151. Photocycloadditions of 2-(Trimethylsilyloxy)-1,3-butadiene to 2-Cycloalkenones

Access to the Basic Pentalenolactone Skeleton[1])

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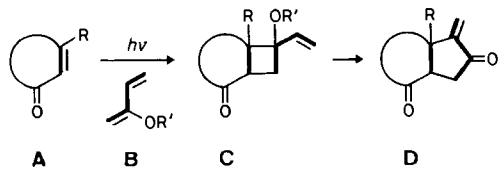
The [2 + 2] photocycloaddition of 2-(trimethylsilyloxy)-1,3-butadiene to a number of 2-cycloalkenones proved to be quite a general reaction leading to good yields of the cycloadducts *(Table)*. This finding is surprising since dienes, in general, are better known as quenchers of enone triplets rather than as photochemical reactants. Both the high substrate concentrations, which can be employed in these cycloadditions, and the remarkable regio- and stereoselectivity of the processes qualify them as valuable for syntheses. In a first application, the photoproducts **1a, b** were transformed in three steps into a viable precursor **4** of the pentalenolactone-G and -H antibiotics.

1. The Synthetic Principle. – The present work is the result of a search for a pentaannulation method involving α,β-enones to proceed with high stereo- and regioselectivity. This objective is accomplished by a two-step sequence which consists of consecutive addition of 2-cycloalkenones **A** to an appropriately substituted diene **B** in a [2 + 2] photoreaction and subjecting the adducts **C** to a C_1 ring expansion (→**D**; *Scheme 1*).

Scheme 1. *Pentaannulation Sequence* via *Consecutive Addition of 2-(Trimethylsilyloxy)-1,3-butadiene to 2-Cycloalkenones and Ring Enlargement of the Vinylcyclobutane*



2. Photocycloadditions of 2-Trimethylsilyloxybutadiene to 2-Cycloalkenones. – While 1,3-dienes have received much attention in ground-state chemistry as important reactants for cycloadditions, their use was comparatively subordinate in combination with excited-state chemistry [2][2]). In fact, they mainly serve in mechanistic studies as triplet quenchers. In this context, *Cantrell* [4] showed that, *e.g.*, 1,3-butadiene should be used with great caution in quenching of enone triplets, since it competitively adds to the enone C=C bond in a [2 + 2] process. Considering the remarkably high yield of this

[1]) Preliminary communication: [1].

[2]) For a summary of related studies in the field of dienone photochemistry, see [3].

addition reaction one could, in turn, anticipate its synthetic value, if the major obstacle, the lack of regio- and stereocontrol in the [2 + 2] process, could be overcome. At this point, we considered the known substituent effects in photochemical cycloadditions of olefins to α,β-unsaturated ketones where substantially enhanced selectivities are observed, if the olefins are alkoxy-substituted [5]. We thought of probing potentially similar effects in the diene-related photochemistry and, therefore, reacted 2-(trimethylsilyloxy)-1,3-butadiene with a variety of 2-cycloalkenones (see the *Table*). A literature search revealed that the use of this particular diene finds precedent in the work of *Tsuda* and coworkers [6] where it has been successfully added to a unique and rather complex enone-resembling chromophor. In our hands, the [2 + 2] photocycloaddition of 2-(trimethylsilyloxy)-1,3-butadiene to a number of standard enones proved to be a more general reaction leading, without exception, to preparatively valuable yields. It should also be noted that these cycloadditions can readily be accomplished in the presence of a five-fold excess of diene only and within relatively short reaction times of 40–48 h. Such conditions have not been met in other cases where a 20-fold excess of diene and irradiation times of several days are required to achieve high yields of cycloadducts [4] [6].

The irradiations were conducted at 300 or 350 nm (*Rayonet* reactor with RPR-3000- or -3500-Å lamps, respectively), depending on sufficient enone absorption, and in cyclohexane or dimethoxyethane solution. Surprisingly high substrate concentrations, *i.e.* 0.1M of enone and 0.5M of diene, could be employed in these reactions. Excitation with 350-nm light was advantageous, where possible, to give cleaner and higher conversions than at 300-nm irradiation, because formation of secondary products *via* consecutive *Norrish*-type-I cleavage and disproportionation is largely suppressed at the longer wavelength. As expected, no change of the cycloadduct ratios was observed upon variation of the excitation wavelength (300-nm *vs.* 350-nm irradiation).

In the [2 + 2] cycloadditions, the steering effect of the silyloxy group selects dominantly for a single regioisomer, coupled with a strong stereochemical control[3]).

The chemoselection invariably favours the substituted part of the diene, *i.e.* C(1) and C(2). Adducts obtained from the addition of C(3) and C(4) of the diene amounted at most to 10% in *Run 4*, and to $< 5\%$ in *Runs 1, 2, 6,* and *7*. No such isomeric adducts were at all formed in *Runs 3* and *5 (Table)*.

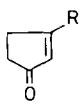
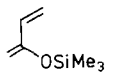
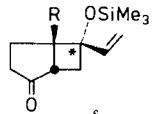
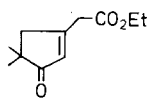
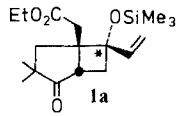
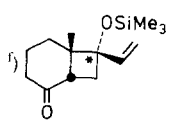
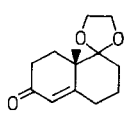
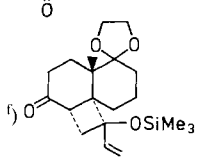
Important stereocontrol factors seem to be the substituents at C(3) of the enone and its ring size. Substituents with increasingly complex O functionalities exert less efficient stereocontrol (*Runs 1, 3,* and *5*). A similar trend was observed upon changing from five- to six-membered enones within the same substitution pattern (*cf. Run 2* with *Run 6*).

The mechanistic details of the reaction cascade of excited α,β-enones in cycloadditions are not yet fully unravelled. Upon laser-flash excitation of cyclic α,β-enones at either 265 or 353 nm, transients absorbing in the 280–320-nm range are observed [8] [9]. They are attributed to π,π^* triplets with considerable twisting about the C=C bond [8–10]. However, these transients and in particular the species absorbing at 280 nm were found not to be involved in the formation of cycloadducts [10]. Instead, another triplet intermediate is proposed to precede the transient which is ultimately intercepted by alkenes, and which is suggested to be a twisted ground state biradical [11][4]). An alternative mechanism, originally proposed by *Corey* and *de Mayo,* invokes a charge-transfer triplet

[3]) A preliminary investigation of 7-membered analogs in this series revealed rather complex product compositions as a result of competing enone dimerization, [2 + 2] and [4 + 2] cycloadditions.

[4]) Evidence for trapping of a *transoid*-cyclohexenone species by furan upon excitation of *Pummerer*'s ketone has recently been presented [12].

Table. *Photocycloaddition Products Formed by Reaction of Various Enones with 2-(Trimethylsilyloxy)-1,3-butadiene*

Run	Enone[a])	Diene[b])	λ_{irr}[c]) [nm]	Products	Yield[d]) [%]	Recovered enone [%]	Ratio of stereoisomers(*) (mayor isomer as depicted)[e])
							
1	R = OMe	„	300	R = OMe[f])	84	12	6:1
2	R = Me	„	350	R = Me[f])	79	10	19:1
3	R = OCOCH(OMe)Ph	„	300	R = OCOCH(OMe)Ph	75	15	5:1[g])
4	R = H	„	300	R = H[h])	76	37	10:1
5		„	350	 **1a**	65	16	12:1
6		„	350	 [f])	63	18	9:1
7		„	300	 [f])	90	72	10:1

[a]) All materials are commercially available or obtained by standard preparation except for *Runs 3* and *5*[2]).

[b]) Preparation: see [7].

[c]) *Rayonet* reactor with *RPR-3000-* or *-3500-*Å lamps.

[d]) Yields refer to the mixture of stereoisomers and are based on % of consumed enone.

[e]) Structure assignment by ^{1}H-NMR decoupling and NOE (R and vinyl protons). The isomeric composition is determined for the crude mixtures by GLC and ^{1}H-NMR.

[f]) < 5% isomers formed by the addition of C(3) and C(4) of the diene.

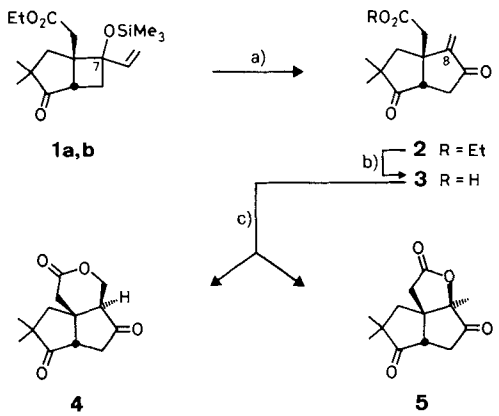
[g]) Mixture of four diastereoisomers in a 1:1:5:5 ratio. Configuration of major components at C(*) as depicted; note: no diastereoisomeric induction triggered by the mandelic-acid residue.

[h]) *Ca.* 10% of isomers formed by the addition of C(3) and C(4) of the diene.

exciplex [13] and would accordingly seem to operate only with enones which are incapable of adoption of *transoid*-geometries [11]. Intriguingly, the present type of cycloadditions leads, within the limits of detection of NMR, exclusively to *cis*-fused products, even when reacting a 'flexible' 2-cycloalkenone such as the 3-methylcyclohexenone *(Run 6)*. Hence, potential interception of *transoid*-enone intermediates by 2-(trimethylsilyloxy)-1,3-butadiene lacks, in absence of *trans*-fused adducts, at least chemical evidence. Intervening formation of a triplet exciplex would, therefore, – and in view of the highly chemo- and stereoselective modes of addition – seem to be a sound hypothesis for further mechanistic investigations.

3. Synthetic Application: Preparation of a Potential Pentalenolactone Precursor 4 *(Scheme 2)*. – Both the high substrate concentrations, which can be employed in the above photoreactions, and the distinct regioselectivity of the addition processes qualify this novel annulation method as a valuable synthetic tool to serve, for example, as a basis to prepare five- and six-membered cycles *via* enlargement of the vinylcyclobutane moiety. The synthesis of densely functionalized cyclopentanoid compounds from the photoproducts was explored first with the aim to assemble the basic skeleton of the pentalenolactones, a family of natural products[5]).

Scheme 2. *Synthesis of a Pentalenolactone Precursor* **4** *from the Photoproducts* **1a, b** (all compounds shown are racemic and the yields refer to chromatographically purified materials)



a) 3.3 mol-% $PdCl_2(PhCN)_2$, *ca.* 2 equiv. 1,4-benzoquinone; analogously to [15]; 72% yield.
b) 5% HCl in acetone, r.t., 48 h; 78%.
c) 125–130°, 1.5 h: **4** in 30% yield; TsOH, toluene, reflux: **5** in 41% yield.

The mixture of the C(7)-stereoisomeric photoproducts **1a** (see the *Table*) and **1b** (C(7) epimer of **1a**) was subjected to a Pd(II)-mediated ring expansion (see *Scheme 2*). A known procedure [15] for the rearrangement of vinylcyclobutanols to cyclopentenones was successfully adopted here for the transformation of the trimethylsilyl derivatives **1a, b** to **2** without the need to cleave the Me_3SiO group in **1** prior to the treatment with $Pd(PhCN)_2Cl_2$. Equally successful were so far analogous Pd(II)-mediated ring expansions on the photoproducts of *Runs 2, 4,* and *6*. The ester **2** was, in the further course of the planned synthesis, hydrolyzed to **3** which, upon heating to 125–130° for 1.5 h, gave rise to

[5]) For excellent surveys on polyquinane chemistry, see [14].

an equilibrium of the δ-lactone **4** and its progenitor **3**. If, on the other hand, the reaction was conducted in toluene at 80° and in presence of TsOH as a catalyst, a mixture of **4** and the γ-lactone **5** resulted. Further heating of this reaction mixture at 110° provided **5** as the sole and evidently thermodynamically favoured product. The control over the reaction modes seems to depend strongly on the acidity of the reaction medium, a fact, which in view of further optimizations, still needs additional exploration. It should be noted, however, that our result, the lactonization to **4**, strikingly contrasts an unsuccessful attempt by *Magnus* and coworkers to obtain the δ-lactone in competition with favourable formation of γ-lactone of a closely related skeleton [16].

The availability of lactone **4** secures, in our opinion, a promising route to the synthesis of the pentalenolactone-G and -H antibiotics, especially in view of a recent conversion of the parent lactol methyl ether of **4** to pentalenolactone-G methyl ester [17]. Continuing work concerns further synthetic development in the project as well as the study of the reactivity of other dienes in presence of 2-cycloalkenones [18].

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Experimental Part

General. The solvents were purified using standard procedures. All reactions were run under Ar. Prep. TLC was carried out on 2-mm silica plates *(Merck)*. GLC: *Carlo-Erba-4100* instrument equipped with a flame-ionization detector coupled to a *Spectra Physics Autolab System I* integrator; *OV 101* glass capillary columns of 20- and 35-m length; N_2 as carrier gas. Flash chromatography (FC) was performed on silica gel (*Merck*, 0.063–0.2 mm). UV spectra (cyclohexane): *Perkin-Elmer Lambda 5* spectrophotometer; λ_{max} (ε); in nm. IR spectra: in $CHCl_3$, unless stated otherwise, on a *Perkin-Elmer-298* instrument; in cm^{-1}. ^{1}H-NMR spectra and ^{13}C-NMR (100.6 MHz): in $CDCl_3$, unless stated otherwise; *Bruker-AM-400* instrument; chemical shifts in ppm rel. to TMS (= 0 ppm) and coupling constants J in Hz. MS (in m/z): *Varian MAT CH5* instrument at 70 eV. The elemental analyses were performed by *Dornis* and *Kolbe*, Mülheim a.d. Ruhr.

General Procedure for the Photocycloadditions of 2-(Trimethylsilyloxy)-1,3-butadiene to Various 2-Cycloalkenones (*Runs 1–7* in the *Table*). The photoreactions were carried out in 50–100 ml 1,2-dimethoxyethane or cyclohexane solns., flushed with Ar (15 min) prior to irradiation, with 0.1M enone and 0.5M 2-(trimethylsilyloxy)-1,3-butadiene [7]; reaction temp. 8–10° (water-cooled reaction vessel); reaction time: 40–48 h. The reactions were run in a *Rayonet* reactor equipped with *RPR-3000-* (quartz vessel used) or -3500-Å lamps (*Pyrex* vessel used) and monitored by GLC and TLC. Purification and separation of the product mixtures were performed by FC (silica gel, 50-fold).

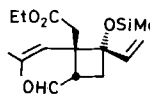
Run 1: 5-Methoxy-6-(trimethylsilyloxy)-6-vinylbicyclo[3.2.0]heptan-2-one. Chromatography (pentane/Et_2O 5:1) gave the separate C(6) stereoisomers. *Major stereoisomer:* IR: 1725, 1625. ^{1}H-NMR: 6.12 (*dd*, J = 10, 17, 1 H); 5.32 (*d*, J = 17, 1 H); 5.22 (*d*, J = 10, 1 H); 3.16 (*s*, 3 H); 2.59 (*m*, 1 H); 2.53–2.40 (*m*, 4 H); 2.15 (*m*, 1 H); 1.70 (*m*, 1 H); 0.06 (*s*, 9 H). NOE at 5.32, 5.22, 2.59, when irradiated at 3.16. ^{13}C-NMR: 217.57, 89.33, 79.04 (3 *s*); 139.69, 45.84 (2 *d*); 113.74, 37.67, 32.13, 23.07 (4 *t*); 51.56, 1.71 (2 *q*). MS: 254 (M^+, $C_{13}H_{22}O_3Si$), 223, 207, 199, 185, 127 (100). *Minor stereoisomer:* ^{1}H-NMR: 6.03 (*dd*, J = 10, 17, 1 H); 5.27 (*d*, J = 10, 1 H); 5.15 (*d*, J = 17, 1 H); 3.34 (*s*, 3 H); 2.65 (*m*, 1 H); 2.57–2.30 (*m*, 4 H); 2.07 (*m*, 1 H); 1.61 (*m*, 1 H); 0.12 (*s*, 3 H). NOE at 2.65, when irradiated at 3.34. ^{13}C-NMR: 218.39, 86.36, 81.36 (3 *s*); 139.89, 47.24 (2 *d*); 116.15, 38.12, 25.93, 18.63 (4 *t*); 53.92, 2.11 (2 *q*). IR and MS: identical with those of the major isomer.

Run 2: 5-Methyl-6-(trimethylsilyloxy)-6-vinylbicyclo[3.2.0]heptan-2-one. Chromatography (pentane/Et_2O 8:1) gave partial separation of the C(6) stereoisomers. *Major stereoisomer:* IR: 1725, 1625. ^{1}H-NMR: 5.95 (*dd*, J = 10, 17, 1 H); 5.20 (*d*, J = 17, 1 H); 5.19 (*d*, J = 10, 1 H); 2.60 (*m*, 2 H); 2.40 (*m*, 2 H); 2.10 (*m*, 3 H); 1.03 (*s*, 3 H); 0.10 (*s*, 9 H). ^{13}C-NMR: 200.80, 77.38, 51.96 (3 *s*); 141.03, 45.77 (2 *d*); 113.39, 38.57, 35.40, 28.10 (4 *t*); 21.29, 1.74 (2 *q*). MS: 238 (M^+, $C_{13}H_{22}O_2Si$), 169, 142, 127, 85, 75 (100), 73, 55, 45, 27. Anal. calc. for $C_{13}H_{22}O_2Si$: C 65.49, H 9.30, Si 11.78; found: C 65.44, H 9.30, Si 11.77.

Run 3: 4-Oxo-7-(trimethylsilyloxy)-7-vinylbicyclo[3.2.0]hept-1-yl 2-Methyl-2-phenylacetate. Four stereoisomers were formed in a 1:1:5:5 ratio, the major components having the C(7) configuration shown in the *Table*. Chromatography (hexane/Et_2O 3:2) gave a clean but inseparable 1:1 mixture of the major components. IR: 1725, 1625. ^{1}H-NMR: 7.36 (br. *s*, 5 H); 5.97 (*dd*, *J* = 10, 17, 0.5 H); 5.64 (*dd*, *J* = 10, 17, 0.5 H); 5.24 (*d*, *J* = 17, 0.5 H); 5.16 (*d*, *J* = 10, 0.5 H); 5.10 (*d*, *J* = 17, 0.5 H); 4.92 (*d*, *J* = 10, 0.5 H); 4.67 (*s*, 0.5 H); 4.65 (*s*, 0.5 H); 3.35 (*s*, 3 H); 3.15–1.10 (*m*, 7 H); 0.18 (*s*, 4.5 H); 0.15 (*s*, 4.5 H). MS: 388 (M^+, $C_{21}H_{28}O_5Si$), 239, 142, 127, 121 (100), 73.

Run 4: 6-(Trimethylsilyloxy)-6-vinylbicyclo[3.2.0]heptan-2-one. Chromatography (pentane/Et_2O 8:1) gave partial separation of the stereoisomers. *Major stereoisomer:* IR: 17.30, 1625. ^{1}H-NMR: 6.06 (*dd*, *J* = 10, 17, 1 H); 5.20 (*dd*, *J* = 1, 17, 1 H); 5.10 (*dd*, *J* = 1, 10, 1 H); 2.70–1.78 (*m*, 8 H); 0.09 (*s*, 9 H). MS: 224 (M^+, $C_{12}H_{20}O_2Si$), 196, 155, 142, 127, 85, 75, 73 (100), 55.

Run 5: Ethyl 2-(3,3-Dimethyl-4-oxo-7-(trimethylsilyloxy)-7-vinylbicyclo[3.2.0]hept-1-yl)acetate (**1a, b**). The enone component for this reaction, ethyl 2-(4,4-dimethyl-3-oxocyclopent-1-enyl)acetate, was prepared by *Reformatsky* addition of α-(zincbromoethyl)acetate to 4,4-dimethylcyclopent-2-en-1-one [19] and oxidation of the resulting tertiary allylic alcohol with pyridinium chlorochromate [18]. Chromatography of the mixture of photoproducts (petroleum ether/AcOEt 17:1) gave the clean C(7) stereoisomers **1a** *(Table)* and **1b** besides 4% of a product from *Norrish* fragmentation. Notably, this separation procedure serves analytical purposes only and is not required for the synthesis of **4**. *Major stereoisomer* **1a**: 283 (52), 227 (232). IR: 1730, 1625. ^{1}H-NMR: 5.92 (*dd*, *J* = 11, 18, 1 H); 5.21 (*dd*, *J* = 1, 11, 1 H); 5.20 (*dd*, *J* = 1, 18, 1 H); 4.03 (*q*, *J* = 7, 2 H); 2.71 (*dd*, *J* = 10, 12, 1 H); 2.68 (*d*, *J* = 15, 1 H); 2.56 (*dd*, *J* = 6, 10, 1 H); 2.42 (*s*, 2 H); 1.97 (*dd*, *J* = 6, 12, 1 H); 1.69 (*d*, *J* = 15, 1 H); 1.19 (*s*, 3 H); 1.18 (*t*, *J* = 7, 3 H); 1.01 (*s*, 3 H); 0.03 (*s*, 9 H). ^{13}C-NMR: 222.9, 171.5, 78.4, 49.8, 41.7 (5 *s*); 140.7, 44.5 (2 *d*); 114.8, 60.3, 40.7, 40.5, 34.8 (5 *t*); 27.7, 26.6, 14.1, 1.85 (4 *q*). MS: 338 (M^+, $C_{18}H_{30}O_4Si$), 269, 142, 127 (100), 75, 73, 29. Anal. calc. for $C_{10}H_{30}O_4Si$: C 63.86, H 8.93, Si 8.30; found: C 63.95, H 8.90, Si 8.19. *Minor stereoisomer* **1b**: IR: 1725, 1625. ^{1}H-NMR: 5.90 (*dd*, *J* = 11, 18, 1 H); 5.24 (*dd*, *J* = 1, 11, 1 H); 5.04 (*dd*, *J* = 1, 18, 1 H); 4.09 (*q*, *J* = 7, 2 H); 2.94 (*d*, *J* = 16, 1 H); 2.84 (*dd*, *J* = 5.5, 10.5, 1 H); 2.51 (*d*, *J* = 16, 1 H); 2.43 (*dd*, *J* = 5.5, 13, 1 H); 2.31 (*dd*, *J* = 10.5, 13, 1 H); 2.17 (*d*, *J* = 15, 1 H); 1.83 (*d*, *J* = 15, 1 H); 1.24 (*t*, *J* = 7, 3 H); 1.05 (*s*, 3 H); 0.99 (*s*, 3 H); 0.06 (*s*, 9 H). ^{13}C-NMR: 223.4, 172.3, 80.4, 49.2, 47.3 (5 *s*); 140.4, 44.5 (2 *d*); 115.8, 60.0, 42.3, 39.6, 32.7 (5 *t*); 28.1, 24.3, 14.2, 1.7 (4 *q*). UV and MS: identical with those of the major isomer. Norrish *product* (structure *vide infra*): IR: 1700. ^{1}H-NMR: 9.95 (*d*, *J* = 2, 1 H); 6.00 (*dd*, *J* = 11, 17, 1 H); 5.26 (*dd*, *J* = 1, 17, 1 H); 5.21 (*d*, *J* = 1.5, 1 H); 5.20 (*dd*, *J* = 1, 11, 1 H); 4.04 (*q*, *J* = 7, 2 H); 2.87 (*d*, *J* = 15, 1 H); 2.78 (*ddd*, *J* = 2, 8, 10, 1 H); 2.59 (*d*, *J* = 15, 1 H); 2.38 (*dd*, *J* = 10, 12, 1 H); 2.26 (*dd*, *J* = 8, 12, 1 H); 1.69 (*d*, *J* = 1.5, 3 H); 1.58 (*d*, *J* = 1.5, 3 H); 0.05 (*s*, 9 H). ^{13}C-NMR: 223.5, 138.4, 78.0, 55.4 (4 *s*); 204.3, 140.8, 120.3, 50.1 (4 *d*); 114.0, 60.1, 42.4, 32.4 (4 *t*); 25.7, 21.1, 14.1, 1.7 (4 *q*). MS: 338 ($M^{+\cdot}$, $C_{18}H_{30}O_4Si$), 269, 142, 127 (100), 75, 73, 29.



Norrish product

Run 6: 6-Methyl-7-(trimethylsilyloxy)-7-vinylbicyclo[4.2.0]octan-2-one. Prep. TLC (petroleum ether/AcOEt 5:1) gave partial separation of the stereoisomers. *Major stereoisomer:* IR: 1708, 1630. ^{1}H-NMR: 5.86 (*dd*, *J* = 10, 17, 1 H); 5.28 (*dd*, *J* = 2.5, 17, 1 H); 5.16 (*dd*, *J* = 2.5, 10, 1 H); 2.40–1.60 (*m*, 9 H); 1.15 (*s*, 3 H); 0.09 (*s*, 9 H). MS: 252 (M^+, $C_{14}H_{24}O_2Si$), 183, 182, 142, 127, 117, 110, 85, 82, 75, 73 (100), 55.

Run 7: Wieland-Miescher *Ketone Adduct.* (*9,9-(Ethylenedioxy)-2-(trimethylsilyloxy)-2-vinyltricyclo-[6.4.0.0^{1,4}]dodecan-5-one*). Prep. TLC (petroleum ether/AcOEt 5:1) gave partial separation of the stereoisomers. *Major stereoisomer:* IR: 1710, 1630. ^{1}H-NMR: 6.25 (*dd*, *J* = 10, 17, 1 H); 5.12 (*dd*, *J* = 1, 17, 1 H); 5.08 (*dd*, *J* = 1, 10, 1 H); 3.93 (*m*, 4 H); 2.50–1.28 (*m*, 13 H); 1.20 (*s*, 3 H); 0.01 (*s*, 9 H). MS: 364 (M^+, $C_{20}H_{32}O_4Si$), 142, 127, 99 (100), 73.

Ethyl 2-(3,3-Dimethyl-8-methylidene-4,7-dioxobicyclo[3.3.0]oct-1-yl)acetate (**2**). Procedure adopted from [15]. A soln. of **1a**/**1b** (605 mg, 1.8 mmol), $PdCl_2$ ($PhCN)_2$ (31 mg, 0.06 mmol), and *p*-benzoquinone (356 mg, 3.3 mmol) in THF (65 ml) was refluxed for 3 h. Then, brine (50 ml) and Et_2O (50 ml) were added, and the mixture was extracted. The separated brine layer was repeatedly extracted with Et_2O, and the combined org. portions were dried ($MgSO_4$) and evaporated. The crude material was purified by FC (silica gel, 100-fold; petroleum ether/AcOEt 6:1), and pure **2** isolated (344 mg, 72% yield) besides a minor portion of the $\Delta^{5,6}$-8-methyl-isomer of **2** (30 mg, 6% yield).

Data of **2**: IR: 1735, 1725, 1720, 1630. ^{1}H-NMR: 6.16 (*s*, 1 H); 5.47 (*s*, 1 H); 4.07 (*q*, *J* = 7, 2 H); 3.01 (*dd*, *J* = 2.5, 11, 1 H); 2.82 (*dd*, *J* = 11, 19, 1 H); 2.73 (*d*, *J* = 16, 1 H); 2.65 (*d*, *J* = 16, 1 H); 2.63 (*dd*, *J* = 2.5, 19, 1 H);

2.27 (*d*, *J* = 14, 1 H); 2.19 (*d*, *J* = 14, 1 H); 1.20 (*t*, *J* = 7, 3 H); 1.13 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR: 222.5, 204.5, 170.4, 151.2, 45.9, 42.9, (6 *s*); 51.2 (*d*); 120.1, 60.8, 49.8, 46.6, 39.4 (5 *t*); 26.4, 26.0, 14.1 (3 *q*). MS: 264 (M^+, $C_{15}H_{20}O_4$), 208, 197, 177, 161, 149, 124, 79, 55, 43, 27 (100). Anal. calc. for $C_{15}H_{20}O_4$: C 68.16, H 7.63; found: C 68.13, H 7.67.

2-(3,3-Dimethyl-8-methylidene-4,7-dioxobicyclo[3.3.0]oct-1-yl)acetic Acid (**3**). A soln. of **2** (160 mg, 0.6 mmol) in acetone (10 ml) and 5% HCl (3 ml) was stirred at r.t. for 48 h. Then, acetone was evaporated, the residue brought to pH 8 with Na_2CO_3 soln. and extracted with Et_2O. The Et_2O layer was dried ($MgSO_4$) and evaporated to yield unreacted **2** (29 mg, 18%). The H_2O layer was acidified with 10% HCl soln. to pH 3 and extracted with AcOEt which, upon drying ($MgSO_4$) and evaporation, afforded clean **3** (112 mg, 78% yield). IR: 3500–2500, 1735, 1730, 1720, 1630. ^{1}H-NMR: 9.45 (*s*, 1 H); 6.15 (*s*, 1 H); 5.50 (*s*, 1 H); 2.99 (*dd*, *J* = 2.5, 11, 1 H); 2.80 (*dd*, *J* = 11, 20, 1 H); 2.78 (*d*, *J* = 16, 1 H); 2.69 (*d*, *J* = 16, 1 H); 2.56 (*dd*, *J* = 2.5, 20, 1 H); 2.24 (*d*, *J* = 14, 1 H); 2.16 (*d*, *J* = 14, 1 H); 1.10 (*s*, 3 H); 0.86 (*s*, 3 H). ^{13}C-NMR: 222.6, 204.7, 175.1, 151.0, 45.9, 45.6 (6 *s*); 51.1 (*d*); 151.1, 49.8, 46.1, 39.4 (4 *t*); 26.2, 25.8 (2 *q*).

Formation of Lactones **4** *and* **5** (*3,3-Dimethyl-10-oxatricyclo[6.4.0.0^{1,8}]dodecane-4,7,11-trione* and *10,10-dimethyl-4-oxatricyclo[6.3.0.0^{1,5}]undecane-3,6,9-trione*, resp.). A neat sample of **3** (60 mg, 0.25 mmol) was heated to 125–130° for 1.5 h, then cooled to r.t. and extracted with sat. $NaHCO_3$ soln. and $CHCl_3$. The org. layer was dried ($MgSO_4$) and evaporated to afford **4** (18 mg, 30% yield; > 97% purity). Acidification of the aq. layer with 10% HCl soln. to pH 3 and extraction with AcOEt, which was dried ($MgSO_4$) and evaporated, gave unreacted **3** (39.6 mg, 66%).

If a soln. of **3** (60 mg, 0.25 mmol) and TsOH (10 mg) in toluene (5 ml) was refluxed for 10 h, the toluene evaporated, and the reaction worked up as previously described, the γ-lactone **5** was isolated from the $CHCl_3$ layer (25 mg, 41% yield). The aq. layer contained unreacted **3**.

Data of **4**: IR: 1735, 1720. ^{1}H-NMR: 4.53 (*dd*, *J* = 3.3, 11.8, 1 H); 4.37 (*dd*, *J* = 4.6, 11.8, 1 H); 2.84 (*dd*, *J* = 3.8, 10.8, 1 H); 2.77 (*d*, *J* = 15, 1 H); 2.72 (*dd*, *J* = 3.8, 19.8, 1 H); 2.71 (*d*, *J* = 15, 1 H); 2.57 (*dd*, *J* = 10.8, 19.8, 1 H); 2.43 (*dd*, *J* = 3.3, 4.6, 1 H); 2.17 (*d*, *J* = 13.6, 1 H); 2.08 (*d*, *J* = 13.6, 1 H); 1.21 (*s*, 3 H); 1.09 (*s*, 3 H). ^{13}C-NMR: 220.2, 214.2, 170.4, 46.0, 43.0 (5 *s*); 54.2, 53.1 (2 *d*); 66.3, 50.2, 41.6, 40.6 (4 *t*); 27.2, 26.1 (2 *q*). MS: 236 (M^+, $C_{13}H_{16}O_4$), 193, 177, 165, 153, 135, 125 (100), 96, 79, 55, 43.

Data of **5**: IR: 1780, 1755, 1740. ^{1}H-NMR: 3.04 (*dd*, *J* = 13, 18.5, 1 H); 2.96 (*d*, *J* = 17, 1 H); 2.91 (*ddd*, *J* = 1, 5, 13, 1 H); 2.87 (*d*, *J* = 17, 1 H); 2.40 (*dd*, *J* = 5, 18.5, 1 H); 1.98 (*dd*, *J* = 1, 14, 1 H); 1.80 (*d*, *J* = 14, 1 H); 1.37 (*s*, 3 H); 1.16 (*s*, 3 H); 1.10 (*s*, 3 H).

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