

377. The Nuclear Magnetic Resonance Spectra of Some Vinyl Ethers.

By J. FEENEY, A. LEDWITH, and L. H. SUTCLIFFE.

The ^1H nuclear magnetic resonance spectra of eleven alkyl vinyl ethers have been obtained at 16.2 and 40.00 Mc./sec., and the spectral parameters have been evaluated by means of an ABC-type analysis. The coupling constant between the geminal vinyl hydrogen atoms has been correlated with the electron-withdrawing power of the alkyl group. No evidence for rotational isomerism was found.

ALTHOUGH the alkoxy-group is electronegative, it shows a strong mesomeric effect when adjacent to an unsaturated linkage. This effect results in vinyl ethers' being susceptible to electrophilic attack. For example, crystalline isotactic polymers of high molecular weight can be obtained by cationic polymerisation.¹ Infrared,² Raman,³ and nuclear magnetic resonance spectroscopy^{4,5} have all been used to study the influence of alkoxy-groups on vinyl systems. Vinyl ethers might show rotational isomerism (cf. Ia, b) result-



from the partial double-bond character in the C-O bond. Both rotational isomerism and electron-attracting properties of substituents are probably important in understanding the mechanism of stereospecific polymerisation of vinyl ethers.⁶ In the present investigation by high-resolution nuclear magnetic resonance spectroscopy the aim was to obtain more detailed information about these factors by examining a group of closely related compounds.

EXPERIMENTAL

Materials.—Cyclohexyl, furfuryl, methyl, t-butyl, and isopropyl vinyl ether were kindly presented by British Oxygen Company, Morden, Surrey. They were redistilled before use. The n-butyl, ethyl, 2-ethylhexyl, i-butyl, and 2-chloroethyl derivatives were obtained from Light and Company and were fractionally distilled before examination. The decalin compound was generously provided by Dr. J. Rasburn of Manchester College of Science and Technology.

Spectroscopy.—The ^1H resonance spectra were obtained at both 40.00 and 16.2 Mc./sec. by using a Varian V4300B spectrometer. Tetramethylsilane (5%) was added as an internal reference to the liquids before they were sealed in Pyrex tubes of 5 mm. outside diameter. At least three recordings of each spectrum were made and absorption-band separations were measured by means of the side-band technique.⁷ 2-Ethylhexyl vinyl ether was examined over the temperature range $+100^\circ$ to -100° with the aid of a temperature-controlled probe similar to that described by Brownstein.⁸

RESULTS

All the compounds gave typical ABC-type⁹ spectra, in agreement with previous work reported on vinyl ethers;^{4,5,10} part of the ^1H resonance spectrum of i-butyl vinyl ether measured

¹ Schildknecht, *Ind. Eng. Chem.*, 1958, **50**, 107; Natta, Dall'Asta, Mazzanti, Giannini, and Cesca, *Angew. Chem.*, 1959, **71**, 205; Vandenberg, Heck, and Breslow, *J. Polymer Sci.*, 1959, **41**, 519.

² Bray and Tarrant, *J. Amer. Chem. Soc.*, 1957, **79**, 6533; Potts and Nyquist, *Spectrochim. Acta*, 1959, **9**, 629.

³ Batner, *Bull. Acad. Sci. U.S.S.R.*, 1947, 123.

⁴ Banwell and Sheppard, *Mol. Phys.*, 1960, **3**, 351.

⁵ Brugel, Ankel, and Fruckeberg, *Z. Elektrochem.*, 1960, **64**, 1121.

⁶ Bawn and Ledwith, unpublished work.

⁷ Arnold and Packard, *J. Chem. Phys.*, 1951, **19**, 1608.

⁸ Brownstein, *Canad. J. Chem.*, 1959, **37**, 1119.

⁹ Bernstein, Pople, and Schneider, *Canad. J. Chem.*, 1957, **35**, 65.

¹⁰ Bishop and Richards, *Mol. Phys.*, 1960, **3**, 114.

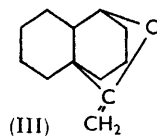
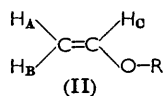
at 40.00 Mc./sec. is reproduced in the Figure, and the chemical shifts of the absorption bands in the spectrum are given in Table I.

TABLE I.

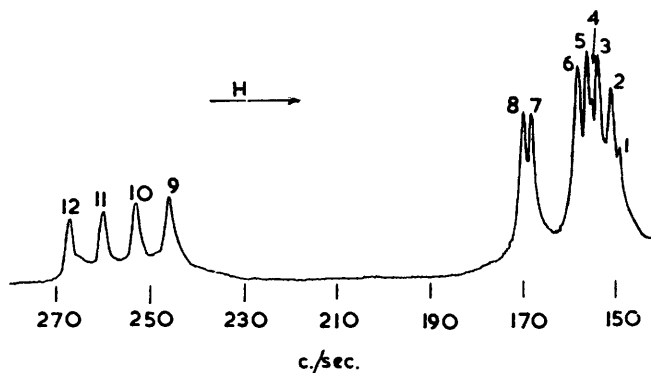
Frequencies of the ABC part of the 40.00 Mc./sec. ^1H resonance spectrum of *i*-butyl vinyl ether. The bands are to low fields of the internal reference, tetramethylsilane.

Band no.	1	2	3	4	5	6	7	8	9	10	11	12
Frequency (c./sec.)...	150.0	151.6	154.6	156.3	157.0	158.8	169.2	170.7	247.6	254.0	261.0	268.0

Designating the molecules as (II), it was possible to evaluate the coupling constants J_{AB} , J_{AC} , and J_{BC} and the chemical shifts τ_A , τ_B , and τ_C by use of the iterative method described by Reilly and Swalen.¹¹ The relative signs of the coupling constants were decided from a comparison of the observed and the calculated intensities of bands derived from different



combinations of the signs of the coupling constants. Unfortunately, a change in the relative sign of J_{AB} brings about only small changes in intensity; our results agree with those of other workers,^{4,5,12} who report negative values of J_{AB} in vinyl ethers.



The ^1H resonance spectrum obtained at 40.00 Mc./sec. for the vinyl group in *i*-butyl vinyl ether.

DISCUSSION

The chemical shifts of the terminal ethylenic hydrogen atoms are all 20–30 c./sec. to higher fields than the ^1H resonance bands of simple olefins. This increase in shielding is evidence for the reduction of double-bond character in the vinyl grouping.^{4,10} The terminal hydrogen atoms of the decalyl vinyl ether (III) possess the normal chemical shift of a terminal ethylenic group. Here, the alkoxy-group cannot transmit its influence because twisting of the $=\text{C}-\text{O}-\text{C}$ grouping is required in order that π -orbitals may overlap with the sp^3 -lone pairs of the oxygen atom. In the decalyl derivative, such twisting is prevented completely by ring strain.

Karplus *et al.*¹³ have shown that the coupling constant between geminal hydrogen atoms increases as the s -character of the carbon atom between them decreases. Hence

¹¹ Reilly and Swalen, *J. Chem. Phys.*, 1960, **32**, 1378.

¹² Castellano and Waugh, *J. Chem. Phys.*, 1961, **34**, 295.

¹³ Karplus, Gutowsky, and Grant, *J. Chem. Phys.*, 1958, **31**, 1278.

the J_{AB} values can be used as a guide to the hybridisation of the terminal vinyl carbon atom, which is an indication of the degree of resonance present. Apart from the decalin derivative, the vinyl ethers have been arranged in Table 2 with the electron-withdrawing power of the alkyl groups increasing from top to bottom. It will be seen that the decrease of J_{AB} from one compound to another follows this order closely: Banwell and Sheppard⁴ obtained similar results for a more widely differing series of vinyl compounds. Thus resonance effects are strongest when the alkyl group is most electropositive. The differences in the chemical shifts of the respective vinyl hydrogen atoms are seen to be small and no correlation with degree of resonance is possible. However, in ordinary vinyl compounds the hydrogen atoms *cis* and *trans* to the substituent are shielded to different extents, the *trans*-position being affected most by the substituent.¹⁴ The magnitude of the chemical-shift difference, $\tau_A - \tau_B$, between the terminal hydrogen atoms is seen to diminish with

TABLE 2.
¹H Spin-spin coupling constants (c./sec.) and chemical shifts (τ values)
 for molecules (II).

R	J_{AB}	J_{AC}	J_{BC}	τ_A	τ_B	τ_C	$\tau_A - \tau_B$
"Decalyl" *	± 1.2	—	—	5.65	5.12	—	0.525
t-Butyl	-0.1	6.2	13.2	6.15	5.80	3.72	0.355
iso-Propyl	-1.2	6.9	13.7	6.12	5.85	3.75	0.264
Cyclohexyl	-1.6	5.7	14.7	6.15	5.90	3.87	0.266
Furfuryl	-1.9	6.6	14.2	6.15	5.90	3.60	0.252
2-Ethylhexyl	-1.8	6.1	12.9	6.20	5.95	3.60	0.249
i-Butyl	-1.7	6.3	14.2	6.12	5.93	3.56	0.190
n-Butyl	-1.8	6.9	14.4	6.05	5.85	3.47	0.190
Ethyl	-1.7	6.9	14.9	6.12	5.93	3.55	0.187
Methyl	-2.2	6.6	14.4	6.15	6.00	3.62	0.154
2-Chloroethyl	-2.7	6.6	16.2	5.95	5.83	3.50	0.120

* The *cis* coupling constant, J_{AC} , is arbitrarily taken as positive, and the signs of the other two coupling constants in a particular molecule are quoted with reference to this. J values are precise to ± 0.2 c./sec. τ values are precise to ± 0.05 p.p.m.

increasing electron-withdrawing power of the alkyl group. This correlation appears to be in opposition to that found from the J_{AB} values, but the understanding of the origin of the latter is more soundly based.

Resonance effects in vinyl ethers, as represented by structures (Ia and b) will, of course, be most favourable when the olefinic π -orbital and a lone-pair p -orbital on the oxygen atom are coplanar. Inspection of molecular models shows that this condition is most readily available in the case of the methyl vinyl ether. For all other vinyl ethers, however, such coplanarity requirements are more difficult to satisfy owing to steric interaction between the alkyl substituent (R) and the H_C atom. If this steric effect were the only consideration then the resonance effect should be greatest for methyl vinyl ether and least for t-butyl vinyl ether. The results presented here show this expected steric inhibition of resonance to be of minor importance—on the assumption that the correct sign has been given to the J_{AB} values.

The infrared investigation of 2-ethylhexyl vinyl ether carried out by Bray and Tarrant² led to postulation of two rotational isomers. Our measurements of the nuclear magnetic resonance spectrum of the compound over the temperature range $+100^\circ$ to -100° gave no indication of two conformations. It seems that if there are two isomeric forms, then the vinyl groups are shielded identically, as it is unlikely that the barrier to interconversion is too low to affect the populations of the states at -100° .

The authors are indebted to Drs. J. H. Binks and J. Lee for helpful discussion.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
 THE UNIVERSITY, LIVERPOOL.

[Received, October 3rd, 1961.]

¹⁴ Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon, London, 1959, p. 120; Reddy and Goldstein, *J. Amer. Chem. Soc.*, 1961, **83**, 2045.