280. *Detection of the Epoxide Group by Infrared Spectroscopy.*

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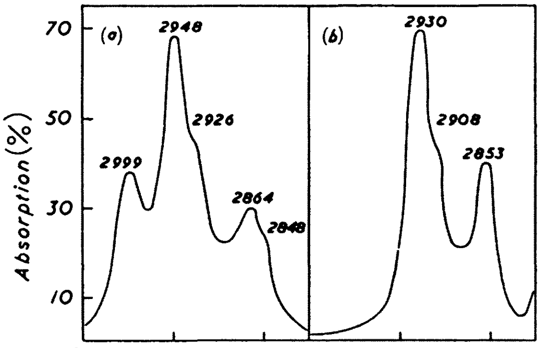
For partially alkylated ethylene oxides of moderate molecular weight a characteristic C–H stretching band can be detected in the 3050—2990 cm.$^{-1}$ region of the infrared spectrum. Correlations between band position and epoxide structure are discussed.

The need for reliable methods of diagnosing the presence of epoxide groups in organic molecules has prompted many efforts to utilise infrared measurements for this purpose.[1] Various regions of the spectrum between 1300 and 650 cm.$^{-1}$ have been studied but, although some success has been achieved in relating certain bands to various types of epoxide structures, no general correlations have emerged. The reasons for this failure have been discussed.[1c]

Recent work on a related problem, detection of the *cyclo*propane group,[2] has shown that more reliable information can be obtained from the 3000 cm.$^{-1}$ region. It is known that decreasing the ring size of alicyclic systems increases the C–H stretching frequencies of the constituent methylene groups, and in derivatives of *cyclo*propane this leads to stretching bands sufficiently well separated from the main C–H absorption to appear as distinct peaks at about 3045 cm.$^{-1}$. With this in mind we examined the spectra of epoxides shown in the Table over the 3200—2800 cm.$^{-1}$ region.

Table.—Most of the compounds were examined in CCl_4 solution on a Perkin-Elmer model 21 double-beam spectrometer fitted with a calcium fluoride prism : those marked * refer to CS_2 solutions and a sodium chloride prism. (The close correspondence between the results for a few cases studied under both conditions shows that the higher resolution of a calcium fluoride prism is not necessary for the correlations discussed below.) The figures in parentheses are molecular extinction coefficients (mole^{-1} l. cm.$^{-1}$). No intensity values are given for shoulders (sh) on the sides of main bands.



a, 1 : 2-*Epoxy*cyclo*hexane.*
b, cyclo*Hexane.*

Compounds 1—7 have a 1 : 2-disubstituted epoxide group attached to an acyclic nucleus (Ia) or to a *cyclo*hexane ring (Ib), and in each case there is a separate peak (~3000 cm.$^{-1}$) on the high-frequency side of the main group of C–H stretching bands (2985—2850 cm.$^{-1}$). This peak is absent in corresponding substances lacking the epoxide function, as is made clear (see Figure) by comparing *cyclo*hexene oxide (no. 4) with *cyclo*hexane. When the

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[1] See, *inter al.*, (*a*) Field, Cole, and Woodford, *J. Chem. Phys.*, 1950, **18**, 1298; (*b*) Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 277; (*c*) Günthard, Heusser, and Fürst, *Helv. Chim. Acta*, 1953, **36**, 1900; (*d*) Patterson, *Analyt. Chem.*, 1954, **26**, 823.

[2] For leading references see (*a*) Wiberley and Bunce, *ibid.*, 1952, **24**, 623; (*b*) Slabey, *J. Amer. Chem. Soc.*, 1954, **76**, 3604; Cole, *J.*, 1954, 3807, 3810.

Infrared frequencies ($cm.^{-1}$) *of epoxides* (*intensities in parentheses*).

No.	Compound	Epoxide bands		Other CH stretching bands					
1	1 : 2-Epoxypropane (III; R = H)	3050 (30)	3000 (60)	2975 sh		2931 (30)			
2	1 : 2-Epoxy-2-methylpropane (III; R = Me)	3045 (30)		2981 (70)	2972 (75)	2935 (40)	2922 (40)		
3	*trans*-3 : 4-Epoxyhexan-1-ol *		2990 (110)		2955 (80)		2905 (40)		
4	1 : 2-Epoxy*cyclo*hexane		2999 (80)			2948 (190) 2926 sh			2864 (60) 2848 sh
5	*cis*-2 : 3-Epoxy*cyclo*hexanol		3004 (45)			2949 (105)			2866 (35) 2850 sh
6	3 : 4-Epoxy*cyclo*hexanol * †		3002 (60)			2942 (95)			2858 (20)
7	3 : 4-Epoxy*cyclo*hexyl acetate * †		2995 (55)		2955 (55)				
8	1 : 2-Epoxy*cyclo*pentane	3037 (45)		2980 sh	2963 (80)	2927 (55)			2856 (25)
	bicyclo[2 : 2 : 1]*Heptane derivatives* (IV).								
9	R = OH *	3033 (35)		2975 (125)			2910 (50)		
10	R = OAc *	3031 (35)		2977 (115)				2880 (15)	
11	R = CO_2Me *	3029 (40)			2955 (205)	2940 sh			2871 (25)
12	R = $CH_2{\cdot}OAc$ *	3031 (45)			2970 (140)			2880 (40)	
	Steroids.								
13	2α : 3α-Epoxycholestane	Not detectable			2955 sh	2939 (635)			2874 (250) 2856 sh
14	5α : 6α-Epoxycholestane	,,	,,			2940 (670)	2910 sh		2868 (320)
15	5β : 6β-Epoxycholestane	,,	,,			2945 (645)	2915 sh		2870 (320)

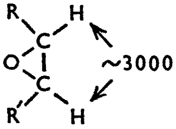
* NaCl prism, CS_2 solution. † Mixture of *cis* and *trans* isomers.

Materials: Nos. 3, 6, 7 and 9—12, Henbest and Nicholls, unpublished work; 5, Henbest and Wilson, *Chem. and Ind.*, 1956, 659; the remainder were prepared by published methods.

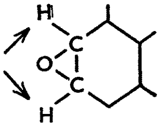
oxide group is fused to a five-membered ring (II) (nos. 8—12) a similar characteristic band appears, but at higher frequency (~3035 cm.$^{-1}$). [Formulæ (Ia), (Ib), and (II) are used to represent compounds 1—12, the *bicyclo*heptane group being considered for the present purpose as more closely related to *cyclo*pentane than to *cyclo*hexane.]

From the Figure it can be seen that the epoxide band is superimposed on a rising background which develops into the main C–H stretching bands. It is to be expected therefore that as the relative intensity of the main group increases, it will be more difficult to pick out the epoxide band. An example of this increase occurs when the epoxide ring is included in polycyclic systems such as steroids (compounds 13—15). Here there are more methyl and methylene groups for each epoxide unit and at comparable concentrations the epoxide peak is " swamped " by the main (broad) C–H bands which, although reaching their maxima below 2950 cm.$^{-1}$, have strong and rapidly rising absorptions at 3000 cm.$^{-1}$. Thus the failure to detect an epoxide band in 2α : 3α-epoxycholestane (Ib; no. 13) is not surprising: it does, of course, limit the applicability of the correlation to compounds with a reasonable (at present, unspecified) epoxide : methyl–methylene ratio.

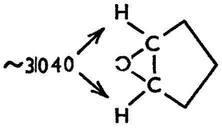
Although the vibrations responsible for the epoxide bands listed in the Table cannot be identified with certainty the results show that systematic correlations between band position and epoxide environment are to be expected. Probable assignments (see formulæ) can be developed as follows. The epoxide bands almost certainly arise from the C–H stretching vibrations of methylene and methine groups contained in epoxide rings (*i. e.*, –CH_2·O– and $>$CH·O–). In compounds 3—7 the epoxide rings are connected to unstrained systems and contain only the latter (methine) type of group. The band occurring at about 3000 cm.$^{-1}$ in each case may then be ascribed to epoxy-methine C–H stretching. When the methine groups are linked to the more strained *cyclo*pentane and *bicyclo*heptane nuclei (compounds 8—12) the frequency is raised to 3040—3030 cm.$^{-1}$. This increase is paralleled by a similar situation found in the olefinic C–H stretching frequencies of different types of 1 : 2-disubstituted *cis*-ethylenic centres: thus acyclic *cis*-olefins and *cyclo*hexene derivatives give bands near 3020 cm.$^{-1}$, whereas *cyclo*pentene and *bicyclo*heptene compounds absorb at higher frequencies (3075—3045 cm.$^{-1}$).[3]



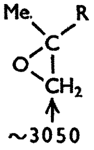
(Ia)



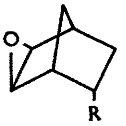
(Ib)



(II)



(III)



(IV)

The frequencies of these epoxy-methine bands are higher than those of normal methine groups which have weak stretching bands around 2900 cm.$^{-1}$. Two separate factors may contribute to this effect, *viz.*, inclusion of the methine group in a three-membered ring, and direct attachment to oxygen. [That an increase should be caused by placing the methine group in a small ring is reasonable by analogy with the corresponding shifts in the bands of cyclic methylene groups.[4] Support for the oxygen's effect is found in the higher frequencies of methine groups in acyclic ethers ($>$CH·O–) than for hydrocarbons.[5]]

Propylene oxide (no. 1) containing a methine and a methylene group in an epoxide ring gives two peaks. From the results with compounds 1—5 it seems reasonable to associate the 3000 cm.$^{-1}$ band again with the methine group: the intensity of the band is approximately half that shown by the other open-chain epoxide (no. 3) containing *two* methine groups. The second band (3050 cm.$^{-1}$) of propylene oxide corresponds closely with the single peak (3045 cm.$^{-1}$) of *iso*butylene oxide (no. 2), and the bands are therefore attributed

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[3] Henbest, Meakins, Nicholls, and Wilson, *J.*, 1957, 997.
[4] Roberts and Chambers, *J. Amer. Chem. Soc.*, 1951, **73**, 5030.
[5] Pinchas, *Analyt. Chem.*, 1955, **27**, 2.

to the epoxy-methylene group present in both compounds. It is to be noted that such a simple analysis cannot be applied to a highly symmetrical molecule such as ethylene oxide where the C–H vibrations are strongly coupled. Thus ethylene oxide, previously studied in the vapour state,[6] gives a complex spectrum in CCl_4 solution with bands at 3018 (35), 3002 (35), 2959 (10), and 2922 (20) cm.$^{-1}$.

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[6] Thompson and Cave, *Trans. Faraday Soc.*, 1951, **47**, 946.