parameters were identical with those previously reported for this substance.[5i]

B. By LiI Opening of 15b. Vinylaziridine **15b** (7 mg) was dissolved in acetone containing 25 mg of LiI and the mixture refluxed for 8-10 h. Aqueous workup and extraction with methylene chloride gave 6 mg of pyrolizidine **1** contaminated with material resembling imine **27**. Pyrrolizidine **1** proved to be a rather sensitive material. Although isolated several times by chromatography, we were unable to obtain analytically pure samples. All spectra were contaminated with decomposition products of unknown composition.

2-Carboethoxy-2,3-dehydropyrrolizidine (2). The condensate from the pyrolysis of **13** was chromatographed on silica gel with hexane/EtOAc (20:80). Pyrrolizidine **2** (R_f = 0.51, EtOAc/hexane, 80:20) was obtained as a clear oil, which decomposed within 2 weeks of storage: IR (neat) 1720, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.27 (t, 3 H, J = 7 Hz), 1.5 (m, 1 H), 1.75 (m, 2 H), 1.95 (m, 1 H), 2.45 (m, 1 H), 2.72 (m, 1 H), 2.98 (m, 1 H), 3.25 (m, 1 H), 3.96 (m, 1 H), 4.16 (q, 2 H, J = 7 Hz), 6.84 (t, 1 H, J = 2 Hz); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.2 (CH_3), 25.5 (CH_2), 32.7 (CH_2), 35.7 (CH_2), 52.2 (CH_2), 60.4 (CH_2), 64.5 (CH), 117.2 (CH), 144.7 (C), 162.4 (C); mass spectrum (70 eV, rel intensity), m/e 181 (M^+) (72), 179 (30), 152 (42), 134 (25), 108 (B), 80 (75).

Anal. Calcd for $C_{10}H_{15}O_2N$: 181.1102. Found: 181.1112.

1-Aza-2-[1-(2-Carboethoxyvinyl)]bicyclo[3.1.0]hexane (16). Azidodiene **14** (0.980 g, 47 mmol) was refluxed in dry toluene for 4 h, during which time a stoichiometric volume of nitrogen was expelled from the reaction mixture. Removal of solvent in vacuo without heating afforded 0.8 g of **16** (94%), which could be used in the next step. The crude product was contaminated with imine **34** (<8%). Attempts to purify **16** by flash chromatography led to extensive decomposition or transformation of **16** to **34**. Flash chromatography of the crude mixture yielded 122 mg (14%) of analytically pure **16**: IR (neat) 1730, 1660, 1590 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.2 (t, 3 H, J = 7 Hz), 1.4-2.1 (m, 5 H), 2.4 (dd, 1 H, J = 4.1 Hz), 3.0 (m, 2 H), 4.1 (q, 2 H), 5.92 (d, 1 H, J = 16 Hz), 6.6 (dd, 1 H, J = 16, 6 Hz); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 13.5 (CH_3), 19.5 (CH_2), 25.4 (CH_2), 36.9 (CH), 48.8 (CH), 52.0 (CH_2), 59.4 (CH_2), 120.5 (CH), 147.3 (CH), 165.4 (C); mass spectrum (70 eV, rel intensity), m/e 181 (M^+) (5), 177 (2), 152 (4), 124 (10), 108 (B), 84 (30).

Anal. Calcd for $C_{10}H_{15}NO_2$: 181.1102. Found: 181.1064.

4β-Carboethoxy-4α-pyrrolizidine (35a). Chromatographed vinylaziridine **16** (90 mg, 0.49 mmol) was evaporated through a horizontally situated hot tube (1 × 40 cm) at 450 °C and 10^{-5} mmHg, and the condensate was collected in a trap cooled with liquid N_2. The total time of evaporation was kept under 2 min by gently warming the distillation flask. The ^1H NMR of the product (80 mg, 89%) indicated the presence of only pyrroline **17** [^1H NMR δ 4.6 (d, 1 H, J = 5.5 Hz) 5.85 (m, 1 H)] and trace amounts of pyrroline **18** [^1H NMR δ 5.6 (m, 2 H)] in a ratio of at least 95:5. Thin-layer chromatography showed a clean conversion of **16** (R_f = 0.75, Al_2O_3, $CHCl_3$) to **17** (R_f = 0.38, Al_2O_3, $CHCl_3$) and **18** (R_f = 0.1, Al_2O_3, $CHCl_3$). Because of the instability of enamines of the type **17**, no attempts were made at isolation of this substance. The pyrolysis mixture (70 mg) was hydrogenated over 5% Pd/C (25 mg) in HOAc (3 mL) at 23 psi for 24 h. The mixture was filtered through Celite, the filter washed with EtOH, and the filtrate evaporated to yield 66 mg (73%) of clear oil **35a**: IR (neat) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.27 (t, 3 H, J = 7 Hz), 1.5 (m, 1 H), 2.25 (m, 4 H), 2.75 (m, 2 H), 3.0 (m, 1 H), 3.4 (q, 1 H, J = 8 Hz), 3.6 (m, 1 H), 3.75 (m, 1 H), 4.2 (q, 2 H, J = 7 Hz), 4.38 (q, 1 H, J = 8 Hz). Spectral data of this material were identical with those reported for **35a**, which was prepared by the method of Robins.[5i] Repetition of this preparation and hydrogenation of the intermediate pyrrole gave **35a**, identical with the material obtained in the pyrolysis/hydrogenation sequence.

4α-Carboethoxy-4α-pyrrolizidine (35b). The product of hydrogenation **35a** (45 mg) (>90% pure) was adsorbed on basic alumina and slowly eluted (~2 h) through a column (1 × 25 cm) with CH_2Cl_2. Evaporation of solvent gave pure **35b**: ^1H NMR ($CDCl_3$, 270 MHz) δ 3.72 (q, 1 H, J = 8 Hz), 4.11 (q, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 14.3 (CH_3), 26.4 (CH_2), 26.9 (CH_2), 28.4 (CH_2), 47.4 (CH_2), 53.7 (CH_2), 55.5 (CH_2), 60.4 (CH_2), 66.0 (CH), 173.4 (C). The ^{13}C NMR chemical shifts of this material matched exactly those reported by Pinnick for the trans isomer of **35**.[5x]

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Supplementary Material Available: Experimental procedures and data for compounds **20b**, **20c**, **24c**, zinc alkoxide, and lithium alkoxide equilibration data (3 pages). Ordering information given on any current masthead page.

Sterically Hindered Free Radicals. 14.[1] Substituent-Dependent Stabilization of Para-Substituted Triphenylmethyl Radicals[2]

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Abstract: This is a contribution to the problem of stabilization of free organic radicals by resonance in general and to the recent discussion of "captodative" stabilization in particular. It has been found that substituent-dependent relative stabilities of 4,4'-disubstituted triarylmethyl radicals **1** can be sensitively determined by ESR spectroscopic measurement of the equilibria of dissociation of the quinonoid dimers **2** in 21 cases. Most of the compounds **1** and **2** were prepared for the first time. Both donor and acceptor substituents act as stabilizers; in combination they cooperate. A quantitative evaluation based on ESR, ENDOR, and UV/vis data leads to a Hammett-like equation containing $\sigma^\bullet$ and σ parameters which is discussed.

Many attempts, beginning in 1920,[4] have been made in order to define what resonance stabilization of a radical means. Kinetic studies have been developed for measuring the relative stabilities of free organic radicals, beginning with important approaches by

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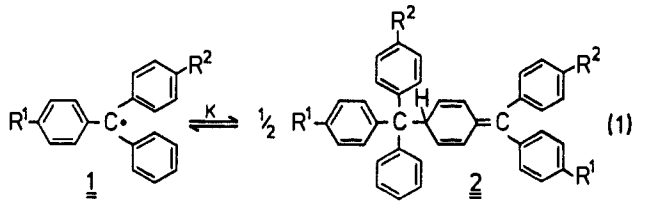
Ziegler and co-workers.[5] They demonstrated that UV spectroscopic measurements of radical–dimer equilibria as well as kinetic trapping experiments with trityl radicals and other scavengers supply consistent thermodynamic data.

In recent years, a new concept of radical stabilization has been promoted by Viehe and co-workers,[6,7] who postulated that the simultaneous influence of a donor and an acceptor substituent at a radical center leads to an enhanced stabilization of this radical in relation to the corresponding symmetrically disubstituted derivatives. This concept of "captodative" radical stabilization has been discussed intensively during the last few years. There are approaches essentially for synthetic application[8] as well as theoretical studies[9,10] and physicochemical measurements[11,12] dealing with quantitative aspects of this concept. However, there are also experimental[12] and theoretical studies[10] not revealing with certainty a particular stabilization in captodative radicals. Therefore we decided to make a contribution to this problem by taking the first and classical "stable free radical", Gomberg's triphenylmethyl,[13] as a model system, using our experience with monosubstituted trityls[1] and thus continuing Ziegler's work with modern spectroscopic methods.

In earlier approaches,[7] more or less complicated irreversible chemical reactions with implications given by (sometimes unknown) details of the mechanism and transition state are used. In other cases, the geometry of and steric or electronic influences on the transition state such as dipole–dipole interactions might be altered by the substituents bound directly to the radical center. We have chosen, therefore, as our test reaction a reversible one and the kinetically simplest one for a radical: the dissociation–recombination of a dimer R–R $\rightleftharpoons$ 2R·. In our opinion, the substituents to be investigated should not be bound directly to the radical center in order to avoid direct interaction during the reaction because of polar or steric effects but should be separated by a phenyl group which transmits the electronic influences. One should then accept that relatively small effects of the substituents will be measured but that these will not suffer from the interference of the factors mentioned above; see eq 1.



(1)

Thus we arrived at Gomberg's triphenylmethyl **1a**[13] and prepared its para-substituted derivatives **1b–u**, mostly for the first time, in order to examine the effects of substituents including a new approach to the captodative stabilization concept.

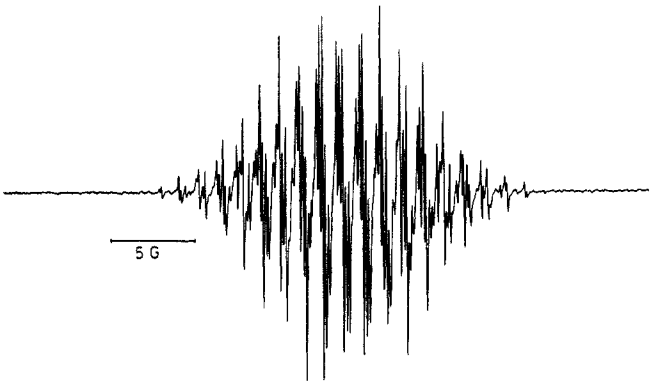


Figure 1. ESR spectrum of the trityl radical **1i** in benzene at 25 °C.

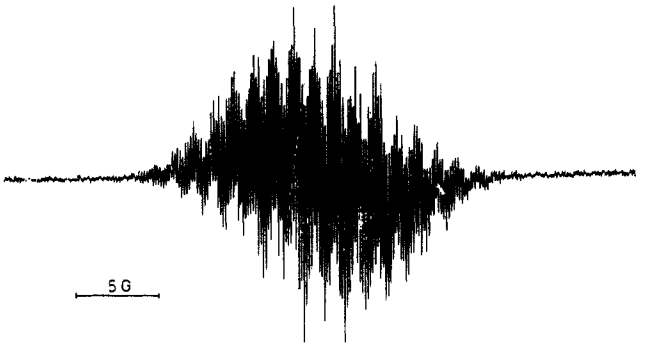


Figure 2. ESR spectrum of the trityl radical **1u** in benzene at 25 °C.

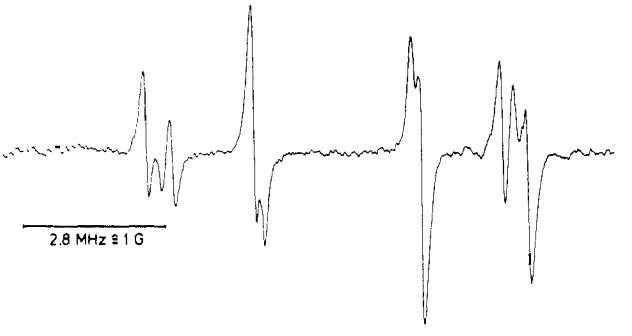


Figure 3. ENDOR spectrum of the trityl radical **1i** in toluene at −60 °C.

Results

The 4,4′-substituted trityl systems **1** have been prepared by means of Grignard or Grignard-analogous reactions. It was therefore necessary, for example, to protect carbonyl substituents. The synthesic strategy is explained by Scheme I.

The introduction of benzoyl groups required carbonyl protection using noncyclic ethers in order to avoid steric hindrance; see Scheme II. Numerous intermediates had to be prepared for the first time: for details, see the Experimental Section. The free radicals **1** have been generated from the corresponding pure, crystalline chlorides **3** by quantitative halogen abstraction with copper powder under standard conditions. This includes high purity of **3**, the constant use of the same solvent benzene at 25 °C, the very low concentration of 0.01 M, the careful exclusion of air, and the 5–10-fold repetition of each individual estimation. In solution, temperature-dependent monomer–dimer equilibria occur, which could be evaluated by means of ESR, UV/vis, IR, and NMR spectroscopies. All steric problems during formation of the exclusively quinonoid dimers **2**, characterized mainly by ^{13}C and ^{1}H NMR spectroscopies at low temperature, and the dissociation of **2** remain constant (in every case, the dimer formation takes place via a nonsubstituted phenyl moiety). This is indicated, too, by the dissociation entropy values ΔS_{diss} (see below)

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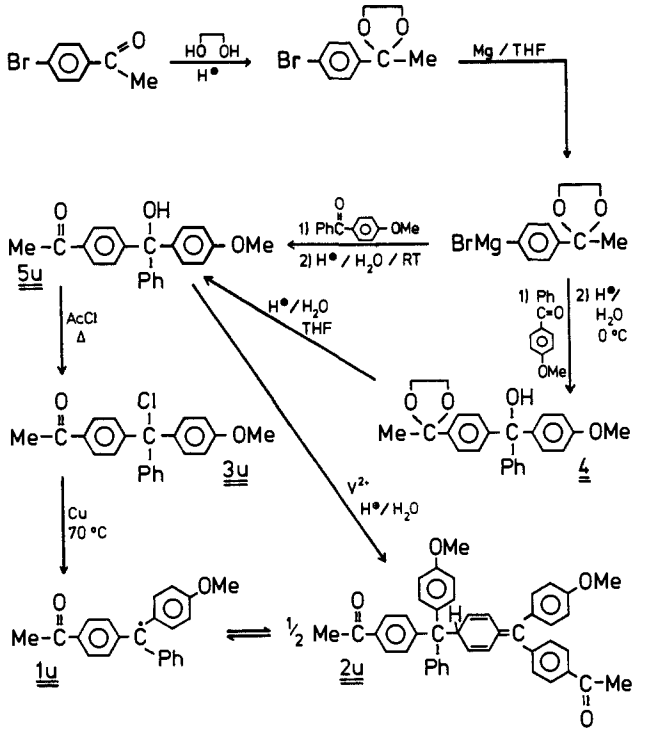
Table I. ESR Data of Para-Substituted Radicals **1a–u** (a = Coupling Constants in Gauss; l = Total Line Width in Gauss)

1	R^1, R^2	a_o^H	a_m^H	a_p^H	$a_o^H(R^1)$	$a_m^H(R^1)$	$a_o^H(R^2)$	$a_m^H(R^2)$	a^{R^1}	a^{R^2}	l	g factor	ref
a	H, H	2.6	1.1	2.8	2.6	1.1	2.6	1.1	$a_p^H = 2.8$	$a_p^H = 2.8$	30[a]	2.0026	17
b	H, *t*-Bu	2.6	1.3	2.6	2.6	1.3	2.6	1.3	$a_p^H = 2.6$	$a_{Me}^H = 0.1$	25		1
c	*t*-Bu, *t*-Bu	2.6	1.3	2.6	2.6	1.3	2.6	1.3	$a_{Me}^H = 0.1$	$a_{Me}^H = 0.1$	25	2.0033	*d*
d	H, CF_3	2.6	1.1	2.8	2.6	1.1	2.6	1.1	$a_p^H = 2.8$	$a^F = 4.5$	36[b]		1
e	CF_3, CF_3[c]								$a^F = 4.2$	$a^F = 4.2$	44[b]	2.0035	*d*
f	H, CN	2.4	1.1	2.5	2.4	1.1	2.8	1.2	$a_p^H = 2.5$	$a^N = 0.50$	26	2.0030	1
g	CN, CN[c]								$a^N = 0.42$	$a^N = 0.42$	26	2.0034	*d*
h	H, COPh	2.43	1.09	2.63	2.43	1.09	2.87	1.21	$a_p^H = 2.63$	$a_{Ph}^H < 0.004$	28	2.0029	*d*
i	COPh, COPh	2.31	1.06	2.48	2.65	1.17	2.65	1.17	$a_{Ph}^H < 0.004$	$a_{Ph}^H < 0.004$	26		*d*
j	H, COMe	2.4	1.1	2.6	2.4	1.1	2.8	1.3	$a_p^H = 2.6$	$a_{Me}^H = 0.2$	28	2.0028	1
k	COMe, COMe[c]								$a_{Me}^H = 0.15$	$a_{Me}^H = 0.15$	26		*d*
l	H, OMe	2.62	1.15/1.03	2.95	2.62	1.15/1.03	2.62	1.15/1.03	$a_p^H = 2.95$	$a_{Me}^H = 0.32$	26	2.0029	*d*
m	OMe, OMe[c]								$a_{Me}^H = 0.35$	$a_{Me}^H = 0.35$	25		*d*
n	H, Ph	2.47	1.10	2.71	2.47	1.10	2.71	1.21	$a_p^H = 2.71$	$a_{Ph}^H = 0.49, 0.19$	30		18
o	Ph, Ph	2.38	1.07	2.60	2.60	1.17	2.60	1.17	$a_{Ph}^H = 0.46, 0.19$	$a_{Ph}^H = 0.46, 0.19$	29		18
p	H, OPh	2.55	1.15	2.75	2.55	1.15	2.55	1.15	$a_p^H = 2.75$	$a_{Ph}^H < 0.05$	28		19
q	OPh, OPh	2.6	1.1	2.6	2.6	1.1	2.6	1.3	$a_{Ph}^H < 0.05$	$a_{Ph}^H < 0.05$	26		19
r	*t*-Bu, CF_3	2.1	1.3/1.1	2.5	2.1	1.3/1.1	2.5	1.3/1.1	$a_{Me}^H < 0.05$	$a^F = 4.6$	36[b]	2.0034	*d*
s	*t*-Bu, CN	2.62	1.1	2.62	2.62	1.1	2.9	1.16	$a_{Me}^H = 0.09$	$a^N = 0.6$	25	2.0035	*d*
t	OMe, CN	2.34	1.17/0.98	2.51	2.34/2.85	1.17/0.98	2.85	1.17	$a_{Me}^H = 0.32$	$a^N = 0.3$	26		*d*
u	OMe, COMe	2.37	0.97/1.10	2.54/2.73	2.54/2.73	0.97/1.10	2.93	1.21	$a_{Me}^H = 0.33$	$a_{Me}^H = 0.19$	26	2.0035	*d*

[a] The additional H_{para} coupling leads to the slightly enhanced signal width. [b] The great F coupling leads to this enhanced signal width. [c] Couplings could not be assigned unequivocally. ENDOR measurements are in preparation. [d] This work.

Scheme I



remaining constant within mono- or disubstituted species, respectively. 4-Substituents do not cause any steric hindrance. Moreover, the dissociation into radicals is not affected by dipole–dipole interactions because of the great distance between the substituents. Otherwise, a trityl **1** with a donor and an acceptor substituent should dimerize generally more readily than another one with two donors or two acceptors. This is not the case; see below.

The twist angle of about 32° for **1a**[14] is not influenced by 4-substituents. This can be concluded from the unchanged total ESR signal width of mono- and disubstituted triarylmethyl radicals

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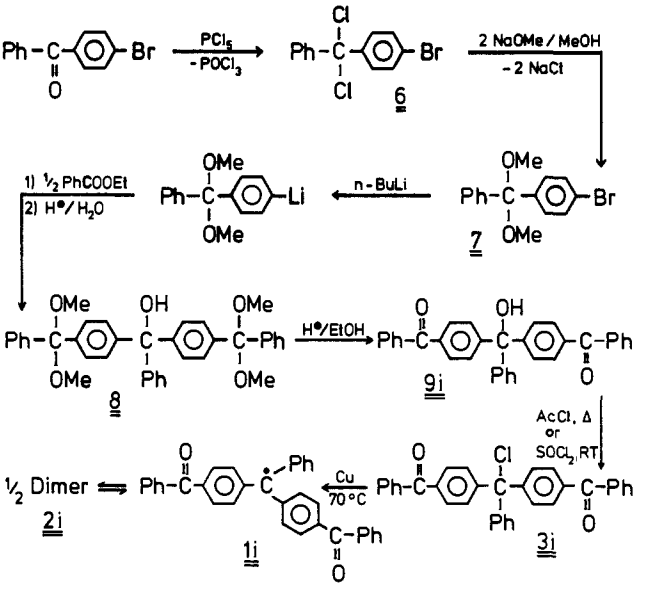
Scheme II



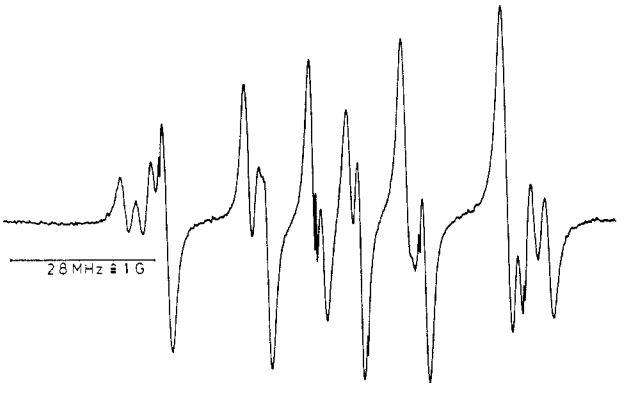


Figure 4. ENDOR spectrum of the trityl radical **1u** in toluene at −60 °C.

as well as from the aromatic hydrogen coupling constants, which are only slightly influenced by para substituents;[15,16] see Table

Table II. Properties of Para-Substituted Triarylmethyl Radicals **1a–u**

1	R^1	R^2	$\sigma^{\cdot,20}$	σ^{21}	100α,[a] %	10^4K,[a] mol·L^{-1}	log K/K_0	ΔH_{diss},[b] kcal·mol^{-1}	ΔS_{diss}^{298}, eu	λ_{max}, nm
a	H	H	0.000	±0	12 ± 1	3.3	0.00	10.7 ± 0.2	20	515
b	H	*t*-Bu	0.036	−0.20	18 ± 1	7.9	0.38	10.2 ± 0.3	20	
c	*t*-Bu	*t*-Bu	0.036	−0.20	36 ± 3	41.0	1.09	8.2 ± 0.2	17	522
d	H	CF_3	0.001	+0.55	17 ± 1	7.0	0.33	10.5 ± 0.2	21	
e	CF_3	CF_3	0.001	+0.55	24 ± 2	15.0	0.66			
f	H	CN	0.043	+0.63	28 ± 2	22.0	0.82	10.0 ± 0.2	21	
g	CN	CN	0.043	+0.63	49 ± 4	94.0	1.45			575
h	H	COPh	0.064	+0.46	33 ± 2	33.0	1.00	10.2 ± 0.2	23	588
i	COPh	COPh	0.064	+0.46	48 ± 4	89.0	1.43	7.6 ± 0.2	16	590
j	H	COMe	0.066	+0.52	27 ± 3	20.0	0.78	10.2 ± 0.3	22	
k	COMe	COMe[c]	0.066	+0.52						
l	H	MeO	0.034	−0.27	24 ± 2	15.0	0.66			
m	MeO	MeO	0.034	−0.27	29 ± 2	24.0	0.86	7.1 ± 0.2	12	523
n	H	Ph		+0.01	31 ± 2	28.0	0.93			
o	Ph	Ph		+0.01	67 ± 4	270.0	1.91	6.8 ± 0.2	16	570
p	H	PhO		−0.30	16 ± 1	6.1	0.27			
q	PhO	PhO		−0.30	25 ± 2	17.0	0.71	9.4 ± 0.3	18	
r	*t*-Bu	CF_3			35 ± 3	38.0	1.06			522
s	*t*-Bu	CN			47 ± 4	84.0	1.41	7.9 ± 0.3	17	563
t	MeO	CN			45 ± 4	74.0	1.35			568
u	MeO	COMe			47 ± 5	84.0	1.41	7.7 ± 0.3	16	

[a] 298 K, 0.01 M benzene solution of the monomer; see Experimental Section. [b] Determined between 280 and 350 K. [c] No measurement because the radical precursor could not be obtained purely.

I. Figures 1 and 2 illustrate as selected examples that the shape of the well-resolved ESR spectra depends on the nature of their substituents. The interpretation of the rather complicated ESR spectra has been reconfirmed in some elucidating cases by ENDOR spectroscopy,[16] which leads to much clearer spectra (see Figures 3 and 4). The coupling constants derived from ESR and ENDOR spectra are always consistent, though it seems in a few examples not to be possible yet to assign all of them clearly; see Table I. The *g* factors of ESR spectra always lie between 2.0026 and 2.0035, indicating the radicals to be C-centered.

The estimation of the degree of dissociation α by ESR has been found to be very sensitive for determining K, much more than any determination of ΔH_{diss}; see Table II. For the equilibrium

$$R\text{–}R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^{\cdot} + R^{\cdot}$$

K is

$$K = \frac{[R][R]}{[R\text{–}R]} = \frac{4\alpha^2}{1-\alpha}C^0 \qquad (2)$$

(C^0 = dimer concentration weighed in). The dissociation enthalpy ΔH_{diss} can be calculated from van't Hoff's equation (3); ΔS_{diss} can be estimated from the expression (4). The equilibrium constant K is expected under these conditions to reflect the substituent-dependent stabilization of the radicals **1b–u** in relation to the unsubstituted derivative **1a**.

$$\frac{d \ln K}{dT} = \frac{\Delta H_{diss}}{RT^2} \qquad (3)$$

$$\Delta G = -RT \ln K = \Delta H - T\Delta S \qquad (4)$$

Our results substantiate that donor as well as acceptor substituents act as radical stabilizers, regardless of whether they do so by inductive or by mesomeric effects or by both of these. Two donors and even two acceptors cooperate, giving approximate additivity; see Table II. This is a striking difference compared with many polar reactions, where, e.g., the effect of methyl groups on the rate of bromination of alkenes is geometric rather than arithmetic,[22] and with polar reactions including free-radical (nucleophilic) additions to olefins,[23] where a donor and an acceptor neutralize each other. In our case a donor and an acceptor cooperate, also giving approximate additivity; see Table II. Details will be discussed below.

UV/vis absorption maxima of radicals **1** likewise show a resonance stabilization power of the 4-positioned substituents indicated by a bathochromic shift of 5–75 nm; see Table II.

Thermodynamic and spectroscopic data illustrate clearly that substituents developing the strongest radical stabilization power, which is about 4 kcal/mol, are found amongst those with π-electrons, as can be seen from the dissociation energy values ΔH_{diss}.[24]

Discussion

As follows from the data in Table II, mono-4-substituted trityls are further stabilized, considerably by introducing a second 4-substituent. The magnitude of this additional stabilization depends on the nature of this second substituent, and therefore a substituents first and second effects are seen to be not always identical.

A second phenyl group obviously exceeds the stabilization power of the first one. For *tert*-butyl or phenoxy substituents, a similar

(15) Sinclair, J.; Kivelson, D. *J. Am. Chem. Soc.* **1968**, *90*, 5074.
(16) Lehnig, M., unpublished work from this laboratory. To be published in detail elsewhere.
(17) Landolt-Börnstein, T. *II/9b: Magnet. Eigenschaften freier Radikale*; Fischer, H., Hellwege, K.-H., Eds.; Springer Verlag: Berlin-Heidelberg, 1977; Section 4.8.1, p 718f, and literature cited there.
(18) Maki, A. H.; Allendorfer, R. D.; Danner, J. C.; Keys, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 4225.
(19) Dünnebacke, D. Diploma Thesis, University of Dortmund, 1985.
(20) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221. A careful review and discussion of earlier attempts to establish a $\sigma^{\cdot}$ scale based on kinetic schemes is given there. (a) **Note Added in Proof**: When this paper was in press, the $\sigma^{\cdot}$ values given in ref 20 were improved in part: Arnold, D. R.; Nicholas, A. M. De P.; Snow, M. S. *Can. J. Chem.* **1985**, *63*, 1150. When these new and more precise values are used, some quantitative adaptations of eq 5 and 6, Figures 5 and 6, and Tables III and IV follow. Since it was too late to do this at present, and since neither our general discussion nor the conclusions are affected, we shall publish the improved material mentioned together with new[27a] and extended data in due time.
(21) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191. Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. Extensive discussion is given in: Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York and London, 1978; pp 439–546.
(22) Atkinson, J. R.; Bell, R. P. *J. Chem. Soc.* **1963**, 3260.
(23) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.
(24) One might imply that a 4 kcal/mol effect is not too important for demonstrating the stabilization discussed here. In other fields, however, even smaller effects are decisive. For example, after 25 years of research in rationalizing the stereo- and regioselectivity of Diels–Alder reactions, the energy differences between the possible transition states have been found to be not more than 1–5 kcal/mol: Gleiter, R.; Böhm, M. C. In *Stereochemistry and Reactivity of Systems Containing π Electrons*; Watson, W. H., Ed.; Verlag Chemie: Deerfield Beach, FL, 1983; p 138.

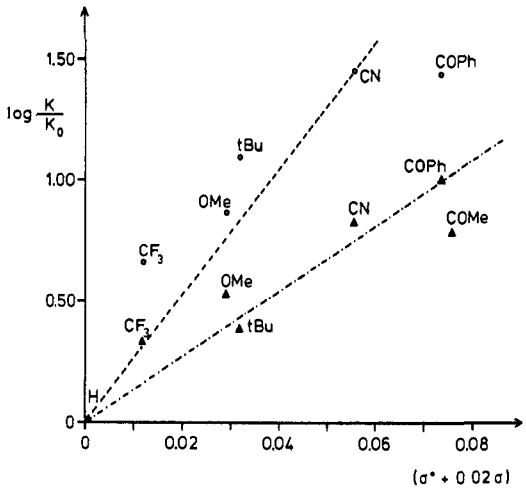


Figure 5. Hammett plot for mono- (▲) and disubstituted (○) trityl radicals **1** using two parameters $\sigma^{\cdot}$ and σ.

effect can be noticed. In any case, in our system a substituent's second effect mostly seems to be greater than its first one, but not smaller, as has been recently concluded from results with another system.[11b] The behavior is, in contrast, more or less specific for a certain substituent and has to be elucidated in the future.

A second methoxy substituent seems to cause a special effect: The dissociation energy value drops down to 7.1 kcal·mol^{-1}, indicating a strong radical stabilization exceeding additivity but not affecting the monomer–dimer equilibrium to the same extent. This is illustrated, too, by a deviation of the dissociation entropy value. A comparable effect is also known from 1,4-bis(methoxy)-substituted butadienes which show an unexpectedly low reactivity in Diels–Alder reactions.[25]

Discussing a substituent's second effect in relation to its first one in our model system, it should be considered that the number of possible reactive sites for dimer formation is reduced from four to two as substitution increases. This can be concluded, too, from the entropy decrease for disubstituted (ca. 16 eu) vs. monosubstituted (ca. 21 eu) examples and might be one reason that a second substituent reduces the ΔH_{diss} value to a greater extent (ca. 2–3 kcal/mol) than the first one (ca. 0.5 kcal/mol).

In order to examine the validity of a Hammett-type equation for our results, we used substituent constants $\sigma^{\cdot}$, developed recently on the basis of ESR data of para-substituted benzylic radicals;[20,20a,26] see Table II. We found a reasonable agreement by introducing a slight polar factor containing the "classical" Hammett values σ,[21,27] leading to an extended Hammett expression (5)[20a] with $\rho \approx 13$ for mono- and $\rho \approx 26$ for disubstituted trityls; see Figure 5 (The exact additivity of the ρ values might be fortuitous, if one considers the discussion in the foregoing paragraph).

$$\log \frac{K}{K_0} = \rho(\sigma^{\cdot} + 0.02\sigma) \qquad (5)$$

Only the $\sigma^{\cdot}$ values established at present[20,20a] could be applied. It would be of interest to have additional ones for the other substituents under investigation. For example, for Ph the rather high $\sigma^{\cdot}$ value of about 0.062 may be assumed from our results.[27a]

The factor 0.02 in eq 5 has been found by iteration from +0.16 to −0.16 to be the optimum; see Figure 6. Given that the K data

Table III. Comparison of Experimental Data with Those Calculated by Equation 6

1	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u
X	H	*t*-Bu	H	CF_3	H	CN	H	COPh	H	COMe	H	OMe	H	Ph	H	OPh	*t*-Bu	*t*-Bu	MeO	MeO
Y	*t*-Bu	*t*-Bu	CF_3	CF_3	CN	CN	COPh	COPh	COMe	COMe	OMe	OMe	Ph	Ph	OPh	OPh	CF_3	CN	CN	COMe
log $K_{X,Y}/K_0$ found	0.38	1.09	0.33	0.66	0.82	1.45	1.00	1.43	0.78		0.66	0.86	0.93	1.91	0.27	0.71	1.06	1.41	1.35	1.41
log $K_{X,Y}/K_0$ calcd by eq 6	0.39	0.79	0.15	0.30	0.69	1.50	0.92	1.80	0.93	1.89	0.48	0.96	*a*	*a*	*a*	*a*	0.54	1.08	1.03	1.29
Δ	+0.01	−0.30	−0.18	−0.36	−0.13	+0.05	−0.08	+0.37	+0.15		−0.18	−0.10					−0.52	−0.33	−0.32	−0.12

[a] No $\sigma^{\cdot}$ values are available.

Table IV. Comparison of Experimental Data with Those Calculated by Equation 7

1	c	e	g	i	m	o	q	r	s	t
X	*t*-Bu	CF_3	CN	COPh	OMe	Ph	OPh	*t*-Bu	*t*-Bu	MeO
Y	*t*-Bu	CF_3	CN	COPh	OMe	Ph	OPh	CF_3	CN	CN
log $K_{X,Y}/K_0$ found	1.09	0.66	1.45	1.43	0.86	1.91	0.71	1.06	1.41	1.35
log $K_{X,Y}/K_0$ calcd by eq 7	1.10	0.66	1.45	1.43	0.86	1.91	0.72	0.88	1.27	1.16
Δ	+0.01	±0.00	±0.00	±0.00	±0.00	±0.00	+0.01	−0.18	−0.14	−0.19

(25) Rücker, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663.

(26) The validity of radical stability calculations from ESR coupling constants a^H has been shown for benzyl radicals by: Fischer, H. *Z. Naturforsch., A* **1964**, *19a*, 866; **1965**, *20a*, 428.

(27) In principle, all Hammett values are to be used in aqueous media. But no systematic adaptation for other solvents is available. Since we use exclusively the same solvent (benzene) and since the factor is only 0.02 here, the use of the classical values seems acceptable. (a) Stewen, U., unpublished work from this laboratory.

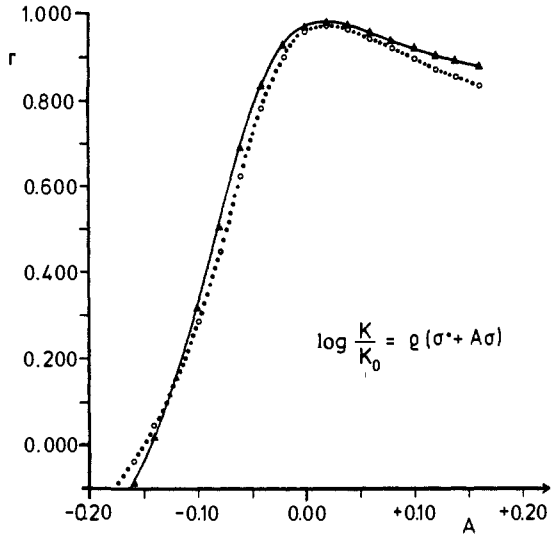


Figure 6. Optimization of the Hammett expression (4) for our results by iteration with various factors (r = correlation coefficient, (▲) monosubstituted, (○) disubstituted trityl radicals **1**).

fit eq 5 and given that the substituent effects within the disubstituted species are arithmetic, eq 6 for the data of para-disubstituted derivatives should follow:[20a]

$$\log \frac{K_{X,Y}}{K_0} = \rho[(\sigma_X^{\cdot} + \sigma_Y^{\cdot}) + 0.02(\sigma_X + \sigma_Y)] = \rho\sigma_{X,Y}' \qquad (6)$$

$$\rho \approx 12.3$$

The results are shown in Table III. The deviations of the calculated data from the experimental data Δ value are not substantial and are not significantly different for symmetrically substituted radicals, e.g., **1c**, **1e**, and those where X is a donor and Y is an acceptor, **1r–u**. A weak effect might be derived, however, from the average Δ values, which are predicted by eq 6 to be too low by −0.33 for **1r–u** and only by −0.07 for all symmetrically disubstituted radicals (supposing that the value for **1r**, −0.52, does not depend on a specific effect such as those discussed above).

This is, at first, surprising, because the combined action of donor and acceptor substituents should enhance the radical stability more than additively and substantially more than symmetric substitution (X = Y) is capable of, following the concept of captodative radical stabilization.[5] This cannot be concluded from our results which demonstrate at present only a weak (if any) additional captodative effect. Table III illustrates that trityls **1** can be stabilized, in principle, by symmetric para substitution to the same extent as by captodative substitution: the stability of **1c** ($R^1 = R^2 = t$-Bu), for example, is not exceeded by the captodative derivative **1r** ($R^1 = t$-Bu, $R^2 = CF_3$), but on the other hand, **1r** is more stable than **1e** ($R^1 = R^2 = CF_3$). For trityls **1g** ($R^1 = R^2 = CN$), **1s** ($R^1 = CN$, $R^2 = t$-Bu), and **1c** ($R^1 = R^2 = t$-Bu), the situation is the same, as well as for **1g** ($R^1 = R^2 = CN$), **1t** ($R^1 = CN$, $R^2 = MeO$), and **1m** ($R^1 = R^2 = MeO$).

Equation 7 and Table IV represent an additional quantitative method of evaluation (neglecting, for the present, the entropy effects discussed above) by comparing the experimental results with the sums of the average data of the individual substituents.

$$\left(\log \frac{K_{X,Y}}{K_0}\right)_{calcd} = \frac{1}{2}\left[\left(\log \frac{K_{X,H}}{K_0} + \log \frac{K_{Y,H}}{K_0}\right) + \left(\log \frac{K_{X,X}}{K_{X,H}} + \log \frac{K_{Y,Y}}{K_{Y,H}}\right)\right] \qquad (7)$$

The captodative radicals appear to be slightly more stable than one may calculate from the average values of the symmetrically disubstituted trityls: They are in between the latter in all the examples investigated so far but slightly above the average. This is illustrated clearly by Figure 7, and this is our suggestion for a new definition of captodative stabilization effects in C-centered radicals.

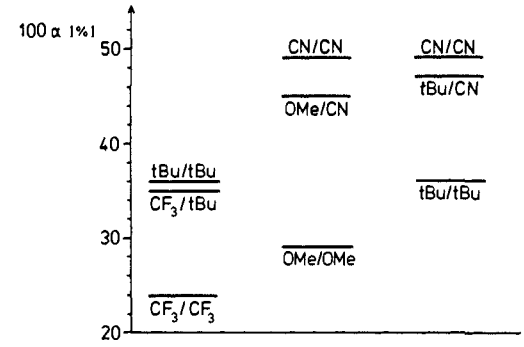


Figure 7. Relative stabilities of para-disubstituted trityl radicals **1c**, **1e**, **1g**, **1m**, and **1r–t**.

There are also other possible methods for analyzing the experimental data.[28] We intend to use and to compare them when we have investigated further substituents with respect to their individual radical-stabilizing power.

Experimental Section

General Information. All reactions with compounds sensitive to air or moisture were carried out under dry argon. ESR spectra were recorded on a Varian E-109 E spectrometer, equipped with a variable-temperature accessory. ENDOR spectra were recorded on a Bruker ER electron nuclear double-resonance spectrometer at 213 K,[16] ^{13}C and ^1H NMR spectra at low temperature on a Bruker AM-300 (^1H = 300 MHz), all other ^1H NMR spectra on a Varian EM-360 A spectrometer (60 MHz). Chemical shifts were measured in parts per million (ppm) against Me_4Si. IR spectra were obtained from Perkin-Elmer 325 and 577 spectrometers, UV/vis data from a Philips Unicam SP 1800 spectrometer, and melting points from a Büchi SMP 20 (uncorrected).

Preparation of Radical Precursors Ar_3CCl 3. The corresponding carbinol Ar_3COH (0.2–0.3 M) is refluxed in dry toluene, while excess freshly distilled acetyl chloride, diluted with a few milliliters of dry toluene, is added dropwise in through the condenser. The refluxing is continued until the OH peak at δ 3.3 (^1H NMR) has disappeared. The volatile components are evaporated at 0.001 torr/20 °C. The residue crystallizes and is recrystallized from dry petroleum ether (bp 60–90 °C) in the presence of one or two drops of acetyl chloride.

Preparation of Dimers 2 by Reduction of the Corresponding Carbinols with V^{2+}. (a) VCl_2 Solution.[29] V_2O_5 (9.1 g) is dissolved under argon in 85 mL of concentrated hydrochloric acid, and 13 g of Zn dust is added in portions under vigorous stirring (take care because of foaming). Then the volume is made up to 100 mL with degassed water.

(b) Reduction.[30] VCl_2 solution (4 mL) (0.1 N) is added dropwise to 1.0 g of the carbinol in 20 mL of absolute acetone or THF. After 10 min, 50 mL of degassed water is added, and the precipitate is collected under argon, washed with ice-cold methanol, and dried at 0.001 torr.

Preparation of Dimers 2 by Reduction of Corresponding Chlorides 3 with Cr^{2+}.[31] $CrSO_4 \cdot 5H_2O$ (1.7 g) in 10 mL of degassed water is added at −10 °C to 1.0 g of triarylmethyl chloride **3** in 60–70 mL of absolute DMF. A yellow solid is deposited from the green solution, completely so after addition of 40–50 mL of degassed water; it is separated by suction under argon and washed first with water and then with ice-cold methanol and finally with *n*-hexane.

Preparation of Radical Solutions and ESR Determination of Spin Concentrations. A 0.01 M solution of the corresponding triarylmethyl chloride **3** in carefully dried and degassed benzene is stirred under careful exclusion of air with the 5-fold amount of Cu powder for 1 h at 70 °C. Exclusion of light is also necessary in order to avoid disproportionation.[32] After the solution cools, Cu and Cu_2Cl_2 precipitate out. The deeply

(28) We are grateful to one of the referees who made very useful suggestions concerning the methods to be used.
(29) Srikantan, B. S. *J. Ind. Chem. Soc.* **1957**, *34*, 74.
(30) Conant, J. B.; Bigelow, N. M. *J. Am. Chem. Soc.* **1931**, *53*, 676.
(31) Hillgärtner, H.; Neumann, W. P.; Schulten, W.; Zarkadis, A. K. *J. Organomet. Chem.* **1980**, *201*, 197.
(32) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic: London and New York, 1968.

Table V. Determination of ΔH_{diss} of Radical **1q**

T, °C	$10^{-3}T^{-1}$, K^{-1}	α	ln K
8	3.56	0.150	−7.544
23	3.38	0.247	−6.425
35	3.25	0.331	−5.721
49	3.11	0.400	−5.234
66	2.95	0.495	−4.635
25	3.36	0.245	−6.444

colored solution is clear and may directly be used for a Beilstein test and ESR measurements. Only freshly prepared solutions should be used.

For the Beilstein test, 2 mL of the solution is evaporated. A negative result is essential. The sensitivity of this test is established to lie at least in the microgram region.[33]

Spin concentrations are determined from overmodulated ESR signals at defined temperatures using a benzene solution of pure DPPH[34] as a reference sample,[35] which has been calibrated by iodometric titration[36] and UV/vis spectroscopy. At least five similar experiments should give consistent ESR data not exceeding a limit of error of 10%. Evaluation is done with a computer program (Hewlett-Packard). After the sample is heated from 8 to 66 °C, it is cooled to room temperature to examine the reproducibility of the measurement; see Table V.

[4-(2-Methyl-1,3-dioxolan-2-yl)phenyl](4-anisyl)phenylmethanol (4). To 3.6 g (0.15 mol) of magnesium, activated with 1,2-dibromoethane under argon, is added dropwise a solution of 34.4 g (0.15 mol) of 4-bromoacetophenone ethylene acetal in 150 mL of dry THF.[37] After the solution is refluxed for 1 h, a solution of 31 g (0.15 mol) of 4-methoxybenzophenone in 100 mL of dry THF is added dropwise. Then the reaction mixture is refluxed for 1 h. After hydrolysis with ice and diluted hydrochloric acid and extraction with Et_2O, the organic layer is separated, washed with aqueous $NaHSO_3$–$NaHCO_3$ solution and water, and then dried over $MgSO_4$. After the solvent is evaporated, the residue is dissolved in a little cyclohexane. After addition of a few milliliters of acetone, the product crystallizes, yielding 29.5 g (54%) pure **4**: mp 122 °C; IR (KBr) 3450 (OH), 1255 (C–O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (s, 3 H, Me), 2.82 (s, 1 H, OH), 3.70–4.04 (m, 7 H, CH_2, OMe), 6.74–7.53 (m, 13 H, Ar). Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.56; H, 6.43. Found: C, 77.31; H, 6.89.

(4-Acetylphenyl)(4-anisyl)phenylmethanol (5). **4** (10.0 g) (27 mmol) in 220 mL of THF is refluxed 6 h with 100 mL of water and 1.0 g of 4-toluenesulfonic acid. Then the organic solvent is removed by destillation, causing crystallization of **5** from the remaining water. **5** is collected by suction and washed with petroleum ether (30–60 °C): yield 8.1 g (91%); mp 170 °C dec; IR (KBr) 3455 (OH), 1655 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H, Me), 2.85 (s, 1 H, OH), 3.74 (s, 3 H, OMe), 6.77–7.98 (m, 13 H, Ar); ^{13}C NMR (acetone-d_6) δ 27.04 (COMe), 55.80 (OMe), 82.00 (Ar_2PhCOH), 128.08–130.39 (Ar), 136.91–159.94 (Ar), 197.80 (C=O); MS (70 eV), *m/e* 332 (82%, M), 315 (10, M − OH), 255 (85, M − Ph), 227 (19, M − COPh), 213 (100, M − PhCOMe), 197 (8, M − COPh − OH), 147 (37, HOCPhCOMe), 135 (43, HOCPhOMe), 119 (7, HOCPhC), 106 (48, HOCPh), 77 (25, Ph), 43 (25, COMe). Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.83; H, 6.27.

Preparation of 5 without Isolating 4. The Grignard reaction described above is followed by hydrolysis with half-concentrated hydrochloric acid under cooling to maintain the mixture at room temperature. **5** precipitates from petroleum ether (bp 30–60 °C), forming colorless crystals: yield 20.9 g (43%); mp 170 °C dec; IR, NMR, and MS data are consistent with those given above.

(4-Acetylphenyl)(4-anisyl)chlorophenylmethane (3u) is obtained from 1.7 g (5.2 mmol) of **4** in 50 mL of toluene and 2.0 mL (28.0 mmol) of acetyl chloride following the general procedure. The crude product crystallizes in the presence of *n*-pentane. It is recrystallized from petroleum ether (bp 60–90 °C)/acetone (10:1) and washed with a little ice-cold Et_2O containing a drop of acetyl chloride to yield 1.4 g (77%) of pure **3u**: mp 160–163 °C; IR (KBr) 1685 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 3 H, Me), 3.85 (s, 3 H, OMe), 6.80–7.98 (m, 13 H, Ar). Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 75.32; H, 5.46. Found: C, 75.94; H, 5.88.

3-[(4-Acetylphenyl)(4-anisyl)phenylmethyl]-6-[(4-acetylphenyl)(4-anisyl)methylene]-1,4-cyclohexadiene (2u). Reduction of 1.0 g (2.9 mmol) of **5** in 20 mL of dry THF is carried out at −20 °C with VCl_2 following the general procedure. The orange precipitate is washed with ice-cold methanol and *n*-hexane and dried at 0.001 torr: yield 0.8 g (83%); mp 157 °C (under argon); ^1H NMR ($CDCl_3$; −20 °C) δ 2.53 (s, 6 H, Me), 3.72 (s, 6 H, OMe), 5.51 (s, 1 H, H_{aliph}), 6.75 (dd, 4 H, H_{olef}), 6.95 (d, 2 H, Ar), 7.01–7.29 (m, 13 H, Ar), 7.38 (d, 2 H, Ar), 7.82 (dd, 4 H, Ar); ^{13}C NMR ($CDCl_3$; −20 °C) δ 26.80 (COMe), 55.49 (OMe), 55.77 (Ar_2PhC—CH), 81.69 (Ar_2PhC), 113.51 (MeOC=C), 126.67–130.56 (HC_{arom}, HC_{olef}), 134.80–152.22 (CC_{arom}, C_{olef}), 158.06, 158.89 (MeOC).

(4-Bromophenyl)dichlorophenylmethane (6).[38] 4-Bromobenzophenone (78.3 g) (0.3 mol) and PCl_5 (62.6 g) (0.3 mol) are heated to 150 °C for 2 h. Then the reaction mixture is fractionated, yielding 85.9 g (91%) of **6** as a yellow liquid: bp 148–150 °C (0.1 torr); $[n]^{20}_D$ 1.6255.

(4-Bromophenyl)dimethoxyphenylmethane (7).[39] **6** (85.0 g) (0.27 mol) is added within 4 h to a solution of NaOEt (0.54 mol) in 500 mL of methanol. The reaction mixture is stirred for 2 h, and the precipitated NaCl is filtered by suction under argon. After evaporation of the solvent, the residue is treated with a little methanol, which causes crystallization at 0 °C. The product **7** is washed with cold methanol: yield 45.0 g (56%); mp 48 °C; IR (KBr) no C=O absorption; ^1H NMR (CCl_4) δ 3.07 (s, 6 H, Me), 7.20–7.60 (m, 9 H, Ar). Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92. Found: C, 59.21; H, 5.32.

Bis(1-dimethoxyphenyltolyl)phenylmethanol (8). **8** (12 g) (39.1 mmol) in 50 mL of dry Et_2O is added to 40 mmol of *n*-BuLi in about 70 mL of dry Et_2O at −35 °C. The green reaction mixture is allowed to reach a temperature of −10 °C within 2 h, and 2.5 g (17.0 mmol) of ethyl benzoate in 10 mL of dry Et_2O is added dropwise, which changes the color of the reaction mixture from green to yellow. After 2 h of stirring at −10 °C, the mixture is kept at room temperature overnight and is then refluxed for 3 h. After hydrolysis with ice and dilute HCl, the organic layer is washed with a concentrated aqueous solution of $NaHCO_3$ and with water and is dried over magnesium sulfate. After evaporation of the solvent, the oily residue crystallizes in the freezer: yield 12.4 g (57%); mp 145 °C; IR (KBr) 3400–3600 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 2.50 (s, OH), 3.00 (s, 12 H, Me), 6.91–7.39 (m, 23 H, Ar). Anal. Calcd for $C_{37}H_{36}O_7$: C, 79.25; H, 6.47. Found: C, 80.11; H, 6.89.

Bis(4-benzoylphenyl)phenylmethanol (9i). A solution of 11.0 g (19.6 mmol) of **8** in 100 mL of ethanol is refluxed together with 50 mL of diluted hydrochloric acid for 2 h. The ethanol is evaporated and the residue extracted with ether. The combined extracts are washed with concentrated aqueous $NaHCO_3$ solution and with water and are dried over magnesium sulfate. After evaporation of the solvent, the residue solidifies in the freezer and is recrystallized from a 1:1 mixture of ether and petroleum ether (bp 30–60 °C) yielding 6.3 g (69%) of **9i**: mp 145 °C; IR (KBr) 3440 (OH), 1650 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.40 (s, 1 H, OH), 7.30–7.89 (m, 23 H, Ar). Anal. Calcd for $C_{33}H_{24}O_3$: C, 84.59; H, 5.16. Found: C, 84.39; H, 5.01.

Bis(4-benzoylphenyl)chlorophenylmethane (3i). A solution of 3.5 g (7.5 mmol) of **9i** in 30 mL of dry toluene is treated with 3.0 mL (42 mmol) of acetyl chloride following the general procedure (50 h). The residue is extremely sensitive to moisture and is recrystallized several times under argon from a 1:1 mixture of dry cyclohexane and dry toluene. The pure product **3i** crystallizes at 4–5 °C within several days: yield 1.1 g (31%); mp 130 °C; IR (KBr) no OH absorption, 1655 (C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 7.28–7.85 (m, Ar); MS (70 eV), *m/e* 452 (91%, M − Cl), 375 (24, M − Cl − Ph), 347 (69, M − Cl − PhCO), 271 (25, M − Cl − PhCO − H), 241 (18, M − Cl − 2PhCO), 165 (23, Ph_2C), 105 (100, PhCO), 77 (20, Ph). Anal. Calcd for $C_{33}H_{23}O_2Cl$: C, 81.39; H, 4.76. Found: C, 80.71; H, 4.40.

Reaction of 9i with Thionyl Chloride. To 1.0 g (2.1 mmol) of **9i** is added 0.3 mL (4.2 mmol) of thionyl chloride at room temperature. The reaction mixture is stirred until gas evolution is complete (about 6 h). The volatile components are evaporated, and the residue is recrystallized as described above: yield 0.8 g (76%) of **3i**; mp 130 °C; IR and NMR data are consistent with those given above. Anal. Calcd for $C_{33}H_{23}O_2Cl$: C, 81.39; H, 4.76. Found: C, 80.55; H, 4.34.

Bis(4-*tert*-butylphenyl)chlorophenylmethane (3c)[40] is prepared from 3.7 g (10 mmol) of bis(4-*tert*-butylphenyl)phenylmethanol[40,41] in 15 mL

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of dry toluene and 1.5 mL (21 mmol) of acetyl chloride following the general procedure (85 h). The oily residue is treated with petroleum ether (60–90 °C) to precipitate colorless crystals, which are washed with a little petroleum ether (30–60 °C): yield 3.6 g (92%) of **3c**; mp 162 °C [lit.[41] mp 162–163 °C]; IR (KBr) no OH absorption, 2960 (Me) cm^{-1}; ^1H NMR (CCl_4) δ 1.31 (s, 18 H, *t*-Bu), 7.15 (m, 13 H, Ar); MS (70 eV), *m/e* 355 (100%, M – Cl), 340 (83, M – Cl – Me), 325 (23, M – Cl –2Me), 298 (15, M – Cl – *t*-Bu), 166 (10, Ph_2C), 135 (16, *t*-BuPh), 57 (14, *t*-Bu). Anal. Calcd for $C_{27}H_{31}Cl$: C, 82.94; H, 7.73. Found: C, 83.00; H, 8.10.

3-[Bis(4-*tert*-butylphenyl)phenylmethyl]-6-[bis(4-*tert*-butylphenyl)-methylene]-1,4-cyclohexadiene (2c). Reduction of 1.0 g (2.7 mmol) of bis(4-*tert*-butylphenyl)phenylmethanol[40,41] is carried out with VCl_2 according to the general procedure: yield 0.95 g (98%) of **2c** as yellow crystals with mp 160–162 °C (under argon); ^1H NMR (CCl_4, –20 °C) δ 1.30 (s, 36 H, *t*-Bu), 5.08 (s, 1 H, C—C—H), 5.90 (d, J = 10.5 Hz, 2 H, C=C—H), 6.23 (d, J = 10.5 Hz, 2 H, C=C—H), 6.71–7.39 (m, 21 H, Ar); ^{13}C NMR (CCl_4/acetone-d_6, –20 °C) δ 34.36 (CMe_3), 37.45, 37.48 (CMe_3), 46.13 (Ar_2PhC—CH), 64.80 (Ar_2PhC), 127.04–134.65 (HC_{Ar}, HC_{olef}), 139.72–151.83 (C_{Ar}, C_{olef}).

Reduction of 3c with Cr^{2+}. **3c** (1.0 g) (2.6 mmol) in 70 mL of dry DMF is treated with 1.7 g (7.2 mmol) of $CrSO_4 \cdot 5H_2O$ in 10 mL of degassed water at –10 °C according to the general procedure. The precipitate is collected by suction under argon and washed with water, ice-cold methanol, and finally *n*-hexane: yield 0.55 g (60%) of **2c**; mp 159–160 °C (under argon); NMR data are consistent with those given above.

Dissociation of 2c. A solution of **2c** in absolute toluene (about 10^{-4} M) shows the ESR spectrum of the radical **1c**. The degree of dissociation of a 5×10^{-3} M solution of **2c** in absolute benzene is α = 33% at 25 °C: UV/vis (C_6H_6) λ_{max} 522 nm.

Bis[4-(trifluoromethyl)phenyl]phenylmethanol. A solution of 22.5 g (0.1 mol) of 4-(trifluoromethyl)bromobenzene in 150 mL of dry ether is cooled to 0 °C, and 0.1 mol of *n*-BuLi in ether or *n*-hexane is added slowly so that the temperature of the reaction mixture does not rise above 5 °C.[42] Then a solution of 6.0 g (39.6 mmol) of ethyl benzoate (distilled) in 50 mL of dry ether is added dropwise at 0 °C, and the reaction mixture is refluxed overnight. After hydrolysis with ice and dilute hydrochloric acid and extraction of the aqueous layer with ether, the combined organic phases are washed with concentrated aqueous solutions of $NaHSO_3$ and $NaHCO_3$ and with water and are dried over sodium sulfate. The solvent is evaporated and any remaining ethyl benzoate is removed at 0.001 torr. The residue is used for preparation of **3e** without further purification: IR (film) 3420 (OH) cm^{-1}, no C=O absorption; ^1H NMR (CCl_4) δ 2.9 (s, 1 H, OH), 7.1–7.5 (m, 13 H, Ar).

Bis[4-(trifluoromethyl)phenyl]chlorophenylmethane (3e). The residue mentioned above is dissolved in 100 mL of dry toluene and is treated with 6.0 mL (84 mmol) of acetyl chloride according to the general procedure (70 h). The oily residue is fractionated by means of Kugelrohr distillation, yielding a colorless liquid (bp 158 °C/0.1 torr) which crystallizes after several days at 4–5 °C: yield 3.8 g of **3e**; mp 58–59 °C; IR (KBr) no OH absorption; ^1H NMR (CCl_4) δ 7.15–7.65 (m, Ar); MS (70 eV), *m/e* 379 (100%, M – Cl), 360 (18, M – Cl – F), 309 (72, M – Cl – CF_3), 239 (33, M – Cl – $2CF_3$), 233 (86, M – Cl – $PhCF_3$), 166 (21, Ph_2C), 147 (20, $PhCF_3$), 119 (18, $PhCH_2F$), 77 (4, Ph). Anal. Calcd for $C_{21}H_{13}ClF_6$: C, 60.81; H, 3.16. Found: C, 61.34; H, 3.54.

Bis(4-cyanophenyl)phenylmethanol is prepared according to ref 43 by reaction of 5.0 g (27.5 mmol) of 4-bromobenzonitrile in 125 mL of THF and 35 mL of *n*-hexane with 27.5 mmol of *n*-BuLi in *n*-hexane followed by reaction with 5.7 g (27.5 mmol) of 4-cyanobenzophenone in 30 mL of THF. The solvents are evaporated, and the residue crystallizes in the presence of petroleum ether (bp 60–90 °C) at –10 °C: yield 4.3 g (53%); mp 177 °C (from 1-propanol) IR (KBr) 3420 (OH), 2240 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30 (s, 1 H, OH), 7.10–7.60 (m, 13 H, Ar). Anal. Calcd for $C_{21}H_{14}NO$: C, 85.11; H, 4.76; N, 4.73. Found: C, 85.86; H, 4.95; N, 4.98.

Bis(4-cyanophenyl)chlorophenylmethane (3g). A solution of 1.0 g (3.4 mmol) of bis(4-cyanophenyl)phenylmethanol in 15 mL of toluene is treated with 0.7 mL (9.8 mmol) of acetyl chloride following the general procedure (14 h). After addition of a little petroleum ether (bp 30–60 °C), **3g** crystallizes at 4 °C overnight. It is recrystallized from petroleum ether (bp 60–90 °C): yield 0.8 g (71%); mp 172 °C; IR (KBr) 2230 (CN) cm^{-1}; ^1H NMR (CCl_4) δ 7.32–7.52 (m, Ar). Anal. Calcd for $C_{21}H_{13}ClN_2$: C, 76.71; H, 3.99; N, 8.52. Found: C, 77.34; H, 4.40; N, 9.01.

Bis(4-cyanophenyl)phenylmethyl 1g and Its Dimer 2g. A solution of the radical prepared according to the general procedure is filtered under argon and evaporated. The red, oily residue could not be brought to crystallization and becomes colorless in the presence of air: IR (film under argon) 2220 (CN) cm^{-1}, no C=C=N absorption; UV/vis (C_6H_6, under argon) λ_{max} 575 nm.

Bis[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]phenylmethanol. Ethyl benzoate (9.6 g) (64 mmol) (distilled) in 20 mL of dry THF is added dropwise at 40 °C to 128 mmol of a Grignard solution prepared from 4-bromoacetophenone ethyleneacetal in dry THF as described above.[37] An exothermic reaction takes place, and after complete addition of the ethyl benzoate, the red reaction mixture is refluxed for 2 h. After the mixture cools and hydrolysis with ice and dilute hydrochloric acid takes place, the aqueous layer is extracted with ether, and the combined organic phases are washed with a concentrated aqueous $NaHCO_3$ solution and with water. After the mixture is dried over magnesium sulfate, the solvent is evaporated. The residue is recrystallized from toluene yielding 14.0 g (53%) with mp 139–140 °C: IR (KBr) 3450 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 1.50 (s, 6 H, Me), 2.80 (s, 1 H, OH), 3.51–3.98 (m, 8 H, CH_2), 7.02–7.48 (m, 13 H, Ar). Anal. Calcd for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.61; H, 6.95.

Bis(4-acetylphenyl)phenylmethanol. Bis[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]phenylmethanol (4.4 g) (10.2 mmol) is dissolved in 80 mL of THF and refluxed for 12 h together with 50 mL of water and 0.5 g of 4-toluenesulfonic acid; the reaction progresses by ^1H NMR spectroscopy. After addition of ether, the mixture is washed with concentrated aqueous $NaHCO_3$ solution and with water, dried over magnesium sulfate, and evaporated, whereby the product precipitates as colorless crystals, which are recrystallized from toluene: yield 3.3 g (94%); mp 161 °C; IR (KBr) 3340 (OH), 1680, 1655 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (s, 6 H, Me), 3.30 (s, 1 H, OH), 7.11–8.00 (m, 13 H, Ar). Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.89; H, 6.12.

Bis(4-acetylphenyl)chlorophenylmethane (3k). To 1.0 g (2.9 mmol) of bis(4-acetylphenyl)phenylmethanol, 0.3 mL (4.2 mmol) of thionyl chloride is added. The reaction mixture is stirred until no further gas is evolved (6 h). The volatile components are evaporated at 0.001 torr, yielding crude **3k** as a yellowish, amorphous solid. All attempts to purify the product as well as other methods of preparation (AcCl, AcBr) were unsuccessful: IR (KBr) no OH absorption, 1680 (C=O) cm^{-1}; ^1H NMR (CCl_4) δ 2.65 (s, 6 H, Me), 7.31–8.19 (m, 13 H, Ar). Anal. Calcd for $C_{23}H_{13}ClO_2$: C, 79.63; H, 5.52. Found: C, 78.91; H, 5.89.

3-(Di-4-anisylphenylmethyl)-6-(di-4-anisylmethylene)-1,4-cyclohexadiene (2m) and Its Dissociation. Di-4-anisylchlorophenylmethane[44] (2.0 g) (6.0 mmol) reduced with $CrSO_4 \cdot 5H_2O$ following the general procedure: yield 1.1 g (60%) of **2m** as orange, instable crystals with mp 51 °C (under argon): ^1H NMR ($CDCl_3$, –25 °C) δ 3.77, 3.80 (2s, OMe), 5.10 (s, H_{aliph}), 5.95 (d, H_{olef}), 6.35 (d, H_{olef}), 6.82–7.38 (m, Ar); ^{13}C NMR ($CDCl_3$, –25 °C) δ 43.39 (Ar_2PhC—CH), 54.53;, 54.88 (OMe), 60.90 (Ar_2PhC), 110.87–113.11 (MeO—C=HC_{arom}), 125.21–130.27 (Ar), 131.57, 132.24 (HC_{olef}), 133.90–147.11 (C_{arom}, C_{olef}), 156.52–157.86 (MeO—C_{arom}). Dissociation: A $\sim 10^{-4}$ M solution of **2m** in benzene shows the ESR spectrum of **1m**. The degree of dissociation α estimated at 25 °C is about 26%; UV/vis (C_6H_6) λ_{max} 523 nm.

Bis(4-biphenylyl)chlorophenylmethane (3o)[45] is prepared from 2.0 g (4.7 mmol) of bis(4-biphenylyl)phenylmethanol[46] in 20 mL of toluene and 2.0 mL (28 mmol) of acetyl chloride according to the general procedure and to ref 45. After addition of a little petroleum ether (90–120 °C), **3o** precipitates at 0 °C as colorless crystals: yield 2.0 g (98%); mp 133 °C [lit.[45] mp 131.5 °C]; IR (KBr) no OH absorption. Anal. Calcd for $C_{31}H_{23}Cl$: C, 86.40; H, 5.38. Found: C, 86.21; H, 5.30.

Bis(4-biphenylyl)phenylmethyl (1o) and Its Dimer 2o. The radical **1o** is generated from a 0.1 M benzene solution of **3o** according to the general procedure. After evaporation of the solvent, the red, oily residue, which is decolorized in the presence of air, is characterized spectroscopically: ^1H NMR (CCl_4/$CDCl_3$, –20 °C) δ 5.50–5.85 (m, H_{aliph}, H_{olef}), 6.27 (d, H_{olef}), 7.12–7.45 (m, Ar); ^{13}C NMR (CCl_4/$CDCl_3$, –20 °C) δ 80.88 (Ar_2PhC), 126.33–130.11 (HC_{arom}, HC_{olef}), 140.08–144.95 (C_{arom}, C_{olef}); UV/vis (C_6H_6) λ_{max} 540–570 nm.

(4-*tert*-Butylphenyl)[4-(trifluoromethyl)phenyl]phenylmethanol. 4-(Trifluoromethyl)benzophenone[47] (9.0 g) (36 mmol) is dissolved in 75 mL of dry ether, and 40 mmol of *tert*-butylphenyllithium[48] in ether is added dropwise at room temperature. After refluxing for 4 h and hydrolysis with ice and dilute hydrochloric acid, the aqueous layer is extracted with ether, and the combined organic layers are dried over sodium

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sulfate. After evaporation the oily residue is purified by column chromatography (40 cm of Al_2O_3 neutral, Woelm activity II; *n*-hexane). Elution with toluene gives a product which is pure (DC) but does not crystallize: IR (KBr) 3440 (OH) cm^{-1}; ^1H NMR (CCl_4) δ 1.30 (s, 9 H, *t*-Bu), 2.60 (s, 1 H, OH), 7.01–7.59 (m, 13 H, Ar).

(4-*tert*-Butylphenyl)[4-(trifluoromethyl)phenyl]chlorophenylmethane (3r). The oily methanol mentioned above is dissolved in 100 mL of dry toluene and is treated with 10.0 mL (140 mmol) of acetyl chloride in 25 mL of dry toluene according to the general procedure (45 h). Addition of a little petroleum ether (bp 60–90 °C) to the oily residue causes crystallization within several days in the freezer. The product is washed with a small amount of cold petroleum ether (bp 60–90 °C): yield 8.1 g (56% based on 4-(trifluoromethyl)benzophenone); mp 83 °C; IR (KBr) no OH absorption; ^1H NMR (CCl_4) δ 1.31 (s, 9 H, *t*-Bu), 7.00–7.59 (m, 13 H, Ar); MS (70 eV), *m/e* 367 (100%, M – Cl), 352 (100, M – Cl – Me), 337 (39, M – Cl – 2Me), 310 (9, M – Cl – *t*-Bu), 240 (20, M – Cl – $PhCF_2$), 233 (17, M – Cl – Ph-*t*-Bu), 165 (19, Ph_2C, 127 (20, $PhCF_2$), 57 (41, *t*-Bu). Anal. Calcd for $C_{24}H_{22}ClF_3$: C, 71.55; H, 5.50. Found: C, 72.03; H, 5.79.

Reduction of 3r with Cr^{2+} is carried out according to the general procedure with 1.0 g (2.5 mmol) of **3r** in 60 mL of DMF at –10 °C and 1.7 g (7.2 mmol) of $CrSO_4 \cdot 5H_2O$ in 10 mL of degassed water. Precipitation is completed by addition of a further 40 mL of water; the orange product is collected by suction under argon and washed with water and a little ice-cold methanol: yield 0.4 g (43%); mp 95 °C (under argon; above 85 °C discoloration begins); ^1H NMR ($CDCl_3$, –20 °C) δ 1.29 (s, 18 H, *t*-Bu), 5.15 (s, 1 H, H_{aliph}), 6.01 (d, 2 H, H_{olef}), 6.38 (d, 2 H, H_{olef}), 6.85–8.00 (m, 21 H, Ar); ^{13}C NMR ($CDCl_3$, –20 °C) δ 31.27 (CMe_3), 34.47 (CMe_3), 43.18 (HC_{aliph}), 62.68 (Ar_2PhC), 122.78–132.78 (HC_{arom}, H_{olef}), 136.39–151.11 (C_{arom}, C_{olef}).

(4-*tert*-Butylphenyl)(4-cyanophenyl)chlorophenylmethane (3s). (4-*tert*-Butylphenyl)(4-cyanophenyl)phenylmethanol[49] (10.0 g) (29.2 mmol) in 80 mL of toluene is treated with 10.0 mL (140 mmol) of acetyl chloride following the general procedure (48 h). Addition of a little *n*-pentane initiates crystallization at 5 °C. The crude product is washed with *n*-pentane and recrystallized from *n*-hexane; first the impurities are precipitated, followed by the product as colorless crystals: yield 7.6 g (72%); mp 90 °C; IR(KBr) no OH absorption, 2240 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9 H, *t*-Bu), 7.10–7.50 (m, 13 H, Ar); MS (70 eV), *m/e* 324 (94%, M – Cl), 309 (100, M – Cl – Me), 294 (23, M – Cl – 2Me), 268 (12, M – Cl – 2Me – CN), 206 (26, M – Cl – Me – PhCN), 191 (20, PhCPhCN), 165 (8, Ph_2C), 104 (51, PhCN) 77 (14, Ph), 57 (9, *t*-Bu), 42 (12, Me_2C). Anal. Calcd for $C_{24}H_{22}ClN$: C, 80.10; H, 6.16; N, 3.89. Found: C, 79.81; H, 5.90; N, 3.90.

(4-*tert*-Butylphenyl)(4-cyanophenyl)phenylmethyl (1s) and Its Dimer 2s. A 0.1 M radical solution (2·1s $\rightleftharpoons$ 2s) obtained according to the general procedure is evaporated. The red, oily residue which becomes colorless in the presence of air is characterized spectroscopically under argon: IR (film) 2240 (CN) cm^{-1}; no C=C=N absorption; ^1H NMR (CCl_4, –20 °C) δ 1.35, 1.40 (2s, 18 H, *t*-Bu), 5.15 (s, 1 H, H_{aliph}), 6.00 (d, 2 H, H_{olef}), 6.23 (d, 2 H, H_{olef}), 7.10–7.79 (m, 21 H, Ar); ^{13}C NMR ($CCl_4/CDCl_3$, –20 °C) δ 31.05, 31.25 (CMe_3), 34.27 (CMe_3), 79.56 (Ar_2PhC), 111.30 (CN), 124.54–131.71 (HC_{arom}, HC_{olef}), 140.52–150.48 (C_{arom}, C_{olef}).

(4-Anisyl)(4-cyanophenyl)phenylmethanol is prepared according to ref 43 by reaction of 5.0 g (27.5 mmol) 4-bromobenzonitrile with 27.5 mmol of *n*-BuLi and 5.9 g (27.5 mmol) of 4-methoxybenzophenone. After removal of the solvent, the residue is dissolved in ether and a little petroleum ether (bp 30–60 °C) is added causing a permanent turbidity. After standing overnight, the clear solution is decanted and concentrated by evaporation to initiate crystallization. Further product fractions are obtained from the mother liquors: yield 5.5 g (63%) of colorless crystals with mp 104 °C; IR (KBr) 3460 (OH), 2840 (CH_{aliph}), 2240 (CN), 1030 (OC_{arom}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.05 (s, 1 H, OH), 3.70 (s, 3 H, OMe), 6.71–7.49 (m, 13 H, Ar). Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.30; H, 5.15; N, 4.40.

(4-Anisyl)(4-cyanophenyl)chlorophenylmethane (3t). A solution of 1.0 g (3.2 mmol) of (4-anisyl)(4-cyanophenyl)phenylmethanol in 15 mL of toluene is transformed to **3t** with 0.5 mL (7.0 mmol) of acetyl chloride according to the general procedure (18 h). After removal of the volatile components, the residue is dissolved in a small amount of dry cyclohexane under argon. After addition of a little dry petroleum ether (bp 90–120 °C), colorless crystals precipitate at –10 °C within 3 days. The product **3t** is recrystallized from petroleum ether (bp 60–90 °C): yield 0.7 g (69%); mp 87 °C; IR (KBr) no OH absorption, 2840 (CH_{aliph}), 2230 (CN), 1250 (OC_{arom}) cm^{-2}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 3 H, OMe), 6.80 (dd, 4 H, Ar), 7.25 (s, 5 H, Ph), 7.51 (dd, 4 H, Ar). Anal. Calcd for $C_{21}H_{16}ClNO$: C, 79.36; H, 5.08; N, 4.41. Found: C, 78.84; H, 4.68; N, 4.24.

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