$3H$-2,1-Benzoxathiole-1,1-dioxide, an Unusual By-Product from the Jacobsen Reaction[1]

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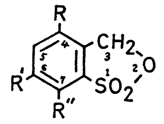
Since the discovery of the non-conventional chlorination of hexamethylbenzene,[2] substitution on the alkyl side-chain of polyalkyl aromatics under ionic conditions has been a problem of interest. However, the character and scope of the unusual reaction have not yet fully been understood because of the paucity of relevant findings.[3] We would like to report on an example of anomalous substitution product, *3H-2,1-benzoxathiole-1,1-dioxide*, which has been obtained from the Jacobsen reaction of some dichloroxylenes and monochlorotrimethylbenzenes.

2,5-Dichloro-*p*-xylene was dissolved in 20%-fuming sulfuric acid and the dark mixture was kept at 65—70°C for 14 hr to complete isomerization. Quenching with water, extraction of the insoluble part with ether and the subsequent removal of the solvent gave a light brown crystalline solid which was recrystallized from ethanol to yield white needles (*ca.* 1—2%), mp 170—171°C. The elemental analysis was in good agreement with the composition $C_8H_6Cl_2O_3S$ (M= 253; Found: C, 37.98; H, 2.30; O, 19.24; S, 12.34%. Calcd for $C_8H_6Cl_2O_3S$: C, 37.94; H, 2.37; O, 18.97; S, 12.65%); its mass spectrum showed revealing fragment ion peaks at m/e 252, 187, 176, 159, 141, and 125. Its infrared spectrum (KBr disk) contained absorptions at 755, 870, 896, 975, 1120 (CH_2-O), 1191 (SO_2), 1242, 1278, 1358 (SO_2), and 1453 cm^{-1}. Its ^1H NMR spectrum (100 MHz, $CDCl_3$) exhibited three singlet peaks at 7.51 (CH_3), 4.60 (CH_2), and 2.45 τ (aromatic H) of relative intensities 3 : 2 : 1. The elemental analysis and spectral data were compatible only with the structure of dichloro-methyl-$3H$-2,1-benzoxathiole-1,1-dioxide, and ^1H NMR spectral comparison with the reference compounds allowed for the ring substituents to be arranged as shown in formula I (R=R′ ′=Cl, R′=CH_3). Similar products were obtained from 4,5-dichloro-*o*-xylene and 4,6-dichloro-*m*-xylene in a smaller amount.



(I)

Ease of the formation of the cyclic ester seems to depend on the orientation of substituents. Thus, 5-chloropseudocumene gave a mixture of three isomeric sultones, of which 4-chloro-6,7-dimethyl-3H-2,1-benzoxathiole-1,1-dioxide (I, R=Cl, R′=R″ =CH_3) was the major component, while chloromesitylene and 5-chlorohemimellitene did not afford any detectable amount of ester but were mostly converted into intractable polymeric substance. Some physical properties of these cyclic esters are summarized in the Table. A noteworthy feature of these products is the preferential sulfo-oxylation on the methyl group attached to the more positively polarized ring carbon ortho to chlorine atom. Similar trends have been observed in the diarylmethane formation,[4] as well as the side-chain nitro-oxylation of polyalkylbenzene derivatives.[5] The sultones were usually formed in a small amount and their separation from the accompanying polymeric by-product was often troublesome. The cyclic ester may share the intermediate with diarylmethane,[6] but the mode of its formation is not clear at present.

TABLE 1. PHYSICAL PROPERTIES OF SOME $3H$-2,1-BENZOXATHIOLE-1,1-DIOXIDES FORMED IN THE JACOBSEN REACTION OF DICHLOROXYLENES AND MONOCHLOROTRIMETHYLBENZENES[a)]

$3H$-2,1-Benzoxathiole-1,1-dioxide (I)			Mp (°C)	^1H NMR spectra ($CDCl_3$, τ)		
R	R′	R″		Aromatic H	CH_2	CH_3
CH_3	Cl	Cl	205—211	2.45	4.65	7.73
Cl	Cl	CH_3	213—214	2.36	4.64	7.40
Cl	CH_3	CH_3	172—173	2.53	4.60	7.75 7.40
CH_3	Cl	CH_3		2.53	4.60	7.60 7.47
CH_3	CH_3	Cl		2.63	4.67	7.57 7.57

a) The orientation of substituent groups has been assigned on the basis of ^1H NMR spectral comparison with reference compounds.

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[1] The Reaction of Polysubstituted Aromatics. Part XXVIII. Part XXVII: This Bulletin, **45**, in press (1972).

[2] E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Amer. Chem. Soc.*, **87**, 3953 (1965).

[3] Formation of the side-chain substituted products has so far been reported in the nitration, chlorination, bromination, sulfonation and positive hydroxylation of certain polyalkylbenzenes and their derivatives.

[4] H. Suzuki, This Bulletin, **42**, 2618 (1969).

[5] H. Suzuki and K. Nakamura, *ibid.*, **44**, 227 (1971); H. Suzuki, K. Nakamura, and M. Takeshima, *ibid.*, **44**, 2248 (1971).

[6] H. Suzuki and Y. Tamura, *Chem. Commun.*, **1969**, 244.