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TWO CRYSTALLINE DIMERIC PEROXIDES FROM SENSITIZED PHOTOOXIDATION OF 2,5-DIMETHYLFURAN

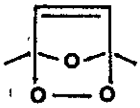
Yueh-Hsiung Kuo*, Kae-Shyang Shih, Gene-Hsiang Lee, and Yu Wang
Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Abstract - Sensitized photooxidation of 2,5-dimethylfuran was carried out in acetone and dichloromethane. Two crystalline dimeric peroxides were isolated after purified on silica gel. The elucidation of the structures of two dimeric peroxides was based on their spectral and chemical data and X-ray analysis.

Recently, Gollnick and Griesbeck[1] described the photooxidation of 2,5-dimethylfuran 1a in various solvents with tetraphenylporphin (TPP) and rose bengal as sensitizer at 13°C. It yielded ozonide 2. However ozonide 2 dimerized slowly to peroxide 3 [mp 143°C(decomp.)] in CCl_4 and $CFCl_3$. In our laboratory, so far we have completed the studies of photooxygenation of 1b[2],1c, 1d,1e[3], and 1f[4]. It is interesting to compare the photooxygenation of furan derivatives and their product distribution as well as to study the sensitized photooxygenation of 2,5-dimethylfuran 1a. From photooxygenation of 1a, we obtained ozonide 2 in $CFCl_3$ at -78°C. The nmr data of this compound match the ones given previously[1]. It can then be reduced with dimethyl sulfide at the same temperature to give cis-diacetylethylene. At room temperature in $CFCl_3$, however we obtained another product , the nmr data of which were the same as 3[1] which could be reduced with triphenyl phosphine to give trans-diacetylethylene but not with dimethyl sulfide. Two dimeric products were obtained from the sensitized photooxidation of 2,5-dimethylfuran 1a. A solution of 2,5-dimethylfuran (6.4g) and methylene blue (100mg) in acetone (110ml) was irradiated with a 500 W incandescent lamp for 2 days at 10-15°C by cooling with water while oxygen gas was slowly bubbling through the solution. The reaction mixture was then coated on silica gel (15g) and the components were separated by chromatography on silica gel : compound 5 (3.8%), 4 (<1%), 6 (36.2%) and 7 (<1%), were isolated accordingly. Similarly, photooxidation of 1a (6.5g) in dichloromethane solution yielded 5 (3.1%), 4 (<1%), 6(33.1%) and 7 (<1%) after irradiation for 2 days. The first product 5 was found to be a mixture of 5 and isomer of 5.

The compounds 4, 6 (mp 74-76°C) and 7 (mp133-135°C) are identified[5] as cis-diacetylethylene, trans-diacetylethylene, and 2-hydroxy-5-hydroperoxy-2,5-dimethyldihydrofuran, respectively, The mixture of 5 and isomer of 5 cannot be separated by chromatography. Fortunately, the amount of compound 5 is slightly *more than isomer of 5 when isolated from acetone solution,* and the opposite is true in dichloromethane solution. Thus 5 (mp 157-158°C) and isomer of 5 (mp 123-125°C) were separated and further purified by recrystallizations from methanol three times. The molecule formula of both compounds, $C_{12}H_{16}O_6$, was determined from their elemental analysis and similar mass spectral data (m/z 256(0.2%), 139(2%), 113(25%), 112(30%), 97(100%), 69(9%) and 43(35%)). *They also give the similar* pattern of ir spectrum ($_{max}$ 3100,2990,1625,1280,1100,965 and 885cm^{-1}), but they give slightly different nmr spectra: compound 5 [^{1}H nmr ($CDCl_3$) 1.53 and 1.66 (each 6H,s), and 5.85 and 6.09 (each 2H,d,J=6Hz): ^{13}C nmr ($CDCl_3$) 21.6, 21.8, 115.5, 114.3, 131.1 and 135.0] and isomer of 5 [^{1}H nmr ($CDCl_3$) 1.47 and 1.70 (each 6H,s), and 5.96 and 6.03 (each 2H,s,)]

1



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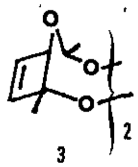

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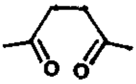

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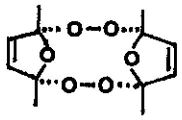
1a R1=R2=Me
1b R1=H,R2=CH_2OCOPh
1c R1=H,R2=COMe
1d R1=H,R2=COOMe
1e R1=H,R2=COOEt
1f R1=R2=CH_2OBZ



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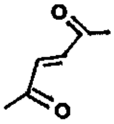

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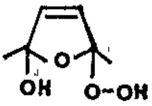

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Both compounds are inert to $NaBH_4$ and PPh_3 reduction, but can be reduced by catalytic hydrogenolysis with 10% Pd-C in methanol to give 2,5-hexanedione [$_{max}$ 1710 cm^{-1}, ^{1}H nmr ($CDCl_3$) 2.19(6H,s) and 2.71(4H,s)]. Each compound also gave positive acidic KI test and yielded the reduction product 6. Based on the above results, compound 5 and isomer of 5 are stereoisomeric and are considered to have resulted from decomposition of 3 by SiO_2, but the exact structure may be different from a symmetric skeleton like 3, based on the physical data. Compound 3 and 5 expressed different chemical properties. The former one can be reduced with Ph_3P, but the latter one shows stable with Ph_3P even with $NaBH_4$. In high

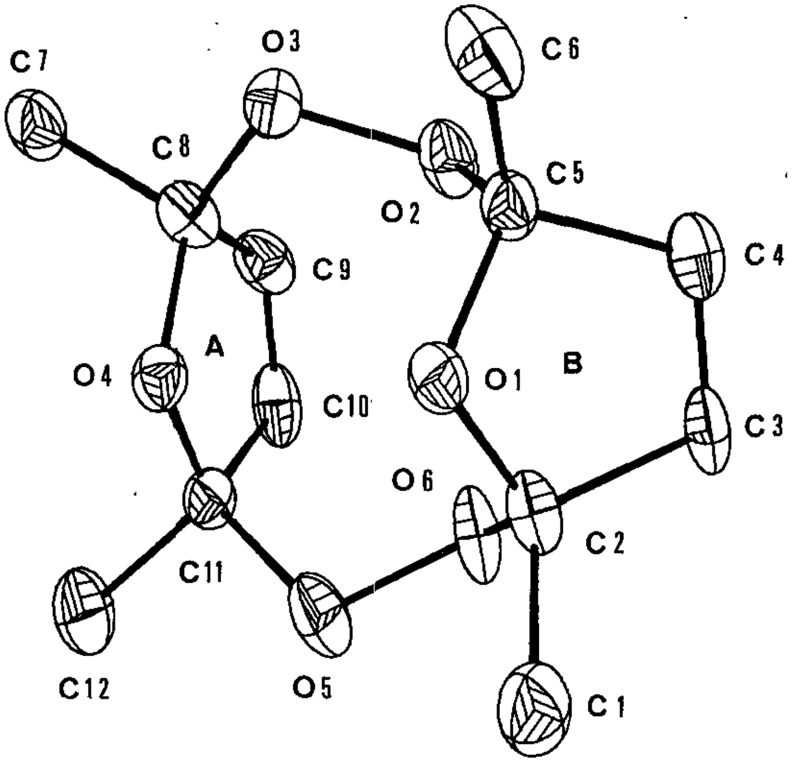

Fig 1

TABLE : BOND LENGTHS (Å) AND BOND ANGLES (°) OF COMPOUND 5

ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH	ATOM1	ATOM2	LENGTH
O1	C2	1.39(1)	O1	C5	1.40(1)	O2	O3	1.497(9)
O2	C5	1.40(1)	O3	C8	1.40(1)	O4	C8	1.45(1)
O4	C11	1.36(1)	O5	O6	1.476(9)	O5	C11	1.43(1)
O6	C2	1.46(1)	C1	C2	1.55(1)	C2	C3	1.52(1)
C3	C4	1.31(1)	C4	C5	1.55(1)	C5	C6	1.50(1)
C7	C8	1.49(1)	C8	C9	1.45(1)	C9	C10	1.27(1)
C10	C11	1.53(1)	C11	C12	1.51(1)			

ATOM1	ATOM2	ATOM3	ANGLE	ATOM1	ATOM2	ATOM3	ANGLE
C2	O1	C5	108.9(7)	O3	O2	C5	107.1(6)
O2	O3	C8	109.0(7)	C8	O4	C11	113.1(7)
O6	O5	C11	110.7(7)	O5	O6	C2	109.7(6)
O1	C2	O6	113.1(8)	O1	C2	C1	112.3(8)
O1	C2	C3	105.6(8)	O6	C2	C1	107.9(8)
O6	C2	C3	102.1(7)	C1	C2	C3	115.5(9)
C2	C3	C4	107.5(9)	C3	C4	C5	108.8(9)
O1	C5	O2	111.0(8)	O1	C5	C4	103.3(8)
O1	C5	C6	109.9(8)	O2	C5	C4	100.8(8)
O2	C5	C6	114.8(8)	C4	C5	C6	116.3(9)
O3	C8	O4	110.3(7)	O3	C8	C7	103.9(8)
O3	C8	C9	116.3(8)	O4	C8	C7	110.1(8)
O4	C8	C9	101.9(8)	C7	C8	C9	114.4(9)
C8	C9	C10	112.7(9)	C9	C10	C11	109.7(9)
O4	C11	O5	113.6(7)	O4	C11	C10	102.6(8)
O4	C11	C12	113.1(9)	O5	C11	C10	111.8(8)

concentration, compound 3 decomposes spontaneously, and 5 is stable in *high* concentration with different sovents. In order to verify the structure of the dimers, compound 5 was submitted to X-ray *crystallographic analysis.* Compound 5 crystallized in monoclinic space group $P\ 2_1/c$. Cell parameters : a=8.294(2), b=10.591(4), c=14.987(6)Å, β=100.69(3)°. Intensity data were collected with MoKα (λ=0.7107Å) radiation up to 2 of 50°. A total of 2270 data were obtained, among which 1011 reflections were observed (>3σ) and were used in the subsequent analyses. The final agreement index is R(F)=0.10. The sample decayed 22% in the beam throughout the experiment. The molecular structure is illustrated in Fig 1. Bond lengths and angles are listed in the table. All the carbon-carbon, carbon-oxygen and oxygen-oxygen bonds are as expected. The relative conformation of the two monomer parts are slightly different: firstly, the planarity of one furan ring A (in Fig 1) is better than the other ring B. The dihedral angle between the two planes is 77.9°. *Secondly, the torsion angles* around C9-C10 are different from those around C4-C3; for example, C7-C8-C9-C10 and C12-C11-C10-C9 are 17° and 18° smaller than C6-C5-C4-C3 and C1-C2-C3-C4 respectively. That means that the methyl groups of ring B are bent more away from the ring plane than those of ring A. This results can further support the observed ^{1}H nmr data. i.e. the methyl proton of ring A gives a slightly different chemical shift than those of ring B. The ethylene protons somehow represent the coupling between two neighboring protons. Strictly speaking, there is no symmetry required for the molecule in solids, so there is a minor difference, even between the two ethylene protons. However the difference between ring A and B is far more than the two neighboring protons. Therefore more complex nmr spectra namely two doublets are expected. It is believed that the *isomer of 5 has a* similar structure but with different configuration (probably trans-isomer of 5). *As for 3, it may represent* more symmetric dimer, i.e. same configuration of ring A and B. The dihedral angle between two ring planes may vary and the torsion angles around the C-C double bond could differ. Therefore 3 gives slightly different nmr spectra. The exact comparison has to rely on the crystal structures of the two.

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REFERENCES

1. K.Gollnick and A.Griesbeck, Tetrahedron, 1985, **41**, 2057.

2. Y.H.Kuo and K.S.Shih, Heterocycles, 1986, **24**, 1361.

3. Y.H.Kuo, Chemistry Express, 1986, **1**, 475.

4. Y.H.Kuo and C.J.Shieh, Heterocycles, 1986, **24**, 1271.

5. T.Noguchi, K.Takayama, and M.Nakano, Biochem. Biophys. Res. Commun., 1977, **78**, 418.

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