# 205. Strained Ketenes from α-Bromoacyl Phosphates. (Tricyclo[4.4.1.0$^{1,6}$]undeca-3,8-dien-11-ylidene)methanone and its Heptacyclic Dimer: a Dispirobridged Dipropellane (1,1″,4,4″,5,5″,8,8″-Octahydrodispiro[[4a,8a]methanonaphthalene-9,1′-cyclobutane-3′,9″-[4a,8a]methanonaphthalene]-2′,4′-dione)

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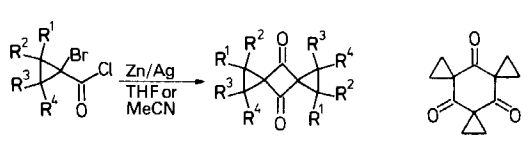
Dehalogenation of the mixed anhydride **6** of 11-bromotricyclo[4.4.1.0$^{1,6}$]undeca-3,8-diene-11-carboxylic acid (**4**) and of diethyl hydrogen phosphate with Zn-Ag couple in THF gave the dispiro-fused dipropellane **8** (1,1″,4,4″,5,5″,8,8″-octahydrodispiro[[4a,8a]methanonaphthalene-9,1′-cyclobutane-3′,9″-[4a,8a]methanonaphthalene]-2′,4′-dione) in 58% yield. Unlike other dispiro[2.1.2.1]octane-4,8-diones (see **2a-e**), the new cyclodimer **8** is an $O_2$-sensitive compound. The 11-bromobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylic acid (**13**) was prepared and converted into the acyl phosphate **14**, which in turn was reduced with Zn-Ag couple in THF/MeOD to give the deuterated ester **16**. Other cyclopropylidenemethanones could be generated and dimerized advantageously by the Zn-induced reduction of the mixed anhydride of the 1-bromocyclopropanecarboxylic acid and diethyl hydrogen phosphonate.

**1. Introduction.** – Recently, a number of dispiro[2.1.2.1]octane-4,8-diones **2** have been prepared by Zn-promoted dehalogenation of 1-bromocyclopropanecarbonyl chlorides **1** in THF [1] and MeCN *(Scheme 1)* [2]. Under special conditions (Zn-Ag couple, MeCN, reflux) and with selected cyclopropane precursors, we have also obtained cyclic trimers and their rearrangement products [2]. For example, the simple trispiro[2.1.2.1.2.1]-dodecane-4,8,12-trione (**3**) has been isolated from **1e** [3]. Triketone **3** contains one distal cyclopropane C–C bond of 143.7 pm, *i.e.* a very short cyclopropane C–C bond (survey and collective discussion of the *Cambridge Crystallographic Data File* with respect to 'free' cyclopropanes, see [4]).

In view of intense current activity in the field of ketene cycloadditions [5], it was of interest to attempt the dehalogenation of sterically more hindered 1-bromocyclopropane-

*Scheme 1*



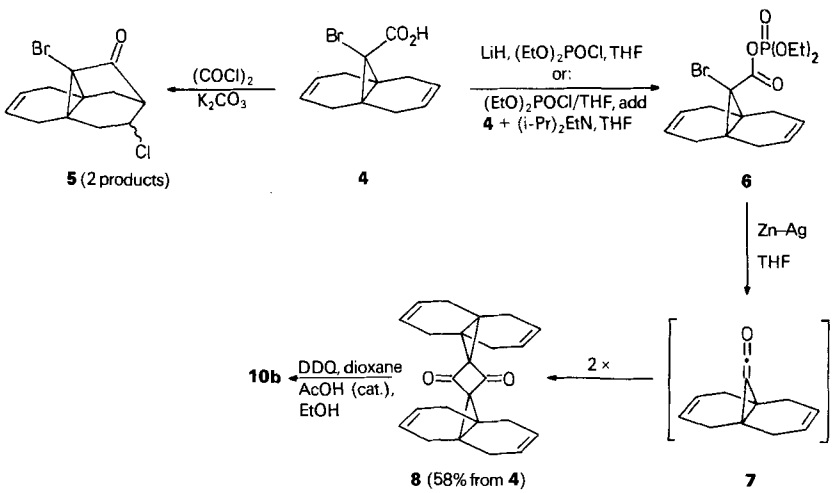

**1** **2** **3**

**a** $R^1 = R^2 = R^3 = R^4 = Me$
**b** $R^1 = R^2 = Me$; $R^3 = R^4 = H$
**c** $R^1R^4 = -(CH_2)_4-$; $R^2 = R^3 = H$
**d** $R^1 = R^2 = R^3 = H$; $R^4 = SiMe_3$
**e** $R^1 = R^2 = R^3 = R^4 = H$

carbonyl chlorides and to study the effect of steric hindrance and additional strain on the generation of the cyclopropylidenemethanone intermediates and on the ease of dimerization.

**2. Results.** – As a test case, we chose the crystalline 11-bromotricyclo[4.4.1.$0^{1,6}$]-undeca-3,8-diene-11-carboxylic acid (**4**). However, various attempts to convert **4** into its acyl chloride failed. Instead two isomeric tetracyclic ketones **5** were formed, apparently by ready nucleophilic intervention of the neighbouring double bond *(Scheme 2)*.

*Scheme 2*



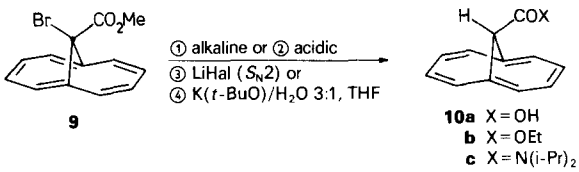

Therefore, a milder method of acyl activation had to be developed which was not conducive to the cyclization of **4** to **5**. In principle, numerous methods for acyl activation are known in peptide chemistry [6]. For a number of reasons (see *Chapt. 3*), we decided to use phosphate [7] as a leaving group. The mixed anhydride **6** of **4** and diethyl hydrogen phosphate was prepared by two simple methods. *i*) Exposure of **4** to LiH in THF gave a thick suspension of lithium carboxylate which was added to a solution of diethyl phosphochloridate ($(EtO)_2POCl$) in THF. *ii*) $(EtO)_2POCl$ in THF was cooled to 0°, and the mixture of **4** and $(i\text{-}Pr)_2EtN$ in THF was added. The resulting mixture was kept in a refrigerator overnight, the precipitate was filtered off under Ar to give a solution of the desired **6** in THF (*cf.* [7]).

Either solution of **6** was immediately subjected to dehalogenation with Zn-Ag couple (→[7]→**8**). After chromatography on silica gel, the heptacyclic dimer **8** was obtained as white crystals. The double-decker dispirodione **8** proved to be surprisingly sensitive to $O_2$ at room temperature. On exposure to air, white crystalline **8** visibly turned yellow with decomposition. NMR spectra of pure **8** could be recorded under Ar.

Various attempts to dehydrogenate **8** with generation of a dimeric aromatic annulene (*cf.* dimer of **15**) were not successful [8]. Reaction of **8** with DDQ (4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile) in dioxan containing some EtOH gave a mixture of polar products, including ethyl ester **10b**.

As another possible precursor of annulenoid dimers, 11-bromo-1,6-methano[10]-annulene-11-carboxylic acid (**13**) was considered. Previously, various attempts to saponify the known methyl ester **9** failed [9]. We have confirmed that other possible conditions ($S_N2$ dehalogenation with $I^-$ ion or $K(t\text{-BuO})/H_2O$) gave also **10a**, in accord with the experiments of *Straube* [9] *(Scheme 3)*. Apparently, the carbonyl C-atom in α-bromocarboxylic ester **9** is highly hindered and saponification is invariably accompanied by reductive loss of the Br-atom.

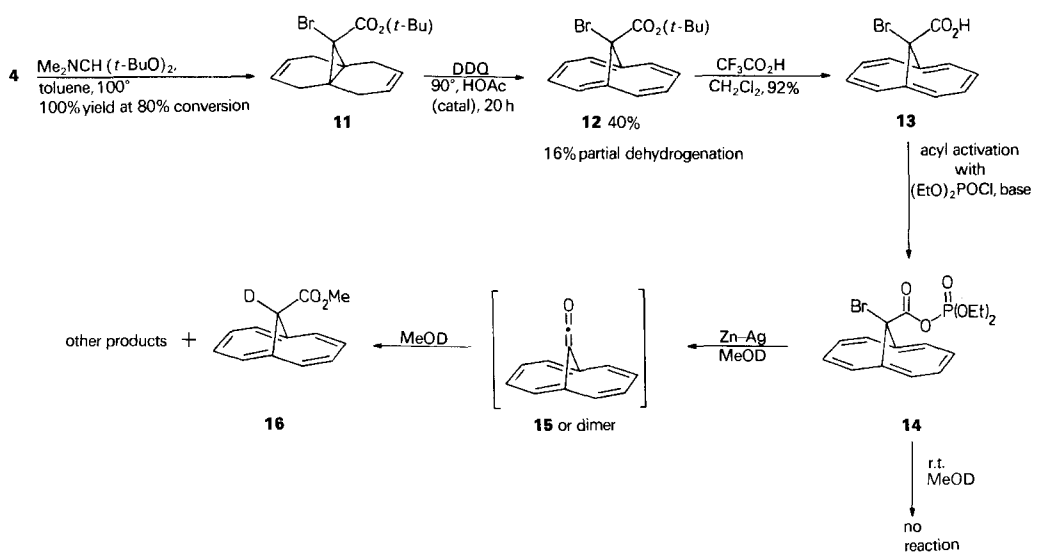
*Scheme 3*




Attempts to convert **4** into functionalized annulene **13** by dehydrogenation with DDQ yielded a mixture of partially dehydrogenated carboxylic acids and the desired **13** which were, however, difficult to separate. Therefore, a detour was taken. Following the procedure of *Widmer* [10] and using higher concentrations of reagents, we converted α-bromocarboxylic acid **4** into its *t*-butyl ester **11** (80% isolated yield; 100% with respect to recovered **4**; *Scheme 4*). After double dehydrogenation with DDQ, annulene ester **12** could be isolated and then hydrolyzed to the desired 1-bromocarboxylic acid **13** under mild acidic conditions at 0° (92% yield).

Conversion of α-bromocarboxylic acid **13** into **14** and dehalogenation with Zn-Ag couple in MeOD/THF gave the deuterated methyl ester **16**. Under identical conditions,

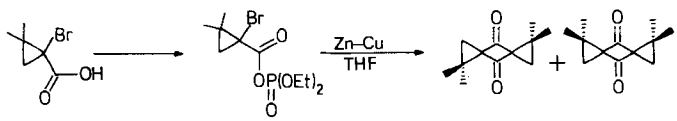
*Scheme 4*



but without Zn-Ag couple, **14** did not react with MeOD/THF. Therefore, we assume that ketene **15** is generated and then trapped by MeOD.

The successful preparation of crowded diketone **8** encouraged us to use α-bromoacyl phosphates as ketene precursors in other cases. For example [11], treatment of carboxylic acid **17** with $(EtO)_2POCl$ in the presence of $(i\text{-}Pr)_2EtN$ afforded the mixed anhydride **18** in a smooth reaction *(Scheme 5)*. Formation of the symmetric anhydride was suppressed by adding the mixture of α-bromocarboxylic acid **17** and $(i\text{-}Pr)_2EtN$ very slowly into a vigorously stirred suspension of $(EtO)_2POCl$ in THF. The formed $(i\text{-}Pr)_2EtN \cdot HCl$ was insoluble in THF and filtered off and the resulting solution used directly for the generation of ketene. The mixed anhydride **18** could also be characterized spectroscopically and isolated in satisfactory purity [7]. Zn-Ag couple induced dehalogenation of **18** gave mainly *'anti'*-**2b**; *'syn'*-**2b** was the minor isomer (*'anti'*/*'syn'* 9:1).

*Scheme 5*




**17** **18** *'anti'*-**2b** *'syn'*-**2b**

**3. Discussion.** – Considering $pK_a$ values of the leaving groups, the success of the acyl-phosphate method is surprising at first sight. Since HCl ($pK_a$ −7) is a much stronger acid than $H_3PO_4$ ($pK_a$ 2.15, first acidity constant), $Cl^-$ ion should be a much better leaving group than diethyl-phosphate ion $(EtO)_2PO_2^-$, consistent with the easy conversion of **4** into **5**. Furthermore, whereas in peptide chemistry the acyl-activated intermediate has the thermodynamic advantage of forming a strong amide bond, in the case at hand this is not so, and a highly strained ketene has to be formed first of all.

The quality of $(EtO)_2PO_2^-$ as a leaving group is probably improved by complexation with $ZnHal_2$, *i.e.* a *Lewis* acid which is generated *in situ*. Another factor likely to facilitate departure of $(EtO)_2PO_2^-$ is delocalization of negative charge over the anion on acyl-O bond breaking. This factor was previously encountered for *p*-toluenesulfonates 4-$MeC_6H_4SO_3R$, insofar as increasing C–X bond breaking in the transition favours *p*-toluenesulfonate ($TsO^-$) over $Br^-$ ion as a leaving group, *i.e.* the ratio of rate constants $k_{TsO}/k_{Br}$ is a criterion for the extent of C–X bond breaking in the transition state of nucleophilic substitution, becoming very large for ionic, $S_N1$-like transition states [12].

The ease and high yield (58%) in forming double propellane **8** from 1-bromocyclopropanecarboxylic acid **4** suggest that steric factors do neither impede the generation of ketene **7** nor affect the subsequent dimerization to **8**. In fact, relief of steric strain may actually facilitate generation of **7**, and it may also promote the reductive loss of the Br-atom on saponification (**9**→**10a**).

The sensitivity of the sandwiched dispiro-fused dione **8** to heating and $O_2$ is of interest. By comparison, the permethylated tricyclic dispiro[2.1.2.1]octane-4,8-dione **2a** is a very stable compound which survives vapourization on various GLC columns, although pentacyclic, doubly cyclohexane-fused dione **2c** tends to decompose on GLC. Apparently, there is *no steric stabilization* of **8** by screening of the 1,3-dicarbonyl grouping. On

the contrary, the stability of the dispiro[2.1.2.1]octane-4,8-dione system seems to be severely affected by the two propella[4.4.1]undeca-3,8-diene moieties. Presumably, additional strain is introduced by the four cyclohexenoid brackets in heptacyclic dione **8**.

The formation of ethyl ester **10b** on reaction of **8** with DDQ underlines the fragility of the 1,3-dicarbonyl grouping in **8**. However, it is not clear wether **8** is cleaved first and then dehydrogenated or *vice versa*.

**4. Conclusions.** – Dialkyl 1-bromocyclopropanecarbonyl phosphates are useful cyclopropylidenemethanone precursors. The mixed anhydrides can be isolated in principle, yet in the subsequent Zn-induced reduction, diethyl-phosphate ion is a sufficiently good leaving group which allows generating the ketene under mild conditions. Diethyl-phosphate ion is $H_2O$-soluble and can be removed easily on workup. Starting from the 1-bromocyclopropanecarboxylic acid, the yield of ketene dimer amounts to *ca.* 50%. The acyl chloride forming step which requires a distillation and tends to lower overall yields is circumvented. Thus, the preparation of sensitive ketene dimers such as **8** is also realizable.

We thank Dr. *K.L. Loening* for advice on nomenclature and the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of our work.

## Experimental Part

*1,1'',4,4'',5,5'',8,8''-Octahydrodispiro[[4a,8a]methanonaphthalene-9,1'-cyclobutane-3',9''-[4a,8a]methanonaphthalene]-2',4'-dione* (**8**). The 11-bromotricyclo[4.4.1.0$^{1,6}$]undecan-3,8-diene-11-carboxylic acid (**4**) [13] (0.54 g, 2 mmol) in abs. THF (5 ml) was added dropwise into an excess of LiH which had previously been washed with light petroleum ether. The formation of the lithium carboxylate was followed with a bubble counter and was complete after reaction overnight. The resulting suspension was syringed at 0° into a soln. of $(EtO)_2POCl$ (0.38 g, 2.2 mmol) in THF (5 ml) within 30 min. The resulting clear soln. was allowed to reach r.t. and was stirred for another 30 min. On addition of freshly prepared Zn-Ag couple [14] (400 mg, 6 mmol), the reaction started immediately and was over in 30 min. Less reactive Zn-Ag couple required brief refluxing. After being cooled to r.t., the mixture was filtered through a short column of silica gel and rinsed with $Et_2O$. After evaporation, chromatography ($Et_2O$/light petroleum ether 1:2) gave **8**, white crystals (200 mg, 58%). M.p. 165°, after recrystallization from EtOH under Ar. The compound could be stored for longer periods at −20°, but turned yellow on exposure to $O_2$. IR ($CCl_4$): 3030*m*, 2980*w*, 2900*m*, 2830*w*, 1720*vs*, 1430*m*, 1190*s*, 1135*s*, 660*s*. $^1$H-NMR ($CDCl_3$): 5.56 (br. *s*, 8 olef. H); 2.00–3.00 (*m* (sym.), 8 $CH_2$). $^{13}$C-NMR ($CDCl_3$; under Ar): 203.01 (C=O); 122.83 (olef. C); 68.03 (spiro C); 46.71 (cycloprop. C); 33.93 ($CH_2$). MS (70 eV, 110°): 344 (11, $M^+$); 290 (4); 214 (32); 186 (22); 172 (5); 131 (78); 130 (86); 129 (100); 115 (57); 91 (90). Anal. calc. for $C_{24}H_{24}O_2$ (344.4): C 83.69, H 7.02; found: C 82.59, H 7.06.

tert-*Butyl 11-Bromotricyclo[4.4.1.0$^{1,6}$]undecan-3,8-diene-11-carboxylate* (**11**). In a flame-dried, round-bottomed flask filled with Ar, **4** (1.08 g, 4 mmol) was supended in abs. toluene (5 ml) and heated to 100°. $Me_2NCH(t\text{-}BuO)_2$ (4 ml, 17 mmol) was added dropwise within 1 h. After stirring for 20 h at 100°, the mixture was treated with a further portion of $Me_2NCH(t\text{-}BuO)_2$ (0.4 ml, 1.7 mmol) and heated for 15 h at 100°. After cooling and addition of $Et_2O$ (30 ml), the mixture was washed with 15 ml of sat. $NaHCO_3$ soln. (3 ×), and polar impurities were removed by column filtration (basic $Al_2O_3$, act. I). After removal of the solvent, the residue was sublimated at 110°/0.05 Torr in a 'Kugelrohr' apparatus to give **11** (1.04 g, 80%). IR (KBr): 3030*w*, 2980*w*, 2900*w*, 2895*w*, 1718*s* (C=O), 1370*m*, 1265*m*, 1250*m*, 1240*m*, 1160*s*. $^1$H-NMR ($CDCl_3$): 5.54–5.63 (br. *t*, 2 olef. H); 5.39–5.51 (*m*, 2 olef H); 2.05–2.94 (br. *q*, 4 $CH_2$); 1.44 (*s*, $(CH_3)_3C$). $^{13}$C-NMR ($CDCl_3$): 166.69 (*s*, C=O); 123.93, 125.28 (2 *d*, olef. C); 80.97 (*s*, $(CH_3)_3C$); 48.68 (*s*, C(9), C(10)); 30.40, 31.23 (2 *t*, $CH_2$); 27.59 (*q*, $CH_3$); 23.68 (*s*, C(11)). MS: 270, 268 (20); 216, 214 (100); 189 (31); 170 (19); 143 (54); 128 (51); 57 (50). Anal. calc. for $C_{16}H_{21}BrO_2$ (325.3): C 59.09, H 6.51; found: C 59.17, H 6.51.

tert-*Butyl 11-Bromobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylate* (**12**). A soln. of 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ = dichlorodicyanobenzoquinone; 4 g, 17.6 mmol) and a drop of AcOH in abs. dioxane (10 ml) was heated to 90°. Ester **11** (1.75 g, 5.34 mmol) in dioxane (5 ml) was added

dropwise and the mixture stirred for 20 h at 90° and allowed to cool down. The precipitated hydroquinone was filtered off and washed with $CH_2Cl_2$ (3 × 50 ml). The combined org. phase was washed with sat. aq. $NaHCO_3$ (4 × 30 ml) and sat. NaCl soln., dried ($MgSO_4$), and evaporated to leave a semisolid mass which consisted of three substances. Chromatography over basic alumina (act. III, $Et_2O$/pentane) gave a mixture of two partially dehydrogenated *t*-Bu esters (280 mg, 16%) and **12** (685 mg, 40%). M.p. 120°. UV (MeOH): 255 (58), 290 (9), 385 (1). IR ($CHCl_3$): 2980*w*, 2940*w*, 1730*s* (C=O), 1370*m*, 1270*m*, 1255*m*, 1160*s*. $^1$H-NMR ($CDCl_3$): 7.03–7.26 (*m*, 4 H); 6.73–6.87 (*m*, 4 H); 1.28 (*s*, $(CH_3)_3C$). $^{13}$C-NMR ($CDCl_3$): 165.0 (*s*, C=O); 128.5 (*d*, C(2), C(5)); 127.1 (*d*, C(7), C(10)); 126.5 (*d*, C(3), C(4)); 124.5 (*d*, C(8), C(9)); 113.1 (*s*, C(1), C(6)); 81.6 (*s*, $(CH_3)_3C$); 62.7 (*s*, C(11)); 27.3 (*q*, $CH_3$). MS (50°): 322, 320 (0.2, $M^+$); 266, 264 (5); 248, 246 (3); 221, 219 (7); 186 (17); 185 (100); 141 (23); 140 (23); 139 (40); 128 (25); 115 (13); 57 (26). Anal. calc. for $C_{16}H_{17}BrO_2$ (321.2): C 59.83, H 5.33; found: C 59.33, H 5.36.

*11-Bromobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylic Acid* (**13**). Ester **12** (310 mg, 0.96 mmol) in $CH_2Cl_2$ (5 ml) was treated at 0° with $CF_3COOH$ (3 ml) in $CH_2Cl_2$ (2 ml). After 70 min, **12** had disappeared (TLC). The mixture was taken up in $CH_2Cl_2$ (15 ml), and the org. phase washed with $H_2O$ (5 × 10 ml) and sat. aq. NaCl soln. dried ($MgSO_4$), and evaporated: 235 mg (92%) of **13**. M.p. 156° (dec.). UV (MeOH): 255 (62), 285 (11), 388 (1). IR (KBr): 2930*m*, 1710*s* (C=O), 1245*m*, 975*m*. $^1$H-NMR ($(D_6)$DMSO): 11.10–12.60 (br., $CO_2H$); 7.17–7.49 (*m*, 4 H); 6.71–7.11 (*m*, 4 H). $^{13}$C-NMR ($(D_6)$DMSO): 166.8 (*s*, C=O); 128.5 (*d*, C(2), C(5)); 126.7 (*d*, C(7), C(10)); 126.5 (*d*, C(3), C(4)); 124.3 (*d*, C(8), C(9)); 113.1 (*s*, C(1), C(6)); 62.9 (*s*, C(11)). MS (110°): 266, 264 (1, $M^+$); 221, 219 (5); 185 (100); 157 (15); 155 (13); 140 (95); 128 (76); 115 (34). HR-MS: 185.0602 ($M^+$ – Br, calc. 185.0603).

*11-Bromobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carbonyl Diethyl Phosphate* (**14**). *Method A.* $(EtO)_2POCl$ (259 mg, 1.5 mmol) was dissolved in abs. THF (3 ml) in a flame-dried, Ar-filled flask. A mixture of **13** (398 mg, 1.5 mmol) and $(i\text{-}Pr)_2EtN$ (245 mg, 1.9 mmol) in abs. THF (5 ml) was added dropwise within 30 min at 0°. The mixture was stirred for 8 h at r.t., a solid being precipitated. After 10 h in a refrigerator, precipitation was complete. The solid was filtered off under inert gas and washed with abs. THF (2 ml), resulting in a soln. of **14** in 10 ml of THF (TLC showed only traces of **13**). This soln. (1 ml) was subjected to flash chromatography (FC) on silica gel (10 g) with $Et_2O$, giving **14** (29 mg, 48%) as a sensitive light yellow oil, besides **13** (11 mg, 28%). IR ($CHCl_3$): 3005*w*, 2930*m*, 2860*w*, 1775*m* (C=O), 1285*m* (P=O), 1170*m* (OEt), 1040*s* (P–O), 1000*m* (P–O), 950*m* (P–O). $^1$H-NMR ($CD_2Cl_2$): 7.03–7.41, 6.80–7.00 (2 *m*, 8 H); 4.17 (*q*, $J$ = 7, $CH_2$); 4.08 (*q*, $J$ = 7, $CH_2$); 1.34 (*t*, $J$ = 7, $CH_3$); 1.33 (*t*, $J$ = 7, $CH_3$). MS (80°): 321 (6, $M^+$ – Br); 293 (11); 265 (3); 248, 246 (6); 232 (4); 220, 218 (6); 185 (13); 141 (23); 140 (60); 139 (100); 128 (23); 115 (16).

*Method B.* A soln. of **13** (220 mg, 0.83 mmol) in abs. THF (5 ml) was added dropwise to LiH (8 mg, 1 mmol) under Ar. After the mixture had been stirred for 40 h at r.t., evolution of gas (bubble counter) had ceased. The resulting thick suspension of Li carboxylate was added dropwise, at 0° within 30 min, into $(EtO)_2POCl$ (143 mg, 0.83 mmol) in abs. THF (5 ml) under Ar. After being stirred for a further 30 min at 0° and then 30 min at r.t., the soln. showed traces of **13** only.

*Methyl [11-$^2$H]Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylate* (**16**). A soln. of **14** (0.14 mmol) in abs. THF (2 ml) was prepared *(Method A)* and MeOD (50 ml) added. After 1 h at r.t., no reaction was discernible. After Zn-Ag couple (100 mg) had been added, the educt disappeared after 5 min. FC (silica gel, $Et_2O$/pentane) gave, apart from some amide **10c** (2.2 mg, 3%), **16** (19.1 mg, 38%) as a major product. IR ($CHCl_3$): 3040*w*, 3020*w*, 2950*w*, 2920*w*, 2840*w*, 1730*s* (C=O), 1430*m*, 1250*m*, 1035*m*. UV (MeOH): 250 (100), 290 (18), 385 (1). $^1$H-NMR ($CDCl_3$): 7.38–7.55, 6.90–7.20 (each *m*, 8 H); 3.23 (*s*, $COOCH_3$); 0.46 (*s*, 0.2 H, nondeuterated ester). $^{13}$C-NMR ($CD_2Cl_2$): 167.5 (*s*, C=O); 129.6 (*d*, C(2), C(5)); 128.4 (*d*, C(7), C(10)); 126.6 (*d*, C(3), C(4)); 125.7 (*d*, C(8), C(9)); 115.9 (*s*, C(1), C(6)); 51.3 (*q*, $CH_3O$); 48.9 (*d* and *t*, (weak)). MS: 201 (6, $M^+$), 200 (2), 169 (6), 142 (100), 141 (42), 128 (14), 116 (36), 115 (36). HR-MS: 201.0899 ($M^+$, calc. 201.1281).

Alternatively, Zn-Ag couple (100 mg) was added to a soln. of **14** (0.25 mmol) in abs. THF (2 ml). After 10 min, **14** had disappeared. *Inter alia* **10a** and **10c** were discernible. After MeOD (50 µl) had been added and the mixture stirred for 1 h at r.t., **16** (3 mg, 6%) was identified.

*Oxidative Cleavage of Dione* **8** *to* **4**. A soln. of **8** (780 mg, 2.3 mmol; recrystallized from EtOH and dried at a vacuum pump) in dioxane (8 ml), was added dropwise into a soln. of DDQ (4.1 g, 18 mmol) and AcOH (100 µl) in dioxane (20 ml) and heated under reflux. After 2 h, **8** had disappeared to give polar substances and a nonpolar product. The precipitated hydroquinone was filtered off, and after chromatography (silica gel, $Et_2O$/pentane), *ethyl bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene-11-carboxylate* (**10b**; 35 mg, 7%) was isolated. UV (MeOH): 255 (126), 290 (16), 390 (1). IR ($CCl_4$): 3040*w*, 2960*w*, 2920*w*, 1740*m* (C=O), 1250*w*, 1220*m*. $^1$H-NMR ($CDCl_3$): 7.33–7.61 (*m*, 4 H); 6.88–7.17 (*m*, 4 H); 3.74 (*q*, $J$ = 7, $CH_2$); 1.03 (*t*, $J$ = 7, $CH_3$); 0.48 (*s*, CH). MS: 214 (3, $M^+$), 191 (2), 184 (2), 168 (3), 140 (100), 128 (13), 115 (38).

*1,1,6,6-Tetramethyldispiro[2.1.2.1]octane-4,8-dione* (**2**). According to *Method A* (see **14**), 1-bromo-2,2-dimethylcyclopropanecarboxylic acid (**17**) was converted into anhydride **18**. A flame-dried flask was charged with **18**

(2.97 g, 0.01 mol) in abs. THF (50 ml), Zn dust (0.03 mol), and CuCl (0.5 mg). The mixture was stirred for 20 h, diluted with $Et_2O$ (100 ml), and filtered. The filtrate was washed with $Et_2O$ and the org. phase washed with sat. aq. $NaHCO_3$ (100 ml) and dil. $H_2SO_4$ soln. (20 ml), dried ($MgSO_4$), and evaporated. Column chromatography gave *'anti'*-**2b** (475 mg, 49%) and *'syn'*-**2b** (43 mg, 9%). For the assignment of *'syn'*/*'anti'*, see [11].

*'anti'*-**2b**: IR ($CCl_4$): 1723*s*. $^1$H-NMR ($CDCl_3$): 1.93 (*s*, 2 $CH_2$); 1.42 (*s*, 4 $CH_3$). $^{13}$C-NMR ($CDCl_3$): 207.5 (*s*); 59.6 (*s*); 41.9 (*s*); 36.1 (*t*); 20.6 (*q*). MS: 192 (73, $M^+$), 178 (15), 177 (100), 175 (18), 149 (42), 135 (24). HR-MS: 192.1163 (calc. 192.1158).

*'syn'*-**2b**: $^1$H-NMR: identical with that of *'anti'*-**2b**. $^{13}$C-NMR: C=O not visible; 60.2 (*s*); 42.3 (*s*); 36.6 (*t*); 20.9 (*q*).

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