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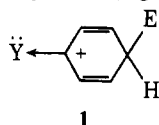
## Isoinductive Resonance Substituents for Mechanism Studies. I. Application to the Norbornyl Tosylate Solvolysis Problem

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**Abstract:** A series of isoinductive resonance substituents for  $\pi$ -electron donation has been developed. Substituents which donate  $\pi$ -electron density by  $\sigma$ - $\pi$  conjugation, being carbon substituents, do not vary greatly in inductive effect. One such substituent,  $-\text{CH}_2\text{Sn}(\text{CH}_3)_3$ , having a  $\sigma^+ = -0.92$  and the inductive effect of a methyl group, when substituted at the 1-position accelerates *exo*-2-norbornyl *p*-nitrobenzoate solvolysis by a factor of  $6 \times 10^5$ . This result strongly supports the theory that there is  $\sigma$  delocalization in the transition state for this solvolysis and demonstrates the usefulness of  $\sigma$ - $\pi$  conjugating substituents in mechanism studies.

The separation of resonance and inductive contributions to the total electron-donating effect of substituents on electron-deficient aromatic systems (e.g., 1) has been attempted



in many ways, most of which have employed Y groups of widely varying electronegativities.<sup>2,3</sup> While this separation into  $\sigma^{\text{R}^+}$  and  $\sigma^{\text{I}}$  components has met with considerable success in aromatic systems, the extension of this concept to presumed  $\sigma$ -delocalized systems such as cyclopropylcarbinyl or 2-norbornyl cations has led to ambiguity and disagreement.<sup>4-9</sup> This ambiguity apparently stems from the widely varying and unpredictable response of such  $\sigma$  systems to both inductive and resonance effects.

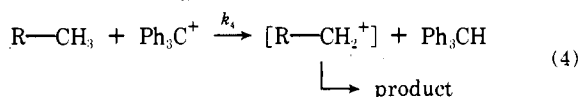
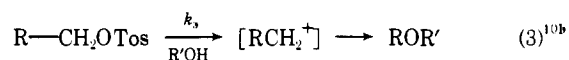
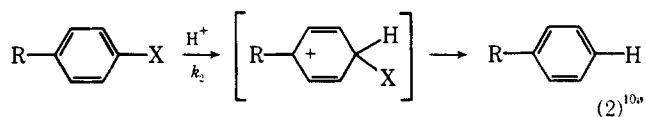
Rather than attempting to develop  $\sigma^{\text{R}^+}$  for each new system, we decided to devise a series of isoinductive  $\pi$  electron donating substituents with which such separation would be unnecessary. This approach is based upon our observation that  $\sigma$ - $\pi$  conjugation of bent or polarized  $\sigma$  bonds afford  $\sigma^+$  values of carbon substituents from  $\sigma^+ = -0.2$  to  $-1.2$ .<sup>10</sup> For example,  $\sigma^+_{p\text{-homocubyl}} = -0.75$ ,<sup>10h</sup> and  $\sigma^+_{p\text{-CH}_2\text{SnMe}_3} = -0.92$ .<sup>10a</sup> Furthermore, a wide ranging series of  $\sigma^+$  substituents with  $\sigma^+$  values increasing in increments of about 0.05 can be easily attached to most chemical systems. But the important quality of these  $\sigma$ - $\pi$  conjugating substituents is that, because they are all carbon substituents, their inductive effects are almost invariant and very near that of

$\text{CH}_3$ . Thus, the  $\sigma^{\text{I}}_{\text{R}}$  values of  $-\text{CH}_2\text{PbPh}_3$ ,  $-\text{CH}_2\text{SnMe}_3$ , and  $-\text{CH}_3$  are all  $-0.3$  as determined by charge transfer from  $\text{PhCH}_2\text{R}$  to TCNE.<sup>10a,11</sup> A selected list of  $\sigma^+$  values of  $\sigma$ - $\pi$  conjugating substituents is shown in Table I.

Because all these substituents have  $\sigma^{\text{I}}$  values near  $-0.3$ , we can define an isoinductive  $\sigma^+$  constant<sup>12</sup>

$$\text{isoinductive } \sigma^+ \equiv (\sigma^+)_{\text{I}} \equiv (\sigma^+)_{\sigma^{\text{I}} = -0.3} \equiv \left( \frac{\partial \ln k}{\partial \sigma^+} \right)_{\sigma^{\text{I}}} \quad (1)$$




We have already shown excellent correlation of the  $\sigma^+$  values of these kinds of substituents (R) in reactions such as 2, 3, and 4.



In these cases, the electron deficiency was either localized on a carbon p orbital<sup>10h,13</sup> or delocalized in a  $\pi$  system.<sup>10a,b,d</sup>

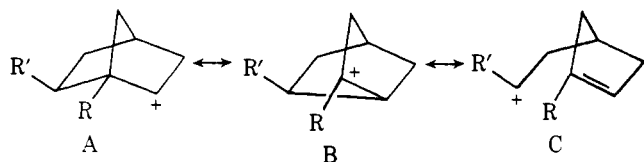
We now turn to the application of these substituents to presumed  $\sigma$ -delocalized (nonclassical) systems where the usual  $\sigma^+$  or  $\sigma^{\text{R}}$  values have not been applicable.

Table I.  $\sigma^+p$ -R of  $\sigma$ - $\pi$  Conjugating Substituents

Group (R)	$\sigma^+$	Ref
-Me	-0.30	12
-OMe	-0.78	12
	-0.52	10h
	-0.71	10h
	-0.75	10h
-CH <sub>2</sub> SiPh <sub>3</sub>	-0.4	10a, 12
-CH <sub>2</sub> GePh <sub>3</sub>	-0.6	10a, 12
-CH <sub>2</sub> SnPh <sub>3</sub>	-0.75	10a, 12
-CH <sub>2</sub> PbPh <sub>3</sub>	-1.0	10a, 12
-CH <sub>2</sub> SiMe <sub>3</sub>	-0.62	10a
-CH <sub>2</sub> SnMe <sub>3</sub>	-0.92	10a
-CH <sub>2</sub> HgC <sub>6</sub> H <sub>11</sub>	-1.2	10a

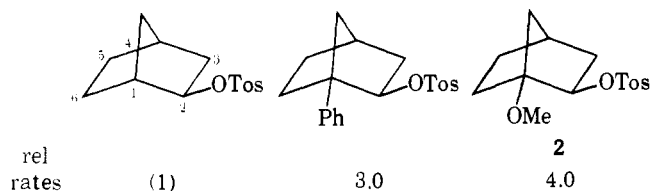
The response of *exo*-2-norbornyl tosylate solvolysis to substituent effects (especially  $\sigma^+$  substituents) has been the source of controversy.<sup>5,6,14,15</sup> The usual valence-bond representation of the 2-norbornyl cation (or its preceding transition state) is the resonance hybrid of eq 5.<sup>14</sup>

$$\Psi_{\text{cation}} = a\psi_A + b\psi_B + c\psi_C \quad (5)$$



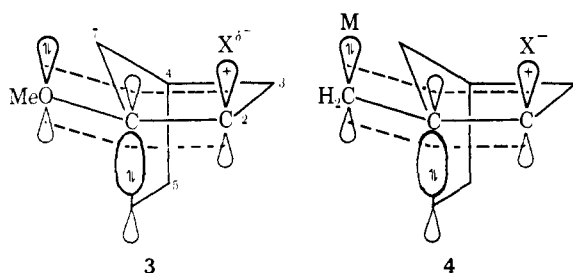
A frequently employed corollary states that, if R' or R are  $\pi$  electron donating substituents and they do not accelerate the formation of the cation, this means that, in the parent system where R = R' = H, the coefficients *b* and *c* are zero and the ion is localized at C<sub>2</sub> (classical).<sup>6</sup>

The following relative rates<sup>7,16</sup> have been thus interpreted by Brown and coworkers<sup>6</sup> as evidence for the localized structure represented by A above:



Conversely, because the 1-methoxy substituent decelerates the rate of *endo*-2-norbornyl tosylate solvolysis, Schleyer and coworkers interpreted these same data as evidence for stabilization of the norbornyl cation by the 1-methoxy substituent.<sup>4</sup> They suggested that the contribution of inductive electron withdrawal by the methoxy group essentially balances its  $\pi$ -donating properties in this system.

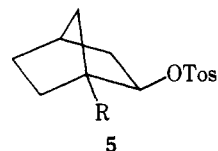
Rewriting the norbornyl cation (transition state) in terms of molecular orbital interactions, we have the system shown in which departure of X<sup>-</sup> is creating electron deficiency at C<sub>2</sub>:



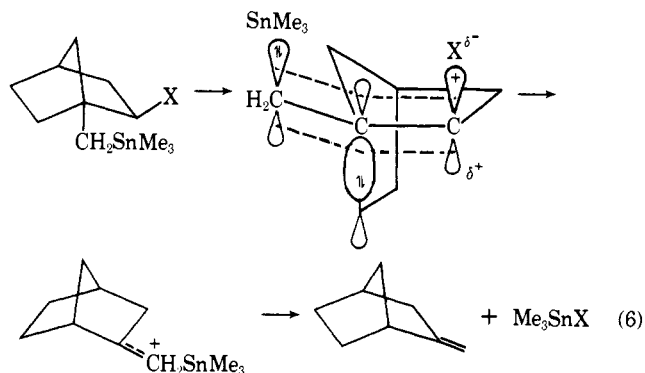
We can now rephrase the question concerning the effect of the methoxy group. Is the C<sub>1</sub>-C<sub>6</sub> bond delocalized to the C<sub>2</sub> electron deficiency sufficiently to interact with the MeO lone pair? According to Brown, the answer is "no" because no rate acceleration is observed. According to Schleyer, the answer is "yes" because the endo compound is retarded.

The obvious solution to this dilemma is to substitute for MeO- an equally good  $\pi$ -donating group which is not electronegative as in 4, in which case large acceleration will result if the interpretation of Schleyer et al. is correct.

We chose the -CH<sub>2</sub>SnMe<sub>3</sub> ( $\sigma^+ = -0.92$ ) for its large electron-donating ability, for its tendency to stabilize only electron-deficient centers,<sup>10k,17</sup> and for its convenient attachment to the norbornyl system. If the 1-methyl group (R = Me in 5), a member of our ( $\sigma^+$ )<sub>1</sub> series, affords its accel-



eration (a factor of 50)<sup>7</sup> in the same way it supplies electrons for aromatic electrophilic substitution (i.e., through its  $\sigma^+p$ -Me = -0.3),<sup>12</sup> then the -CH<sub>2</sub>SnMe<sub>3</sub> should accelerate *exo*-2-norbornyl tosylate by more than 10<sup>5</sup> by the interactions shown in eq 6 and should lead to the products indi-



cated because of the tendency for loss of R<sub>3</sub>Sn<sup>+</sup> from cations.<sup>13</sup>

## Results

We have therefore prepared 1-trimethyltinmethyl-*exo*-2-norborneol by the route shown in Scheme I. The stereochemistry of the first step is well established.

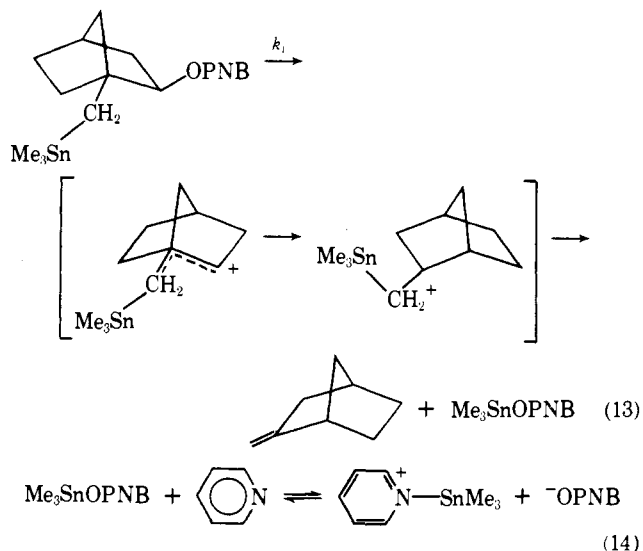
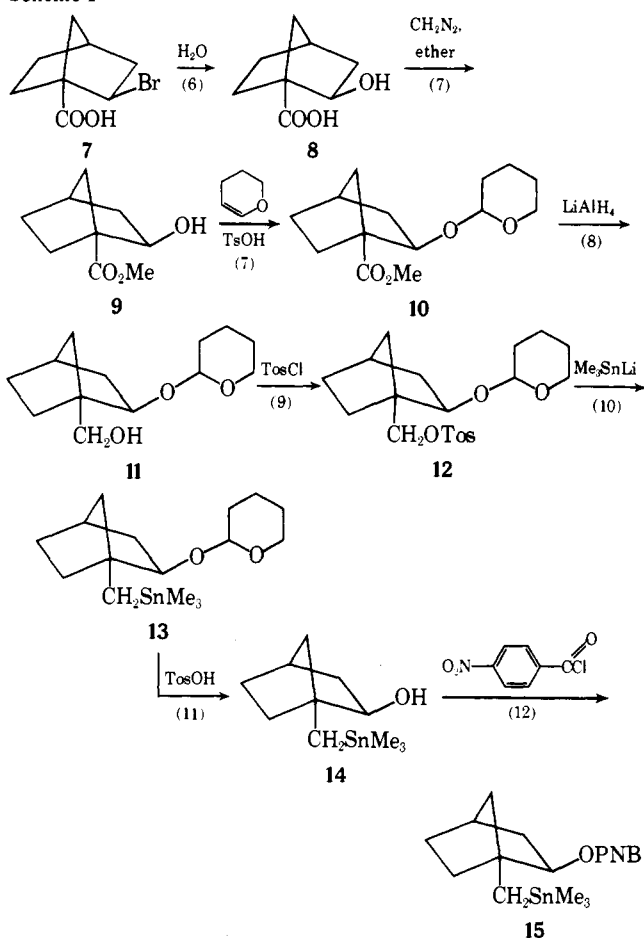
We first prepared the ditosylate of the glycol related to 12, but reactions with trimethyltinlithium gave either no reaction or an intractable mixture. We now believe that either of the tin tosylates would be unstable.

The less reactive *p*-nitrobenzoate ester 15 was prepared and solvolyzed in aqueous acetone. Preliminary results indicated complete disappearance of the ester in 5 days at 100° in (7:3) acetone-water, indicating a rate in excess of 10<sup>-5</sup> sec<sup>-1</sup>. Rates of solvolysis in 80% acetone-20% water, as determined by conductivity, are shown in Table II. The product of this solvolysis, produced in 91% yield after 20 half-lives at 100°, was identified as 2-methylenenorbornane. This excludes the possibility of carbonyl-oxygen bond hydrolysis or cyclopropane formation and shows that the reaction proceeds as shown in eq 13 and 14.

## Discussion

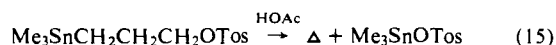
In order to compare the rather fast rate of this solvolysis with that of norbornyl tosylate, we have resorted to a direct comparison of our rate with that of 2-methyl-2-norbornyl *p*-nitrobenzoate,  $k_1 = 1.96 \times 10^{-6}$  sec<sup>-1</sup> at 50° in 60%

Scheme 1



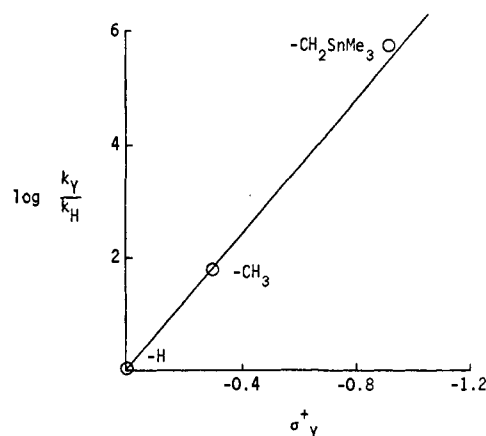
aqueous dioxane.<sup>20</sup> Extrapolation of the data in Table I to 50° indicates  $k_1 = 9.3 \times 10^{-7} \text{ sec}^{-1}$ . A correction factor of 22 between 80% acetone and 60% dioxane<sup>21</sup> gives  $k_1 = 2.1 \times 10^{-5} \text{ sec}^{-1}$  at 50°. This rate is 11 times that of 2-methyl-*exo*-2-norbornyl *p*-nitrobenzoate which is in turn reported to be accelerated by 55,000 by the 2-methyl substituent.<sup>20</sup> Therefore the Me<sub>3</sub>SnCH<sub>2</sub>- group accelerates "norbornyl *p*-nitrobenzoate" solvolysis by 600,000!<sup>22</sup>

There are other possibilities for acceleration of primary tosylate solvolysis by a  $\gamma$ -trimethyltin group. Kuivila and coworkers<sup>25</sup> have observed a small acceleration (about 500) in the reaction shown in eq 15.

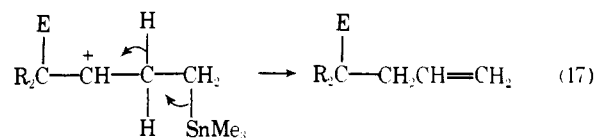
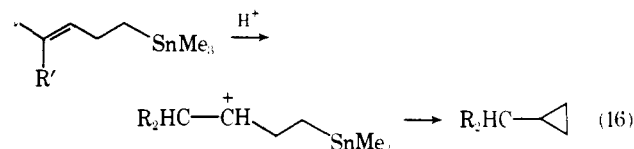
Table II. Rates of Solvolysis of 1-Trimethylstannylmethyl-*exo*-2-*p*-nitrobenzoyloxynorbornane (15)<sup>a</sup>

Temp, °C	$k$ , sec <sup>-1</sup> × 10 <sup>4</sup>	$\Delta H^\ddagger = 23.5 \text{ kcal/mol}$
-110	2.46 ± 0.07	
100	1.012 ± 0.05	
90	0.445 ± 0.018	

<sup>a</sup>In 80% acetone–20% water containing  $1.2 \times 10^{-3} M$  pyridine and about  $10^{-3} M$  of 15.

Figure 1. Plot of  $\log k_Y/k_H$  for substitution of Y at the 1-position on *exo*-2-norbornyl-*p*-nitrobenzoate against  $\sigma^+_Y$ .

However, we found no cyclopropyl product and the geometry for this kind of participation cannot be attained in structure 4. Furthermore, Peterson, Robbins, and Hansen<sup>26</sup> have shown that the rather facile reaction 16 is not accompanied by any of reaction 17. This suggests that the effect we observed here is not to be expected in unstrained compounds.



Although any quantitative correlation might be fortuitous, it is interesting to plot the accelerations caused by 1-substituents having similar inductive effects against  $\sigma^+_Y$  as we do for H, Me, and -CH<sub>2</sub>SnMe<sub>3</sub> in Figure 1. The slope of this line,  $\rho = -6$ , shows that this reaction is indeed very sensitive to substitution at the 1-position. This large acceleration also confirms Schleyer's<sup>4</sup> postulate that the resonance effect of the 1-MeO substituent is large but is essentially cancelled by its large inductive effect. Our finding also emphasizes the need to carefully explore the nature of substituent effects on  $\sigma$ - $\pi$  conjugated systems.

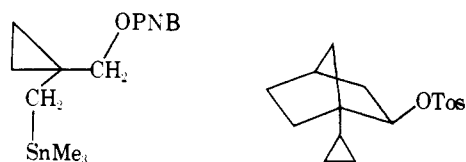
We are assuming, with some confidence, that the -CH<sub>2</sub>SnMe<sub>3</sub> will not accelerate the solvolysis of the endo compound. No other 1-substituent has done so.<sup>27</sup> If this is correct, then the *exo*/*endo* rate ratio of the 1-CH<sub>2</sub>SnMe<sub>3</sub>-2-norbornyl tosylates should be  $\sim 600,000 \times 1600 \approx 10^9$ !

The acceleration we observed was predicted (perhaps not quantitatively) on the basis of delocalization of the C<sub>1</sub>-C<sub>6</sub> bond in norbornyl cation formation, and this acceleration can in no way relate to any "steric hindrance to the leaving group" in the endo compound.<sup>6</sup> In our study there is a 600,000-fold acceleration which is due to delocalization

through the  $\sigma$  system to the 2-norbornyl position. One of the basic tenets proposed by Brown and coworkers, that substituent effects do not reveal  $C_1$ - $C_6$  delocalization, is now untenable as is the conclusion that there is no such delocalization.

But the conclusion which we reach in this study is that substituents which have widely varying  $\sigma^+$  values and constant  $\sigma^1$  values can be effectively employed as mechanistic probes where other kinds of  $\sigma^+$  substituents have given ambiguous results.

If these ( $\sigma^+$ ); substituents show such large stabilization of delocalized or "nonclassical" ion precursors, then we should predict large accelerations in the solvolyses of compounds such as those shown:



In fact the rates of such 1-R-2-*exo*-norbornyl tosylate solvolyses should be predictable from the  $\sigma^+$  values in Table I.

We conclude that  $\sigma$ - $\pi$  conjugating substituents afford a very versatile series of isoinductive activating groups for definitive mechanistic probes and synthetic applications.

## Experimental Section

**exo-2-Bromobicyclo[2.2.1]heptyl-1-carboxylic acid (7)** was prepared by the method of Kwart and Null<sup>28</sup> and converted, through the alcohol **8** to the ester **9** as described by Wilt and Wagner.<sup>9</sup>

**Preparation of *exo*-2-Tetrahydropyranyloxybicyclo[2.2.1]heptyl-1-methanol (11).** The hydroxy ester **9** (5 g) was dissolved in 15 ml of diethyl ether and this added dropwise to 3.78 g (0.045 *M*) of dihydropyran and 0.31 g (0.0018 *M*) of *p*-toluenesulfonic acid monohydrate in 30 ml of ethyl ether.<sup>29</sup> After an hour at room temperature, the solution was washed with saturated sodium carbonate, dried over sodium sulfate, and distilled to yield 3.3 g (70% yield), bp 110–115° (0.3 mm), of clear liquid (**10**). This 3.3 g (0.013 *M*) of ester was stirred for 48 hr at room temperature with 0.5 g (0.013 *M*) of lithium aluminum hydride in 30 ml of ethyl ether. Hydrolysis with 10% aqueous sodium hydroxide produced a white ether insoluble powder which was filtered off. Drying and evaporation of the dried ether solution left 2.8 g (>98%) of an oil (**11**) whose infrared spectrum showed hydroxy but no carbonyl absorption. There were broad NMR absorptions at  $\delta$  1–2, 2.1, 3.4–4.0, and 4.6. The methyl ester singlet at  $\delta$  3.6 was absent.

**Preparation of *exo*-2-Tetrahydropyranyloxy-1-trimethylstannylmethylbicyclo[2.2.1]heptane (13).** The alcohol **11** (2.8 g, 0.0124 *M*) in 25 ml of dry pyridine was treated with 2.3 g (0.0124 *M*) of redistilled tosyl chloride at room temperature for 20 hr. The reaction mixture was dissolved in ether, washed successively with ice-water, cold 1% aqueous hydrochloric acid (twice), 10% sodium carbonate, and water, and then dried over sodium sulfate. Evaporation of the solvent and recrystallization of the residue from low boiling petroleum ether produced 4.1 g (66% yield) of **12** in two crops, mp 67–69°. This product had the typical tosylate NMR singlet at  $\delta$  2.4 and doublets at  $\delta$  7.1 and 7.6 in addition to the broad absorptions mentioned above. This tosylate (**12**), 0.3 g (0.0008 *M*), was dissolved in dry tetrahydrofuran under argon and treated with 0.002 *M*  $(CH_3)_3SnLi$  in tetrahydrofuran from a standard solution of this reagent. After 20 hr at 45°, the solvent was evaporated, the residue taken up in ethyl ether, and this washed with cold water, dried, and evaporated. Thin layer chromatography on silica gel revealed three products which were shown to be hexamethylditin, the desired compound **13**, and starting material **12** in order of decreasing *R<sub>f</sub>*. Using column chromatography on silica gel with successive elution with hexane (for  $Me_6Sn_2$ ), 1% ether in hexane, 2% ether in hexane for (**13**), and 10% ether in hexane for (**12**), about 60% yield of **13** was obtained. Spectra were: ir 760, 990, 1045, 1080, 1115, 1355, 1360, 1430, 3000  $cm^{-1}$ ; NMR ( $CDCl_3$ ,  $Me_4Si$ )  $\delta$  0.15 (9 H, s), 1.60 (4 H, m), 3.70 (16 H, m), 4.60 (1 H, s).

**Preparation of *exo*-2-*p*-Nitrobenzoyloxy-1-trimethylstannylmethylnorbornane (15).** To 0.3 equiv of *p*-toluenesulfonic acid monohydrate in methanol was added 1 equiv of **13**. After 15 min, the methanol was evaporated, the residue taken up in ether, and this washed with dilute sodium bicarbonate solution, dried, and evaporated to an oil (**14**): NMR ( $CCl_4$ ,  $Me_4Si$ )  $\delta$  0.20 (9 H, s), 1.20 (11 H, m), 3.55 (2 H, m). Addition of  $D_2O$  reduced the area at  $\delta$  3.55 to 1 H.

To 0.4 g (0.00014 *M*) of the alcohol **14** in 10 ml of pyridine was added 0.27 g (0.00014 *M*) of *p*-nitrobenzoyl chloride (recrystallized from hexane) and the solution left at room temperature for 1 day. The reaction mixture was dissolved in ethyl ether, washed successively three times with 1% aqueous hydrochloric acid and water, and then dried over magnesium sulfate and evaporated to give a tan solid. This product was taken up in hot hexane, filtered to remove *p*-nitrobenzoic acid, and crystallized. **15**: yield 40–60% in several runs; mp 94–95°; ir 875, 930, 1025, 1105, 1200, 1285, 1350, 1525, 1600, 1725, 3000  $cm^{-1}$ ; NMR ( $CDCl_3$ ,  $Me_4Si$ )  $\delta$  0.20 (9 H, s), 1.40 (11 H, m), 4.70 (1 H, m), 8.32 (4 H, s).

Anal. Calcd for  $C_{18}H_{25}NO_4Sn$ : C, 49.30; H, 5.72; N, 3.20. Found: C, 49.46; H, 5.66; N, 3.40.

**Solvolysis Product.** A sealed ampoule containing 40 mg of **15** in about 10 ml of 80% acetone–20% water by volume was heated at 100° for 40 hr and analyzed by gas-liquid chromatography at 80°. A 10 ft  $\times$  0.25 in. column of 20% QF-1 on 80–100 gas Chrom Z column was used. Only one peak other than those of the solvents was observed. Collection of this peak and taking its ir and NMR spectra showed it to be 2-methylenenorbornane.<sup>30</sup> NMR ( $CDCl_3$ ,  $Me_4Si$ )  $\delta$  0.9–1.8 (6 H, m), 1.8–2.1 (2 H, m), 2.28 (1 H, s), 2.60 (1 H, s), 4.53 (1 H, d), 4.80 (1 H, d).

Gas-liquid chromatography peak area comparisons between the reaction mixture and a standard solution of 2-methylenenorbornane indicated a 91% yield of this compound from solvolysis.

**Solvolysis Rate Measurements.** Solutions (about 5 ml) of **15** in 80% acetone (redistilled)–20% water by volume which were about  $10^{-3}$  *M* in **15** and  $1.2 \times 10^{-3}$  *M* in pyridine were sealed in ampoules in duplicate and placed in the appropriate temperature baths. At intervals the ampoules were quickly cooled and opened, conductance was measured at 25° on an RC-16BZ conductance bridge, and the ampoules were resealed and returned to the bath. Plots of  $\log(C_\infty - C)$  vs. time were linear for at least 5 half-lives.

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## References and Notes

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## Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XX.

### 2,4,6-Tri(*tert*-butyl)benzyl, -anilino, -phenoxy, and -phenylthiyl Radicals<sup>1</sup>

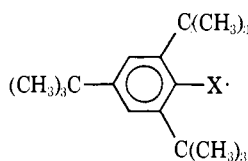
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**Abstract:** The title radicals have been generated, and their kinetic behavior has been examined. The EPR parameters for the benzyl and anilino radicals indicate that the benzylic and amino hydrogens are coplanar with the aromatic rings. The benzyl radical decays rapidly with second-order kinetics ( $k = (5 \pm 2) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  at  $24^\circ$ ) to give the bibenzyl. The anilino radical exists in equilibrium with the hydrazine ( $\Delta H = -13.1 \pm 0.5 \text{ kcal/mol}$ ,  $\Delta S = -27 \pm 2 \text{ gibbs/mol}$ ). The rate constant for anilino decay to its dimer can be represented by  $\log(k_{-1}/\text{M}^{-1} \text{ sec}^{-1}) = 6.3(\pm 1.0) - 2.5(\pm 0.8)/\theta$ , where  $\theta = 2.3RT \text{ kcal/mol}$ , and that for decomposition of dimer to two anilino radicals by  $\log(k_1/\text{sec}^{-1}) = 12.2 - 15.6/\theta$ . The phenylthiyl radical is also in equilibrium with its dimer at ambient temperatures ( $\Delta H = -23.3 \text{ kcal/mol}$ ), but the phenoxy radical shows no sign of dimerization even at  $-100^\circ$ . The behavior of these four radicals is discussed in terms of the strengths of the bonds formed by head-to-head dimerization.

In several previous papers in this series, we have shown that radical lifetimes can be dramatically increased by steric protection of the radical center.<sup>4</sup> Each of these papers was confined to radicals of a single type. That is, each dealt with radicals in which the atom that formally bore the unpaired electron was held constant, and the size of the surrounding groups was varied.

Equally dramatic changes in radical lifetimes can be achieved by holding to the same basic molecular structure and altering the atom carrying the unpaired electron. This is because the mutual bonding capacities of different atoms are not all the same. In the present paper, we illustrate this phenomenon by reporting on the kinetic behavior of the 2,4,6-tri(*tert*-butyl)benzyl, -anilino, -phenoxy, and -phenylthiyl radicals.



X = CH<sub>2</sub>, NH, O, S

The 2,4,6-tri(*tert*-butyl)phenoxy ( $\text{Ar}\ddot{\text{O}}$ )<sup>5,6</sup> is a well-known blue-colored radical that is readily prepared by oxidation of the phenol with a variety of reagents. It can be stored at room temperature in concentrated solutions (e.g., 1 M in benzene) for prolonged periods of time, in the absence of air. The pink-colored 2,4,6-tri(*tert*-butyl)anilino

radical ( $\text{Ar}\ddot{\text{N}}\text{H}$ ) has also been examined in some detail,<sup>7-12</sup> particularly with respect to its EPR<sup>7,8,10-12</sup> and uv-visible<sup>7,9</sup> spectra. In solution (at  $<10^{-4} \text{ M}$ ) it "can be preserved for several days when the solvent is *n*-hexane but the stability is less in cyclohexane".<sup>7</sup> The isoelectronic tri(*tert*-butyl)benzyl radical ( $\text{Ar}\ddot{\text{C}}\text{H}_2$ ) has not been previously reported. It was readily obtained from tri(*tert*-butyl)toluene or tri(*tert*-butyl)benzyl chloride which have been recently synthesized.<sup>13,14</sup> Tri(*tert*-butyl)phenylthiyl ( $\text{Ar}\ddot{\text{S}}$ ) has been previously studied, but there are conflicting reports as to its lifetime in solution.<sup>15-17</sup>

#### Experimental Section

**General.** The kinetic EPR procedure has been adequately described in previous papers in this series.<sup>1</sup> Unless otherwise stated, all materials were prepared and handled in an argon atmosphere.

**Materials.** The  $\text{ArOH}$  was a (purified) commercial sample (K & K Laboratories). Standard literature procedures were used to prepare  $\text{ArCH}_3$ ,<sup>13</sup>  $\text{ArNH}_2$ ,<sup>18</sup>  $\text{ArSH}$ ,<sup>19</sup> and  $\text{ArNO}$ .<sup>20</sup> The disulfide  $\text{ArSSAr}$  was prepared by oxidizing  $\text{ArSH}$  with silver oxide and was purified by vacuum sublimation, mp  $233^\circ$  (lit.<sup>19</sup>  $233^\circ$ ).

Hexa(*tert*-butyl)bibenzyl ( $\text{ArCH}_2\text{CH}_2\text{Ar}$ ) was prepared by reaction of  $\text{ArCH}_2\text{Cl}$ <sup>13</sup> (0.1 g) with finely divided sodium in paraffin wax at  $120^\circ$  under  $\text{N}_2$  for 30 min.<sup>4d,21,22</sup> In this time, the NMR signal due to the  $\text{CH}_2\text{Cl}$  protons disappeared. Column chromatography on acidic alumina yielded 0.04 g of the crystalline hydrocarbon  $\text{ArCH}_2\text{CH}_2\text{Ar}$ : mp  $228^\circ$ ; proton NMR spectrum in  $\text{CDCl}_3$  (in parts per million downfield from  $\text{Me}_4\text{Si}$ ) 1.20 (*p*- $\text{C}(\text{CH}_3)_3$ ) and 1.22 (*o*- $\text{C}(\text{CH}_3)_3$ ) (totalled 54 H), 3.40 (4 H,  $-\text{CH}_2\text{CH}_2-$ ), 7.48 (4 H, aryl *m*-H). The elemental analysis was poor (Anal. Calcd for