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THE PHOTOCHEMISTRY OF 2,3,11,12-TETRAPHENYL-2,3,11,12-DIDEHYDRO-18-CROWN-6

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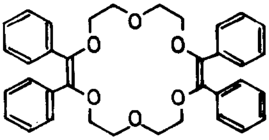
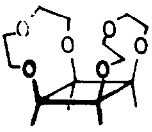
Summary: Upon UV irradiation the Z - stilbene units of the title compound undergo oxidative cyclization to phenanthrene rings or Z-E - isomerization. New crown ethers containing two phenanthrene rings or one phenanthrene ring and one E- or Z-stilbene unit were synthesized.

The photochemistry of the unsaturated crown ether 1 [1] appeared to us a possible access to crown derived basket or cage structures like 2 or 3 [2]. We report in this communication on photochemical conversions of 1 which do, however, take a different pathway.



1



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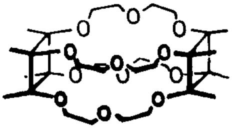

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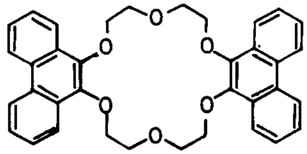
The electronic absorption spectrum of 1 exhibits absorption bands at 300 nm (ε = 17 200) and 245 (ε = 9 800). The variations of the photochemical parameters in our experiments were as follows [3]: irradiation of 1 in benzene solution (*ca.* 1.25×10^{-2} *M*) at one or both absorption maxima, in the presence or absence of oxidizing agents or triplet sensitizers, and further, irradiation of 1 or its sodium iodide complex in the solid state.

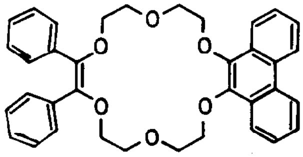
Under all conditions, the only isolated products were the new crown ethers 4, 5 and 6 and unreacted 1. The product mixtures were seperated by low pressure liquid chromatography on a Lobar (Merck) packed silica gel column using CH_2Cl_2 /CH_3CN (9:1) as eluting solvent. Thin layer chromatography revealed the presence of a number of lower molecular weight fragments of 1, but species like 2 and 3 were not detected in any of the experiments.

When a benzene solution of 1 was irradiated for 48 h in a quartz vessel in the absence of sensitizers and under rigorous exclusion of oxygen, it remained largely (90 %) unchanged, some fragments and small amounts of 4, 5 and 6 being formed.

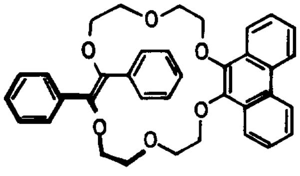
Oxygen as well as ketonic triplet sensitizers serve as oxidants promoting the phenanthrene ring formation by oxidation of the intermediate dihydrophenanthrenes [4]; when 1 is irradiated in benzene with catalytic amounts of iodine and oxygen bubbling through the solution [5], 4 is obtained as the sole crown ether in 50-60 % yield after 5 h. Various amounts of 4, 5 and 6 are obtained if the irradiation is interrupted earlier. The yield of 6 never exceeds 0.5 % .



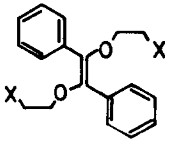
4, m.p. 245 °C



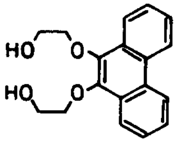
5, m.p. 218 °C



6, m.p. 228 °C



11 (a:X=OH;b:X=OTos)



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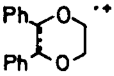
The structures of the new crown ethers 4, 5 and 6 were confirmed by their spectroscopic properties [6]. In their ^{1}H - nmr spectra all three species show three typical multiplets (4:2:2) for the phenanthrene protons which are virtually identical in chemical shift and splitting pattern with those of 9,10-dimethoxyphenanthrene [7], and which are the only aromatic proton signals of 4. The spectrum of 5 appears like composed of two halves of each 1 [1] and 4 with the phenyl signal as a singlet. The nmr spectrum of 6 is more complicated: the phenyl protons are split into two multiplets (3:2) as is always noted in E-stilbene derivatives [8], and the methylene protons appear as three multiplets (12:2:2).

The mass spectrum of 1 (m/z 564,M$^{\cdot+}$,100%) contains the key fragments 7 (m/z 238,70%) and 8 (m/z 105,97%); the corresponding fragments of 4 (m/z 560,M$^{\cdot+}$,45%) are 9 (m/z 236,100%) and 10 (m/z 180,65%).



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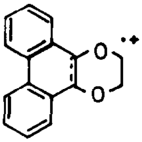
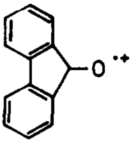
$\text{Ph-C-O}^{\cdot+}$

8



9



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The mass spectra of 5 and 6 are identical except for the relative intensities of the fragment ions (m/z 562, M$^{\cdot+}$, 52% for 5, 77% for 6); they show all four fragments 7-10 thus indicating the presence of the phenanthrene as well as the stilbene moieties.

In its ir spectrum 5 has the typical C=C stretching frequency of Z-stilbenediol derivatives at 1630 cm^{-1} [8], in addition to the phenanthrene 9,10-stretching vibration at 1620 cm^{-1} which is shared by all crowns 4-6 and also by 9,10-dimethoxyphenanthrene.

With these data, the structures of 4 and 5 are well established. As 6 is the first example of a crown ether with a trans - double bond its structure was further confirmed by an independent synthesis: E-α,β-bis(2-hydroxyethoxy-)stilbene, 11a [9], was irradiated in the presence of iodine and oxygen to give the diol 12 [10]. Cyclization of 12 with the ditosylate 11b (sodium hydride in refluxing THF [11]) gave 12 % of the crown ether 6 which was in all respects identical with the material obtained photochemically from 1.

References and notes

[1] A.Merz, Angew.Chem. 89, 484 (1977); Angew.Chem.Int.Ed.Engl. 16, 467 (1977).

[2] For similar structures from photochemical cyclization reactions see: H.Krauch, S.Fariad and D.Hess, Chem.Ber. 99, 1880 (1966).

[3] Irradiations were carried out in a falling thin film quartz reactor using a Philips HPK 125 W low pressure mercury lamp and UV filters as needed.

[4] E.V.Blackburn and J.C.Timmons, Quart.Rev. 23, 482 (1969).

[5] C.S.Wood and F.B.Mallory, J.Org.Chem. 29, 3373 (1964).

[6] Molecular formulae were established by correct elemental analyses and high resolution mass spectra. ^{1}H-nmr spectra (in CD_2Cl_2, δ - values vs. TMS, int.Stand.):
4: 4.05-4.22,4.39-4.62, symm.m.,16 H; 7.53-7.76,m,8H; 8.13-8.38,m,4H; 8.54-8.79,m,4H.

5: 3.80-4.04,symm.m,8H; 4.04-4.21,4.40-4.60,symm.m,8H; 7.20,s,10H; 7.53-7.78,m,4H; 8.15-8.35,m,2H; 8.57-8.80,m,2H.
6:4.00-4.12,m,12H; 4.12-4.40,m,2H; 4.60-4,88,m,2H; 7.01-7.52,m,6 phenyl-H; 7.52-7.85, m, 4 phenyl-H + 4 phenanthrene-H; 8.10-8.38,m,2H; 8.53-8.78,m,2H.

[7] m.p. 39 °C; obtained in 95 % yield from iodine catalyzed photocyclization of E- or Z-α,β-dimethoxystilbene [8] ;^{1}H-nmr ($CDCl_3$): 4.10,s,6H;7.48-7.78,m,4H;8.13-8.40,m,2H; 8.53-8-80,m,2H.

[8] A.Merz and R.Tomahogh, J.Chem.Research 1977, (S) 273, (M) 3070.

[9] A.Merz, M.Eichner and R.Tomahogh, subsequent paper in this issue.

[10] 12: m.p. 102 °C, 85 % yield; ^{1}H-nmr ($CDCl_3$): 3.8-4.1,4.1-4.5,symm.m,10H; 7.3-7.7,m,4H; 7.9-8.3,m,2H; 8.4-8.7,m,2H).

[11] K.E.Koenig, G.M.Lein, P.Stuckler, T.Kaneda and D.J.Cram, J.Amer.Chem.Soc. 101, 3553 (1979).

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