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THE QUESTION OF PENTAPHENYLETHYL: AN AM1 STUDY

WILLIAM B. SMITH

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

Semi-empirical AM1 theoretical calculations were carried out on the pentaphenylethyl and 9-tritylfluorenyl free radicals, related radicals and their precursor hydrocarbons. Previous reports of the preparation of the former radical have been questioned, although the existence of the second is on secure ground. Based on simple energy considerations, it is concluded that pentaphenylethyl should be as readily prepared. However, the acidity of the precursor hydrocarbon is considerably less than that of 9-tritylfluorene, and possible radical decomposition via dissociation to triphenylmethyl and diphenylcarbene is calculated to be more facile than the corresponding decomposition of 9-tritylfluorenyl. A previous postulation of a rapid phenyl equilibration of the pentaphenylethyl radical is shown to be untenable.

INTRODUCTION

The pentaphenylethyl[1a] (**I**) and 9-tritylfluorenyl[1b] (**II**) free radicals were first reported as isolable solid free radicals by Schlenk and Mark in 1922. The initial preparation of **I** was subsequently questioned by Dorfman,[2] who failed in attempts to prepare the radical. Several years ago, attempts were made to characterize both of these pentaarylethyl radicals by means of ESR spectroscopy.[3] Neither of the preparations of Schlenk and Mark produced a radical attributable to pentaphenylethyl. The reaction of tritylsodium with the dichlorofluorene did give the 9-tritylfluorenyl radical, not as the initially reported purple solid, but rather as the brown matrix in which a non-ESR-active purple solid was deposited. A more reliable preparation of 9-tritylfluorenyl was via the anion of the corresponding hydrocarbon and oxidation with dibromotetramethylethane (the Ziegler method).[4] Application of the Ziegler method with pentaphenylethane under a wide variety of conditions usually gave the ESR spectrum of the trityl radical. On two occasions a much more complex spectrum was observed which required the postulation of a rapidly equilibrating pentaphenylethyl system for explanation. In contrast, the radicals generated from 1,1-bis(4-*tert*-butylphenyl)-2,2,2-triphenylethane and pentakis(4-*tert*-butylphenyl)ethane were both readily prepared and characterized by ESR spectroscopy as substituted benzhydryl radical analogs. The ESR spectrum of the 9-tritylfluorenyl indicated no delocalization into the trityl group. Dilution of the initial preparation produced a complex series of spectral changes yielding the ESR spectrum of the trityl radical. Fluorenone was isolated in one case from the reaction mixture. It was presumed that a decomposition of **II** into trityl and fluorenylidene was occurring. The photolysis of diazofluorene in the presence of trityl radical was demonstrated to form 9-tritylfluorenyl.

Over the years, many attempts at preparing substituted derivatives of pentaphenylethane have been reported.[5] Invariably, these have been shown to lead to products of attack on the aromatic rings or to cleavage of the central carbon–carbon bond. The preparation of pentaphenylethyl may pose some inherently more difficult steps compared with the preparation of 9-tritylfluorenyl, or possibly **I** may possess inherently greater chemical reactivity than **II**.

Powerful tools for theoretical calculations are now commonly available, and it seemed reasonable to turn to these methods in searching for answers to the questions above. Given the size of these molecules, *ab initio* calculations were judged impractical, and semi-empirical methods were chosen as the most reasonable line of attack.

COMPUTATIONAL METHODS

Heats of formation of arylalkanes and their corresponding radicals were calculated by MOPAC version 6 using the AM1 Hamiltonian.[6,7] The radicals and carbenes were calculated by the half-electron method of Dewar *et al.*[8] These results are given in Table 1. The choice of the AM1 vs PM3[9] Hamiltonian was dictated

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by the fact that when applied to six alkyl free radicals for which experimental heats of formation are available, AM1 gave an average deviation of ±6·0 kcal mol^{-1} vs ±7·4 kcal mol^{-1} for PM3 (1 kcal = 4·184 kJ). Further, Lluch *et al.*[10] have provided convincing arguments that the RHF AM1 half-electron method provides meaningful results in free radical calculations. The AM1 results for toluene, benzyl radical and the singlet and triplet states of diphenylcarbene and fluorenylidene have been published previously,[11] and the results in Table 1 are in excellent agreement with these values.

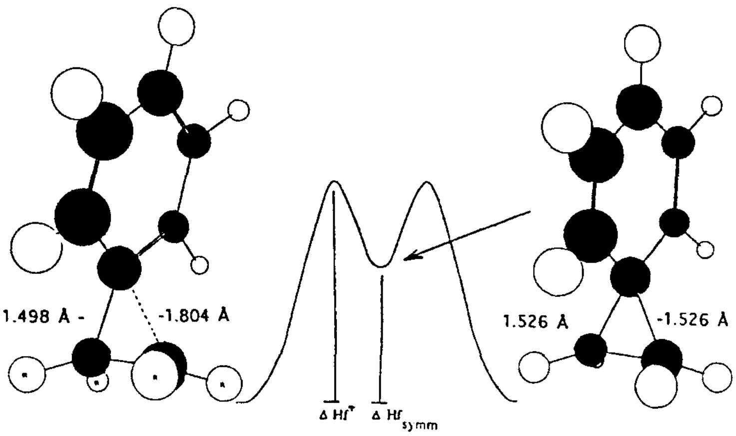
The reaction pathway for phenyl migration in the 2-phenylethyl and pentaphenylethyl radicals was explored by saddle calculations using the method of Dewar *et al.*[12] The calculated transition structures were refined by the eigenvector following routine of Baker.[13] A force calculation on the transition structure for the 2-phenylethyl radical gave one negative root for the force matrix and one negative frequency. As a confirmation of this result, the migration of phenyl in the 2-phenylethyl radical was carried out by a linear synchronous transit[14] at the level of UMP2/6–31G* using Gaussian 92 for Windows.[15] Again, the transition structure was refined by the optimization routine embedded in the program. The transition structures from these studies were all so closely related that only the geometry for the 2-phenylethyl radical is shown in Figure 1 along with the energies of interest. A referee suggested that the semi-empirical study might profit by using the MNDO Hamiltonian since this method gives more accurate results for three-membered rings than the AM1 Hamiltonian. In fact, the enthalpy of activation for the phenyl migration was reduced by only 1·5 kcal mol^{-1}.

RESULTS AND DISCUSSION

The heats of formation for a series of arylalkyl radicals and their precursor hydrocarbons are given in Table 1, as are the bond dissociation energies (BDE). These results meet the intuitively reasonable expectation that increasing phenyl substitution provides increasing radical stabilization.

According to the data in Table 1, pentaphenylethyl is stabilized by about 8 kcal mol^{-1} over the 9-tritylfluorenyl radical when referred to their hydrocarbon precursors. In a similar fashion, diphenylmethyl is thermochemically more stable than fluorenyl. On the basis of radical energetics alone there would appear to be no reason for the preparation of pentaphenylethyl to have proven so elusive.

In contrast to the preparation of pentaphenylethyl, both 1,1-bis(4-*tert*-butylphenyl)-2,2,2-triphenylethyl and pentakis(4-*tert*-butylphenyl)ethyl were readily prepared.[3] Pearson and Martin[15] had reported the photobromination of p-*tert*-butyltoluene to be twice as fast as toluent itself and suggested that the *tert*-butyl group helped stabilize the benzyl radical. However, calculations on the 1,1-bis(4-*tert*-butylphenyl)-2,2,2-triphenylethyl radical and its hydrocarbon precursor (Table 1) indicate no enhanced stabilization effect.



R	ΔHF‡	ΔHF$_{symm}$
-H	33.28	23.25
-Ph	35.51	24.89

Figure 1. Energy plot for the migration of phenyl for the 2-phenylethyl radical (R = H) and pentaphenylethyl (R = Ph). Heats of formation are in kcal mol^{-1}

Table 1. Heats of formation (kcal mol^{-1}) of various polyphenylated species

Species	ΔH_f	BDE[a]
$PhCH_3$	14·42	—
$PhCH_2^{\cdot}$	52·03[b]	37·61
Ph_2CH_2	42·17	—
$Ph_2CH^{\cdot}$	73·46	31·29
$Ph_2C^{\cdot\cdot}$		
Singlet	131·56	—
Triplet	119·19	—
Bis(4-*tert*-butylphenyl)methane	5·26	—
Bis(4-*tert*-butylphenyl)methyl	36·48	31·22
Ph_3CH	74·90	—
$Ph_3C^{\cdot}$	100·24	25·34
Ph_3CCHPh_2	155·86	—
$Ph_3CC^{\cdot}Ph_2$	177·05	21·19
$Ph_3CCH(C_6H_4C_4H_9)_2$	119·61	—
$Ph_3CC^{\cdot}(C_6H_4C_4H_9)_2$	140·87	21·26
Fluorene	54·36	—
Fluorenyl	89·15	34·79
Fluorenylidene		
Singlet	153·51	—
Triplet	153·07	—
9-Tritylfluorene	157·24	—
9-Tritylfluorenyl	186·80	29·56
Diphenyl-(9′-phenylfluorenyl)methyl	179·32	22·08

[a] The bond dissociation energy (BDE) equals the difference in energy (kcal mol^{-1}) of the radical and its precursor hydrocarbon.
[b] Experimental value 47·8 kcal mol^{-1} from Ref. 21.

Two alternative possibilities offer themselves as explanations for the failure to generate pentaphenylethyl. First, in Ziegler and Schell's procedure[4] the amount of radical produced will depend on the ease of anion production and the stability of the anion prior to oxidation. A comparison of pKa versus the energy differences[16] between anion and hydrocarbon ($\Delta HF_{(anion\text{-}RH)}$) for the series toluene, diphenylmethane and triphenylmethane allows an estimation of the pKa differences between 9-tritylfluorene and pentaphenylethane with the former being more acidic by ca. 10^3. When solutions of pentaphenylethane were allowed to stand with *tert*-butyl lithium and then quenched with D_2O only small amounts of deuterium incorporation were noted implying a very small concentration of the pentaphenylethyl anion. Furthermore, Bachman and Osborn[18] had established that pentaphenylethane was readily cleaved to smaller fragments by sodium-potassium alloy.

Another possible explanation for the failure to detect pentaphenylethyl is the rapid decomposition of the radical once it has been formed. Photochemical halogenation of pentaphenylethane with either chlorine or bromine leads only to cleavage products.[5,18] Furthermore, 9-tritylfluorenyl was found to decompose with traces of oxygen either via a peroxide intermediate or by a prior dissociation to triphenylmethyl and fluorenylidene.[3] The latter process was shown to be a distinct possibility by virtue ofthe observation that triphenylmethyl and diazofluorene formed the radical upon photolysis. The heats of formation both triplet and singlet diphenylcarbene and fluorenylidene are given in Table 1. These values are in excellent agreement with the previously published values of Dannenberg *et al.*[11] Comparison of the lower energies of the triplet carbenes indicates the dissociation of pentaphenylethyl is *ca* 24 kcal mol^{-1} less endothermic than that of 9-tritylfluorenyl. One may assume that this difference is reflected to some extent in the activation energies for the dissociation process (Hammond's postulate). Hence it is possible that pentaphenylethyl is considerably more sensitive to photochemical or thermal dissociation than the 9-tritylfluorenyl radical.

A final point may be raised in consideration of the pentaphenylethyl radical. The structure of the radical is amenable to dimerization in the sense analogous to the Jacobson dimer[20] now accepted as the triphenylmethyl dimer. This cannot be the case when the *para* positions are blocked by *tert*-butyl groups. There may be not enough radical present in the pentaphenylethyl case to allow detection.

Lastly, the question of a rapidly equilibrating phenyl radical system is addressed. A careful search of the literature failed to reveal any calculations of energy barriers or intermediates for the phenyl migration process. The energy surface for phenyl migration was explored following a saddle calculation. For both the 2-phenylethyl radical and the pentaphenylethyl radical symmetrical intermediates were found which were formed via unsymmetrically bridged transition structures (Figure 1). The relevant energies are also given there. The geometries for the two transitions structures were essentially the same. The same statement applies to the result of a linear strategic transit search carried out at the UMP2/6–31G* level on the 2-phenylethyl system. The calculated barriers were of sufficient height to preclude the earlier postulation of a rapid phenyl flipping process.[3] This contention is supported by the fact that while the phenyl migration in the 9-tritylfluorenyl system is exergonic, no evidence of such a migration was observed in the study of 9-tritylfluorenyl.

The following conclusions follow from this study. Based on energy considerations, there is no obvious reason why pentaphenylethyl cannot be prepared. However, rapid phenyl group equilibration is not a reasonable mechanism for radical stabilization. It may be presumed the radical observed in our earlier study[3] was some artifact of the preparation. The addition of *p*-*tert*-butyl groups to the conjugated phenyls enhances the stability of these radicals only in the sense that it inhibits dimerization or other reactions involving these *para* positions. At this time, the best evidence is that an unsubstituted pentaphenylethyl radical has *not* been prepared.

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