20 J. Am. Chem. Soc. 1985, 107, 20-28

ENDOR Studies of Novel Di- and Triphenylmethyl Radicals Generated from Galvinols

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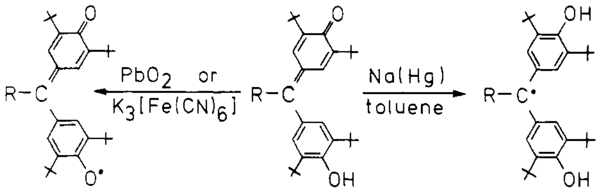
Abstract: A novel method is described which allows the generation of di- and triphenylmethyl radicals by reduction of galvinols with a sodium amalgam. The hyperfine coupling constants of these radicals including their signs have been determined by EPR, ^{1}H, ^{2}H, ^{13}C ENDOR, and TRIPLE experiments, and assignments to molecular positions are given. A pronounced temperature dependence of hydroxy proton coupling constants has been observed and is discussed in terms of torsional oscillations. The effect of phenyl hyperconjugation is demonstrated in highly twisted phenyl groups; i.e., the meta proton coupling constant becomes larger than the ortho and para coupling constants. The structures and dynamic behavior of these radicals have been investigated and compared with the corresponding galvinoxyl radicals. The mechanism of spin density transfer into alkyl groups is discussed.

Triarylmethyl radicals are commonly prepared by the reaction of a triarylmethyl halide with a metal,[1] but a variety of procedures involving the oxidation of a triarylmethyl carbanion, the reduction of a triarylmethyl carbenium ion, and the thermal or photolytic decomposition of a suitable precursor are known.[2] In this paper we report on a novel pathway which provides *para*-hydroxy-substituted di- and triphenylmethyl radicals by the reduction of galvinols. Upon oxidation, galvinols yield the well-known galvinoxyl radicals, e.g., Coppinger's radical or Yang's biradical.[3] Whereas upon reaction with alkali metals in ethereal solvents galvinols yield diamagnetic anions or in some cases radical dianions,[4] we have found that persistent neutral radicals are formed upon treatment with a sodium amalgam in hydrocarbon solvents. Since a multitude of galvinols are accessible via an organometallic synthetic pathway,[5] this procedure allows the generation of various novel triphenylmethyl radicals and of diphenylmethyl radicals with bulky alkyl substituents.



It will be shown that the structure of these radicals can be proven by means of EPR and ENDOR spectroscopy in combination with deuterium and ^{13}C labeling. Since the prominent novel structural feature is the presence of hydroxy groups in the para positions and steric interference with the neighboring *tert*-butyl groups might be expected, a detailed analysis of the hydroxy proton hyperfine coupling will be given. Thus, its temperature dependence and deuterium isotope effects have been studied. Furthermore, the fact that a wide variety of substituents can be introduced into these radicals allows a systematic investigation of the dependence of the structure, the spin density distribution, and the dynamic behavior on the nature of the substituent. For instance, it may be expected that the twist angle of a phenyl ring will be increased upon introduction of substituents (e.g., methyl or phenyl groups) into the ortho positions. It is known that the usual sequence of phenyl proton coupling constants ($|a_o| \simeq |a_p| > |a_m|$) may be altered in highly twisted phenyl groups; i.e., the meta proton coupling becomes the largest, an effect known as "phenyl hyperconjugation".[6,7] Regarding the alkyl-substituted diphenylmethyl-type radicals, the large π-spin population at the central position allows the investigation of spin density transfer into alkyl side chains. Finally, the properties of the di- and triphenylmethyl-type radicals will be compared with those of the respective galvinoxyls which have been studied extensively.[8,9] This comparison is particularly interesting since the steric requirements are the same whereas the electronic structure is quite different in these two types of radicals.

Experimental Section

Preparation of Compounds. The synthesis of most of the galvinols which serve as precursors of the radicals dealt with in the present paper has been reported previously, including the ^{13}C-labeled compounds (**1c**, **2c**, **5c**, **6c**, and **9c**) (Figure 1).[5,8-10] The preparation of selectively deuterated galvinols (**1e** and **2e**) is described elsewhere.[11]

1-[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]-2,4,6-trimethylbenzene (4a). A mixture of 5.0 g (14 mmol) of finely powdered (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 9 mL of *n*-butyllithium in *n*-hexane (20%), and 2.15 mL of (N,N,N',N'-tetramethyldiamino)ethane was treated with 1.00 g (5.6 mmol) of 2,4,6-trimethylbenzoic acid methyl ester at -5 °C. Elimination of the trimethylsilyl groups with methanol/HCl yielded 1.9 g (63%) of **4a**: mp 198 °C (from acetic acid); mass spectrum (80 eV), *m/e*

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(10) Compound **3a** was erroneously described as 2,6-dimethylphenylgalvinol in ref 8. The NMR spectrum establishes that **3a** is actually the 2,4-isomer, 1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]-2,4-dimethylbenzene: mp 217 °C, anal; ^{1}H NMR (CDCl$_3$) δ 7.31 (d, 1 H, J = 2 Hz), 6.96 (s, 2 H), 6.8–7.0 (m, 3 H), 6.75 (d, 1 H, J = 2 Hz), 5.40 (s, 1 H), 2.31 (s, 3 H, *p*-Me), 1.88 (s, 3 H, *o*-Me), 1.32 (s, 18 H), 1.24 (s, 9 H), and 1.12 (s, 9 H); mass spectrum (80 eV), *m/e* 526 (M$^+$). The EPR/ENDOR spectra of the galvinoxyl radicals **3g** and **4g** are very similar; coupling constants (in megahertz; toluene, 200 K) are as follows: **3g**, 3.71 (2 H), 3.63 (1 H), 3.52 (1 H), 0.38, and 0.14; **4g**, +3.75 (2 H), +3.57 (2 H), –0.39, and +0.15. Therefore, the conclusions drawn in ref 8 with respect to the dynamic behavior of "2,6-dimethylphenylgalvinoxyl" remain valid.

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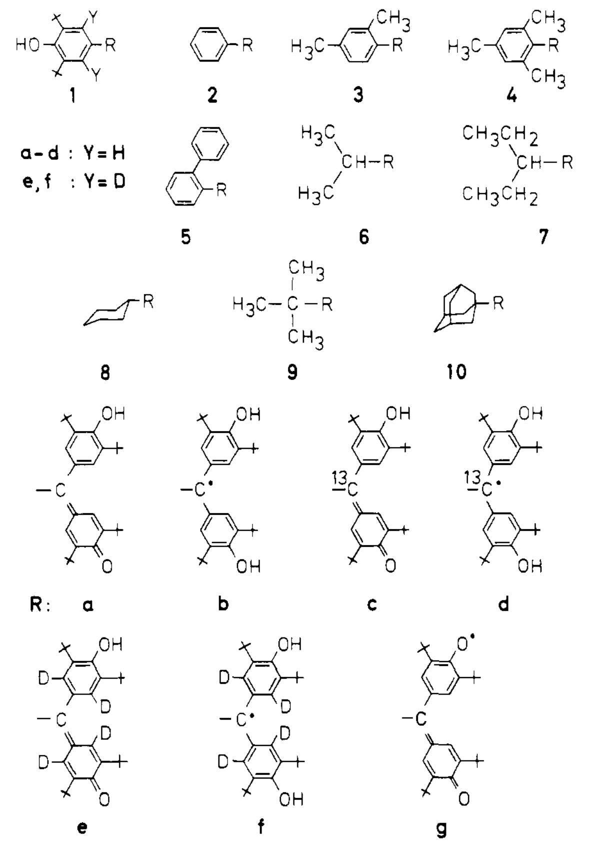

Figure 1. Numbering scheme of compounds. The following isotopically labeled radicals have been investigated: **1d**, **2d**, **5d**, **6d**, **9d**, **1f**, and **2f**.

540 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 1 H, J = 2 Hz, quinoid), 7.07 (s, 2 H), 6.90 (s, 2 H, mesityl), 6.72 (d, 1 H, J = 2 Hz, quinoid), 5.45 (s, 1 H, OH), 2.33 (s, 3 H, p-Me), 2.00 (s, 6 H, o-Me), 1.40 (s, 18 H), 1.33 (s, 9 H), and 1.16 (s, 9 H). Anal. Calcd: C, 84.39; H, 9.69. Found: C, 84.54; H. 9.53.

Generation of Radicals. The radicals were prepared by shaking deoxygenated solutions of the galvinols in anhydrous toluene or isopentane (ca. 10^{-3} mol L^{-1}) with a sodium amalgam for about 2 min. In a competitive reaction, an insoluble (di-) sodium salt formed. **1b** partially deuterated at the hydroxylic positions was obtained by treatment of a solution of **1a** in absolute toluene with finely divided sodium to give the disodium salt (under nitrogen; alternatively, the dilithium salt was prepared by means of n-butyllithium), hydrolysis with D_2O, separation of the organic layer, removal of D_2O by azeotropic distillation, and generation of the radical as described above.

Instrumentation. The mass spectra were recorded on a 711 Varian-MAT spectrometer. The ^{1}H NMR spectra were taken on a Bruker WH-270 in $CDCl_3$, internal standard tetramethylsilane. EPR spectra were recorded on a Bruker ER 200D EPR spectrometer. The ENDOR and TRIPLE spectrometer, basically consisting of a Bruker ER 220D EPR spectrometer equipped with a Bruker cavity (ER 200ENB), home-built NMR facilities, and a Nicolet signal averager, has been described elsewhere.[12] A microwave power level of 2 mW was applied and an rf power level of about 30–50 W (field strength 0.3–0.4 mT in the rotating frame) in ^{1}H ENDOR and 120–180 W (0.7–0.8 mT) in ^{13}C ENDOR experiments (not constant over the frequency range).

Results and Discussion

Tris(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl Radical (1b). Figure 2 (top) shows the EPR spectrum of the radical obtained by treatment of **1a** with a sodium amalgam in toluene. The well-resolved hyperfine pattern, a septet of quartets, indicates hyperfine interaction with two sets of six and three equivalent protons, respectively. The spectrum exhibits a remarkable temperature dependence: The quartet splitting decreases with decreasing temperature; finally each quartet collapses to a single line, whereas the septet splitting remains almost unchanged. In Figure 2 (bottom) the ENDOR spectrum of this radical is depicted, showing two pairs of lines separated by the "septet" and "quartet" hyperfine coupling constant, respectively, and a signal at the free proton frequency. The latter is attributed to protons with a coupling constant smaller than the ENDOR line width ($|a|$ < 60 kHz). It is noteworthy that ENDOR spectra with an excellent signal-to-noise ratio could be obtained throughout the temperature range of the liquid phase of toluene (190–370 K; optimum ENDOR response at about 220 K), thus allowing an accurate measurement of the temperature dependences of the coupling constants ($|a_1|$ decreases from 7.19 MHz (190 K) to 7.14 MHz (370 K), $|a_2|$ increases almost linearly from 0.14 MHz (200 K) to 1.10 MHz (370 K), vide infra). Relative signs of the two coupling constants were determined by general TRIPLE resonance[13] and turned out to be opposite. Moreover, this technique allowed the resolution of the smallest splitting ($|a_3| \simeq 0.03$ MHz).

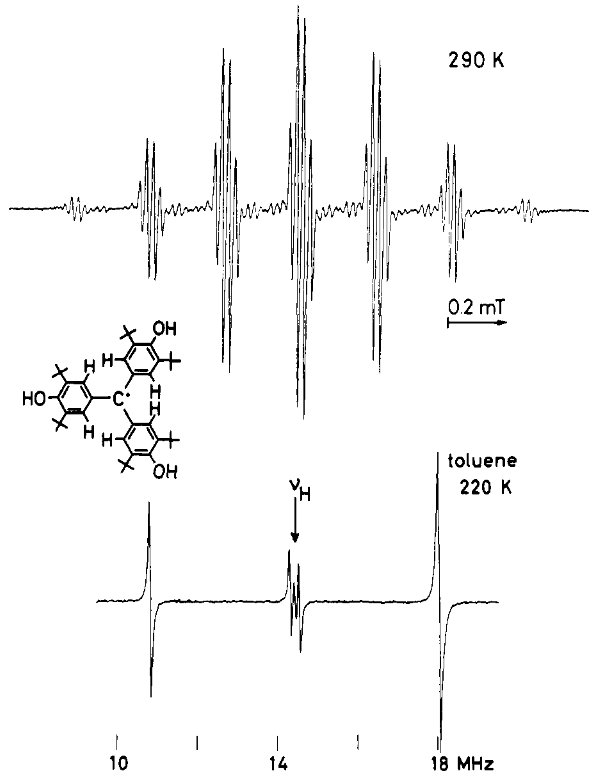

Figure 2. EPR (top) and ENDOR (bottom) spectra of **1b**.

In order to prove the structure of the radical, isotopic labeling experiments were performed. The radical from **1e**, deuterated at the six ring positions, gave an ENDOR spectrum showing one pair of ^{2}H ENDOR signals ($|a_D|$ = 1.094 MHz, 200 K) instead of the pair of ^{1}H ENDOR signals belonging to the largest splitting ($|a_H|$ = 7.19 MHz; the ratio a_H/a_D = 6.57 corresponding roughly to the ratio of the gyromagnetic ratios, γ_H/γ_D = 6.5144). Thus, it must be concluded that radical **1b** (**1f**) has threefold symmetry with six equivalent ring protons (or deuterons). Since the radical is soluble in nonpolar hydrocarbons such as toluene or isopentane (it does not form in protic or ethereal solvents), it can be assumed that it is a neutral radical. Therefore, the structure of a triphenylmethyl radical is proposed, bearing *tert*-butyl groups in the meta and hydroxy groups in the para positions. Deuteration of the hydroxylic positions proved to be rather difficult, since an excess of D_2O (as in most exchange experiments, e.g., in NMR) could not be applied. Starting with **1a**-d_2, deuterated at the hydroxylic positions, a radical with extensively (but not completely) deuterated hydroxy groups was obtained. Thus, the OH and OD coupling constants could be measured simultaneously by ENDOR: a_{OH} = 0.69 MHz and a_{OD} = 0.062 MHz (300 K), yielding $a_{OH}/a_{OD} = 11 \pm 1$. This ratio deviates enormously from the

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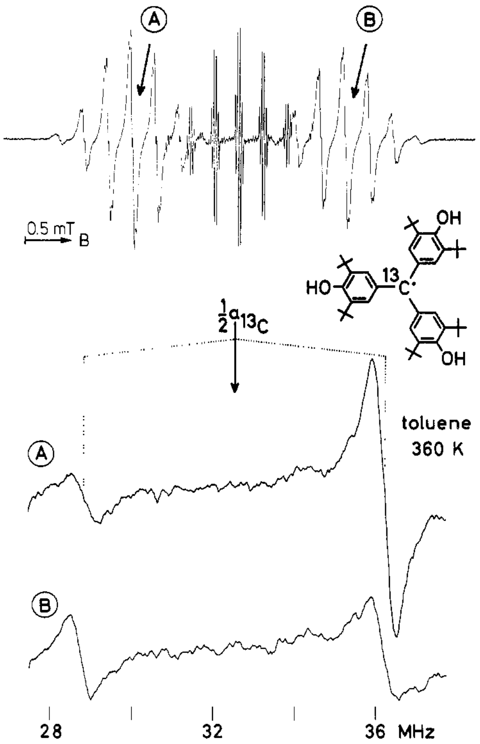

Figure 3. EPR (top) and ^{13}C ENDOR (bottom) spectra of **1d** (90% enrichment of ^{13}C). The ENDOR spectra were taken at two different field settings (A and B).

calculated ratio (6.5), i.e., a pronounced isotope effect is observed (vide infra).

Figure 3 (top) shows the EPR spectrum of radical **1d** which is ^{13}C-labeled at the central position (90% enrichment). It is remarkable that the signals of the central septet, due to unlabeled radicals (10%), have about the same height as those of the septets in the wings because of larger line widths of the latter. From the theory of EPR line widths[14] it is known that such a line broadening which depends on the nuclear spin state M_I (or rather on M_I^2) is caused by a modulation of the dipolar hyperfine interaction through molecular tumbling in solution. Consequently, not only the isotropic hyperfine coupling of the central ^{13}C atom ($|a_C|$ = 63.8 MHz (300 K)) but also the hyperfine anisotropy is large; i.e., there is a substantial π spin population at the central position as expected for triphenylmethyl-type radicals. ^{13}C ENDOR spectra of **1d** taken at different field settings are depicted in Figure 3 (bottom). According to the ENDOR resonance condition

$$\nu_{\mathrm{ENDOR}} = |\nu_n \pm a/2| \qquad (1)$$

each spectrum shows a pair of ^{13}C ENDOR lines centered about $a_C/2$ and separated by twice the free nuclear resonance frequency of ^{13}C (ν_C) since $|a_C/2| > \nu_C$. It is evident that the ENDOR signal amplitudes depend markedly on the field setting; i.e., the high-frequency ^{13}C ENDOR signal is more intense than the low-frequency signal when a low-field EPR component (A) is saturated and vice versa for the high-field setting (B). (Since the rf power is not frequency-independent in our experimental setup, the observed amplitudes of the low-frequency signals are too small relative to the high-frequency signals.) Such behavior is usually found for nuclei exhibiting a large hyperfine anisotropy and is caused by cross-relaxation effects $W_{x2} > W_{x1}$.[15] In particular, this phenomenon has been observed with the ^{13}C-labeled triphenylmethyl radical, and a detailed discussion has been given.[16] As Figure 4 shows, ^1H ENDOR signals of **1d** could also be recorded, but their detection proved to be much more difficult than in the case of the unlabeled radical **1b** (cf. Figure 2). Moreover, the amplitudes of the ^1H ENDOR signals also depend on the field setting (A and B in Figure 3); i.e., the cross-relaxation effect due to the ^{13}C nucleus also influences the ^1H ENDOR spectrum. It has been shown previously that this effect can be employed for

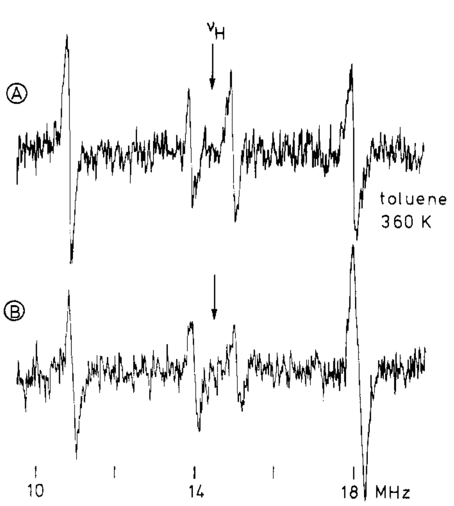

Figure 4. ^1H ENDOR spectra of **1d** taken at two different field settings (A and B), cf. Figure 3.

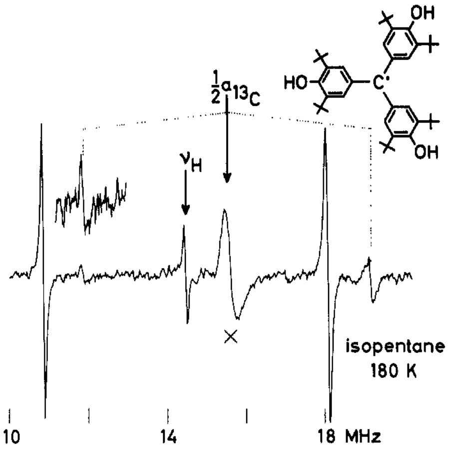

Figure 5. ENDOR spectrum of **1b** exhibiting ^{13}C ENDOR signals in natural abundance, obtained with a field setting on a respective satellite line in the EPR spectrum. (The broad signal marked by x is not an ENDOR line but an image of an EPR peak.)

Table I. Comparison of ^1H and ^{13}C Hyperfine Coupling Constants (MHz) of **1b** with Data of Triphenylmethyl Radicals[a]

position	**1b**	TPM[b]	HTB–TPM[c]
o-^1H	−7.19	−7.304	7.20
m-^1H	(−0.03)[d]	+3.203	
p-^1H	(+0.14)[e]	−7.997	7.85
central ^{13}C	+64.41[f]	+66.87[g]	65.9
attached ^{13}C	30.68		31.7
o-^{13}C			18.2
m-^{13}C	9.55		9.0
p-^{13}C			11.5
g	2.002818	2.002588[h]	

[a] Measured by ENDOR, solvent toluene (200 K), accurate within ± 0.01 MHz, unless stated otherwise. Conversion of units: 1 G ≙ 0.1 mT ≙ 2.803 MHz. [b] Triphenylmethyl radical. [c] Tris(3,5-di-*tert*-butylphenyl)methyl radical in benzene at 298 K; EPR data from ref 21. [d] *tert*-Butyl protons. [e] Hydroxy protons; this coupling constant is strongly temperature-dependent; see text and Figure 10. [f] At 330 K; temperature coefficient $da/dT = +18 \pm 1$ kHz/K. [g] At 300 K; temperature coefficient $da/dT = +17.0 \pm 0.3$ kHz/K, from ref 16. [h] From ref 22; the measured *g* value of **1b** (toluene, 290 K; $\pm 1 \times 10^{-5}$) has been calibrated relative to this value.

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Table II. Hyperfine Coupling Constants (MHz) of Radicals **2b**–**5b**[a]

position	**2b**, 210 K	**3b**, 230 K	**4b**, 230 K	**5b**, 210 K
o-^{1}H	−7.24	−8.16	−8.87	−8.71(2 H) −7.17(1 H) −7.07(1 H)
p-OH	+0.12	+0.25	+0.29	+0.18
o'-^{1}H	−7.05	−4.56 +2.16[c]	+0.98[c]	−4.80[d,e]
m'-^{1}H	+3.11	+2.70 +2.60	+2.52	+2.85
p'-^{1}H	−7.88	+4.56[c]	+1.55[c]	−4.91[d]
central ^{13}C	+65.56[b]			+66.98[b]

[a] Measured by ENDOR; solvent, toluene; accurate within ±0.01 MHz. Signs were determined by general TRIPLE. [b] At 350 K. [c] Methyl protons. [d] Assignment might be interchanged. [e] Phenyl substituent: +0.69 (1 H), −0.38, and −0.24 MHz.

the determination of relative signs in a way exactly analogous to a general TRIPLE experiment.[17,18] Since the coupling constant of the central ^{13}C atom in the triphenylmethyl radical is known to be positive,[16] this experiment establishes the absolute signs of the ^{1}H coupling constants in **1d**; see Table I.

It should be mentioned that further ^{13}C coupling constants of (unlabeled) **1b** could be extracted not only from the positions of ^{13}C "satellite lines" in the EPR spectrum but also from ^{13}C ENDOR signals observed in natural abundance. An example is given in Figure 5. The assignment of these coupling constants to molecular positions (see Table I) is based on the multiplicities deduced from the intensities of the EPR satellite lines and on the observed relaxation behavior; details of this method will be reported elsewhere.[19]

A comparison of the experimental hyperfine data of **1b** collected in Table I with those of the triphenylmethyl radical establishes the structure of **1b**. Furthermore, from the fact that the g value of **1b** is only slightly larger than that of the unsubstituted radical, whereas galvinoxyls have g values of about 2.0046,[20-22] it can be concluded that the π-spin populations at the oxygen atoms are small. Judging from the temperature dependence of the EPR signal amplitudes of **1b**, this radical does not dimerize noticeably. The mechanism of the formation of **1b**, however, could not yet be elucidated with certainty. It requires obviously the uptake of a hydrogen atom, i.e., a one-electron reduction followed by protonation. This reaction takes place only in sufficiently dry hydrocarbon solvents and does not proceed quantitatively; in a side reaction the (di-) sodium salt forms and precipitates. In alcoholic or ethereal solvents, only the latter reaction is observed; the diamagnetic dianion is soluble in these solvents. The origin of the proton required to form **1b** could not be established so far; it might be due to traces of water still present in absolute toluene (dried over Na/K; sample preparation on a high-vacuum line) or alternatively stem from another molecule of **1a**. Since no deuterium is incorporated when the reaction is performed in perdeuteriotoluene, a reaction with the solvent can be ruled out.

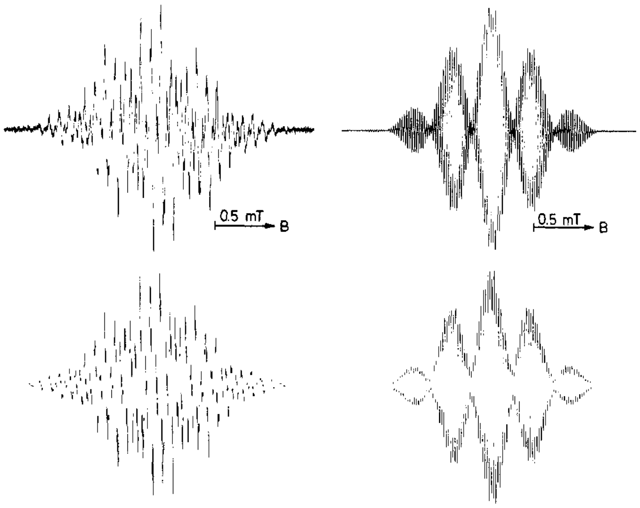

Figure 6. Top: EPR spectra of **3b** (left; toluene, 230 K) and **4b** (right; toluene, 260 K). Bottom: Computer simulations.

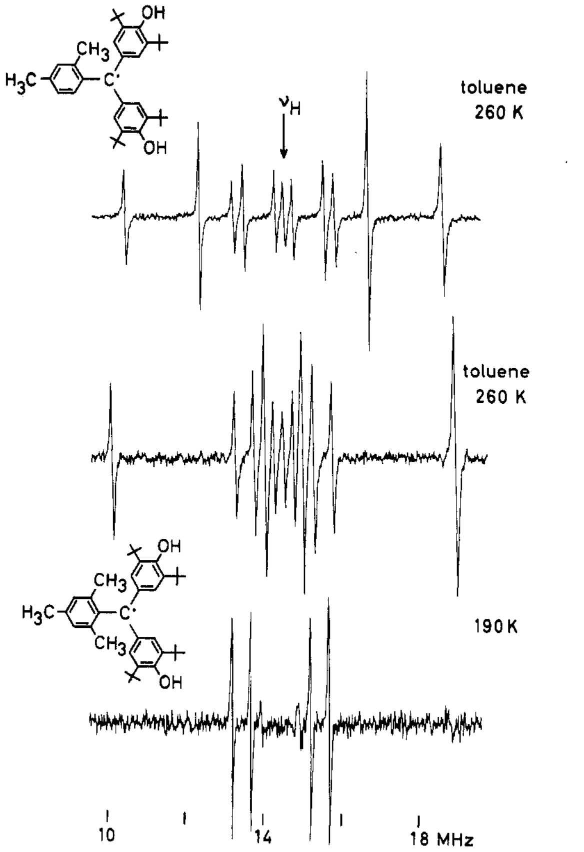

Figure 7. ENDOR spectra of **3b** (top) and of **4b** taken at two different temperatures (center and bottom).

Other Triphenylmethyl Radicals. Apart from **1b** which has been described in detail in the previous section, a variety of triphenylmethyl radicals, e.g., **2b**–**5b**, is accessible by reduction of (substituted) phenylgalvinols. In **2b**, the threefold symmetry found in **1b** is lost; therefore, the six ortho protons are no longer equivalent. An unequivocal assignment of all coupling constants to molecular positions could be achieved by means of ^{1}H and ^{2}H ENDOR studies of the selectivity deuterated radical **2f** and computer simulations of the EPR spectrum; see Table II. Since the temperature dependence of the coupling constants of the hydroxy protons in **2b** and all other radicals of this series are similar to that found for **1b**, their ENDOR signals are easily recognized. Relative signs of the proton hyperfine coupling constants of all radicals described here have been determined by general TRIPLE experiments. The ^{13}C coupling constant of the central ^{13}C atom in **2d** has been measured by ^{13}C ENDOR; see Table II.

It was of interest to investigate the influence of steric hindrance on the geometries and spin density distributions caused by substitution of the ortho positions of the phenyl ring. Therefore, the radicals **3b**–**5b** have been studied. The EPR and ENDOR spectra of **3b** and **4b** are depicted in Figures 6 and 7; the data are collected in Table II. Unequivocal assignments of all hyperfine coupling constants of these two radicals to molecular positions can be given based on the multiplicities accessible from computer simulations of their EPR spectra; see Figure 6 (bottom), with the exception

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Table III. Hyperfine Coupling Constants (MHz) of Radicals **6b–10b**[a]

position	**6b**, 230 K	**7b**, 250 K	**8b**, 210 K	**9b**, 240 K	**10b**, 305 K
o-^{1}H	−10.19 (2 H) −6.50 (2 H)	−9.14 (2 H) −7.65 (2 H)	−10.50 (2 H) −6.07 (2 H)	−7.51 (4 H)[e]	−7.29 (4 H)[e,g]
p-OH	+0.55 (1 H) +0.35 (1 H)	+0.55[c]	*c*	+0.35 (2 H)	+0.76 (2 H)
alkyl β	+19.65 (1 H)	+10.68 (1 H)	+21.45 (1 H)		
alkyl γ	+0.40 (6 H)	−1.60 (2 H) +0.82 (2 H)	−1.87 (4 H)[d]	+0.52 (9 H)	−1.58 (6 H)
alkyl δ		+0.27 (6 H)	+2.06 (2 H)[d] +0.33[d]		+1.63 (3 H)[d] −0.10[d]
central ^{13}C	74.7[b]			81.89[f]	

[a] See footnote *a*, Table II. The number of equivalent protons is given in parentheses. [b] At 300 K (EPR). [c] The hydroxy protons are probably inequivalent. [d] Assignment to molecular positions not established experimentally. [e] Broad ENDOR signals; see text. [f] At 350 K (ENDOR). [g] Inequivalence observed at low temperatures; −12.74 MHz (2 H) at 210 K.

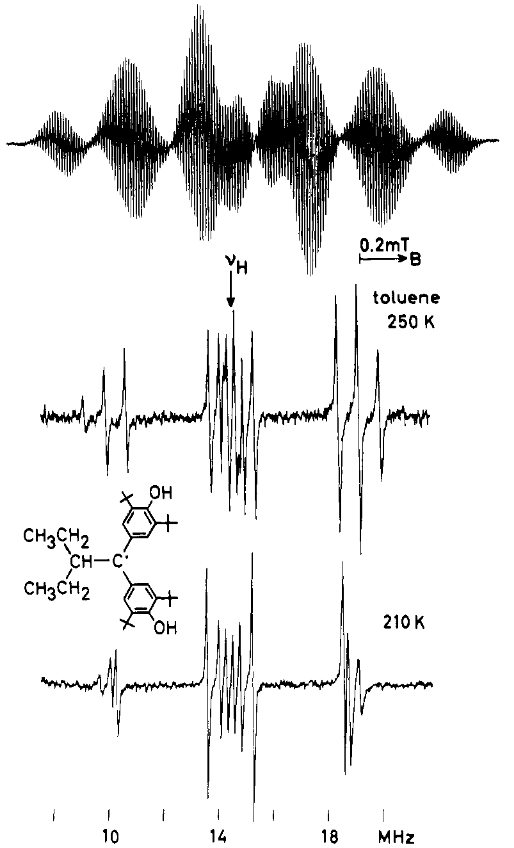

Figure 8. EPR spectrum (top; toluene, 290 K) and ENDOR spectra of **7b** (center and bottom).

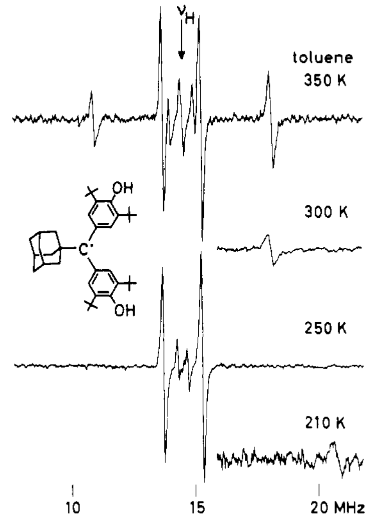

Figure 9. ENDOR spectra of **10b** taken at four different temperatures. Note the temperature dependence of the line width and position of the high-frequency signal.

of the two methyl groups in the ortho and para positions of **3b**. The assignment given in Table II is based on a comparison with **4b**, taking into account the relative magnitudes of the coupling constants and the relaxation behavior of the ENDOR signals. Figure 7 (bottom) shows the ENDOR spectrum of **4b** taken in toluene at 190 K, i.e., in a highly viscous solvent giving rise to a long correlation time for rotational diffusion of the radicals. It is known from the theory of the ENDOR response[23] that only ENDOR signals from nuclei exhibiting exceptionally small hyperfine anisotropies can be detected under these conditions. This phenomenon has occasionally been employed to identify freely rotating methyl groups.[24] The spectrum under consideration shows two pairs of intense sharp ENDOR signals and a much weaker pair in the middle. The intense signals are due to the methyl group in the para position of the phenyl ring and to the ring protons in the meta positions, the weak signals belong to the methyl groups in the ortho positions (vide infra). The relaxation behavior of the protons in **3b** is similar, although the differences in signal intensities are less pronounced.

Regarding the *ortho*-phenyl-substituted radical **5b**, a pronounced inequivalence of the four ring protons in the basic dihydroxydiphenylmethyl moiety is found. Moreover, the widths of the respective ENDOR lines are strongly temperature-dependent, and at 285 K coalescence to a single pair of signals is observed. This line-shape effect is characteristic of dynamic processes;[25,26] i.e., the phenyl substituent causes steric hindrance of internal rotations (vide infra). Similarly, the ENDOR spectra indicate a hindered rotation of the phenyl substituent itself, but this effect could not be traced accurately because of overlapping lines, the more so since the hydroxy proton signals with strongly temperature-dependent positions appear in the frequency range under consideration. The ^{13}C coupling constant of the central carbon atom in **5d** is somewhat larger than in **2d**; see Table II.

Diphenylmethyl Radicals. Radicals of the diphenylmethyl series (**6b–10b**) have been generated from several alkyl galvinols. So far persistent radicals could only be obtained with voluminous alkyl groups. Attempts to prepare these types of radicals from unsubstituted galvinol or from cyclopropylgalvinol failed, and the isopropyl and cyclohexyl derivatives, **6b** and **8b**, are the least stable in this series, decaying rapidly at room temperature.

Figure 8 shows EPR and ENDOR spectra of **7b**. It is evident that the coupling constants of this radical are strongly temperature-dependent; however, a dynamic line broadening could not be observed up to 305 K. The multiplicities and hence the assignments of the coupling constants to molecular positions have been determined by means of computer simulations of the EPR

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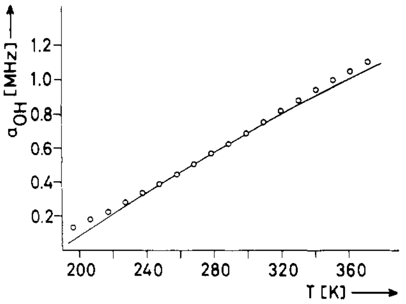

Figure 10. Temperature dependence of the hydroxy proton hyperfine coupling constant of **1b**. The experimental data points are denoted by circles; the solid line represents the calculated dependence based on a theoretical model; see text.

spectrum. The data are collected in Table III. Radicals **6b** and particularly **9b** and **10b** exhibit dynamic line-shape effects. For example, ENDOR spectra of **10b** taken at four different temperatures are depicted in Figure 9. The ENDOR signals belonging to the four phenyl ring protons, which are only slightly broader than the other signals at 350 K, are broadened increasingly with decreasing temperature and become too broad to be observable at 250 K. At 210 K, a signal can be observed again, but the coupling constant is now much larger (12.74 MHz) and must be assigned to two equivalent protons. The ENDOR lines due to the other two protons, which should exhibit a coupling of roughly 1.8 MHz, could not be resolved because of overlap with neighboring signals. Corresponding to the ENDOR spectra, the EPR spectra of **10b** show an alternating line-width effect. The ^{13}C coupling constants of the central carbon atoms of the labeled compounds **6d** and **9d** have been measured. A comparison of Tables II and III demonstrates that they are significantly larger than those of the triphenylmethyl series. Obviously the magnitude of this coupling constant increases with increasing steric hindrance.

Temperature Dependence of Hydroxy Proton Couplings. A salient feature of the radicals described here is the pronounced temperature dependence of the hydroxy proton couplings. A plot for **1b** is given in Figure 10, and essentially the same dependence is found for the other radicals, provided that different spin populations in the hydroxyphenyl groups are taken into account. At first sight it might be assumed that a steric interaction with the neighboring *tert*-butyl groups is responsible for the effect and that this interaction forces the hydroxy proton out of the plane. However, it will be shown that the potential minimum corresponds to a planar conformation.

Hyperfine coupling to hydroxy protons and its temperature variation has been studied extensively in small molecules such as hydroxymethyl.[27,28] β-Proton hyperfine couplings generally show a pronounced dependence on the torsional angle which is ascribed to the hyperconjugative mechanism of spin density transfer, usually of the form[29]

$$a_\beta = (B_0 + B_2 \cos^2 \theta)\rho_\alpha \qquad (2)$$

where θ is the dihedral angle between the X–H bond (X = C and O) and the $2p_z$ orbital on the α-carbon atom. In order to account for the temperature dependence, it is assumed that the rotation of the X–H group is restricted by a potential barrier which in the case of C_2 symmetry can be represented by

$$V(\theta) = \frac{V_2}{2}(1 - \cos 2(\theta - \theta_0)) \qquad (3)$$

where θ_0 corresponds to the minimum of the potential well. The observed coupling is the average of the expectation values of a_β for all torsional states weighted by their populations. In the classical approach assuming Boltzmann statistics one obtains[30]

$$\bar{a}_\beta = \frac{\int_{-\pi}^{\pi} a_\beta(\theta) \exp(-V(\theta)/k_BT)d\theta}{\int_{-\pi}^{\pi} \exp(-V(\theta)/k_BT)d\theta} \qquad (4)$$

It should be mentioned, however, that a rigorous treatment involving rotating groups with a small moment of inertia requires the application of a quantum-mechanical procedure.[27,31] We adopt the classical approach to estimate the rotational barrier V_2. Since meaningful results cannot be obtained by a fit procedure if all parameters are allowed to vary, it is necessary to make some assumptions. An INDO calculation yielded the following parameters for hydroxymethyl ($\rho_C \simeq 1$): $B_0 = -4.6$ MHz and $B_2 = 116.2$ MHz;[27] $\rho_C = 0.0810$ ($\rho_O = 0.0058$) was obtained from an HMO–McLachlan calculation for **1b**.[32] Consequently, the potential minimum must correspond to the planar conformation ($\theta_0 = 90°$: $a_{OH} = -0.37$ MHz, whereas $a_{OH} = 9.04$ MHz for $\theta_0 = 0°$). When only V_2 was allowed to vary, a reasonable fit of the calculated curve to the experimental points could not be achieved. Since B_0 depends on the spin population at the oxygen atom and the above-given value proved to be inadequate; even in the case of hydroxymethyl, it was also varied. A least-squares fitting procedure yielded $B_0 = -12.5$ MHz and $V_2 = 8.4$ kJ/mol; the calculated temperature dependence is depicted in Figure 10 together with the experimental points. Since the classical approach is not strictly adequate, the agreement with the experimental data is not perfect and the obtained parameters should only be regarded as semiquantitative. Nonetheless, it can be concluded that the potential barrier V_2 in **1b** is considerably smaller than in the hydroxymethyl radical (quantum-mechanical approach: 16.7 kJ/mol, classical approach: 28.9 kJ/mol).[27] In the latter, the barrier is probably due to a certain amount of double-bond character of the C–O bond which should be smaller in **1b** (HMO π-bond order: 0.254). In view of the preferred conformation and the potential barrier, steric interactions between the hydroxy proton and the neighboring *tert*-butyl groups apparently do not play an important role in **1b**.

It is noteworthy that both in the hydroxymethyl radical[27] and in **1b**, a pronounced isotope effect is found when the hydroxylic position is deuterated, i.e., the observed ratio a_{OH}/a_{OD} deviates considerably from the calculated ratio $\gamma_H/\gamma_D = 6.5144$. For the hydroxymethyl radical a ratio of 6.05/1.06 = 5.7 has been reported, whereas for **1b** a ratio of 0.69/0.062 = 11 has been determined. At first sight, the isotope effect seems to operate into opposite directions in these cases. However, deuteration has the same effect as a decrease in temperature in both cases which is reasonable since the excursion of a deuteron from its equilibrium position in an oscillating motion is known to be smaller than that of a proton owing to its higher mass. Whereas the absolute magnitude of a_{OH} in the hydroxymethyl radical increases with decreasing temperature (hence $a_{OH}/a_{OD} < 6.5$), the coupling constant actually decreases as in the case of **1b** since its sign is certainly negative.[27]

An extrapolation of the experimental points plotted in Figure 10 toward lower temperatures suggests that a_{OH} should change signs. This assumption could not be verified, however, since the respective ENDOR signals could not be detected below 200 K even when the low-melting solvent isopentane was used. This failure can be attributed to the fact that the viscosity of the solvents becomes too high at low temperatures, giving rise to short relaxation times T_{2e} and thus to a decrease of the ENDOR enhancement particularly for small hyperfine couplings.[33]

Evaluation of Twist Angles. Comparison with Galvinoxyls. The triphenylmethyl radical has been studied extensively, e.g., by EPR,[34] EPR in liquid crystals,[35] ENDOR,[36] and X-ray analysis

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(32) Parameters: $\lambda = 1.2$, $h_O = 2.0$, $k_{C-O} = 0.8$, and $\beta_{12} = 0.866\beta$ (twist angles 30°).

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Table IV. Calculated Spin Populations for Di- and Triphenylmethyl Radicals with Various Twist Angles[a]

	triphenylmethyl radicals			diphenylmethyl radicals		
θ_1	30°	30°	30°	25°	20°	0°
θ_2	30°	30°	30°	25°	40°	70°
θ_3	30°	50°	70°			
central	0.5235	0.5858	0.6491	0.6397	0.6829	0.7765
o	0.0958	0.1039	0.1107	0.1199	0.1352	0.1631
m	−0.0358	−0.0397	−0.0440	−0.0477	−0.0545	−0.0712
p	0.0884	0.0945	0.0986	0.1068	0.1193	0.1377
o'	0.0958	0.0560	0.0164	0.1199	0.0877	0.0175
m'	−0.0358	−0.0222	−0.0071	−0.0477	−0.0367	−0.0087
p'	0.0884	0.0504	0.0143	0.1063	0.0765	0.0140

[a] HMO–McLachlan calculation with $\lambda = 1.2$ and $k(\theta) = \cos\theta$.

(tris(*p*-nitro) derivative),[37] and it is now generally accepted that the phenyl rings are twisted by about 30° ("propeller" conformation). Additional evidence for this notion was obtained from a ^{2}H ENDOR investigation of perdeuteriotriphenylmethyl dissolved in a liquid crystal.[38] These experiments allow the determination of deuterium quadrupole splittings which depend on the deuterium quadrupole coupling constant (essentially constant for aromatic C–D bonds, $e^2qQ/h = 180 \pm 10$ kHz), the order parameters, and the orientation of the C–D bond axis. In the case of perdeuteriotriphenylmethyl, resolved quadrupole splittings were only observed for the para positions ($\delta_Q = 35 \pm 2$ kHz), whereas an estimate of $\delta_Q \simeq 15$ kHz for the ortho and meta positions was obtained from line-width studies (solvent: smectic A phase of 4-cyano-4′-octylbiphenyl, 294 K). *This result is not compatible with a planar structure of the radical* but can be explained if twisting of the phenyl rings by about 30° is assumed since this would reduce the quadrupole splittings for the ortho and meta positions appropriately but leave that for the para positions unaltered.

In principle, it should be possible to estimate the twist angles in (substituted) triphenylmethyl radicals by comparison of the experimental hyperfine coupling constants with data from quantum-mechanical calculations. However, an inspection of the large number of papers dealing with this problem demonstrates that reliable values for the twist angles cannot be obtained in this way, at least not from the proton hyperfine data alone.[21] Thus, the best overall agreement with an HMO–McLachlan calculation using standard parameters ($\lambda = 1.2$, $Q^{H}{}_{CH} = -2.7$ mT in the McConnell relationship, eq 5) is obtained for a planar structure, although the ordering $|a_o| > |a_p|$ is wrongly predicted.[36]

$$a_H = Q^{H}{}_{CH}\rho_C \qquad (5)$$

Agreement can also be achieved for a twisted structure ($\theta \simeq 30°$) provided that unusually large values of $Q^{H}{}_{CH}$ (−3.12 mT)[39] or λ (1.45)[40] are used or an anomalously low electronegativity of the central carbon atom is assumed.[41] Although these calculations correctly predict the meta proton coupling constant, this result is actually wrong since it has been recognized that delocalization of the unpaired π-electron spin density into the σ system of twisted phenyl rings ("phenyl hyperconjugation") may not be neglected.[42] Experimental evidence of the fact that the π-spin population in the meta positions is indeed smaller than predicted has been obtained in the investigation of the tris(*m*-tolyl)methyl radical which exhibits an "unusually" small hyperfine coupling constant of the methyl protons (2.35 MHz).[39]

Nevertheless, a comparison of the experimental data of the radicals under study with calculated spin populations should be instructive and give an insight into their structures. Results of HMO–McLachlan calculations for tri- and diphenylmethyl radicals with various twist angles are collected in Table IV. For the sake of generality, data are given for unsubstituted radicals; when the *para*-hydroxy groups are taken into account,[32] the absolute magnitudes of the spin populations are reduced by ca. 10% (para), 5% (meta), and 1% or less for all other positions. In the following discussion of the triphenylmethyl derivatives **1b**–**5b**, it will be assumed that the two (in **1b** three) 3,5-di-*tert*-butyl-4-hydroxyphenyl groups are twisted by ca. 30°. A comparison of the hyperfine coupling constants of **1b** and **2b** with those of the unsubstituted triphenylmethyl radical (Tables I and II) shows no substantial deviations; minor differences may be attributed to substituent effects. On the other hand, the spin populations in the unique phenyl ring are evidently reduced when substituents are introduced into the ortho positions of this group (**3b**–**5b**, Table II). Correspondingly, the ortho proton coupling constants of the hydroxyphenyl groups indicate a smaller but significant increase of spin population in these groups. Since the para proton coupling constants are not affected by π–σ delocalization,[42] they should be best suited for estimating the twist angle. In **3b** and **4b** the para position is substituted by a methyl group, but it is normally found that the absolute magnitude of the coupling constant of a freely rotating methyl group is almost the same as that of a respective α proton whereas the sign is opposite. Therefore a McConnell-type relation (eq 5) with $Q^{H}{}_{CCH_3} \simeq +2.9$ mT applies;[43] this relation holds, for example, for the tris(*p*-tolyl)methyl radical.[31] When the data are calibrated relative to the triphenylmethyl radical, the following twist angles are obtained for the ortho-substituted phenyl groups: ca. 50° in **3b** and **5b** and ca. 70° in **4b**. Thus, the steric hindrance of an *ortho*-phenyl substituent is about the same as that of an *ortho*-methyl substituent, but additionally it gives rise to an inequivalence of the two hydroxyphenyl groups.

In contrast to the para proton coupling constants, the meta proton coupling constants decrease only from 3.11 to 2.52 MHz in the series **2b**–**4b**. In **4b** the meta coupling is in fact the largest coupling in the phenyl group. This is the typical situation of phenyl hyperconjugation which has been observed and discussed previously, e.g., in studies of the radical anion and cation of rubrene[6] and the radical anion of 9,10-dixylylanthracene.[7] It should be pointed out that the anomalously large meta proton coupling constants in highly twisted phenyl rings are only due to σ-spin density from π–σ mixing, whereas the π spin populations at the meta carbon atoms are small as predicted from pure π-MO theories. Therefore, the *anisotropic* hyperfine interaction of the meta protons should be small. Evidence for this prediction has been obtained in the present study by an investigation of the relaxation behavior of the ^{1}H ENDOR signals of **4b**. From the observation that the meta proton ENDOR signals are unusually narrow and intense under experimental conditions, resulting in

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long rotational correlation times (see Figure 7, bottom), it can be concluded that the hyperfine anisotropy must be extraordinarily small.[23] On the other hand, the *ortho*-methyl groups exhibit an unusually large dipolar hyperfine interaction which is attributed to the fact that these groups are located in close proximity to the central carbon atom which bears a large π spin population. Finally it should be noted that the isotropic *ortho*-methyl proton coupling constants in **3b** and **4b** are exceptionally small. Although we have no definitive explanation for this finding, we attribute it to some kind of "through-space" interaction. The same behavior was encountered in the study of ditolyl- and dixylylanthracene radical anions.[7]

The two hydroxyphenyl groups in the diphenylmethyl radicals **6b–8b** are clearly inequivalent due to different twist angles; see Table III. The same is true for **9b** and **10b**, although an internal dynamic process results in an apparent equivalence at elevated temperatures. An evaluation of the twist angles has to be based on a discussion of the ortho proton coupling constants which convey merely information about the differences between the twist angles. A comparison with calculated spin populations (Table IV) yields the following estimates: 25°/35° in **7b**, 20°/40° in **6b** and **8b**, and 0°/70° in **9b** and **10b**. It should be noted that the coupling constants, particularly in **7b**, are strongly temperature-dependent due to a temperature dependence of the preferred conformation and/or torsional oscillations. The radicals **9b** and **10b** (at low temperatures) are actually best described as benzyl-type radicals (ortho proton coupling constant in the benzyl radical: 14.43 MHz[44]); at elevated temperatures, equilibration of the two hydroxymethyl groups is rapid on the EPR/ENDOR time scale. The ^{13}C coupling constants of the central carbon atoms prove to be a sensitive probe of the steric hindrance or the transitions from a triphenylmethyl- via a diphenylmethyl- to a benzyl-type radical, respectively, as the increase from 65.56 to 81.89 MHz in the series **2b**, **5b**, **6b**, and **9b** shows (Tables II and III). This increase is in qualitative agreement with the predicted increase in π-spin population at the central carbon atom (Table IV).

Regarding the alkyl groups in the radicals **6b–8b**, information about the torsional angle is accessible from the β-proton coupling constant. The angular dependence is described by eq 2, although the angular function should be replaced by an average $\langle\cos^2\theta\rangle$, taking into account torsional oscillations. Since the parameters in eq 2 are not accurately known, it is a common procedure to compare the β-proton coupling constant with that of the corresponding radical in which the alkyl group is replaced by methyl ($\langle\cos^2\theta\rangle = {}^1/_2$).[31] Actually the methyl proton coupling constant of the 1,1-bis(3,5-di-*tert*-butylphenyl)-1-ethyl radical, which should be a good model, has been published, $a_{CH_3} = 43.2$ MHz.[45] Thus, the alkyl groups in the radicals **6b–8b** prefer to adopt conformations with dihedral angles $\theta > 45°$, and the following average values of $\langle\theta\rangle$ (calculated from $\langle\cos^2\theta\rangle$) are obtained: ca. 60° for **6b** and **8b** and ca. 70° for **7b**.

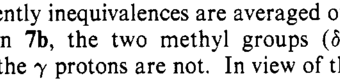
It is interesting to compare the structures of the di- and triphenylmethyl radicals **1b–10b** with those of the corresponding galvinoxyl radicals **1g–10g** since any effects of steric hindrance are the same whereas the electron spin distribution is completely different. Thus, HMO theory predicts a node of the singly occupied molecular orbital (SOMO) at the central carbon atom in galvinoxyls, whereas the maximum spin population is found at this position in the di- and triphenylmethyl radicals. This very different behavior becomes evident in a comparison of the ^{13}C coupling constants of the central carbon atoms: +64.4 MHz in **2b** vs. −27.7 MHz in **2g**[9a] and +81.9 MHz in **9b** vs. −17.0 MHz in **9g**[9b] (note the different signs).

On the other hand, the geometries of the two types of radicals are very similar. Thus, the twist angles deduced for the diphenylmethyl radicals **6b–8b** do not deviate significantly from those of the corresponding galvinoxyls **6g–8g**.[9b] Moreover, the dynamic behavior of the radicals **5b–10b** is qualitatively similar to that of the galvinoxyls **5g–10g**.[8,9] In particular, it had been stated previously that the two "galvinoxyls" **9g** and **10g** are best described as equilibrating phenoxyls.[9b] The present results demonstrate that the respective diphenylmethyl radicals (**9b** and **10b**) should likewise be regarded as equilibrating benzyl radicals. Although a quantitative comparison of activation energies is beyond the scope of this paper, it can be concluded that the dynamic behavior of both the galvinoxyls and the di- and triphenylmethyl radicals is mainly governed by steric effects and not by electronic influences.

Spin Density Transfer into Alkyl Groups. The β-proton hyperfine coupling constants of the alkyl groups of radicals **6b–8b**, which can be accounted for by a hyperconjugative mechanism of spin density transfer, have been discussed above. In this section the γ- and δ-proton coupling constants shall be considered. Since the alkyl groups are attached to a center bearing large π-spin population, these couplings are relatively large; see Table III. It should be emphasized that the signs of all couplings have been determined by means of general TRIPLE experiments and that in most cases an assignment to molecular positions could be given based on the multiplicities deduced from computer simulations of the EPR spectra.

The two methyl groups (γ protons) of the isopropyl moiety in **6b** are equivalent despite the low symmetry of the radical (vide supra). Apparently inequivalences are averaged out by torsional oscillations. In **7b**, the two methyl groups (δ protons) are equivalent but the γ protons are not. In view of the equivalence of the methyl groups in both radicals we conclude that the methylene groups in **7b** are equivalent whereas the two γ protons in each methylene group are inequivalent (diastereotopic). An unambiguous assignment to positions within the cyclohexyl group of **8b** cannot be given. In analogy to an INDO study of 9-cyclohexylanthracene[46] and to an investigation of cyclohexyl *tert*-butyl nitroxide,[47] we assume that the axial and equatorial γ protons are equivalent. This assignment is supported by the result for the adamantyl moiety in **10b** where the six γ protons are equivalent for symmetry reasons and a similar coupling constant is found.

From an inspection of Table III it is evident that the γ-proton coupling constants of radicals **6b–10b** vary substantially and even change sign. Since the π-spin populations at the central carbon atoms are not that much different in these radicals, it must be concluded that a strong conformational dependence of the γ-proton couplings is responsible for this variation. The sterical dependence of long-range splittings has long been recognized,[48] and γ-proton coupling constants have been rationalized in terms of different spin-density-transfer mechanisms, namely spin polarization and spin delocalization (homohyperconjugation).[49] The latter mechanism is most important for the W-plan arrangement giving



rise to a large positive value, whereas negative γ-proton coupling constants are found for most conformations including the anti-W arrangement. In accordance with this concept, negative γ-proton couplings have been observed in **8b** and in **10b** where the geometry is approximately anti-W, whereas small positive values have been measured for the freely rotating *tert*-butyl group in **9b** and for the methyl groups in **6b**.

Conclusions

Concluding, we can state that *para*-hydroxy-substituted di- and triphenylmethyl radicals which are accessible from galvinols by

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reduction have similar structures and exhibit a similar dynamic behavior as the corresponding galvinoxyl radicals which are generated by oxidation of the parent galvinols. On the other hand, the spin density distributions in these two types of radicals are completely different. This allows the investigation of different properties. Thus, phenyl hyperonjugation can be studied in ortho-substituted triphenylmethyl-type radicals whereas the phenyl proton coupling constants in the respective galvinoxyls are too small for this purpose. Moreover, the mechanism of spin density transfer into alkyl groups can be investigated in diphenylmethyl-type radicals because of the large spin population at the central carbon atom. In this context, the potential of the general TRIPLE method for a determination of signs of hyperfine coupling constants proved to be of great value.

Acknowledgment. We thank Dr. K. Schubert and M. Sordo for samples of the ^{13}C-labeled and deuterated galvinols, respectively. H. K. gratefully acknowledges financial support by Deutsche Forschungsgemeinschaft (Normalverfahren) and Fonds der Chemischen Industrie. B. K. gratefully acknowledges a Liebig stipend of the Fonds der Chemischen Industrie.

Registry No. 1a, 2887-52-7; **1b**, 93403-31-7; **1d**, 93403-32-8; **2a**, 56523-92-3; **2b**, 93425-33-3; **3a**, 93403-33-9; **3b**, 93403-34-0; **4a**, 93425-34-4; **4b**, 93425-35-5; **5a**, 61937-92-6; **5b**, 93425-36-6; **6a**, 74853-85-3; **6b**, 93403-35-1; **7a**, 79320-49-3; **7b**, 93403-36-2; **8a**, 79320-50-6; **8b**, 93403-37-3; **9a**, 61937-90-4; **9b**, 93403-38-4; **10a**, 93403-39-5; **10b**, 93403-40-8; (2,6-di-*tert*-butyl-4-bromophenoxy)trimethylsilane, 27329-74-4; 2,4,6-trimethylbenzoic acid methyl ester, 2282-84-0; triphenylmethyl, 2216-49-1; sodium amalgam, 11110-52-4.

Two-Dimensional NMR Spectroscopy of Tetra-*o*-tolylcyclopentadienone. Complete Rotamer Assignment

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Abstract: A slow-exchange 2D NMR experiment on tetra-*o*-tolylcyclopentadienone allows the making of a complete rotamer assignment and leads to stronger experimental evidence to the uncorrelated rotation of the *o*-tolyl rings in the α position as the threshold mode.

Recently we presented a detailed ^{1}H and ^{13}C NMR study on the stereochemistry of tetra-*o*-tolylcyclopentadienone (compound **1**).[4] We proposed a static stereochemistry, based on a molecular framework, in which the four peripheral *o*-tolyl rings are perpendicular to the central cyclopentadienone ring, at least on the NMR time scale. Thus compound **1** exists as a mixture of ten rotamers. Their characteristics are given in Table I and in Table I of ref 4. Therefore, a total of 16 methyl resonances is expected, in achiral solvents[4] when internal rotations are frozen out, 8 being due to the α *o*-tolyl rings and the 8 others to the β ones.

In the ^{1}H spectra recorded in the slow-exchange region of **1** (−60 to −30 °C), we observed at most 14 signals, with important overlapping or tailing. It was, therefore, impossible to make any assignments of these signals to the rotamers they arise from; neither we could assert whether two signals are missing because of accidental isochronies or because one of the rotamers is much less populated than the others.[4]

In a medium-temperature range, we observed four residual[5-7] methyl signals, two almost isochronous low-field α ones and two high field β ones, assignable to two residual isomers.[4] This partial coalescence is due to internal rotations of *o*-tolyl rings becoming rapid on the NMR time scale. This behavior was shown to be compatible with only four out of the ten possible modes of internal rotations of **1**: two three-ring rotations, M_7 and M_8, and two one-ring rotations, M_1 (the α one ring rotation) and M_2 (the β one ring rotation). We excluded M_7 and M_8, though NMR indistinguishable from M_2 and M_1, respectively, for steric reasons. We preferred M_1 as the threshold mode rather than M_2 exclusively on the basis of qualitative activation barrier considerations.[4]

The aim of this paper is to propose a complete rotamer assignment together with strong two-dimensional NMR evidence for the α one-ring rotation as the threshold mode.

Figure 1 presents the methyl region of a resolution-enhanced[4,8,9] (Lorentz–Gauss) 500-MHz ^{1}H spectrum, recorded in $CDCl_3$ at −43 °C, with our signal numbering, our rotamer assignment, and the constitution α or β of the methyl group that the signal arises from (see also Table I). Signals with double numbering are pairs of isochronous resonances (see below).

The 500-MHz spectrum of Figure 1 compared fairly well with the 270-MHz spectrum at −40 °C of Figure 4 of ref 4 except for two details: (1) the well-separated signals 9 and 10 in the 500-MHz spectrum are isochronous in the 270-MHz spectrum of ref 4; and (2) the two isochronous signals 15 and 16 in the 500-MHz spectrum at −43 °C are well separated in the 270-MHz spectrum at −40 °C. We attribute the latter observation to a strong temperature dependence of the chemical shift of signal 15.

Figure 2 represents identical contour plots of the slow-exchange 500-MHz 2D spectrum, recorded at −43 °C, to which we have superimposed the networks, indicating, respectively, which α and

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