

MOLECULAR ORBITAL CORRELATION OF ARYLMETHYL CHLORIDE ATOM ABSTRACTION BY STANNYL RADICALS *

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Summary

A series of monochloromethylated polycyclic benzenoid hydrocarbons have been treated with triphenyltin hydride and AIBN initiator at 70°C. Under these conditions the only observable reaction is reduction of the starting materials to methylarenes. A significant range of relative rates (factor of 40) has been found among the compounds studied. All relative rates yielded an excellent correlation when plotted against PPP-SCF calculated energy differences. The present work shows the ability of such calculations to treat processes involving nucleophilic radicals.

It is known that most linear free energy relationships, such as the Hammett equation, can relate reactivity trends to electronic changes caused by structural variation. These changes may combine inductive (and/or field) effects with conjugative and mesomeric interactions. It has been pointed out that the study of series of related unsubstituted polycyclic, benzenoid molecules rather than substituted benzenes allows for the separation of these two modes of interactions [1]. The inductive effects of such polycyclic groups should be equivalent as they are derived from alternant systems [2]. Thus, any changes in reactivity encountered among the aforementioned compounds can be traced solely to differences in abilities to conjugatively stabilize the intermediate if the usual assumption of constant entropy factors throughout the series is maintained. This should also allow for possible correlation of experimental data with calculated energy differences. This latter consideration, while frequently discussed in texts relating molecular orbital theory to organic chemistry [2-4], is not associated with a large set of different examples. Still, those investigations which have been carried out, at least for simple arylmethyl systems, have yielded

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encouraging results. Such reactions may be schematically represented by eq. 1 with the understanding that the mechanistic step need not be first order as



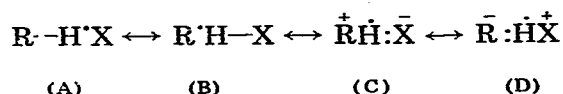
shown.

Early studies in arylmethyl reactivity dealt with the formation of ionic intermediates. The generation of the corresponding radicals was first accomplished by direct hydrogen abstraction using bromotrichloromethane (eq. 2) [5]. Similar results were later found for hydrogen abstraction using bromine atom [6] and even for the generation of arylmethyl type radicals by radical additions



to polycyclic vinylarenes [7]. An overall review of the molecular orbital correlation of these relative reactivities has also appeared [8].

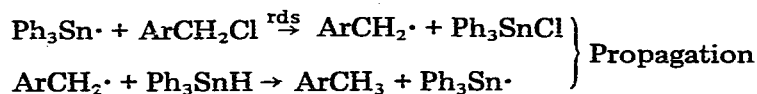
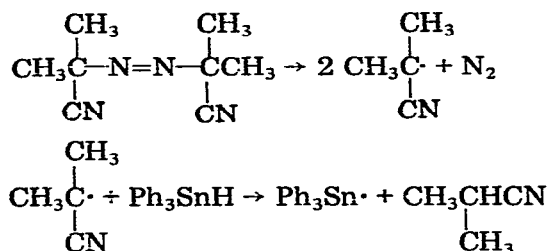
Rather good molecular orbital correlations are reported in all the above instances. All these processes involve "electrophilic" radicals. The classical representation for hydrogen abstraction by such a species includes contributions from the charge separated canonical structure, C [9]. It might logically follow



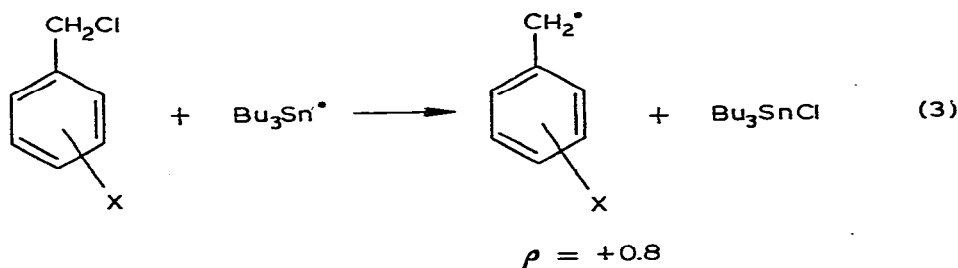
that the transition state for hydrogen abstraction by "nucleophilic" radicals would conversely resemble canonical form D and show rate acceleration by electron-withdrawing groups in R. Though a fairly large body of data seems to support this view [10], this interpretation has been challenged [11].

In order to see whether the formation of arylmethyl radicals by some reaction utilizing nucleophilic species could be treated by a molecular orbital approach, we undertook the investigation of chlorine atom abstraction from a series of arylmethyl chlorides by triphenyltin radicals. This synthetically valuable reaction is utilized in the reduction of organic halides. The reaction scheme utilizing AIBN as an initiator is shown in Scheme 1.

SCHEME 1



The reactive center of the attacking radical is on an electropositive element. Trialkyl- and triaryl-tin radicals show nucleophilic properties in many reactions [12]. Most important, in the present context, are the reductions of substituted benzyl chlorides (eq. 3) which exhibit positive rho values [13,14].



The relative rates of chlorine abstraction were determined by standard competitive techniques involving the monitoring of disappearance of starting materials. Tin radicals are known to add to alkenes [12,15] and the stannylation of reactive sites in polycyclics must be considered as a possible, though not probable, route for consumption of certain reactants [16]. A similar aromatic substitution was shown to significantly compete with hydrogen abstraction from 9-methylantracene [17]. Ring stannylation does not appear to be a significant problem. In competitive studies between the anticipated least reactive halide, benzyl chloride, and the most susceptible polycyclic, anthracene, no reaction of the hydrocarbon could be determined under conditions leading to 95% reactivity of the former compound. The ultimate products of the chloride abstraction, methylarenes, were similarly shown to be unreactive toward stannyl radicals or the precursor hydride.

The actual course of the reaction was followed by ^1H NMR spectroscopy. Signals from protons in the chloroarylmethylene groups (δ 4.8–5.5 ppm) are distinct from those of the corresponding benzyl chloride (δ 4.5 ppm). The decrease in intensity of these signals relative to that of an unreactive internal standard, diphenylmethane (δ 4.0 ppm), are used directly to evaluate the ratio of rate constants by standard formulation [18]. The signals for product arylmethanes (δ 2.3 to 3.0 ppm) could also be clearly observed. Material balance between halide consumed and hydrocarbon formed was approximately 90%. The region of the NMR spectrum beyond δ 5.0 ppm was inaccessible due to solvent (benzene) absorption. All reactions were run in replicate, under a nitrogen atmosphere at reduced pressure, at 70°C. Starting reaction mixtures were prepared in the approximate molar ratio 1/1/1/0.1/20 for arylmethyl chloride/benzyl chloride/diphenylmethane/triphenyltin hydride/AIBN initiator/benzene. Reaction times varied from 1–3 h. This corresponded to 15–70% reaction of the starting halides. Table 1 contains the relative rate data obtained in these experiments.

The logarithms of the relative rate data may be plotted against calculated energy differences between arylmethyl radicals and the corresponding arene. The calculations may be carried out at any desired level of sophistication.

Prior work in our laboratories has successfully made use of an open-shell PPP-SCF approach [5,7,8]. The results of these calculations are shown in Table

TABLE 1

RELATIVE RATES OF CHLORINE ABSTRACTION FROM HOMOCYCLIC ARYLMETHYL CHLORIDES BY THE TRIPHENYLSTANNYL RADICAL AT 70°C

System	Relative rate	ΔE (SCF) ^a	$\Delta\Delta E$ (SCF)
Phenyl	1.00	4.633	0
2-Naphtyl	1.88 ± 0.11	4.679	0.046
1-Naphtyl	3.29 ± 0.48	4.757	0.124
9-Phenanthryl	3.79 ± 0.24	4.784	0.151
1-Anthracyl	7.95 ± 0.20	4.917	0.284
9-Anthracyl ^b	38.68 ± 2.19	5.109	0.476

^a All energies given in electron volts. ^b Run vs. the 1-anthracyl system and corrected to reference compound.

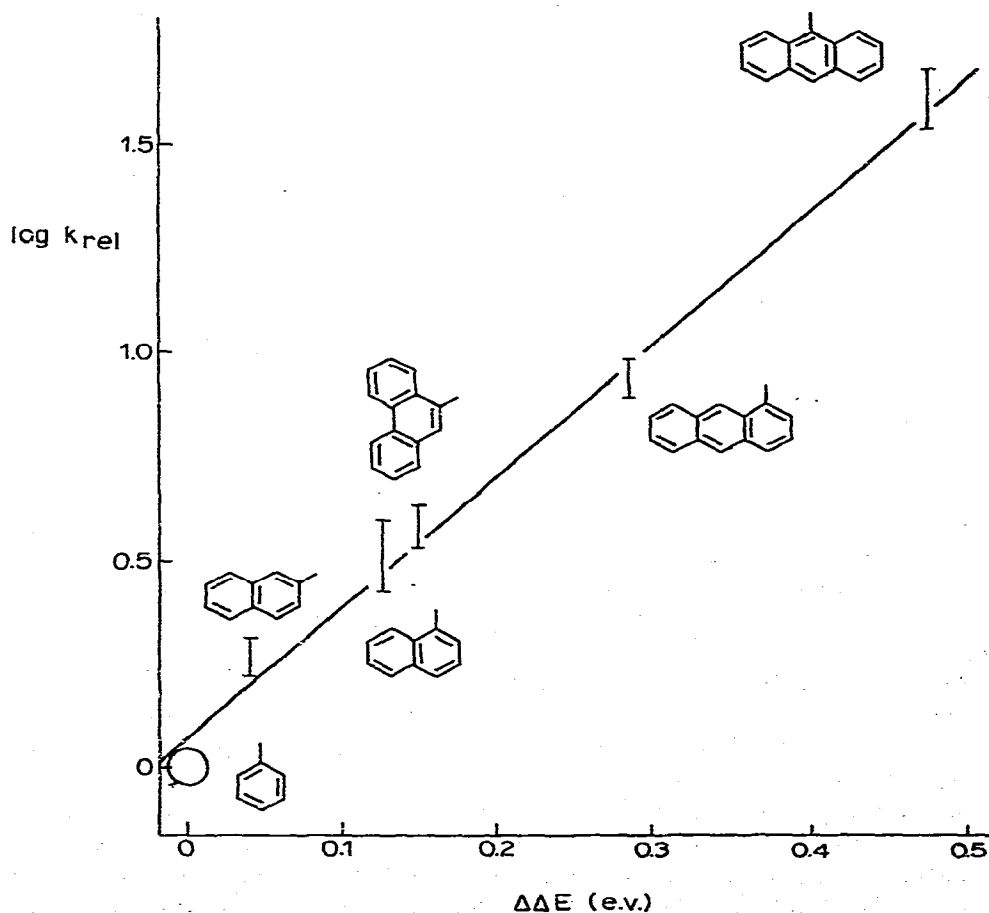


Fig. 1. Logarithms of relative rates vs. calculated relative energy difference for radical formation.

1. It should be mentioned that the present calculated energies differ slightly from those reported in the earlier citations [5]. This is due to both modest changes in empirical input parameters and to improved computer techniques which allow energy minimization with respect to bond length variation. Also given are the energies expressed relative to the benzene→benzyl system. These are found in the column labeled $\Delta\Delta E$ of Table 1. The results are illustrated in Fig. 1. An excellent correlation is obtained with a coefficient of 0.99 and a standard deviation from the regression of only 0.11.

The overall success of the correlation reaffirms the conclusion that appreciable intermediate character is developed in the transition state for halogen abstraction [19]. The possible inference that the abstractions of benzylic halogens by Group IVA radicals are independent of resonance effects [20] cannot be justified. Atom abstraction by a nucleophilic radical appears to be just as amenable to molecular orbital correlations as the previously discussed electrophilic hydrogen abstraction examples. A comparison of sensitivities toward substrate modification in the hydrogen and halogen abstraction studies shows the latter process to be 60% of the former. This might have been adduced from the earlier Hammett studies, however, temperature differences in those cases make direct comparison tenuous. It is most probable that radical character is much more developed in the transition state for hydrogen abstraction.

The general similarity in behavior between the two systems argues that the use of stannyl radicals may effectively serve as a means of generating interesting arylmethyl radicals which are not accessible by routes utilized to date. Hetero-aryl methyl radicals in particular might now be investigated.

Experimental

Materials. Triphenyltin hydride was prepared from the corresponding commercially available chloride [21]. Several of the arylmethyl chlorides were commercially available or could be prepared from easily obtained alcohols by treatment with thionyl chloride. Diphenylmethane, benzene and AIBN were commercially obtained. All materials were purified before use. Physical properties agree with those in the literature. Impurities could not be detected by gas chromatography.

Equipment: All analyses were carried out on a Standard Varian Associates HA100 instrument.

Kinetic procedure. Reaction mixtures of two arylmethyl chlorides, diphenylmethane, triphenyltin hydride, AIBN and benzene in a ratio of 1/1/1/0.1/2.0 were prepared. Samples were divided among several tubes which were degassed by repeated freeze-thaw cycles and finally sealed under a reduced pressure of nitrogen. Samples were reserved for starting material analysis. The remaining samples were allowed to react at 70°C in a constant temperature bath for periods of 1–3 h. All analyses were by NMR after small amounts of TMS were added to the samples.

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