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Proton exchange in compounds of low acidity is often difficult in a practical method because of high kinetic barriers associated with removal of the hydrogen. Toluene and toluene derivatives were shown by Streitwieser to have
undergo slow H/D exchange processes. We now report a general method based on our previous studies on PTC/OH' systems for exchanging very weak carbon acid protons under readily obtainable conditions.

**Results and Discussion**

Until very recently, only compounds as acidic as fluorene (pK_a = 23) underwent PTC reactions under conditions which favor the interfacial mechanism. It seemed, therefore, that fluorene represents a compound of the lowest limit of acidity suitable for such a reaction. This behavior of an interfacial mode can be rationalized by the thermodynamic parameters of the following process:

\[ 2\text{NaOH} + H^+ \rightarrow \text{Na}^+ + \text{NaOH}_2\text{H}_2\text{O} \quad K = 10^{23} \]

Thus, an acid of a pK_a value up to 23 should react with solid NaOH to give the sodium salt. The empirical limit for exchange on a practical time scale is therefore represented by the fluorene molecule (pK_a = 23). On the other hand, we have recently reported that very weak carbon acids (pK_a = 34) do undergo rapid reactions operative under PTC/OH' conditions. We rationalized this expansion of the acidity range of compounds capable of undergoing this process by assuming that the reaction occurs via an extraction mechanism. We have shown that the hydroxide ion can be extracted into the organic phase with the appropriate catalyst under PTC conditions.

This process affords an increased basicity of the hydroxide ion, relative to that of the hydroxide ion acting at the interface, and hence enables the abstraction of a proton from compounds of very low acidity. The intrinsic basicity of the relatively unsolvated hydroxide ion is much greater than that which can be achieved in a solvent such as water or alcohol. This property could be employed for H/D exchange studies as well as for many deuterated compounds. The increased basicity of the OH' or OD' ions is obtained by the employment of an organophilic catalyst, a hydrophilic counterion (to avoid catalyst poisoning), and very high concentrations of the aqueous base. In an ideal system the extracted OD' ion is followed by just a few molecules of D_2O as the NaOD pasty solution acts as a dessicant which "dries" the ion pair. This high base concentration should also promote the base into the organic phase used in neat form an increase of 5-10% was obtained (see Experimental Section). Not studied. This compound is rather insoluble in hexane, and therefore 1 mL of solvent was added.

The hydrogen–deuterium exchange of the substituted toluenes (Table I) shows the following trend. chloro-, bromo-, and iodotoluene afford relatively good yields (39–62%) when substituted in the para or meta position; however, para substitution affords lower yields (5–16%). o- or m-Fluorotoluene afford deuteration exchange in low yields (4% and 12%, respectively), whereas no exchange was detected with p-fluorotoluene. The fact that m-fluorotoluene exchanges to a higher degree is in accord with Streitwieser's reported studies of lithium cyclohexylamide in cyclohexylamine. 9-Nitrotoluene affords 80% H/D exchange of the methyl group, while p-nitrotoluene gave 40% and the meta isomer did not afford any exchange product.

An exchange experiment carried out on 2,4-dichlorotoluene afforded 42% of the deuterated compound. This observation emphasizes the small contribution of the p-chloro substituent to the enhancement of the substrate acidity. As a practical method for the preparation of compounds with a high degree of deuteration one can repeat the exchange procedure. In this manner repetition of the H/D exchange of, for example, o-bromotoluene enhanced the degree of exchange from 62% to 81%.

The greater H/D exchange of m-fluorotoluene is consistent with Klein's hypothesis that two groups in the

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* One run (hexane), percentage of exchanged methyl group protons of the isolated compound as estimated by 'H NMR. For liquid substrates used in neat form an increase of 5–10% was obtained (see Experimental Section). Not studied. 

meta position to each other are stabilized relative to the ortho and particularly to para isomers when the substituents carry interacting lone pairs with the aromatic ring. This stabilization is caused by a polarization which results in a charge alternation around the ring by donor–acceptor interactions. The results of both the fluorine and the nitro-substituted toluenes agree with this hypothesis since that nitrogen is an acceptor that stabilizes the system in the ortho and para positions. The results in Table I reflect two effects, one of them is the effect discussed above and the other one is a field effect exerted by the electron-negative substituent. The sequence of the reactivities of halogen–substituted toluene seems to follow the size of the halogen atom and its ability to disperse the charge withdrawn by the inductive effect.

The degree of exchange was deduced from the decrease in the respective resonance area of the proton spectrum relative to an internal standard which does not undergo such a process (aromatic protons or hexamethylbenzene). The position of the exchanged hydrogen and the degree of exchange of the methyl protons were elucidated from proton-decoupled $^{13}$C NMR spectra. The $^{1}J_{C-H}$ (as well as $^{3}J_{P-D}$) coupling pattern allowed for the assignment of the particular carbon atom which has undergone the process and the degree of exchange of its protons. The $^{1}H$ NMR spectrum of the substituted toluenes shows a mixture of starting material as well as mono- and diddeuterated products, as deduced from patterns composed of a triplet and quintuptet shifted to high field. Additional support to the exchange process is given by mass spectroscopy. Electron-impact spectra obtained on a GC/MS spectrometer showed evidence for the existence of deuterated molecules in representative cases.

The proton–deuterium exchange process was also carried out on aromatic halogen derivatives which have more than one methyl group. The introduction of an additional methyl group is expected to decrease the degree of the exchange. Reaction of neat 2-bromo-1,3-dimethylbenzene (1) (2-bromo-m-xylene) showed 45% deuterium exchange. The $^{1}H$ NMR spectrum shows a complex pattern of the methyl resonance at 2.36 ppm which is composed of a triplet and a quintuplet ($J = 2 \pm 0.3$ Hz) shifted to high field, thus pointing at a mixture of singly and doubly deuterated methyl groups. In the $^{13}$C NMR spectrum, the methyl singlet at 23.52 ppm is split in the exchanged molecule to an unsymmetrical pattern composed of five lines ($J = 19.3 \pm 1.6$ Hz), thus exhibiting that more than one hydrogen atom of the methyl group has been exchanged. However, reaction under the standard conditions (hexane solution) afforded only 14% of the deuterated product. Neat 1-bromo-2,4-dimethylbenzene (2) gave an overall exchange of 36%. The o-methyl group is deuterated to a higher extent relative to the para position (59% and 13%, respectively). The o- and the p-methyl singlets of 2 (2.31 ppm and 2.23 ppm, respectively) show a pattern composed of a triplet and a quintuplet ($J = 2 \pm 0.3$ Hz) shifted to high field. In the $^{13}$C NMR spectrum, the o-methyl group appears as a superposition of a triplet and a quintuplet, while the p-methyl appears as a triplet ($J = 19.3 \pm 1.6$ Hz). Here again, when the reaction is carried out in hexane solution at the standard conditions, the yield decreased significantly (11% total exchange, 16% at the ortho position and 5% at the para position).

Neat 1-bromo-2,4,6-trimethylbenzene (3) afforded only 13% of total exchange of the methyl group hydrogen atoms. In the $^{13}$C NMR spectrum, only the o-methyl group ($\delta = 23.36$ ppm) shows a split pattern ($J = 19.3 \pm 1.6$ Hz), thus showing that the p-methyl group did not undergo an exchange process. Reaction in hexane afforded only the starting materials. The introduction of an additional methyl group to the aromatic ring decreases the acidity to a greater extent. Therefore, 1-iodo-2,3,5,6-tetramethylbenzene (4) (iododurene) did not show any H/D exchange.

### Conclusion

A practical method for H/D exchange is obtained via extractive hydroxide ion initiated phase-transfer catalysis. The reaction of NaOD/D$_2$O system allows the easy production of compounds that otherwise would require very strong bases and appropriate solvents. The strong basicity of OD$^-$ ion is attributable to its relative freedom from water molecules when OD$^-$ is extracted into the depth of the organic layer.

### Experimental Section

**Materials.** Substituted toluenes, 2-bromo-1,3-dimethylbenzene, and 1-bromo-2,4,6-trimethylbenzene were prepared by standard procedures according to the literature. The catalyst tetrabutylammonium hydrogen sulfate (TBA)$\text{HSO}_4^{-}$ was purchased from Sigma Chemical Co. Sodium deuterioxide (NaOD) was prepared by a careful addition of sodium metal to D$_2$O under nitrogen atmosphere. Toward the end of the reaction heating is required. The past NaOD/D$_2$O solution was titrated with standard solution of HCl to show that the solution contained 65% w/w of NaOD.

**NMR Spectra.** The NMR spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.138 and 75.46 MHz for $^{1}H$ and $^{13}C$, respectively. The field/frequency stabilizations were maintained by locking to the solvent (CDCl$_3$) deuterium. The free induction decay signals were digitized and accumulated on an Aspect 1000 computer (Spectrospin/Novabiochem). The degree of exchange was obtained from the relative band areas before and after the process. In the substituted toluenes, the aromatic protons served as a internal standard. In other cases hexamethylbenzene (Fluka) served as internal standard.

### H/D Exchange Experiments. General Procedure

Unless otherwise stated, reactions were carried out in a standard reaction vial (55 mm high and 21 mm diameter) with strong magnetic stirring. The stirring bar was Teflon coated (10 mm long and 3 mm diameter). In a typical reaction 3 mmol of substrate were added to 0.5 mL of hexane, 0.6 mmol of catalyst (20 mol %), and 2.86 g of NaOD/D$_2$O was stirred at room temperature for 20 h, followed by three extractions with water, dried with MgSO$_4$, and filtered and the filtrate was evaporated to dryness under vacuum. These operations afforded a solution which is free from catalyst and its decomposition products.

**Reaction of 2-Bromo-1,3-dimethylbenzene (2-Bromo-m-xylene), 1.** Into the standard vial were added 0.785 g (4.24 mmol) of 1, 0.574 g (1.69 mmol, 40 mol %) of (TBA)$\text{HSO}_4^{-}$, and 2.55 g of NaOD/D$_2$O. The reaction mixture was stirred magnetically for 19 h at room temperature. The workup was carried out according to the standard procedure. In addition, the reaction was carried out also in a solvent under the previously described conditions: $^{1}H$ NMR $\delta 7.00$ (m, aromatic), 2.35 (superimposed, s, t, q, $^{3}J_{H-D} = 2$ Hz); $^{13}$C NMR $\delta 137.96$ (s), 127.42 (s), 126.40 (s), 22.99 (superimposed s, t, q, $^{J}_{C-H} = 19.3$ Hz).

**Reaction of 1-Bromo-2,4-dimethylbenzene (2).** A mixture of 0.827 g (4.47 mmol) of 2, 0.61 g (1.8 mmol, 40 mol %) of (TBA)$\text{HSO}_4^{-}$, and 2.86 g of NaOD/D$_2$O was stirred at room temperature with a magnetic stirrer in the standard vial for 23 h. The standard workup procedure was applied. In addition, this reaction

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was also carried out in a solvent: \(^1\)H NMR \(\delta_3 7.35\) (J\(_{AB} = 8.2\) Hz), \(\delta_2 6.8\) (J\(_{AB} = 8.2\) Hz, J = 1.96 Hz), 7.00 (d, J = 19.6 Hz), 2.27 (superimposed, s, t, q, J = 2 Hz), 2.27 (s), 2.19 (t, J = 2 Hz); \(^{13}\)C NMR \(\delta 137.19\) (a), 136.81 (a), 131.89 (a), 131.49 (a), 127.96 (a), 121.42 (a), 21.91 (superimposed, s, t, q, J = 19.3 Hz).

**Reaction of 1-Bromo-2,4,6-trimethylbenzene (2-Bromomesitylene, 3).** A mixture of 0.769 g (3.88 mmol) of 3, 0.525 g (1.54 mmol; 40 mol %) of (TBA)HSO\(_4\) and 5.370 g of NaOD/D\(_2\)O was stirred magnetically in the standard vial for 28 h at room temperature. The standard workup procedure was applied. The same reaction was also carried out in a solvent: \(^1\)H NMR \(\delta 6.76\) (s), 2.29 (s), 2.15 (s); \(^{13}\)C NMR \(\delta 137.57\) (a), 135.93 (a), 128.85 (a), 124.06 (a), 23.08 (superimposed, s, t, J = 19.3 Hz), 20.38 (s).

**Reaction of 1-Iodo-2,3,5,6-tetramethylbenzene (1-Iodo-

Magnesium in Methanol: Substitute for Sodium Amalgam in Desulfonylation Reactions

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Synthetic equivalents of acetylene in the Diels-Alder reaction are of special utility in view of the low reactivity of acetylene itself toward most dienes. Recently\(^1\) cis-and trans-1,2-bis(phenylsulfonyl)ethylenes (1, Ar = C\(_6\)H\(_4\)) have been recommended for this purpose, with eventual reductive elimination of the activating sulfone functions by treatment with sodium amalgam. In connection with a study of some general routes to substituted derivatives of ethenoanthracene 3, we examined the utility of cis- and

\[
\text{ArSO}_{2}\text{CH} = \text{CHSO}_{2}\text{Ar} 
\]

\(\text{trans-1 (Ar = p-C}_6\text{H}_4\text{C}_6\text{H}_4\)}\) in this system. In the initial Diels-Alder reaction trans-1 proved far more reactive than the corresponding cis isomer\(^2\) and was therefore used exclusively in this study. Not wishing to be faced, in expectation of eventual large-scale work, with the tedious handling of massive quantities of toxic metallic mercury, we devised a simple method of desulfonylation involving treatment of the appropriate bis(sulfone) with an excess of magnesium in methanol at 50 °C for several hours. Under these conditions adduct 2 gave 8 in 62% yield accompanied by 21% of the corresponding dihydro derivative 4. For comparison, under the same conditions the analogous dichloro compound 5 gave only 27% of 3.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{(C}_6\text{H}_4\text{SO}_{2}\text{)}_2\text{C}_6\text{H}_4 & \quad \text{R} \\
\text{R} & \quad \text{H} \\
\text{R} & \quad \text{R} \\
\text{C}_6\text{H}_5 & \quad \text{H} \\
\end{align*}
\]

The simplicity of this technique encouraged us to extend it to 1,1-bis(sulfones) as well as simple monosulfones. Application to 6a and 6b gave the expected hydrocarbons n-propylbenzene and n-butylbenzene in yields of 64% and 81%, respectively. Phenyl \(\beta\)-phenethyl sulfone gave ethylbenzene in 68% yield. The fate of the sulfonyl residues was not determined in any of these conversions. The magnesium turnings used in this study were activated by treatment with dilute hydrochloric acid. Turnings activated in this way were especially reactive in the Grignard reaction as well as these desulfonylation processes.

**Experimental Section\(^3\)**

(Z)-1,2-Bis[(4-methylphenyl)sulfonyl]ethene. Obtained by oxidation of the corresponding bisthio ether by the method of Truce and McManimie.\(^4\) The precursor was most simply prepared from vinylidene chloride by the technique of Truce and Boudakian\(^5\) except that refluxing the \(p\)-toluenethiol for a 4-day period with lithium isopropoxide in isopropyl alcohol took the place of the sealed tube reaction. The sulfone was obtained in an overall yield of 40%: mp 152–155 °C (lit.\(^4\) mp 149 °C); \(^1\)H NMR

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