order of magnitude of the present benzyl anion studies, but *opposite in sign*. We conclude that the orbital following perturbation as proposed is too large by at least an order of magnitude. We also conclude that although deuterium substitution has some of the properties of a normal electron-donating substituent in terms of gross direction and order of magnitude, variations of magnitude cannot be analyzed as simple substituent effects and have limited usefulness as probes of electronic structure.

Acidity of Hydrocarbons. XXVI. Rates of Exchange of *m*- and *p*-Trimethylsilyltoluene-α-*d* and -α-*t* with Lithium Cyclohexylamide in Cyclohexylamine[1,2]

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Abstract: Deuterium and tritium exchange rates were determined for *m*- and *p*-trimethylsilyltoluenes in cyclohexylamine catalyzed by lithium cyclohexylamide at 25°. Tritium exchange rates relative to toluene-α-*t* are: *meta*, 1.01, $k_D/k_T = 3.3 \pm 0.3$; *para*, 4.57, $k_D/k_T = 3.0 \pm 0.1$. These results confirm the conjugative electron withdrawal of a silyl group. Equivalent σ^- values are: *m*-$(CH_3)_3Si$, 0.00; *p*-$(CH_3)_3Si$, +0.17.

Because silicon is more electropositive than carbon, it is expected to have an electron-donating inductive effect.[4,5] Several studies, however, have demonstrated that a conjugating trimethylsilyl group can have an electron-withdrawing effect.[6] From a study of the acidities of substituted anilinium ions and phenols, for example, Benkeser and Krysiak[7] found an enhancement of acidity by a *p*-trimethylsilyl group equivalent to σ^- values of +0.07 to +0.11. Similarly, in a study of base-catalyzed cleavages of substituted benzylsilanes, Eaborn and Parker[8] found a ninefold rate acceleration by a *p*-trimethylsilyl group that further demonstrates this electron-withdrawing effect.

These results prompted the present study of base-catalyzed exchange of trimethylsilyl-substituted toluenes with lithium cyclohexylamide (LiCHA) in cyclohexylamine. Our previous studies of isotope effects,[9,10] mechanism,[11] and substituent effects[12] have shown that this reaction proceeds through a benzyllithium intermediate and that the transition state is highly carbanionic. Hence, this system is well suited for a further characterization of the electrical effects of a silyl group.

Results and Discussion

The *m*- and *p*-trimethylsilyltoluene-α-*d*(*t*)'s were prepared by straightforward syntheses. The kinetic determinations were patterned after our previous vacuum-line procedures. Because of the difficulty of assaying the base concentration accurately, the pseudo-first-order experimental rate constants are always more accurate than the second-order rate constants. Accordingly, our current practice is to include some standard compound in every kinetic run in order to obtain relative rates directly. In addition, a mixture of deuterated and tritiated compounds is used, and the exchange of both isotopes is followed in order to obtain two independent relative rates and to obtain directly the primary isotope effect, k_D/k_T. A high value for this ratio provides a monitor for the absence of internal return which could render less significant the derived relative substituent rates.[12-14]

In the present study *o*-fluorotoluene was used as the internal standard for *p*-trimethylsilyltoluene; its rate relative to toluene, 12, has been determined previously.[12] It was desirable not to have toluene itself in the system in at least one case because it would be the product of a nucleophilic reaction of cyclohexylamide ion on silicon with subsequent cleavage of the silicon–aryl bond. The importance of such a cleavage reaction had to be determined. In fact, this cleavage does occur but at a rate an order of magnitude slower than the benzylic hydrogen exchange.

The results are summarized in Table I. The primary isotope effects indicate the mechanism is the same as for toluene for which $k_D/k_T = 2.8$; that is, that the carbon–hydrogen bond is largely broken at the transi-

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[2] Paper XXV: A. Streitwieser, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **89**, 3767 (1967).

[3] On leave from the Institute of Chemical Process Fundamentals, Prague, Suchdol 2, Czechoslovakia.

[4] J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Am. Chem. Soc.*, 71, 2923 (1949).

[5] C. Eabor and S. H. Parker, *J. Chem. Soc.*, 939 (1954).

[6] H. Soffer and T. DeVries, *J. Am. Chem. Soc.*, 73, 5817 (1951).

[7] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

[8] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 126 (1955).

[9] A. Streitwieser, Jr., W. C. Langworthy, and D. E. Van Sickle *J. Am. Chem. Soc.*, **84**, 251 (1962).

[10] A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962).

[11] A. Streitwieser, Jr., D. E. Van Sickle, and L. Reif, *ibid.*, **84**, 258 (1962).

[12] A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

[13] D. J. Cram, C. A. Kingsbury, and B. Rickborn, *ibid.*, **83**, 3688 (1961).

[14] Y. E. Hofman, A. Schriesheim, and R. E. Nickols, *Tetrahedron Letters*, 1745 (1965).

Table I. Rate Constants for LiCHA-Catalyzed Exchange at 25°

$YC_6H_4CH_2D(T)$			10^5k_{exp}, sec^{-1}			k_{rel}[b]		
Y	Concn, *M*	*c*,[a] *M*	k_D	k_T	k_D/k_T	D	T	σ[c]
p-$(CH_3)_3Si$	0.114	0.125	17.5 ± 0.4	5.90 ± 0.11	3.0 ± 0.1	4.70	4.57	+0.17
o-F	0.231		44.6 ± 1.1	15.5 ± 0.3	2.88 ± 0.08	(12)[d]	(12)[e]	
m-$(CH_3)_3Si$	0.106	0.118	3.70 ± 0.05	1.13 ± 0.07	3.3 ± 0.3	1.00	1.01	0.00
H	0.190		3.71 ± 0.11	1.13 ± 0.02	3.3 ± 0.1			

[a] Formal concentration of LiCHA. [b] Rates relative to toluene-*α-d* and -*α-t*, respectively. [c] Calculated from k_{rel} and ρ = 4.0. [d] Assumed to be the same as the tritium rate; *cf.* ref 12. [e] Reference 12.

tion state and that the central carbon is highly carbanionic. The electron-withdrawing effect of the *p*-trimethylsilyl group is shown by its rate relative to toluene of close to five. Using $\rho = 4.0$ as previously established for substituted toluenes[12] the equivalent σ value, which should be considered to be a σ^-, is +0.17. This value is close to that obtained by Eaborn and Parker, +0.19,[8] but is greater than that which applies to anilinium ions and phenols (*vide supra*). This variation indicates that the degree of electron withdrawal may depend on the electron supply. This limitation of a single-term Hammett equation suggests the application to anionic systems of a two-parameter Yukawa and Tsuno equation.[15]

$$\log \text{relative rate} = \rho[\sigma + r(\sigma^- - \sigma)]$$

However, the data at present are insufficient to justify this extension.

The conjugative electron withdrawal by the *p*-trimethylsilyl group is probably due to π overlap between the aryl p_z and silicon $d_{x,z}$ orbitals, as has been suggested previously. The absence of a net effect for the *m*-trimethylsilyl group suggests the operation even here of conjugative electron withdrawal that just compensates for the normal electron-donating inductive effect. Note that σ_I for $(CH_3)_3Si$ is -0.15[8,16] and that σ_m is usually close to σ_I.

Experimental Section

***p*-Trimethylsilylbenzoic Acid.** The reaction of *p*-bromophenylmagnesium bromide with trimethylchlorosilane in ether gave 44% of crude product which, even after distillation, contained substantial amounts of *p*-bis(trimethylsilyl)benzene and *p*-dibromobenzene as determined by glpc analysis (20% XF-1150 on Chromosorb W at 157° using an Aerograph 1520). The Grignard reagent from 52 g of crude product in tetrahydrofuran was carbonated with Dry Ice. Crystallization from heptane gave 24 g of pure acid, mp 116–117° (lit.[17] 117–118°).

***p*-Trimethylsilyltoluene-*α-d(t)*.** The above acid was esterfied with methanol and sulfuric acid and reduced with lithium aluminum hydride in ether. The resulting alcohol was stirred with 333 g of thionyl chloride for 15 min in an ice bath. The excess thionyl chloride was removed under vacuum, and the remaining oil was distilled, bp 129–131° (19–20 torr). The product, 20.8 g, was 89% pure by glpc analysis, the principal impurities being thionyl chloride, benzyl chloride (1%), and *p*-chlorobenzyl chloride (1.5%). This product was converted to the Grignard reagent in ether and quenched with tritium-enriched water and deuterium oxide. Distillation through a small column gave 14.5 g, bp 114–116° (65 torr), and consisted of 94.5% d_1 with a tritium activity of 1.08 × 10^5 dpm/μl. The only impurities found (glpc—20% SF-96 on Chromosorb W at 120°) were toluene and *p*-chlorotoluene, <0.1%. The infrared spectrum showed a $(CH_3)_3Si$ group (strong band at 850 cm^{-1} and splitting of the band at 1245 cm^{-1}). The nmr showed four aromatic protons at δ = 6.87 ppm, a triplet at δ = 1.80 ppm (2 H), and the trimethylsilyl singlet at δ = −0.19 ppm.

***m*-Trimethylsilylbenzoic Acid.** This was prepared in the same way as the *para* isomer starting with 128 g of *m*-dibromobenzene. The product acid was crystallized from heptane, yield 21.3 g, mp 112–113° (lit.[17] 110–111°).

***m*-Trimethylsilyltoluene-*α-d(t)*.** The acid was esterified with diazomethane, reduced, and converted to the chloride, and the Grignard reagent was quenched as for the *para* isomer. The product, 14.9 g, had bp 114.6–115.0° (65 torr), 95.7% d_1, 8.59 × 10^4 dpm/μl, and was pure by glpc analysis (20% Dow 710 on Chromosorb W at 150°). The nmr showed a multiplet of four aromatic protons at δ = 6.83 ppm, a triplet at δ = 1.81 ppm (2 H), and a singlet (9 H) at δ = −0.19 ppm.

***o*-Fluorotoluene-*α-d(t)*.** The Grignard reagent from *o*-fluorobenzyl chloride was quenched with tritium-enriched water and deuterium oxide. Distillation gave a product, bp 112.0°, having 94.7% d_1 and 1.9 × 10^5 dpm/mg. The nmr spectrum showed a multiplet (4 H) centered at δ = 6.42 ppm and a triplet (2 H) at δ = 1.63 ppm.

Toluene-*α-d(t)* has been described previously in this series.

Kinetics. The procedure for preparing the reaction mixture, isolating the kinetic aliquots, and titrating for base was essentially that published previously.[18] The tritium content of the aliquot mixture was determined by radio gas chromatography. The effluent from an Aerograph 1520 passed through a proportional-flow counter tube.[12] The area of each glpc peak was measured with an Aerograph digital integrator 470, and the radioactivity pulses were counted by a Nuclear Chicago digital integrator. The ratio of counts per unit area was reproducible to 1%. For the deuterium analyses, the low-voltage mass spectrum was taken. In the cases of the silyltoluenes both the parent ion and M − 15 ($CH_3C_6H_4SiMe_2^+$) were used and gave good agreement.

The first-order rate constants were computed by Perrin's[19] program (for k_T) and by DeTar's[20] LSKIN1 program.

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(15) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

(16) O. Exner and Y. Jonas, *Collection Czech, Chem. Commun.*, **27**, 2296 (1962).

(17) R. G. Severson, R. Y. Rossump, D. R. Lindberg, and R. D. Engberg, *J. Am. Chem. Soc.*, 79, 6540 (1957).

(18) A. Streitwieser, Jr., and R. A. Caldwell, *ibid.*, **87**, 5394 (1965).

(19) A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965).

(20) D. F. DeTar and C. E. DeTar, to be published; modified by H. A. Hammond.