Sterically Hindered Free Radicals. 18.[1] Stabilization of Free Radicals by Substituents As Studied by Using Triphenylmethyls

Wilhelm P. Neumann,* Alicia Penenory,[2] Ulrich Stewen, and Manfred Lehnig

Contribution from the Lehrstuhl für Organische Chemie I of the University of Dortmund, Otto-Hahn-Str. 6, D-4600 Dortmund 50, Federal Republic of Germany.
Received September 19, 1988

Abstract: The relative stabilization of 10 4-mono- and 24 4,4′-disubstituted triphenylmethyl radicals **1** has been measured by recording the degree of dissociation of the corresponding quinonoid dimers **2** by means of ESR. The following substituents or combinations of two of them have been used: H, CF_3, *t*-Bu, OMe, OPh, CN, COPh, COMe, Ph, SMe, and NO_2. Both donors and acceptors enhance the stability in the ground state of the radicals, which is evaluated in terms of $\sigma^\bullet$ values and a Hammett-like equation. Two donors act additively, as do two acceptors. No specific synergism of a donor with an acceptor (capto-dative stabilization) has been found. Most efficient for the relative stabilization are the electroneutral substituents Ph and SMe. Most of the ESR spectra of these trityls are new. An exact assignment became possible via the corresponding ENDOR spectra, which are listed in detail. Many of the substituted trityls including dimers and precursors have been prepared for the first time.

In recent years, free radicals became important intermediates in highly selective organic synthesis, mainly in regio- and stereoselective C–C couplings. Thus, multistep radical reactions including ring closures (tandem reactions) are carried out in one-pot procedures with high yields and enantioselectivity.[3] A thorough knowledge of stability and stabilization effects of free radicals is desired, and new impact is given to basic research in this field.[4]

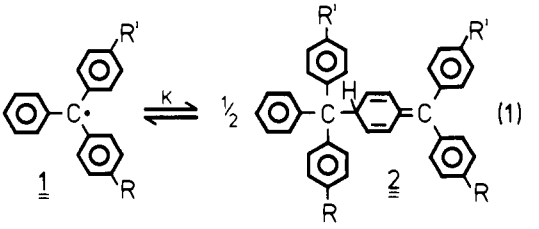
We have studied the electronic effects (inductive and resonance effects) of a considerable number of substituents on the stability of carbon-centered radicals.[5,6] There are earlier investigations aimed at this goal,[4,7] but the substituent-dependent influences measured are based only on few combinations of substituents. Moreover, the latter are often bound directly to the radical center, causing steric and other proximity effects thus restricting the general validity of the approaches.

In order to avoid these problems we have separated the substituents from the radical center by a spacer that transmits the electronic effects. We selected para-substituted derivatives of Gomberg's classical triphenylmethyl. This allowed access to the kinetically most uncomplicated test reaction for the stability of a radical, the dissociation–recombination equilibrium.[6]

We now wish to report our results with 10 important substituents and with 24 combinations of them and a detailed evaluation of specific substituent effects. This enables us to give a well-founded experimental examination and quantification of the cooperation of substituents (additive, less or more than additive).

Results

In order to rationalize stabilizing (or destabilizing) effects of the substituents R or combinations R/R′ or R′/R′ the latter have been located in para positions of trityl radicals **1**, and the equilibrium constant K has been determined in eq 1 by measuring the free-radical concentration in solutions of the corresponding dimer

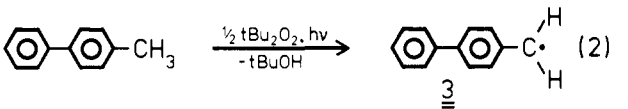


(1)

2 by means of ESR.[6] Very pure compounds are needed for this work. Most of the quinonoid trityl dimers **2** and their precursors are new. To estimate the influence of substituents R and R′ and to compare and verify our results of the equilibrium measurements with another independent radical-stabilization scale, we have found it best to use and to complete the $\sigma^\bullet$ scale of Arnold and Nicholas.[8] This scale, indicating spin density changes, is based on measuring substituent-dependent variations of the α-coupling constant a_R in para-substituted benzyl radicals with respect to that of the unsubstituted radical, a_H:[8,9]

$$\sigma^\bullet = 1 - (a_H/a_R)$$

One of the most important substituents to be discussed here is the phenyl group, which exhibits a high stabilizing effect.[4,10] For a quantification its $\sigma^\bullet$ value that is required for comparison with other substituents, see Table I. After fruitless attempts by others and us,[11] we succeeded by the use of sensitizing *p*-methoxyacetophenone and by filtering heat and short-waved UV off by a circulating methanol system at 25 °C (eq 2).



(2)

The ESR spectrum gave the very high value of $\sigma^\bullet_{Ph} = 0.062$ and a stabilization energy[8] of about 1.5 kcal/mol, in comparison with the unsubstituted benzyl radical.

(1) Part 17: Neumann, W. P.; Stapel, R. *Chem. Ber.* **1986**, *119*, 3432.
(2) Penenory, A., on leave from the University of Córdoba, Argentine, as Alexander von Humboldt Fellow 1986/88.
(3) Neumann, W. P. *Synthesis* **1987**, 665. Curran, D. P. *Synthesis* **1988**, 417; 489. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986.
(4) Viehe, H. G.; Janousek, Z.; Merényi, R. *Substituent Effects in Radical Chemistry*; NATO ASI Series C, D. Reidel: Dordrecht, 1986; Vol. 189.
(5) Neumann, W. P.; Stapel, R. *Chem. Ber.* **1986**, *119*, 3422.
(6) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762.
(7) Viehe, H. G.; Merényi, R.; Janousek, Z. *Pure Appl. Chem.* **1988**, *60*, 1635.
(8) Nicholas, A. M. De P.; Arnold, D. R. *Can. J. Chem.* **1986**, *64*, 270.
(9) Fischer, H. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1964**, *19a*, 866; **1965**, *20a*, 428.
(10) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254.
(11) Dinçtürk, S.; Jackson, R. A.; Townson, M.; Ağirbaş, H.; Billingham, N. C.; March, G. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1121. Stewen, U. Diploma Thesis, University of Dortmund, 1986.

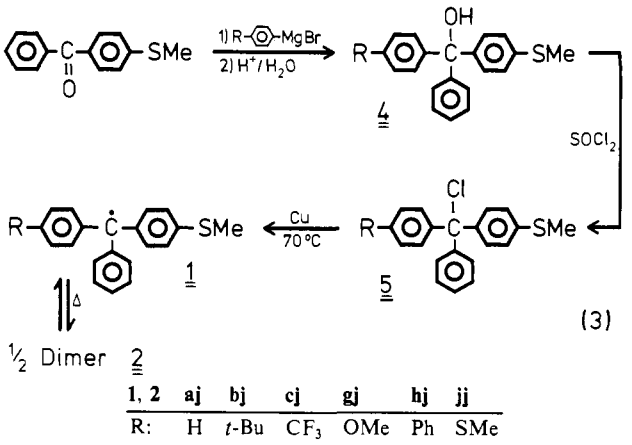
0002-7863/89/1511-5845$01.50/0

Table I. Linear Free Energy Relationship

1	R	R′	σ[19]	$\sigma^{\bullet}$[8,13]	($\sigma^{\bullet}$ + 0.01σ)	log K[a]
aa	H	H	0.00	0.0000	0.0000	−3.48
ab	H	tBu	−0.20	0.0080	0.0055	−3.10
ac	H	CF_3	0.54	−0.0086	−0.0019	−3.15
ad	H	CN	0.70	0.0400	0.0488	−2.66
ae	lH	COPh	0.42	0.0554	0.0607	−2.49
af	H	COMe	0.50	0.0597	0.0660	−2.70
ag	H	OMe	−0.28	0.0185	0.0150	−2.82
ah	H	Ph	−0.01	0.0615[a]	0.0614	−2.56
ai	H	OPh	−0.32	0.0185	0.0145	−3.21
aj	H	SMe	0.00	0.0630	0.0630	−2.78
ak	H	NO_2	0.78	0.0630[a]	0.0710	−2.55
bb	tBu	tBu	−0.20	0.0080	0.0055	−2.39
cc	CF_3	CF_3	0.54	−0.0086	−0.0019	−2.82
dd	CN	CN	0.70	0.0400	0.0488	−2.03
ee	COPh	COPh	0.42	0.0554	0.0607	−2.05
gg	OMe	OMe	−0.28	0.0185	0.0150	−2.63
hh	Ph	Ph	−0.01	0.0615[a]	0.0614	−1.57
ii	OPh	OPh	−0.32	0.0185	0.0145	−2.78
jj	SMe	SMe	0.00	0.0630	0.0630	−1.72

[a] This work.

Another very important substituent is the methylthio group,[10,12] $\sigma^{\bullet}_{SMe}$ = 0.063,[13] but SMe-substituted trityls had to be prepared for the first time. We followed eq 3 and obtained pure products.



½ Dimer 2

1, 2	aj	bj	cj	gj	hj	jj
R:	H	t-Bu	CF_3	OMe	Ph	SMe

Warming of the quinonoid α,para dimers **2** (see eq 1) gave the trityls **1** (see eq 3 and Table II). In the case of **2jj**, R = R′ = SMe, we observed an irreversible degradation at 70 °C, forming mainly the methane (4-$SMeC_6H_4)_2C(Ph)H$ and two minor unidentified products. Since no hydrogen abstraction from the solvent benzene takes place, the H in the methane probably comes from the radical **1jj**.[14] In the presence of oxygen, a peroxide of **1jj** arises and upon heating the methanol (4-$SMeC_6H_4)_2C(Ph)OH$ is formed by fragmentation of the peroxide. At 45 °C, however, we got reproducible ESR values. The SMe derivatives mentioned in eq 3 are stable at 70 °C, including the precursor of **2jj**, the chloride **5jj**.

The availability of these dimers allowed us to quantify the stabilizing influence of a SMe group, alone or in combination with other residues R mentioned in eq 3; see Table II and Figures 1 and 2.

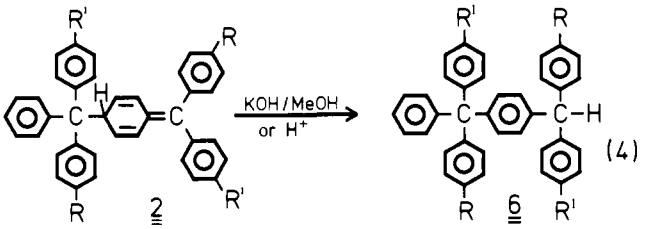
For the nitro group, a $\sigma^{\bullet}$ value is not available. Also our attempts to generate the 4-nitrobenzyl radical remained unsuccessful, but from our extended Hammett plot (Figure 1) we assume $\sigma^{\bullet}_{NO_2} \approx 0.063$. This high value is also expected from other considerations.[4,10]

We generated for the first time the 4-nitrotrityl **1ak** and its dimer **2ak**. They are stable at least up to 70 °C: Reproducible ESR data, see Table II, were obtained from a reheated probe which had sat at 20 °C for 3 mo.

Our attempts to generate the bis(4-nitro)trityl, starting from bis(4-nitrophenyl)methane, remained unsuccessful. The low-yield product was impure, and the ESR spectrum was not reliable.

Besides the radicals **1** and the dimers **2** already mentioned, we prepared 12 others with R/R′ = CF_3/OMe, *t*-Bu/CF_3, *t*-Bu/CN, CN/OMe, COMe/OMe, *t*-Bu/OMe, *t*-Bu/OPh, COPh/OPh, CN/Ph, OMe/Ph, CF_3/Ph, and *t*-Bu/Ph (see Table II) and obtained well-resolved ESR spectra. Often, a satisfactory simulation of the very complicated ESR spectra was possible only by using the ENDOR data.[15] In every case, the dimers of **1** were formed according to eq 1 via α,para dimerization giving the quinonoids **2**. No α,α (giving ethane-like dimers) or α,ortho dimerizations have been observed.

All quinonoid dimers **2** investigated so far rearrange easily to the benzoid products **6** via a 1,5-H shift, both by base[16] (yields up to 94%) and by acid catalysis;[17] see eq 4. This rearrangement



is known from other examples[5,18] and is commonly acknowledged as additional proof for a quinonoid structure such as **2**.

Discussion

It is the aim of this work to investigate the effects of substituents on monomer–dimer equilibria in trityl radicals. Moreover, our test system fulfills the following conditions, which ensure its more general validity for a better understanding of radical stabilization: (a) Our chemical equilibrium reaction (1) demonstrates substituent-dependent reactivity of a carbon-centered radical and is free of implications and complications given in other systems by often unknown details of the mechanism and kinetics. (b) The nonkinetic method enables us to quantify sensitively the substituent-dependent effects and to compare them with other stabilization scales. (c) We include as many substituents (or combinations thereof) as possible in order to find general relations and to exclude abberations by an individual behavior of a single substituent. We think that condition a is fulfilled, as seen below, by the trityl system and the reversible dissociation–recombination as shown in eq 1. In contrast, most of the approaches known so far[4,7] are based on kinetic measurements of irreversible reactions assuming that changing the stability of the radical (whatever this means in the specific case) by changing the substituent is the only influence on the rate measured. Point b is connected with the earlier attempts to correlate a certain substituent with the reactivity of a radical as it is usual for polar reactions by using a Hammett equation.

We found this $\sigma^{\bullet}$ scale[8,9] (see above) best suited to fulfill point b. This scale offers values for a considerable number of substituents (enlarged now by Ph and NO_2, see above), so satisfying also point c. Most of the published sets of radical stabilization parameters[4] contain much less or only a few members. An additional reason for selecting Arnold's scale is the presence of the benzyl moiety in our system, and the fact that the substituents

(12) Luedtke, A. E.; Timberlake, J. W. *J. Org. Chem.* **1985**, *50*, 268. Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978, p 183. Griller, D.; Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1817.

(13) Arnold, D. R.; Nicholas, A. M. De P.; Snow, M. S. *Can. J. Chem.* **1985**, *63*, 1150.

(14) Disproportionations of several 4-alkylated trityls are described: Marvel, C. S.; Rieger, W. H.; Mueller, M. B. *J. Am. Chem. Soc.* **1939**, *61*, 2769.

(15) Lehnig, M.; Stewen, U. *Tetrahedron Lett.* **1989**, *30*, 63.

(16) Staab, H. A.; Brettschneider, H.; Brunner, H. *Chem. Ber.* **1970**, *103*, 1101.

(17) Takeuchi, H.; Nagai, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 753.

(18) Hillgärtner, H.; Neumann, W. P.; Schulten, W.; Zarkadis, A. K. *J. Organomet. Chem.* **1980**, *201*, 197. Wittig, G.; Hopf, W. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 760. Wittig, G.; Petri, H. *Liebigs Ann. Chem.* **1934**, *513*, 26.

Table II. Properties of Para-Substituted Triarylmethyl Radicals **1aa–hj** (a = Coupling Constants[d] in Gauss)

1	R	R′	100α,[a] percent	10^3 K,[a] mol/L	ΔG,[b] kcal/mol	λ_{max}, nm	a_p^H	a_o^H	a_m^H	a_o^H(R)	a_m^H(R)	a_o^H(R′)	a_m^H(R′)	$a_{R,R'}$
aa	H	H[c]	12 ± 1	0.33	4.75	515	2.86	2.61	1.14	2.61	1.14	2.61	1.14	
ab	H	tBu	18 ± 1	0.79	4.23	508	2.85	2.60	1.14	2.60	1.14	2.60	1.14	H: 0.11
bb	tBu	tBu	36 ± 3	4.05	3.26	522	2.88	2.59	1.13	2.59	1.13	2.59	1.13	H: 0.10
ac	H	CF_3	17 ± 1	0.70	4.30	525	2.76	2.54[e]	1.13[e]	2.54[e]	1.13[e]	2.54[e]	1.13[e]	F: 4.68
cc	CF_3	CF_3	24 ± 2	1.52	3.85	527	2.70	2.53[e]	1.13[e]	2.53[e]	1.13[e]	2.53[e]	1.13[e]	F: 4.36
ad	H	CN	28 ± 2	2.18	3.63	558	2.62	2.38	1.06	2.38	1.06	2.86	1.16	N: 0.47
dd	CN	CN	49 ± 4	9.42	2.76	573	2.64	2.30	1.12	2.64	1.12	2.64	1.12	N: 0.42
ae	H	COPh	33 ± 2	3.25	3.39	588	2.60	2.41	1.08	2.41	1.08	2.85	1.23	-
ee	COPh	COPh	48 ± 4	8.86	2.80	590	2.46	2.28	1.04	2.64	1.16	2.64	1.16	-
af	H	COMe	27 ± 3	2.00	3.68	-	-	-	-	-	-	-	-	-
ag	H	OMe	24 ± 2	1.52	3.85	-	2.93	2.58[e]	1.16	2.58[e]	1.16	2.58[e]	1.02	H: 0.31
gg	OMe	OMe	29 ± 2	2.37	3.58	523	2.92	2.57[e]	1.04[e]	2.57[e]	1.04[e]	2.57[e]	1.04[e]	H: 0.32
ah	H	Ph[c]	31 ± 2	2.79	3.49	-	2.72	2.48	1.10	2.48	1.10	2.72	1.21	H: 0.19/0.49
hh	Ph	Ph[c]	67 ± 4	27.21	2.14	570	2.60	2.38	1.07	2.60	1.17	2.60	1.17	H: 0.19/0.46
ai	H	OPh	16 ± 1	0.61	4.39	-	2.84	2.60[e]	1.12[e]	2.60[e]	1.12[e]	2.60[e]	1.12[e]	H: 0.05
ii	OPh	OPh	25 ± 2	1.67	3.79	-	2.83	2.62[e]	1.10[e]	2.62[e]	1.10[e]	2.62[e]	1.10[e]	H: 0.05
aj	H	SMe	25 ± 1	1.67	3.79	-	2.73	2.50	1.10	2.50	1.10	2.83	1.21	H: 0.43
jj	SMe	SMe	61 ± 4	19.08	2.35	610	2.61	2.41	1.13[e]	2.61	1.13[e]	2.61	1.13[e]	H: 0.41
ak	H	NO_2	31 ± 2	2.79	3.49	625	2.64	2.31	1.04	2.31	1.04	2.87	1.18	N:[e]
bc	tBu	CF_3	35 ± 3	3.77	3.31	522	2.73	2.52	1.13[e]	2.52	1.13[e]	2.52	1.13[e]	H: 0.09 F: 4.73
bd	tBu	CN	47 ± 4	8.34	2.84	563	2.60	2.41	1.07	2.41	1.07	2.88	1.21	H: 0.09 N: 0.57
bg	tBu	OMe	28 ± 2	2.18	3.63	526	2.88	2.58	1.09[e]	2.58	1.09[e]	2.58	1.09[e]	H: 0.09/0.33
bh	tBu	Ph	30 ± 4	2.57	3.53	530	2.73	2.46	1.08	2.46	1.08	2.73	1.21	H: 0.09/0.16/0.48
bi	tBu	OPh	29 ± 2	2.37	3.58	524	2.86	2.58[e]	1.12	2.58[e]	1.12	2.58[e]	1.12	H: 0.09
bj	tBu	SMe	37 ± 2	4.35	3.22	556	2.74	2.50	1.10	2.50	1.10	2.74	1.20	H: 0.09/0.42
cg	CF_3	OMe	25 ± 3	1.67	3.79	-	2.72	2.50[e]	1.07[e]	2.50[e]	1.07[e]	2.50[e]	1.07[e]	H: 0.35 F: 4.72
ch	CF_3	Ph	29 ± 3	2.37	3.58	526	2.64	2.43	1.13[e]	2.64	1.13[e]	2.64	1.13[e]	H: 0.18/0.47 F: 4.45
cj	CF_3	SMe	38 ± 2	4.66	3.18	530	2.64	2.42	1.12[e]	2.42	1.12[e]	2.79	1.12[e]	H: 0.46 F: 4.55
dg	CN	OMe	45 ± 4	7.36	2.91	568	2.53	2.35	0.96	2.85	1.20	2.35	0.96	H: 0.32 N:[e]
dh	CN	Ph	42 ± 5	6.08	3.02	570	2.49	2.30	1.15[e]	2.74	1.15[e]	2.49	1.15[e]	H: 0.17/0.45 N: 0.45
ei	COPh	OPh	37 ± 4	4.35	3.22	594	2.40	2.33	1.03	2.80	1.20	2.33	1.03	H: 0.03
fg	COMe	OMe	47 ± 5	8.34	2.84	-	-	-	-	-	-	-	-	-
gh	OMe	Ph	50 ± 5	10.00	2.73	-	2.71	2.46	1.01	2.46	1.01	2.71	1.19	H: 0.17/0.31/0.49
gj	OMe	SMe	26 ± 3	1.83	3.74	-	2.70	2.48	0.99	2.48	0.99	2.79	1.14	H: 0.31/0.43
hj	Ph	SMe	47 ± 1	8.34	2.84	600	2.61	2.37	1.05	2.61	1.17	2.61	1.17	H: 0.19/0.45

[a] 298 K, 0.01 M benzene solution of the monomer. [b] See the text. [c] Maki, A. H.; Allendoerfer, R. D.; Danner, J. C.; Keys, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 4225. [d] ENDOR data of radicals **1** at 200 K in toluol. [e] Further splittings not resolved.

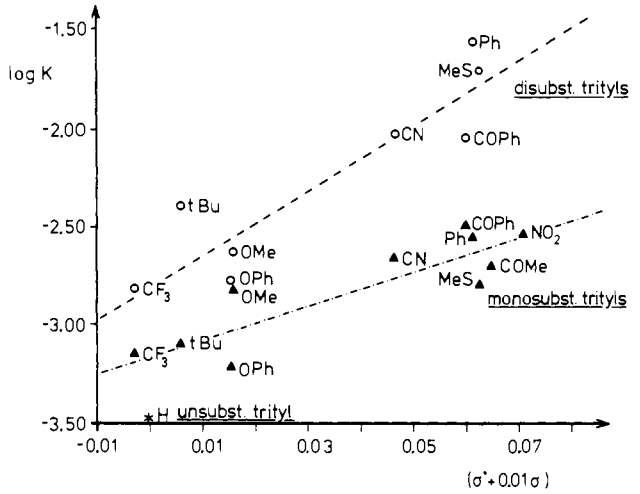


Figure 1. Hammett-like free energy relationship between log K of eq 1 and substituent effects (σ^* + 0.01σ) for mono (▲) and identically disubstituted (O) trityl radicals **1**. The values are taken from Table I.

are located in the para position in both systems.

A reasonable quantitative correlation between log K of eq 1 and σ^* (see Table I) was obtained for all of the 10 substituents we have investigated, as Figure 1 shows. This indicates a Hammett-like free energy relationship. A correlation coefficient r = 0.87 for monosubstituted trityls is not too exciting, but is accepted in Hammett-like relations.[19,20] This fulfills point c (for details see below).

Table III. Comparison of Experimental and Calculated ΔG Data for Substituent Combinations R/R′

1	R	R′	ΔG_{found}, kcal/mol	ΔG_{calcd}, kcal/mol	$\Delta\Delta G$, kcal/mol	group[a]
bc	*t*-Bu	CF_3	3.31	3.56	−0.25	a
bd	*t*-Bu	CN	2.84	3.01	−0.17	a
bg	*t*-Bu	OMe	3.63	3.42	+0.21	c
bh	*t*-Bu	Ph	3.53	2.70	+0.83	c
bi	*t*-Bu	OPh	3.58	3.53	+0.05	b
bj	*t*-Bu	SMe	3.22	2.81	+0.41	c
cg	CF_3	OMe	3.79	3.72	+0.07	b
ch	CF_3	Ph	3.58	3.00	+0.58	c
cj	CF_3	SMe	3.18	3.10	+0.08	b
dg	CN	OMe	2.91	3.17	−0.26	a
dh	CN	Ph	3.02	2.45	+0.57	c
ei	COPh	OPh	3.22	3.30	−0.08	b
gh	OMe	Ph	2.73	2.86	−0.13	a
gj	OMe	SMe	3.74	2.97	+0.77	c
hj	Ph	SMe	2.84	2.25	+0.59	c

[a] See the text.

While polar effects influence radical reactions,[21] it was necessary to verify the linear free energy relationship (Figure 1) by introducing the polar Hammett σ-factor. In fact the coefficient A = 0.01, optimized by iteration, indicates that in our system polar effects are of minute importance.

As a further requirement for c, we have investigated not less than 24 combinations of substituents R/R′, eight with identical ones and 16 with combinations of different ones; see Tables II and III and Figures 1 and 2. For identically disubstituted trityls, a r = 0.91 is acceptable and the conclusions discussed below are meaningful.

(19) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985, p 242.
(20) Isaacs, N. S. *Physical Organic Chemistry*; J. Wiley: New York, 1987.
(21) Minisci, F. in ref 4, p 391.

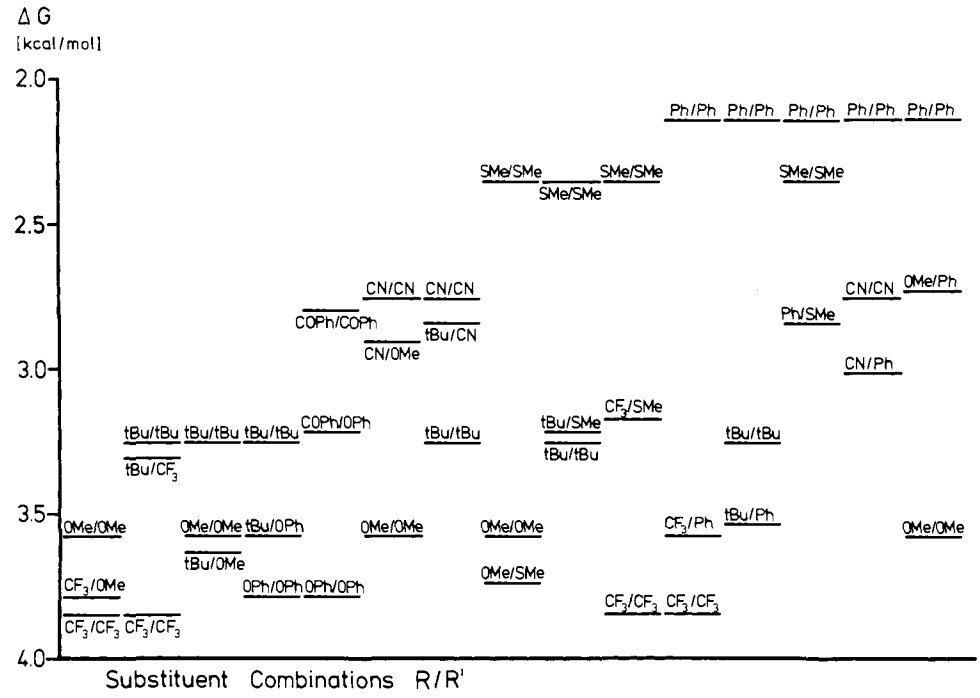


Figure 2. Relative stabilities of 4,4′-disubstituted trityl radicals **1bc–1hj** in terms of ΔG^{298}. (Increasing values indicate decreasing stabilities.) The values are taken from Table II.

We have measured the dissociation degrees α at 298 K and the equilibrium constants K of eq 1 in benzene for the dimers **2** at different temperatures which yielded the ΔH_{diss} and ΔS_{diss} values. ΔH_{diss} varies for disubstituted trityls between 7.3 and 9.4 kcal/mol, and ΔS_{diss} varies between 15 and 21 eu. While the margin of error is ±1.5 kcal/mol, measurements of ΔH_{diss} are not sensitive enough for deducing detailed information about specific stabilization of the radical.

The estimation of K enables us to calculate the most important thermodynamic value, the free energy, ΔG, of the equilibrium reaction, eq 1 (error ≤±0.1 kcal/mol).[20] It is much more sensitive toward substituent-dependent stabilization than ΔH_{diss}:

$$K = \frac{4\alpha^2}{1-\alpha} c_{dimer} \qquad \Delta G = -RT \ln K = \Delta H - T\Delta S$$

Increasing ΔG^{298} values indicate decreasing radical stabilities.

The number of reactive sites for dimerization drops from four (**1aa**, R = R′ = H) to three for the monosubstituted to two for the disubstituted trityls **1**. This implies different entropy factors. By the same reason, K_o ($R^1 = R^2 = H$) for **1aa** cannot be used as a standard;[6] a log K is plotted directly instead of log (K/K_o). We derive a Hammett-like plot as shown in Figure 1, with the three individual groups just mentioned, and therefore arrive at an extended Hammett equation (eq 5). All substituents inves-

$$\log K = \rho(\sigma^{\bullet} + A\sigma) + C \qquad (5)$$

tigated cause higher dissociation of the dimer **2**, hence stabilizing the radical **1**. None is destabilizing it. The radical stabilizing power of a substituent has nothing to do with its electron-attracting or -releasing power: electron-neutral substituents; see Table I, such as Ph and SMe, are among the most powerful ones, as are strongly electron-attracting ones such as NO_2. For monosubstituted trityls **1**, R = H, R′ ≠ H, one finds $\rho \approx 8.5$, and for disubstituted trityls, R = R′ ≠ H, $\rho \approx 16$. The doubling of the slope in the linear free energy relationship indicates the additivity of the effect of equal substituents in average. Individual deviations are also noticed,[22] e.g. with the donor MeO or the acceptor COPh. No antagonism of two like substituents as it has been claimed from kinetic data in other systems[7] can be seen.

Regarding Figure 1, additional arguments for the self-consistency of our test system can be derived. If a dipole–dipole repulsion in a dimer **2** is the reason of enhanced dissociation, the most electron attracting and withdrawing substituents should have the strongest impact, whereas the electron-neutral ones should have less or none. This is clearly not the case. A further argument is given by the good constancy of the ^{13}C NMR data of the central C–C group.

Changing of twisting of the three aryl nuclei in **1** by substituents might be another implication. This can be excluded by the good constancy of the relation between para and ortho or meta proton ESR couplings compared with those of **1aa**, as well as by the total line width of the ESR signals. Numerous of the very complicated ESR signals, due to the high number of coupling protons, could be assigned and simulated only after comprehensive ENDOR measurements; see Table II.

The spin density at the para position of the unsubstituted ring in the doubly substituted trityls gives only a weak response to the kind of the substituents. Nevertheless qualitatively the variations are the same as observed in other systems.[13] COPh, Ph, NO_2, SMe, and CN groups decrease the spin density, while *t*-Bu, OMe, CF_3, and OPh substituents have only a slight effect.

An exceptionally efficient stabilization of radicals by combination of a donor with an acceptor has been claimed in the related concepts of push–pull,[23] mero-,[24] and capto-dative stabilization.[7] Thus, a pair of donors and a pair of acceptors as well should stabilize considerably less than additively, and an acceptor plus a donor should stabilize much more. Only in recent time, however, experimental examinations have been undertaken to verify this claim;[4,6,25,26] see also above.

From our ΔG values (see Table II), we are now able to quantify the stabilization by a certain substituent combination R/R′, and

(22) Earlier attempts[6] with much less data seemed to indicate a substituent's second effect being somewhat bigger than the same substituent's first effect.

(23) Balaban, A. T.; Frangopol, P. T.; Frangopol, M.; Negoita, N. *Tetrahedron* **1967**, *23*, 4661. Stanciuc, G.; Caproiu, M. T.; Caragheorgheopol, A.; Caldararu, H.; Balaban, A. T.; Walter, R. I. *J. Magn. Reson.* **1987**, *75*, 63.

(24) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *J. Chem. Soc. Perkin Trans. 1* **1974**, 1422.

(25) Birkhofer, H.; Hädrich, J.; Beckhaus, H.-D.; Rüchardt, Ch. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 573. Beckhaus, H.-D.; Rüchardt, Ch. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 770.

(26) If the capto-dative effect is fundamentally enthalpic, the ΔG criterion is not unambiguous and could partly be masked by entropic influences.

we calculate $\Delta\Delta G$ from the difference between the expected (ΔG_{calcd}) and the found values:

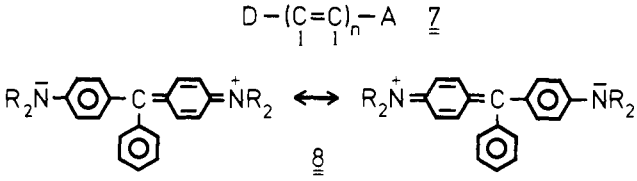
$$\Delta G_{calcd}(R/R') = 0.5\ [\Delta G_{found}(R/R) + \Delta G_{found}(R'/R')]$$

$$\Delta\Delta G = \Delta G_{found}(R/R') - \Delta G_{calcd}(R/R')$$

Three groups of R/R′ combinations are observed; see Table III and Figure 2: (a) very slightly exceeding additivity: four examples (*t*-Bu/CF_3, **1bc**; CN/OMe, **1dg**; *t*-Bu/CN, **1bd**; OMe/Ph, **1gh**),[27] $\Delta\Delta G \approx -0.2$ kcal/mol. (b) Additivity, arithmetic average: four examples (COPh/OPh, **1ei**; CF_3/SMe, **1cj**; CF_3/OMe, **1cg**; *t*-Bu/OPh, **1bi**), $\Delta\Delta G \approx 0$ kcal/mol. (c) Below average, in part markedly below: seven examples (*t*-Bu/OMe, **1bg**; *t*-Bu/SMe, **1bj**; CF_3/Ph, **1ch**; *t*-Bu/Ph, **1bh**; CN/Ph, **1dh**; Ph/SMe, **1hj**; OMe/SMe, **1gj**), $\Delta\Delta G \approx 0.2$–0.8 kcal/mol.

In our 15 examples, in no case did the combined effect of two different substituents R/R′ exceeds that of R/R or R′/R′, regardless of whether they are donors or acceptors or neither. In four examples, the mixed combination remains even underneath of both of the identical ones (*t*-Bu/OMe in **1bg**, *t*-Bu/Ph in **1bh**, Ph/SMe in **1hj**, OMe/SMe in **1gj**). Nothing like a thermodynamic capto-dative effect can be seen. What we derive from Figure 2 and Table III is an individual cooperation of the substituents' specific feature for a certain combination of substituents.

The stabilization concepts mentioned are, as it seems, derived from the principle of resonators in the dyestuff chemistry.[28] There, a donor D and an acceptor A are in resonance across the complete π-system connecting them, **7**. Their effect is the highest when both are equivalent as in triphenylmethanes **8**.



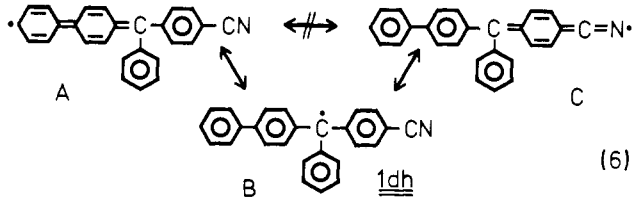
7

8

This concept cannot be transferred to a radical system like ours as it is evidenced now. Our ESR and ENDOR measurements (see Table II), are backing this: The high F coupling of the CF_3 group when combined with H in **1ac** of 4.68 G is not noticeably altered, neither by an inductive donor *t*-Bu in **1bc** (4.73 G) nor by the mesomeric one, Ph, in **1ch** (4.45 G). The Ph group in **1ah** (0.19/0.49 G) is not affected by the donors OMe (0.17/0.49 G) in **1gh**, *t*-Bu (0.16/0.48 G) in **1bh**, or the acceptor CN in **1dh** (0.17/0.45 G). Also the CN coupling in **1ad** (0.47 G) does not reflect the participation of an additional Ph in **1dh** (0.45 G).

This follows also from the lack of solvent dependence of the ESR couplings. Dipolar resonance forms of the radicals **1**, therefore, are not involved: **1dh**, e.g., exhibits $a_p^H = 2.49$ G in benzene ($\epsilon = 2.28$) and in 1,2-dichlorobenzene ($\epsilon = 9.93$) as well.

The two mesomeric forms A and C of **1dh**, eq 6, are not synergetic in analogy to **8**, but cooperate independently with B.



(6)

Moreover, they can disturb one another: the thermodynamic stability of **1dh** is markedly below the expected average value ($\Delta\Delta G = 0.57$ kcal/mol); see Figure 2 and Table III. It follows that there is not a single resonance system across the whole molecule like in **7** or **8** but two partial ones, A ↔ B and B ↔ C, contributing more or less additively to the stability of **1**.

It is made clear now that no valid conclusions in relation to radical stability can be derived from the donor or acceptor strength of a substituent. The two most efficient combinations are those of two identical, electron-neutral substituents (Ph/Ph, **1hh**; SMe/SMe, **1jj**) but also the two less efficient ones (CF_3/CF_3, **1cc**; OPh/OPh, **1ii**). For a rationalization quantum chemical calculations are needed, but they are not available at present.

Capto-dative (and the like) effects observed during certain free radical reactions[4,7] seem to be, therefore, related to activated states influencing *irreversible* reactions and not to the ground-state thermodynamic stability[25,26] of a radical as we have measured in our *equilibrium* reaction (1).

Experimental Section

All reactions with air-sensitive compounds were carried out under dry argon. Instrumental equipment, the preparation of radical solutions, and the quantitative ESR technique have been published.[6] The determination of α is based on 5–10 independent measurements.

(A) Radical Precursors Ar_3CCl 5. The carbinol or its solution in dry benzene and a 4–10-fold amount of freshly distilled $SOCl_2$ at 20 °C give a deeply colored mixture which is stirred until gas evolution ceases. After evaporation, the viscous residue is recrystallized.

(B) Benzoids 6 by Rearrangement of the Quinonoid Dimers 2. Ar_3CCl **5** (5.3 mmol) in 30 mL of dried and degassed benzene is stirred with the 10-fold amount of Cu powder for 1 h at 70 °C. The hot, deeply colored solution is treated with 20 mL of a saturated solution of KOH in dry, degassed methanol and refluxed for additional 3 h. After cooling, the Cu and Cu_2Cl_2 is filtered off, and the benzene layer is separated, washed with water, and dried over Na_2SO_4. After evaporation, the remaining solid is recrystallized.

(C) Quinonoid Dimers 2. A degassed suspension of 1 mmol of **5** diluted in 2.0 mL of $CDCl_3$ and 0.5 g of Cu powder is heated for 1 h at 60 °C. After cooling and precipitation of Cu and Cu_2Cl_2, the clear, deeply colored solution is directly used for ^1H and ^{13}C NMR.

ESR Measurement of 4-Phenylbenzyl 3. 4-Biphenylylmethane (0.4 g, 2.38 mmol), DTBP (0.3 mL, 1.63 mmol), and 4-anisoylbenzene (sensitizer) (45 mg, 0.3 mmol), carefully degassed in a quartz tube, are irradiated by the focused light of a Hanovia 1-kW Hg lamp in the cavity of a Varian E-109E spectrometer at 25 °C. To avoid early decomposition by short-waved UV (<250 nm) and the intense irradiation heat, the UV light is filtered through cooled MeOH. During the 4-h scan time, the sample is exchanged every 1 h to insure a sufficient radical concentration. a_α^H 15.25 G, a_o^H 5.00 G, a_m^H 1.81 G, $a_{o'}^H = a_{p'}^H$ 1.06 G, $a_{m'}^H$ 0.36 G, confirmed by simulation.

(4-Biphenylyl)(4-*tert*-butylphenyl)phenylmethanol (4bh). To 2.68 g (0.11 mol) of Mg, activated with 1,2-dibromoethane under argon, 23.5 g (0.11 mol) of 1-bromo-4-*tert*-butylbenzene in 45 mL of Et_2O is added dropwise. After 1 h of reflux, 17.0 g (66 mmol) of 4-benzoylbiphenyl in 350 mL of Et_2O is added dropwise at 20 °C, and the mixture is refluxed for an additional 2 h. After hydrolysis with ice and diluted hydrochloric acid and extraction with Et_2O, the organic layer is separated, washed with saturated aqueous $NaHSO_3/NaHCO_3$ and water, and then dried over $MgSO_4$. After evaporation, the viscous residue crystallizes from Et_2O/petroleum ether (bp 60–90 °C) (1:5) at 4 °C: yield 18.0 g (70%); mp 127–128 °C; IR (KBr) 3580 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9 H, *t*-Bu), 2.80 (s, 1 H, OH), 6.90–7.70 (m, 18 H, Ar); ^{13}C NMR ($CDCl_3$) δ 31.32, 34.36 (CMe_3), 81.65 (Ar_2PhCOH), 124.75–128.64 (HC_{arom}), 139.68–149.92 (C_{arom}). Anal. ($C_{29}H_{28}O$) C, H.

(4-Biphenylyl)(4-*tert*-butylphenyl)chlorophenylmethane (5bh) is prepared by following procedure A from 10.0 g (25 mmol) of **4bh** and 4.0 mL (50 mmol) of $SOCl_2$. The red, oily residue is dissolved in CH_2Cl_2, and a little *n*-pentane is added, causing a permanent turbidity. After several days at 4 °C, colorless crystals of **5bh** precipitate. It is recrystallized from benzene: yield 4.5 g (44%); mp 108–110 °C; IR (KBr) no OH absorption; ^1H NMR (CCl_4) δ 1.30 (s, 9 H, *t*-Bu), 6.90–7.60 (m, 18 H, Ar); ^{13}C NMR ($CDCl_3$) δ 31.29, 34.41 (CMe_3), 81.28 (Ar_2PhCCl), 124.58–130.06 (HC_{arom}), 140.15–150.55 (C_{arom}); MS (70 eV) *m/e* 376 (80, M − Cl), 375 (100, M − Cl − H), 361 (15, M − Cl − Me), 346 (8, M − Cl − 2 Me), 319 (9, M − Cl − *t*-Bu). Anal. ($C_{29}H_{27}Cl$) C, H.

1-[(4-Biphenylyl)(4-*tert*-butylphenyl)phenylmethyl]-4-[(4-biphenylyl)(4-*tert*-butylphenyl)methyl]benzene (6bh) is prepared according procedure B: yield 1.65 g (83%); mp 150–153 °C (diluted EtOH); ^1H NMR (CCl_4) δ 1.38 (s, 18 H, *t*-Bu), 5.50 (s, 1 H, H_{aliph}), 6.90–7.70 (m, 35 H, Ar); ^{13}C NMR ($CDCl_3$) δ 31.39, 34.32, 34.39 (CMe_3), 55.73 (Ar_3CH), 64.09 (Ar_4C), 124.24–131.57 (HC_{arom}), 138.33–149.00 (C_{arom}); MS (70 eV) *m/e* 751 (35, M), 674 (100, M − Ph), 618 (49, M −

(27) In the first three of these examples, a minute variation in spin density indicates a similar effect.[15]

(28) Zollinger, H. *Color Chemistry*; VCH Verlagsgesellschaft: Weinheim, 1987.

$PhCMe_3$), 598 (45, M − Biph), 375 (91, 1/2 M), 299 (54, 1/2 M − Ph), 242 (31, 1/2 M − $PhCMe_3$). Anal. ($C_{58}H_{54}$) C, H.

3-[(4-Biphenylyl)(4-*tert*-butylphenyl)phenylmethyl]-6-[(4-biphenylyl)(4-*tert*-butylphenyl)methylene]-1,4-cyclohexadiene (2bh). Procedure C is followed: ^1H NMR ($CDCl_3$; −25 °C) δ 1.15, 1.17 (2 s, 18 H, CMe_3), 5.05 (s, 1 H, H_{allyl}), 5.90 (s, 2 H, H_{olef}), 6.25 (d, 2 H, H_{olef}), 6.78–7.52 (m, 31 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 31.18, 31.38, 34.13, 34.35 (CMe_3), 42.42 (Ar_2PhCCH), 61.92, 62.34 (Ar_2PhC), 121.8–130.9 (HC_{arom}, HC_{olef}), 135.8–148.4 (C_{arom}).

(4-Biphenylyl)[4-(trifluoromethyl)phenyl]phenylmethanol (4ch). 4-Benzoylbiphenyl (11.5 g, 44 mmol) in 300 mL of Et_2O is added at 0 °C to [4-(trifluoromethyl)phenyl]lithium,[29] prepared from 7 mL (50 mmol) of 4-(trifluoromethyl)bromobenzene in 50 mL of Et_2O and 50 mmol of *n*-BuLi in *n*-hexane. After hydrolysis with ice and dilute hydrochloric acid and extraction with ether, the combined organic phase is washed with saturated aqueous $NaHSO_3$ and $NaHCO_3$ and with water and dried over $MgSO_4$. After evaporation, the viscous residue is used for preparation of **5ch** without further purification: IR (film) 3510 (OH) cm^{-1}, no C=O.

(4-Biphenylyl)[4-(trifluoromethyl)phenyl]chlorophenylmethane (5ch) is prepared by following procedure A with 10.0 g (24 mmol) of **4ch** dissolved in 10 mL of benzene and 5.0 mL (70 mmol) of $SOCl_2$: yield 7.8 g (75%); mp 122–123 °C (petroleum ether (bp 60–90 °C)); IR (KBr) no OH; ^1H NMR (CCl_4) δ 6.80–7.75 (m, 18 H, Ar); MS (70 eV) *m/e* 387 (100, M − Cl), 317 (6, M − Cl − CF_3), 309 (17, M − Cl − Ph), 241 (42, M − Cl − CF_3 − Ph), 77 (3, Ph), 69 (8, CF_3). Anal. ($C_{26}H_{18}ClF_3$) C, H.

1-[(4-Biphenylyl)[4-(trifluoromethyl)phenyl]phenylmethyl]-4-[(4-biphenylyl)[4-(trifluoromethyl)phenyl]methyl]benzene (6ch) is prepared according to procedure B: yield 1.6 g (87%); mp 128 °C (MeOH); ^1H NMR (CCl_4) δ 5.55 (s, 1 H, H_{aliph}), 6.85–7.90 (m, 35 H, Ar); MS (70 eV) *m/e* 774 (100, M), 697 (67, M − Ph), 629 (77, M − $C_6H_4CF_3$), 621 (21, M − Biph), 387 (67, 1/2 M). Anal. ($C_{52}H_{36}F_6$) C, H.

3-[(4-Biphenylyl)[4-(trifluoromethyl)phenyl]phenylmethyl]-6-[(4-biphenylyl)[4-(trifluoromethyl)phenyl]methylene]-1,4-cyclohexadiene (2ch). Procedure C is used: ^1H NMR ($CDCl_3$, −25 °C) δ 5.07 (d, 1 H, H_{allyl}), 6.01–6.30 (m, 4 H, H_{olef}), 6.81–7.46 (m, 31 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 42.12, 42.31 (Ar_2PhCCH), 61.31, 61.78 (Ar_2PhC), 123.65–129.73 (HC_{arom}, HC_{olef}, CF_3), 138.77–147.74 (C_{arom}).

(4-Anisyl)[4-(trifluoromethyl)phenyl]phenylmethanol (4cg). 4-Anisoylbenzene (18.5 g, 87.1 mmol) in 200 mL of Et_2O is added dropwise at 0 °C to 4-(trifluoromethyl)phenyllithium[29] prepared from 12.2 mL (87.1 mmol) of 4-(trifluoromethyl)bromobenzene in 50 mL of Et_2O and 87.1 mmol of *n*-BuLi in *n*-hexane. After usual workup the viscous residue is crystallized from *n*-hexane: 17.0 g (54%) of **4cg**; mp 62–65 °C; IR (KBr) 3470 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 2.65 (s, 1 H, OH), 3.75 (s, 3 H, OMe), 6.58–7.68 (m, 13 H, Ar). Anal. ($C_{21}H_{17}F_3O_2$) C, H.

(4-Anisyl)[4-(trifluoromethyl)phenyl]chlorophenylmethane (5cg) is prepared with procedure A from 8.0 g (22.3 mmol) of **4cg** in 8 mL of benzene with 5 mL (70 mmol) of $SOCl_2$: 7.5 g (89%); mp 103 °C (*n*-hexane); IR (KBr) no OH; ^1H NMR (CCl_4) δ 3.80 (s, 3 H, OMe), 6.65–7.70 (m, 13 H, Ar); ^{13}C NMR ($CDCl_3$) δ 55.15 (OMe), 80.49 (Ar_2PhCCl), 113.16–130.80 (HC_{arom}), 123.98 (q, CF_3, ^1J_F = 272.1 Hz), 136.61–159.22 (C_{arom}). Anal. ($C_{21}H_{16}ClF_3O$) C, H.

1-[4-Anisyl[4-(trifluoromethyl)phenyl]phenylmethyl]-4-[4-anisyl[4-(trifluoromethyl)phenyl]methyl]benzene (6cg). Procedure B is used: yield 1.7 g (94%); mp 95 °C (diluted MeOH); ^1H NMR (CCl_4) δ 3.75 (s, 6 H, OMe), 5.48 (s, 1 H, H_{aliph}), 6.60–7.66 (m, 25 H, Ar); ^{13}C NMR ($CDCl_3$) δ 55.18, 55.23 (OMe), 55.40 (Ar_2PhCH), 64.04 (Ar_3PhC), 112.95–132.01 (HC_{arom}), 124.22 (q, CF_3, ^1J_F = 272.12 Hz, ^2J_F = 31.79 Hz), 134.96–158.31 (C_{arom}); MS (70 eV) *m/e* 682 (96, M), 605 (91, M − Ph), 537 (100, M − $PhCF_3$), 341 (81, 1/2 M). Anal. ($C_{42}H_{32}F_6O_2$) C, H.

3-[(4-Anisyl)[4-(trifluoromethyl)phenyl]phenylmethyl]-6-[(4-anisyl)-[4-(trifluoromethyl)phenyl]methylene]-1,4-cyclohexadiene (2cg). Procedure C is applied: ^1H NMR ($CDCl_3$, −25 °C) δ 3.80, 3.82 (s, 6 H, OMe), 5.14 (s, 1 H, H_{allyl}), 6.03–6.40 (m, 4 H, H_{olef}), 6.80–7.61 (m, 21 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 43.29 (Ar_2PhCCH), 54.80 (OMe), 62.00 (Ar_2PhC), 112.87–131.32 (HC_{arom}, HC_{olef}, CF_3), 132.30–158.27 (C_{arom}).

(4-*tert*-Butylphenyl)(4-phenoxyphenyl)phenylmethanol (4bi). 4-Phenoxybenzophenone (19.2 g, 70 mmol) in 200 mL of Et_2O is added dropwise within 2 h at 20 °C to (4-*tert*-butylphenyl)lithium,[30] prepared from 12.1 mL (70 mmol) of 1-bromo-4-*tert*-butylbenzene in 100 mL of Et_2O and 70 mmol of *n*-BuLi in *n*-hexane at −10 °C. After usual workup the viscous residue is used for preparation of **5bi** without further purification: IR (film) 3530 (OH) cm^{-1}, no C=O; ^1H NMR (CCl_4) δ 1.25 (s, 9 H, *t*-Bu), 2.70 (s, 1 H, OH), 6.63–7.75 (m, 18 H, Ar).

(4-*tert*-Butylphenyl)(4-phenoxyphenyl)chlorophenylmethane (5bi) is prepared with procedure A from 10.0 g (24 mmol) of crude **4bi** in 25 mL of benzene with 7.3 mL (100 mmol) of $SOCl_2$: 4.5 g (44%); mp 102 °C (petroleum ether, bp 60–90 °C); IR (KBr) no OH; ^1H NMR (CCl_4) δ 1.33 (s, 9 H, *t*-Bu); 6.70–7.55 (m, 18 H, Ar). Anal. ($C_{29}H_{27}ClO$) C, H.

(4-Anisyl)(4-*tert*-butylphenyl)phenylmethanol (4bg). 4-Anisoylbenzene (11.9 g, 56 mmol) in 100 mL Et_2O is dropped within 1 h at 20 °C to (4-*tert*-butylphenyl)lithium[30] prepared from 9.7 mL (56 mmol) of 4-bromo-*tert*-butylbenzene in 100 mL of Et_2O and 56 mmol of *n*-BuLi in *n*-hexane at −10 °C. After refluxing of the green mixture for 2 h, the usual workup follows. The viscous residue is used for preparation of **5bg** without further purification: ^1H NMR (CCl_4) δ 1.30 (s, 9 H, *t*-Bu), 2.45 (s, 1 H, OH), 3.68 (s, 3 H, OMe), 6.55–7.40 (m, 13 H, Ar).

(4-Anisyl)(4-*tert*-butylphenyl)chlorophenylmethane (5bg) is prepared by using procedure A and 10.0 g (27 mmol) of crude **4bg** in 25 mL of benzene with 7.3 mL (100 mmol) of $SOCl_2$: 5.7 g (58%); mp 139 °C (benzene/*n*-pentane, 1:5); IR (KBr) no OH; ^1H NMR (CCl_4) δ 1.35 (s, 9 H, *t*-Bu), 3.75 (s, 3 H, OMe), 6.62–7.40 (m, 13 H, Ar); MS (70 eV) *m/e* 330 (24, M − Cl), 329 (100, M − Cl − H). Anal. ($C_{24}H_{25}ClO$) C, H.

(4-Biphenylyl)(4-cyanophenyl)phenylmethanol (4dh). 4-Bromobenzonitrile (5.0 g, 28 mmol) in 125 mL of THF and 35 mL of *n*-hexane is transformed into (4-cyanophenyl)lithium by reaction of 28 mmol of *n*-BuLi in *n*-hexane at −100 °C.[30] After 15 min of stirring at −100 °C, 7.1 g (28 mmol) of 4-benzoylbiphenyl in 50 mL of THF is added within 30 min. While slowly warming up, the reaction mixture changes from yellow to blue. Before usual workup the mixture is stirred for additional 3 h. The residue is dissolved in CH_2Cl_2, and a little *n*-pentane is added, causing a permanent turbidity. The product crystallizes at 4 °C, yielding 6.5 g (65%) of **4dh**: mp 127–128 °C; IR (KBr) 3410 (OH), 2215 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.95 (s, 1 H, OH), 7.18–7.80 (m, 18 H, Ar). Anal. ($C_{26}H_{19}NO$) C, H, N.

(4-Biphenylyl)(4-cyanophenyl)chlorophenylmethane (5dh) is prepared by following procedure A with 2.0 g (5.5 mmol) of **4dh** in 7 mL of benzene and 1.8 mL (25 mmol) of $SOCl_2$: 0.9 g (43%); mp 117 °C; IR (KBr) no OH, 2215 (CN) cm^{-1}; ^1H NMR (CCl_4) δ 7.00–7.70 (m, 18 H, Ar); MS (70 eV) *m/e* 379 (5, M), 344 (100, M − Cl), 266 (17, M − Cl − Ph), 241 (20, M − Cl − Ph − CN), 190 (8, M − Cl − Biph). Anal. ($C_{26}H_{18}ClN$) C, H, N.

[4-(Methylthio)phenyl]diphenylmethanol (4aj).[31] IR (film) 3470 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 2.43 (s, 3 H, SMe), 2.50 (s, 1 H, OH), 7.10 (s, 4 H, Ar), 7.20 (s, 10 H, Ar).

[4-(Methylthio)phenyl]chlorodiphenylmethane (5aj) is prepared by following procedure A with 9.8 g (32 mmol) of crude **4aj** and 24 mL (320 mmol) of $SOCl_2$: 8.2 g (79%); mp 85–86 °C; IR (KBr) no OH; ^1H NMR ($CDCl_3$) δ 2.47 (s, 3 H, SMe), 7.15 (s, 4 H, Ar), 7.28 (s, 10 H, Ar). Anal. ($C_{20}H_{17}ClS$) C, H.

1-[[4-(Methylthio)phenyl]diphenylmethyl]-4-[[4-(methylthio)phenyl]-phenylmethyl]benzene (6aj) is prepared according to procedure B: 0.76 g (50%); mp 129–130 °C (EtOH); ^1H NMR (CCl_4) δ 2.50 (s, 6 H, SMe), 5.50 (s, 1 H, H_{aliph}), 7.00–7.50 (m, 27 H, Ar).

Bis[4-(methylthio)phenyl]phenylmethanol (4jj). 4-Methylthiobenzophenone (15.0 g, 66 mmol) in 250 mL of Et_2O is added dropwise at 20 °C to 66 mmol of [4-(methylthio)phenyl]magnesium bromide in 200 mL of Et_2O. After refluxing for 3 h and usual workup, the residue is steam distilled and recrystallized from petroleum ether (bp 60–90 °C), yielding 16.7 g (72%) of **4jj**: mp 110 °C (lit.[31] mp 111 °C); IR (KBr) 3440 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 2.43 (s, 7 H, SMe, OH), 7.13 (s, 8 H, Ar), 7.23 (s, 5 H, Ar).

Bis[4-(methylthio)phenyl]chlorophenylmethane (5jj). Procedure A is used with 3.0 g (8.5 mmol) of **4jj** and 6.5 mL (87 mmol) of $SOCl_2$: 2.8 g (89%); mp 120–121 °C (lit.[31] mp 122 °C) (*n*-hexane/CH_2Cl_2 (3:1)); IR (KBr) no OH absorption; ^1H NMR ($CDCl_3$) δ 2.55 (s, 6 H, SMe), 7.23 (s, 8 H, Ar), 7.37 (s, 5 H, Ar). Anal. ($C_{21}H_{19}ClS_2$) C, H.

1-[Bis[4-(methylthio)phenyl]phenylmethyl]-4-[bis[4-(methylthio)-phenyl]methyl]benzene (6jj). Procedure B is applied, but the radical solution is prepared at 45 °C: yield 0.5 g (30%); mp 95–96 °C (EtOH); ^1H NMR (CCl_4) δ 2.50 (s, 12 H, SMe), 5.40 (s, 1 H, H_{aliph}), 6.90–7.60 (m, 25 H, Ar). Anal. ($C_{42}H_{38}S_4$) Calcd: C, 75.2. Found: C, 72.2.

(4-Anisyl)[4-(methylthio)phenyl]phenylmethanol (4gj). 4-Methylthiobenzophenone (10.0 g, 44 mmol) in 200 mL of Et_2O is added dropwise at 20 °C to 46 mmol of 4-anisylmagnesium bromide in 150 mL of Et_2O. After refluxing for 4 h, the mixture is worked up in the usual way to give 8.4 g (57%) of orange crystals from petroleum ether (bp 60–90 °C)/CH_2Cl_2 (5:1) at 0 °C: mp 74–75 °C; IR (KBr) 3480 (OH) cm^{-1};

(29) Soloski, E. J.; Tamborski, C. *J. Organomet. Chem.* **1978**, *157*, 373.
(30) Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339.
(31) Brand, K.; Stallmann, O. *J. Prakt. Chem.* **1924**, *107*, 358.

^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H, SMe), 3.33 (s, 1 H, OH), 3.50 (s, 3 H, OMe), 6.27–7.33 (m, 18 H, Ar).

(4-Anisyl)[4-(methylthio)phenyl]chlorophenylmethane (5gj). Procedure A is applied with 3.0 g (9.0 mmol) of **4gj** and 6.5 mL of $SOCl_2$. After evaporation, the residue is dissolved in Et_2O, and a small amount of *n*-hexane is added, causing a permanent turbidity. Colorless crystals precipitated within 2 days at 0 °C: 2.4 g (75%); mp 95–97 °C; IR (KBr) no OH; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H, SMe), 3.78 (s, 3 H, OMe), 6.67–7.50 (m, 13 H, Ar). Anal. ($C_{21}H_{19}ClOS$) C, H.

[4-(Methylthio)phenyl][4-(trifluoromethyl)phenyl]phenylmethanol (4cj). n-BuLi (50 mmol) in *n*-hexane is added slowly to 11.3 g (50 mmol) of 4-(trifluoromethyl)bromobenzene in 30 mL of Et_2O between −5 and 5 °C.[29] 4-(Methylthio)benzophenone (11.0 g, 48 mmol) in 200 mL of Et_2O is dropped to the cold mixture. After refluxing overnight and usual workup, **4cj** remains as a brownish oil, which is used for preparation of **5cj** without further purification: 13.5 g (75%) of crude **4cj**: IR (film) 3460 (OH) cm^{-1}; ^{1}H NMR (CCl_4) δ 2.30 (s, 3 H, SMe), 3.10 (s, 1 H, OH), 6.60–7.60 (m, 13 H, Ar).

[4-(Methylthio)phenyl][4-(trifluoromethyl)phenyl]chlorophenylmethane (5cj). Procedure A is applied with 13.0 g (35 mmol) of crude **4cj** and 20 mL (0.27 mol) of $SOCl_2$. The brownish, oily residue is fractionated (bp 174 °C/0.4 Torr), crystallizing after several days at 4 °C: 3.8 g of **5cj**; mp 71–72 °C; IR (KBr) no OH; ^{1}H NMR (CCl_4) δ 2.50 (s, 3 H, SMe), 7.10–7.80 (m, 13 H, Ar). Anal. ($C_{21}H_{16}ClF_3S$) C, H.

(4-Biphenylyl)[4-(methylthio)phenyl]phenylmethanol (4hj). 4-(Methylthio)benzophenone (7.5 g, 33 mmol) in 125 mL of Et_2O is dropped at 20 °C to 35 mmol of 4-biphenylylmagnesium bromide in 125 mL of Et_2O. After refluxing for 5 h and usual workup, the viscous residue is used for preparation of **5hj** without further purification: 10.6 g (80%) crude **4hj**; IR (film) 3450 (OH) cm^{-1}, no C=O; ^{1}H NMR (CCl_4) δ 2.30 (s, 3 H, SMe), 2.90 (s, 1 H, OH), 6.70–7.80 (m, 18 H, Ar).

(4-Biphenylyl)[4-(methylthio)phenyl]chlorophenylmethane (5hj). Procedure A is used with 6.8 g (18 mmol) of crude **4hj** and 13 mL (175 mmol) of $SOCl_2$: 4.3 g (61%); mp 125–126 °C (*n*-hexane, CH_2Cl_2 (3:1)); IR (KBr) no OH; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H, SMe), 7.10–7.80 (m, 18 H, Ar). Anal. ($C_{26}H_{21}ClS$) C, H.

1-[(4-Biphenylyl)[4-(methylthio)phenyl]phenylmethyl]-4-[(4-biphenylyl)[4-(methylthio)phenyl]methyl]benzene (6hj). Procedure B is followed: yield, 0.81 g (40%); mp 147–148 °C (CCl_4); ^{1}H NMR (CCl_4) δ 2.10 (s, 6 H, SMe), 5.30 (s, 1 H, H_{aliph}), 6.70–7.50 (m, 35 H, Ar). Anal. ($C_{52}H_{42}S_2$) C, H.

(4-*tert*-Butylphenyl)[4-(methylthio)phenyl]phenylmethanol (4bj). 4-Methylthiobenzophenone (10.0 g, 44 mmol) in 200 mL of Et_2O is added at 20 °C to 46 mmol of (4-*tert*-butylphenyl)magnesium bromide in 75 mL of Et_2O. After refluxing 5 h and usual workup, the residue is steam distilled. The oily product crystallizes at 0 °C with a small amount of *n*-hexane: 13.5 g (85%); mp 102–103 °C (*n*-hexane); IR (KBr) 3565 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H, *t*-Bu), 2.13 (s, 3 H, SMe), 3.30 (s, 1 H, OH), 6.90 (s, 4 H, Ar), 7.03 (s, 9 H, Ar).

(4-*tert*-Butylphenyl)[4-(methylthio)phenyl]chlorophenylmethane (5bj). Procedure A is applied with 2.7 g (7.5 mmol) of **4bj** and 6.5 mL (87 mmol) of $SOCl_2$: 1.7 g (60%); mp 92–93 °C (*n*-hexane); IR (KBr) no OH; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9 H, *t*-Bu), 2.47 (s, 3 H, SMe), 7.13 (s, 4 H, Ar), 7.27 (s, 9 H, Ar). Anal. ($C_{24}H_{25}ClS$) C, H.

1-[(4-*tert*-Butylphenyl)[4-(methylthio)phenyl]phenylmethyl]-4-[(4-*tert*-butylphenyl)[4-(methylthio)phenyl]methyl]benzene (6bj). Procedure B is applied: 0.99 g (54%); mp 132–133 °C (EtOH); ^{1}H NMR (CCl_4) δ 1.40 (s, 18 H, *t*-Bu), 2.50 (s, 6 H, SMe), 5.50 (s, 1 H, H_{aliph}), 6.90–7.50 (m, 25 H, Ar). Anal. ($C_{48}H_{50}S_2$) C, H.

3-[(4-*tert*-Butylphenyl)diphenylmethyl]-6-[(4-*tert*-butylphenyl)-phenylmethylene]-1,4-cyclohexadiene (2ab). Procedure C is applied: ^{1}H NMR ($CDCl_3$, −25 °C) δ 1.17, 1.20 (2 s, *t*-Bu), 4.99 (s, 1 H, H_{allyl}), 5.84–6.24 (m, 4 H, H_{olef}), 6.76–7.34 (m, 23 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 30.25, 33.18, 33.36 (*t*-Bu), 42.69 ($ArPh_2CCH$), 61.26 ($ArPh_2C$), 123.42–129.42 (HC_{arom}, HC_{olef}), 136.10–148.88 (C_{arom}).

3-[(4-Benzoylphenyl)diphenylmethyl]-6-[(4-benzoylphenyl)phenylmethylene]-1,4-cyclohexadiene (2ae). Procedure C is applied: ^{1}H NMR ($CDCl_3$, −25 °C) δ 5.20 (s, 1 H, H_{allyl}), 6.08–6.37 (m, 4 H, H_{olef}), 7.00–7.95 (m, 33 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 43.42 (Ar_2PhCCH), 62.83 (Ar_2PhC), 127.31–132.52 (HC_{arom}, HC_{olef}), 136.46–149.33 (C_{arom}), 196.01 (COPh).

3-[Bis(4-cyanophenyl)phenylmethyl]-6-[bis(4-cyanophenyl)-methylene]-1,4-cyclohexadiene (2dd). Procedure C is followed: ^{1}H NMR ($CDCl_3$, −25 °C) δ 5.16 (s, 1 H, H_{allyl}), 5.99–6.22 (m, 4 H, H_{olef}), 7.00–7.75 (m, 21 H, Ar); ^{13}C NMR ($CDCl_3$, −25 °C) δ 42.95 (Ar_2PhCCH), 62.85 (Ar_2PhC), 111.59 ($C_{arom}CN$), 117.68 (CN), 126.71–132.21 (HC_{arom}, HC_{olef}), 142.20 −148.60 (C_{arom}).

Acknowledgment. Dr. A. Penenory thanks the Alexander von Humboldt Foundation for the Fellowship, Dr. M. Lehnig is grateful to the BRUKER Analytische Messtechnik, Rheinstetten, FRG, for having been able to do the ENDOR measurements in their laboratories. We are grateful to Ch. Hauschild for experimental assistance, to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support, and to Dr. Kim M. Baines (on leave from the University of Toronto) for stylistic improvements.