66. The Hydrolysis of Ethyl 1-Methyl-2,4-cyclopentadiene-1-carboxylate by Nonenzymatic and Enzymatic Methods. Carbon-Carbon *vs.* Carbon-Oxygen Bond Cleavage

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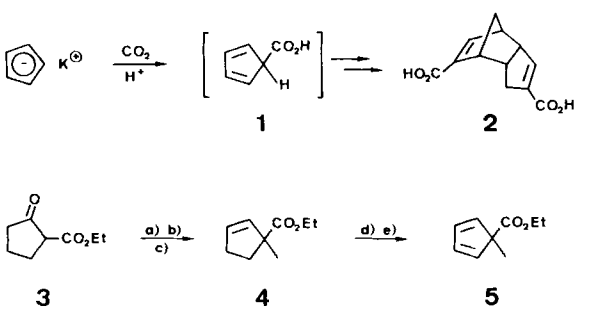
The title ester **5** is shown to undergo C–C bond cleavage under the conditions of basic ester hydrolysis (KOH/EtOH) with formation of potassium ethyl carbonate (**6**) and the tautomeric methylcyclopentadienes **7** and **8**. In contrast, porcine liver esterase (PLE, *EC 3.1.1.1*) cleanly hydrolyses **5** to give the isolable 1-methyl-2,4-cyclopentadiene-1-carboxylic acid (**13**). The latter undergoes thermal dimerization with conservation of the geminal-substitution pattern. The configuration of the *Diels-Alder* adduct **17** is ascertained by it photochemical transformation into bishomocubane dicarboxylic acid **12**, easily distinguished by its C_2 symmetry. Under the conditions of acid-catalyzed hydrolysis, dimerization of ester **5** and polymerization prevail, unless low acid concentration is used. The dimer **9** of **5** has one ester function that is reluctant to undergo basic hydrolysis.

Simple cyclopentadienecarboxylic acids are a relatively unknown class of compounds. The parent symmetric member **1** and tautomers of it, derived by 1,5-sigmatropic rearrangement [1], are likely to be intermediates in the formation of *Thiele*'s acid (**2**). The latter is obtained by reaction of potassium cyclopentadienide with CO_2, followed by acidic workup [2]. The correct structure of this dimer **2** was established only many decades after its first preparation [2c]. Fifteen years ago, a straightforward synthesis of a cyclopentadiene carboxylate, *viz.* the title ester **5**, was reported [3]. Introduction of a CH_3 group at C(1) was shown to protect this formal derivative of **1** reasonably well against both 1,5-sigmatropic rearrangement and dimerization. The synthesis, extended in our laboratory to other geminally disubstituted cyclopentadienes [4], starts from the commercially available β-keto ester **3**. The protecting CH_3 group and the first double bond are introduced in early steps. Allylic bromination of the ester **4** followed by elimination of HBr gives the fairly stable ester **5** (*Scheme 1*). To our knowledge, no attempt has been

Scheme 1



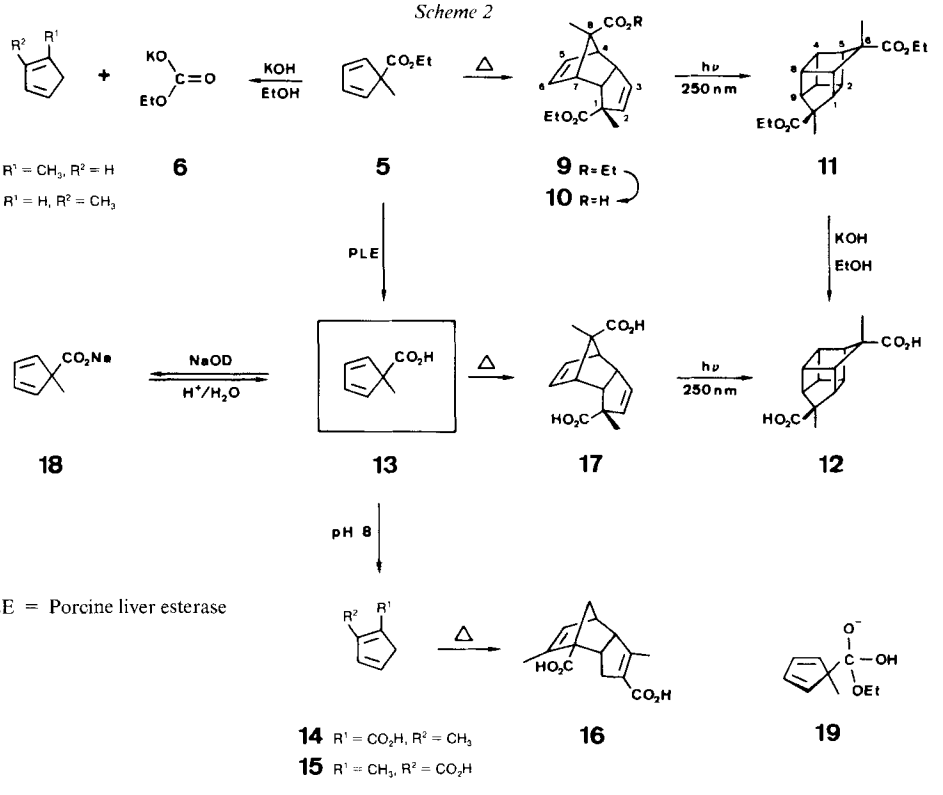
a) Na, CH_3I;
b) $NaBH_4$;
c) P_2O_5;
d) *N*-bromosuccinimide;
e) Al_2O_3; overall yield 23% [3].

made to transform this ester into the corresponding acid. The chances of obtaining by this route a stable cyclopentadienecarboxylic acid looked promising. In this communication we wish to report on our efforts to achieve this target.

Results. – When we attempted to saponify ester **5** with KOH/EtOH at 25°, we obtained potassium ethyl carbonate (**6**; 82%) and a mixture of the tautomeric methylcyclopentadienes **7** (36%) and **8** (41%; *Scheme 2*). The colorless monoester salt **6** which precipitates from the reaction mixture was unambiguously identified by comparison of its ^{1}H-NMR and ^{13}C-NMR spectra with those of a sample prepared by a known route [5]. The methylcyclopentadienes **7** and **8** were shown by GC and ^{1}H-NMR spectroscopy to be identical with authentic material obtained by cracking of the commercially available dimer. The use of LiOH or NaOH in EtOH did not alter the course of this reaction. Again, C–C bond cleavage was the overall outcome.

When acid-catalyzed hydrolysis of ester **5** was attempted (boiling in 2M aq. H_2SO_4), we obtained small amounts of the dimer **9** (8%) and an untreatable tar. The previously unknown *Diels-Alder* adduct **9** can, of course, be prepared more economically, in 85% yield, by heating of the neat ester **5** to 120° (*Scheme 2*). The ^{1}H-NMR spectrum of **9** immediately revealed that the geminal-substitution pattern of the starting material **5** was conserved in the dimer. The configuration at its quaternary centers C(1) and C(8) was first deduced from the lanthanide induced shift effects (LIS) of the ^{1}H-NMR signals. The configurational assignment found corroboration in the markedly different reactivities

Scheme 2



PLE = Porcine liver esterase

the two ester functions of **9** show towards KOH/EtOH. Whereas the ethoxycarbonyl group at C(8) was readily saponified, the ester function at C(1) of **9** was reluctant to do so. It survived boiling for 24 h in 3.5M KOH/EtOH. Acidic workup gave the monoacid **10** in 78% yield. Clearly, the remaining ester function of **10** is oriented towards the cavity of the tricyclic skeleton, and thereby efficiently protected against further attack.

The ultimate structural proof with respect to the relative configuration at the quaternary centers of dimer **9** was provided by a photochemical rearrangement (*cf.* [2c] [6]). Irradiation of **9** (250 nm, acetone) gave the symmetric bishomocubane derivative **11**, which belongs to point group C_2 and is chiral (*Scheme 2*). Consequently, the ^{1}H-NMR signals of the two ethoxycarbonyl groups appear as a single ABM_3 spin pattern of double intensity. Moreover, the two CH_3 groups of **11** are isochronous in both the ^{1}H-NMR and the ^{13}C-NMR spectrum.

For reasons we shall deal with below, the bishomocubane diester **11** was converted into the corresponding diacid **12**. Both ester functions of compound **11**, in contrast to those of its precursor **9**, are readily saponified with KOH/EtOH (*Scheme 2*).

At this stage of our study, it was obvious that the hydrolysis of ester **5** required either much milder conditions than those chosen so far, or an entirely different approach. Hence, we decided to investigate enzymatic methods [7]. Porcine liver esterase (PLE; *EC 3.1.1.1*), well known for its broad substrate tolerance [8], was chosen for that purpose.

A mixture of ester **5** and PLE in phosphate buffer solution was stirred at 25° and monitored at pH 8 by continuous titration with 1M NaOH. After 1 h, consumption of base had ceased and the mixture was worked up. ^{1}H-NMR spectroscopic examination revealed that the desired 1-methyl-2,4-cyclopentadiene-1-carboxylic acid (**13**) was formed as the main product. It was accompanied by small amounts of the short-living isomeric acids **14** and **15** (ratio **13**/**14**/**15** 22:2:1). Isolation of the target acid **13** was made easy by the fact that the equilibrating acids **14** and **15** precipitated at room temperature within 1 h by virtue of a dimerization reaction. We tentatively assign structure **16** to the ensuing diacid. Its ^{1}H-NMR spectrum ((D$_6$)DMSO) shows two CH_2 groups, a single olefinic proton, and three bridgehead H-atoms. Both CH_3 groups are vinylic and show the appropriate allylic and homoallylic scalar couplings, respectively. Decisive for our choice of structure **16** was a modest NOE enhancement (7%) observed for the olefinic proton upon spin saturation of the CH_3-C(3) resonance.

The principal product of enzymatic cleavage, *i.e.* acid **13**, was isolated in 66% yield by medium-pressure chromatography (silica gel, hexane/Et_2O 4:1) and fully characterized by standard spectroscopic methods. To our knowledge, it is the first example of the preparation of a simple cyclopentadienecarboxylic acid.

When we attempted to distil this acid at 100°/12 Torr, we obtained its dimer **17**. The configuration at the quaternary centers of this *Diels-Alder* product is analogous to that of the diester **9**. This was evident from the similarity of its ^{1}N-NMR spectrum with that of **9** and found confirmation in the photochemical transformation of **17** into a bishomocubane diacid, identical with compound **12** described above (*Scheme 2*).

The behavior of acid **13** when dissolved in basic media is complex. Preliminary studies show that the events are both solvent- and pH-dependent. Acid **13** undergoes slow rearrangement at pH 8 in a 0.1M phosphate buffer solution to give the isomeric acids **14** and **15** (*ca.* 50% conversion in 5 h at 25°). This finding clearly accounts for the formation of these two by-products during the PLE-promoted ester hydrolysis of **5**. Yet, acid **13**

forms a fairly stable salt **18** when dissolved in 0.5M $NaOD/D_2O$. Upon re-acidification after 5 h at 25°, the starting material **13** was recovered in 93% yield. In striking contrast, acid **13** when dissolved in 0.5M KOH/EtOH undergoes mainly decarboxylation and to a small extent (< 8%) rearrangement into the salts of acids **14** and **15.**

Acid **13**, moreover, was found to be reasonably stable at 25° in dioxane/0.5M aq. H_2SO_4 1:1. Recovery after 24 h was 89%. This finding encouraged us to re-examine the acid-catalyzed hydrolysis of ester **5** under these mild conditions. The ester is indeed cleaved to give acid **13**, the amount of undesired by-products being modest. However, the reaction is extremely slow, after 3 d, only half of the ester was consumed with *ca.* 45% of **13** being formed.

Discussion. – Normally, basic ester hydrolysis is a very simple transformation. Ethyl cyclopentadienecarboxylate **5** clearly is an exception as it undergoes C–C bond cleavage rather than the usual ethoxide release. It is likely that this breakdown occurs at the stage of the anionic intermediate **19** (see *Scheme 2*), which has two adjacent quaternary centers. Formation of an aromatic leaving group, *i.e.* methyl cyclopentadienide, and of potassium ethyl carbonate (**6**), can cooperate ideally with release of strain. Our findings suggest that intermediate **19** can be reached both from the ester **5** or upon dissolution of acid **13** in KOH/EtOH. It must be kept in mind, however, that potassium ethyl carbonate (**6**) is not necessarily a primary reaction product. Any source of CO_2 would give rise to its formation under the present reaction conditions. This ester salt could exert thermodynamic control over a reversible reaction step, simply by virtue of its insolubility in ethanolic medium. Nevertheless, support for the involvement of **19** as a key intermediate of the decarboxylation step is provided by the relatively high stability of carboxylate **18** in H_2O (pH 13.5). This salt does not decarboxylate nor does it rapidly isomerize.

The behavior of ester **5** in KOH/EtOH is reminiscent of the reversible addition of some allylic *Grignard* compounds to ketones [9] and of the thermal breakdown of homoallylic alcoholates [10]. In both cases, strain release and formation of anionic allylic leaving groups bring about a similar C–C bond rupture.

None of these difficulties and abnormalities are encountered when ester **5** is hydrolyzed by PLE. The ease with which the enzyme accepts and cleaves this achiral neopentyl-type ester is impressive. Clearly, whenever chemical methods fail or meet with difficulties, enzymatic methods should be exploited.

Finally, acid-catalyzed hydrolysis is feasible in principle, but within the admissible temperature and concentration range it can not compete in rate with the enzymatic procedure.

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Experimental Part

General. Photolyses: *Srinivasan-Griffin* reactor (*Rayonet-RPR-100*) with *RPR*-lamps 2537 Å; quartz vessels with internal H_2O cooling. GC: *Perkin-Elmer-900;* glass columns. IR spectral (cm^{-1}): *Perkin-Elmer IR-257.* UV spectra (λ[nm] (ε)): *Kontron Uvikon-820.* NMR spectra: *Bruker WM-360* (8.46 Tesla) or *Varian XL-200* (4.7 Tesla); chemical shifts in δ [ppm] relative to internal TMS, unless stated otherwise; apparent scalar coupling constants J in Hz; multiplicities for ^{13}C under off-resonance decoupling or according to attached proton test (APT). MS (*m/z* (% relative to base peak)): *Finnigan-4023* with *INCOS* data system; electron impact, 70 eV.

Basic Hydrolysis of **5**. Under N_2, 420 mg (2.76 mmol) of **5** [3] were dissolved in a soln. of 280 mg (5.0 mmol) of KOH in 5 ml of 95% EtOH and stirred for 10 h at 25°. A colorless precipitate was filtered, washed with ice-cold EtOH and dried *i.v.*: 289 mg (82%) of *potassium ethyl carbonate* (**6**), identical by ^{1}H-NMR (D_2O) and ^{13}C-NMR (D_2O) with an authentic sample [5]. The filtrate was pre-purified by flash distillation (25°/12 Torr). GC (*SE-30*, 5% on *Chromosorb-W*, 3 m, 50°; toluene as integration standard): one single peak for **7**/**8** (total yield 77%), of identical retention time with the one of the dedimerization product (200°) of commercial methylcyclopentadiene dimer (*Fluka*). An anal. sample of **7**/**8** was obtained by prep. GC (*SE-30, 5%* on *Chromosorb-W*). ^{1}H-NMR (360 MHz, $CDCl_3$): ratio **7**/**8** = 0.88.

*Diethyl 3a,4,7,7a-Tetrahydro-1,8-dimethyl-4,7-methano-1*H*-indene-1,4-dicarboxylate* (**9**). Neat **5** (2.43 g, 16 mmol) was heated under N_2 for 3 h to 120°. Medium-pressure chromatography (silica gel, hexane/Et_2O 4:1) gave **9** (2.07 g, 85%) as a colorless oil. UV (EtOH): 207 (700), 230 (sh). IR ($CHCl_3$): 2940 *m*, 1725 *s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.13 (*s*, 3 H); 1.23 (*s*, 3 H); 1.25 (*t*, *J* = 7.2, 3 H); 1.28 (*t*, *J* = 7.2, 3 H); 2.67 (*dd*, *J* = 8, 4, H–C(7a)); 2.88 (*m*, H–C(4)); 3.15 (*m*, H–C(7)); 3.52 (*m*, H–C(3a)); 4.05–4.25 (*m*, 2 *ABM*$_3$ type, 4 H); 5.35 (*dd*, *J* = 5.8, 2.1, H–C(3)); 5.62 (*m*, H–C(6)); 5.65 (*dd*, *J* = 5.8, 1.8, H–C(2)); 5.74 (*m*, H–C(5)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 14.06 (CH_3); 14.16 (CH_3); 18.0 (CH_3); 29.78 (CH_3); 51.17 (CH); 51.61 (CH); 51.72 (CH); 52.24 (CH); 55.78 (C); 60.05 (CH_2); 60.29 (CH_2); 69.40 (C); 129.5 (CH); 130.4 (CH); 134.2 (CH); 137.1 (CH); 176.1 (C); 176.3 (C). MS: 304 (18, $C_{18}H_{24}O_4$), 259 (7), 231 (16), 185 (16), 152 (100), 93 (49), 80 (46).

*1-Ethyl Hydrogen 3a,4,7,7a-Tetrahydro-1,8-dimethyl-4,7-methano-1*H*-indene-1,4-dicarboxylate* (**10**). Ester **9** (204 mg, 0.66 mmol) was dissolved in a soln. of 1.0 g (17.8 mmol) of KOH in 5 ml of 95% EtOH and heated under reflux for 10 h. After evaporation the mixture was hydrolyzed, washed once with Et_2O, and acidified at 0° with 2N HCl to pH 1. The product was exhaustively extracted with Et_2O, washed twice with brine, and dried ($MgSO_4$). Medium-pressure chromatography (silica gel, hexane/Et_2O 1:1) gave **10** (142 mg, 78%) as a colorless oil. IR ($CDCl_3$): 3500*w*, 2990*m*, 1726*s*, 1700*s*, 1240*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.20 (*s*, 3 H); 1.29 (*t*, *J* = 7.1, 3 H); 1.34 (*s*, 3 H); 2.73 (*dd*, *J* = 8, 4, H–C(7a)); 2.94 (*m*, 1 H); 3.26 (*m*, 1 H); 3.57 (*m*, H–C(3a)); 4.19 (*q*, *J* = 7.1, 2 H); 5.44 (*dd*, *J* = 6, 2, 1 H); 5.68 (*dd*, *J* = 6, 2, 1 H); 5.82 (*AB* with further fine structure, H–C(5), H–C(6)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 14.06 (CH_3); 18.0 (CH_3); 29.78 (CH_3); 51.23 (CH); 51.67 (CH); 51.71 (CH); 52.54 (CH); 55.75 (C); 60.15 (CH_2); 69.62 (C); 129.6 (CH); 131.0 (CH); 134,5 (CH); 136.4 (CH); 176.2 (C); 183.3 (C). MS: 276 (24, $C_{16}H_{20}O_4$), 230 (26), 203 (45), 152 (82), 124 (46), 106 (45), 93 (62), 80 (60), 79 (100).

Diethyl 6,10-Dimethylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dicarboxylate (**11**). A soln. of **9** (502 mg, 1.65 mmol) in 50 ml of acetone was deoxygenated with Ar and irradiated in a quartz vessel with internal H_2O cooling with light of wavelength 250 nm for 1.5 h. Evaporation of the solvent and medium-pressure chromatography (silica gel, hexane/Et_2O 6:1) gave **11** (447 mg, 89%) as a colorless oil. UV (EtOH): 215 (450). IR (CCl_4): 2990*s*, 1730*s*, 1260*s*, 1115*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.96 (*s*, 6 H); 1.25 (*t*, *J* = 7, 6 H); 2.54 (*m*, 2 H); 2.78 (*m*, 4 H); 2.96 (*m*, 2 H); 4.13 (*m* of *ABM*$_3$ type, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 14.15 (CH_3); 15.46 (CH_3); 37.01 (CH); 43.27 (CH); 45.60 (CH); 53.95 (CH); 59.96 (CH_2); 60.34 (C); 176.0 (C): MS: 304 (7, $C_{18}H_{24}O_4$), 231 (50), 185 (35), 157 (50), 152 (100), 93 (50), 80 (58).

6,10-Dimethyl-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dicarboxylic Acid (**12**). A soln. of **11** (202 mg, 0.66 mmol) in a soln. of 200 mg (3.6 mmol) of KOH in 5 ml of 95% EtOH was heated to reflux for 10 h. After evaporation, the crude salt was dissolved in H_2O and washed once with Et_2O. The aq. phase was acidified under ice cooling with 2M HCl to pH 1 and extracted exhaustively with Et_2O. The combined Et_2O extracts were washed twice with brine and dried ($MgSO_4$). Evaporation gave **12** (128 mg, 78%) as colorless prisms of m.p. 280° (dec.). IR (KBr): 3450*s* (br.), 2990*s* (br.), 1700*s*, 1470*m*, 1410*m*, 1280*s*. ^{1}H-NMR (360 MHz, CD_3OD): 0.96 (*s*, 6 H); 2.57 (*m*, 2 H); 2.75 (*m*, 4 H); 2.95 (*m*, 2 H). ^{13}C-NMR (50.3 MHz, CD_3OD): 15.93 (CH_3); 38.17 (CH); 44.53 (CH); 46.90 (CH); 55,25 (CH); 61.52 (C); 180.0 (C). MS: 202 (5, $C_{14}H_{16}O_4$), 157 (11), 142 (10), 125 (55), 124 (100), 96 (30), 79 (80). Anal. calc. for $C_{14}H_{16}O_4$ (248.27): C 67.72, H 6.50; found: C 67.69, H 6.48.

1-Methyl-2,4-cyclopentadiene-1-carboxylic Acid (**13**) *from* **5** *by Enzymatic Cleavage*. A beaker was charged at 25° with 40 ml of 0.1M phosphate buffer (pH 8.0), 0.5 ml of a commercial suspension of PLE (5 mg; *ca.* 650 U relative to ethyl butyrate as standard) in 3.2M $(NH_4)_2SO_4$ (*Fluka*), and 1.25 g (8.2 mmol) of **5** [3]. The (dropping) pH was kept at 8 by continuous titration with 1M NaOH (pH electrode *Ingold*) under stirring. The reaction was virtually complete after 1 h and comsumption of 7.7 ml of 1M NaOH (0.94 equiv.). The mixture was washed with 25 ml of Et_2O and then acidified with 2M HCl to pH 3: The products were exhaustively extracted with Et_2O, washed twice with brine, and dried ($MgSO_4$). Removal of the Et_2O left a colorless oil (856 mg) consisting by ^{1}H-NMR ($CDCl_3$) of **13** (88%), **14** (8%), and **15** (4%). When a soln. of this oil in $CHCl_3$ was allowed to stand for 1 h at 25°, colorless crystalline **16** (82 mg, 8% based on **5**) precipitated. Filtration gave a $CHCl_3$ soln. of **13** of > 95% purity. Medium-pressure chromatography (silica gel, hexane/Et_2O 4:1) yielded **13** (678 mg, 66%) as a colorless oil. IR (CCl_4): 3530w, 3080*s* (br.), 2990*s* (br.), 1705*s*, 1460*w*, 1410*m*, 1280*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.50 (*s*, 3 H);

6.41 (narrow *AA'BB'*, 4 H); 9.8 (br. *s*, 1 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.9 (CH_3); 62.0 (C); 131.6 (CH); 140.0 (CH); 179.3 (C). MS: 124 (43, $C_7H_8O_2$), 96 (15), 81 (100), 79 (92), 77 (48).

2-Methyl-1,3-cyclopentadiene-1-carboxylic Acid (**14**; transient species recorded in presence of **13** and **15**): ^{1}H-NMR (360 MHz, $CDCl_3$): 2.40 ('*t*', *J* = 2.4, 3 H); 3.36 (*m*, 2 H); 6.48 (*dt*, *J* = 5.1, 1.6, 1 H); 6.67 (br. *dt*, *J* = 5.1, 1.6).

2-Methyl-1,4-cyclopentadiene-1-carboxylic Acid (**15**; transient species recorded in presence of **13** and **14**): ^{1}H-NMR (360 MHz, $CDCl_3$): 2.42 (*s*, 3 H); 3.18 ('*t*', *J* = 1.5, 2 H); 6.20 (*dt*, *J* = 5.5, 1.5, 1 H); 6.71 (*dt*, *J* = 5.5, 1.5, 1 H).

*3a,4,7,7a-Tetrahydro-3,6-dimethyl-4,7-methano-1*H*-indene-2,7-dicarboxylic Acid* (**16**). M.p. 207–209° (dec.). IR (KBr): 3420 (br.), 2950*m*, 2930*m*, 1700*s*, 1680*s*, 1635*s*, 1300*m*, 1265*m*. ^{1}H-NMR (360 MHz, (D_6)DMSO; (D_5)DMSO at 2.51 ppm as secondary ref.): 1.59 (*d*, *J* = 8.0, H–C(8)); 1.66 (*d*, *J* = 1.6, CH_3–C(6)); 1.71 (*d*, br. *J* = 8.0, H–C(8)); 1.85 (br. *d*, *J* = 17, H–C(1)); 1.96 (br. *s*, CH_3–C(3)); 2.32 (*ddm*, *J* = 17, 9.6, couples with CH_3–C(3), H'–C(1)); 2.8 (*m*, H–C(4), H–C(7a)); 3.61 (br. *d*, *J* = 8.1, H–C(3a)); 5.72 (*m*, H–C(5)); 12.2 (br. *s*, 2 H). ^{13}C–NMR (50.3 MHz, (D_6) DMSO): 15.48 (CH_3); 15.62 (CH_3); 34.89 (CH_2); 40.39 (CH); 44.84 (CH); 54.83 (CH_2); 62.08 (CH); 63.54 (C); 127.97 (CH); 129.60 (C); 142.8 (C); 152.46 (C); 166.62 (C); 174.65 (C). MS: no $M^{+\cdot}$ ($C_{14}H_{16}O_4$) at 248, 230 (3), 124 (35), 96 (14), 79 (100).

*3a,4,7,7a-Tetrahydro-1,8-dimethyl-4,7-methano-1*H*-indene-1,4-dicarboxylic Acid* (**17**). Neat **13** (200 mg, 0.16 mmol) was heated under Ar for 3 h to 100°. The viscous mixture was dissolved in 3 ml of $CHCl_3$ and kept for 3 d in the refrigerator (5°), whereupon **17** had precipitated as colorless cubic crystals of m.p. 220–221° (dec.): 112 mg, 56%. From the mother liquor, 48 mg (24%) of unreacted **13** were recovered. **17:** UV (EtOH): 215 (440). IR (KBr): 3500*m* (br.), 3080*s* (br.), 3000*s* (br.), 1700*s*, 1450*m*, 1410*m*, 1280*s*, 1250*s*. ^{1}H-NMR (360 MHz, CD_3OD): 1.19 (*s*, 3 H); 1.25 (*s*, 3 H); 2.78 (*dd*, *J* = 8, 4, 1 H); 2.84 (*m*, 1 H); 3.16 (*m*, 1 H); 3.62 (*m*, 1 H); 5.37 (*dd*, *J* = 5.5, 2, 1 H); 5.62 (*dd*, *J* = 5.5, 2, 1 H); 5.64 (*m*, 2 H). ^{13}C-NMR (50.3 MHz, CD_3OD): 18.57 (CH_3); 30.37 (CH_3); 52.55 (CH); 52.94 (CH); 53.0 (CH); 53.99 (CH); 56.85 (C); 70.68 (C); 130.76 (CH); 132.28 (CH); 135.14 (CH); 138.29 (CH); 180.16 (C); 180.44 (C). MS: 248 (13, $C_{14}H_{16}O_4$), 230 (15), 202 (4), 124 (83), 96 (48), 79 (100), 57 (56).

12 *from* **17**. A soln. of **17** (45 mg, 0.18 mmol) in 10 ml of acetone was deoxygenated with Ar and irradiated in a quartz vessel with internal H_2O cooling with light of wavelength 250 nm for 2 h. Removal of the solvent gave **12** in practically quant. yield, identical by ^{1}H-NMR and IR with the material obtained from **11**.

Sodium 1-Methyl-2,4-cyclopentadiene-1-carboxylate (**18**) *from* **13**. Acid **13** (20 mg, 0.16 mmol) was dissolved in 2 ml of 0.5M NaOD in D_2O, prepared from Na_2O/D_2O. One quarter of this soln. was analyzed by ^{1}H-NMR (360 MHz): **18** (HDO at 4.6 ppm as secondary reference): 1.10 (*s*, 3 H); 6.05 (*AA'BB'*, 2 H); 6.15 (*AA'BB'*, 2 H). The spectrum remained virtually unchanged over 5 h at 25°. Only after 24 h had partial decomposition to yet unknown products occurred.

The remaining ¾ of the soln. of **18** was kept for a total of 5 h at 25° and then acidified under ice cooling with 2M HCl to pH 2. Extraction with Et_2O followed by workup as described above gave 14 mg (93%) of **13**. Contamination with rearrangement or dimerization products was less than 4% by ^{1}H-NMR (360 MHz).

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