J. Chem. Soc. (B), 1968

An Infrared Study of Competitive Intramolecular Hydrogen Bonding in a Series of Benzyl Alcohols

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The competitive behaviour of various π -electron systems (carbon-carbon triple bond and double bond and the benzene ring) as basic sites for intramolecular hydrogen bonding has been investigated for a series of benzyl alcohols by infrared studies.

HYDROGEN bonding, $OH \cdots \pi$, both inter- and intramolecular, is well authenticated.¹ Several π -electron

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¹ The following are representative: (a) A. Allerhand and P. von R. Schleyer, J. Amer. Chem. Soc., 1963, 85, 866; (b) V. Prey and H. Berbalk, Monatsh., 1951, 82, 990; (c) A. W. Baker and A. T. Shulgin, J. Amer. Chem. Soc., 1959, 81, 4524; (d) G. Eglinton, J. Martin, and W. Parker, J. Chem. Soc., 1965, 1243; (e) M. R. Basila, E. L. Saier, and L. R. Cousins, J. Amer. Chem. Soc., 1965, 87, 1665; (f) Z. Yoshida and E. Osawa, *ibid.*, p. 1467; (g) T. Cairns and G. Eglinton, J. Chem. Soc., 1965, 5906; (h) A. T. McPhail and G. A. Sim, Chem. Comm., 1965, 124; (i) G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960; (j) M. Tichy, Adv. Org. Chem., 1965, 5, ch. 3. systems participate in hydrogen bonding, e.g., $-C\equiv N$,^{1a} $-C\equiv C-$,^{1b}-CH=CH-,^{1c,d} and benzene rings.^{1 $\leftarrow j$}

The asymmetry and rather low frequency of the hydroxy-group stretching absorption (*ca.* 3620 cm.⁻¹) of benzyl alcohol (IX) is now interpreted ² as being due to the overlapping of two bands, one near 3632 and a more intense one at 3615 cm.⁻¹, corresponding to free OH

² (a) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, J. Amer. Chem. Soc., 1958, **80**, 6691; (b) D. S. Trifan, R. Bacskai, P. von R. Schleyer, and C. Wintner, Abstracts, 135th National Meeting of the Amer. Chem. Soc., Boston, Mass., April 1959, p. 98-O; (c) P. von R. Schleyer, C. Wintner, D. S. Trifan, and R. Bacskai, Tetrahedron Letters, 1959, No. 14, 1; (d) M. Oki and H. 1wamura, Bull. Chem. Soc. Japan, 1959, **32**, 955. [conformer (i)] and an OH $\cdots \pi$ intramolecularly bonded OH [conformer (ii)], respectively. Several α -aromatic alcohols have been shown 2b, c to exist largely or entirely in the ring bonded form in dilute carbon tetrachloride solution. Ring substituents have little effect on Δv , but affect significantly the position of the free-bonded equilibrium; 'electron-withdrawing' groups reduce the proportion of bonded conformer in the equilibrium whereas 'electron-repelling' groups in general increase the proportion of bonded conformer. This demonstrates clearly that a hydrogen bond between the hydroxygroup and the π -electrons is being formed, since the proportion of bonded conformer parallels directly the availability of the π -electrons for hydrogen bonding. It has also been shown 2d that conformer (ii), with the hydrogen bonded to C-1 of the benzene ring, correctly represents the $OH \cdots \pi$ intramolecularly hydrogen bonded species.

The present study deals with the series of benzylic alcohols (I)—(VIII), with benzyl alcohol (IX) as reference. The alcohols contain the benzyl alcohol system ortho-substituted with a CH_2-CH_2 , a cis-CH=CH, a trans-CH=CH, or a C=C, so there is the opportunity for interaction with these unsaturated groups, in addition to, or in competition with, bonding to the parent benzene ring. Furthermore, in some cases there is the possibility of interaction with the other benzene ring or the other benzyl alcohol grouping. Quite complex bands due to the hydroxy-group stretching absorptions were therefore expected, and their interpretation affords some appreciation of the energetic and steric requirements of the benzylic hydroxyl for intramolecular hydrogen bonding.

The acetylenic alcohols (I) and (II) were prepared from the corresponding benzylic bromides (Xa) and (Xb) through lithium aluminium hydride reduction of the acetates (Xd) and (Xe). They were hydrogenated, using the Lindlar catalyst, to the corresponding *cis*stilbene alcohols (III) and (IV). Refluxing of a carbon tetrachloride solution of the *cis*-alcohols (III) and (IV) with a trace of iodine furnished the *trans*-stilbene alcohols (V) and (VI), and hydrogenation of (I) and (II) over palladium-carbon gave the alcohols (VII) and (VIII).

RESULTS AND DISCUSSION

Intermolecular Hydrogen Bonding.—All the compounds were examined at various concentrations in carbon tetrachloride. In some cases, e.g., the diols (IV), (VI), and (VIII) (Figure), the lowest concentrations which could be handled still showed a band of lower intensity than that with the previous higher concentration; it was then assumed that it would disappear on further dilution and could be ascribed to an intermolecular hydrogen bond. In the case of the alcohol (I), the associated ³ (a) J. Pitha, J. Joska, and J. Fajkoš, Coll. Czech. Chem. Comm., 1963, 28, 2611; (b) A. J. Baker, G. Eglinton, A. G. Gonzalez, R. J. Hamilton, and R. A. Raphael, J. Chem. Soc., 1962, 4705; (c) W. S. Bennet, G. Eglinton, and S. Kovac, Nature, 1967, 214, 776. band is still detectable at 3mM but has completely disappeared at 0.9mM. The diols self-associate more strongly than the alcohols, and (IV), (VI), and (VIII) associate so strongly that 9-cm. cells and very dilute solutions had to be used before intermolecular bonding disappeared. The compounds presumably have OH groups which are suitably orientated for some form of cyclic complexes involving dimeric, trimeric, and tetrameric species (cf. the novolaks ^{1g}). Further studies are required to elucidate the factors which bring about abnormally persistent association of this type.³

Intramolecular Hydrogen Bonding.—Except in cases where there is abnormally persisent intermolecular association, the spectra of the alcohols and diols (Figure) in dilute solution in carbon tetrachloride are interpretable solely in terms of the various conformations adopted by the individual molecule in its solvent cage.



Proportions $\binom{0}{0}$ of individual conformers

(i)				
ÓН	(ii)	(iii)	(iv)	(v)
free	$OH \cdots ring A$	$OH \cdots X$	$OH \cdots ring B$	$OH \cdots Y$
35	40	25		
25	40	15		20
25	50	15 *	10 *	
25	50	15 *	10 *	Not obsd.
20	55	15 *	10 *	
20	55	15 *	10 *	Not obsd.
10	75		15	
20	60		10	10
35	65			
	(i) OH free 35 25 25 25 20 20 10 20 35	$\begin{array}{cccc} (i) & (ii) \\ OH & (ii) \\ free OH \cdots ring A \\ 35 & 40 \\ 25 & 40 \\ 25 & 50 \\ 25 & 50 \\ 25 & 50 \\ 20 & 55 \\ 20 & 55 \\ 10 & 75 \\ 20 & 60 \\ 35 & 65 \end{array}$	$\begin{array}{ccccccccc} (i) & (ii) & (iii) \\ OH & (ii) & (iii) \\ free OH \cdots ring A & OH \cdots X \\ 35 & 40 & 25 \\ 25 & 40 & 15 \\ 25 & 50 & 15 \\ 25 & 50 & 15 \\ 25 & 50 & 15 \\ 20 & 55 & 15 \\ 20 & 55 & 15 \\ 10 & 75 \\ 20 & 60 \\ 35 & 65 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

These percentage figures for the conformer populations (corrected to nearest 5%) can only be approximate since the extinction coefficients for the individual conformers cannot be measured. They are measured on full curves, and not for broken curves.

* Tentative assignments. \dagger The percentage figures in these cases represent a summation of the conformations of both hydroxy-groups (see text) and are obtained by treating the ε^a values as for one hydroxy-group.

The observed $\nu(OH)$ data are in Table 2 and illustrated in the Figure. Each spectrum is composed of several bands, some of which, because of their breadth or close separation, merge and produce an asymmetric band with shoulders. Nevertheless, it is possible to assign to these absorptions approximate values for the frequency (ν) , half-band width $(\Delta \nu_1^{a})$, and intensity (ϵ^a) by graphical band construction.⁴ The method is illustrated for four ⁴ M. Öki and H. Iwamura, *Bull. Chem. Soc., Japan*, 1959, **32**, 950.

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Hydroxy-group stretching absorption, ν(OH), for the alcohols (I)—(IX) in CCl₄ solution; concentrations and cell lengths are in Table 2 (a)(i) and (b)(i) (I) and (II) in CHCl₃; 15 and 6.5mM, respectively; both in 0.5-cm. cells
(a)(ii) and (b)(ii) (I) and (II) in CCl₄; 0.9 and 1.3mM, respectively; cell lengths 6 and 2 cm., respectively

An asterisk (*) denotes intermolecular association.

of the alcohols in the Figure. Such treatment is helpful in treating bands of complex shape, but is necessarily subjective and ideally requires curve analysis or curve construction with digital or analogue computers.⁵ The premise on which such band analysis is based is, of course, that a group X-H, which is vibrating in a symmetrical environment, will give rise to a symmetrical (Lorentz) absorption band.⁶

Compounds (I) and (II) were also examined in chloroform solution. Chloroform causes slight lowering and broadening of the free $\nu(OH)$ of dissolved alcohols, and reduction of self-association at a given concentration compared with that in carbon tetrachloride.⁷ The resultant broadening [Figure (a), (b)] has obliterated the environment of the two hydroxy-groups. The systematic basis for the assignments follows.

Literature studies ² give $\nu(OH)$ for benzyl alcohol as 3635 and 3618 cm.⁻¹ for conformers (i) and (ii) respectively. Benzyl alcohol (IX) provides valuable data for comparison with the alcohol (VII). The only additional basic site available to the proton for hydrogen bonding is the second benzene ring, which is attached to the first by a saturated two-carbon chain, and we can confidently suggest a mixture of conformers (i), (ii), and (iv), with the assigned ν (OH) 3648, 3611, and 3533 cm.⁻¹, respectively. All three are presumed to be interconvertible.

For the diol (VIII) the only feature additional to those

TABLE 2

Hydroxy-group	stretching	absorption	(cm1)	in CCL	solution ·	t
			(/			

	Concn. Cell (mM) (cm.)	Conformer (i)		Conformer (ii)		Conformer (iii)		Conformer (iv)			Conformer (v)						
		(cm.)	$\widetilde{\nu(OH)}$	$\Delta \nu_1^{a}$	εª	v(OH)	$\Delta \nu_1^a$	εª	v(OH)	$\Delta \nu_{i}^{a}$	εª	v(OH)	$\Delta \nu_1^{a}$	εª	v(OH)	$\Delta \nu_1^{\mathbf{a}}$	εª
(\mathbf{I})	$3 \cdot 4$	2	3637	26	30	3618		35	[3595]		20						
(ÌI)	1.3	2	3637	23	40	3617	28	65	[3580]		20				3507	90	35
ÌII	$4 \cdot 3$	2	[3635]		20	3618	18	40	`3 5 80 `*		10	[3535] *		5			
(IV)	0.8	6	[363 8]		30	3619	22	65	3585 *		20	[3535] *		10			
(V)	2.9	2	3640		15	3618	20	40	[3580] *		10	[3535] *		5			
(ÌVI)	0.4	9	3640		25	3618	23	65	3584*		20	[3535] *		15			
ÌII	0.2	9	3648		5	3611	18	50				3533		10			
III	0.2	9	[3640]		25	3618	20	80				3535	_	15	3575		15
IX)	1.5	2	[3635]		30	3618	18	60									

Figures in square brackets are only approximate owing to difficulty in measurement.

Each compound was run at several concentrations in the range 90-0.2mm with cell paths 0.05-9 cm. The results [except for (I)] are for the lowest concentration examined. Intermolecular bonding, $\nu(OH)$ ca. 3480 cm.⁻¹ (broad) was then almost completely eliminated; for example, compound (VI) has e^a ca. 2 units for this band at 0.2mm.

* Tentative assignment. $\dagger \epsilon^{a}$ to nearest 5 l. mole⁻¹ cm.⁻¹; in the case of the diols they are for the two hydroxy-groups together.



detail revealed in the carbon tetrachloride spectra for (I) and (II). Also noteworthy is the shift to lower frequency of the band due to intermolecular bonding $(\Delta v \ ca. \ 35 \ cm.^{-1})$ for (I).

Assignments for the individual absorption bands (Figure) are in Table 2, and Table 1 gives a summary of estimates of the approximate proportions of individual conformers. In the diols, where Y = OH, conformers (i)—(v) are no longer adequate representations. One of the hydroxy-groups can be treated systematically as in (i)—(v), but the other (Y) could be free, or bonded to one of the benzene rings, or bonded to the carboncarbon triple or double bond. We cannot at present estimate the proportions of the individual conformers representing the permutations of the intramolecular

in (VII) is the second hydroxy-group, and the only additional band (3575 cm.⁻¹) is presumably due to OH ··· OH intramolecular hydrogen bonding. It is surprising that the absorption is at such high frequency in view of the close approach which is possible between the two groupings. However, the low intensity is understandable in terms of the high degree of conformational freedom (cf. hexane-1,6-diol, which does not display intramolecular bonding 8).

For the acetylenic alcohol (I), the alcohol (VII) was used for comparison, and it is clear that $OH \cdots \pi$ (second aromatic ring) bonding has been eliminated, since the other aromatic ring is held rigidly at too great a distance for intramolecular bonding with the hydroxyproton ($0 \cdots C$ distance is *ca*. 4 Å from Dreiding models).

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⁵ Product Bulletin, Chem. Eng. News, 1965, 43, 50.
⁶ R. N. Jones and C. Sandorfy, 'Chemical Applications of Spectroscopy,' ed. W. West, Interscience, New York, 1956, ch. 4. Z

⁷ J. C. D. Brand and G. Eglinton, 'Applications of Spectro-scopy to Organic Chemistry,' Oldbourne Press, London, 1965. ⁶ W. F. Baitinger and P. von R. Schleyer, Abstracts, 145th

National Annual Meeting of the Amer. Chem. Soc., New York, September 1963, p. 37-Q.

The shoulder at *ca.* 3595 cm.⁻¹ is assigned as OH $\cdots \pi$ (carbon-carbon triple bond).

The diol (II), which corresponds to the previously described alcohol (I), has an additional basic site for bonding—to the OH—and the consequent $OH \cdots OH$ intramolecular hydrogen bond accounts for the prominent band at 3507 cm.⁻¹. The OH $\cdots \pi$ (carboncarbon triple bond) band is still present as a small peak at ca. 3580 cm.⁻¹ (Figure). This diol is particularly interesting, since the two benzene rings are linked by the rigid triple bond and, although free to rotate round its axis, have much less conformational freedom than those in (VIII). Of course, the CH₂OH groups are nominally free to rotate with respect to the benzene rings to which they are attached, but when both are at almost closest approach, the $O \cdots O$ distance is *ca.* 2.5 Å, and the situation appears (from models) to be ideally suited to $OH \cdots OH$ intramolecular bonding.

The carbon-carbon double bond link between the two aromatic rings introduces several new features. The rigid and cylindrically symmetrical acetylene unit of (I) and (II) is replaced by the cis- or trans-double bond. These structural changes bring about complications arising from (a) hydrogen-hydrogen interactions: steric restriction of coplanarity of the benzene ring and the double bond, (b) the directional availability of the π electrons (double bond) required for hydrogen bonding, and (c) additional conformational freedom which means that several different conformations of the interacting group are possible [e.g., in the cis-alcohol (III), the hydroxy-group could be orientated so as to produce 'free' OH, bonded $OH \cdots \pi$ (parent aromatic ring), bonded $OH \cdots \pi$ (double bond) at various angles, and OH $\cdots \pi$ (other aromatic ring), again at various angles]. The observed bands for the alcohols (III)-(VI) are in Tables 1 and 2. In the diols (IV) and (VI), OH · · · OH intramolecular bonding appears to be absent [compare the acetylenic diol (II)]. Also, the band at ca. 3535 cm.⁻¹ in the trans-alcohols (V) and (VI), assigned to conformer (iv), was not expected on the basis of models, since the second ring appears to be almost out of bonding range. Another possible interpretation of this band is that there could be two possible sites on the double bond to which the proton may bond, e.g., to each carbon atom of the double bond.

The assignments of the observed bands for these *cis*and *trans*-stilbene alcohols (III)—(VI) are tentative owing to the conformational complexities.

Conclusion.—The spectra reveal that flexible molecules of this type, bearing several basic sites, adopt a number of conformations which can be detected by the characteristic OH stretching frequencies of the hydroxygroups forming the intramolecular hydrogen bonds. The relative proportions of these conformations are sensitive to the functional groups present, partly as a result of the variations in the electron density available for hydrogen bonding, and partly as a consequence of

⁹ T. Cairns, G. Eglinton, and S. M. McGeachin, *J. Chem. Soc.*, 1965, 1235.

the changes in the flexibility of the molecules. It is surprising that the assigned frequency values for conformers (iii) have such similar values, in view of the differing geometries and bonding sites involved. The same remark also holds for conformers (iv). Another striking feature is the predominance of conformer (ii) $[v(OH) \ ca.\ 3617 \ cm.^{-1}]$ in spite of the alternative basic sites available to the hydrogen of the hydroxy-group for bonding. Further studies with carefully chosen

molecules, and computer analysis of the absorption

bands, should permit more precise evaluation.

EXPERIMENTAL

Measurements.—Quantitative i.r. spectra were recorded linearly in cm.⁻¹ as percentage transmission with a Unicam SP 100 double-beam infrared spectrophotometer equipped with an SP 130 sodium chloride prism-grating double monochromator (3000 lines/in.) operated under a vacuum.⁹ The routine i.r. spectra of solutions, liquid films, and Nujol mulls were recorded on a Unicam SP 200 and the u.v. spectra on a Unicam SP 800 spectrophotometer. N.m.r. spectra were recorded on a Perkin-Elmer RS10 (60 Mc.), and mass spectra on an A.E.I. MS 9 spectrometer. Melting points were recorded on a Kofler microscope hot-stage.

Materials.—Thin layer chromatography (t.l.c.) was carried out on Kieselgel G (Merck). Petroleum refers to the light petroleum fraction of b. p. $40-60^{\circ}$ unless otherwise stated. AnalaR carbon tetrachloride was used for the quantitative i.r. measurements without further purification, and AnalaR chloroform was freed from ethanol by passing over blue silica gel immediately before use.

2-Bromomethyl-2'-methyldiphenylacetylene (Xb) and 2,2'di(bromomethyl)diphenylacetylene (Xc).- 2,2'-Dimethyldiphenylacetylene¹⁰ (Xa), m. p. 27° (715 mg.), N-bromosuccinimide (715 mg.), and dibenzoyl peroxide (10 mg.) in dry carbon tetrachloride (5 ml.) were heated under reflux for 18 hr. The mixture was cooled, succinimide was filtered off, and evaporation of the solvent gave a crude solid which was chromatographed on silica (30 g.). Elution with carbon tetrachloride-petroleum (1:4) gave the monobromide (Xb) (160 mg., 28%), needles, m. p. 63-65° (from pentane), molecular ions, mass spectrometry(ms), at m/e 284 and 286 (ratio 1:1) ($C_{16}H_{13}Br$ requires M, 285), λ_{max} (EtOH) 288 and 304 mµ (log ε 4.04 and 3.93). Elution with carbon tetrachloride gave the dibromide (Xc) (410 mg., 56%), needles, m. p. 126-127° (from acetic acid) (lit., 11 127-128°) (Found: C, 52.7; H, 3.4. Calc. for C₁₆H₁₂Br₂: C, 52.8; H, $3\cdot3\%$), molecular ion (ms) at m/e 362, 364, and 366 (ratio 1:2:1) (Calc. for $\rm C_{16}H_{12}Br_2:~\ensuremath{M}$, 364), $\lambda_{\rm max.}$ (EtOH) 292 and 312 mµ (log ε 4.17 and 4.05), complex multiplet centred at τ 2.63 (8H; benzenoid) and a singlet at 5.2 (4H; CH₂Br).

2-Acetoxymethyl-2'-methyldiphenylacetylene (Xd).—A solution of 2-bromomethyl-2'-methyldiphenylacetylene (Xb) (249 mg.) and fused sodium acetate (300 mg.) in acetic acid (3 ml.) was heated under reflux for 4 hr., cooled, and poured into water, and the neutral fraction isolated with ether. Evaporation gave the monoacetate (Xd) as a colourless oil, b. p. 220°/0·2 mm. (block) (201 mg., 87%), molecular ion (ms) at m/e 264, (C₁₈H₁₆O₂ requires M, 264), v(CO)

¹⁰ J. Coops, G. J. Hoijtink, Th. J. E. Kramer, and A. C. Faber, *Rec. Trav. chim.*, 1953, **72**, 781.

¹¹ H. A. Staab and F. Graf, Tetrahedron Letters, 1966, 751.

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(film) 1740 cm.⁻¹, λ_{max} . (EtOH) 271, 277, 285, 294, and 304 mµ (log ε 4·10, 4·15, 4·26, 4·12, and 4·18).

2,2'-Di(acetoxymethyl)diphenylacetylene (Xe).—A solution of 2,2'-di(bromomethyl)diphenylacetylene (Xc) (100 mg.) and fused sodium acetate (225 mg.) in acetic acid (3 ml.) was treated as in the preceding experiment, yielding the diacetate (Xe) (90 mg., 99%), needles, m. p. 83.5—84.5°, on sublimation at 240°/0.1 mm., molecular ion (ms) at m/e 322 (C₂₀H₁₈O₄ requires M, 322), v(CO) (Nujol) 1740 cm.⁻¹, λ_{max} . (EtOH) 271, 277, 285, 294, and 304 mµ (log ε 4.05, 4.09, 4.19, 4.07, and 4.12).

2-Hydroxymethyl-2'-methyldiphenylacetylene (I).— The monoacetate (Xd) (195 mg.) in dry ether (3 ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (80 mg., 6 equiv.) in ether (6 ml.). The mixture was stirred and heated under reflux for 2 hr., cooled, and a saturated aqueous solution of ammonium sulphate was added. Isolation with ether gave the *alcohol* (I) (141 mg., 86%), needles, m. p. 63—64° (from petroleum), molecular ion (ms) at m/e 222 (C₁₆H₁₄O requires M, 222). T.I.c. (silica; 1:4 ethyl acetate-petroleum) showed one spot, $R_{\rm F}$ 0·3, v(OH) (melted film) 3400 cm.⁻¹, $\lambda_{\rm max}$. (EtOH) 271, 277, 285, 294, and 340 mµ (log ε 4·16, 4·21, 4·31, 4·17, and 4·23).

2,2'-Di(hydroxymethyl)diphenylacetylene (II).—Addition of a solution of the diacetate (Xe) (70 mg.) in dry ether (2 ml.) to a stirred suspension of lithium aluminium hydride (50 mg., 6 equiv.) in dry ether (5 ml.), as in the preceding experiment, gave the diol (II) (48 mg., 93%), needles, m. p. 127—128° (from water), molecular ion (ms) at m/e 238 (C₁₆H₁₄O₂ requires M, 238). T.l.c. as in the preceding experiment showed one spot, $R_{\rm F}$ 0.05, $\lambda_{\rm max}$. (EtOH) 271, 277, 285, 294, and 304 mµ (log ε 4.32, 4.36, 4.48, 4.35, 4.40), v(OH) (Nujol) 3400 cm.⁻¹.

2-Hydroxymethyl-2'-methyl-cis-stilbene (III).—The acetylenic alcohol (I) (11 mg.) in ethanol was hydrogenated using the Lindlar catalyst until 1 mol. of hydrogen had been absorbed, and the product extracted with ethanol. Evaporation gave the cis-alcohol (III), needles, m. p. 41—42° (from petroleum), molecular ion (ms) at m/e 224 (C₁₆H₁₆O requires M, 224). T.1.c. (25% silver nitrate on silica; 3:7 ethyl acetate-petroleum) showed one spot, $R_{\rm F}$ 0.6, $\lambda_{\rm max}$. (EtOH) 264 mµ (log ε 3.95), v(OH) (Nujol) 3400 cm.⁻¹. 2,2'-Di(hydroxymethyl)-cis-stilbene (IV).—The acetylenic

2,2'-Di(hydroxymethyl)-cis-stilbene (IV).—The acetylenic diol (II) (10.5 mg.) in ethanol was hydrogenated as in the preceding experiment, to give the cis-diol (IV), needles, m. p. 106—107° (from water), molecular ion (ms) at m/e240 (C₁₆H₁₆O₂ requires M, 240). T.l.c. as in the preceding experiment showed one spot, $R_{\rm F}$ 0.2, $\lambda_{\rm max}$ (EtOH) 262 mµ (log ε 3.97), v(OH) (Nujol) 3400 cm.⁻¹.

2-Hydroxymethyl-2'-methyl-trans-stilbene (V).—A solution of the cis-alcohol (III), in carbon tetrachloride containing a trace of iodine, was heated under reflux for 4 hr., cooled, washed with aqueous sodium thiosulphate solution, dried, and filtered. Evaporation gave the trans-alcohol (V), needles, m. p. 47—48° (from petroleum), molecular ion (ms) at m/e 224 (C₁₆H₁₆O requires M, 224). T.l.c. as in the preceding experiment showed one spot, $R_{\rm F}$ 0.55, $\lambda_{\rm max}$. (EtOH) 291 m μ (log ε 4.37), γ (CH) for CH=CH trans, (CS₂) 960 cm.⁻¹, ν (OH) (Nujol) 3400 cm.⁻¹.

2,2'-Di(hydroxymethyl)-trans-stilbene (VI).—The cis-diol (IV) was isomerised as in the preceding experiment, to give the trans-diol (VI), needles, m. p. 158—159° (from water) (lit.,⁶ 162°), molecular ion (ms) at m/e 240 (Calc. for C₁₆H₁₆O₂: M, 240). T.l.c. as in the preceding experiment showed only one spot, $R_{\rm F}$ 0·15, $\lambda_{\rm max}$ (EtOH) 288 mµ (log ε 4·33), γ (CH) for CH=CH trans, (CS₂) 965 cm.⁻¹, v(OH) (Nujol) 3400 cm.⁻¹.

2-Hydroxymethyl-2'-methylbibenzyl (VII).—The acetylenic alcohol (I) (9·4 mg.), in ethanol, was hydrogenated over 5% palladium-charcoal until 2 mol. of hydrogen had been absorbed, and the product extracted with ethanol. Evaporation gave the *alcohol* (VII), needles, m. p. 33—34° (from petroleum), molecular ion (ms) at m/e 226 (C₁₆H₁₈O requires M, 226). T.l.c. as in the preceding experiment showed one spot $R_{\rm F}$ 0·75, v(OH) (Nujol) 3400 cm.⁻¹.

2,2'-Di(hydroxymethyl)bibenzyl (VIII).—The acetylenic diol (II) (10·1 mg.), in ethanol, was hydrogenated with 2 mol. of hydrogen as in the preceding experiment, giving the diol (VIII), needles, m. p. 150—151° (from water) (lit.,¹² 151°), molecular ion (ms) at m/e 242 (Calc. for $C_{16}H_{18}O_2$: M, 242). T.l.c. as in the preceding experiment showed one spot, $R_{\rm F}$ 0·27, v(OH) (Nujol) 3400 cm.⁻¹.

We thank Mrs. F. Lawrie for the quantitative infrared measurements, and the British Petroleum Company for a research grant (I. D. C.).

[7/1488 Received, November 16th, 1967]

¹² E. D. Bergmann and Z. Pelchowicz, J. Amer. Chem. Soc., 1953, 75, 4281.