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THE PHOTODIMERIZATION OF BENZO(b)THIOPHEN-3-METHYL 1-OXIDE

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The photochemical behaviour of benzo(b)thiophen 1,1-dioxide and some of its derivatives have been reported by different authors (1-4). It was found that these compounds generally photodimerize in both head-to-head and head-to-tail fashion, with the exception of benzo(b)thiophen-3-carboxylic acid 1,1-dioxide which gives the anti head-to-head dimer (5). In the same respect the recent photodimerization of 1-methylindene by DEKKER and al (6) gave the anti head-to-head dimer whereas indene produced the anti head-to-head and anti head-to-tail dimer (7).

These results prompted us to report on the photochemistry of benzo(b)thiophen-3-methyl 1-oxide 1 (8). Irradiation of 1 in benzene at 313nm gave two isomers in 40% yield in the proportion of 3/5. However, irradiation at 366nm and using benzophenone as a sensitizer gave the same isomers in the same amount but with an over all yield of 80%. The molecular ions of the two isomers, which have been separated by elution on SiO_2 95-5 ether-methanol, are 328 which agree with the formula $C_{18}H_{16}O_2S_2$. The I.R. spectrum shows the characteristic frequency of the sulfoxide group for both isomers at 1040-1060cm^{-1} as a doublet and the disappearance of the C=C double bond in 1.

For the major isomer 2a the m.p. is 224-26°C and the ^{1}H-NMR spectrum (solvent $CDCl_3$) shows a two protons singlet at δ 4.75ppm, six protons singlet at δ 1.20ppm, besides 8 aromatic protons at δ 7.4-8ppm.

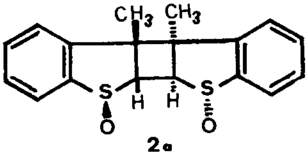
The minor isomer 2b (m.p.250 decomp.) has ^{1}H-NMR spectrum (solvant $CDCl_3$) with two doublets at δ 4.4ppm (1H J_{AB} 6Hz) and δ 3.6ppm (1H J_{AB} 6Hz), two singlets at δ 1.0ppm (3H,methyl) δ 1.35ppm (3H,methyl) besides 8 aromatic protons at δ 7.4-8ppm.

Oxidation of the two isomers with m-chloroperbenzoic acid converts them to sulfone 3 which is identified by ^{1}H-NMR spectrum {solvent : DMSO d_6 ; δ 7.7-8ppm (8H,aromatic), δ 4.08ppm (2H,cyclobutane) and δ 1.25ppm (6H,2-methyl)}, and by elementary analysis as well as by a molecular ion of 360. Compound 3 is identical to that obtained by photodimerization of benzo(b)thiophen-3-methyl 1,1-dioxide which gave only one dimer as contrasted with benzo(b)thiophen 1,1-dioxide which produced the two anti-configurated head-to-head and head-to-tail dimers. (1-3).

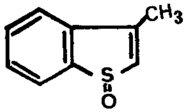
Epimerization of 2a in 2 volumes of tetrahydrofuran and 1 volume of concentrated HCl converts it to 2b and 2c. The latter cannot be purified from the former due to its lack of stability but it has been identified by ^{1}H-NMR spectrum {solvent $CDCl_3$; δ 7.3-8.15ppm (8H,aromatic), δ 3.25ppm singlet (2H,cyclobutane), δ 1.35ppm singlet (6H,2-methyl)} as well as by IR. Moreover the oxidation of the mixture of 2b and 2c gave the sulfone 3.

From these results we deduce the possible structures for these two isomers as shown in scheme 1.

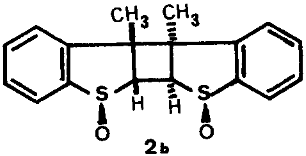
To determine the stereochemistry of the two S – O bonds for these dimers we used the lanthanide induced chemical shift effect (9.10). By complexation with the oxygen atom of the sulfoxide group there is a large shift for protons cis to oxygen. We observe a large proton shift for 2a (Δ_{Eu}= -0,70 ; R_p=0,1) (11) and a large proton shift for only one of the protons in 2b (Δ_{Eu}= -1,10 and Δ_{Eu}= -0,40 ; R_p=0,1) (11) which indicates that in 2a all the protons are cis to the sulfoxide groups, whereas in 2b one proton is cis and the other is trans. Thus, in 2a, the molecule is symmetric and the two protons as well as the two methyl groups show singlet peaks in the ^{1}H-NMR, whereas in 2b the molecule is asymmetric and the two protons show AB quartet and the methyl groups are split. In that respect the ^{13}C NMR spectrum of 2a consists of 9 peaks whereas in 2b all the carbons are different giving 18 different peaks. All these peaks have been easily attributed.



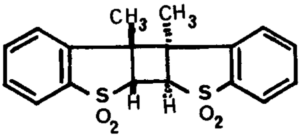
2a



1



2b



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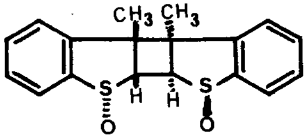

2c

On these spectral informations, oxidation products and epimerization, we assign the photodimers of 1 to be 2a and 2b. While 2c is expected to be a product of the photodimerization of 1, we are unable to detect it and it can be produced only by epimerization.

Irradiation of various compounds in this serie is underway and should give more information about the reactivity of benzo(b)thiophen 1-oxide derivatives.

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11.- $\Delta_{Eu} = \delta_{CDCl_3} + \delta_{(CDCl_3 + Eu(Fod)_3)}$; R_p : molar ratio Eu(Fod)$_3$/substrate.