Tetrahedron Letters No.8, pp. 651-654, 1969. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF BROMOSULTONES

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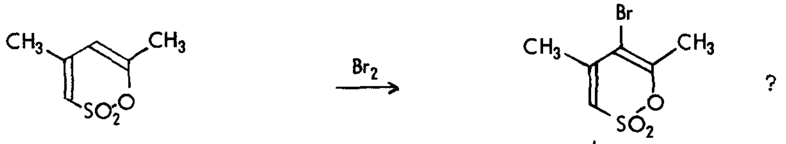
(Received in USA 20 November 1968; received in UK for publication 16 January 1969)

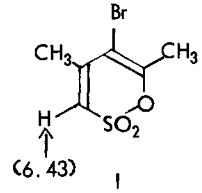
In connection with our studies on the use of furans in organic synthesis, it was desirable to prepare the known bromosultone I (1). Treatment of the sultone of mesityl oxide, II, with one equivalent of bromine as described (2) gave material isolated in 63% yield by column chromatography (3) (Silicar CC7, 200-300 mesh; eluant, 1:4 = ether: pet ether). It had the following characteristics: m. p. 77-78° (reported m. p. 74-75° (2)); $\lambda_{max}^{CHCl_3}$ 8.72, 7.33 ($-SO_2-O-$) and 6.04 ($>C=C<$) μ; $\lambda_{max}^{CHCl_3}$ 278 mμ (ε 7390); the nmr spectrum (deuterochloroform solution) showed absorption for one proton as a singlet at δ = 5.72 ppm (-CH=) and for six protons as a singlet at 2.09 ppm (allylic $-CH_3$'s) (4).



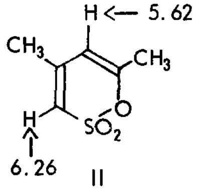
II I

Having on hand nmr spectra of several other sultones, we became convinced that the compound does not have the 5-bromo structure I tentatively assigned (2). The following nmr data is relevant:

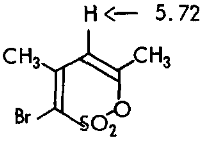
Chemical shifts in ppm downfield from TMS



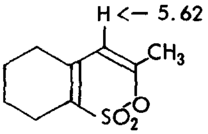
I



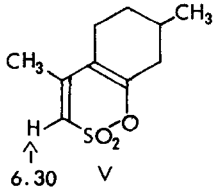
II



III



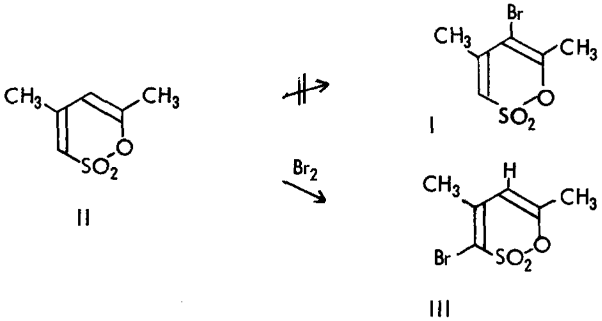
IV



V

An initial assignment of the ring protons in II was made by comparison with compounds IV and V (5). It was apparent that the lone vinyl hydrogen atoms at 5.62 and 6.30 ppm in IV and V correlated, respectively, with the vinyl hydrogens in II at positions 5 and 3. Since the bromosultone obtained had its vinyl hydrogen at 5.72 ppm, we reasoned by analogy that the hydrogen at position five had been preserved during the bromination reaction, being shifted a little upfield from 5.62 ppm. Accordingly, we assigned to this bromosultone structure III. Inherent in this line of reasoning, of course, was the assumption that a replacement of either ring hydrogen atom of II by bromine would not have a large effect upon the chemical shift of the remaining hydrogen.

Suspecting at this point that the sultone (II) of mesityl oxide, with one equivalent of bromine, undergoes a substitution reaction in the three position to produce the bromosultone III, and thus being unable to obtain the desired bromosultone I, an unambigous synthesis of I was undetaken.



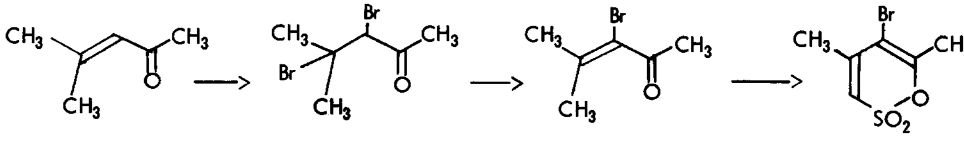
II

I

III

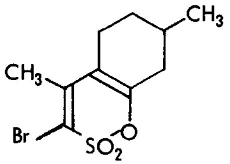
Mesityl oxide (VI) was first converted into 3-bromomesityl oxide (VII) by a method similar to that of Doeuvre (6). Bromination of mesityl oxide in pentane, careful removal of the solvent <u>in vacuo</u>, treatment of the residue with one equivalent of KOH in 80% ethanol, followed by a water/methylene chloride workup afforded as a colorless oil, 3-bromo-4-methyl-3-pentene-2-one: b.p. 58-61°/10 mm (reported b.p. 70°/18 mm (6)). The nmr spectrum (carbon tetrachloride solution) showed three, three-proton singlets at 1.99, 2.02 and 2.38 ppm. When this bromomesityl oxide was treated with acetic anhydride-sulfuric acid (7), bromosultone I could be isolated (8) in 3% yield by column chromatography (200-300 mesh Silicar CC7; eluant, 1:9 = ether: pet ether). Recrystallization from ether-pentane afforded material with the following characteristics (9): m.p. 62-63°; $\lambda_{max}^{CHCl_3}$ 8.75, 7.44 (-SO_2-O-), and 6.19 ($>$C=C$<$)μ ; $\lambda_{max}^{CHCl_3}$ 285 mμ (ϵ 3780). The nmr spectrum (deuterochloroform solution) showed absorption for six protons as two singlets at 2.16 and 2.34 ppm (allylic CH_3's) and for one proton as a singlet at 6.43 ppm (-CH=C$<$). Thus our earlier assumption about the nmr of authentic I was confirmed; and both possible isomeric bromosultones from mesityl oxide have been synthesized and characterized.

Unambiguous Synthesis of I

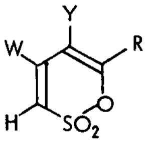


VI VII I

Preliminary evidence seems to indicate that facile substitution of bromine in the free, three position of dienic sultones is a general phenomenon. Bromination of the sultone of pulegone affords VIII, m.p. 107-109°; $\lambda_{max}^{CCl_4}$ 8.48, 7.25 ($-SO_2-O-$) and 6.07 ($>C=C<$)μ ; $\lambda_{max}^{CHCl_3}$ 284 mμ (ϵ 8740)(10). The nmr spectrum (deuterochloroform solution) showed absorption for three protons as a singlet at 2.09 ppm, (allylic CH_3), for three protons as a doublet at 1.03 ppm ($>CH-C\underline{H}_3$), and for seven protons as complex multiplets from 1.28 to 2.45 ppm.



VIII



IX

With regard to establishing the generality of this reaction, itshould be noted that there are no published examples of a dienic sultone having more than two hydrogens attached directly to the ring. Furthermore, only two types of sultone having a free, three position are known. With the synthesis of III and VIII it is established that all of these known substitution types, IX (W = R, Y = R or H), undergo bromination by substitution. Obviously, it would be desirable to study less-substituted sultones. To this end, we have devised a new general method for the synthesis of hitherto unknown, monosubstituted sultones IX (W = Y = H)(11). Further work is in progress to study the bromination of these intriguing compounds.

Acknowledgments

For financial assistance, we are indebted to the Office of General Research at the University of Georgia. Our appreciation is extended to Mr. Courtney Pape for recording NMR spectra.

REFERENCES AND FOOTNOTES

1. For the relationship of diene sultones to furans *see* T. Morel and P. E. Verkade, *Rec. trav. chim.* *67*, 539 (1948).
2. R. H. Eastman and D. Gallup, *J. Am. Chem. Soc.*, *79*, 864 (1948).
3. Chromatography improves the stability of the bromosultone remarkably; *see* reference (2).
4. NMR spectral data were, of course, unavailable at the time of the original structural assignment. Our spectra were recorded on a Varian HA 100 instrument.
5. T. Morel and P. E. Verkade, *Rec. trav. chim.* *68*, 619 (1949).
6. J. Doeuvre, *Bull. chim. soc. Fr.* *39*, 1549 (1962).
7. These are the usual reagents for sultone formation from α,β-unsaturated ketones - see reference (5).
8. Another product is eluted with ether: pet ether = 1:4. It has not yet been identified but it is definitely not a sultone.
9. *Anal.* Calcd. for $C_6H_7BrO_3S$: C, 30.14; H, 2.95. Found: C, 30.06; H, 2.97.
10. *Anal.* Calcd. for $C_{10}H_{13}BrO_3S$: C, 40.96; H, 4.46. Found: C, 40.78; H, 4.39.
11. W. E. Barnett, results to be published.