Interannular Interactions in Para-Substituted Diphenylmethane Anion Radicals

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Abstract: Methylene esr hyperfine splittings (hfs) are found to be sensitive probes for 1,3-interannular interactions in diarylmethane anion radicals. 1,3 spin delocalizing interactions enhance $a_{\mathrm{CH_2}}$ by amounts that range up to 100% for symmetrically delocalized species. In this work, enhancements of 29% for the *p,p'*-ditrimethylsilyl and ditrimethylgermyldiphenylmethane anion radicals and of 10% for the corresponding monosubstituted anion radicals were observed. The delocalization, though present, is highly unsymmetrical, the ratio of spin densities on the two aryl rings being 46 in the former and 1600 in the latter two cases. No detectable enhancements in $a_{\mathrm{CH_2}}$ were found for the *p*-mono- and *p,p'*-diphenyl-, cyano-, and nitro-substituted cases. Electron exchange competition equilibria further support the proposal of stabilizing 1,3-interannular interactions in the digermane and disilane anion radicals. These two anion radicals are found to be much more thermodynamically stable than their monosubstituted counterparts, a circumstance inexplicable in terms of substituent effects on wholly localized anion radicals. Special stabilities are not found in anion radicals that fail to show enhanced methylene hfs. It is concluded that measurable stabilizations can arise from delocalizing interannular interactions even in an unsymmetrical species in which charge and spin density delocalization onto the second phenyl ring is quite small.

Attractions between carbon atoms not canonically bonded are usually weak and rather difficult to demonstrate. The work presently reported involves a search for interannular interactions in several mono- and di-para-substituted diphenylmethane anion radicals using esr spectroscopy and electron exchange equilibrium experiments.

Results and Discussion

The parent diphenylmethane anion radical (DPM$\cdot^-$) has already been investigated.[1,2] Its esr hyperfine splittings (hfs) suggest a typical alkyl benzene anion radical. Cases of both slow and rapid equilibration of the odd electron between the two phenyl rings have been observed,[2] depending on the medium involved, without significant alterations in the basic spin distribution. Nevertheless, electron exchange competition equilibria demonstrate a special stability for DPM$\cdot^-$.[2] The unexpected order of thermodynamic stabilities (relative to the respective neutral hydrocarbons) DPM$\cdot^-$ > benzene anion radical > toluene anion radical was found. The special stability of DPM$\cdot^-$ was attributed to an interannular attraction which might be largely ionic (electrostatic polarization of the second ring) or covalent. The latter would imply delocalization of the odd electron by the second phenyl ring. Despite the fact that hfs from the second ring were not resolved in these esr spectra, we favor an attraction with a substantial covalent component. Such a conclusion requires that interactions which lead to significant (say 500–2000 cal) stabilizations may perturb spin densities only nominally. The data for the substituted DPM anion radicals will provide further support for this conclusion. The available data do not distinguish between 1,3 and 1,5 (between ortho,ortho' positions) interactions. The latter, however, are favored by spin density considerations and, concordantly with this, the 2,2-diphenylpropane anion radical actually undergoes an ortho cyclization reaction, giving the 9,9-dimethylfluorene anion radical.[2]

First-order perturbation theory gives $\Delta E_{1,3} = \beta_{\mathrm{rs}}\rho_{\mathrm{r}}$, where ρ_{r} is the spin density at the atom r (see diagram) attached to the methylene group in the localized form of the anion radical. Though its small ρ_{r} makes DPM$\cdot^-$ relatively inhospitable to a 1,3 interaction, para-substituted DPM derivatives are readily constructed which are much more suitable in this respect. Specifically, para groups with electron-withdrawing resonance effects increase ρ_{r} by preferentially stabilizing a symmetric benzene-like ABMO which has a much larger ρ_{r} than the antisymmetric one occupied in alkylbenzene anion radicals and in DPM$\cdot^-$. In addition, they are remote from the interaction site and should not interfere sterically. Finally, an excellent criterion for interannular interaction, the magnitude of the methylene hfs ($a_{\mathrm{CH_2}}$), is available in these systems.

If a 1,3 interaction be operative, the system should spend more time in the conformation(s) in which the interaction is maximized. π Overlap would be maximized, in a DPM$\cdot^-$ type radical, in a coplanar conformation, whereas σ–π overlap would be maximized in a folded conformation. It is well known that β hfs (such as the methylene hfs) are sensitive to conformation.[3] In particular, the folded conformation (in which the phenyl rings face each other symmetrically) should be characterized by a smaller ($^1/_2$) and the coplanar one by a larger ($^3/_2$) methylene hfs than the free rotation value (observed for a methyl group in the analogous arylmethane anion radical). Whereas a theoretically based preference is sometimes expressed[4] for σ–π 1,3 overlap, it is not definitely known which should prevail from any experimental demonstration. It would, however, be very coincidental if both minima were of exactly the same depth. Therefore it appeared likely that some conformational bias would result from an interannular 1,3 interaction and be reflected experimentally in the magnitude of $a_{\mathrm{CH_2}}$. In the case of

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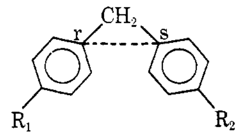
no covalent 1,3 interaction a bias should still exist, based upon steric and torsional effects. Therefore the "normal" conformational bias would have to be ascertained quantitatively and 1,3 interaction deduced by deviations therefrom. Even independently of any conformational effects, quantum mechanics predicts that a symmetrically delocalized radical will have a β hfs twice as large as a localized (including a rapidly equilibrating localized) species.[5,6] This holds because a_{CH_2} is proportional to the square of the sums of the coefficients at all vicinal positions in the MO occupied by the odd electron. Thus $a_{CH_2} = Q(c_r + c_s)^2$. In the localized form $c_s = 0$ and $c_r = \underline{1}$, hence $a_{CH_2} = Q$; in the delocalized form, $c_r = \sqrt{2}/2 = c_s$, and $a_{CH_2} = 2Q$. The ratio ranges between 1 and 2 for unsymmetrically delocalized species. The aforementioned theoretical considerations have been amply verified by experiment, especially in the case of the cyclohexadienyl radical.

The ten para-substituted or para,para′-disubstituted DPM anion radicals below were therefore synthesized and their esr spectra measured and analyzed. The choice and location of substituents were guided by the desire to vary and maximize ρ_r.



1a, $R_1 = R_2 = NO_2$
b, $R_1 = NO_2$; $R_2 = H$
2a, $R_1 = R_2 = CN$
b, $R_1 = CN$; $R_2 = H$
3a, $R_1 = R_2 = Ph$
b, $R = Ph$; $R_2 = H$
4a, $R_1 = R_2 = SiMe_3$
b, $R_1 = SiMe_3$; $R_2 = H$
5a, $R_1 = R_2 = GeMe_3$
b, $R_1 = GeMe_3$; $R_2 = H$

The five substituents involved, *viz.*, nitro, cyano, trimethylsilyl, trimethylgermyl, and phenyl, have in common the ability to preferentially stabilize an s-like orbital, as discussed previously, thus situating relatively large fractions of odd electron density at the position para to to the substituent, whence the 1,3 interaction may occur. The relevant data are contained in Table I. The quantity designated *C*(R) is an experimental criterion based on the methylene hfs, being defined as a_{CH_2}/a_{CH_3}, where a_{CH_2} is the methylene hfs of the substituted DPM$\cdot^-$ concerned and a_{CH_3} is the methyl (free rotation) hfs of the correspondingly substituted toluene anion radical. This ratio corrects for variations in a_{CH_2} due to changes in ρ_r with substituent. The validity of the *C*(R) index has been discussed in several papers.[3,7,8] Published[9-11] methyl hfs of para substituted toluene anion radicals were used for the calculation of *C*(R) except for the case of *p*-trimethylsilyltoluene and *p*-trimethylgermyltoluene. In the former case a literature value was available,[12] but the methyl hfs was redetermined in MTHF–crown in order to check on the possibility of a solvent effect on this hfs. The value obtained (8.75 G) was not greatly different (8.43) from that previously observed in DME. Note, in addition, that the exact magnitude of the methyl hfs has no direct bearing on the relative *C*(R) values of the mono- and disubstituted diarylmethane anion radicals. The *p*-trimethylgermyltoluene anion radical has not been reported. Neither were our attempts to generate this radical from its substrate successful. Therefore the para hfs of the trimethylgermylbenzene anion radical[13] was used as an approximation to the desired methyl hfs. The para hfs in the trimethylsilylbenzene anion radical (8.09) is quite close to the methyl hfs of the *p*-trimethylsilyltoluene anion radical in the same solvent, DME (8.43).

Table I. Esr Hyperfine Splittings of Diarylmethane Anion Radicals[a]

Compound	Number	a_{CH_2}	a_o	a_m	a_x
Dinitro	**1a**	2.8	3.2[b]	1.0[b]	(N) 10.3
Mononitro	**1b**	2.8	3.3	1.1	(N) 10.9
Dicyano	**2a**	6.30	3.44[b]		(N) 1.77
Monocyano	**2b**	6.20	3.54[b]	0.49	(N) 2.06
Diphenyl	**3a**	3.79	1.30[c]		(*p*-Ph–H) 2.61
Monophenyl	**3b**	3.79	2.61[c]	0.40[c]	(*p*-Ph–H) 5.22[b]
Disilane	**4a**	7.75	1.00[b]	1.00[b]	($-CH_3$) 0.1
Monosilane	**4b**	6.8	2.8[b]	1.3[b]	($-CH_3$) 0.2
Digermane	**5a**	7.50	1.0		($-CH_3$)–
Monogermane	**5b**	6.30	2.1		($-CH_3$)–

[a] By potassium reduction in DME (**1**, **2**) or MTHF–crown (**3**, **4**, **5**) solvent. [b] The ortho and meta designation is with respect to the substituent. [c] Ortho, meta, and para refer to the phenyl–phenyl bond of the biphenyl moiety (phenyl is the substituent).

The values of *C*(R) observed for **1a**$\cdot^-$, **1b**$\cdot^-$, **2a**$\cdot^-$, and **2b**$\cdot^-$ are 0.72, 0.72, 0.69, and 0.69, respectively. Since all four species are localized (*i.e.*, slowly equilibrating; see ring hfs) and since, in addition, any interannular interactions should be larger in the **a** than in the **b** members of the series and for cyano than nitro (ρ_r factor) it appears that any 1,3 interactions in these four species must be miniscule indeed. Therefore it does seem valid to speak of a normal value for *C*(R), in the absence of interannular interactions. Further, the magnitude of *C*(R) suggests that *the folded conformation is favored over the coplanar one.*

Species **3b**$\cdot^-$ is also localized and has *C*(R) = 0.70 essentially as before, but **3a**$\cdot^-$ shows equivalent aryl rings. However, *C*(R) is still 0.70. The latter species may thus be classified as rapidly equilibrating localized. It is not particularly surprising, incidentally, that equilibration is faster here than in **1a**$\cdot^-$ and **2a**$\cdot^-$, since there is, in **3a**$\cdot^-$, no polar substituent available to pair with the metal ion. No doubt the metal ion still interacts quite strongly with the negatively charged aryl ring, rendering the system instantaneously unsymmetrical and hampering the 1,3 interaction.

It is important to note that six cases in all exhibit the normal *C*(R) = 0.705 ± 0.015. Some of these have polar substituents, and others do not; some are slowly and others rapidly equilibrating. The value of ρ_r varies from 0.15 to 0.33. It appears reasonable to conclude that 1,3 interactions are, to an outstandingly

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good approximation, absent in all six of these cases. No doubt ion pairing plays at least some part in minimizing 1,3 interactions. An interesting but unanswered question is whether any of the free ions of **1**–**3a**$\cdot^-$ would have substantial interannular interactions.

The silyl and germyl cases were considered, on theoretical grounds, to be the best hopes for observing 1,3 interactions. They, with the cyano group, engender the largest ρ_r's and, in advantage over the cyano group, these substituents are not highly polar. Moreover, they are bulky and could tend to resist tight ion pairing. In fact, **4a**$\cdot^-$ and **5a**$\cdot^-$ do have equivalent aryl rings and display the quantum mechanically expected enhancement in C(R) [0.89 and 0.91, respectively]. The **b** components are, of course, not visibly delocalized as viewed from the ring hfs, but nevertheless have the slightly elevated C(R) values 0.78 and 0.77, respectively. Apparently, then, **4a**$\cdot^-$ and **5a**$\cdot^-$ do support an interannular interaction. A smaller interaction is also likely for **4b**$\cdot^-$ and **5b**$\cdot^-$. It should be noted that even if the **b** series were wholly localized the data would still decisively impute interannular delocalization to the **a** series. Thus, if the **b** ions were fully localized, they should have identical C(R) values to those of rapidly equilibrating localized versions of the **a** ions. The observed enhancement is 29%, not 100% as expected for symmetrically delocalized ions. Consequently, unless there is a large counterbalancing conformational shift, **4a**$\cdot^-$ and **5a**$\cdot^-$ are indicated to be *unsymmetrically delocalized.* This appears eminently logical for an ion pair and suggests that the metal ion still prefers to sit over one of the aryl rings at a time. This analysis also helps explain the results in the **b** series which would, of course, be even more unsymmetrical. The hfs from the other ring might then be too small to resolve. Thus, absence of hfs from a second ring should probably not be used to conclusively rule out small interannular interactions. The validity of this assertion is dramatically illustrated by the following calculation. The quantum mechanical enhancement factor for β hfs is given by $(c_r + c_s)^2/c_r^2 + c_s^2$. Experimentally, this factor is found to be 1.29 (29%) for the disilane anion radical. It emerges that $c_r/c_s = 6.75$ and, more importantly, $c_r^2/c_s^2 = 45.6$, that is, $\rho_r = 45.6\rho_s$. In other words, C_s has only 2% of the spin density present at C_r. Interaction with the s orbital of the second ring (containing C_s) should place about equal spin densities at C_s and the para portion of that ring ($C_{p'}$). Assuming a maximum hfs of 9 G for an s-type benzene ABMO (such as is observed in the monosilane), this small ρ_s would correspond to $a_{p'} \approx 0.2$ G. This is the hfs which should be observed if the disilane were not rapid equilibrating and if the line width were sufficiently narrow. The 1.10 enhancement factor observed with the monosilane and germane corresponds to $c_r/c_s = 40$, $c_r^2/c_s^{\ 2} = 1600$, and to a $a_{p'} = 0.05$ G. Thus, methylene hfs are quite sensitive to even small extents of delocalization, and such delocalization need not even produce readily observable ring hfs.

Considerable thought has been given to possible flaws in the foregoing experiments and arguments, and it may be to some purpose to mention a few which were considered. In addition to the emphasized effects of conformation and delocalization, C(R) is also affected by changes in the spin density distribution. The utility of the C(R) index is, of course, based upon the assumption that such differences are negligible. That this is valid to an excellent approximation for the arylmethane series as compared to the localized diarylmethane series is easily verified by a comparison of the ring hfs in the two series. Deviations are in the range 0–5%, whereas the increase in C(R) is 28%. Further, the increase in C(R) of 15% in the disilane and digermane as compared to the monosilane and monogermane is also significant. The differences in hfs between the localized cases of disubstitution and their corresponding monosubstitution cases are seen to be very small indeed. In most of these, *e.g.*, the nitro and cyano cases, the second substitutent represents a far greater perturbation than do the silyl and germyl groups. Therefore the second substituent in a localized disilane or digermane should cause even less change in the spin densities than in the other three cases, in which changes are demonstrably negligible.

Competition Experiments. Independent confirmation of the conclusions based on the C(R) results was sought *via* competition experiments. If, *e.g.*, **4a**$\cdot^-$ is appreciably stabilized by a 1,3 interaction, the electron affinity of **4a** should be greater than that of **4b**. If the anion radicals of both of these systems are localized, there should be very little difference in their stabilities and, as will be argued below, any differences should actually lean in favor of **4b**$\cdot^-$. This conjecture was tested by reducing varying proportions of **4a**:**4b** with potassium in 2-methyltetrahydrofuran (MTHF) containing 1 mol of dicyclohexyl-18-crown-6 ether per mol of disilane, which was always the minor component. This solvent combination was initially used to assure that reduction was halted before either component was totally reduced.[2] The method was retained, even after it was determined that ordinary anion radical solvents alone (*e.g.*, DME) give identical results, because the desired anion radicals were much more stable in this medium than in the usual solvents. This may be partly due to the lower temperatures accessible in MTHF (−130°), but some other effect is also operative since **4a**$\cdot^-$, for example, is much more stable at −60° in MTHF–crown than in DME. Perhaps the anion radical is simply more tightly ion paired to the metal in MTHF and thereby more stabilized. In any case the effect is great enough to be noteworthy.

Reduction of 1:2 and 1:5 proportions of **4a**:**4b** under these conditions gave, after short or long reaction times, only radical **4a**$\cdot^-$. The esr spectra of **4a**$\cdot^-$ and **4b**$\cdot^-$ are quite different and readily distinguishable. Only when a 1:10 ratio of the two was used did the **b** species appear. Apparently **4a**$\cdot^-$ is subject to a stabilization effect present to a lesser degree in **4b**$\cdot^-$. This procedure was repeated for the germanes, and identical results were obtained.

In contrast, when a 1:1 mixture of **3a**:**3b** was reduced, both radicals were observed. When the proportion is 2:1, **3a**$\cdot^-$ is observed, and when 1:2, **3b**$\cdot^-$ is observed. The competition experiments directly reflect relative energies and decisively confirm the special stabilities of the disilane and digermane anion radicals and the absence thereof in **3a**$\cdot^-$. The nitro and cyano cases were not studied, since both the mono and di series are localized and give nearly identical spectra.

It is important to record that the trimethylsilyl group is a weak electron donor ($\sigma = -0.02$ to -0.07) in Hammett correlations.[14] Its presence on the second, neutral ring in a localized disilane anion radical should therefore cause a destabilization. The trimethylgermyl group is neutral ($\sigma = 0.0$). The previous conclusions are thus fortified by more detailed considerations of substituent effects. It might be mentioned that σ^- is positive ($+0.09$)[15,16] for trimethylsilyl. That is, when its conjugative ability is more fully called out than in normal Hammett correlations the group is feebly electron attracting. This is observed in, *e.g.*, the ionization of *p*-trimethylsilylphenols or anilinium ions. However, it is only in the nonclassical version of **4a**$\cdot^-$ that the second trimethylsilyl group is present in the conjugated system having the odd electron. In other words, localized **4a**$\cdot^-$ is a σ situation, the delocalized version a σ^- situation. Since both the disilane and digermane anion radicals are *solely* formed upon reduction of 5:1 mixtures of the relevant mono- and disubstituted substrates, it is certain that they are both favored by factors of at least 10 in their respective equilibria. Even should the silyl and germyl groups somehow have acquired a small positive σ value in the present circumstances, an untenably large ρ value would be required in order to account for effects of the observed magnitude. For example, if $\sigma = +0.02$, $\rho \geq 50$ would be required. Such a large ρ would be unprecedented and especially so for a reaction in which the substituent is so remote from the sites of charge accrual. For example, the benzoic acid ionization, which has $\rho = 1.00$ in water, has approximately a full unit of negative charge added to two positions two atoms removed from the benzene ring bearing the substituent. The anion radicals here involved have only *ca.* $^1/_3$ unit this close. Therefore even if the change in solvent engendered a tenfold increase in ρ (also unprecedented), the expected reaction constant would still be only about 3. Finally, the finding of comparable stabilities for **3a**$\cdot^-$ and **3b**$\cdot^-$. provides experimental verification that ρ, and therefore substituent effects, are small for a localized anion radical. It is therefore concluded that a substituent effect on the stability of a localized anion radical could not be responsible for the observed special stabilities of the disilane and digermane anion radicals.

A further competition reaction was carried out in which disilane **4a** was forced to compete with an equimolar amount of trimethylsilylbenzene. The esr spectrum was a composite of the spectra of both anion radicals. Apparently the interannular stabilization in **4a**$\cdot^-$ approximately nullifies its inductive destabilization by the electron-donating methylene bridge.

Ring Spin Densities. The ring spin densities, as reflected by the ring hfs, in **4a**$\cdot^-$,**b**$\cdot^-$ provide still another clue suggesting delocalization in the former. A small 1,3 interaction might be expected to produce a small perturbation in the wave functions. Specifically, this perturbation should be in the direction of the homobiphenyl anion radical. The ortho hfs should therefore be decreased and the meta increased.[17] This is exactly as observed (Table I) in **4a**$\cdot^-$ as compared to **4b**$\cdot^-$. In the monosilane anion radical the ortho splitting is more than twice the meta splitting, as is typically observed in silylbenzene anion radicals. In the disilane case they are nearly equal. The hfs of the latter must be multiplied by two in order to compare them with the figures for **4b**$\cdot^-$. The effect is not observable in the germane case where the ortho and meta hfs are already equal in the monosubstituted anion radical. However, the failure to resolve the ortho and meta hfs here may simply be a matter of the rather large (0.50 G) line width of the digermane spectrum.

It should be stressed that the DPM systems discussed in this paper are not particularly ideally suited, geometrically, for 1,3 overlap. The substituents have been chosen and situated to optimize the wave function toward such overlap, but the geometry is only mediocre in terms of proximity. Therefore, the demonstration of these effects in these particular systems implies that similar effects may exist in other systems. It further suggests that systems which have especially propitious geometries for 1,3 overlap in addition to favorable orbital characteristics, may have even larger stabilization energies. The development of techniques for demonstrating and measuring the magnitudes of these interactions is a worthy and significant challenge.

Experimental Section

Nmr spectra were recorded on a Varian A-60 spectrometer, infrared spectra on a Beckman IR-5 spectrometer, and mass spectra on a CEC-DuPont 21-491 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Esr spectra were obtained on a Varian V-4502 X-band spectrometer equipped with a temperature control apparatus. Esr samples were made up using standard vacuum line techniques. Solvents were stored on the line over NaK and distilled into the vessels. Alkali metals were distilled into the vessels from sidearms. The crown ether (dicyclohexyl-18-crown-6) was furnished by DuPont, Elastomer Chemicals Department.

The mono- and dinitro compounds **1a** and **1b** were obtained from Columbia Organic Chemicals and were used without further purification. The precursors *p*-bromodiphenylmethane and *p,p'*-dibromodiphenylmethane were obtained from K & K Laboratories and Aldrich Chemical Co., respectively.

***p,p'*-Dicyanodiphenylmethane (2a).** Following the method of Friedman and Shechter,[18] *p,p'*-dibromodiphenylmethane (2.00 g, 6.2 mmol) was combined with cuprous cyanide (1.31 g, 14.6 mmol) and dimethylformamide (5.0 ml). The mixture was refluxed for 6 hr, after which the aqueous acidic ferric chloride work-up method was followed by extraction with 10-ml portions of benzene and ethyl ether. The combined organic extracts were subjected to normal work-up procedures, and removal of the solvents by rotovap left a yellow oil which upon chromatography on silica gel with Skelly B elution gave, after evaporation of solvent, white cottony needles of the dinitrile **2a** (0.52 g, 38.8%): mp 166–167° (lit.[19] 165°); ir ($CHCl_3$) 2245 cm^{-1} (sharp, $C\equiv N$ stretch); nmr ($CDCl_3$) τ 5.91 (s, $-CH_2-$, 2 H), and 2.36–2.77 (q_{AB}, $J = 8.5$ Hz, aryl, 8 H); mass spectrum m/e 218 (M).

***p*-Cyanodiphenylmethane (14b).** Similarly, reflux of *p*-bromodiphenylmethane (2.50 g, 1.00 mmol) with cuprous cyanide (1.10 g, 1.20 mmol) in dimethylformamide (1.52 ml) yielded after work-up and recrystallization from pentane the nitrile **2b** (0.99 g, 50.8%) as white crystals: mp 49–50° (lit.[20] 50–52°); ir (CCl_4) 2250 cm^{-1} (sharp, $C\equiv N$ stretch); nmr (CCl_4) τ 6.06 (s, $-CH_2-$, 2 H) and 2.49–3.09 (m, aryl, 9 H).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.75. Found: C, 86.73; H, 6.01.

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p,p'-Di(trimethylsilyl)diphenylmethane (4a). Magnesium turnings (0.67 g, 28.0 mg-atoms) and a stirring bar were placed in the bottom of a 100-ml, three-neck flask, fitted with a stopper, addition funnel, and a Vigreux column topped with a T-tube, through which dry nitrogen is introduced. After flame-drying the apparatus, THF (5 ml, distilled from sodium) was pipetted into the flask, and a solution of p,p'-dibromodiphenylmethane (3.00 g, 9.2 mmol) and 1,2-dibromoethane (0.86 g, 4.6 mmol) in 25 ml of THF was added dropwise with stirring. After addition was complete, the mixture was refluxed for 6 hr more, or until magnesium consumption was complete. To the Grignard reagent was added, dropwise, trimethylsilyl chloride (1.99 g, 18.3 mmol) in 10 ml of THF. The mixture was refluxed for 12 hr, and after cooling water and ethyl ether were added, followed by normal work-up procedures. A viscous oil was obtained, which upon vacuum distillation yielded, after a forerun of diphenylmethane and monosilane **4b**, the disilane **4a** (0.92 g, 32.0%) as a clear oil: bp 123° (15 μ); nmr (CCl_4) τ 9.79 (s, $-CH_3$, 18 H), 6.21 (s, $-CH_2$, 2 H), 2.94 and 3.61 (q_{AB}, J = 7.5 Hz, aryl, 8 H); mass spectrum m/e 312 (M).

p-(Trimethylsilyl)diphenylmethane (4b). Likewise, treatment of p-bromodiphenylmethane (2.50 g, 10.0 mmol) with magnesium metal (0.73 g, 29.6 mg-atoms) along with 1,2-dibromoethane (1.10 g, 5.8 mmol) in THF, followed by addition of trimethylsilyl chloride (2.20 g, 20.4 mmol), yielded upon work-up and distillation the monosilane **4b** (2.00 g, 82.3%) as a clear viscous liquid: bp 95° (20 μ); nmr (CCl_4) 9.79 (s, $-CH_3$, 9 H), 6.21 (s, $-CH_2$, 2 H), 2.97 (s, monosubstituted aryl, 5 H), 2.60 and 2.94 (q_{AB}, disubstituted aryl, 4 H).

p,p-Di(trimethylgermyl)diphenylmethane (5a). Similarly, the Grignard reagent formed from p,p-dibromodiphenylmethane (3.00 g, 9.2 mmol) and magnesium turnings (0.85 g, 35.0 mg-atoms), accelerated by 1,2-dibromoethane (3.46 g, 18.4 mmol), reacted with trimethylgermyl bromide (3.8 g, 19 mmol) to give, in addition to the by-products diphenylmethane and the monogermane **5b**, the digermane **5a** (0.89 g, 24.1%), a viscous clear oil: bp 152° (50 μ); nmr (CCl_4) 9.79 (s, $-CH_3$, 18 H), 6.27 (s, $-CH_2-$, 2 H), 2.81 and 3.06 (q_{AB}, J = 7.5 Hz aryl, 8 H); mass spectrum m/e 402 (M).

Anal. Calcd for $C_{19}H_{28}Ge_2$: C, 67.44; H, 7.09. Found: C, 67.18; H, 7.09.

p-(Trimethylgermyl)diphenylmethane (5b). Mixing together in THF p-bromodiphenylmethane (2.50 g, 10.1 mmol), 1,2-dibromoethane (1.90 g, 10.1 mmol), magnesium metal (0.50 g, 20.6 mmol), and after Grignard formation, trimethylgermyl bromide (2 g, 10 mmol) afforded after work-up and distillation the monogermane **5b** (1.10 g, 37.9%) as a clear viscous liquid: bp 125° (00 μ); nmr (CCl_4) τ 9.79 (s, $-CH_3$, 9 H), 6.35 (s, $-CH_2-$, 2 H), 3.08 (s, monosubstituted aryl, 5 H), 3.05 and 2.78 (q_{AB}, J = 7.5 Hz, disubstituted aryl, 4 H); mass spectrum m/e 286 (M).

Anal. Calcd for $C_{16}H_{20}Ge$: C, 56.81; H, 7.05. Found: C, 57.17; H, 6.84.

p-Phenylbenzhydrol. To a stirred solution of biphenyl-4-carboxaldehyde (5.00 g, 27.5 mmol) in 50 ml of dry ethyl ether was added dropwise 3 M ethereal phenylmagnesium bromide (20 ml, 55 mmol) over a 30-min period. After addition was complete a large amount of solid and viscous material had formed and 20 ml of THF (distilled over sodium) was added which partially liquefied the reaction mixture. After 3 hr reflux, water and dilute HCl were added until two clear layers were obtained. Upon work-up the organic fraction yielded a brown oil which could not be crystallized. Nmr showed no detectable starting aldehyde, but the relative areas of aryl and suspected methine H's showed the presence of large amounts of impurities. Chromatography (silica gel) after five 50-ml portions of Skelly B, and two of 75% Skelly B-25% benzene, yielded a fraction which showed an encouraging aryl/methine nmr ratio, and after two recrystallizations from Skelly B the alcohol was obtained (0.45 g, 6.3%) as white crystals: mp 95°; nmr ($CDCl_3$) τ 7.51 (s, $-OH$, 1 H), 4.24 (s, methine, 1 H), 2.30–2.88 (m, aryl, 14 H); mass spectrum m/e 260 (M).

p-Phenyldiphenylmethane (3b). The p-phenylbenzhydrol (0.45 g, 17.3 mmol) in 20 ml of ethyl ether was added dropwise under nitrogen to a stirred mixture of $LiAlH_4$ (0.25 g, 66.8 mmol) and $AlCl_3$ (0.91 g, 68.3 mmol) in 50 ml of ethyl ether and refluxed gently 4 hr. After cooling, water was added dropwise until hydrogen evolution ceased and a clean light gray precipitate formed. The solid was removed by suction filtration; the flask and solid were washed twice with 10-ml portions of ethyl ether. The combined ether fractions were dried with sodium sulfate and rotovaped to give white crystals (mp 73–80°) which were recrystallized from hexane to give the hydrocarbon product **3b** (0.21 g, 51.2%) as white crystals: mp 83–84° (lit.[21] 85°); nmr ($CHCl_3$) τ 6.01 (s, $-CH_2-$, 2 H), and 2.30–2.91 (m, aryl, 14 H); mass spectrum m/e 320 (M).

p,p'-Diphenylbenzhydrol. To a flame-dried flask containing magnesium turnings (0.56 g, 64.2 mg-atoms) and 5 ml of ethyl ether was added dropwise a solution of p-bromobiphenyl (7.50 g, 32.2 mmol) and 1,2-dibromoethane activator (6.05 g, 32.2 mmol) in 50 ml of ethyl ether. After 4 hr reflux, Grignard formation was essentially complete, as judged by magnesium consumption, and to the flask was added, over a 30-min period, ethyl formate (1.19 g, 16.1 mmol) in 20 ml of ethyl ether. After addition was complete, the reaction mixture was refluxed for 1.5 hr, followed by the addition of water and dilute HCl, and the separation of the two layers. Suspended in the organic fraction was a powdery white solid which was removed by suction filtration. The filtrate was dried with sodium sulfate and rotovaped to give a yellow solid. This material was leached four times with 50-ml portions of Skelly B and then recrystallized twice from ethyl ether to give the alcohol (0.80 g, 14.8%) as white crystals: mp 142–144°; nmr (DMSO-d_6) τ 6.71 (s, $-OH$, 1 H), 4.21 (s, methine, 1 H), and 2.22–2.75 (m, aryl, 18 H); mass spectrum m/e 336 (M).

Bis(p-biphenylyl)methane (3a). In a reduction procedure similar to that for the monophenylbenzhydrol, the p,p-diphenylbenzhydrol (0.72 g, 2.23 mmol) was added to a mixture of $LiAlH_4$ (0.34 g, 8.92 mmol) and $AlCl_3$ (1.19 g, 8.92 mmol), refluxed for 4 hr, and then quenched with water and filtered. The work-up yielded after recrystallization from Skelly B–ether the hydrocarbon **3a** (0.53 g, 73.8%), as a white powder: mp 161–162° (lit.[22] 162°); nmr ($CDCl_3$) τ 5.93 (s, $-CH-$, 2 H), and 2.28–2.86 (m, aryl, 18 H); mass spectrum m/e 320 (M).

Acknowledgment. The authors are grateful to the Welch Foundation for supporting this research (F-149).

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