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CARBON-CARBON BOND CLEAVAGE IN AN EPOXIDE. A MINOR PRODUCT FROM THE ACID TREATMENT OF ENDRIN

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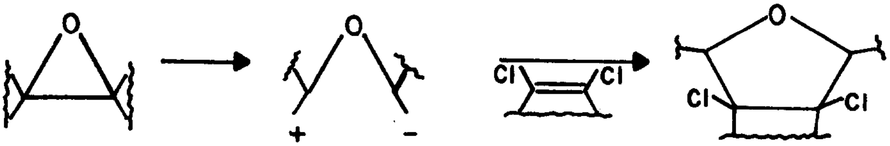
During a systematic NMR spectral examination of the transformation products of the polychlorocyclodiene insecticides, we had occassion to repeat the preparation of a number of compounds. On treatment of endrin 1 with sulfuric acid we noticed besides formation of ketoendrin 2 (2) the consistent appearance of a product (6-8%) to which we now assign structure 3a on the basis of analytical (3) and spectral data. Thus, its infrared spectrum indicated the absence of the characteristic ClC = CCl stretching frequency at 1600 cm^{-1} as well as indicating the absence of a hydroxyl or carbonyl group. Both the ^1H and ^{13}C nmr spectra suggested a symmetrical molecule. The assignments made are given in Tables 1 and 2 and compared with the nmr spectra of endrin. Of particular utility in the assignment of structure is the signal at δ93.6 in the ^{13}C nmr spectrum of 3a assigned to the 4 and 5 carbon atoms. On comparison with the signal for the same carbon atoms as endrin (δ47.2) it becomes apparent that the epoxide group is no longer present in 3a. Only this structure accounts for all the observations made.

Reaction of 3a with excess lithium aluminum hydride yielded compound 3b whose ^1H and ^{13}C nmr spectral assignments are given in Tables 1 & 2. The stereochemistry at C-11 is assigned by analogy to a similar reduction in the endrin series and on the basis of the observations that the nmr signals not affected by replacement of chlorine by hydrogen are those at positions 2 and 7 in endrin and in 3a.

The formation of 3a is of interest since it involves C-C cleavage of the epoxide followed by cycloaddition with a dichloroolefin. Such a process would appear to proceed via the carbonyl ylid 4. However, in this case the intermediacy of 4 can be questioned since both thermal and photochemical reaction of endrin failed to provide 3a in our hands, these conditions being more likely for carbonyl ylid formation (4).



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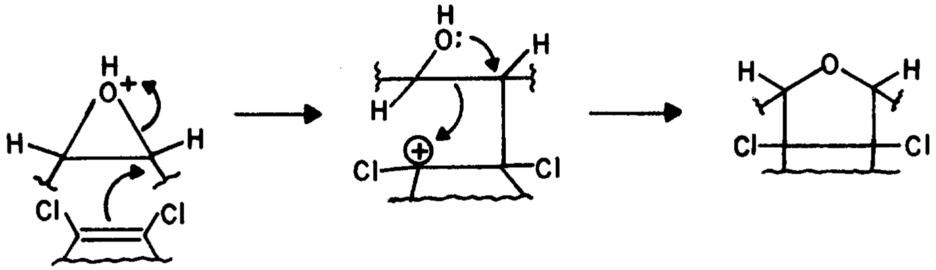
An alternate pathway utilising acid catalysis can be represented as follows:



Undoubtedly the proximity of the dichloroolefin to the strained epoxide in the cage system of endrin plays the major directing role in the reaction.

Table 1

^{1}H nmr assignments* for 3a, 3b, endrin (1) and 11-exo-dechloro-endrin

COMPOUND

SIGNAL	3a	3b	Δδ	ENDRIN(1)	11-dechloro	Δδ
H-2/H-7	3.25	2.98	-0.27	3.23	3.00	-0.23
H-3/H-6	2.88	2.89	0.01	2.89	2.92	0.03
H-4/H-5	4.80	4.62	-0.18	3.30	3.34	0.04
H-12a	1.95	1.87	-0.08	0.93	0.91	-0.02
H-12s	1.43	1.32	-0.11	1.79	1.77	-0.02
H-11	-	4.60	-	-		

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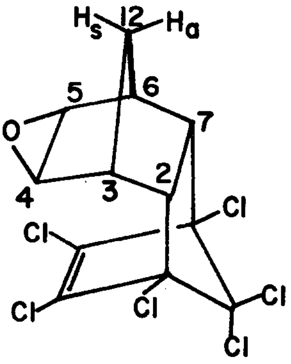
*δ in $CDCl_3$.ref. TMS. Assignments checked by decoupling.

Table 2

^{13}C nmr assignments* for 3a, 3b, endrin(1) and 11-exo-dechloro-endrin

			COMPOUND					
SIGNAL	3a	$^1J(^{13}C-^1H)/Hz$	3b	$^1J(^{13}C-^1H)Hz$	ENDRIN(1)	$^1J(^{13}C-^1H)Hz$	11-exo-dechloro-endrin	$^1J(^{13}C^1H)Hz$
C-12	27.5	136.3	27.2	136.3	29.9	140.3	29.7	139.9
C-4/C-5	93.6	164.1	92.5	162.4	47.2	192.9	46.9	194.0
C-3/C-6	57.4	152.3	55.8	150.2	54.7	144.4	55.7	141.0
C-2/C-7	40.4	143.5	41.5	144.0	39.3	149.5	39.5	154.9
C-1/C-8	79.2		73.2		79.6		WITH $CDCl_3$	
C-10/C-9	87.8		90.1		132.5		131.2	
C-11	100.0		76.6	163.6	108.8		87.7	166.0

*δ (ppm/TMS/$CDCl_3$)



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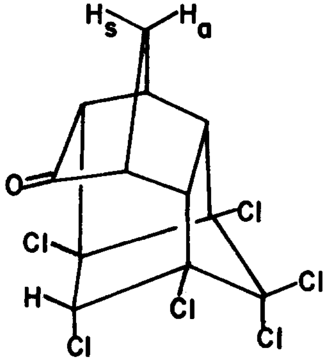

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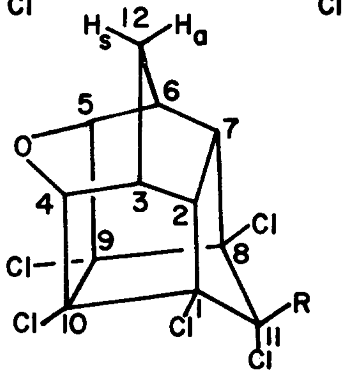

3aR=Cl
bR=H

Numbering assigned by analogy to endrin only (5)

References and Notes

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3. m.p. 286°, M^+ (mass spectral 378). Anal. C, 37.93; H, 2.12; 0, 4.20; Cl, 55.57; $C_{12}H_8OCl_6$ requires C, 37.84, H, 2.12, 0,4.30, Cl, 55.9.
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5. The systematic name for 3a is 2,3,4,4,5,6 - hexchloro-12-oxapentacyclo $[5.4.1.1.^{8,11}0^{3,10}.0^{5,9}]$ tridecane. We thank Prof. P.M. Laughton for his assistance in this matter.

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