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Thermal aromatizational rearrangements of 4,4-dimethyl-1-(4-trichloromethyl-4-methylcyclohexa-2,5-dienylidene)cyclohexane-2,6-dione

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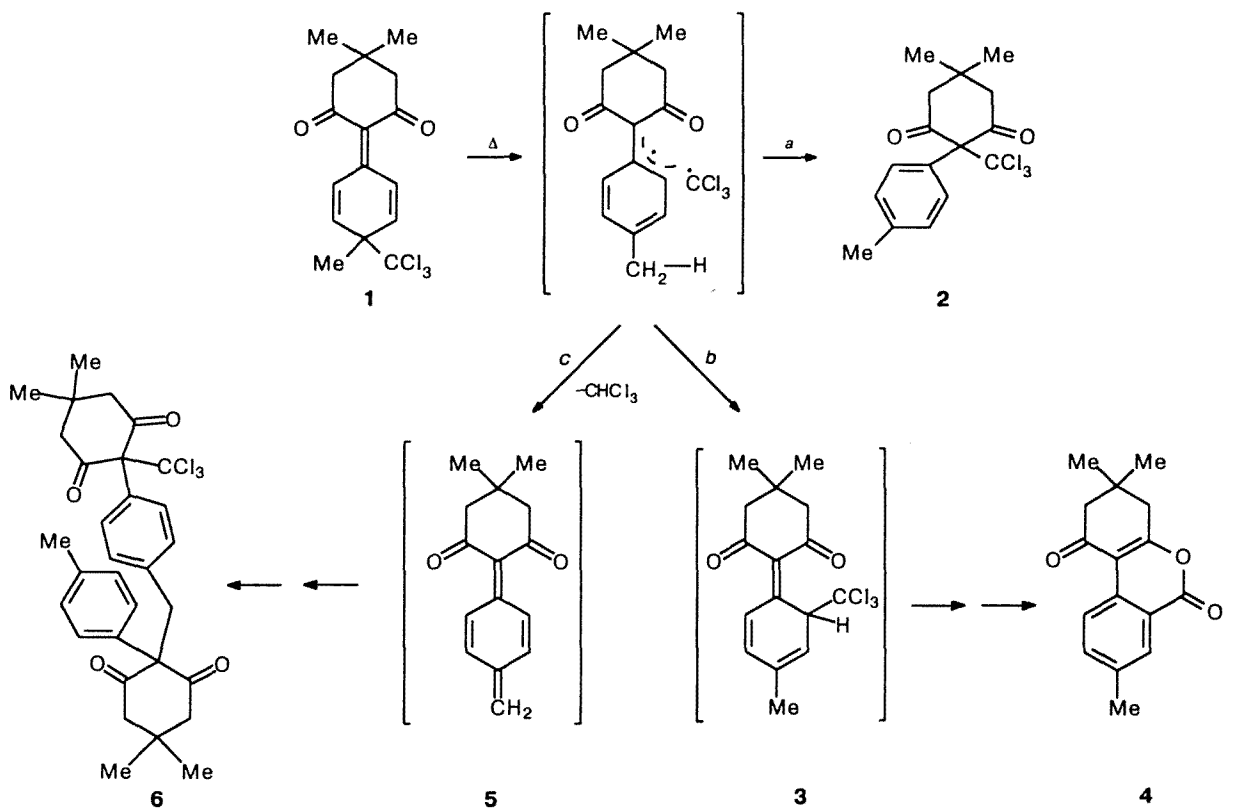
Thermal transformations constitute an important branch of organic chemistry.[1] We discovered new aromatizational rearrangements of trienedione (**1**)[2] (Scheme 1) that occur under thermolysis conditions at 180—185 °C

Scheme 1



† Deceased.

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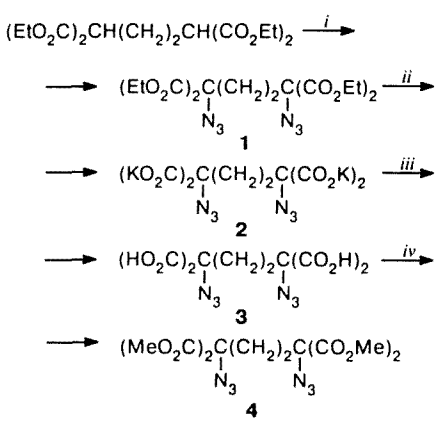
Tetraethyl ethylenebis(azidomalonate) (**1**) was synthesized for the first time by azide transfer from tosyl azide[1] onto ethylenebis(malonate) dianion.[2] Transformations of compound **1** afforded ethylenebisazidomalonic acid (**3**), its salt (**2**), and its ester **4** (Scheme 1), which are of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



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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