Tetrahedron Letters, Vol. 33, No. 52, pp. 8127-8130, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

4,5-Dimethylene -1,2-dioxane and Derived Diels-Alder Adducts

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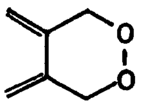
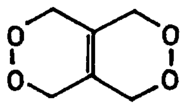
Abstract : 4,5-Dimethylene-1,2-dioxane (**1**) was prepared by zinc-induced debromination of 4,5-bis (bromomethyl)-1,2-dioxacylohexa-4-en (**4**) obtained from 2,3-bis (bromomethly-1,3-butadiene (**3**) by reaction with singlet oxygen. Diels-Alder additions of **1** with singlet oxygen, dimethyl acetylenedicarboxylate and N-methyl-1,2,4-triazoline-3,5-dione gave adducts **2**,**6** and **8** respectively. 3,4-Disubtituted furans **5** and **9** were obtained from peroxides **4** and **8** by cobalt (II) tetraphenylporphyrin catalyzed rearrangement.

This paper reports the syntheses of the previously unknown 4-5-dimethylene-1,2-dioxane (1) and the symmetric bisperoxide 3,4,8,9-tetraoxa-1(6)-bicyclo[4.4.0]decene (2).



1

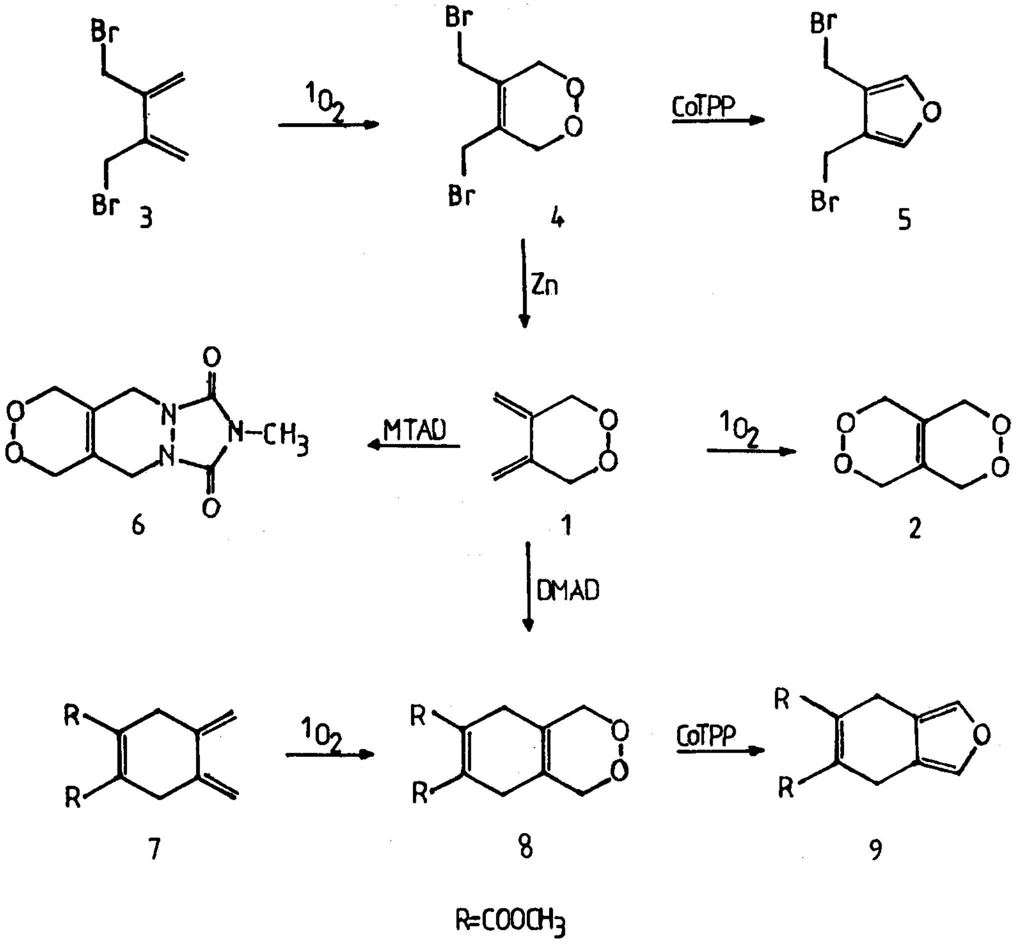


2

Compound **1** contains exocyclic diene and 1,2-dioxane moieties both of which can be readly functionalized. The diene moiety can react with different dienophiles and form 4,5-substituted cyclohexane (or cyclohexene) annelated-1,2-dioxanes. 3,4-Disubstituted furans can be prepared from the rearrangement of this cycloadduct. Such a sequence is of use in the synthesis of various subtituted multicyclic molecules. 3,4-Disubstituted furans are generally obtained from vinyloxiranes or α-thiometylene ketones[1,2]. These methodologies require the use of anhydrous solvent, strong organic bases and low reaction temperatures.

Compound **1** is also of interest for the potential use of furans obtained from rearrangement of the cycloadduct of diene **1** with 1,4-benzoquinone derivatives as precursors of cage molecules which can be formed from intramolecular cycloaddition.

Compounds 1 and 2 were synthesized as in Scheme 1. The photooxygenation reaction of 2,3-bis (bromomethyl)-1,3-butadiene[3] (3) using tetraphenylporphyrin (TTP) as sensitizer in chloroform at room temperature gave a 40 % yield of 4,5-bis(bromomethyl)-1,2-dioxacyclohexa-4-en (4). 4,5-Dimethylene-1,2-dioxane was obtained from 4 by zinc-induced debromination in a yield of 80%.



Scheme: 1

It was found that although 1 polimerized quite rapidly in the free state, it was stable in solution for at least one week and reactions in solution were carried out with a very low extent of polimerization.

Tablo 1. Selected Physical Data of 1,2,4,5,6,8,9

Compound	^{1}H-NMR(CDCl$_3$) δ ppm			M.P °C	IR cm^{-1}
1	5.45	s.	vinyl methylene (2H)	–	
	4,9	s.	vinyl methylene (2H)	–	
	4,7	s.	allylic methylene	–	
2	4,5	s.		–	
4	4,7	br.s.	peroxide (4H)		
	4,1	br.s.	bromomethyl (4H)	95-96	2860,1460,1190 1030,580
5	7,5	br.s.	furan (2H)		
	4,5	br.s	bromomethyl (4H)	72-74	1540,1425,1210 1040,805
6	4,55	br.s	peroxide ring (4H)		
	4.05	br.s	diaza ring (4H)	120-122	2850,1690
	3,1	s.	N-methyl (3H)		1465,750
8	4,4	s.	peroxide ring (4H)	169-170	2870,1715,1430
	3,8	s.	(6H)		1265,1055
	2,9	s.	methylenic (4H)		
9	7,4	br.s	furan (2H)		1720,1430,1270
	3,85	s.	(6H)		1060, 760
	3,35	br.s.	(4H)		

3,4,8,9-Tetraoxa-1(6)-bicyclo[4.4.0]decene (2) was prepared from the reaction of 1 with singlet oxygen under the usual conditions in chloroform at room temperature. Endoperoxides[4] are of both synthetic and theoretical importance.

The Diels-Alder reactions of 1 with dimethylacetylenedicarboxylate (DMAD) and with N-methyl-1,2,4-triazoline-3,5-dione (MTAD) were carried out in ether at room temperature. Although DMAD addition took three days MTAD addition took place rapidly, and adducts 8 (70% yield) and 6 (90% yield) were obtained respectively.

To confirm the structure of 1 in a chemical way, dimethyl 4,5-dimethylenecyclohexene-1,2-dicarboxylate (7) was synthesized using the method given in the literature[3b]. Spectroscopic data and m.p. of the product **8** obtained by the singlet oxygenation of **7** were found to be identical with those of DMAD adduct of **1**.

Cobalt(II)tetraphenylporphyrin (CoTPP) is known to catalyze the rearrangement of unsaturated bicyclic endoperoxides[5]. Foote[6] used CoTPP to catalyze the rearrangement of monocyclic endoperoxides and obtained furans. Following the same methodology we prepared furans **5** and **9** in quantitative yield by the treatment of the peroxides **4** and **8** with 5-10 mol % CoTPP in chloroform.

The reaction of 1 with alkenes and quinones are being further studied.

ACKNOWLEDGMENT : We are greteful to the Turkish Scientific and Technical Research Council (TÜBİTAK Grant No.TBAG-973) for financial support.

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(Received in UK 15 June 1992)