in the melt or on solid supports (cellulose or chitosan, mol. weight 30000), the products being separated by chromatography on SiO_2. Transformation *a* into compound **2** (27—41%) may be considered to be an example of the Auwers rearrangement,[3] and rearrangement *b* yielding product **4** (2—14%) can formally be explained by the 1,3-migration of the CCl_3 group *via* intermediate **3** followed by hydrolysis and lactonization. Rearrangement *c* to give product **6** (2—13%) probably occurs *via* the intermediate unstable quinonemethide **5**, which then undergoes double radical recombination. The contribution of pathway *a* to the processes observed virtually does not depend on the reaction conditions. In the melt, pathway *c* markedly dominates over pathway *b*; conversely, on solid supports (cellulose is somewhat more active than chitosan), the latter competitively suppresses rearrangement *c* almost completely. The structures of the new products were determined by the data of elemental analysis, ^{1}HNMR and IR spectroscopy, and mass spectrometry. In the case of compound **4**, MS-FAB and X-ray diffraction were also used.

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Ethylenebis(azidomalonates)

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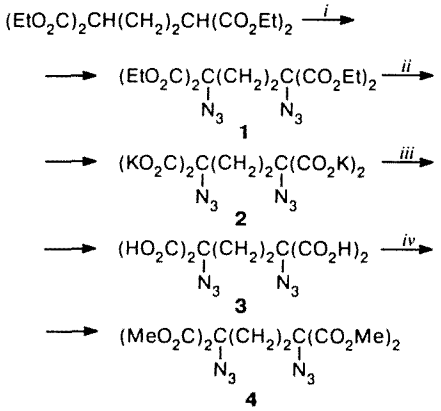
Tetraethyl ethylenebis(azidomalonate) (**1**) was synthesized for the first time by azide transfer from tosyl azide[1] onto ethylenebis(malonate) dianion.[2] Transformations of compound **1** afforded ethylenebisazidomalonic acid (**3**), its salt (**2**), and its ester **4** (Scheme 1), which are of interest as synthons and photoactive reagents.

Bisazide **1**, yield 39 %, white crystals, m.p. 44—46 °C. Found (%): N, 19.67. $C_{16}H_{24}N_6O_8$. Calculated (%): N, 19.63. IR (in thin film), ν/cm^{-1}: 2130 (N_3); 1755 (CO) (*cf.* monoazidomalonates[1]). ^{1}H NMR ($CDCl_3$), δ: 1.34 (t, 12 H, Me, ^3J = 7.0 Hz); 1.90 (s, 4 H, 2 CH_2); 4.31 (q, 8 H, 4 CH_2O). ^{13}C NMR ($CDCl_3$), δ: 13.7 (q, Me, ^1J = 128.1 Hz); 27.9 (t, $(CH_2)_2$, ^1J = 135.2 Hz); 70.6 (s, CN_3); 62.6 (t, CH_2O, ^1J = 144.1 Hz); 166.5 (s, CO). Salt **2**, yield 94 %, white crystals, m.p. >270 °C (dec.). ^{1}H NMR (D_2O), δ: 1.73 (s, CH_2). Acid **3**, yield 95 %, white crystals, m.p. >169 °C (dec.). ^{1}H NMR (acetone-d_6), δ: 2.01 (s, CH_2). ^{13}C NMR (CD_3OD), δ: 28.9 (t, CH_2, ^1J = 135.0 Hz); 74.0 (s, CN_3); 172.5 (s, CO). Methyl ester **4**, yield 97.7 %, white crystals, m.p. 85—87 °C. IR (CCl_4), ν/cm^{-1}: 2110 (N_3); 1735—1700 (CO).

Scheme 1



$$(EtO_2C)_2CH(CH_2)_2CH(CO_2Et)_2 \xrightarrow{i} (EtO_2C)_2\underset{N_3}{C}(CH_2)_2\underset{N_3}{C}(CO_2Et)_2\ (\mathbf{1}) \xrightarrow{ii} (KO_2C)_2\underset{N_3}{C}(CH_2)_2\underset{N_3}{C}(CO_2K)_2\ (\mathbf{2}) \xrightarrow{iii} (HO_2C)_2\underset{N_3}{C}(CH_2)_2\underset{N_3}{C}(CO_2H)_2\ (\mathbf{3}) \xrightarrow{iv} (MeO_2C)_2\underset{N_3}{C}(CH_2)_2\underset{N_3}{C}(CO_2Me)_2\ (\mathbf{4})$$

Reagents and conditions: *i*. NaH in anhydrous dioxane, 2 h, 40 °C, then TsN_3, boiling for 15 h. *ii*. 4 equiv. of KOH in MeOH, 12 h, 20 °C. *iii*. conc. HCl in Et_2O, 1 h, 20 °C. *iv*. CH_2N_2 in Et_2O/MeOH.

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^{1}H NMR ($CDCl_3$), δ: 1.92 (s, 4 H, 2 CH_2); 3.82 (s, 12 H, 4 MeO). ^{13}C NMR ($CDCl_3$), δ: 28.3 (t, CH_2, ^1J = 133.7 Hz); 53.5 (q, MeO, ^1J = 148.2 Hz); 71.0 (s, CN_3); 167.16 (s, CO).

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3,7-Diaza-2,6-dioxobicyclo[3.3.1]nonane-1,5-dicarboxylates: complete autoassembly and NMR studies

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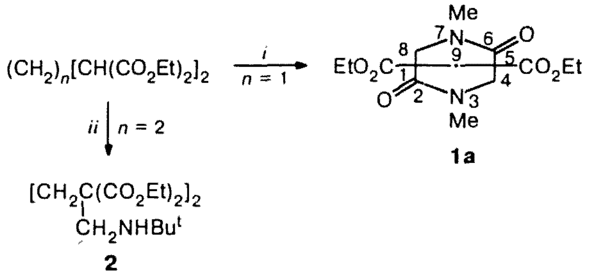
To develop further the principle of complete autoassembly of cage structures,[1] we have studied the synthesis of the bicyclic dilactam **1a** (*cf.* the known data[2]) by aminomethylation of methylenebismalonate.[3] The intermediate formation of the corresponding diamino tetraester was confirmed by the preparation of the sterically hindered analog **2** from ethylenebismalonate[3] under the same conditions (Scheme 1).

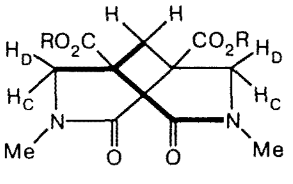
Diester **1a** readily undergoes transesterification to give its analog **1b** (MeOH/MeONa, 0.5 h at 20 °C, yield 84 %, m.p. 205—207 °C). Exhaustive alkaline hydrolysis of diester **1a** gave derivatives **1c**,**d**, and partial hydrolysis of **1a**,**b** yielded compounds **3a**,**b** and **4a**,**b**.

The compositions and structures of compounds **1**—**4** were confirmed by the data of elemental analysis and ^{1}H and ^{13}C NMR spectroscopy.

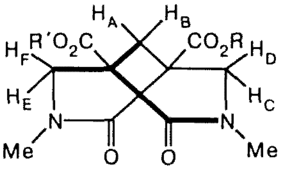
Scheme 1



Reagents and conditions: *i.* 1 equiv. of 1,3,5-trimethylhexahydro-1,3,5-triazine in the presence of CF_3CO_2H, 20 h at 100 °C. *ii.* 1 equiv. of 1,3,5-tris(*tert*-butyl)hexahydro-1,3,5-triazine under the conditions described in *i.*



1b—d



3a,**b**, **4a**,**b**

R = Me (**1b**), K (**1c**), H (**1d**)

R = Et, R' = K (**3a**), H (**3b**)
R = Me, R' = Na (**4a**), H (**4b**)

1a. Yield 75 %. M.p. 103—104 °C (*cf.* Ref. 2). **2.** Yield 75 %. M.p. 80 °C. ^{1}H NMR (CD_3OD), δ: 1.06 (s, 18 H, 2 Bu^t); 1.25 (t, 12 H, 4 Me, ^3J = 7.0 Hz); 1.83 (s, 4 H, 2 CH_2); 3.0 (s, 4 H, 2 CH_2N); 4.17 (q, 8 H, 4 CH_2O, ^3J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.96 (qt, $\underline{C}H_3CH_2O$, ^1J = 127.2 Hz, ^2J = 2.2 Hz); 25.75 (tt, $(CH_2)_2$, ^1J = 132.2 Hz, ^2J = 3.6 Hz); 28.74 (q.sept., $\underline{Me}_3C$, ^1J = 125.0 Hz, ^3J = 4.4 Hz); 43.93 (t, CH_2N, ^1J = 138.1 Hz); 49.85 (br.s, $\underline{C}(CO_2Et)_2$); 58.22 (s, $\underline{C}Me_3$); 60.9 (tq, CH_2O, ^1J = 148.2 Hz, ^2J = 4.4 Hz); 170.83 (br.s, CO). Yield of the picrate 60 %, m.p. 177—178 °C. Found (%): N, 11.21. $C_{38}H_{54}O_{22}N_8$. Calculated (%): N, 11.49.

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