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STUDIES ON THE POLARITY OF THE TRI-n-BUTYLTIN RADICAL

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Summary

A satisfactory Hammett correlation was observed for the radical reduction of substituted benzyl halides by tri-n-butyltin hydride. The magnitude of the positive ρ value was comparable to that observed for other nucleophilic radicals.

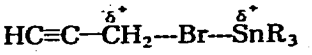
Recently, there has been renewed interest in probing polar effects in free radical reactions by use of the Hammett equation [1]. The renewed interest recieved impetus, in part, from a suggestion by Zavitsas and Pinto that the observed Hammett correlations for hydrogen abstraction at benzylic carbon did not result from charge separation at the transition state [2]. Zavitsas and Pinto suggested that substituents acted to change the carbon—hydrogen bond dissociations energies. Because electron-withdrawing substituents strengthened the benzylic C—H bonds, Zavitsas and Pinto argued that only negative ρ values could be observed. Subsequent to this suggestion, Pryor and co-workers reported a positive ρ value for abstraction of benzylic hydrogen by t-butyl radical [3]. Since then, several other examples of positive ρ values have been reported [4]. Even though some of the experimental data used to determine the positive ρ values have been questioned, the positive values appear to be valid [5]. There have been many examples of hydrogen abstraction at benzylic carbon by electrophilic radicals [2,6], but examples of abstraction by nucleophilic radicals are still scarce. In order to evaluate the spectrum of polar effects displayed in free radical reactions, more examples of nucleophilic radicals need to be studied by use of the Hammett equation or by other means.

A reaction related to hydrogen abstraction is the reduction of benzyl halides by tri-n-butyltin hydride. This reaction proceeds by a free radical mechanism [7]. Propagation steps for the reaction can be represented as shown in eq. 1 and 2.

$$RX + {}^{\cdot}SnR_3 \rightarrow R^{\cdot} + XSnR_3 \quad (1)$$

$$R^{\cdot} + HSnR_3 \rightarrow RH + {}^{\cdot}SnR_3 \quad (2)$$

It has been proposed that the organotin radical is nucleophilic [7]. For example, reduction of propargyl bromide occurs more readily than reduction of allyl bromide with organotin hydride. This is consistent with a partial polar nature of the transition state leading to the propargyl radical, I.



$$HC{\equiv}C{-}\overset{\delta^+}{C}H_2{-}{-}{-}Br{-}{-}{-}\overset{\delta^+}{Sn}R_3$$

(I)

Since the allyl group is less electronegative than the propargyl group, the latter should be more effective in stabilizing a partial negative charge [7]. Polar effects in free radical hydrostannation of unsaturated compounds are more difficult to assess. As olefinic substituents become more electron-withdrawing, a polar addition takes place [8]. Evaluation of relative rate data is made more difficult because of the reversibility of organotin radical addition to olefins [9]. Hammett correlations have been made on organotin hydride reductions of acyl halides and on additions to aldehydes and ketones [10—12]. These studies are consistent with the idea of a nucleophilic organotin radical but give little information about the magnitude of the polar nature of the organotin radical compared to other nucleophilic radicals. Kuivila and Menapace showed that trifluoromethylbenzyl chloride was reduced by organotin hydride more readily than benzyl chloride [13]. Nagai and co-workers demonstrated that halide abstraction by silyl radicals could be correlated with Taft's substituent parameters [14]. Few quantitative studies have been made for benzyl halide abstraction. Interestingly, Kochi found no substituent correlation for the reduction of substituted benzyl chlorides with chromium(II) [15].

Results and discussion

Relative rates for tri-n-butyltin hydride reduction of a series of benzyl chlorides (eq. 3) are summarized in Table 1. A Hammett plot for the data in Table 1 is presented in Fig. 1.

$$XC_6H_4CH_2Cl + (n\text{-}C_4H_9)_3SnH \rightarrow XC_6H_4CH_3 + (n\text{-}C_4H_9)_3SnCl \qquad (3)$$

The positive ρ value of 0.81 ($r = 0.98$) supports the concept of a nucleophilic radical. In addition, the data add to the evidence that polar effects in benzyl

TABLE 1

RELATIVE REACTIVITIES OF SUBSTITUTED BENZYL HALIDES, $XC_6H_4CH_2Cl$, WITH TRI-n-BUTYLTIN HYDRIDE

X	k/k_0
p-CH_3	0.67 ± 0.13
m-CH_3	0.81 ± 0.07
H	1.00
p-F	1.00 ± 0.03
p-Cl	1.78 ± 0.20
m-Cl	1.63 ± 0.14
p-CN	3.27 ± 0.30

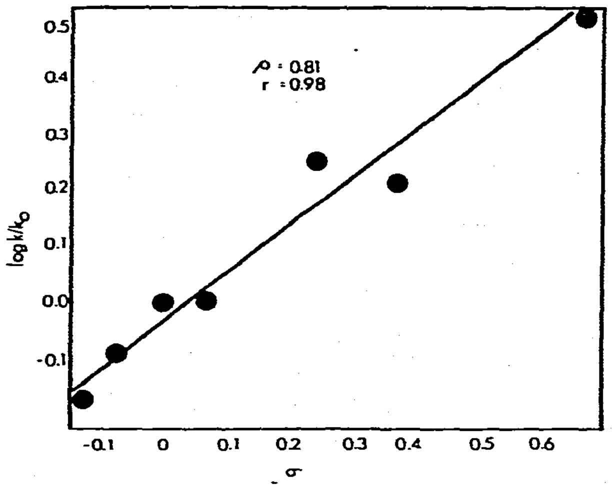


Fig. 1. Hammett plot for reduction of benzyl chlorides.

systems are real, and are not manifestations of benzylic bond dissociation energies. This example also provides one of the few positive ρ values observed for abstraction at benzylic carbon. Pryor has reported a value of 0.99 for abstraction of benzylic hydrogen by t-butyl radical [3]. Pryor [4a] and Henderson [4b] have reported values of 0.50 and 0.47 for abstraction of benzylic hydrogen by undecyl radical. The evidence in this study effects clear support for a nucleophilic organotin radical, and demonstrates that the polar effect is comparable to that shown by other nucleophilic radicals. Halide abstraction appears to be a promising tool for evaluating polar effects in free radical reactions at benzylic carbon. A transition state model consistent with the data reported here may be represented by structures II⟷III.

$$[R^{\cdot}\text{---}\dot{C}l\text{---}{}^{\cdot}SnR_3] \leftrightarrow [R\!:^{-}\text{---}\dot{C}l\text{---}{}^{+}SnR_3]^{\ddagger}$$

(II) (III)

There is one recent study of benzylic halide abstraction [16]. Migita and co-workers observed ρ values of 0.13, 0.05, and −0.19 for reaction of benzyl bromide with phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals. In contrast to us, they concluded there was little need to invoke a canonical structure bearing negative charge on the benzyl carbon.

Experimental

For each kinetic run, a solution of 0.04 mol of substituted benzyl chloride, 4.6 g (0.036 mol) of benzyl chloride, and 3.9 g of anisole was diluted to 100 ml with 1,2-dimethoxyethane. The solution was thoroughly mixed, and was divided into three equal parts which were added to three 25 ml pyrex flasks. Each pyrex flask contained 1.4 g (0.005 mol) of tri-n-butyltin hydride. The flasks were flushed with nitrogen, sealed, placed in a constant temperature bath at 25 ± 0.10°C for 4 h, and irradiated with UV light. The light source was a 100-Watt, medium pressure mercury vapor lamp which was placed in a quartz cylinder in the center of the bath. This method has been shown to be effective in promoting free radical organotin hydride reactions [13]. Consumption of the organotin hydride was indicated by the disappearance of the tin hydrogen band at 1815 cm^{-1} in the infrared spectrum. The reaction mixture was analyzed before and after the reaction by GLC using anisole as the internal standard. Relative rates were calculated by standard methods [17], using eq. 4, where $[C_x]_i$ and $[C_x]_f$ are the

$$k_x/k_o = \log \frac{[C_x]_i/[C_x]_f}{[C_o]_i/[C_o]_f} \tag{4}$$

initial and final concentrations of substituted benzyl chloride and $[C_o]_i$ and $[C_o]_f$ are the initial and final concentrations of benzyl chloride.

Kuivila and Menapace have shown that the relative rates of organotin hydride reductions of halides do not vary with changes in concentration of the reactants [14]. Products were identified, and product yields were also monitored by GLC for reduction of *p*-methylbenzyl chloride and for *p*-chlorobenzyl chloride. Within experimental error, the reactants were accounted for as reduction products or unreacted starting material. The ρ value and correlation coefficient (r) were obtained from a least squares analysis.

Analyses were carried out on a F and M Model 810 Gas Chromatograph with an eight foot stainless steel column packed with 10% Apiezon L on 60—80 mesh Chromosorb P. The temperature was programmed at 8°/min from 120 to 210°C.

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