IR (film): $\tilde{\nu}$ = 2932 cm^{-1}, 1718, 1615, 1451, 1370, 1158, 998, 850. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.16–2.06 (m, 10H, cyclohexyl H), 1.51 [s, 9H, $C(CH_3)_3$], 2.61–3.03 [m, 1H, $CH(CH_2)_2$], 6.06, 6.27 (d, ^2J = 1.5 Hz, 2H, 2 vinyl H). – MS (70 eV): *m/z* (%) = 238 (0) [M^+], 182 (59), 165 (20), 164 (33), 57 (100).

1,1-Dimethylethyl 4-Methyl-2-methylene-3-oxohexanoate (**12f**): The allylic alcohol **11f** (0.43 g) was allowed to react at –78°C for 15 min. Work up as described above gave **12f** as a light yellow oil (120 mg, 29%). – IR (film): $\tilde{\nu}$ = 2974 cm^{-1}, 1718, 1616, 1460, 1370, 1152, 849. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 1.10 (d, ^3J = 7 Hz, 3H, $CHCH_3$), 1.52 [s, 9H, $C(CH_3)_3$], 1.62–1.86 (m, 2H, $CHCH_2CH_3$), 2.91–3.09 [m, 1H, $CH(CH_3)CH_2$], 6.10, 6.29 (d, ^2J = 1 Hz, 2H, 2 vinyl H). – ^{13}C NMR ($CDCl_3$): δ = 11.44 (q, CH_2CH_3), 15.59 (q, $CHCH_3$), 25.31 (t, CH_2CH_3), 28.06 [q, $C(CH_3)_3$], 45.19 (d, $CHCH_3$), 82.91 [s, $C(CH_3)_3$], 129.83 (t, $C=CH_2$), 144.39 (s, $H_2C=C$), 164.18 (s, C-1), 204.36 (s, C=O). – MS (70 eV): *m/z* (%) = 212 (0) [M^+], 156 (18), 141 (16), 57 (100).

1,1-Dimethylethyl 2-Methylene-3-oxo-3-phenylpropanoate (**12g**): The allylic alcohol **11g** (0.47 g) was allowed to react at –78°C for 15 min. Work up as described above gave a yellow oil (370 mg, 79%). – IR (film): $\tilde{\nu}$ = 2979 cm^{-1}, 1724, 1679, 1599, 1450, 1370, 1248, 1148, 988, 851, 729, 694. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35 [s, 9H, $C(CH_3)_3$], 6.03, 6.58 (d, ^2J = 1 Hz, 2H, 2 vinyl H), 7.38–7.67 (m, 3H, arom. H), 7.78–7.93 (m, 2H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 27.75 [q, $C(CH_3)_3$], 82.12 [s, $C(CH_3)_3$], 128.46 (d, 2 arom. C), 129.06 (d, 2 arom. C), 130.21 (t, $C=CH_2$), 133.24 (d, arom. C), 136.85 (s, arom. C), 143.55 (s, $C=CH_2$), 163.41 (s, C-1), 193.36 (s, C=O). – MS (70 eV): *m/z* (%) = 232 (0.4) [M^+], 231 (3), 176 (57), 175 (15), 105 (100), 57 (71).

1,1-Dimethylethyl 3-(4-Bromophenyl)-2-methylene-3-oxopropanoate (**12h**): The allylic alcohol **11h** (0.63 g) was allowed to react at

−78°C for 15 min. Work up as described above gave **12h** as white needles (520 mg, 83%), m.p. 62°C. – IR (film): $\tilde{\nu}$ = 2976 cm^{-1}, 1724, 1666, 1587, 1402, 1371, 1292, 1254, 1155, 995, 855, 786. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.38 [s, 9H, $C(CH_3)_3$], 6.05, 6.59 (d, ^2J = 1 Hz, 2H, 2 vinyl H), 7.56–7.76 (m, 4H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 27.27 [q, $C(CH_3)_3$], 82.31 [s, $C(CH_3)_3$], 128.36 (s, C-Br), 130.52 (d, 2 arom. C), 130.56 (t, $C=CH_2$), 131.76 (d, 2 arom. C), 135.57 (s, arom. C), 142.98 (s, $C=CH_2$), 163.07 (s, C-1), 192.24 (s, C=O). – MS (70 eV): *m/z* (%) = 312/310 (1) [M^+], 311/309 (10), 357/355 (22), 256/254 (31), 238/236 (20), 57 (100).

$C_{10}H_7O_3$ Calcd. 255.9558 Found 255.9559 (MS)

$C_{14}H_{15}BrO_3$ (311.19) Calcd. C 54.05 H 4.86
Found C 53.76 H 4.87

Nucleophilic Additions to **12g**. – *1,1-Dimethylethyl 2-Hydroxymethyl-3-oxo-3-phenylpropanoate* (**13**): A 25-ml flask equipped with a reflux condenser was charged with **12g** (0.46 g, 2 mmol) in 5 ml of acetone. After addition of water (5 ml, 280 mmol) and refluxing the mixture for 3 d, the solvent was distilled off. The residue was taken up in ether, washed with water and dried ($MgSO_4$). Flash chromatography (ether/light petroleum ether, 3:1) gave **13** as a colorless oil (0.22 g, 44%). – IR (film): $\tilde{\nu}$ = 3500 cm^{-1}, 2980, 1725, 1670, 1595, 1450, 1368, 1250, 1150, 1049, 840, 690. – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.37 [s, 9H, $C(CH_3)_3$], 2.20–2.53 (br. s, 1H, CH_2OH), 4.14 (d, ^3J = 5.5 Hz, 2H, $CH_XCH_AH_B$), 4.44 (dd, J_{AX} = 5.5 Hz, J_{BX} = 6 Hz, 1H, $CH_XCH_AH_B$), 7.42–7.66 (m, 3H, arom. H), 7.88–8.11 (m, 2H, arom. H). – MS (70 eV): *m/z* (%) = 250 (0) [M^+], 193 (15), 176 (6), 175 (4), 105 (100).

1,1-Dimethylethyl 2-(Methoxymethyl)-3-oxo-3-phenylpropanoate (**14**): Enone **12g** (0.46 g, 2 mmol), 5 ml of acetone and methanol (11.5 ml, 280 mmol) were refluxed for 1 d. Work up as described above gave **14** as a colorless oil (0.35 g, 66%). – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1730, 1685, 1595, 1445, 1365, 1250, 1150, 845, 730, 690. – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.36 [s, 9H, $C(CH_3)_3$], 3.36 (s, 3H, OCH_3), 3.94 (d, ^3J = 7 Hz, 2H, $CH_XCH_AH_B$), 4.55 (dd, J_{AX} = 6.5 Hz, J_{BX} = 7 Hz, 1H, $CH_XCH_AH_B$), 7.42–7.63 (m, 3H, arom. H), 7.92–8.02 (m, 2H, arom. H). – MS (70 eV): *m/z* (%) = 264 (0) [M^+], 207 (20), 176 (8), 175 (7), 105 (100), 77 (41).

1,1-Dimethylethyl 3-Oxo-3-phenyl-2-[(phenylamino)methyl]propanoate (**15**): A 10-ml flask was charged with **12g** (0.46 g, 2 mmol) in 5 ml of acetone. After addition of aniline (0.37 g, 4 mmol) the mixture warmed up spontaneously and the reaction was over after 1 min (TLC control). Work up as described and flash chromatography (ether/light petroleum ether, 1:3) gave **15** (370 mg, 46%). – IR (film): $\tilde{\nu}$ = 3414 cm^{-1}, 2978, 1729, 1686, 1604, 1509, 1449, 1370, 1252, 1152, 751, 693. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.32 [s, 9H, $C(CH_3)_3$], 3.79, 3.81 (dd, J_{AB} = 0 Hz, J_{AX} = J_{BX} = 3.3 Hz, 2H, $CH_XCH_AH_B$), 4.57 (dd, *J* = 3.3 Hz, 1H, $CH_XCH_AH_B$), 6.57–6.78 (m, 3H, arom. H), 7.10–7.23 (m, 2H, arom. H), 7.37–7.62 (m, 3H, arom. H), 7.90–8.01 (m, 2H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 27.78 [q, $C(CH_3)_3$], 42.77 (t, CH_2N), 54.53 (d, $CHCH_2$), 82.47 [s, $C(CH_3)_3$], 113.16 (d, 2 arom. C), 117.88 (d, arom. C), 128.53 (d, 2 arom. C), 128.66 (d, 2 arom. C), 129.39 (d, 2 arom. C), 133.42 (d, arom C), 136.62 (s, arom. C), 147.30 (s, arom. C), 166.03 (s, C-1). – MS (70 eV): *m/z* (%) = 325 (0.4) [M^+], 268 (2), 231 (4), 176 (34), 175 (10), 105 (100), 77 (53).

Hetero Diels-Alder Reactions of **12** *with 2,3-Dihydrofuran:* The keto ester **12** (2 mmol) and 2,3-dihydrofuran (0.28 g, ca. 0.3 ml, 4 mmol) in acetonitrile (3 ml) were stirred at room temp. After the given reaction time the solvent was distilled off and the crude product was purified (flash gel, ether/light petroleum ether, 1:5).

1,1-Dimethylethyl 6-Ethyl-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran-5-carboxylate (**17a**): The keto ester **12a** (0.37 g, 2 mmol) and 2,3-dihydrofuran (0.28 mg, 4 mmol) were allowed to react as described above. After 10 h, **17a** was isolated as a light yellow oil (200 mg, 40%). – IR (film): $\tilde{\nu}$ = 2975 cm^{-1}, 1703, 1627, 1456, 1367, 1177, 1088, 1050, 1017, 935. – ^1H NMR (300 MHz, C_6D_6): δ = 1.24 (t, ^3J = 7 Hz, 3H, CH_2CH_3), 1.31–1.46 (m, 2H, OCH_2CH_2), 1.46 [s, 9H, $C(CH_3)_3$], 1.78–1.93 (m, 1H, OCHCH), 2.27 (dd, J_{AB} = 18 Hz, J_{AX} = 6 Hz, 1H, $CCH_AH_BCH_X$), 2.44 (dd, J_{AB} = 18 Hz, J_{BX} = 1 Hz, 1H, $CCH_AH_BCH_X$), 2.83 (m, 2H, CH_2CH_3), 3.55 (ddd, J_{AB} = J_{AC} = J_{AD} = 8.5 Hz, 1H, $OCH_AH_BCH_CH_D$), 3.83 (ddd, J_{AB} = J_{BC} = 8.5 Hz, J_{BD} = 4 Hz, 1H, $OCH_AH_BCH_CH_D$), 5.10 (d, ^3J = 4 Hz, 1H, OCHCH). – ^{13}C NMR (C_6D_6): δ = 12.23 (q, CH_2CH_3), 22.95 (t, $C=CCH_2CH$), 26.84 (t, OCH_2CH_2), 27.53 (t, CH_2CH_3), 28.28 [q, $C(CH_3)_3$], 36.91 (d, OCHCH), 67.86 (t, OCH_2), 78.98 [s, $C(CH_3)_3$], 99.19 (s, C–CO), 100.70 (d, OCH), 166.20 (s, C=O), 167.31 (s, EtC). – MS (70 eV): *m/z* (%) = 254 (3) [M^+], 197 (24), 180 (13), 179 (13), 70 (100).

1,1-Dimethylethyl 2,3,3a,7a-Tetrahydro-6-(2-phenylethyl)-4H-furo[2,3-b]pyran-5-carboxylate (**17d**): Keto ester **12d** (0.52 g, 2 mmol) and 2,3-dihydrofuran (0.28 g, 4 mmol), reaction time 15 h: yellow oil; yield 240 mg (36%) of **17d**. – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1690, 1638, 1452, 1365, 1170, 1065, 994. – ^1H NMR (300 MHz, C_6D_6): δ = 1.17–1.41 (m, 2H, OCH_2CH_2), 1.45 [s, 9H, $C(CH_3)_3$], 1.79–1.93 (m, 1H, OCHCH), 2.27 (dd, J_{AB} = 17.5 Hz, J_{AX} = 6.5 Hz, 1H, $CCH_AH_BCH_X$), 2.40 (dd, J_{AB} = 17.5 Hz, J_{BX} = 1.5 Hz, 1H, $CCH_AH_BCH_X$), 2.93–3.22 (m, 4H, $PhCH_2CH_2$), 3.54 (ddd, J_{AB} = J_{AC} = J_{AD} = 8 Hz, 1H, $OCH_AH_BCH_CH_D$), 3.79 (ddd, J_{AB} = J_{BC} = 8 Hz, J_{BD} = 4.5 Hz, 1H, $OCH_AH_BCH_CH_D$), 5.08 (d, ^3J = 4 Hz, 1H, OCHCH), 7.00–7.31 (m, 5H, arom. H). – ^{13}C NMR (C_6D_6): δ = 23.13 (t, C-5), 27.59 (t, OCH_2CH_2), 28.45 [q, $C(CH_3)_3$], 34.11, 35.02 (t, $PhCH_2CH_2$), 36.99 (d, OCHCH), 68.07 (t, OCH_2), 79.26 [s, $C(CH_3)_3$], 100.24 (s, C–CO), 100.73 (d, OCH), 126.16 (d, arom. C), 127.72/128.04, 128.36/128.55 (d, 4 arom. C), 142.00 (s, arom. C), 164.12 (s, C=CO), 167.37 (s, C=O). – MS (70 eV, 50°C): *m/z* (%) = 330 (10) [M^+], 274 (44), 257 (17), 256 (13), 70 (100).

$C_{12}H_{12}O_3$ Calcd. 204.0786 Found 204.0786 (MS)

1,1-Dimethylethyl 6-Cyclohexyl-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran-5-carboxylate (**17e**): Keto ester **12e** (0.48 g, 2 mmol) and 2,3-dihydrofuran (0.28 g, 4 mmol), reaction time 20 h: light yellow wax; yield 330 mg (54%) of **17e**. – IR ($CHCl_3$): $\tilde{\nu}$ = 2980 cm^{-1}, 1688, 1612, 1450, 1366, 1070, 945. – ^1H NMR (300 MHz, C_6D_6): δ = 1.25–1.85 (m, 12H, 6 CH_2), 1.46 [s, 9H, $C(CH_3)_3$], 1.85–1.98 (m, 1H, OCHCH), 2.29 (dd, J_{AB} = 17.5 Hz, J_{AX} = 6.5 Hz, 1H, $OCH_AH_BCH_X$), 2.49 (dd, J_{BX} = 2 Hz, 1H, $CCH_AH_BCH_X$), 3.55 (ddd, J_{AB} = J_{AC} = J_{AD} = 8 Hz, 1H, $OCH_AH_BCH_CH_D$), 3.83 (ddd, J_{AB} = J_{BC} = 8 Hz, J_{BD} = 3.5 Hz, 1H, $OCH_AH_BCH_CH_D$), 3.78–3.91 (m, 1H, CH–C=), 5.14 (d, ^3J = 3.5 Hz, 1H, OCHCH). – ^{13}C NMR (C_6D_6): δ = 23.30, 26.41, 26.73, 27.61, 30.11, 30.19 (t, 7 CH_2), 28.49 [q, $C(CH_3)_3$], 37.18 (d, OCHCH), 40.89 (d, CH–C=), 67.98 (t, OCH_2), 79.16 [s, $C(CH_3)_3$], 99.09 (s, C–CO), 101.15 (d, OCH), 167.75 (s, C=CO), 168.28 (s, C=O). – MS (70 eV): *m/z* (%) = 308 (2) [M^+], 307 (6), 251 (32), 234 (11), 233 (21), 83 (100).

$C_{18}H_{28}O_4$ Calcd. 308.1988 Found 308.1988 (MS)

$C_{18}H_{28}O_4$ (308.20) Calcd. C 70.13 H 9.09
Found C 69.86 H 9.05

1,1-Dimethylethyl 6-Phenyl-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran-5-carboxylate (**17g**): Keto ester **12g** (0.46 g, 2 mmol) and 2,3-dihydrofuran (0.28 g, 4 mmol), reaction time 17 h: white needles, m.p. 80–82°C, yield 420 mg (70%) of **17g**. – IR (KBr): $\tilde{\nu}$ = 2981 cm^{-1}, 1677, 1638, 1596, 1366, 1307, 1080, 967, 880, 698. – The ^1H and ^{13}C signals were assigned by 2D spectroscopy. ^1H NMR (C_6D_6): δ = 1.18 [s, 9H, $C(CH_3)_3$], 1.29–1.45, 1.45–1.63

(m, 2H, OCH_2CH_2), 1.82–1.95 (m, 1H, OCHCH), 2.39 (dd, J_{AB} = 17.5 Hz, J_{AX} = 7 Hz, 1H, $CCH_AH_BCH_X$), 2.69 (dd, J_{BX} = 1.5 Hz, 1H, $CCH_AH_BCH_X$), 3.52 (ddd, $J_{AB} = J_{AC} = J_{AD}$ = 8 Hz, 1H, $OCH_AH_BCH_CH_D$), 3.81 (ddd, $J_{AB} = J_{BC}$ = 8 Hz, J_{BD} = 3 Hz, 1H, $OCH_AH_BCH_CH_D$), 5.16 (d, ^3J = 4 Hz, 1H, OCHCH), 7.01–7.12 (m, 3H, arom. H), 7.36–7.45 (m, 2H, arom. H). – ^{13}C NMR (C_6D_6): δ = 23.13 (t, $C{=}CCH_2$), 27.37 [q, $C(CH_3)_3$], 27.58 (t, OCH_2CH_2), 36.79 (d, OCHCH), 68.18 (t, OCH_2), 79.52 [s, $C(CH_3)_3$], 101.67 (d, OCH), 102.40 (s, $C{=}CO$), 127.38 (d, 2 arom. C), 128.40 (d, 2 arom. C), 136.83 (s, arom. C), 159.42 (s, Ph-C), 167.80 (s, C=O). – MS (70 eV): *m/z* (%) = 302 (1) [M^+], 245 (40), 228 (17), 227 (56), 70 (100).

$C_{10}H_8O_3$ Calcd. 176.0473 Found 176.0473 (MS)

$C_{18}H_{22}O_4$ (302.40) Calcd. C 71.50 H 7.33
Found C 71.10 H 7.30

1,1-Dimethylethyl 6-(4-Bromophenyl)-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran-5-carboxylate (**17h**): Keto ester **12h** (0.62 g, 2 mmol) and 2,3-dihydrofuran (0.28 g, 4 mmol), reaction time 3 h: white needles, m.p. 73–75°C, yield 600 mg (79%) of **17h**. – IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1}, 1694, 1643, 1586, 1367, 1303, 1085, 882, 757. – ^{1}H NMR ($CDCl_3$): δ = 1.20 [s, 9H, $C(CH_3)_3$], 1.76–1.98, 2.02–2.21 (m, 2H, OCH_2CH_2), 2.52–2.72 (m, 3H, CCH_2CH), 3.99 (ddd, $J_{AB} = J_{AC} = J_{AD}$ = 8.5 Hz, 1H, $OCH_AH_BCH_CH_D$), 4.16 (ddd, $J_{AB} = J_{BC}$ = 8.5 Hz, J_{BD} = 3 Hz, 1H, $OCH_AH_BCH_CH_D$), 5.51 (d, ^3J = 4 Hz, 1H, OCHCH), 7.17–7.26 (m, 2H, arom. H), 7.42–7.52 (m, 2H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 23.49 (t, $C{=}CCH_2$), 27.76 [q, $C(CH_3)_3$], 27.93 (t, OCH_2CH_2), 37.14 (d, OCHCH), 63.56 (t, OCH_2), 80.29 [s, $C(CH_3)_3$], 101.45 (d, OCH), 103.32 (s, $C{=}CO$), 123.94 (s, CBr), 130.03 (d, 2 arom. C), 130.88 (d, 2 arom. C), 135.87 (s, arom. C), 158.46 (s, $C{=}CO$), 167.59 (s, C=O). – MS (70 eV, 60°C): *m/z* (%) = 382/380 (5) [M^+], 325/323 (19), 307/305 (31), 279/277 (4), 257/255 (14), 70 (100).

$C_{18}H_{21}BrO_4$ (381.29) Calcd. C 56.71 H 5.55
Found C 56.56 H 5.54

CAS Registry Numbers

9a: 123-38-6 / **9b**: 123-72-8 / **9c**: 590-86-3 / **9d**: 104-53-0 / **9e**: 2043-61-0 / **9f**: 96-17-3 / **9g**: 100-52-7 / **9h**: 1122-91-4 / **11a**: 135513-92-7 / **11b**: 135513-93-8 / **11c**: 135513-94-9 / **11d**: 135513-95-0 / **11e**: 135513-96-1 / **11f**: 135513-97-2 / **11g**: 135513-98-3 / **11h**: 135513-99-4 / **12a**: 135514-00-0 / **12b**: 135514-01-1 / **12c**: 135514-02-2 / **12d**: 135514-03-3 / **12e**: 135514-04-4 / **12f**: 135535-69-2 / **12g**: 135514-05-5 / **12h**: 135514-06-6 / **13**: 135514-08-8 / **14**: 135514-09-9 / **15**: 135514-10-2 / **16a**: 135514-07-7 / **17a**: 135514-11-3 / **17d**: 135514-12-4 / **17e**: 135514-13-5 / **17g**: 135514-14-6 / **17h**: 135514-15-7 / $H_2C{=}CHCO_2tBu$: 1663-39-4 / DABCO: 280-57-9 / 3-hydroxyquinuclidine: 1619-34-7 / 2,3-dihydrofuran: 1191-99-7

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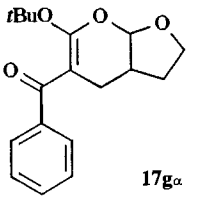
[14] Structure **17gα** was considered initially as an alternative to that of hetero Diels-Alder adduct **17g**, since the ^{1}H signal of the *t*-butyl group was shifted upfield, δ 1.14, as compared to δ 1.36 in the starting compound **12g**. However, closer scrutiny showed that the ketone carbonyl was directly involved in the cycloaddition, because the ^{13}C NMR spectrum of the cycloadduct showed only one lowfield singlet at δ 168.5, but none at δ ≈ 200, which would have been characteristic of ketone carbonyl. Apparently, the upfield shift of the *t*-butyl signal is caused by the anisotropic effect of the neighboring phenyl group in **17g**. We thank Dr. *Victor Wray*, Gesellschaft für Biotechnologische Forschung, Braunschweig-Stöckheim, for discussion; see also M. Yamauchi, S. Katayama, O. Baba, T. Watanabe, *J. Chem. Soc., Chem. Commun.* **1983**, 281.



17gα

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