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THE SYNTHESIS OF EXO,EXO-11-OXATETRACYCLO[4.4.1.0.^{2,5}0^{7,10}]UNDECA-3,8-DIENE. THE STEREOCHEMISTRY OF THE TRICYCLO[6.2.0.0^{3,6}]DECANE DERIVATIVE OBTAINED BY THE PHOTODIMERISATION OF DIMETHYL TRANS,TRANS-PENTA-1,4-DIEN-3-ONE-1,5-DICARBOXYLATE

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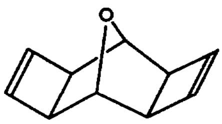
We report the synthesis of *exo,exo*-11-oxatetracyclo[4.4.1.0.^{2,5}0^{7,10}]undeca-3,8-diene (1). This molecule contains ten CH units in addition to the oxygen bridge, and is a potential precursor of fully unsaturated C_{10}-hydrocarbons which are of theoretical interest. The corresponding diaza analogue 2 (which contains two additional phenyl substituents) [3] and the etheno analogue 3 [4] have been synthesised recently by Paquette *et al*.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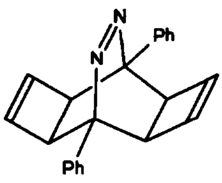

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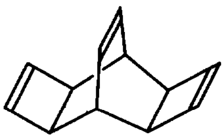
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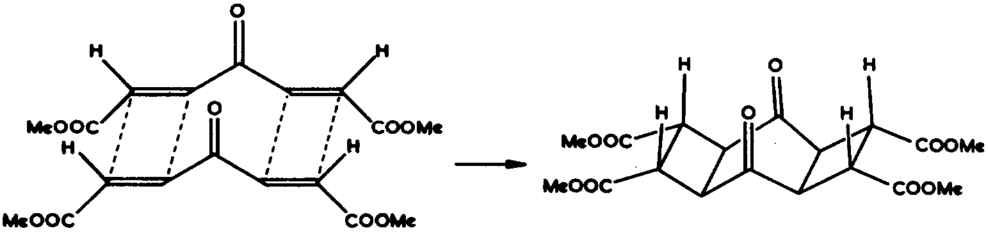
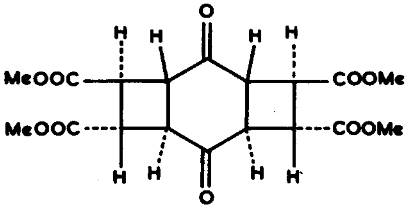
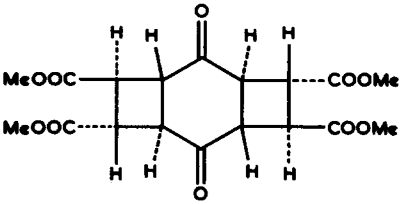
Irradiation of crystalline dimethyl *trans,trans*-penta-1,4-dien-3-one-1,5-dicarboxylate (4) with a Hanovia Type L ultraviolet lamp (450 W), using a vycor filter, gave tetramethyl tricyclo[6.2.0.0^{3,6}]decane-2,7-dione-4,5,9,10-tetracarboxylate (**5a**, mp 242-243°) [5] in 69% yield. The indicated stereochemistry follows from the stereochemistry of the derived oxides **7** and **1**, discussed below.



4 **5a**



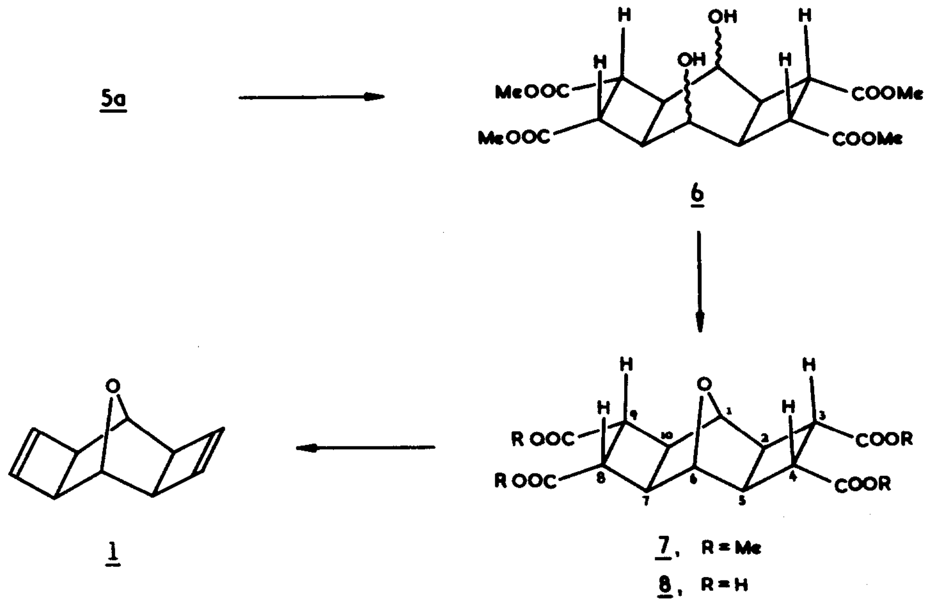
5b



5c

Corse *et al.*[6] have postulated the "*all-trans*" stereochemistry **5b** or **5c** for the dimer on the basis of the nmr spectrum, which however is equally compatible with the "*cis*" stereochemistry **5a**. Moreover, the *trans*-junction between the 4- and 6-membered rings in **5b** or **5c** would make the substance less stable than the corresponding *cis*-fused compound, and it would be expected that epimerisation of the ring junctions adjacent to the carbonyl groups would occur under basic conditions.[7] In practice, the dimer was recovered unchanged after treatment with boiling pyridine, confirming the *cis*-fused stereochemistry.

Reduction of **5a** with an excess of sodium borohydride in THF at room temperature for 48 hr gave the diol **6** (viscous liquid) in 72% yield as a mixture of stereoisomers; repeated crystallisation from chloroform-hexane resulted in 21% of one pure isomer, mp 239-242°.[8] Dehydration of **6** (mixture of stereoisomers) with phosphoryl chloride in pyridine at 0-100° led to *ca* 20% of the oxide **7**,[9] mp 209.5 - 210.5°.[8] The nmr spectrum (CDCl$_3$) showed a 2-H singlet at τ 5.65 (H^1, H^6), a 12-H singlet at 6.32 (CH_3), and a 8-H symmetrical A_2B_2 multiplet centred at 7.00; this multiplet consisted of 4-H multiplets at τ 6.78 (H^3, H^4, H^8, H^9), and 7.22 (H^2, H^5, H^7, H^{10}). The assignment of the A_2B_2 multiplet was substantiated by partial exchange of

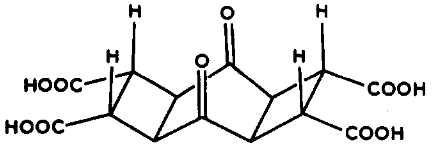


H^3, H^4, H^8, and H^9 in the corresponding tetra-acid 8 (see below) with D by treatment with NaOD in D_2O. The spectrum of the product showed an A_2B_2 multiplet in which the lower field part was now less intense than the higher field part. The simplicity of the nmr spectrum of 7 indicates that the molecule possesses a high degree of symmetry. The fact that H^1 and H^6 are not split significantly shows that the dihedral angle between these protons and H^2, H^5, H^7, and H^{10} is *ca* 90°, and the cyclobutane rings must therefore be *cis* *exo*-fused. The fact that the carbomethoxy groups in 7 are on the opposite side to the oxide bridge follows from the probable mode of formation of 5a (see formula 4), and the fact that no isomerisation is to be expected in passing from 5a to 7.

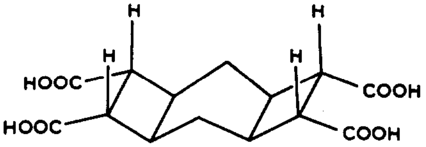
Saponification of 7 in dioxan with aqueous hydrochloric acid at *ca* 100° for 7 hr gave 75% of 8 as a monohydrate, mp > 330°.[8] Attempted oxidative decarboxylation of 8 with lead tetra-acetate in pyridine [10] gave no 1, but this transformation could be brought about electrolytically.[11] A vigorously stirred solution of 8 (1 g) in 15% aqueous pyridine (100 ml) and triethylamine (1.3 g) was electrolysed for 2½ hr between two stationary concentric cylindrical platinum wire gauze electrodes at 50-80 volts dc (initial current 0.6 amp) with external ice cooling. Isolation with ether and distillation at 55° (bath temp.) (12 mm) gave 1 (21 mg, 5%) as a colourless liquid which rapidly turned yellow at room temp. in air; homogeneous by glc;

mass spectrum, m/e 146.0734 (calcd for $^{12}C_{10}{}^{1}H_{10}{}^{16}O$: 146.0732). The nmr spectrum of 1 ($CDCl_3$) confirmed the assigned structure and stereochemistry, showing a 4-H singlet at τ 4.09 (olefinic), a 2-H singlet at 6.20 ($>$CH-O-) and a 4-H singlet at 7.30 (allylic).

By comparison, electrolysis of 9 (obtained from 5a by acid hydrolysis) or 10 (obtained from 5a by successive formation of the bisethylenedithioketal, Raney nickel desulphurisation, and acid hydrolysis) gave none of the corresponding diolefin. The difference may be due to the greater rigidity of 8 compared with 9 or 10.



9



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Notes and References

1. To whom inquiries should be addressed.

2. Taken in part from the Ph.D. thesis of G.A. Bullock, 1968. Financial support by the Petroleum Research Fund and the National Science Foundation is gratefully acknowledged.

3. L.A. Paquette and J.F. Kelly, Tetrahedron Letters, 4509 (1969).

4. L.A. Paquette and J.C. Stowell, ibid., 4159 (1969).

5. See F. Straus, Ber., 37, 3294 (1904); H. Stobbe and E. Färber, ibid., 58, 1548 (1925); H. Midorikawa, Bull. Chem. Soc. Japan, 26, 302 (1953).

6. J. Corse, B.J. Finkle, and R.E. Lundin, Tetrahedron Letters, 1 (1961).

7. See E.J. Corey, R. Mitra, and H. Uda, J. Am. Chem. Soc., 86, 485 (1964).

8. All crystalline new substances gave satisfactory elemental analyses, and showed ir and nmr spectra compatible with the assigned structures.

9. About 75% of 6 was recovered. Only one of the three possible stereoisomers of 6 can form the oxide 7, and the recovered 6 probably consists mainly of the other two isomers.

10. See C.M. Cimarusti and J. Wolinsky, J. Am. Chem. Soc., 90, 113 (1968) and references quoted there.

11. See P. Radlick, R. Klem, S. Spurlock, J.J. Sims, E.E. van Tamelen, and T. Whitesides, Tetrahedron Letters, 5117 (1968); H.H. Westburg and H.J. Dauben, ibid., 5123 (1968).