

Base-induced Electrocyclic Opening of Some Heterocyclic Compounds

By H. KLOOSTERZIEL,* MRS. J. A. A. VAN DRUNEN, and P. GALAMA

[Koninklijke Shell-Laboratorium, Amsterdam (Shell Research N.V.)]

Summary Dihydrofuran, dihydrothiophen and its 1,1-dioxide, and dihydrobenzoxepin lose a proton and yield open anions upon reaction with KNH_2 .

THE electrocyclization of a pentadienyl to a cyclopentenyl anion and of the all-*trans* heptatrienyl to the cycloheptadienyl anion has been reported.^{1,2} Corresponding ring openings have now been observed for a number of heterocyclic compounds.

described³ all-*trans*-anion. This anion and (IIIa) do not interconvert on being kept at room temperature for several months.

2,5-Dihydrothiophen (Ib) and its 1,1-dioxide (Ic) reacted similarly to give the open anions (IIIb) and (IIIc).

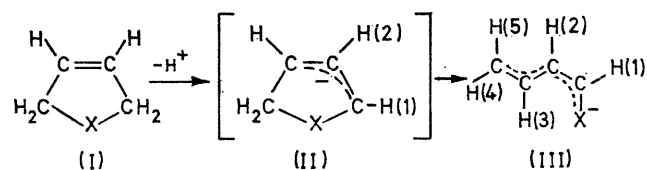
The conclusions drawn from the spectral data are confirmed by chemical evidence. Thus, addition of (Ib) to KNH_2 in NH_3 , followed by addition of methyl iodide, gives *cis*-1-methylthiobutadiene in high yield.

N.m.r. spectral data of anions (III)

X	H(1)	Chemical shifts (δ in p.p.m.)					Coupling constants (c./sec.)				
				H(2)	H(3)	H(4)	H(5)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	
O	7.32	4.30	6.82	3.86	4.22	4.5	11.0	10.2	17.2	3.3	
S	7.05	5.81	7.20	4.55	4.72	8.1	10.8	10.2	17.5	3.0	
SO_2	5.80	6.11	7.05	5.18	5.24	10	11	10	17	2	

2,5-Dihydrofuran (Ia) was added to slightly more than one equivalent of KNH_2 in liquid ammonia at -60° to -40° , and the n.m.r. spectrum of the resulting solution was recorded at -60° within 10 min. It was found that (Ia) had been completely converted to an anion (five protons). The spectrum cannot be ascribed to the dihydrofuran anion (IIa)—which would in any case be too strong a base to occur to any extent in liquid ammonia—since H(1) of (IIa) should appear at high field (due to the negative charge) as a doublet due to coupling with H(2) (at low field). In fact it is the signal at lowest field ($\delta = 7.32$) that is a doublet (due to coupling with the proton at $\delta = 4.30$). The data (Table) are consistent with the assignment of the *cis*-1, *trans*-2-butadienyl anion structure (IIIa) to the anion.

The anion (IIIa) is a geometrical isomer of the previously



a: X=O; b: X=S; c: X=SO₂

The ring of 2,3-dihydro-oxepin opens up analogously to give the *cis*-1, *trans*-2, *cis*-3, *trans*-4-hexa-1,3,5-trien-1-olate anion. This reaction is very likely similar to the crucial step in the conversion of 2,3-dihydro-1-benzoxepin by excess of sodium methoxide to *o*-*cis*-butadienyphenol.⁴

(Received, June 9th, 1969; Com. 805.)

¹ R. E. Bates and D. A. McCombs, *Tetrahedron Letters*, 1969, 977.

² H. Kloosterziel and Mrs. J. A. A. van Drunen, *Rec. Trav. chim.*, in the press.

³ G. J. Heiszwolf and H. Kloosterziel, *Rec. Trav. chim.*, 1967, 86, 807.

⁴ E. E. Schweizer, D. M. Crouse, and D. L. Dalrymple, *Chem. Comm.*, 1969, 354.