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FACILE CONSTRUCTION OF TERPENOID FRAMEWORKS BY CYCLO-ADDITIONS WITH METHYL 2-CHLOROCYCLOPROPYLIDENACETATE

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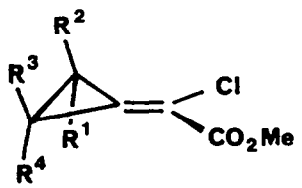
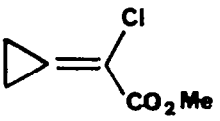
Abstract - Methyl 2-chlorocyclopropylidenacetate (**2-Cl**) smoothly [2+4]cycloadds to cyclopentadiene and 2,3-dimethylbutadiene at room temperature. With the donorsubstituted cyclohexadienes **6**, **9** at elevated temperatures (60, 120°C respectively) **2-Cl** reacts without any observable regioselectivity. In contrast, **2-Cl**, when treated with lithium cyclohexadienolates **13** undergoes completely regioselective iterative Michael additions with subsequent intramolecular γ-elimination to give tricyclic γ-ketoesters **16** in good to excellent yields. The products **16** can readily be transformed to multifunctional bicyclo[2.2.2]octane as well as bicyclo[3.2.1]octane derivatives **17**. A rationalization of the unprecedented reactivity of **2-Cl** on the basis of its available structural features (IP(π), $^1J_{C,C}$, C=C bond length) is offered.

Modern strategies for convergent syntheses of complex organic molecules require multifunctional building blocks, which combine versatility with high chemo- and stereoselective reactivity.[1] In this respect, 2-chlorocyclopropylidenacetates **1-Cl**, readily accessible in two short steps from olefin adducts of thermally ring-opened tetrachlorocyclopropene,[2] deserve particular attention. Especially the unsubstituted **2-Cl** and its recently prepared α-thiosubstituted analogues **2-SR**[3] fulfil several of these requirements, in that they contain four types of functionality - the carbonyl group, the α-substitutent, the double bond and the cyclopropane moiety - and are highly reactive [2+2]-[2b,4] and [2+4]-cycloaddends[2a] as well as Michael acceptors.[3,5] This report describes Diels-Alder and iterative aprotic Michael additions onto **2-Cl**, which are convenient for the construction of bi- and tricyclic terpenoid skeletons.[6]



1 – Cl



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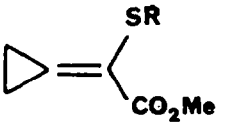
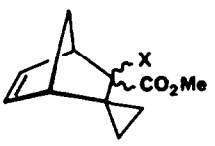


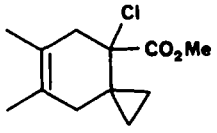
2 – SR

[4+2]-Cycloadditions of 2-Cl

Methyl 2-chlorocyclopropylidenacetate (**2-Cl**) adds to cyclopentadiene at room temperature; the reaction is complete within 5 h and gives endo/exo-**3-Cl** (endo/exo = 2.8:1) in 90% yield. The α-phenylthio derivative **2-SPh** is about equally reactive (r.t., 3 h, 81%, endo/exo = 1.4:1),[3b] while the unsubstituted methyl cyclopropylidenacetate **2-H** reacts more slowly (r.t., 4 d, 84%, endo/exo = 3.2:1).[3b] With 2,3-dimethylbutadiene **2-Cl** at room temperature yields **4** (79%), at elevated temperature (125°C) **4** (76%) was obtained along with a small amount (2-4%) of its dehydrochlorination product **5**. On one side **2-Cl**, in its [2+4]-cycloadditions onto 1-methoxy-3-trimethylsiloxy-1,3-butadiene and 2-trimethylsiloxy-5-methylfuran , shows a reasonably high regioselectivity,[7] as expected for a



3 X = Cl, SPh, H



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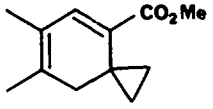

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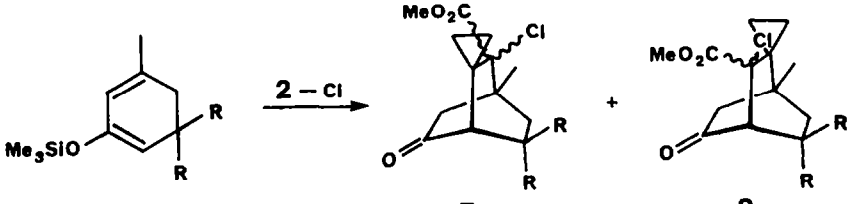


6 R = H **7** **8**

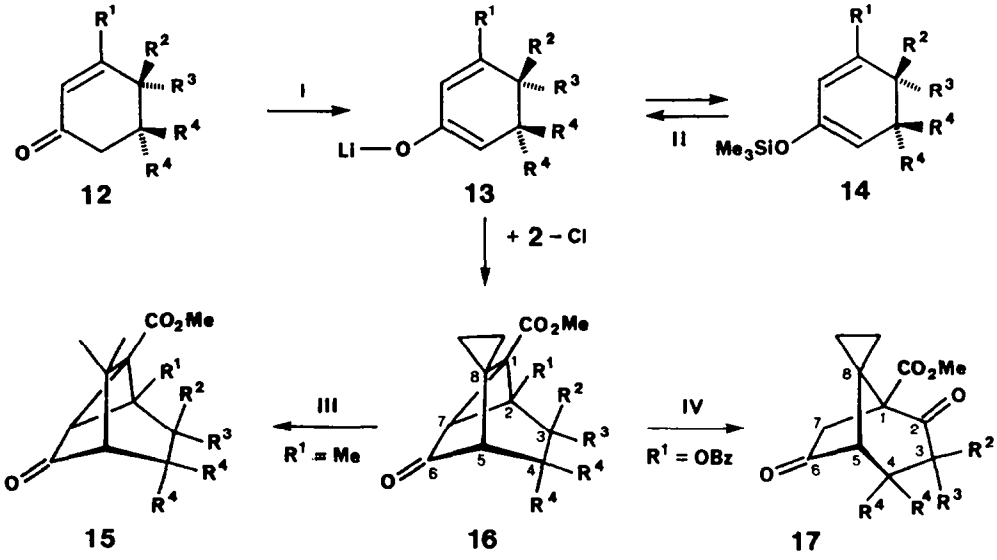
9 R = Me **10** **11**

HOMO-LUMO controlled concerted reaction.[8] With 4-methylcyclohexa-1,3-dien-2-ol trimethylsilyl ether, however, it gave a complex mixture containing about equal amounts of both regioisomeric adducts **7**, **8** and the tricyclic ketoester **16a** (after acidic work-up). Each regioisomer **7** and **8** was a mixture of endo- and exo-diastereomers; an assignment was not possible, since they could be separated only on an analytical scale by capillary vpc and showed virtually identical mass spectra. In an independent experiment with **6**, a 25% yield of **16a** was isolated in a pure form. The trimethylcyclohexadiene **9** also yielded, after acidic work-up, the tricyclic ketoester **16c** as the main product (28% isolated), which like **16a** apparently formed by an intramolecular nucleophilic displacement of chloride in the enolate of **10** (see below). The byproduct, which had the same molecular mass as **16c**, but a distinctly different ^{1}H-NMR spectrum, could not be identified due to its small quantity. These thermal [4+2]-cycloadditions were not pursued any further, since the iterative Michael additions of dienolates onto **2-Cl** occur at low temperatures with complete regio- and stereoselectivity and much better yields (see below).

Iterative Aprotic Michael Additions[6]

Lithium cyclohexadienolates **13**, generated from the corresponding cyclohexenones **12** with lithium diisopropylamide or from the enol trimethylsilyl ethers **14** with methyllithium or butyllithium, smoothly add to **2-Cl** to give tricyclic γ-ketoesters **16** (see scheme 1) in good to excellent yields (see table 1). Except for the addition of unsubstituted cyclohexadienolate **13d**, the yields of cycloadducts are in the range of those from other acrylates[9] and

better than those from α-bromocrotonate.[10] Thus, in the best cases like **16e** and **16f** with yields of 79 and 92% respectively, the two reactants must have combined in a sequence of events in which three new C,C-bonds were formed with an extremely high efficiency (>92% for each step). It is especially noteworthy that methyl 3,3-dimethylacrylate does not react with any of the cyclohexadienolates **13** nor with the trimethylsilyl enol ether **6**. The addition of the considerably more reactive cyclopropylidenacetate **2-Cl**,[3a] however, can be utilized to achieve the same goal by subsequent catalytic hydrogenation, as was demonstrated



Scheme 1. Methyl 6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'-carboxylates **16** from **2-Cl** (for conditions see table 1; III: H_2, Pt, AcCH, r.t.; IV: H_2/Pd-C, EtOAc).

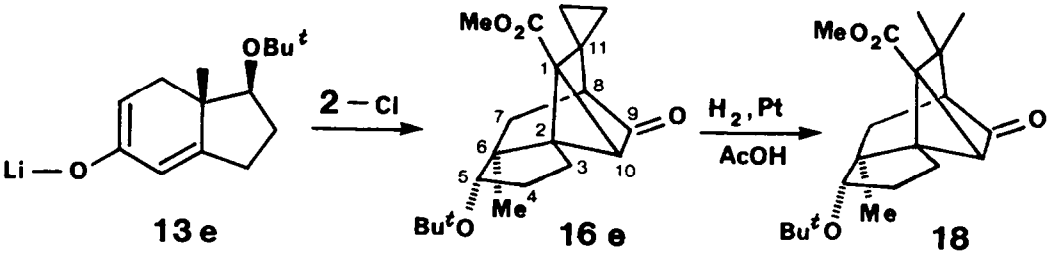
Table 1. Tricyclic ketoesters **16** from **2-Cl** and lithium cyclohexadienolates **13** (see scheme 1).

Cpd.	R^1	R^2	R^3	R^4	Yield [%] (Method[a])		Isolation[b]
a)	CH_3	H	H	H	68	(II)	A,B
b)	H	CH_3	CH_3	H	52	(II)	B
c)	CH_3	H	H	CH_3	75	(II)	B
d)	H	H	H	H	34	(I)	B
e)	$-(CH_2)_2CH(OBu^t)-$[c]		CH_3	H	79/94	(I/II)	B
f)	OBz	H	H	H	92	(I)	C
g)	$OSiMe_3$	H	H	H	(32)	(I)[d]	C

[a] I: **12**, LDA, THF, -78°C; II: **14**, THF, MeLi/Et_2O or BuLi/hexane, -40°C, then r.t.. [b] A: Recrystallization; B: Kugelrohr distillation; C: Chromatography. [c] Enolate from (1S,7aS)-1-tert-butoxy-7a-methyl-1,2,3,6,7,7a-hexahydro-5H-inden-5-one. [d] After acidic work-up, only the retro aldol product **17** (R^2-R^4 = H) was isolated.

with the adducts **16a** and **16e**, the latter arising from the enolate **13e** of (1S,7aS)-1-tert-butoxy-7a-methyl-1,2,3,6,7,7a-hexahydro-5H-inden-5-one.[11] When hydrogenated over PtO_2 in acetic acid, compound **16e** cleanly gave the gem-dimethyl derivative **18** (56%), while **15** obtained from **16a** (67% crude) partially

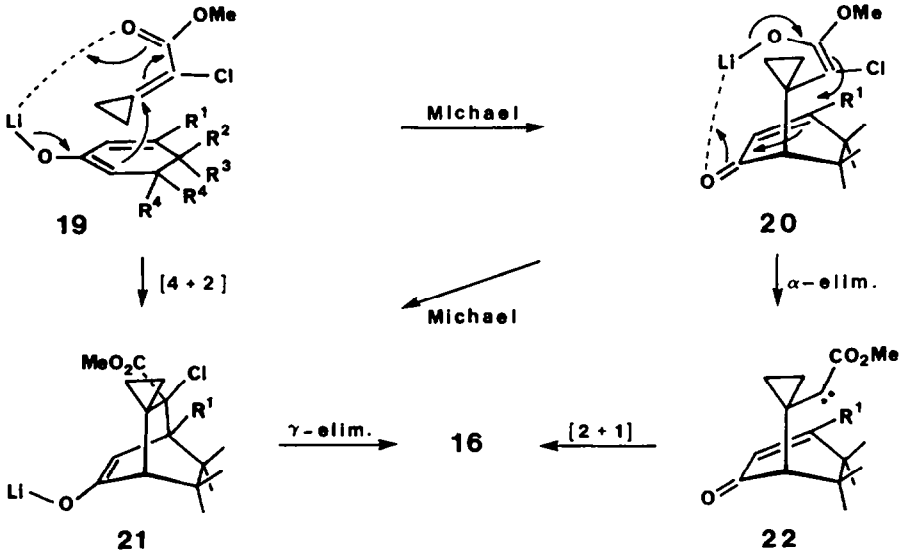
underwent further hydrogenation under these conditions. The skeletal three-membered ring in **16** can be opened in two different ways, depending on the nature of the substituent R^1. With R^1 = H,Me reductive cleavage of C^1-C^7 (e.g. with lithium in liquid ammonia) can produce bicyclo[2.2.2]octane derivatives as shown by Hagiwara et al..[10b] The 2-benzyloxy derivative **16f** after reductive removal of the benzyl group by catalytic hydrogenation undergoes a retro aldol reaction opening the C^2-C^7 bond to quantitatively give the bicyclo[3.2.1]octane derivative **17f** (R^2-R^4 = H). The 2-trimethylsiloxy derivative **16g** could not be



13e **16e** **18**

isolated after acidic work-up, but yielded the retro aldol product **17f** (R^2-R^4 = H) right away. Thus, **2-Cl** can be used as a reactive multifunctional building block to construct bi- and tricyclic skeletons of a variety of - largely terpenoid - natural products.

Mechanistically, the formation of the tricyclic products **16** from **13** and **2-Cl** can be rationalized in three different ways. It can either be initiated by a sequence of two Michael additions[12] starting from a preoriented complex **19** to predominantly give **21** via **20** with a chloro substituent anti to the enolate moiety, so that subsequent γ-elimination can occur. **21** with the proper confi-



Scheme 2. Mechanistic rationalization of the formation of tricyclic products **16** from **2-Cl** and cyclohexadienolates.

guration at C^2 could also be formed by a concerted [4+2]-cycloaddition with the typical endo selectivity of a Diels-Alder reaction. If the first Michael addition of **13** to **2-Cl** were faster than the concerted cycloaddition, the intermediate **20** could also α-eliminate chloride ion to yield a carbomethoxy carbene

22, which subsequently undergoes an intramolecular cheletropic addition to give **16**. It is difficult to decide between the first two alternatives, but the latter appears to be less likely.

Structural Features of 2-Cl and Discussion

In order to gain some insight into the reasons underlying the outstanding reactivity of **2-Cl**,[2b] several physical measurements were employed. In the IR spectrum of **2-Cl** both the νC=C and the νC=O band coincide at 1730 cm^{-1}. This is to be expected for a molecule like **2-Cl**, which consists of a methylenecyclopropane (νC=C 1730 cm^{-1}) and an α,β-unsaturated ester (νC=O 1730 cm^{-1}) moiety.

The He(I)-PE spectrum of **2-Cl** reveals a π-ionization energy of 9.48 eV. Surprisingly, this is only insignificantly lower than that of methylenecyclopropane (IP(π) = 9.52),[13] but definitely lower than that of a simple acrylate (10.72 eV).[14] Qualitatively, one would expect the LUMO energy of **2-Cl** to be lower than that of 3,3-dimethylacrylate, as the HOMO energy is lowered by the attachment of the small ring.[15] MNDO calculations,[16] however, predict a LUMO energy of -0.5 eV for **2-Cl** and -0.7 eV for methyl 2-chloro-3,3-dimethylacrylate.

The ^{13}C-NMR spectrum (90.5 MHz, $CDCl_3$) of **2-Cl** with signals at 5.1 (C-3'), 9.3 (C-2'), 52.4 ($\underline{C}H_3$), 114.4 (C-2), 138.7 (C-1') and 162.1 (C-1) indicates the characteristic polarization of an α,β-unsaturated ester. The $^{13}C,^{13}C$-coupling constant across the double bond in **2-Cl** was determined as $^1J_{C,C}$ = 112.3 Hz. This large value, which on the one side is intermediate between those of methylenecyclopropane (95.2 Hz)[17] and bicyclopropylidene (~138 Hz),[18] on the other side distinctly bigger than that of simple acrylates,[19] definitely correlates with a higher s-character in the hybrid orbitals (close to 50%) at C1'. Assuming an additivity of substituent effects, one would expect a $^1J_{C,C}$ for **2-Cl** as a disubstituted methylenecyclopropane of 106.5 Hz.[19]

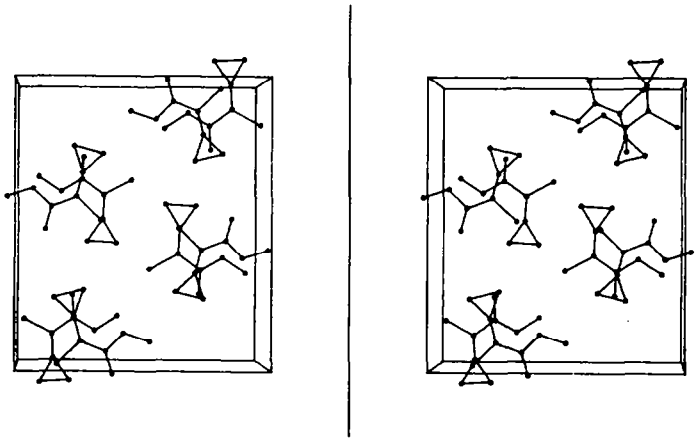


Fig. 1. Stereographical plot of the unit cell of **2-Cl** along [010].

Finally, the structural parameters of **2-Cl** were determined by X-ray diffraction. A crystal was grown from molten **2-Cl** in a X-ray capillary (diameter 0.1 mm) by the Bridgman technique,[20] its space group was Pnma with 8 molecules

in the unit cell and two crystallographically independent molecules in the asymmetric unit (see fig. 1).[21] The structure was solved by direct methods.[22] The independent molecules lie in the mirror planes in y = 0.25 and 0.75 and are completely planar (fig. 2). Within the range of the (rather large) standard deviations the lengths of the C,C single and double bonds in **2-Cl** (see table 2) are the same as those in bicyclopropylidene,[23] the double bond being slightly shortened with respect to those in ethylene and in methylenecyclopropane.[24] This is in accordance with the change in hybridization of C^2 and $C^{1'}$ as indicated by the large $^1J_{C,C}$.

On the basis of these data, the drastically increased Diels-Alder and Michael reactivities of **2-Cl** cannot be explained in a straightforward way. The major contribution appears to be made by a thermodynamic effect. Upon any addition across the double bond, which goes along with a change of hybridization at C^2 and $C^{1'}$, the strain both in the three-membered ring and in the double bond decreases. Although this strain relief fully occurs only in the products, it must be felt in the transition states as well and therefore affects the kinetics of such reactions.

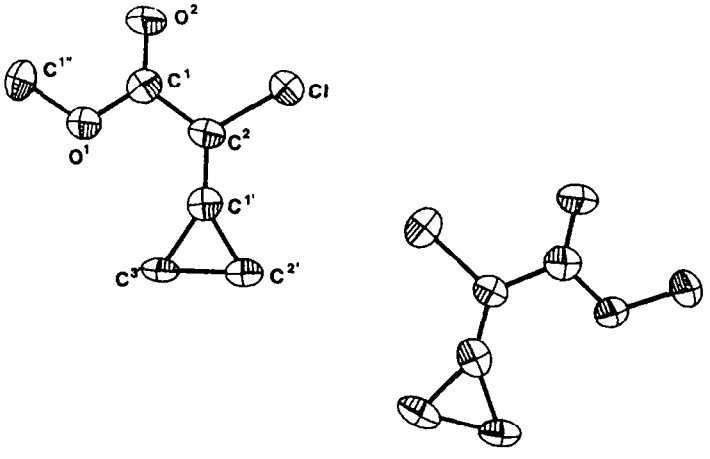


Fig. 2. ORTEP plot of two independent molecules of **2-Cl** (carbon and oxygen atoms only)[21].

Table 2. Bond distances (in pm) and bond angles (in degrees) for crystalline **2-Cl** (standard deviations in parentheses) [2nd independent molecule in the asymmetric unit].[21]

Distance		Angle	
C^1-O^2	121.7(6) [120.4(7)]	Cl-C^2-$C^{1'}$	121.1(4) [119.7(4)]
C^1-O^1	131.8(6) [133.1(6)]	Cl-C^2-C^1	114.9(4) [114.7(4)]
$C^{1''}$-O^1	143.8(6) [144.3(7)]	C^2-C^1-O^2	123.3(5) [125.2(5)]
C^1-C^2	148.0(7) [146.1(7)]	C^2-C^1-O^1	112.9(4) [111.9(5)]
C^2-Cl	173.3(5) [173.4(5)]	O^1-C^1-O^2	123.8(5) [122.9(5)]
C^2-$C^{1'}$	131.1(7) [132.3(7)]	C^1-O^1-$C^{1''}$	116.6(4) [116.0(4)]
$C^{1'}$-$C^{2'}$	145.3(7) [145.8(8)]	C^2-$C^{1'}$-$C^{2'}$	147.8(5) [148.3(5)]
$C^{1'}$-$C^{3'}$	145.7(7) [148.3(8)]	$C^{2'}$-$C^{1'}$-$C^{3'}$	64.3(4) [63.8(4)]
$C^{2'}$-$C^{3'}$	154.8(8) [155.4(9)]	$C^{1'}$-$C^{2'}$-$C^{3'}$	58.0(3) [58.9(4)]
		C^1-C^2-$C^{1'}$	124.0(5) [125.6(5)]
		$C^{1'}$-$C^{3'}$-$C^{2'}$	57.7(3) [57.3(4)]
		C^2-$C^{1'}$-$C^{3'}$	147.9(5) [148.0(5)]

EXPERIMENTAL PART

General remarks. Melting points (uncorrected) were determined in a Büchi SMP-20 apparatus. - ^{1}H-NMR: Bruker WM 250 (250 MHz), WH 270 (270 MHz), WM 400 (400 MHz); δ = 0 for tetramethylsilane, δ = 7.16 for benzene (C_6D_5H), δ = 7.26 for chloroform. - ^{13}C-NMR: Bruker WM 250 (62.88 MHz), AM 360 (90.53 MHz); δ = 0 for tetramethylsilane, δ = 77.0 for chloroform, δ = 128.0 for benzene. - IR: Perkin-Elmer 297, 399; Zeiss IMR 25. - MS and GC/MS: Varian MAT 311A and MAT 112.

Methyl endo/exo-2'-chloro-3'-spirocyclopropane-1,3'-bicyclo[2.2.1]hept-5'-ene]-2'-carboxylate (**3-Cl**): A solution of 2.1 g (13.7 mmol) **2-Cl** and 1.75 g (27.4 mmol) freshly distilled cyclopentadiene in 20 mL dry methylene chloride was stirred at r. t. under an atmosphere of nitrogen for 4 h. The solvent was evaporated and the crude product chromatographed over 100 g silica gel (column 40 x 3 cm) eluting with pentane/ether (10:1), yield 2.7 g (88%) **3-Cl**, R_F = 0.38. An analytically pure sample was obtained by vapor phase chromatography (4 m 10% SE 30, 150°C). Vpc analysis (50 m WG 11, 60-180°C, 3°/min) disclosed a ratio endo/exo = 74/26 (with respect to the methoxycarbonyl group).

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 0.46 (m, 1H(exo)), 0.59 (m, 2H(endo)), 0.75 (m, 1H(exo)), 0.81 (m, 1H(endo)), 0.99 (m, 1H(endo)), 1.07 (m, 1H(exo)), 1.24 (m, 1H(exo)), 1.69 (d, 1H(exo)), 1.71 (d, 1H(endo)), 2.04 (s, 1H(exo)), 2.07 (d, 1H(endo)), 2.07 (s, 1H(endo)), 2.30 (d, 1H(exo)), 3.38 (s, 1H(exo)), 3.51 (s, 1H(endo)), 3.64 (s, 3H(exo)), 3.72 (s, 3H(endo)), 6.17 (m, 1H(exo)), 6.25 (m, 1H(endo)), 6.37 (m, 1H(exo)), 6.61 (m, 1H(endo)). - IR ($CDCl_3$): 3060, 2950, 1730 (νC=O), 1430, 1280, 1240 (νC-O), 1030, 880 cm^{-1}. - GC/MS (70eV): m/z = 212/214 (M^+ (1Cl)), 133 (M^+ -Cl,CO_2), 177 (M^+ -Cl), 145 (M^+ -OCH_3/HCl), 176 (M^+ -HCl). Both diastereomers showed almost identical fragmentation patterns. (Found: C, 62.24; H, 6.04; Cl, 16.53. Calc. for $C_{11}H_{13}ClO_2$ (212.68): C, 62.12; H, 6.17; Cl, 16.67; O, 15.05).

Methyl 4-chloro-6,7-dimethylspiro[2.5]oct-6-ene-4-carboxylate (**4**): A solution of 130 mg (0.89 mmol) **2-Cl** in 2 mL 2,3-dimethyl-1,3-butadiene was stirred at r. t. for 12 d. The excess diene was then removed on a rotatory evaporator and the residue filtered over 5 g aluminum oxide (activity III), yield 160 mg (79%) **4**, colorless oil. -

^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.34 (m, 1H), 0.52 (m, 1H), 0.89 (m, 1H), 1.01 (m, 1H), 1.58 (s, 3H), 1.67 (s, 3H), 1.70 + 2.97 (AB, 1H each, J_{AB} = 16 Hz), 2.34 + 2.57 (AB, 1H each, J_{AB} = 17 Hz), 3.78 (s, 3H). - IR (KBr): 2920, 1710 (νC=O), 1425 (νCH_3(as)), 1270, 1250, 1220 (νC-O), 1105, 890, 830, 770, 740 (νC-Cl). - GC/MS (70eV): m/z = 228/230 (M^+ (1Cl)), 133, 192 (M^+ -HCl), 164 (M^+ -HCl/CO), 177 (M^+ -HCl/CH_3). (Found: C, 62.50; H, 7.33; Cl, 15.45. Calc. for $C_{12}H_{17}ClO_2$ (228.7): C, 63.02; H, 7.49; Cl, 15.50).

In a second run a solution of 200 mg (1.3 mmol) **2-Cl** and 500 mg (6.1 mmol) 2,3-dimethyl-1,3-butadiene in 2 mL $CDCl_3$ was heated in a sealed ampoule to 120-130°C for 10 h. The solvent was evaporated and the black residue chromatographed over 20 g silica gel (column 2 x 20 cm) with petroleum ether/diethyl ether 10:1 to yield 238 mg (76%) **4** and 10 mg (3%) of a by-product, most probably the dehydrochlorination product **5**.

GC/MS (70eV): m/z = 192 (M^+), 160 (M^+ -C_2H_4O), 161 (M^+ -$COCH_3$), 133 (M^+ -CO_2CH_3), 177 (M^+ -CH_3).

Reaction of **2-Cl** with 4-methylcyclohexa-1,3-dien-2-ol trimethylsilyl ether (**6**): A solution of 62 mg (0.4 mmol) **2-Cl** and 83 mg (0.4 mmol) **6** in 0.5 mL [D_8]-toluene in a nmr tube was kept at 60°C over night. After 15 h the signals of the starting material had almost completely disappeared. The mixture was solvolyzed with 3 mL methanol containing 2-3 drops 2N hydrochloric acid and the crude products chromatographed over 10 g silica gel (column 2 x 20 cm) with petroleum ether/diethyl ether 1:1. The main fraction weighed 56 mg (46%) and consisted of a mixture, most probably of the isomeric adducts **7** and **8**. The ^{1}H-NMR spectrum (270 MHz, $CDCl_3$) showed four ester methoxy signals at 3.73, 3.75, 3.79 and 3.80 ppm. GC/MS (70eV): m/z = 256/258 (M^+ (1Cl)), 221 (M^+ -Cl), 214 (M^+ -C_2H_2O), 189, 183, 178; 2 isomers with almost identical fragmentation patterns. m/z = 256/258 (M^+ (1Cl), 225 (M^+ -OCH_3), 221 (M^+ -Cl), 220 (M^+ -HCl), 189, 188; another 2 isomers with almost identical fragmentation patterns.

In an independent experiment, a mixture of 147 mg (1 mmol) **2-Cl** and 250 mg (1.2 mmol) **6** was kept at 60°C under an argon atmosphere over night. After acidic work-up, chromatography over 30 g silica gel with pentane/ether 1:1 gave 56 mg (25%) **16a**, identical with the product obtained from **2-Cl** and the dienolate **13a** (see below).

Reaction of **2-Cl** with 4,6,6-trimethylcyclohexa-1,4-dien-2-ol trimethylsilyl ether (**9**): 82 mg (0.56 mmol) **2-Cl** and 150 mg (0.70 mmol) **9** in 0.5 mL [D_8]-

toluene were heated in a NMR tube. No reaction was observable after 24 h at 70°C, but it was complete after 2 d at 100°C. The mixture was hydrolyzed with a solution of 2-3 drops of 2N hydrochloric acid in 3 mL methanol and the crude product chromatographed over 10 g silica gel (column 2 x 20 cm) eluting with petroleum ether 40-60°/diethylether 1:1. Two fractions were isolated.

Fraction I: 39 mg (28%) methyl 2',4',4'-trimethyl-6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'-carboxylate (**16c**). - ^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.27-0.35 (m, 1H), 0.43-0.52 (m, 1H), 0.90 (s, 3H), 0.87-1.00 (m, 1H), 1.14-1.18 (m, 4H), 1.20 (s, 3H), 1.29 (b, 1H), 1.41-1.51 (m, 1H), 1.69 + 1.73 (AB, 1H, J_{AB} = 14.2 Hz), 2.16 + 2.22 (AB, 1H, J_{AB} = 14.2 Hz), 2.26 (d, 1H), 3.68 (s, 3H). - IR (film): 3070, 2960, 2920, 1725 (νC=O), 1430, 1350, 1240, 1200 (νC-O), 1135, 1080, 970, 900, 880, 795 (νC-Cl) cm^{-1}. - GC/MS (70eV): m/z = 248 (M^+), 220 (M^+ -CO), 205 (M^+ -C_2H_3O), 233 (M^+ -CH_3), 192 (M^+ -CO_2CH_3).

II: 27 mg (19%) unidentified compound. - ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 0.45-0.51 (m, 1H), 0.85-0.92 (m, 4H), 1.00 (d, 1H, J = 1.7 Hz), 1.24-1.32 (m, 5H, containing 2d at 1.26 and 1.29 (J = 12.5 Hz, s at 1.31), 1.83 (d, 3H, J = 1.7 Hz), 2.18 (s, 2H), 2.27 + 2.30 (d, 1H, J = 12.5 Hz), 3.73 (s, 3H), 5.85 (b, 1H). - IR (film): 2950, 2870, 2040, 1720 (νC=O), 1430, 1235 (νC-O), 1020, 720 cm^{-1}. - GC/MS (70eV): m/z = 248 (M^+), 164, 192 (M^+ -CO_2CH_3), 217 (M^+ -OCH_3), 233 (M^+ -CH_3), 205 (M^+ -C_2H_3O).

General Procedure for the Preparation of Lithium Dienolates

Method I (LDA method): An oven-dried round-bottomed flask was charged with dried (LAH) and freshly distilled tetrahydrofuran and 1.1 equivalent of anhydrous diisopropylamine, flushed with argon and cooled to -78°C. To this solution was added with stirring 1.1 equivalent of a 1.8 M solution of n-butyllithium in n-hexane to form LDA, followed after 30 min by a solution of 1 equivalent of the enone in dry THF with a syringe over a period of 15 min to form the lithium dienolate. Methyl 2-chlorocyclopropylidenacetate dissolved in dry THF was added with a syringe. The reaction mixture was slowly warmed-up to r. t. and then quenched with 1.4 equivalents of 1 N hydrochloric acid, diluted with water, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and/or passed through a column of silica gel, concentrated, and the residue distilled in a Kugelrohr.

Method II (trimethylsilyl enolether method): The lithium dienolate was formed as above but then quenched at -78°C with chlorotrimethylsilane (neat) to form the trimethylsilyl enol ether. The reaction mixture was diluted with n-pentane, washed with water, and dried over $MgSO_4$. After removal of the solvent, the remaining oil was distilled under reduced pressure. Freshly distilled trimethylsilyl enol ether was dissolved in dry THF, cooled to -40°C and treated under an inert atmosphere with 1 equivalent of a 2 M solution of methyllithium in ether (or 1.9 M n-butyllithium in hexane) for 30 min yielding an amine free solution of the corresponding lithium dienolate. Reaction conditions and work-up as described above for method 1.

Methyl 2'-methyl-6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'-carboxylate (**16a**): 293 mg (2.0 mmol) **2-Cl** in 5 mL THF were added to a solution of the dienolate, previously prepared from 460 mg (2.5 mmol) TMS-ether **14a** in 25 mL THF using method II (-60°C, n-butyllithium). The reaction was quenched after stirring at r. t. for 1 h. The usual work-up gave 280 mg (68%) **16a**, white crystals, m.p. 91-92°C. -
^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.44-0.62 (m, 2H, cyclopropyl), 0.72-0.8 (m, 1H, cyclopropyl), 1.19 (s, 3H), 1.2-1.27 (m, 1H, cyclopropyl), 1.5-1.54 (m, 1H), 1.95-2.3 (m, 4H), 2.33 (d, J = 1.8 Hz, 1H), 3.67 (s, 3H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 5.4 (t), 9.6 (t), 20 (q), 23.4 (s), 24 (t), 27.9 (t), 42.8 (d), 45.8 (s), 50.4 (d), 51.6 (q), 168 (s), 211.4 (s). - IR (KBr): 3050, 1740, 1715 cm^{-1}. - EI-MS (70eV): m/z = 220 (10%, M^+), 192 (90), 133 (90), 117 (60), 105 (100), 91 (95), 77 (50). - High-res. MS: Found: 220.1095. Calc. for $C_{13}H_{16}O_3$: 220.1099. - Found: C, 70.89; H, 7.32. Calc.: C, 70.89; H, 7.32.

Methyl 3',3'-dimethyl-6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'-carboxylate (**16b**): 588 mg (3.0 mmol) TMS-ether **14b** were treated with 1.6 mL 1.9 M n-butyllithium (method II) in 15 mL dry THF to form **13b**. 270 mg (1.8 mmol) **2-Cl** in 5 mL dry THF were added at -78°C. The reaction mixture was allowed to warm to r. t. over night. Work-up gave 330 mg (52%) **16b** (Kugelrohr, b.p. 140°C/0.01 Torr). -
^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.65-0.37 (m, 2H), 1.15 + 1.30 (2s, 6H), 1.15-1.42 (m, 3H), 1.75 (dd, J = 14 and 3 Hz, 1H), 1.92 (ddd, J = 14, 3 and 1 Hz, 1H), 2.23 (dd, J = 8.8 and 1 Hz, 1H), 2.47 (dd, J = 8.8 and 1.8 Hz, 1H), 3.63 (s, 3H). - IR (film): 1730 cm^{-1}. - EI-MS (70eV): m/z = 234 (20%, M^+), 219 (10), 178 (90), 147 (70), 91 (100), 77 (60). - High-res. MS: Found: 234.1254. Calc. for $C_{12}H_{18}O_3$: 234.1256.

Methyl-2',4',4'-trimethyl-6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]-octane]-1'-carboxylate (**16c**): To a solution of dienolate **13c** prepared from 470 mg (2.2 mmol, method II, butyllithium) **14c** in 20 mL THF and cooling (-60°C) were added 293 mg (2.0 mmol) **2-Cl** in 3 mL THF under an argon atmosphere. Usual work- up after stirring for 1 h at r.t. yielded 370 mg (75%) **16c**, colorless oil, b.p. 140°C/0.01 Torr.

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.26-0.34 (m, 1H, cyclopropyl), 0.42-0.5 (m, 1H, cyclopropyl), 0.88 (s, 3H), 0.88-0.96 (m, 1H, cyclopropyl), 1.13 (d, J = 1.5 Hz, 1H), 1.14 (s, 3H), 1.18 (s, 3H), 1.39-1.48 (m, 1H, cyclopropyl), 1.66, 1.71, 2.14 + 2.20 (AB, J = 14 Hz, 2H), 2.24 (d, J = 1.5 Hz, 1H), 3.66 (s, 3H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 2.35 (t), 3.28 (t), 16.3 (q), 18.5 (s), 27 (2q), 35.2 (s), 35.3 (s), 38.5 (t), 38.6 (d), 43.2 (s), 49.9 (q), 59.2 (d), 173.5 (s, ester), 217.1 (s, ketone). - IR (neat): 3060, 1730 cm^{-1}. - EI-MS (70eV): m/z = 248 (30%, M^+), 233 (50), 220 (100), 205 (60), 192 (40), 177 (30), 161 (40), 145 (70), 133 (30), 119 (40), 105 (60), 91 (40), 83 (40). - High-res. MS: Found: 248.1412. Calc. for $C_{15}H_{20}O_3$: 248.1412.

Methyl 6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'-carboxylate (**16d**): A solution of dienolate **13d** prepared from 0.22 g (2.3 mmol, method I) in 20 mL THF was treated with 300 mg (2.0 mmol) **2-Cl** in 3 mL THF at -40°C and then at r. t. for 1 h. After the usual work-up, the product was isolated by Kugelrohr distillation, yield 140 mg (34%) **16d**, colorless oil (b.p. 130°C/0.02 Torr).

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.35-0.45 (m, 1H, cyclopropyl), 0.55-0.65 (m, 1H, cyclopropyl), 1.12-1.22 (m, 1H, cyclopropyl), 1.38-1.45 (m, 1H, cyclopropyl), 1.48 (m, 1H), 1.85-2.33 (m, 4H), 2.38-2.45 (m, 1H), 2.54 (dd, J = 1.9 and 8.8 Hz, 1H), 3.62 (s, 3H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 5.2 (t), 9.1 (t), 16.3 (t), 22.5 (s), 28.3 (t), 37 (d), 38.2 (s), 39 (d), 51.3 (d), 51.5 (q), 169.6 (s, ester), 211.1 (s, ketone). - IR (neat): 3060, 1730 cm^{-1}. - EI-MS (70eV): m/z = 206 (12%, M^+), 178 (30), 119 (75), 105 (40), 91 (100). - High-res. MS: Found: 206.0944. Calc. for $C_{12}H_{14}O_3$: 206.0943.

Methyl (1S,2R,5S,6S,8S,10R)-5'-tert-butoxy-6'-methyl-9'-oxospiro[cyclopropane-1,11'-tetracyclo[6.2.1.$0^{2,6}$.$0^{2,10}$]undecane]-1'-carboxylate (**16e**): 147 mg (1 mmol) of **2-Cl** in 5 mL THF were added dropwise to a solution of dienolate **13e** prepared from 220 mg (1 mmol) (+)-(1S,7aS)-tert-butoxy-7a-methyl-7,7a-dihydro-5(6H)-indanone **12e** (method I) and stirred at r. t. over night. The usual work-up gave 263 mg (79%) of a viscous oil after Kugelrohr distillation (130°C/0.01 Torr which formed crystals (m.p. 132°C) upon standing. When **13e** was generated using method II, the yield of **16e** was 94%.

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.42 (m, 2H), 0.7-0.82 (m, 1H), 1.03 (s, 3H), 1.19 (s, 9H), 1.2-1.75 (m, 5H), 1.95-2.23 (m, 3H), 2.55 (d, J = 1.5 Hz, 1H), 3.67 (s, 3H), 3.97 (dd, J = 8.4 and 8.8 Hz, 1H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 6.3 (t), 10.8 (t), 21.8 (q), 25.2 (t), 28.7 (3q), 30.9 (t), 36.9 (t), 39.1 (d), 41.7 (s), 45.9 (s), 49.8 (d), 50.6 (s) 51.5 (q), 72.6 (s), 78.1 (d), 168.3 (s, CO_2CH_3), 211.6 (s, C=O). - IR (KBr): 3070, 1745, 1720 cm^{-1}. $[\alpha]_D^{23}$ = +111 (c = 0.4, ethanol). - EI-MS (70eV): m/z = 332 (6%, M^+), 301 (2), 276 (36), 258 (6), 248 (10), 244 (10), 217 (30), 57 (100). Found: C, 72.27; H, 8.53. Calc. for $C_{20}H_{28}O_4$: C, 72.30; H, 8.43.

Methyl 2'-benzyloxy-6'-oxospiro[cyclopropane-1,8'-tricyclo[3.2.1.$0^{2,7}$]octane]-1'- carboxylate (**16f**): 400 mg (2.7 mmol) of **2-Cl** dissolved in 5 mL THF were added to a solution of 2.2 mmol dienolate **13f** (method I) in 20 mL THF at -78°C under argon, and warmed-up to r. t. over night. The usual work-up and chromatography on silica gel (ether-pentane 1:1) gave 578 mg (92%) **16f**, colorless oil (b.p. 150°C/0.01 Torr).

^{1}H-NMR (270 MHz, $CDCl_3$, δ, ppm): 0.47-0.61 (m, 2H), 0.76-0.83 (m, 1H), 1.29-1.35 (m, 1H), 1.55-1.77 (m, 2H), 1.94-2.07 (m, 1H), 2.37-2.65 (m, 2H), 2.85 (d, J = 1.6 Hz, 1'-H, 1H), 3.64 (s, ester Me, 3H), 4.55 + 4.65 (AB, J = 11 Hz, 2H, diastereotopic benzylic H's), 7.2-7.3 (m, aromat. H, 5H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 4.8 (t), 8.9 (t), 20.3 (t), 22.6 (t), 24.1 (s), 41.2 (d), 45.7 (s), 49.9 (d), 51.5 (q), 69.9 (t), 75.4 (s), 127 (d), 127.5 (d), 128 (d), 136.9 (s), 165.8 (s), 207.3 (s). - IR (neat): 1730 cm^{-1}. - EI-MS (70eV): m/z = 312 (2%, M^+), 91 (100). - High-res. MS: Found: 312.1361. Calc. for $C_{19}H_{20}O_4$: 312.1360.

Methyl 2',6'-dioxo-spiro[cyclopropane-1,8'-bicyclo[3.2.1]octane]-1'-carboxylate (**17f**): To a solution of dienolate **13g** formed from 1.01 g (5.5 mmol) of TMS-enolether **14g** in 15 mL THF at -78°C following method II was added a solution of 732 mg (5 mmol) **2-Cl** in 10 mL THF at -60°C. The reaction mixture was allowed to warm-up to r. t. over night, quenched with sat. aqueous NH_4Cl solution, and extracted with methylene chloride. Chromatography on silica gel (ether-pentane 1:1) gave 350 mg (31.5%) **17f**, white crystals, m.p. 85°C (ether-pentane).

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 0.52-0.68 (m, 2H, cyclopropyl), 0.72-0.81 (m, 1H, cyclopropyl), 1.3-1.4 (m, 1H, cyclopropyl), 2.02-2.13 (m, 3H), 2.46-2.67 (m, 2H), 2.72 (AB, J = 19 Hz, 1H, 7'H$_{endo}$), 3.11 (AB, dd, J = 19, 1.4, 1.4 Hz, 1H, 7'H$_{exo}$), 3.73 (s, 3H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 3.9 (t), 8.8 (t), 25.1 (t), 29.7 (s), 33.8 (t), 45.6 (t), 51.5 (q), 53.4 (q), 63.6 (s), 167.7 (s), 204 (s), 213.1 (s). - IR (CH_2Cl_2): 1750, 1725, 1710 cm^{-1}. - EI-MS (70eV): m/z = 222 (20%, M$^+$), 190 (25), 162 (25), 134 (25), 79 (30), 55 (100). Found: C, 64.85; H, 6.35. Calc. for $C_{12}H_{14}O_4$: C, 64.74; H, 6.24.

Catalytic hydrogenation of **16a**: 100 mg (0.46 mmol) **16a** in 5 mL glacial acetic acid were stirred in the presence of 10 mg prehydrogenated PtO_2 under an atmosphere of hydrogen for 48 h. The progress of the reaction was followed by capillary gas chromatography (25 m OV 1701, 170°C), and after completion the catalyst was filtered off, the solution diluted with 100 ml of water and the mixture extracted with pentane (3 times 10 mL). The combined pentane extracts were washed with saturated sodium bicarbonate solution (2 times 50 mL) and 50 mL saturated sodium chloride solution, dried over magnesium sulfate and rotoevaporated. The residue was distilled in a Kugelrohr (120°C/0.04 Torr) to give 67 mg (67%) crude methyl 6'-oxo-2,8,8-trimethyltricyclo[3.2.1.0^{2,7}]octane-1'-carboxylate (**15**) as a colorless oil which partially crystallized upon standing (m.p. 54°C). The crude **15** contained varying amounts (8-35% in different runs) of a product with MG 224 apparently arising from **15** by further hydrogenation.

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 1.05 (s, Me, 3H), 1.16 (s, Me, 3H), 1.39 (s, Me, 3H), 1.65-2.15 (m, 5H), 2.19 (d, J = 2 Hz, 1H, 2-H), 3.75 (s, 3H, ester Me). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 19.4 (q), 20 (q), 22.1 (t), 23.5 (t), 25.7 (q), 37.2 (s), 40.5 (s), 41 (d), 50.2 (s), 50.7 (q), 52.7 (d), 168.8 (s), 212.2 (s). - IR (KBr): 1710 cm^{-1}. - EI-MS (70eV): m/z = 222 (50%, M$^+$), 207 (2), 194 (30), 135 (65), 119 (60), 107 (100), 93 (65), 91 (70). - High res. MS: Found: 222.1257. Calc. for $C_{13}H_{18}O_3$: 222.1256.

Catalytic hydrogenation of **16e**: 180 mg (0.58 mmol) in 5 mL glacial acetic acid were hydrogenated over 60 mg prehydrogenated PtO_2 as described above for **16a**. The progress of the reaction was controlled by thin layer (TLC) and capillary gas chromatography (25 m OV 1701, 250°C, rel. R_T (**16e**) = 1.00, rel. R_T (**18**) = 0.87). **16e** and **18** both had R_F = 0.74 on TLC, but differed in color upon staining with sulfuric acid, **16e** giving a light brown and **18** a red spot. After workup as above, the crude product was recrystallized to yield 100 mg (56%) methyl (1S,2R,5S,6S,8S,10R)-5'-*tert*-butoxy-6,11,11-trimethyl-9-oxotetracyclo-[6.2.1.0^{2,6}.0^{2,10}]undecane-1'-carboxylate (**18**), m.p. 104-105°C.

^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 1.00 (s, 3H), 1.04 (s, 3H), 1.16 (s, 9H), 1.30-1.40 (m, 1H), 1.38 (s, 3H), 1.60-1.70 (m, 2H), 1.90-2.15 (m, 3H), 2.36 (d, J = 1.4 Hz, 1H), 3.71 (s, 3H), 3.98 (t, J = 8.1 Hz, 1H). - ^{13}C-NMR (62.88 MHz, $CDCl_3$, δ, ppm): 22.0 (q), 22.4 (q), 25.7 (t), 27.4 (q), 28.7 (3q), 31.2 (t), 32.2 (t), 37.9 (s), 38.6 (d), 40.9 (s), 51.6 (q), 51.7 (s), 52.4 (s), 53.2 (d), 72.7 (s), 77.7 (d), 169.8 (s), 213.1 (s). - IR (KBr): 1730, 1390, 1365, 1220 cm^{-1}. $[\alpha]_D^{23}$ = -99° (c = 0.3 in EtOH). - MS (70eV): m/z = 334 (M$^+$, 10%), 303 (5), 278 (90), 260 (40), 246 (35), 232 (30), 231 (30), 218 (25), 57 (100). Found: C, 71.83; H, 9.12. Calc. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04.

Catalytic hydrogenation of **16f**: 312 mg (1.34 mmol) **16f** in 20 mL ethyl acetate were stirred under an atmosphere of hydrogen (2 bar H_2) in the presence of 50 mg Pd on C (10%, Fluka, Switzerland) for 48 h. The catalyst was removed by filtration through 1 g of silica gel, the solvent was stripped off and the remaining colorless oil distilled in the Kugelrohr to give 205 mg (98%) **17f**, identical in all respects with the material obtained above from **13g**.

Crystal structure analysis of **2-Cl**:[21] A crystal was grown from molten **2-Cl** in a X-ray tube (0.1 mm diameter) employing the Bridgman technique[20] with a temperature gradient +50/29, slowly lowered to +50/23°C. The space group was Pnma with a = 1517.2 (22), b = 683.1 (13), c = 1326.7 (25) pm, d = 1.416 g cm^{-3}, V = 103.6 cm^3 mol^{-1}. 1437 reflections with $2\theta \leq 55°$ (1192 with $I > 3\sigma(I)$) were recorded on a Syntex P2, automated four circle diffractometer with variable scan speed (1.0 - 29.3° min^{-1}), ω-scan with 1° scan width, MoKα (71.073 pm), graphite monochromator; temperature ±5°C; empirical absorption correction (Ψ-scan) with 6 reflections. Direct methods[22] were used to solve the structure, all atoms except H from E-map, H atoms from ΔF synthesis, R = 0.061 (R_w = 0.057).

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