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Preparation and Cyclopropanation of Selected Oxapolycycles

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Abstract: The Diels-Alder reaction of dimethyl furandicarboxylate **6** with DMAD is investigated and the *exo-exo* bisadduct **8** is fully characterized. Monoadduct **7**, **8**, and test system **12** are cyclopropanated with diazomethane giving **10**, **11**, and **14**. Then **7**, **8**, and **12** are treated with the "latently acceptor substituted" diazomethane **17**. After appropriate transformations cyanocyclopropyl derivatives **18** and **19** are obtained from **7** and **12**. Unexpectedly, **8** also gives **19** by a retro-Diels-Alder reaction thereby frustrating planned further work.

Keywords: Furans, Diels-Alder reactions, Cycloadditions, Cyclopropanation

Oxapolycyclic systems derived from furan are potential precursors of polyfunctional *cis* substituted decalins. These are of interest to us in search for new paths towards certain highly symmetric polycyclic hydrocarbons *via* ring enlargement to bicyclo[5.5.0]dodecanes and further conversions. We report here on the synthesis and reactivity of some new members of this class of compounds.

[4 + 2] cycloadditions of reactive dienophiles with a large variety of furans have been the topic of numerous publications ever since the pioneering work of Diels and Alder, [1] and the monoadducts obtained are useful synthetic intermediates. [2] Application of acetylenic dienophiles in particular allows for one or two consecutive Diels-Alder reactions depending on reaction conditions and stochiometries of the starting materials as at least one of the double bonds in the monoadduct **1** is activated for a second attack (Scheme 1).

* e-mail: dehmlow@post.uni-bielefeld.de; # X-ray structural analysis

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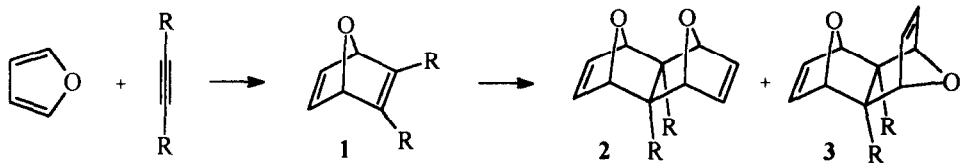
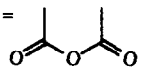
PII: S0040-4020(99)00824-8

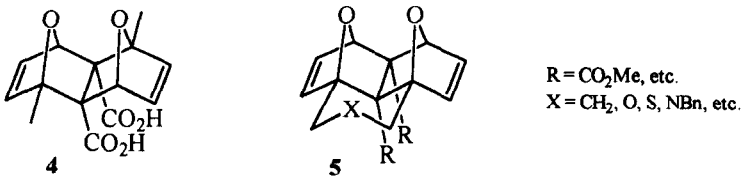


2a R = CO_2Me; **2b** R = CO_2H; **2c** R = COCl; **2d** R = CHO; **2e** R =



Scheme 1.

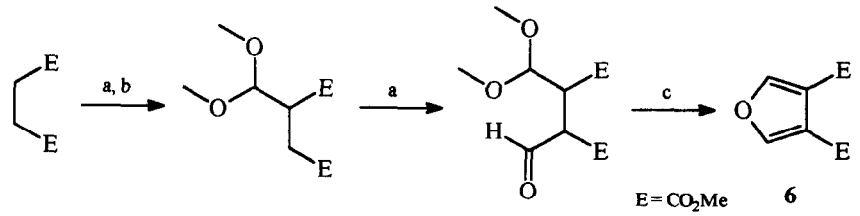
In this connection the preferential synthesis of bisadducts **2** is of special interest because the actual composition of reaction mixtures depends strongly on the thermodynamic and kinetic stabilities of the various species involved in the process. Extensive informations are available, for instance, for the conversion between furan and dimethyl acetylenedicarboxylate (DMAD) in which case a multitude of products are found under various modes of reaction. [3] Whereas compounds **2a** - **2e** [3-7] have been known for some time, much less is found in the literature on higher substituted cycloadducts of this type. Lautens reports on preparation and derivatization of the dicarboxylic acid **4** [8,9] and on several compounds having substitution patterns as indicated in **5** [10] (Figure 1).



R = CO_2Me, etc.
X = CH_2, O, S, NBn, etc.

Figure 1.

The present work concentrates mainly on oxapolycycles derived from dimethyl furan-3,4-dicarboxylate **6**. This compound can be prepared from dimethyl succinate by the shown sequence in four steps with an over-all yield of 40 %. The synthesis was modified after a scheme originally devised by Kornfeld (Scheme 2). [11]

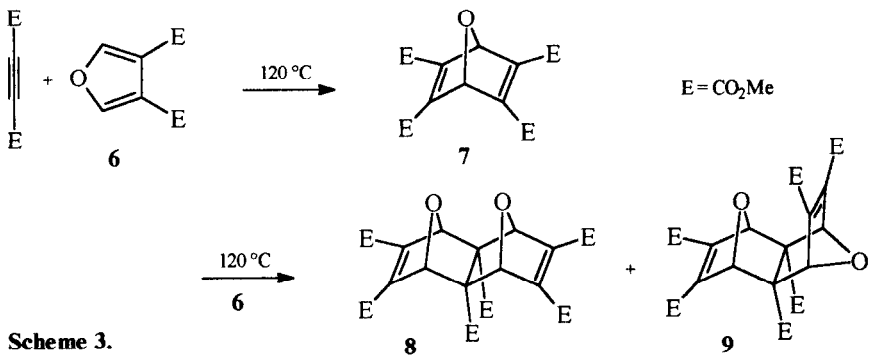


a) NaH, THF, HCO_2Me; b) MeOH, TosOH, $HC(OMe)_3$; c) konz. H_2SO_4

Scheme 2.

To the best of our knowledge only very few [4 + 2] cycloadditions of furan-3,4-dicarboxylates with dienophiles are known. These happen to be acetylenic compounds, to be sure: DMAD [12], cyclooctyne [13], arynes [14], and some perfluorated building blocks [15].

When equimolar amounts of **6** and DMAD are heated tetraester **7** is formed in very good yield indeed. Use of an excess of the diene, however, results in further reaction of **7** with **6**, and certain concentrations of the bisadducts **8** and **9** are formed in a domino fashion (Scheme 3).

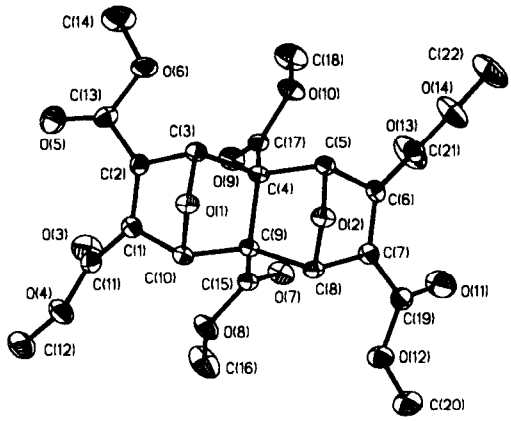


Scheme 3.

For convenience it is best to use a two-step procedure and isolate monoadduct **7** first. This is converted subsequently with a second equivalent of **6**. After about 3h at 120 °C an equilibrium is established within the system, and (according to ^{1}H NMR) the bisadducts **8** and **9** are present at concentrations of ca. 20 % each. Less symmetric *exo-endo* compound **9** is the kinetic product obviously: it is found at constant concentration from a few minutes after starting the reaction. In contrast, the percentage of **8** increases slowly towards the equilibrium level of 20 %. The formation of higher molecular cycloadducts was never observed under any conditions.

Thermodynamically more stable isomer **8** can be crystallized from the reaction mixture selectively, and **8** is obtained as a complex (2:1) with co-crystallized chloroform. This $CHCl_3$ complex formation is probably the very reason, why it is possible to separate **8** from the mixture in this way. After concentration the combined residual liquors can be added to the next run, because the same equilibrium as described above is reached again. As **9** easily undergoes retro-Diels-Alder reaction it was never isolated in substance but was characterized spectrally as a component in the four compound mixture.

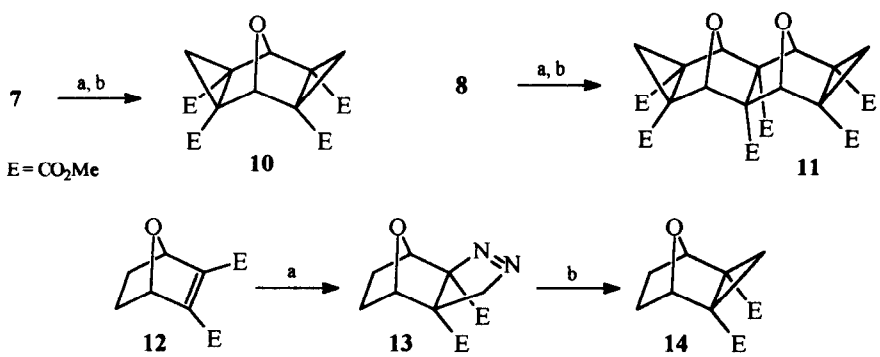
The *exo-exo* stereochemistry of highly symmetrical **8** is apparent from spectroscopy (only 2 methyl ester signals for instance). It was further verified by an X-ray structural analysis [16] (Figure 2), which is distorted partially because of the chloroform in the crystal at three concrete, but different positions.



ORTEP-view of compound **8**

Figure 2.

We wanted to investigate the synthetic potential of **8** more closely towards an eventual formation of a bicyclo[5.5.0]dodecane system over several steps. Martin had biscyclopropanated **7** to **10** by reacting it with an excess of diazomethane and photolyzing the product formed. [17] When **8** was treated similarly, a primary colorless solid had already separated after a few minutes. This was UV irradiated in ethyl acetate to give compound **11** in excellent yield over two steps (Scheme 4).

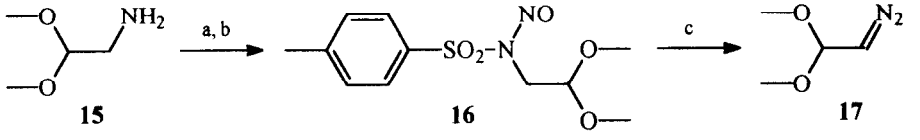


a) excess CH_2N_2; b) hν, EtOAc

Scheme 4.

For comparison purposes compound **12** [18] was transformed likewise into **13** [19] and eventually into **14**. A remarkable differentiation of the ^1H NMR resonances of the cyclopropane CH_2 was observed: whereas the chemical shifts are very similar in **14** they vary more and more when going to **10** and finally to **11**. This may be the result of increasing strain exercised by the ester groups on the underside of the molecule.

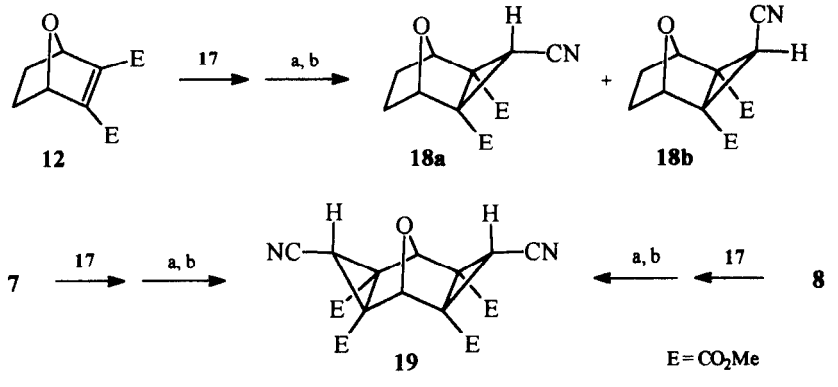
Our planned further reactions call for the introduction of substituents on the cyclopropane units, but we were unable to halocyclopropanate **7**, **8**, or **12**, and diazoacetic esters were unsuitable. Therefore, we used a "latently acceptor substituted" diazomethane carrying an acetal group (compound **17** [20]), which behaves chemically as a simple substituted diazomethane. **17** is related to the respective diethyl and dioxolane derivative originally introduced by Kirmse [21]. In this paper we present an improved and easier synthesis of **17**, which avoids work with N_2O_4 and uses commercially available **15**. This is transformed in two steps into the *N*-nitroso-tosylamide **16**, which in turn is converted into **17** (with KOH/aqueous methanol). **17** is extracted into ether and the etheral solution is used directly for the cycloadditions (Scheme 5).



a) TosCl, NEt_3; b) $NaNO_2$, HOAc, Ac_2O; c) KOH, MeOH, H_2O

Scheme 5.

The raw products formed from **17** with **7**, **8**, and **12** were purified neither before nor after photolysis, but were rather transformed directly into nitriles by Beckmann fragmentation. For this purpose they were treated with hydroxylamine hydrochloride in formic acid (Scheme 6). [22]



a) hv, EtOAc; b) $H_2NOH{\cdot}HCl$, HCO_2H

Scheme 6.

In this way, **12** led to a 6 : 4 mixture of the two possible isomers **18a** and **18b** whereas **7** gave only 1 of the maximally possible 3 isomers. The structure of **18a** was established by ^{1}H NMR, as the cyclopropyl hydrogen (resonance at 2.71 ppm) appears at lower field then the corresponding H atom in the isomer **18b** does (resonance at 2.56 ppm). This effect is attributed to deshielding by the O-bridge. [23 - 25] As the two cyclopropyl hydrogens in **19** appear at 2.72 ppm, it seems quite obvious, that the compound shows the given configuration. It is likely that this is the thermodynamically most stable isomer.

To our surprise and disappointment, the same reaction of **8** did not lead to the respective product. Instead **19** was obtained here as well. Obviously the first 1,3-dipolar addition increases strain in the molecule to such an extent that a retro-Diels-Alder reaction is preferred, and only the newly formed polycycle is able then to react with the excess of the 1,3-dipole. This unexpected result thwarts our further attempts to synthesize specific substituted bicyclo[5.5.0]dodecanes unfortunately.

Experimental Section

General Procedures: Melting points were determined using a Büchi 510 melting point apparatus and are uncorrected. - ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 250-P spectrometer operating at 250 MHz for ^{1}H and at 62 MHz for ^{13}C. Chemical shifts are in ppm relative to TMS as internal standard. - Infrared spectra were recorded on a Mattson Model Genesis FT-IR. - Elemental analyses were performed on a Leco Model CHNS-932. - Mass spectra were recorded on a Fisons Instruments VG AutoSpec with methane as ionization gas. - Dimethyl furan-3,4-dicarboxylate **6** was prepared under standard conditions using the system NaH/THF/HCO_2Me as described in Scheme 2. Compounds **7** [12] and **12** [18] were prepared according to literature procedures. Aminoacetaldehyde dimethylacetale **15** is commercially available.

Hexamethyl exo,exo-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-diene-2,4,5,7,9,10-hexacarboxylate (**8**).

A mixture of 9.21 g (50 mmol) of dimethyl furan-3,4-dicarboxylate **6** and 16.3 g (50 mmol) of tetramethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate **7** was heated at 120 °C for 3h. After cooling, the resultant oil was taken up in $CHCl_3$ (100 ml) and hexane was added to the solution with occasional stirring until tiny colorless crystals separate (180 ml). Then another 20 ml of hexane were added and after 1h at rt the suspension was filtered with suction. The solid was washed twice with 50 ml of $CHCl_3$/hexane (1/3) and recrystallized as described above (18 % yield in each run). All residual liquors were combined and concentrated and the residue was used for another cycloaddition, over-all yield in 10 consecutive runs 22.9 g

(40.1 mmol, 80 %) of **8**; mp 180 °C. - ^{1}H NMR ($CDCl_3$): δ = 3.56 (s, 6H), 3.82 (s, 12H), 5.44 (s, 4H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 52.43, 68.55, 86.04, 146.71, 162.06, 167.93 ppm. - IR (KBr): ν = 3035, 2958, 2846, 1751, 1727, 1434, 1326, 1230, 1130, 948 cm^{-1}. - MS (CI) m/z (%): 511 (1), 449 (2), 327 (12), 295 (53), 267 (17), 185 (16), 153 (100), 94 (15). - Analysis for $C_{22}H_{22}O_{14}$ + 1/2 $CHCl_3$ ($C_{45}H_{45}O_{28}Cl_3$) requires C 47.40 H 3.98, found C 47.50 H 3.91.

Crystals for X-ray analysis were obtained by diffusion crystallisation (chloroform/hexane). Diffractometer used: Siemens P2(1); programs used: Siemens SHELXTL plus / SHELXL-97. Crystal Data for **8**: FW 570.08; crystal size 0.90 x 0.60 x 0.33 mm; space group $P2_1/n$; unit cell dimensions: a = 12.440(3) Å, b = 9.575(2) Å, c = 21.026(4) Å, β = 97.10(2)°; volume 2485.3(9) Å^3; D_{calc} = 1.524 Mg/m^3; F(000) = 1180; absorption coefficient 0.281 mm^{-1}; 2θ-range: 3° – 60°; reflections collected 7511; independent reflections 7209 (R_{int} = 0.0429); R indices (all data) R1 = 0.0955, wR2 = 0.1762.

Hexamethyl exo,exo-13,14-dioxahexacyclo[9.1.0.1^{2,10}.1^{4,8}.0^{3,9}.0^{5,7}]tetradecane-hexakis-anti-1,3,5,7,9,11-hexacarboxylate (**11**).

A solution of 150 mmol diazomethane in 500 ml of diethyl ether was added to 500 ml of dichloromethane at 0 °C. Under stirring, a solution of **8** (15.3 g, 30 mmol) in 500 ml of CH_2Cl_2 was added. After a few minutes a colorless solid separates and the reaction mixture was allowed to warm to rt for 15h. Excess diazomethane was destroyed by the addition of a few ml of HOAc and the suspension was filtered with suction to give 17.1 g (28.8 mmol, 96 %) of crude adduct; mp 250 °C (decomp.). - IR (KBr): ν = 3014, 2956, 1778, 1733, 1577, 1440, 1315, 1276, 1234 cm^{-1}. - Analysis for $C_{24}H_{26}N_4O_{14}$ requires C 48.49, H 4.41, N 9.42, found C 48.29, H 4.23, N 9.09. The material was subjected to photolysis without purification in 2000 ml of EtOAc at 0 °C (Philips HPK 125 W, quartz filter) by adding the solid within 4h in small portions. After another h the reaction mixture was concentrated and the residue was taken up in diethyl ether (100 ml). The colorless solid was separated to give 14.9 g (27.7 mmol, 96 %) of **11**; mp 274 °C (decomp.). - ^{1}H NMR ($CDCl_3$): δ = 1.18 (d, J = 4.3 Hz, 2H), 1.75 (d, J = 4.3 Hz, 2H), 3.57 (s, 6H), 3.70 (s, 12H), 4.77 (s, 4H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 16.52, 35.80, 51.47, 52.12, 67.08, 84.56, 167.40, 167.94 ppm. - IR (KBr): ν = 3010, 2958, 1722, 1438, 1363, 1240, 1143, 979 cm^{-1}. - MS (CI) m/z (%): 540 (8), 508 (25), 507 (100), 229 (21), 197 (10). - Analysis for $C_{24}H_{26}O_{14}$ requires C 53.53, H 4.87, found C 53.38, H 4.79.

Dimethyl 3,4-diaza-10-oxatricyclo[5.2.1.$0^{2,6}$]dec-3-ene-bis-anti-2,6-dicarboxylate (**13**). [19]

To a solution of about 90 mmol diazomethane in 270 ml of diethyl ether 8.49 g (40 mmol) of dimethyl 7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate **12** in ether (100 ml) were added with stirring. After warming to rt for 15h, the excess diazomethane was destroyed with HOAc and the solvent was evaporated. The solid residue was recrystallized from ethyl acetate to give 8.54 g (33.6 mmol, 84 %) of **13**; mp 112 °C. - ^{1}H NMR ($CDCl_3$): δ = 1.79 (m, 2H,), 2.12 (m, 1H), 2.29 (m, 1H), 3.67 (s, 3H), 3.78 (s, 3H), 4.41 (d, J = 4.9 Hz, 1H), 4.69 (d, J = 18.5 Hz, 1H), 4.87 (d, J = 5.2 Hz, 1H), 5.10 (d, J = 18.5 Hz, 1H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 25.27, 26.00, 52.47, 52.79, 58.79, 82.07, 85.33, 88.74, 108.86, 166.46, 170.19 ppm. - IR (KBr): ν = 3018, 2983, 2956, 1733, 1567, 1438, 1288, 1203, 1110, 1010 cm^{-1}. - MS (CI) m/z (%): 255 (59), 223 (52), 195 (100), 166 (76), 135 (89), 107 (50), 79 (57). - Analysis for $C_{11}H_{14}N_2O_5$ requires C 51.97, H 5.55, N 11.02, found C 51.92, H 5.60, N 11.03.

Dimethyl 8-oxatricyclo[3.2.1.$0^{2,4}$]octane-bis-anti-2,4-dicarboxylate (**14**).

Photolysis (as above [*cf.* **11**]) of **13** (8.0 g, 31.5 mmol) at 0 °C for 4h in 2000 ml of ethyl acetate affords after Kugelrohr destillation 5.95 g (26.3 mmol, 83 %) of **14** as a colorless oil; bp 110 °C at 0.1 mbar. - ^{1}H NMR ($CDCl_3$): δ = 1.56 (d, J = 4.6 Hz, 1H), 1.62 (d, J = 4.6 Hz, 1H), 1.75 (m, 2H), 2.24 (m, 2H), 3.70 (s, 6H), 4.52 (m, 2H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 13.92, 27.41, 37.65, 52.07, 77.61, 169.63 ppm. - IR (neat): ν = 2991, 2956, 1727, 1440, 1361, 1265, 1153, 1112, 921 cm^{-1}. - MS (CI) m/z (%): 227 (45), 195 (100), 165 (13), 138 (15), 107 (10), 79 (10). - Analysis for $C_{11}H_{14}O_5$ requires C 58.40, H 6.24, found C 58.10, H 6.41.

N-(2,2-Dimethoxy-ethyl)-N-nitroso-4-tosylamide (**16**).

For the preparation of the tosylamide 104.8 g (550 mmol) of tosyl chloride were suspended in 500 ml of dry diethyl ether. Without cooling, a mixture of triethylamine (76 ml, 550 mmol) and aminoacetaldehyde dimethyl-acetale **15** (52.6 g, 500 mmol) was added as to keep a gentle reflux. After stirring 15h at rt, the triethylamine hydrochloride was removed by washing with saturated $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4 and filtered. Finally the solvent was removed to give a nearly quantitative yield of the corresponding tosylamide as a yellow oil. Without purification, this crude product was taken up in 500 ml of dry diethyl ether and treated with 200 ml of HOAc and 200 ml of Ac_2O. 69.0 g (1.0 mol) $NaNO_2$ were added under stirring at 0 °C in one portion. The reaction was completed by stirring for another 2h at 0 °C and 15h at rt. For workup, the reaction mixture was added cautiously to 500 ml of a saturated solution of $NaHCO_3$ in water. Additional solid $NaHCO_3$ was added until CO_2 evolution ended. Then the ether phase was separated and the remaining

suspension was extracted thoroughly with diethyl ether. The combined organic extracts were washed with $NaHCO_3$ solution and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure at rt until an oil began to separate. The remaining solution (about 250 ml) was kept at 0 °C for several hours, and when crystals appeared 200 ml of hexane were added. The pale yellow solid was isolated and dried *in vacuo* to give 116.2 g (403 mmol, 81 %) of **16**; mp 45 °C. - ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3H), 3.24 (s, 6H), 3.90 (d, J = 5.5 Hz, 2H), 4.36 (t, J = 5.5 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 21.69, 43.94, 54.34, 100.23, 128.42, 130.03, 135.04, 145.97 ppm. - IR (KBr): ν = 2996, 2962, 2935, 2834, 1592, 1523, 1376, 1299, 1191, 1157, 1122, 1060, 921 cm^{-1}. - Analysis for $C_{11}H_{16}N_2O_5S$ requires C 45.82, H 5.59, N 9.72, found C 45.84, H 5.78, N 9.71.

2,2-Dimethoxydiazoethane (**17**).

15.2 g (270 mmol) of KOH were dissolved in a mixture of methanol (100 ml), water (50 ml) and diethyl ether (20 ml) and with vigorous stirring at 0 °C, 25.9 g (90 mmol) of **16** were added in small portions over 15min. After 2h at that temperature, 50 ml of 2N KOH solution and 50 ml of diethyl ether were added to the reaction mixture. Stirring was continued for additional 2h at 0 °C. Then another 50 ml of 2N KOH solution were added to dissolve any solid and the bright yellow ether phase was separated. The aqueous mixture was extracted with ether until the organic phase no longer showed a yellow color. The combined organic extracts were washed with 2N KOH solution (50 ml) and dried over Na_2SO_4. After filtration the etheral solution of **17** was used immediately for the following reactions. The yield of **17** (65-70 mmol, ~ 75 %) was determined by reaction with an excess of 2,4,6-trimethyl benzoic acid. The resulting ester was isolated and identified *via* its ^{1}H NMR.

CAUTION: The reader should be aware of the potential hazard of diazomethane derivatives and should handle compound **17** only in solution under a well ventilated hood.

Dimethyl 3-cyano-8-oxatricyclo[3.2.1.0^{2,4}]octane-bis-anti-2,4-dicarboxylate (**18**).

A solution of 70 mmol of **17** in diethyl ether was prepared. At 0 °C 8.49 g (40 mmol) of **12** were added in one portion. After 15h at rt the excess of the diazo compound was destroyed by the addition of HOAc and thereafter the excess of the acid was removed by washing with $NaHCO_3$ solution. The etheral layer was dried over Na_2SO_4, filtered and concentrated to give the crude adduct. Without further characterization, the pale yellow oil was subjected to photolysis in 1000 ml of ethyl acetate (as above [*cf.* **11**]). Once more the solvent was removed and the cyclopropane system was now taken up in 150 ml of formic acid and 10.4 g (150 mmol) of hydroxylamine hydrochloride were added. The reaction mixture was heated at reflux for 45min and then poured onto 300 ml ice for quenching. Solid K_2CO_3 was added to neutralize the acid. After extraction with

dichloromethane the combined organic extracts were washed with $NaHCO_3$ solution, dried over Na_2SO_4 and filtered. The oil obtained after removal of the solvent was subjected to Kugelrohr destillation (0.1 mbar, 120 °C) and finally crystallized from hexane/*tert.*-butyl methyl ether (5/2). In this way 3.32 g (13 mmol, 33 %) of cyclopropyl nitriles **18** were obtained as an isomeric mixture of **18a** and **18b** (6:4); mp 121 - 122 °C. - **18a** (60%): ^{1}H NMR ($CDCl_3$): δ = 1.89 (m, 2H), 2.26 (m, 2H), 2.71 (s, 1H), 3.76 (s, 6H), 4.84 (m, 2H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 12.43, 26.90, 42.03, 53.03, 77.37, 115.09, 166.20 ppm. - **18b** (40%): ^{1}H NMR ($CDCl_3$): δ = 1.85 (m, 2H), 2.20 (m, 2H), 2.56 (s, 1H), 3.83 (s, 6H), 4.61 (m, 2H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 10.46, 26.87, 40.78, 52.95, 77.86, 115.30, 165.25 ppm. - IR (KBr): ν = 3035, 3016, 2958, 2244, 1743, 1438, 1319, 1268, 1238, 1199, 1157, 1087, 983, 925 cm^{-1}. - MS (CI) m/z (%): 251 (11), 250 (79), 218 (100), 191 (27), 186 (84), 159 (29), 131 (26). - Analysis for $C_{12}H_{13}NO_5$ requires C 57.37, H 5.22, N 5.58, found C 57.37, H 5.28, N 5.53.

Tetramethyl exo,exo-4,8-dicyano-9-oxatetracyclo[5.1.0.1^{2,6}.0^{3,5}]nonane-tetrakis-anti-1,3,5,7-tetracarboxylate (**19**).

Following the three step procedure described for the preparation of compounds **18** 9.79 g (30 mmol) of tetraester **7** were treated with 120 mmol of **17** for 4d. After photolysis in ethyl acetate (as above [*cf.* **11**]), the final conversion of the acetales to nitriles was realized by treatment with 27.8 g (400 mmol) of hydroxylamine hydrochloride in 200 ml of formic acid. Crude **19** was crystallized from chloroform/*tert.*-butyl methyl ether (1/2) to give 2.62 g (6.5 mmol, 22 %) of **19** as tiny colorless crystals; mp 233 - 235 °C. - ^{1}H NMR ($CDCl_3$): δ = 2.72 (s, 2H), 3.77 (s, 12H), 5.24 (s, 2H) ppm. - ^{13}C NMR ($CDCl_3$): δ = 17.38, 43.02, 53.25, 77.75, 113.60, 164.76 ppm. - IR (KBr): ν = 3031, 2958, 2248, 1739, 1446, 1326, 1257, 1230, 1160, 1122 cm^{-1}. - MS (CI) m/z (%): 402 (40), 373 (43), 371 (100), 338 (20), 329 (17), 311 (25), 263 (22). - Analysis for $C_{18}H_{16}N_2O_9$ requires C 53.47, H 3.99, N 6.93, found C 53.47, H 3.97, N 7.18.

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