However, in this way stilbene is present in the product mixtures and the chromatographic analysis is consequently less accurate, because its retention time is similar to that of the corresponding ketones.

Acknowledgments.—We are grateful to Dr. J. S. Lomas, Professor K. Yates, and Professor B. M. Wepster for helpful and critical discussions.

Steric Crowding in Organic Chemistry. II. Spectral and Conformational Properties of Highly Substituted Phenylcarbinols[1]

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A series of highly substituted aryl carbinols ArCOHRR′ (**2–14**) has been prepared. The hydroxyl stretching frequencies of the alcohols in CCl_4 were measured and, although multiple bands were observed in some cases, the spectra were interpreted in terms of a predominant conformation with the oxygen in the plane defined by the carbinol carbon and the aromatic ring. The first overtone of the hydroxyl stretching frequency in the near-infrared showed the same multiple bands. The downfield chemical shift of the hydroxyl protons on addition of DMSO was examined. The magnitude of this shift was smaller in the more crowded compounds. The ρ values for the effect of para substituents on the chemical shifts are about 0.5 for all series examined and are insensitive to the size of attached groups. The effect of tris(dipivalomethanato)europium on the chemical shifts was examined, and the shifts of the aromatic protons were correlated with the distance and angle dependence of the pseudocontact shift equation. The geometries of the Eu complexed alcohols were interpreted in terms of a predominant conformation with a coplanar arrangement of the aryl–C–O–Eu atoms.

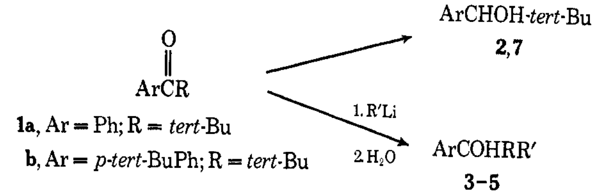
α-Phenylcarbinols display multiplicity in their hydroxyl stretching frequencies in the infrared which has been interpreted in terms of the conformations of the molecules.[3] The nmr chemical shift of the hydroxyl proton of phenylcarbinols in dimethyl sulfoxide (DMSO) solution has also been used as a probe for examining the structures of the carbinols,[4] and the nmr spectra of α-aryldi-*tert*-butylcarbinols have been related to their conformational properties.[5]

The present investigation was designed to examine the role of very bulky substituents on the spectroscopic properties of α-arylcarbinols. The accompanying paper[6] considers the spectral properties and reactivity of ferrocenylcarbinols. The reactivity of the aryl compounds will be presented elsewhere.[7]

Results

A series of highly substituted arylcarbinols (**2–5**, **7**) were prepared by reduction, or by addition of the appropriate alkyllithium to *tert*-butyl aryl ketones (**1a**, **b**) (Table I).

Phenyldi-*tert*-butylcarbinol (**6**) was prepared by the addition of phenyllithium to di-*tert*-butyl ketone to minimize 1,6-conjugate addition to the para position of **1a**, a reaction often observed in the reaction of **1a** with organometallic reagents.[3e,8] Similarly, phenyl-*tert*-butylneopentyl- and phenyldineopentylcarbinols (**8** and **9**) and their derivatives having a para substituent on the phenyl ring (**10–14**) were prepared by the addition of the corresponding aryllithium to *tert*-butyl neopentyl and dineopentyl ketones, respectively.



Hydroxyl stretching frequencies for the alcohols were measured for CCl_4 solutions and are summarized in Table I. The frequencies for compounds **2–7** were measured for 0.4 and 0.04 M solutions. At the higher concentration intramolecular hydrogen bonds around 3500 cm^{-1} could also be observed for **2–4**. The frequencies for compounds **8–15** were measured for 0.004 M solutions. The frequency reported for **6** is somewhat improved over that reported previously.[3e] Compound **6** also showed near-infrared absorption frequencies at 7117 and 7060 cm^{-1} with relative intensities 5 and 3, respectively, for either 0.13 M or 0.03 M solutions in CCl_4.

The nmr spectral parameters of the carbinols in various solvents are also given in Table I. The influence of the concentration of DMSO in CCl_4 on the hydroxyl chemical shift of **2** is given in Table II. Plots of the hydroxyl chemical shifts of the para-substituted aryldineopentylcarbinols and the aryl-*tert*-butylneopentylcarbinols in DMSO *vs.* the σ parameters of the substituents were linear, with ρ values of 0.50 and 0.47, re-

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TABLE I

SPECTRAL PARAMETERS OF ARYLCARBINOLS, ArCOHRR′

					Nmr, δ					
Compd	Ar	R	R′	ν_{max}, cm^{-1} [a]	Solvent	OH	Aromatic	*tert*-Bu	CH_2R	Other
2	Ph	H	*t*-Bu	3619	CCl_4	1.76	7.12	0.84		4.18 (C**H**OH)
					DMSO	5.08[e]	7.25	0.89		4.24 (C**H**OH)[e]
3	Ph	Me	*t*-Bu	3625 (sh)	CCl_4	2.0	7.4 (m)	0.89		1.52 (Me)
				3611	DMSO	4.58	7.2 (m)	0.86		1.50 (Me)
4	Ph	Et	*t*-Bu	3615	CCl_4	1.47	7.2 (m)	0.88	1.8–2.4 (m)	0.63 (Me)[d]
					DMSO	4.24	7.3 (m)	0.80		0.60 (Me)[d]
5	Ph	*i*-Pr	*t*-Bu	3624 (sh)	CCl_4	1.36	7.1 (m)	0.91	2.5 (C**H**Me_2)[f]	0.57, 1.09 (CH**Me**$_2$)[d]
				3612						
					DMSO	4.09	7.2 (m)	0.88		0.58, 1.10 (CH**Me**$_2$)[d]
6	Ph	*t*-Bu	*t*-Bu	3644 (5)	CCl_4	1.72	7.4 (m)	1.07		
				3617 (3)	DMSO	4.16	7.4 (m)	1.02		
7	*p*-*t*-BuPh	H	*t*-Bu	3620	CCl_4	1.97	7.2 (m)	0.84, 1.30		4.19 (C**H**OH)
					DMSO	4.98[e]	7.2 (m)	0.90, 1.33		4.22 (C**H**OH)[e]
8	Ph	*t*-Bu	Np[h]	3641	CCl_4	1.53	7.3 (m)	0.77, 0.85	1.88, 2.10[g]	
					DMSO	3.93	7.3 (m)	0.72, 0.80	1.83, 2.07[g]	
9	Ph	Np	Np	3640.5	CCl_4	1.45	7.3 (m)	0.70	1.71, 1.88[g]	
				3630 (sh)	DMSO	4.02	7.3 (m)	0.65	1.70, 1.87[g]	
10	*p*-Anis	*t*-Bu	Np	3640	$CDCl_3$	1.67	6.80, 7.35[b]	0.78, 0.87	1.90, 2.10[g]	3.80 (OMe)
					DMSO	3.83	6.80, 7.35[b]	0.73, 0.80	1.80, 2.02[g]	3.73 (OMe)
11	*p*-Anis	Np	Np	3641	CCl_4	1.40	6.70, 7.23[b]	0.70	1.59, 1.93[g]	3.75 (OMe)
				3632 (sh)	DMSO	3.90	6.78, 7.35[b]	0.68	1.77[c]	3.72 (OMe)
12	*p*-ClPh	*t*-Bu	Np	3641	CCl_4	1.55	7.18, 7.37[b]	0.78, 0.85	1.88, 2.08[g]	
					DMSO	4.00	7.26, 7.47[b]	0.77, 0.85	1.87, 2.07[g]	
					Pyridine		7.38, 7.68[b]	0.93, 0.98	2.23, 2.67[g]	
13	*p*-ClPh	Np	Np	3638	CCl_4	1.43	7.19, 7.35[b]	0.72	1.65, 1.92[g]	
				3629 (sh)	DMSO	4.15	7.25, 7.49[b]	0.68	1.80[c]	
					Pyridine		7.38, 7.67[b]	0.83	1.97	
14	*p*-F_3CPh	*t*-Bu	Np	3641.5	CCl_4	1.63	7.54[c]	0.77, 0.87	1.92, 2.14[g]	
					DMSO	4.22	7.63	0.73, 0.82	1.88, 2.12[g]	
15	*p*-ClPh	Me	Me	3620 (5)	CCl_4	1.82	7.15, 7.35[b]			1.48 (Me)
				3607 (6)	DMSO	5.02	7.24, 7.56[b]			1.43 (Me)
					Pyridine		7.39, 7.71[b]			1.67 (Me)

[a] CCl_4 solutions. [b] A′A′XX′ quartets. Reported as δ, which was calculated with approximate $J = 9$ Hz in all cases and using an equation for the difference of chemical shifts between protons A and X in an AX system: L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 129, 130. [c] Broad singlet. [d] $J = 7$ Hz. [e] Doublet, $J = 4$ Hz. [f] Heptet, δ 2.50, $J = 7$ Hz. [g] Doublet, $J = 15$ Hz. [h] Neopentyl.

TABLE II

EFFECT OF DMSO ON THE HYDROXYL CHEMICAL SHIFT OF PhCHOH-*tert*-Bu (**2**)[a]

DMSO/2[b]	0.0	0.5	0.75	1.0	1.25	2.75	6.0	11.0	∞
δ (OH)[c]	1.76	2.92	3.28	3.52	3.72	4.12	4.52	4.70	5.08

[a] 0.5 *M* in CCl_4. [b] Mol of DMSO/mol of **2**. [c] Relative to TMS.

spectively. The downfield shifts of the resonances resulting from addition of 0–0.5 mol of the paramagnetic shift reagent tris(dipivalomethanato)europium [Eu(DPM)$_3$] to **12**, **13**, and *p*-chlorophenyldimethylcarbinol (**15**) were determined, and plots of δ for the various protons *vs.* the concentration of the shift reagent were linear in all cases. The slopes of these plots are tabulated in Table III.

TABLE III

Eu(DPM)$_3$ SHIFT GRADIENTS OF RESONANCES[a]

Compd	Ortho H[b]	Meta H[b]	*tert*-Bu	*tert*-BuCH_2	Me
12	2.36	0.20	1.80, 1.68	4.16, 2.48	
13	4.84	0.62	2.26	6.96, 5.82	
15	11.16	2.42			14.54

[a] Shift gradient $\Delta\delta_i$ defined as parts per million downfield/mol of Eu(DPM)$_3$ per mol of carbinol. [b] Refers to the position ortho and meta to the carbinol group, respectively. The lowest field protons experience the largest shifts and are assigned to the ortho positions.

Discussion

The arylcarbinols in CCl_4 display maxima at a high-frequency region around 3640 cm^{-1}, and at a low frequency region around 3615 cm^{-1}. These regions were proposed some time ago[3a] to be characteristic of free and π-bonded hydroxyls; for example, benzyl alcohol has bands at 3632 and 3615 cm^{-1} which were assigned to these types. This viewpoint has been criticized[3b,4a] because the frequency shifts between rotational conformers in some saturated alcohols were equally as large as those in the aromatic cases.[9] Recent results[3c,d,f] for 1-tetralols and chroman-4-ols of known configuration have suggested that π bonding is still a viable explanation for the occurrence of stretching frequencies of benzyl alcohols in the range 3600–3620 cm^{-1}, but such interpretations must be viewed with skepticism.

The first overtone of the hydroxyl stretching frequency occurs in the near-infrared region around 7100 cm^{-1} (1.4 μ). This absorption is perhaps more convenient for examination of multiplicity in the hydroxyl stretching frequency than the more usual infrared measurements, and such spectra of various 1,2-diphenylethanols have been interpreted in terms of both free and π-bonded hydroxyls.[3g] For **6** in CCl_4 we observe bands

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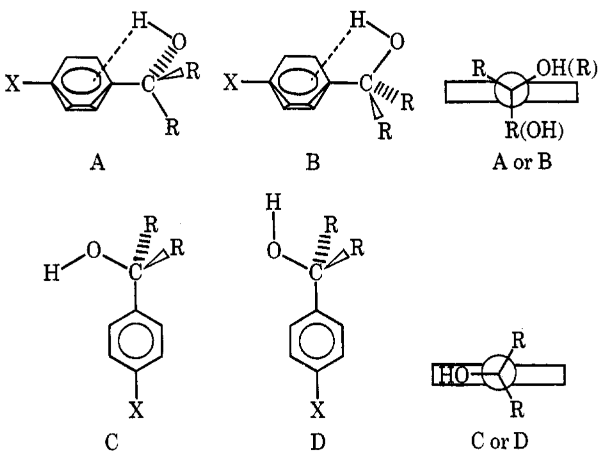
[9] L. Joris, P. v. R. Schleyer, and E. Ōsawa, *Tetrahedron*, **24**, 4759 (1968).

at 7117 and 7060 cm^{-1}, relative intensities 5 and 3, respectively, corresponding to the 3644 and 3617 cm^{-1} bands in the infrared. However, the same caveat given above applies to the interpretation of these near-infrared absorptions as free and π-bonded hydroxyls.

Some possible conformations to be considered for the arylcarbinols are shown as structures A–D (Chart I).

CHART I



In structures A and B all three substituents are staggered around the plane of the phenyl ring, whereas in C and D the C–O bond lies in the plane of the phenyl ring. π bonding of the hydroxyl to the ring should be possible in A and B, although the hydroxyl hydrogen may point away from the ring and be unbonded in these conformations.

The hydroxyl group evidently forms rather strong complexes with DMSO of Eu(DPM)$_3$. Thus addition of DMSO to a CCl$_4$ solution of benzyl alcohol was observed[4a] to lead to shifts of the OH stretching frequency to 3440 cm^{-1}, and the data in Table II show a marked downfield shift of the hydroxyl resonance on addition of DMSO to a CCl$_4$ solution of **2**. Addition of Eu(DPM)$_3$ gives a linear change in chemical shifts with ratios of Eu(DPM)$_3$:alcohol up to 0.8.[10] The hydroxyl absorption is the only resonance markedly shifted by the addition of DMSO (Table I).

The nmr spectra of *p*-anisyldi-*tert*-butylcarbinols show a temperature variation of the aryl resonances ascribed to slow rotation around the aryl–carbinol bond,[5] and give the same behavior in a variety of solvents, including DMSO.[5] Apparently the conformation around the aryl–carbinyl bond is not significantly affected by the presence of DMSO or Eu(DPM)$_3$, which is reasonable in view of the reported[11] insensitivity of the effective size of the hydroxyl group of cyclohexanol upon complexation with DMSO.[11] It would seem that complexation of DMSO to the hydroxyl hydrogen, or Eu(DPM)$_3$ to the oxygen, might lead to a change in the rotational population around the C–O bond to accommodate the bulk of the added molecule, but the evidence on this point is only suggestive.

Sternhell and coworkers[5] have presented convincing evidence that conformations C and D are predominant (within the sensitivity of the nmr spectrometer) for the di-*tert*-butylcarbinols. Thus at lower temperatures the aromatic protons show nonequivalence of the ortho protons and nonequivalence of the meta protons, and this nonequivalence disappears at higher temperatures. This behavior is ascribed to slow rotation around the aryl–carbinol bond, so that the two sides of the molecule are unequally shielded at lower temperatures. The multiplet ir bands for **6** can be ascribed to the presence of C and D, rather than the presence of A or B, for this molecule as was suggested by one of us.[3e] The neopentyl compounds (**8–14**) show neither the nonequivalence of the two halves of the aromatic ring nor any strong ir bands at lower frequencies. Thus conformation D appears favored with these compounds, with a rapid rotation around the aryl–carbinol bond so that the two sides of the ring are equally shielded.

The lower frequencies observed with the less crowded compounds **2–5** and **15** suggest that these compounds do exist at least to some extent in CCl$_4$ solutions in conformations such as A or B with a degree of π bonding to the aromatic ring. Steric interactions would presumably be minimized in conformation A in compounds **2–5**, where the very large *tert*-butyl group would take the position furthest removed from the phenyl ring.

It is readily apparent from Table I that there is a trend in the chemical shifts of the hydroxyl protons in DMSO to higher fields with increasing bulk of the substituents. This is in accord with the trend reported by Ouellette and coworkers,[4a] who found δ values for benzyl alcohol, 1-phenylethanol, cumyl alcohol, and 3-methyl-2-phenylbutanol of 5.15, 5.12, 4.95, and 4.63, respectively. *cis*- and *trans*-1-phenyl-4-*tert*-butylcyclohexanols were reported to give shifts of δ 4.63 and 4.55, respectively.[3d] The strong dependence of chemical shift on the bulk of the alkyl groups suggests that the bonded dimethyl sulfoxide molecule is repelled by the substituents to weaken the complex. The δ values for phenyldi-*tert*-butylcarbinol (**6**), phenyl-*tert*-butylneopentylcarbinol (**8**), and phenyldineopentylcarbinol (**9**) are 4.16, 3.93, and 4.02, respectively, suggesting that **8** has the highest degree of steric crowding in the vicinity of the hydroxyl group. This is in accord with the fact that this system apparently formed the weakest complex with Eu(DPM)$_3$ [the smallest Eu(DPM)$_3$ shift gradient in Table III].

The values of ρ found for the aryldineopentyl and aryl-*tert*-butylneopentyl systems of 0.50 and 0.47, respectively, for the complexation with DMSO, may be compared with the values of 0.41, 0.45, 0.51, and 0.63 reported by Ouellette and coworkers[4a] for the substituted benzyl alcohols, 1-arylethanols, cumyl alcohols, and 3-methyl-2-phenylbutanols, respectively. The trend toward larger ρ values with increasing bulkiness of the groups noted in these latter series[4a] thus is probably only a random variation, as the present results with still larger substituents do not follow this pattern.

The large steric effect of the α substituents shows a rather severe interaction of the complexing DMSO molecule with these groups, but the absence of any steric effect in the *p*-*tert*-butyl substituted derivative **7** indicates that the complexing solvent is not closely associated with the benzene ring. These considerations suggest that conformation E is preferred for the complex, and that the effect of ring substituents on the strength of the hydrogen bond to DMSO is transmitted

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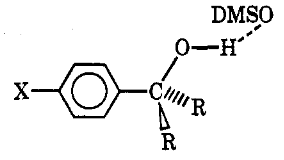
[10] (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971). (b) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3281 (1971).

[11] R. J. Ouellette, *ibid.*, **86**, 4378 (1964).



E

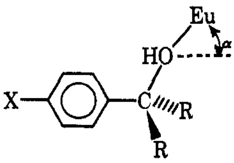
through the bonds of the molecule. This description differs from that proposed by Ouellette and coworkers,[4a] which included π bonding of the DMSO to the aromatic ring.

It has also been suggested[4a] that the H-C-O-H coupling in DMSO is influenced by the size of substituents on the carbinol carbon, in that primary alcohols (benzyl alcohols and ethanol) have couplings of 5.1–5.5 Hz, whereas 1-arylethanols have $J = 4.0$ Hz. However, the fact that compounds **2** and **7** also have $J = 4.0$ Hz establishes that the size of the 1-alkyl substituent does not affect the coupling constant, and suggests that the coupling constants probably reflect only the primary or secondary nature of the carbinol, and that all of the DMSO complexes have conformation E, or conformations related to E by rotation around the aryl–carbinol bond in the case of **2–5**, **7**, and **15**.

The Eu(DPM)$_3$-induced shifts are consistent with the usual[10b] pseudocontact shift dependence for a proton H$_i$ (eq 1), where $\Delta\delta_i$ is the change in chemical

$$\Delta\delta_i = k(3\cos^2\theta_i - 1)R_i^{-3} \qquad (1)$$

shift induced per mole, k is a constant for each compound and temperature, θ defines the H$_i$EuO angle, and R is the H$_i$–Eu distance. Using geometry F for the complex, with the aryl–C–O–Eu system coplanar and rapid rotation around the aryl–C bond, the Eu can be located relative to the H$_o$ and H$_m$ protons of the ring. Use of an O–Eu distance of 3.0 Å and the ratio of the shift gradients $[\Delta\delta_o/\Delta\delta_m = (3\cos^2\theta_o)R_m^3/(3\cos^2\theta_m)\cdot R_o^3]$ from Table III gives calculated angles of α of 45, 61, and 67° for **15**, **13**, and **12**, respectively. Structures where the O–Eu distance and α increase simultaneously owing to repulsion of the bulkier alkyl groups are also consistent with the observed shifts.



F

Experimental Section

General.—Analyses were performed by the Bernhardt Mikroanalytisches Laboratorium, Elbach über Engleskirchen, West Germany, or Shionogi Research Laboratory. Routine infrared spectra were determined using Perkin-Elmer 137, 257, or 337 spectrophotometers and were calibrated against appropriate polystyrene bands. Hydroxyl stretching frequencies were measured with a Perkin-Elmer 621 or a JASCO-DS-403G grating spectrophotometer. Nmr spectra were measured with Varian A-60, A56/60D, or A-60A instruments with tetramethylsilane as an internal standard. Assignments of hydroxy peaks in carbon tetrachloride solution were confirmed by shaking with D$_2$O. Chemical shifts of hydroxyl protons in DMSO solution were determined using the published procedure.[4a] Melting points (capillary) and boiling points are not corrected. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU instrument. Ultraviolet spectra were obtained with a Perkin-Elmer 202 spectrophotometer. Thin layer chromatography (tlc) was carried out on glass plates coated with silica gel with the solvents noted. Gas chromatography (glpc) was performed with a Varian Aerograph 90P-3 or a Hitachi Perkin-Elmer F6-D instrument and the columns and temperatures specified. Analytical data of the arylcarbinols are summarized in Table IV. Near-infrared measurements were made with a Cary 14 spectrophotometer.

TABLE IV

ANALYTICAL DATA FOR ARYLCARBINOLS

			Calcd, %			Found, %		
Compd	Formula	Mol wt	C	H	Cl	C	H	Cl
4	$C_{13}H_{20}O$	192.30	81.20	10.48		80.73	10.21	
5	$C_{14}H_{22}O$	206.33	81.50	10.75		80.88	10.81	
7	$C_{15}H_{24}O$	220.36	81.76	10.98		82.03	10.86	
8	$C_{16}H_{26}O$	234.38	81.99	11.18		82.22	11.17	
9	$C_{17}H_{28}O$	248.41	82.20	11.36		82.27	11.37	
10	$C_{17}H_{28}O_2$	264.39	77.22	10.67		76.99	10.56	
11	$C_{18}H_{30}O_2$	278.42	77.65	10.86		77.39	10.79	
12	$C_{16}H_{25}ClO$	268.82	71.48	9.37	13.19	71.49	9.40	13.46
13	$C_{17}H_{27}ClO$	282.84	72.18	9.62	12.54	72.30	9.55	12.47
14	$C_{17}H_{25}F_3O$	302.37	67.52	8.33	18.85 (F)	67.56	8.34	18.64 (F)

tert-**Butyl Phenyl Ketone** (**1a**).—Pivalyl chloride (106 g, 0.883 mol) was placed in 200 ml of ether in a 1-l. three-neck flask, and phenylmagnesium bromide (350 ml of 3 M solution, 1.05 mol) in ether was added over 20 min with stirring and cooling in an ice bath. The solution was stirred for 6 hr while warming to room temperature, and then refluxed for 40 min. After work-up the infrared spectrum of the crude product revealed a ketone absorption at 1685 cm^{-1} and another band at 1710 cm^{-1}; so aqueous HCl was added and the solution was heated on the steam bath with rapid stirring for 5 hr. After work-up only the ketone absorption appeared in the ir; so the product was fractionally distilled through a 10-cm vacuum-jacketed column with a Nichrome spiral, giving 60.4 g (0.373 mol, 42%) of **1a**, bp 99–108° (13 Torr), which was 96% pure by glpc (10 ft × $^1/_8$ in. 20% DEGS on Chromosorb P, 165°).

Phenyldi-*tert*-butylcarbinol (**6**).[3e]—Phenyllithium (prepared from 0.127 mol of bromobenzene in ether) was added to di-*tert*-butyl ketone (18.1 g, 0.126 mol) in 100 ml of ether with stirring over 20 min at a rate to maintain reflux. The solution was stirred for 3 hr and half the solution was removed, poured into water, extracted with ether, and dried, and the solvent was evaporated. Glpc examination (10 ft × $^1/_8$ in. Carbowax 20M on Chromosorb P, 195°) of the product showed several short retention peaks, the major peak, and a long retention peak (equal to 10% of the major product) which had an identical retention time with **7**.

Distillation of the product failed to give pure material; so **6** was isolated by glpc (10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W, 225°). The remaining half of the reaction product above was added to 100 ml of toluene, the ether was distilled away under a stream of nitrogen, and the toluene solution was refluxed overnight. The product was isolated and found to have the same composition as the first portion by glpc analysis, consistent with the relative stability of the lithium alkoxide.[3e]

Phenylmethyl-*tert*-butylcarbinol (**3**)[12,13] was obtained from the reaction of **1a** with methyllithium in ether, bp 60–64° (0.25 Torr) [lit.[12] bp 128° (20 Torr)], and was purified by glpc (10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W, 215°).

Phenylethyl-*tert*-butylcarbinol (**4**) was obtained from the reaction of **1a** with ethyllithium in ether and purification of the product by glpc (10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W, 225°).

Phenylisopropyl-*tert*-butylcarbinol (**5**) was obtained from **1a** and isopropyllithium in pentane and was purified by glpc (10 ft × $^3/_8$ in. Carbowax 20M on Chromosorb W, 220°).

Phenyl-*tert*-butylcarbinol (**2**) was prepared by NaBH$_4$ reduction of **1a** followed by recrystallization from pentane at −10° and sublimation (120°, 25 Torr), mp 41.5–42.5° (lit.[14] mp 44–45°).

tert-**Butyl *p*-*tert*-butylphenyl ketone** (**1b**) was prepared by the

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reaction of *tert*-butylmagnesium chloride (0.35 mol) with *p*-*tert*-butylbenzoyl chloride (0.40 mol) in refluxing ether. After hydrolysis and recovery of considerable acid the product was distilled to give a center cut of **1b** (6.86 g, 0.0314 mol, 9%): bp 84–87° (0.4 Torr) [lit.[15] mp 103–106° (1 Torr)]; nmr (CCl_4) δ 1.32 (s, sharp, 18, both *tert*-Bu), 7.1–7.8 (m, 4, aromatic); nmr (benzene) δ 1.21 and 1.30 (each s, 9, *tert*-Bu), aromatic obscured. The higher boiling distillation fractions included a solid which could not be identified.

***p*-*tert*-Butylphenyl-*tert*-butylcarbinol (7)** was obtained from the lithium aluminum hydride reduction of **1b**. After recrystallization from pentane at −25°, **7** was obtained as white prisms, mp 90–90.5°.

Preparation of Aryl-*tert*-butylneopentyl- and -dineopentylcarbinols.—*tert*-Butylneopentyl[16] and dineopentyl[17] ketones were prepared by the methods of Whitmore. Phenyllithium was made from lithium metal and bromobenzene in ether and *p*-anisyllithium, *p*-chlorophenyllithium, and *p*-trifluoromethylphenyllithium from *n*-butyllithium and the corresponding bromide. To a solution of the ketone in ether was added a solution of the aryllithium at about −20° under nitrogen atmosphere with vigorous stirring. After standing for 3 hr, the mixture was poured into an ice-cold aqueous ammonium chloride solution and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated to give an α-arylcarbinol. Yields were satisfactory in the case of phenyl derivatives, those for the anisyl-, chlorophenyl-, and trifluoromethylphenyl compounds were not, and the carbinols were isolated from the reaction mixture by thin layer chromatography. All the carbinols thus obtained gave satisfactory analyses and ir and nmr spectra consistent with the structures: **8**, bp 85° (2 mm), 89% yield; **9**, bp 94° (2 mm), 83%; **10**, mp 77–78°, 31%; **11**, mp 63–64°, 44%; **12**, mp 77–78.5°, 40%; **13**, mp 103–104°, 31%; for **14**, mp 53–54°, 43%.

Registry No.—**1a**, 938-16-9; **1b**, 22583-66-0; **2**, 3835-64-1; **3**, 21811-48-3; **4**, 34235-13-7; **5**, 34235-14-8; **6**, 15656-90-3; **7**, 34235-16-0; **8**, 34235-17-1; **9**, 34235-18-2; **10**, 34235-19-3; **11**, 34235-20-6; **12**, 34235-21-7; **13**, 34235-22-8; **14**, 34235-23-9; **15**, 1989-25-9; DMSO, 67-68-5; Eu(DPM)$_3$, 15522-71-1.

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Steric Crowding in Organic Chemistry. III. Spectral Properties, Conformations, and Reactivities of Highly Substituted Ferrocenylcarbinols[1]

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The preparation of a series of highly substituted ferrocenylcarbinols FcCRR′OH (**2**–**8**) has been accomplished. The hydroxyl stretching frequencies of the alcohols in CCl_4 solution showed bands in the region 3560–3583 cm^{-1} which were interpreted in terms of iron-bonded conformations, whereas bands at 3632 cm^{-1} were assigned to nonbonded conformations. Derivatives of the tertiary ferrocenyl carbinols could not be prepared, but the reactivity of the carbinols with acid to form cations was determined. *tert*-Butylferrocenylcarbinyl acetate (**10**) was prepared and found to undergo hydrolysis at a rate 4900 times as slow as methylferrocenylcarbinyl acetate. The depressed reactivity of **10** was attributed to steric hindrance of resonance stabilization.

The reactivity of α-arylcarbinols and their derivatives to form carbonium ions has been a topic of intensive investigation, particularly the electronic effect of substituents on the stability of the positive charge.[3,4] The stabilization by the ferrocenyl substituent is quite large,[4] but there has been considerable controversy as to whether the mode of stabilization by this group involves only hyperconjugative participation of bonding electrons[4h,i] or whether the nonbonding orbitals on iron are also significantly involved.[4a–d] The role of bulky substituents which prevent efficient overlap between the developing p orbital of the carbonium ion and the π system of the aromatic ring has also been examined in phenyl-substituted compounds.[5]

The spectroscopic properties of α-ferrocenylcarbinols have also been instructive regarding configurations and conformations of these compounds, as investigated by infrared[6a,b] and nmr[6c] measurements.

The present investigation was designed to elucidate the effect of very bulky substituents on the spectral properties and reactivity of α-ferrocenylcarbinols, and complements the investigation of the spectral proper-

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