acknowledged.

Preparation and Characterization of Some Pentaarylethyls

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The reaction of triphenylmethylsodium with dichlorodiphenylmethane does not give pentaphenylethyl as previously reported, but when the anion reacts with 9,9-dichlorofluorene, it does form the reported 9-tritylfluorenyl radical which has been characterized by ESR spectroscopy. The radical is better prepared by oxidation of the anion of 9-tritylfluorene. The 9-tritylfluorenyl radical reacts with traces of oxygen to give triphenylmethyl and fluorenone. With light it forms triphenylmethyl and fluorenylidene. The latter was established by photolyzing 9-diazofluorene in the presence of triphenylmethyl with the generation of 9-tritylfluorenyl. Small yields of the persistent pentakis(*p-tert*-butylphenyl)ethyl radical have been prepared, and it is probable that pentaphenylethyl has also.

Pentaphenylethyl was reported as a stable radical isolated as a solid in 1922 by Schlenk and Mark,[1] who formed it by reacting ether solutions of dichlorodiphenylmethane with triphenylmethyl- (trityl) sodium or by the reaction of the disodium adduct of tetraphenylethylene with triphenylmethyl chloride. Since electron spin resonance spectroscopy (ESR) did not exist at the time, they characterized ether solutions of the radical by their reactivity with oxygen and with chlorine, forming a presumed pentaphenylethyl chloride which was reported to give back the radical when treated with copper bronze and also to be hydrolyzed to pentaphenylethyl alcohol. In a subsequent paper,[2] they also reported the isolation of the 9-tritylfluorenyl radical as a purple solid obtained from the reaction of tritylsodium with 9,9-dichlorofluorene.

In 1935, Dorfman[3] reported that numerous attempts to prepare pentaphenylethyl by the dichlorodiphenylmethane route were unsuccessful. He did find the path through tetraphenylethylene satisfactory and determined the electron affinity of the radical by measuring the amount of sodium taken up from a standard sample of sodium amalgam. Similar measurements were made on the purple 9-tritylfluorenyl.

While no reference to pentaphenylethyl per se was made, Gregg and Mayo[4] found the chain-transfer constant in styrene polymerization to be three orders of magnitude larger for pentaphenylethane than for triphenylmethane. Such chain-transfer phenomena involving benzyl-type hydrocarbons are usually discussed in terms of the relative strength of the C–H bonds being broken and might be interpreted in this case as implying an unusually large stabilization for the pentaphenylethyl radical.

Recently, we have studied the photochemical bromination of pentaphenylethane at room temperature.[5] The only products are a quantitative yield of trityl bromide and dibromodiphenylmethane. The pentaphenylethyl radical was proposed as a transient species here, the resultant pentaphenylethyl bromide decomposing to the trityl radical and the bromodiphenylmethyl radical.

The postulation of pentaphenylethyl as a substance of unusual persistence of course begs the question. The diphenylmethyl radical is not persistent, but rather dimerizes to tetraphenylethane. The introduction of steric hinderance in the form of *o*-methyl groups alters the dimerization from ethane formation to the formation of a methylenecyclohexadiene.[6] The same has recently been found true for the 1,1-diphenyl-2,2-dimethylpropyl radical.[7] This mode of dimerization appears to be equally accessible to the pentaphenylethyl radical. Phenyl bridging in radical reactions has never found experimental support unlike the formation of phenonium ions in carbocation processes. A bridged phenyl radical appears to be at best a transition state during phenyl migration.

Experimental Section

All ESR spectra were obtained on a Varian Model E 102A instrument with a 9.5-GHz microwave bridge using a modulation frequency of 100 kHz. Proton and carbon NMR spectra were obtained on Varian EM-390 and JEOL FX-60 instruments, respectively. Unless otherwise noted all NMRs were obtained in deuteriochloroform with tetramethylsilane as an internal standard. Routine mass spectra were obtained on a Finnigan OWA-1020 GC-MS-DS operating after a Perkin-Elmer Sigma-3 gas chromatograph. High-resolution mass spectra were kindly provided by Dr. David Russell of Texas A&M University.

Reactions carried out in the absence of oxygen were conducted in a standard glovebag purged with prepurified nitrogen or argon. Such reactions were frequently carried out in standard Schlenk ware after similar purging.

Reaction of Tritylsodium with Dichlorodiphenylmethane. Tritylsodium was generated by shaking 2.0 g (7.2 mmol) of trityl chloride in 75 mL of ether with sodium amalgam (ca. 2.5%) formed from 0.7 g (30 mmol) of sodium and 2 mL of mercury. After 15 h the dark red solution was filtered under nitrogen, and a solution composed of 0.85 g (3.6 mmol) of dichlorodiphenylmethane in 25 mL of ether was added in small protions. When ca. 2.7 mmol of the dichloro compound had been added, the dark red initial color altered to light red. An ESR analysis of the solution at this

(1) Schlenk, W; Mark, H. *Ber.* **1922**, *55*, 2285.
(2) Schlenk, W.; Mark, H. *Ber.* **1922**, *55*, 2299.
(3) Dorfman, M. *J. Am. Chem. Soc.* **1935**, *57*, 1455.
(4) Gregg, R. A.; Mayo, F. R. *Discuss. Faraday Soc.* **1947**, *2*, 328.
(5) Smith, W. B.; Harris, M. C. *J. Org. Chem.* **1980**, *45*, 355.

(6) Lankamp, H.; Nauta, W. T.; McLean, C. *Tetrahedron Lett.* **1968**, 249.
(7) Smith, W. B.; Branum, G. D.; Saint, C. *J. Org. Chem.*, in press.

time showed only a very concentrated solution of trityl radical. When the mixture was allowed to stand overnight, a gold-colored solid was deposited from the solution. Isolated by filtration, an ether solution of this material gave again the ESR spectrum of trityl. Reduction in the mother liquor volume of the original solution gave more gold-colored solid which again gave only the trityl ESR on dissolution.

The above sequence was repeated a number of times with several variations in the concentration and mode of addition. The only radical ever detected was trityl. In one experiment 1.2 g of trityl chloride was reacted with proportional amounts of all reagents as above. The mixture was allowed to stand for 3 weeks protected from light and air. At the end of this time the solvent was evaporated under vacuum. A ^{13}C NMR was obtained on the crude product. The latter was then chromatographed on a 2 × 50 cm column by using a low-boiling petroleum ether and 10% chloroform–petroleum ether sequentially as the developing solvents. Fractions were monitored by TLC and ^{13}C NMR. Comparison with known samples allowed the identification of collected materials as follows: 0.34 g of triphenylmethane, 0.22 g of tetraphenylethylene, 0.15 g of pentaphenylethane, 0.12 g of 4-trityl-1-(diphenylmethyl)benzene [mp 210–215 °C (lit.[8] mp 225 °C)], and 0.14 g of two unidentified compounds.

Several attempts to prepare pentaphenylethyl by the use of disodium tetraphenylethyl dianion were carried essentially as described by Schlenk and Mark.[4] Again ESR signals only of trityl were observed. Preparative thin-layer chromatography of 0.41 g of crude product from one of these gave a product distribution of 65% tetraphenylethylene, ca. 25% triphenylmethane, and ca. 10% triphenylmethyl peroxide.

Reaction of Tritylsodium with 9,9-Dichlorofluorene. In parallel with the above sequence, 1.4 g (5 mmol) of trityl chloride was converted to the anion with sodium amalgam (0.6 g of sodium in 1 mL of mercury) in 50 mL of ether (6-h reaction time). A solution of 0.33 g (1.4 mmol) of 9,9-dichlorofluorene in 10 mL of ether was added dropwise to the anion solution. The dark red color of the anion was converted to a deep purple. An ESR examination of a small portion of the solution showed the presence of only trityl radical.
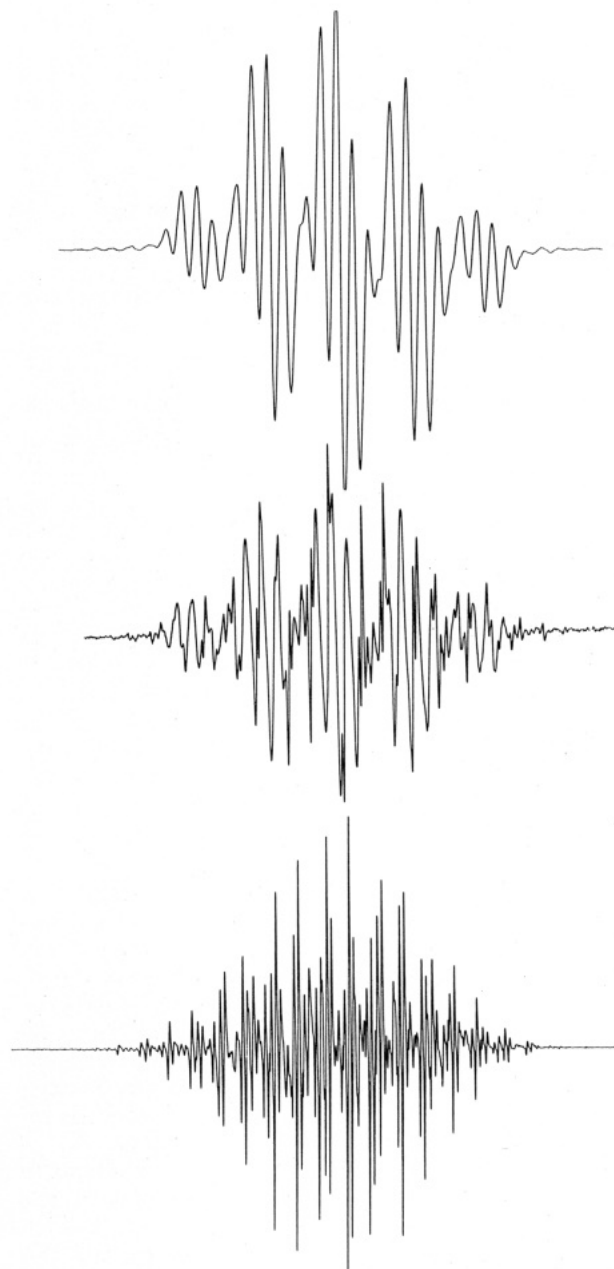
After the mixture had been allowed to stand several hours, a purple solid was deposited. Isolated by filtration under nitrogen, neither the solid nor solutions in ether gave an ESR signal. The ^{13}C NMR of this material was extremely complex in the aromatic region, but signals at 52.3 and 62.9 ppm correspond with those of an authentic sample of 9-tritylfluorene. Analytical TLC of the purple solid indicated at least four substances present. Solutions in chloroform maintained their color integrity about 1 h before slowly turning orange-brown.

In repeat reactions as above, it became noticeable that small amounts of a brown amorphous solid were also being formed. The purple solid could be separated from this material manually in the glovebag. Solutions of this brown material in ether gave an ESR signal (Figure 1, top) attributable to 9-tritylfluorenyl. A spectral simulation was readily achieved with coupling constants as follows: 3.58 (4 H) and 0.78 G (4 H). The g value was 2.0054.

In one experiment the purple solid and brown amorphous material were each formed when 9,9-dichlorofluorene was reacted with 2 equiv of tritylmagnesium bromide.

Dilution and photochemical experiments are described in the text for solutions of the brown material.

Preparation of 9-Tritylfluorenyl by the Method of Ziegler.[9] A solution of 9-tritylfluorene, 21 mg (0.05 mmol), prepared by the coupling of tritylmagnesium bromide and 9-bromofluorene[10]) in 50 mL of tetrahydrofuran (THF) in a Schlenk tube was reacted 0.5 mL of 1.4 M n-butyllithium in hexane. An immediate orange color developed. Treatment of this solution with 90 mg (0.4 mmol) of 2,3-dibromo-2,3-dimethylbutane with swirling for 10 min converted the solution to light brown. The ESR spectrum of this solution was identical with that attributed above to the 9-tritylfluorenyl radical.

(8) Ullman, F.; Borsun, W. *Ber.* **1902**, *35*, 2877.
(9) Ziegler, K.; Schnell, B. *Justus Liebigs Ann. Chem.* **1924**, *477*, 227.
(10) Schmidlin, J. *Ber.* **1910**, *43*, 1140.
(11) Marvel, C. S.; Kaplan, J. F.; Himel, C. M. *J. Am. Chem. Soc.* **1941**, *63*, 1892.

Figure 1. ESR spectrum for 9-tritylfluorenyl (top), after partial dilution (middle), and in dilute solution (bottom). The top spectrum is identical with the simulated spectrum obtained on using the parameters in Table I. The bottom spectrum is identical with that of the trityl radical.

Solutions of the 9-tritylfluorenyl anion prepared as above were stable for up to 3 weeks. These solutions could be used to generate radical at will when treated with dibromide or gave back the hydrocarbon quantitatively when hydrolyzed. Solutions of the radical could be prepared directly in the ESR tube by adding the anion solution to the dibromide in the tube. Solutions of the radical were stable for as long a 5 days in the absence of air.

In one experiment, radical generated from 0.1 g of hydrocarbon in 75 mL of THF was allowed to stand with 35 mL of air overnight. The solvent was evaporated under vacuum, and the brown oily residue was chromatographed as before, yielding a small yellow fraction (10 mg) of fluorenone identified by infrared and ^{13}C NMR.

In another experiment an ESR tube of radical solution was irradiated with a low-pressure mercury lamp. The ESR changes are discussed in the text.

9-[Tris(perdeuteriophenyl)methyl]fluorenyl Radical. A sample of 9-[tris(perdeuteriophenyl)methyl]fluorene was prepared by the following sequence of standard reactions: perdeuteriophenylmagnesium bromide, tris(perdeuteriophenyl)carbinol, conversion to the bromide, and coupling as before to the fluorene.

Generation of the radical as above gave an ESR signal identical with Figure 1 (top).

9-[Tris(4-*tert*-butylphenyl)methyl]fluorenyl Radical. The preparation of tris(4-*tert*-butylphenyl)methyl bromide was prepared from the carbinol[11] by refluxing with excess acetyl bromide in heptane: mp 277–282 °C dec; ^{13}C NMR δ 31.4, 34.6, 80.0, 124.5, 130.4, 143.1, 150.7 ppm; HRMS, *m/e* 411.304 036, calcd for $C_{31}H_{39}$ ($M^+ - Br$) 411.305 136. The bromide was converted to the Grignard and coupled with 9-bromofluorene as before, mp 260–268 °C (vacuum). Anal. ($C_{44}H_{48}$) C, H.

The radical was generated from the anion as described above to give an ESR identical with Figure 1 (top).

Preparation of 9-(9-Phenylfluorenyl)fluorene and the Radical Therefrom. The method of Bachman was used to prepare 9-phenylfluorenyl bromide.[12] A solution of 3.21 g (10 mmol) of the above bromide and 2.45 g (10 mmol) of 9-bromo-fluorene in 150 mL of benzene was added dropwise to 5 mL of mercury while mechanically stirring the reaction. After being stirred overnight, the mixture was filtered through Celite. The inorganic material was washed with additional benzene which was filtered and combined with the reaction product. TLC (20% methylene dichloride in petroleum ether) indicated three major products. The residue obtained upon rotary evaporation of the benzene was taken up in 100 mL of chloroform on a steam cone. Hexane (60 mL) was added to the boiling mixture, maintaining the total volume at ca. 100 mL. When the mixture cooled, solids in two well-defined crystal habits were deposited. After filtration, the mixed crystals were partially separated by boiling with 40 mL of chloroform which retained a considerable amount of the more soluble material upon cooling. The solution was filtered and concentrated to near saturation. Chromatography (2 × 40 cm column) over silica gel with 10% chloroform in petroleum ether gave a series of fractions monitored by TLC and ^{13}C NMR. In this fashion, a fraction (0.46 g) was obtained with the ^{13}C NMR of a pure substance of the desired structure. It was recrystallized from 1:1 chloroform–hexane: yield 0.29 g; mp 275–278 °C; ^{13}C NMR δ 54.1, 62.2, 119.1, 119.7, 125.2, 126.0, 126.8, 127.1, 127.3, 127.5, 128.6, 140.9, 142.0, 143.6, 143.9, 147.9; HRMS, *m/e* 406.170 679, calcd for $C_{32}H_{22}$ 406.172 128.
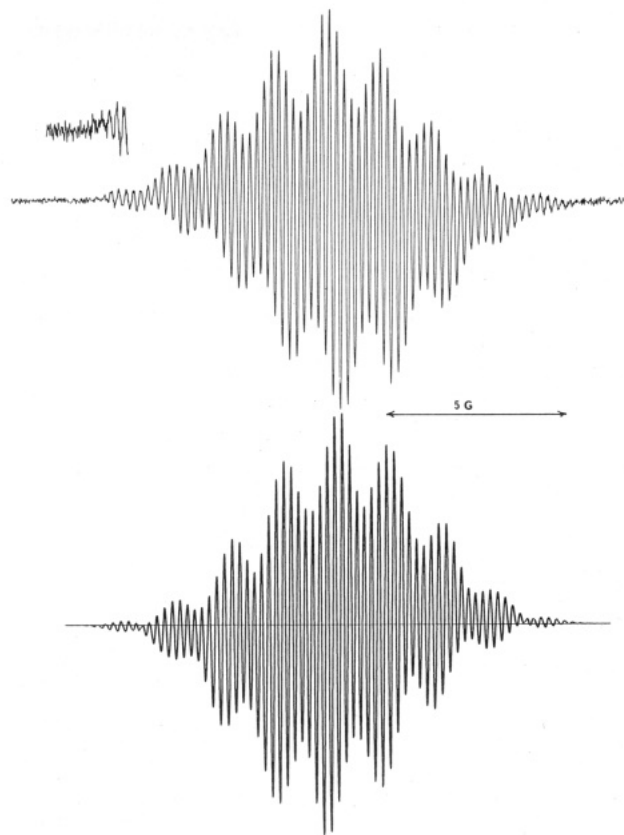
This material in THF was converted to the anion with *n*-butyllithium as above and reacted with 2,3-dibromo-2,3-dimethylbutane, yielding an ESR signal exactly as in Figure 1 (top).

Preparation of the Pentaarylethanes. Pentaphenylethane was prepared by the method of Bachman[13] in which trityl bromide and benzhydryl bromide are stirred with mercury.

Bis(4-*tert*-butylphenyl)methyl bromide was prepared by refluxing 3.75 g (13 mmol) of the corresponding carbinol[14] with 10 mL of acetyl bromide in 50 mL of heptane for 2 h. The hot solution was filtered and concentrated to ca. 40 mL by using a stream of nitrogen. When the mixture was cooled, crystals deposited which were collected (petroleum ether wash) and dried in vacuuo: 3.66 g (78%); mp 136–137 °C; ^{13}C NMR δ 31.3, 34.6, 55.7, 125.5, 128.2, 138.3, 151.1; HRMS, *m/e* 343.104 730, calcd for $C_{20}H_{24}Br$ ($M^+ - CH_3$) 343.106 116.

A solution of tris(4-*tert*-butylphenyl)methyl bromide (2.49 g, 5 mmol) in 100 mL of degased benzene was stirred rapidly with 5 mL of mercury while a solution of benzhydryl bromide (1.22 g, 5 mmol) in 200 mL of benzene was added slowly over a 2-h period. After stirring overnight, the mixture was allowed to settle, and the clear portion was decanted and filtered through Celite. The inorganic salts were washed with portions (3 × 50 mL) of benzene each of which was filtered and added to the original solution. Evaporation to dryness gave 2.74 g of crude product. This was taken up in a minimum of hot chloroform (ca. 40 mL). To this was added 40 mL of hot hexane. Upon cooling 0.81 g (28%) of 1,1-diphenyl-2,2,2-tris(4-*tert*-butylphenyl)ethane deposited: mp 185–202 °C dec (vacuum); ^{13}C NMR δ 31.4, 34.3, 60.6, 61.6, 123.7, 125.7, 127.2, 131.4, 131.6, 143.3, 143.7, 148.5. Anal. ($C_{44}H_{50}$) C, H.

In a similar fashion, 1.63 g (5 mmol) of trityl bromide and 1.78 g (5 mmol) of bis(4-*tert*-butylphenyl)methyl bromide were coupled yielding 2.51 g of crude product. Chromatography through a silica

(12) Bachman, W. E. *J. Am. Chem. Soc.* **1930**, *52*, 3287.
(13) Bachman, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 2135.
(14) Balfe, M. P.; Kenyon, J.; Thain, E. M. *J. Chem. Soc.* **1952**, 790.

Figure 2. ESR spectrum of pentakis(4-*tert*-butylphenyl)ethyl (top) and the simulation using the parameters in Table II.

gel column (development by 8% chloroform in petroleum ether) gave 0.6 g of pure material/g of crude material applied. Crystallization was from chloroform–hexane: mp 175–187 °C dec (vacuum); ^{13}C NMR δ 31.3, 34.2, 58.3, 63.0, 124.2, 125.7, 126.9, 131.0, 131.8, 140.0, 146.1, 148.5. Anal. ($C_{40}H_{42}$) C, N.

By the same procedure tris(4-*tert*-butylphenyl)methyl bromide was coupled with bis(4-*tert*-butylphenyl)methyl bromide yielding pentakis(4-*tert*-butylphenyl)ethane: mp 205–233 °C dec (vacuum); ^{13}C NMR δ 31.4, 34.2, 59.8, 61.7, 123.6, 124.0, 131.1, 131.4, 140.5, 143.6, 148.1, 148.3. Anal. ($C_{52}H_{66}$) C, H.

Application of the Ziegler Procedure To Form Pentaphenylethyls. Attempts to prepare pentaarylethane anions by treatment with *n*-butyl or *tert*-butyllithium solely in THF indicated the materially lessened acidic character of the ethane hydrogens in these compounds compared to their fluorene counterparts. As a result a variety of mixed solvents including THF, diethyl ether, dimethyl sulfoxide (Me_2SO), and hexamethylphosphoramide (HMPT) were tried. Successful combinations are indicated below.

A solution of 4 mg of 1,1-bis(4-*tert*-butylphenyl)-2,2,2-triphenylethane in a mixed solvent composed of THF (30 mL), HMPT (1.5 mL), and 2 drops of Me_2SO was reacted with *n*-butyllithium (0.7 mL, 1.5 M solution in hexane). The solution rapidly became bright red. Approximately 2 mL of this solution was added to ca. 10 mg of 2,3-dibromo-2,3-dimethylbutane in an ESR tube. Initially a weak ESR was observed which resembled one of the artifactual spectra (triplet of pentuplets) described below. When the sample was allowed to stand overnight, the weak signal was replaced with the spectrum identical with that shown in Figure 2. Spectral analysis and computer simulation gave hyperfine coupling constants as follows: 1.69 (4 H), 1.29 (4 H), and 0.22 g (18 H), and *g* = 2.0083. The simulation resembled Figure 2 (bottom) in all details.

In a similar fashion, the pentakis(4-*tert*-butylphenyl)ethyl radical was generated from its ethane. The spectrum is shown in Figure 2 (top), and spectrum analysis plus computer simulation (Figure 2, bottom) gave the following coupling constants: 1.69 (4 H), 1.29 (4 H), and 0.22 g (18 H), and *g* = 2.0084.

It should be noted that the ESR spectrum shown in Figure 2 is quite different from that of the tris(4-*tert*-butylphenyl)methyl
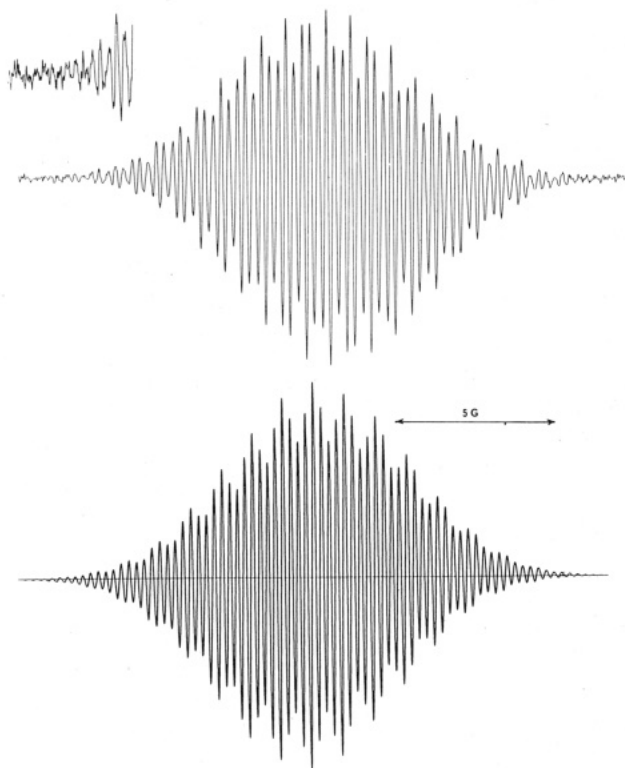
Figure 3. ESR spectrum of the presumed pentaphenylethyl radical and the simulation using the parameters in Table II.

radical which was generated both in the computer from literature parameters and by shaking the bromide with mercury. This point is made because cleavage of pentaarylethyl anions to triarylmethyl anions was found to occur in several cases now to be mentioned.

Two attempts were made to prepare the 1,1-diphenyl-2,2,2-tris(4-*tert*-butylphenyl)ethyl by the procedure above. When *n*-butyllithium was added to the ethane in the mixed solvent, a red color was formed which deepened with time. Addition of this solution after 2 h to the dibromide in the ESR tube produced an ESR identical with an authentic spectrum of tris(4-*tert*-butylphenyl)methyl.

A number of attempts to prepare pentaphenylethyl were conducted under a wide range of solvents, bases, and times. It was quickly realized that when any significant concentration of the anion was prepared and allowed to stand, a cleavage to the trityl anion occurred, as the ESR spectrum of the trityl radical was often our only observation. On other occasions a broad 15-line spectrum was observed as a triplet of pentuplets. A few times a quartet of pentuplets was found. These latter two spectra could not be generated by treating *n*-butyllithium with the dibromide in any combination of THF, HMPT, or Me₂SO. After approximately two dozen attempts, two successive and independent preparations produced a new radical species as now described.

A Schlenk tube containing 6 mg (0.15 mmol) of pentaphenylethane in 30 mL of THF was put through a freeze, pump, thaw cycle and filled with nitrogen. HMPT (1 mL) was added followed by 1 mL of 1.48 M *n*-butyllithium in hexane. A burgundy solution was produced. After 1 h ca. 2 mL of the solution was added to 10 mg of 2,3-dibromo-2,3-dimethylbutane in an ESR tube. Over a period of 22 h the light yellow solution in the region of the dibromide moved up to the midpoint of the tube. The tube was positioned so that the burgundy/yellow interface was just above the cavity (yellow solution in the cavity), and a clear ESR spectrum of the trityl radical was obtained. When the interface was placed so that the burgundy solution was in the cavity, the spectrum shown in Figure 3 (top) was obtained.

Reactions of Trityl Radical with Aryl Carbenes. A solution of trityl radical in THF was prepared by shaking 0.81 g (2.5 mmol) of trityl bromide in 100 mL of THF with ca. 3 mL of mercury. The solution containing the radical was decanted from the inorganic residue into a quartz flask containing 0.5 g (2.6 mmol) of 9-diazofluorene[15] all under nitrogen. Subsequent examination

of similar solutions indicted that in the absence of light this mixture was indefinitely stable.

The flask was irradiated with a low-pressure mercury lamp for 30 min. Nitrogen evolution was evident. Examination of a sample of the reaction mixture produced an ESR very much like that in Figure 1 (middle), indicating a mixture of trityl and 9-tritylfluorenyl radicals. A similar spectrum could be generated by mixing solutions of each of these radicals produced independently. An entirely similar mixed spectrum could be generated in situ by irradiation of the initial reaction mixture with either the mercury lamp or a projector lamp directly in the ESR tube.

In a repeat of the above experiment the reaction mixture was irradiated for 1 h with a 300-W projector. The solvent was evaporated, and the residue was subjected to column chromatography over silica gel with 10% chloroform in petroleum ether for development. A fraction approximating 25% of the residue was identified by proton and ^{13}C NMR as 9-tritylfluorene.

Several attempts were made to prepare pentaphenylethyl by the analogous procedure of photolyzing diphenyldiazomethane in the presence of trityl radical. While nitrogen evolution was observed, the signal from the trityl radical slowly disappeared.

Results and Discussion

Multiple repetitions of the two preparative pathways of Schlenk and Mark[1] failed to produce any ESR-active species other than the trityl radical. Examination of the product mixture formed when tritylsodium was reacted with dichlorodiphenylmethane indicated a variety attributable to the formation and subsequent reaction of trityl and chlorodiphenylmethyl radicals. The formation of a small amount of pentaphenylethane, however, suggests that if pentaphenylethyl was formed, it did not persist under the reaction conditions. Other pathways can be written to account for the ethane formation. As a consequence of these results we turned our attention toward the preparation of the 9-tritylfluorenyl radical.

Treatment of 9,9-dichlorofluorene with tritylsodium produces the reported color change and the precipitation of a purple solid. This material was found to be a complex mixture with no ESR-active component. The concurrent deposition of a brown amorphous material did provide an ESR-active material, the signal being attributable to the 9-tritylfluorenyl radical I (Figure 1, top).
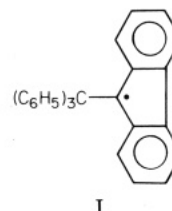
I

Spectrum analysis and simulation for I gave the parameters in Table I. The assumption was made that the hyperfine couplings to positions 1 and 3 and to 2 and 4 are equal, respectively. For comparison the published values for the fluorenyl and the 9,9'-bifluorenyl-9-yl radicals are included. In contrast to the original claim for pentaphenylethyl,[1] it thus appears that 9-tritylfluorenyl[2] is the first solid organic free radical of a persistent nature to be reported. That it was not the reported purple solid is inconsequential. It subsequently became a routine matter to generate solutions of the radical by converting 9-tritylfluorene to the anion with *n*-butyllithium and oxidizing this to the radical with 2,3-dibromo-2,3-dimethylbutane (the method of Ziegler[9]).

The line widths shown in Figure 1 (top) at half-height are ca. 0.3 G. In contrast, line widths for trityl are routinely

(15) Baltzy, R.; Mehta, N.; Russel, P. B.; Brooks, R. E.; Grivsky, E. M.; Steinberg, A. M. *J. Org. Chem.* **1961**, *26*, 3669.

Table I. ESR Values for the
9-Substituted Fluorenyl Radicals

expt	name	position	a_H, G
1	9-trityl[a]	1,3	3.58
		2,4	0.78
2	9-tris(penta-deuteriophenyl)-methyl[b]	1	3.63
		2	0.93
		3	3.45
		4	0.69
3	9-H, i.e., fluorenyl[c]	1	3.98
		2	0.91
		3	3.76
		4	0.64
4	9,9'-bifluorenyl-9-yl[d]	1	3.85
		2	0.76
		3	3.50
		4	0.76

[a] Assignments made by analogy with fluorenyl. Identical ESR values were found for 9-[tris(4-*tert*-butylphenyl)-methyl]fluorenyl and 9-(9-phenylfluorenyl)fluorenyl.
[b] Values established for the resolved spectrum before alteration to the spectrum in expt 1. [c] Reference 17.
[d] Neugebauer, F. A.; Groh, W. R. *Tetrahedron Lett.* 1973, *12*, 1005.

0.1 G or less. The observed broadening might be due to a variety of sources such as electron exchange or unresolved couplings. The latter might arise from electron delocalization into the triphenylmethyl moiety or the failure of the assumption of equality of couplings as noted above.

Several approaches to answer this question were essayed. The following radicals were generated by the Ziegler method from their precursor hydrocarbons: 9-tris(perdeuteriophenyl)methylfluorene, 9-tris(4-*tert*-butylphenyl)methylfluorene and 9-(9'-phenylfluorenyl)fluorene. With one exception the ESR spectra for these radicals were identical with that for 9-tritylfluorenyl, thus eliminating electron delocalization into the 9-substituent as a line-broadening mechanism. The exception was the spectrum generated from one sample of the deuterated tritylfluorene. This sample gave a much better resolved spectrum (line widths of ca. 0.1 G) and, consequently, a more accurate set of hyperfine couplings which are given in Table I and assigned by analogy with the published assignments for fluorenyl. About 30 min after generation, the radical signal decayed to the usual 25-line spectrum. This observation remains an enigma with the one possible clue that the hydrocarbon sample was found to be slightly wet with ethanol from crystallization.

While 9-tritylfluorenyl, either solid or in solution, has a long lifetime in the absence of oxygen and light, an unusual series of alterations were observed while attempting to work with solutions in the ESR tube. Generated by either of the two methods above, solutions of the radical in ether or THF upon dilution begin to break up into a more complex pattern of lines as shown in Figure 1. Initially designed to rule on exchange processes, this puzzling behavior became clear only with the realization that the trityl radical (Figure 1, bottom) was being formed at high dilution, mixtures of trityl and 9-tritylfluorenyl being observed at intermediate dilutions. When carefully deoxygenated solvents were employed, the initial signal showed only a decay in the signal-to-noise ratio, confirming that the sequence displayed in Figure 1 was due to traces of oxygen in the diluting solvent. The process was confirmed by the isolation of fluorenone from the treatment of I with oxygen (eq 1). The decay of peroxyorgano radicals to ketones is a well-known process.

The solutions of I in ether or THF were stable to fluorescent room light. Irradiation of the ESR tube with a low-powered UV light caused a rapid change in the ESR

$$I + O_2 \longrightarrow (C_6H_5)_3C \cdots \xrightarrow[\text{steps}]{\text{several}} (C_6H_5)_3C\cdot + \tag{1}$$
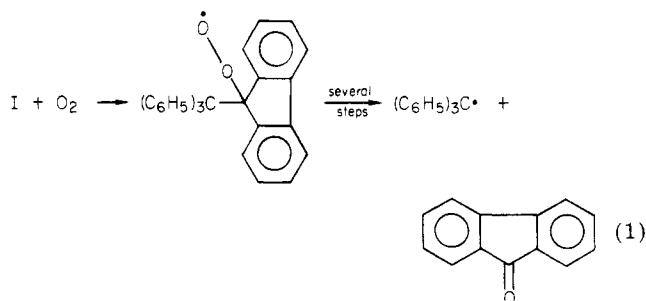
signal that mimicked the sequence shown in Figure 1, the logical inference being that I was undergoing photolytic cleavage to trityl radical and the carbene fluorenylidene (eq 2). In view of the difficulties of product identification

$$I \xrightarrow{h\nu} (C_6H_5)_3C\cdot + \tag{2}$$
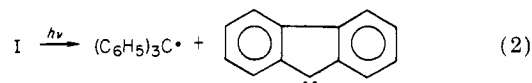
from such dilute radical solutions, the correctness of the above supposition was established by proceeding with the reverse reaction. Solutions of trityl and diazofluorene were stable for up to several days in the absence of light. When irradiated with either UV or visible light nitrogen evolution occurred, and the ESR spectrum changed from that of pure trityl to that shown in Figure 1 (middle), indicating an approximate 1:1 mixture of trityl with I. This composition maintained itself until all of the diazofluorene was consumed. In view of the current confusion regarding the exact sequence of events in the photolysis of diazofluorene,[16] it is pointless to argue the electronic state of the carbene before reaction. Preparative-scale photolysis of the trityl–diazofluorene mixture produced 9-tritylfluorene in ca.. 20% yield.

Simple HMO considerations suggest that pentaphenylethane is less acidic than 9-tritylfluorene and that pentaphenylethyl is the less stable radical. Attempts to generate the anion in THF with *n*-butyl- or *tert*-butyllithium supported this expectation. A variety of ploys were attempted before the addition of HMPT or HMPT plus a small amount of Me$_2$SO was found to produce deep burgundy solutions from the ethane in THF plus the alkyllithium. Complete conversion to the pentaarylethyl anions was probably never achieved. After 1 h, deuteration indicated a maximum of 16% proton replacement on the ethane. After 24 h, complete cleavage to form the triphenylmethyl anion had occurred. Attempts to generate the pentaphenylethyl radical from these solutions were largely negative (see below, however). Depending on the history of the reagents and reaction time, one saw the trityl ESR or a simple 15- or 20-line spectrum which presumably were artifacts resulting from impurities or decompositions.

However, when the same procedure was carried out with 1,1-bis(4-*tert*-butylphenyl)-2,2,2-triphenylethane and with pentakis(4-*tert*-butylphenyl)ethane, respectively, the burgandy solutions gave the rich ESR pattern shown in Figure 2. Spectral analysis and computer simulation gave the spectrum shown in Figure 2 (bottom), a very close replication of the experimental spectra. The ESR parameters are given in Table II as are comparison values for the pertinent couplings of 1,1-diphenylmethyl, 1,1,2,2-tetraphenylethyl, and tris(4-*tert*-butylphenyl)methyl taken from the literature. As seen, the value for the coupling at the ortho position for our two *p*-*tert*-butylphenyl analogues

(16) (a) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* 1982, *104*, 6813. (b) Brauer, B. E.; Grasse, P. B.; Kaufman, K. J.; Schuster, G. B. *Ibid.* 1982, *104*, 6814.

Table II.   ESR Values for the Pentaphenylethyls
and Related Radicals

expt	name	position	a_H, G
1	pentakis(4-*tert*-	2,6	1.69
	butylphenyl)ethyl	3,5	1.29
		CH$_3$	0.22
2	1,1-bis(4-*tert*-	2,6	1.69
	butylphenyl)-2,2,2-	3,5	1.29
	triphenylethyl	CH$_3$	0.22
3	pentaphenylethyl	2,6 (10H)	0.98
		3,5 (10H)	0.26
		4 (5H)	1.92
4	diphenylmethyl[a]	2,6	3.7
		3,5	1.35
		4	4.2
5	1,1,2,2-tetra-	2,4,6	3.02
	phenylethyl[b]	3,5	1.24
6	tris(4-*tert*-	2,6	2.57
	butylphenyl)-	3,5	0.09
	methyl[c]	CH$_3$	0.09

[a] Bassindale, A. R.; Hudson, A.; Bowles, A. J.; Jackson, R. A. *Tetrahedron Lett.* **1973**, *34*, 3185.   [b] Table I, footnote *d*.   [c] van der Hart, W. J. *Mol. Phys.* **1969**, *19*, 75.

is smaller than for the same positions in diphenylmethyl or for 1,1,2,2-tetraphenylethyl. On the basis of arguments already made in the literature, one can say that there is less delocalization and more twist away from planarity in our radicals.[17] This conclusion is supported by the quoted values for tris(4-*tert*-butylphenyl)methyl.

Attempts to prepare 1,1-diphenyl-2,2,2-tris(4-*tert*-butylphenyl)ethyl from ethane failed just as those earlier for pentaphenylethyl had. However, after the successes described above we returned to pentaphenylethyl and on two separate occasions with different reagents prepared the radical shown in Figure 3. As described in the Experimental Section this radical exists in that portion of the ESR tube just above the interface formed by the reacting dibromide and the anion solution. The region below had the yellow color and ESR spectrum of the trityl radical.

Attempts to simulate the experimental spectrum were made by considering ten-spin interactions as in diphenylmethyl. No combination over a wide range of values was even close to the experimental spectrum. Furthermore, there are far too many lines to accommodate a stable phenyl-bridged species. The simulation shown was derived on the assumption of 25 proton spin interactions (ten ortho, ten meta, and five para). The values of best fit are given in Table II. While there is a good similarity between

the experimental and simulated spectra, changes of as little as 0.1 G produce major changes in appearance because of the complex pattern of overlapping lines. The exercise had reached a point of diminishing returns.

The implications of such complete delocalization are the rapid equilibration of the phenyls in pentaphenylethyl (eq 3). The logical test of such a postulation would be observations at lower temperatures. Unfortunately, the geometry of our low-temperature cavity prevented the insertion of the ESR tube to the proper depth.
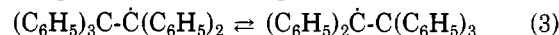
$$(C_6H_5)_3C\text{-}\dot{C}(C_6H_5)_2 \rightleftharpoons (C_6H_5)_2\dot{C}\text{-}C(C_6H_5)_3 \qquad (3)$$

The great difficulty in forming the pentaphenylethyl radical in a reproducible fashion suggests the advancement of the hypothesis of rapid phenyl equilibration on a tentative basis only. The *tert*-butyl substituents are known to stabilize benzyl-type radicals. The photobromination of *p*-*tert*-butyltoluene is nearly twice as fast as that of toluene itself.[18] Furthermore, Ruchart and co-workers[19] have found *p*-tolyl to have a lower radical migratory aptitude than phenyl. Presumably *tert*-butylphenyl would be lower than phenyl also. Consequently, the apparent difference between the two types of pentaarylethyls may be quite real.

(17) Atto, A.; Hudson, A.; Jackson, R. A.; Simmons, N. P. C. *J. Chem. Phys. Lett.* **1975**, *33*, 477.

(18) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142.
(19) Ruchardt, C.; Hecht, R. *Ber.* **1965**, *98*, 2471.