

284. Chemistry of Succinylsuccinic Acid Derivatives. Part I On the Photodimerization of Diethyl Succinylsuccinate

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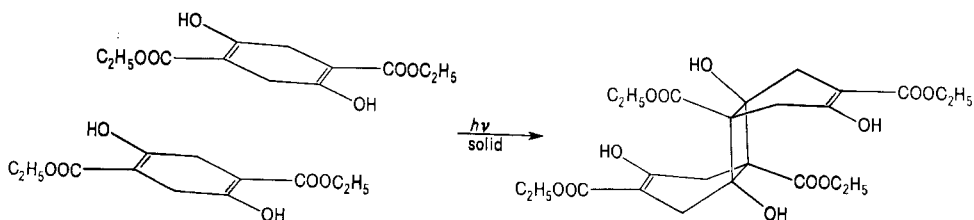
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(5. X. 73)

Summary. Topochemically controlled photochemical dimerization of diethyl succinylsuccinate in the solid is reported. The structure evaluation by elemental and spectroscopic analysis of the product is given. The participation of chelated enols in photochemical cycloadditions in the crystalline solid state is here demonstrated for the first time.

The ground state low molecular [1] as well as macromolecular [2] chemistry of succinylsuccinic esters (1,4-dialkoxycarbonyl-2,5-dihydroxy-cyclohexa-1,4-dienes) is well documented. Their photochemical behaviour has however received no attention until now.

We found that irradiation of powdered triclinic crystals of diethyl succinylsuccinate (DESS) or of their aqueous dispersion with light of $\lambda > 260$ nm, followed by *Soxhlet* extraction of unreacted material, gave a photoproduct according to the following scheme:



The production of *anti*-tricyclo[4.4.0^{1,6}.0^{7,12}]-1,4,7,10-tetraethoxycarbonyl-3,6,9,12-tetrahydroxy-dodeca-3,9-diene in this photoreaction is the first example of dimerization of chelated enols in the solid state²⁾ and it reaffirms the anticipated mechanism of participation of chelated enols in 2+2 cycloadditions [4]. The topochemical control [5] of the reaction is demonstrated by the absence of dimerization in solution, by the analogous solid-state dimerization of dimethyl succinylsuccinate³⁾, as expected from its similar crystal structure [6], by contrast with the photostability³⁾ of 1,4-diethoxycarbonyl-2,5-diamino-cyclohexa-1,4-diene [7] under the same conditions, owing to its obviously different crystal packing.

Traces of diethyl-2,5-dihydroxyterephthalate were also found in the extract. Although aromatization by way of hydrogen atom abstraction from the cyclohexadiene by a photoexcited species is not unfeasible [8], this compound is believed to be a

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²⁾ Enol dimerization in solution was only recently first reported [3].

³⁾ Unpublished results.

thermal rather than a photochemical oxidation product. In an attempt to copolymerize DESS with benzene-1,3-disulfonylchloride, no addition across the enolic double bonds occurred and complete aromatization took place instead (see Experimental). A thermal aromatization was also observed with polymers of the similar 1,4-diethoxycarbonyl-2,5'-diamino-cyclohexa-1,4-diene [9].

Structure evaluation: DESS prepared according to *Aschan* [10] had a m.p. of 131–132°, an Rf value of 0.75⁴⁾ and a UV. absorption at $\lambda_{\max}^{\text{EtOH}} = 241 \text{ nm}$ ($\epsilon \sim 2.0 \times 10^4$). Its mass spectrum⁵⁾ showed the following fragmentation pattern⁶⁾: 256 (72.7, *M*), 238 (8.9, *M* – H₂O), 227 (34.5, *M* – C₂H₅), 211 (32.7, *M* – OC₂H₅), 210 (56.4, *M* – HOC₂H₅), 199 (8.5, *M* – C₂H₅–C₂H₄), 142 (100, *M* – C₂H₅OCOCCHO). The ¹H-NMR. spectra in CDCl₃ at –40° and at 32° had signals due to enol form only and no resonance absorption owing to a possible keto configuration (Table 1).

Table 1. ¹H-NMR. spectrum of DESS in CDCl₃, at 32° (Fig. 1)

Hydrogen	Multiplicity	Shift (ppm)	Integration
H _a	<i>t</i>	1.30	6 H
H _b	<i>q</i>	4.25	4 H
H _c	<i>s</i>	3.15	4 H
H _d	<i>s</i>	12.10	2 H ^{a)}

a) absorption disappears upon addition of D₂O.

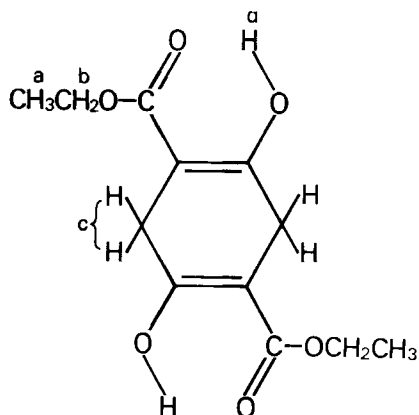


Fig. 1. Lettering of the H atoms of DESS

The photodimer had an Rf value of 0.07 and melted at 162–165°. Its structure elucidation was based on the following data: by vapor phase osmometry the molecular weight was 500 ± 25 , showing the product to consist of no more than two succinylsuccinate units. The UV. absorption at $\lambda_{\max}^{\text{EtOH}} = 253 \text{ nm}$ ($\epsilon \sim 1.0 \times 10^4$) indicated the elimination of half of the original chromophores responsible for the absorption in the monomer, as expected for a cyclobutane dimer. The infrared absorption at 965 cm^{-1}

⁴⁾ On silica gel thin layer plates, with acetone-hexane (1:4) as eluent.

⁵⁾ Sample temperature 80°.

⁶⁾ Data given are mass numbers, relative intensities and tentative assignments of principal ions.

(nujol), originally absent in the spectrum of DESS, could be assigned to the cyclobutane ring [11]. The transformation of two of the chelated enols into tertiary hydroxyls attached to cyclobutane was associated with the appearance of an absorption at 3420 cm^{-1} (DESS had no hydroxylic absorption) and with an additional ester band at 1710 cm^{-1} , in addition to the original chelate ester at 1675 cm^{-1} .

In the mass spectrum the molecular ion $M = 512$ was detected. The intense ion m/e 256 and its fragmentation similar to that of DESS was in accord with the reopening of a cyclobutane ring. Thus, the following fragmentation pattern was observed^{6) 7)}: 512 (0.04, M), 494 (0.17, $M - \text{H}_2\text{O}$), 466 (0.45, $M - \text{HOC}_2\text{H}_5$), 448 (1.8, $M -$

Table 2. $^1\text{H-NMR}$. spectrum of DESS-photodimer in CDCl_3 at 32° (Fig. 2)

Hydrogen	Multiplicity	Shift (ppm)	Integration
$\text{H}_a\text{H}_a'$	<i>m</i>	1.30	12 H
$\text{H}_b\text{H}_b'$	<i>m</i>	4.15	8 H
$\text{H}_c\text{H}_c'$	<i>m</i>	2.3–3.2	8 H
H_d	<i>s</i>	6.32	2 H ^{a)}
H_e	<i>s</i>	12.0	2 H ^{a)}

a) absorption disappears upon addition of D_2O .

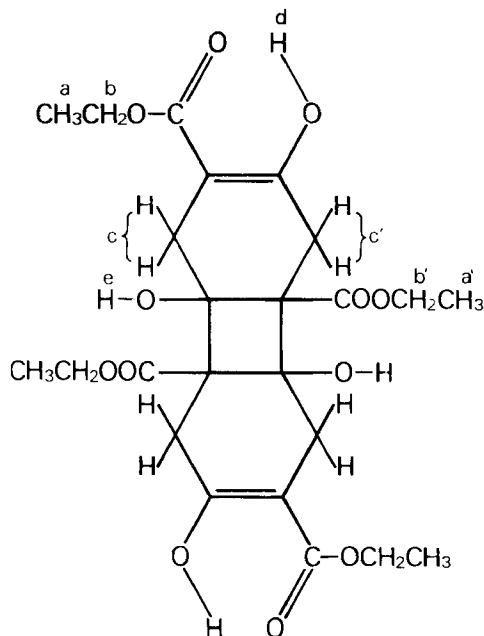


Fig. 2. Lettering of the H atoms of DESS-photodimer

$\text{HOC}_2\text{H}_5 - \text{H}_2\text{O}$), 421 (1.8, $M - \text{HOC}_2\text{H}_5 - \text{OC}_2\text{H}_5$), 420 (2.0, $M - \text{HOC}_2\text{H}_5 - \text{HOC}_2\text{H}_5$), 256 (71.4, $M - M/2$) and further fragmentation as of DESS, with 210 (100.0, $256 - \text{HOC}_2\text{H}_5$).

7) Sample temperature 110° .

The elemental analysis was equal to that expected for DESS (see Experimental). $^1\text{H-NMR}$. analysis (Table 2) showed the photoproduct to contain essentially the same features as those of DESS. A new absorption at 6.32 ppm was assigned to the hydroxylic protons attached to cyclobutane. The allylic hydrogens in the cyclohexene ring became magnetically unequivalent in the product, as evident from the two overlapped *AB* spectra to which they gave rise. Also, the enolic hydrogens lost half of their original intensity, and an equal amount of new hydroxylic hydrogens appeared.

The tentative assignment of the signals in the $^{13}\text{C-NMR}$. spectrum of the photoproduct was based in part on that of DESS and was in accord with the structure of a cyclobutane dimer. The elucidation of the $^{13}\text{C-NMR}$. spectrum of DESS (Table 3) was made by assuming the α and β carbon shieldings of carboethoxy and of hydroxyl to be additive [12] and by superimposing them on the chemical shifts of cyclohexadiene [13]. The estimated chemical shifts of C(1) and C(2) (165 and 94 ppm) compared favourably with those found at 168.25 and 93.25 ppm, respectively.

Table 3. Proton decoupled $^{13}\text{C-NMR}$. spectrum of DESS (Fig. 3)

Carbon	δ (ppm)
C(1) C(1')	168.25
C(2) C(2')	93.25
C(3) C(3')	28.57
C(4) C(4')	171.03
C(5) C(5')	60.71
C(6) C(6')	14.28

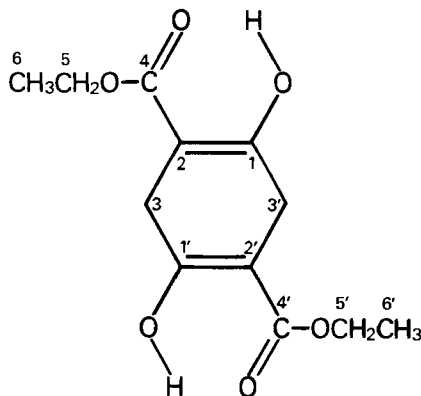


Fig. 3. Numbering of C atoms of DESS

In the spectrum of the photodimer (Table 4) carbons C(16)C(22), C(4)C(10), C(3)C(9), C(17)C(23) and C(18)C(24) remained almost unchanged as compared with DESS, whereas carbons C(5)C(11) and C(2)C(8) experienced a substantial downfield shift. The non-equivalence of these cyclohexene methylenes results from the different electronic environment induced by the neighbouring carbons C(1) and C(3) *vs.* C(4) and C(6), respectively. The two remaining signals, which were originally absent in the monomer, were assigned to the cyclobutane ring. By assuming that a neighbouring hydroxyl causes a greater deshielding than a carboethoxy, the resonance at 76.19 ppm was assigned to carbons C(6)C(12) and that at 55.25 ppm to C(1)C(7).

From the crystal packing of DESS a 'head to tail' configuration was predicted for the photodimer [14]. This was indeed confirmed by a crystal structure analysis of the photoproduct [15].

Temperature variation between -40° and 60° left the $^1\text{H-NMR}$. absorption pattern of the allylic methylene protons unchanged. As no other conformation became apparent, a transformation in solution of the type *syn-syn* \rightleftharpoons *syn-anti* \rightleftharpoons *anti-anti* (see fig. 5) seemed unlikely under these conditions. The *syn-syn* conformation found for the solid crystals was therefore believed to persist in solution.

Table 4. Proton decoupled ^{13}C -NMR. spectrum of anti-tricyclo[4.4.0^{1,6}.0^{7,12}]-1,4,7,10-tetraethoxycarbonyl-3,6,9,12-tetrahydroxy-dodeca-3,9-diene (Fig. 4)

Carbon	δ (ppm)
C(15) C(21)	13.88 ^{a)} , 2 ^{b)}
C(18) C(24)	14.16 ^{2 b)}
C(5) C(11)	32.93 ^{3 b)}
C(2) C(8)	33.80 ^{3 b)}
C(1) C(7)	55.23 ^{a)}
C(17) C(23)	60.51 ^{4 b)}
C(14) C(20)	61.70 ^{a)} , 4 ^{b)}
C(6) C(12)	76.19 ^{a)}
C(4) C(10)	94.52
C(3) C(9)	170.63 ^{5 b)}
C(16) C(22)	172.42
C(13) C(19)	174.68 ^{a)} , 5 ^{b)}

a) carbons with chemical shifts absent in DESS.

b) assignment possible within each other of the equally top-numbered carbons.

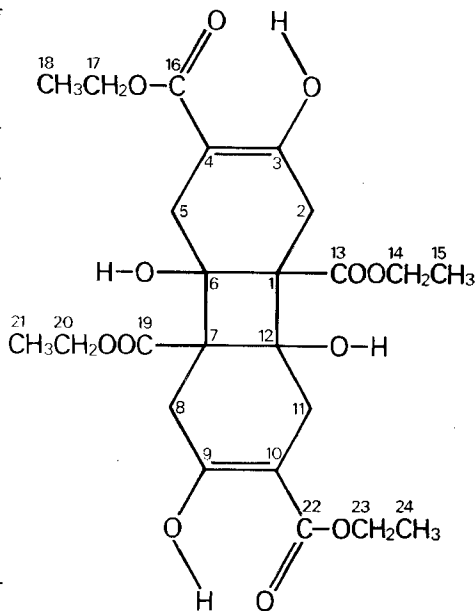


Fig. 4. Numbering of C atoms of the dimer of DESS

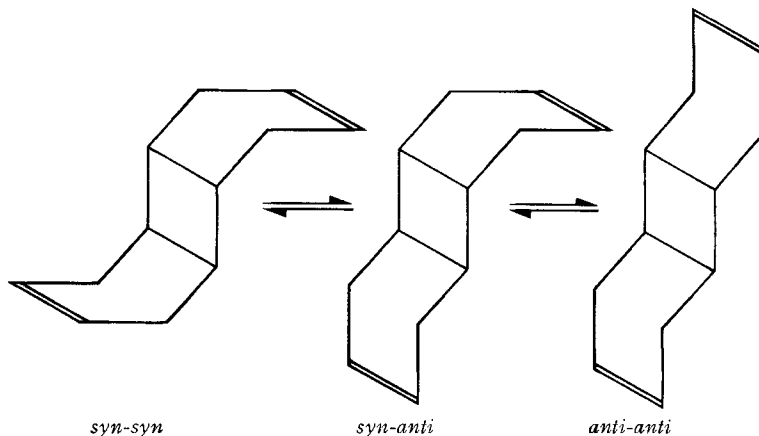


Fig. 5. Conformation of DESS-photodimer

Whereas the unreacted moiety in the photodimer preserved its original chemical character, the substituents on the newly formed cyclobutane are expected to gain in chemical reactivity. This increased reactivity might be utilized in the synthesis of macromolecules possessing the chelating power of DESS. The photoreaction investigated here may be representative for other succinylsuccinic derivatives.

Experimental Part. – *Photochemical procedures:* UV. irradiations were done on solid powder with a 2 kW high pressure mercury lamp through quartz while keeping the DESS in cellophane bags which filtered off part of the short UV. light.

In a typical example irradiation of 100 g DESS, under stirring for 100 h and subsequent Soxhlet extraction with petroleum ether bp 30–50° gave 3 g of pure photodimer. The extract contained unreacted DESS (95 g) and traces of diethyl 2,5-dihydroxyterephthalate. Alternatively, aqueous dispersions of the powder were circulated by means of a peristaltic pump around a 700 W water cooled high pressure mercury lamp irradiating through a 9821 Corex filter ($\lambda > 260$ nm): 20 g of dispersed DESS in 2 l of water were irradiated during 30 h. The dispersion was filtered, dried and liberated from starting material by Soxhlet extraction. 1.8 g of pure photodimer remained.

$C_{24}H_{32}O_{12}$ Calc. C 56.24 H 6.29 O 37.46% Found C 56.22 H 6.38 O 37.20%

Diethyl 2,5-dihydroxyterephthalate – A: 5 g of the Soxhlet extract of the irradiation mixture of DESS was chromatographed on a silica gel column. An acetone-hexane (1:9) solution eluted 16 mg having the following characteristics: m.p. and mixed m.p. (see B below) 136–137°; Rf 0.68⁴). – UV.: $\lambda_{\max}^{\text{EtOH}} = 220$ nm ($\epsilon \sim 1.76 \times 10^4$), 251 nm ($\epsilon \sim 0.97 \times 10^4$), 376 nm ($\epsilon \sim 0.36 \times 10^4$). – MS.⁵)⁶): 254 (23.3, M), 208 (100, M – HOC₂H₅), 180 (30.2, M – HOC₂H₅ – 28), 162 (81.4, M – HOC₂H₅ – HOC₂H₅ or else M – HOC₂H₅ – 28 – H₂O), 134 (21.0, 162 – CO). – NMR. (δ CDCl₃): 1.40 (6H, t, COOCH₂CH₃), 4.42 (4H, q, COOCH₂CH₃), 7.44 (2H, s, aromatic), 10.07 (2H, s, phenolic hydroxyl).

$C_{12}H_{14}O_6$ Calc. C 56.69 H 5.55% Found C 56.67 H 5.66%

B: DESS (12.8 g) and benzene-1,3-disulfonylchloride (13.8 g) were dissolved in 100 ml benzene. Cupric chloride (0.5 g) and triethylammonium chloride (0.5 g) in acetonitrile (1 ml) were added [16], the mixture was flushed with nitrogen and allowed to react in a 200 ml glass lined autoclave at 120° for 12 h, during which the pressure did not rise above 6 bar. Upon cooling, the mixture was thoroughly washed with water, dried over calcium chloride and evaporated to dryness. 11.2 g of a solid remained. The material analyzed as above.

Instrumentation: UV. measurements were done on a Cary 15 spectrophotometer. Mass fragmentation was measured on a Varian CH 7 spectrometer. ¹H and ¹³C-NMR. spectra were taken on a Varian XL-100-15⁷ at 100 MHz and at 25.2 MHz respectively. Chemical shifts are given in ppm downfield from tetramethylsilane. Vapor phase osmometry was done in CH₂Cl₂ solutions at 30°.

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REFERENCES

- [1] A. Hantzsch, Ber. deutsch. chem. Ges. 48, 772 (1915); P. C. Guha, *ibid.* 72, 1359 (1932); H. Batzler & G. Fritz, Chem. Ber. 86, 737 (1953); H. Liebermann, Liebigs Ann. Chem. 404, 272 (1914).
- [2] H. Holtschmidt, Makromol. Chem. 13, 141 (1954).
- [3] G. Mark, F. Mark, P. Margaretha & O. E. Polansky, Tetrahedron Letters 1973, 237.
- [4] P. de Mayo & H. Takeshita, Canad. J. Chemistry 41, 440 (1963).
- [5] M. D. Cohen & G. M. J. Schmidt, J. chem. Soc. 1964, 1996 and references therein cited.
- [6] P. Ganis, C. Pedone & P. A. Temussi, Renc. Acc. Naz. Lincei 35, 68 (1963).
- [7] A. Baeyer, Ber. deutsch. chem. Ges. 19, 428 (1886).
- [8] D. Elad & J. Sinnreich, Chem. Commun. 19, 471 (1965); Tetrahedron 24, 4509 (1968).
- [9] A. Tai, F. Higashi & S. Yokomizo, J. Polymer Sci., A-1, 9, 2481 (1971).
- [10] Aschan, «Chemie der Alicyclischen Verbindungen», Braunschweig, 1905, p. 707 (Beilsteins Handbuch der Organischen Chemie, Fourth Edtn. Berlin, 1927, Vol. 10, p. 894).
- [11] J. M. Derfer, E. E. Pickett & C. E. Boord, J. Amer. chem. Soc. 71, 2482 (1949); L. W. Marrison, J. chem. Soc. 1951, 1614; G. Chiurdoglu, Th. Doehard & M. Duts, Bull. Soc. chim. belges 70, 642 (1961).
- [12] J. B. Stothers, 'Carbon 13-NMR. Spectroscopy', Academic Press, 1972, p. 184.
- [13] L. R. F. Johnson & W. C. Jankowsky, 'Carbon-13 NMR. Spectra', Wiley Interscience, 1972, spectrum 166.
- [14] H. C. Mez & G. Rihs, Helv. 56, 2766, Part II (1973).
- [15] H. C. Mez & G. Rihs, Helv. 56, 2772, Part III (1973).
- [16] J. Sinnreich & M. Asscher, J. chem. Soc., Perkin I, 1972, 1543.