Tetrahedron Letters No. 16, pp. 1051-1054, 1963. Pergamon Press Ltd.
Printed in Great Britain.

NOVEL SIX-RING COMPOUNDS VIA THE REACTION OF KETENE DIETHYLACETAL WITH METHANESULFONYL CHLORIDE

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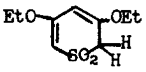
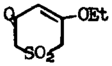
(Received 10 April 1963)

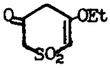
In an earlier communication[1] we reported the synthesis of a four-membered-ring sulfone by the reaction of methanesulfonyl chloride, ketene diethylacetal, and triethylamine. The present report concerns the reaction of methanesulfonyl chloride with two equivalents of ketene diethylacetal in the absence of base to yield 3,5-diethoxy Δ^2, Δ^4 -thiacyclohexadiene-1, 1,-dioxide (I). McElvain[2] had reported a similar cyclization of ketene diethylacetal in the presence of hydrogen flouride to produce 1,1,3,3,5,5 hexaethoxycyclohexane, which was found to lose ethanol readily to form the triethyl ether of phloroglucinol.



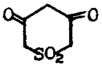
I



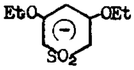
II



IIa



III



IV

Compound I was readily hydrolysed in a high yield to the mono-ketoether of either structure II or IIa. This hydrolysis product was further hydrolyzed, also in high yield, to tetrahydrothiapyran-3,5-dione-1,1-dioxide (III), which

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[1] W.E. Truce, J.J. Breiter, D.J. Abraham, and J.R. Norell, J. Am. Chem. Soc. **84**, 3030 (1962).

[2] S.M. McElvain and J.W. Lanfston, J. Am. Chem. Soc. **65**, 2239 (1943).

has been synthesized by an alternate method.[3] Compound I is sufficiently acidic to react with sodium in T.H.F. to form a deep red color with production of a gas (H_2?). The nature of the anion (probably IV) is now under investigation.

Compound I. A solution of anhydrous ether, two equivalents of ketene diethylacetal, and one equivalent of methanesulfonyl chloride under a nitrogen atmosphere at room temperature was stirred overnight. The yellow ether layer was separated from any solid which appeared, and the ether was removed under vacuum. The resulting yellow oil was evaporated at 25-30° at 1 mm. The solidified pot residue was recrystallized from anhydrous ethyl acetate and pet. ether (b.p. 65-67°) to produce a 20-25% yield of I, m.p. 119-121°. Anal. Calcd. for $C_9H_{14}O_4S$: C, 49.54; H, 6.42; S, 14.68. Found C, 49.31; H, 6.38; S, 14.43. The infrared spectrum of I was consistent with the presence of a sulfone group (7.5 μ and 8.5 μ), $>C=C<$ groups (6.1 μ and 6.3 μ) and ether linkages (9.1 μ). The NMR spectrum (in $CDCl_3$ with tetramethylsilane as the standard) is in full accord with the structure of I. There are two singlets at 5.50 δ and 5.20 δ (two vinyl protons), a quartet centered at 3.90 δ (methylene hydrogens of the ethoxyl groups) and which overlaps a singlet at 3.85 δ (ring methylene protons), and a triplet at 1.35 δ (methyl protons of the ethoxy group.) The relative areas were 1:1:6:6, respectively.

Compound II. Compound I was placed in 95% ethanol with a few drops of dilute aqueous hydrochloric acid. The mixture was heated just until solution occurred and then it was cooled. Compound II precipitated in 75% yield (higher yields by extraction), m.p. 115-116°, mixture m.p. with I 85-115°. The infrared spectrum of II was in agreement with the presence of a carbonyl group at (6.0 μ), a $>C=C<$ group (6.2 μ), and the sulfone group (7.45 μ and 8.6 μ). The "carbonyl" peak at 6.0 μ is indicative of a conjugated ketone[4], thus favoring structure II over IIa. The NMR spectrum (in $CDCl_3$ with

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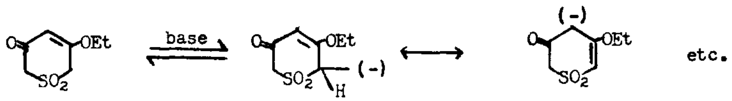
[3] E.A. Fehnel and A.P. Paul, J. Am. Chem. Soc. **77**, 4241 (1955).

tetramethylsilane as the standard) showed a singlet at $5.65\,\delta$ (vinyl proton), a quartet at $4.0\,\delta$ (methylene hydrogens of the ethoxy group), a singlet overlapping the quartet at $3.95\,\delta$ (methylene-ring protons), and a triplet at $1.4\,\delta$ (methyl protons of the ethoxy group). The relative areas were 1:6:3. The overlapping singlet in II was about twice the area of the quartet, i.e., 4:2; whereas, the overlapping singlet in I was about one-half the area of the quartet, i.e., 2:4. This is in full agreement with the structures. The NMR of II in NaOD showed only ethoxyl proton signals. The overlapping singlet at $3.95\,\delta$ and the vinyl proton at $5.65\,\delta$ had disappeared [there was a very strong signal at $4.90\,\delta$ (HOD or H_2O)]. This suggested an exchange of five acidic protons with deuterium as



Compound II slowly decolorized aqueous permanganate as well as bromine in chloroform; but the bromine reaction was fast after the addition of a drop of dilute hydrochloric acid. Compound II has a U.V. maximum at 250 $m\mu$. Anal. Calcd. for $C_7H_{10}O_4S$: C, 44.21; H, 5.26; S, 16.84. Found: C, 43.98; H, 5.49, S, 16.64.

Compound III. When compound II was dissolved in conc. hydrochloric acid and the solvent evaporated, compound III was produced in a 90% yield, m.p. 198-200° (d), soft. at 194°. The U.V. spectrum of III in 0.01 N ethanolic HCl showed a max. at 258 $m\mu$ and in 0.01 N ethanolic sodium ethoxide at 288 $m\mu$ with an isosbestic point at 271 $m\mu$. This compared to the approximated literature[3] values for III of 260 $m\mu$, 285 $m\mu$ and 270 $m\mu$, respectively. The infrared spectrum of III was that expected of a β-diketone[5] with the ketone and olefinic bands at 6.2μ and 6.3μ. The broad and weak enolic O-H band

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[4] L.J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., 1958, p. 136.

occurred at 3.75 μ which is in agreement with the literature[6]. The NMR spectrum of III in D_2O showed only a HOD or H_2O signal at 4.7 δ suggesting complete exchange of the six protons. The NMR spectrum in DMF-$CDCl_3$ solution gave three major signals at 6.5 δ , 5.75 δ, and 4.0 δ with an area of approx. 2:1:6. This suggests a mixture of the mono and dienolic forms of III. When III was placed $NaHCO_3$ it effervesced and formed a blood red color in ferric chloride which agreed with the previous report. Anal. Calcd. for $C_5H_6O_4S$: C, 37.04; H, 3.70; S, 19.75. Found: C, 37.14; H, 3.98; S, 19.60. Disemicarbazone had m.p. 252° (d). Anal. Calcd. for $C_7H_{12}N_6O_4S$: C, 30.43; H, 4.35; N, 30.43; S, 11.59. Found: C, 30.21; H, 4.09; N, 30.86; S, 11.29.

Acknowledgement. --- The authors gratefully acknowledge support of this work by the National Institutes of Health under grant No. CY-4536 and by a Public Health Service fellowship No. GPM15, 549 from the National Institutes of Health, the Division of General Medical Sciences, Public Health Service.

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[5] L.J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., 1958, p. 142.

[6] R.S. Rasmussen, D.D. Tunnicliff and R.R. Brattain, J. Am. Chem. Soc. **71**, 1066 (1949).