

## Hydroxy-group Stretching Bands and Conformations of Substituted Benzyl Alcohols

By A. David Boul and G. Denis Meakins,\* Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford OX1 3QY

The O-H stretching absorptions of aryl-di-t-butylmethanols are composed of three symmetrical bands. These are assigned to an antiperiplanar H-O-C-Ar arrangement, and two synclinal forms which are distinguished by the presence or absence of O-H  $\cdots$   $\pi$ -electron interaction. N.m.r. evidence suggests that interconversion between the synclinal forms, involving only a partial rotation about the Ar-C axis, is rapid at 34 °C; complete rotation is more severely impeded.

The measurement of enthalpy differences confirms the occurrence of intramolecular bonding in benzyl alcohol and dimethylphenylmethanol.

DURING their fundamental work on the relationship between the hydroxy-group stretching frequencies and the conformations of alcohols, Oki and Iwamura<sup>1</sup> established that dilute solutions of benzyl alcohols in non-polar solvents contain free and intramolecularly bonded (O-H  $\cdots$   $\pi$ -electrons) forms. Later, Schleyer and his co-workers<sup>2</sup> refined the general conformational treatment, and extended it to alicyclic systems. Our observation<sup>3</sup> of hydroxy-bands at unusually high frequencies in the spectra of some alcohols having bulky substituents at the hydroxy-bearing carbon atom (*e.g.* di-t-butylmethanol) prompted the present work with  $\alpha\alpha$ -dialkylbenzyl alcohols, the main objects being to compare the di-t-butyl compounds with the  $\alpha\alpha$ -dimethylbenzyl alcohols studied previously<sup>1c</sup> and to investigate the relative stabilities of the rotameric forms of benzyl alcohols. (Although the literature contains several, markedly different, values for the enthalpy difference between the free and bonded forms of 2-phenylethanol,<sup>4</sup> the value for benzyl alcohol does not seem to be available.) The results obtained and the main interpretations are shown in the Scheme.

Reaction of aryl-lithium compounds with di-t-butyl ketone (the procedure used with phenyl-lithium<sup>5</sup>) gave the tertiary alcohols (IV)–(VII) in *ca.* 25% yields. In order to facilitate the spectrometric analysis, compounds with more highly substituted aromatic nuclei were required; two such benzyl alcohols, (VIII) and (IX), were prepared by nitrating the reactive *p*-methoxyphenyl compound (VI).

Benzyl alcohol (I) and the dimethyl compound (II),

<sup>1</sup> M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, (a) 1959, **32**, 950; (b) 1959, **32**, 955; (c) 1962, **35**, 1552.

<sup>2</sup> J. Loris, P. von R. Schleyer, and E. Osawa, *Tetrahedron*, 1968, **24**, 4759.

and derivatives of both having substituents in the aromatic ring, give two hydroxy-bands (A and C, see Scheme) which are known<sup>1b,c</sup> to arise from the conformations shown below the columns of band positions. [The present figures for the frequencies of compounds (I) and (II) agree well with the literature values. In the conformation giving band C the interaction is envisaged<sup>1b,c</sup> as involving the  $\pi$ -electron cloud above C(1) of the aromatic ring rather than C(1) itself.] Previous work,<sup>2,3a</sup> and the relative intensities of the components lead unambiguously to assignments of the two bands (A and B) of di-t-butylmethanol (III). The absorptions of the related benzyl alcohols (IV)–(IX) have *three* components, as exemplified in the Scheme. Comparison with the earlier compounds and predictions from general analyses<sup>1-3</sup> establish that only band A is sufficiently low in frequency to be allocated to the antiperiplanar H-O-C-Ar conformation; the other two bands are then assigned to synclinal arrangements. With compounds (I) and (II) the synclinal form shown in column C does not involve unfavourable interactions between the carbon centres, but substitution of t-butyl groups at the benzylic centre of this form produces severe repulsions between the large alkyl groups and the *ortho*-positions of the aromatic ring. Relief of strain by an out-of-plane twist of the aromatic ring leads to two synclinal forms (columns B and C), of which the one (column C) suitable for O-H  $\cdots$   $\pi$ -electron interaction is correlated with the

<sup>3</sup> (a) F. Dalton, G. D. Meakins, J. H. Robinson, and W. Zaharia, *J. Chem. Soc.*, 1962, 1566; (b) A. D. Boul, J. W. Blunt, J. W. Browne, V. Kumar, G. D. Meakins, J. T. Pinhey, and V. E. M. Thomas, *J. Chem. Soc. (C)*, 1971, 1130.

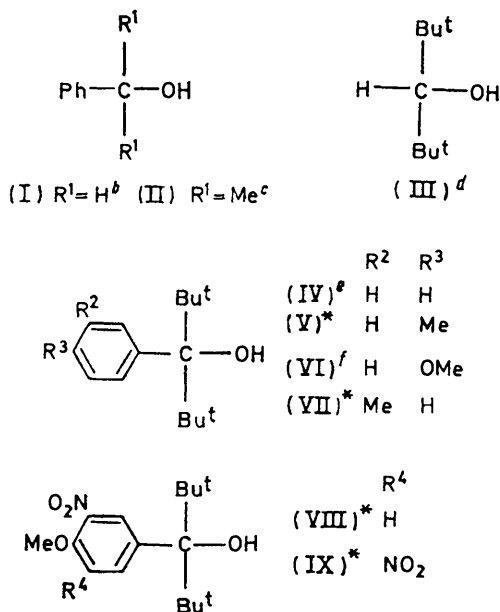
<sup>4</sup> P. J. Krueger and H. D. Mettee, *Tetrahedron Letters*, 1966, 1587.

<sup>5</sup> P. D. Bartlett, T. R. Steadman, T. T. Tidwell, and W. P. Weber, *Tetrahedron Letters*, 1970, 2915.

lower wavenumber component (*ca.* 3628  $\text{cm}^{-1}$ ). The values of the relative intensities of bands B and C suggest

## SCHEME

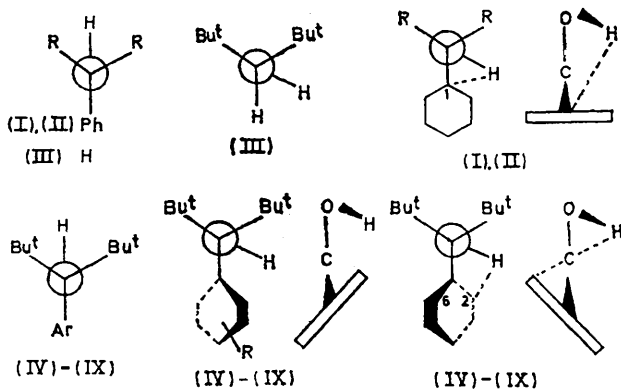
Dilute solutions in  $\text{CCl}_4$  were examined at a spectra slit-width of 2  $\text{cm}^{-1}$  from 253 to 243 K and the curves were resolved into symmetrical components (*ca.* 70% Lorentzian character) as described previously.\* The positions ( $\text{cm}^{-1}$ ) of the component bands are given at 298 K; these are followed in parentheses, by the areas of the components expressed as percentages of the total area of the OH absorptions at 253 K (*i.e.* for each alcohol the combined components have an area of 100% at 253 K).\*



\* Ref. 7. Previous i.r. studies: <sup>b</sup> ref. 1b; <sup>c</sup> ref. 1c; <sup>d</sup> ref. 3a; <sup>e</sup> ref. 5. <sup>f</sup> N.m.r. study: ref. 6.

• New compound.

Compd.	Bands and conformations		
	A	B	C
(I)	3635 (36)		3614 (51)
(II)	3620 (33)		3605 (49)
(III)	3623 (15)	3651 (69)	
(IV)	3614 (22)	3643 (47)	3630 (15)
(V)	3615 (22)	3643 (44)	3630 (18)
(VI)	3615 (21)	3643 (51)	3628 (18)
(VII)	3615 (20)	3643 (39)	3630 (28)
(VIII)	3614 (20)	3643 (55)	3628 (11)
(IX)	3611 (17)	3640 (68)	3623 (3)

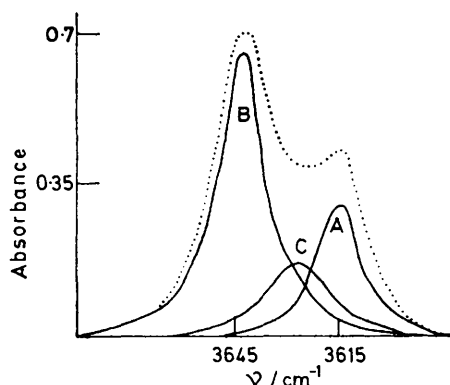


that in form C the hydroxylic hydrogen atom lies above C(2) of the aromatic ring: band C is intensified more by

a 3- than by a 4-methyl group [compounds (VII) and (V)] and is markedly diminished by nitro-groups at positions 3 and 5 [compounds (VIII) and (IX)].

Marked hindrance to rotation about the Ar-C axis of compound (VI) was established by n.m.r. studies: <sup>6</sup> a high temperature (*ca.* 140 °C) was required to obtain a symmetrical AA'BB' pattern for the aromatic protons' signals. This effect is seen more easily with the tetra-substituted benzyl alcohol (IX): the two doublets observed for the aromatic protons at 34 °C collapse to a singlet at 150 °C. In contrast, the t-butyl groups of each compound give one singlet, even at 34 °C. The implications are that libration between forms B and C, involving only a small energy barrier, is rapid, but that complete rotation of the aromatic ring [through the C conformation depicted for compounds (I) and (II)] is more severely impeded. This agrees with the main point of the previous interpretation <sup>6</sup> (restricted rotation of the aryl group), but the present work suggests that the form intermediate between conformations B and C is the time-average of a rapid interconversion rather than a stable conformation.<sup>6</sup>

Application of a standard technique <sup>7</sup> gave reliable values for the enthalpy differences between the conformations of the alcohols (I), (II), and (III). The higher



OH Bands of compound (VI)

Compd.	Forms	$\Delta H^\circ / \text{J mol}^{-1}$
(I)	A $\rightleftharpoons$ C	$-3400 \pm 500$
(II)	A $\rightleftharpoons$ C	$-6900 \pm 500$
(III)	A $\rightleftharpoons$ B	$-800 \pm 500$
(IV)-(IX)	A $\rightleftharpoons$ (B + C)	<i>ca.</i> +2000 †
	B $\rightleftharpoons$ C	<i>ca.</i> -1000 †

† See text.

values for the benzyl alcohols, † especially that of the dimethyl compound (II), confirm that there is attractive interaction in the form giving the lower frequency band (*cf.* the most recent value <sup>4</sup> of  $-4400 \text{ J mol}^{-1}$  for 2-phenylethanol); measurement of  $\Delta H^\circ$  might be used generally to distinguish between conformational heterogeneity

† Dr. J. G. Watkinson (University of Manchester) has kindly informed us of his work leading to a figure of  $-7500 \text{ J mol}^{-1}$  for benzyl alcohol in tetrachloroethylene.

<sup>6</sup> G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 1967, 2539.

<sup>7</sup> D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1972, 1959.

alone, and in conjunction with intramolecular bonding in one form, as the cause of O-H multiplicity.\* With the *t*-butyl compounds the variations in band areas with temperature were not much greater than the possible errors in curve resolution. While little significance should be attached to the  $\Delta H^0$  figures shown in the Scheme, it appears that form A now becomes the thermodynamically most stable conformation.

#### EXPERIMENTAL

Preparative and spectrometric techniques were as described in *J.C.S. Perkin I*, 1973, 1766, and ref. 7, respectively.  $\text{CCl}_4$  used for i.r. spectra (1 cm cells) and, except for one case, n.m.r. spectra (100 MHz), was distilled from  $\text{P}_2\text{O}_5$  and stored over molecular sieves. The alcohols were dried and their purity was checked by t.l.c. immediately before spectrometric examination; solutions were prepared, and cells filled, in a dry box. The constants of compounds (I)–(IV) agreed with the literature values which are given in, or can be found from, the references in the Scheme. Petrol refers to light petroleum, b.p. 60–80°.

**Compounds (V)–(VII).**—4-Bromotoluene (10 g) in  $\text{Et}_2\text{O}$  (15 ml) was added during 20 min to a stirred suspension of Li (1.1 g) in  $\text{Et}_2\text{O}$  (10 ml) under  $\text{N}_2$ . After a further 15 min, 2,2,4,4-tetramethylpentan-3-one (3.8 g) in  $\text{Et}_2\text{O}$  (10 ml) was added, and the solution was boiled under reflux for 3.5 h. Work-up and distillation gave material (3.2 g), b.p. 119–121° at 0.5 mmHg, which was chromatographed on neutral  $\text{Al}_2\text{O}_3$  (200 g). Elution with petrol– $\text{C}_6\text{H}_6$  (3 : 1) and distillation gave 2,2,4,4-tetramethyl-3-*p*-tolylpentan-3-ol (V) (2.1 g),  $n_D^{20}$  1.5182 (Found: C, 82.1; H, 11.1.  $\text{C}_{16}\text{H}_{26}\text{O}$  requires C, 82.0; H, 11.2%),  $\tau$  ca. 2.75 (m, ArH), 7.70 (s, ArMe), and 8.95 (s,  $\text{Bu}^t$ ).

\* The demonstration of intramolecular bonding in cyclopropylmethanol (M. Oki and H. Iwamura, *Tetrahedron Letters*, 1973, 4003) might be supported in this way.

Similarly 3-bromotoluene (7 g) gave the 3-*m*-tolyl compound (VII) (2.2 g), b.p. 124–125° at 0.8 mmHg,  $n_D^{20}$  1.5148 (Found: C, 81.8; H, 11.2%),  $\tau$  ca. 2.8 (m, ArH), 7.68 (s, ArMe), and 8.94 (s,  $\text{Bu}^t$ ).

1-Bromobutane (10 g) in  $\text{Et}_2\text{O}$  (8 ml) was added during 25 min to a stirred suspension of Li (1.5 g) in  $\text{Et}_2\text{O}$  (30 ml) under  $\text{N}_2$ . After 15 min 4-bromoanisole (18.4 g) in  $\text{Et}_2\text{O}$  (10 ml) was added, and after a further 15 min 2,2,4,4-tetramethylpentan-3-one (8.6 g) in  $\text{Et}_2\text{O}$  (10 ml) was added. Subsequent treatment as before gave the 3-*p*-methoxyphenyl compound (VI) (2.85 g), m.p. 109–110° (from petrol) (lit.,<sup>6</sup> 110–111°),  $\tau$  ca. 3.0 (m, ArH), 6.25 (s, OMe), and 8.95 (s,  $\text{Bu}^t$ ) [lit.,<sup>6</sup>  $\tau$  ( $\text{CDCl}_3$ ), ca. 3.0, 6.20, and 8.90].

**Compounds (VIII) and (IX).**—A mixture of 95%  $\text{HNO}_3$  (0.4 g) and  $\text{Ac}_2\text{O}$  (0.8 ml) at 0 °C was added during 5 min to a stirred suspension of compound (VI) (1.2 g) in  $\text{Ac}_2\text{O}$  (2 ml) at 0 °C. After 15 min, work-up gave 3-(4-methoxy-3-nitrophenyl)-2,2,4,4-tetramethylpentan-3-ol (VIII) (0.86 g), m.p. 96–97° (from petrol) (Found: C, 65.0; H, 8.5; N, 4.8.  $\text{C}_{16}\text{H}_{25}\text{NO}_4$  requires C, 65.1; H, 8.5; N, 4.7%),  $\tau$  2.05 [2H, m, ArH(2 + 6)], 3.05 [four-line signal,  $J$  6 and 2 Hz, ArH(5)], 6.07 (s, OMe), and 8.94 (s,  $\text{Bu}^t$ ).

Nitration with 95%  $\text{HNO}_3$  (1.5 g)– $\text{Ac}_2\text{O}$  (3 ml) of compound (VI) (1.06 g) suspended in  $\text{Ac}_2\text{O}$  (2 ml) at 0 °C for 20 h gave 3-(4-methoxy-3,5-dinitrophenyl)-2,2,4,4-tetramethylpentan-3-ol (IX) (0.98 g), m.p. 124–126° (from petrol) (Found: C, 56.7; H, 7.1; N, 8.0.  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_6$  requires C, 56.7; H, 7.1; N, 8.1%),  $\tau$  1.64 and 1.79 [two d,  $J$  2.4 Hz, ArH(2 + 6)], 6.09 (s, OMe), and 8.94 (s,  $\text{Bu}^t$ ). A solution in cyclohexanone showed two doublets ( $\tau$  1.46 and 1.60) each with  $J$  2.4 Hz at 34 °C, a broad signal at 130 °C, and a singlet ( $\tau$  1.53) at 150 °C.

We thank the S.R.C. for a studentship (to A. D. B.).

[3/2512 Received, 10th December, 1973]