that in these cases quenching only proceeds via the singlet encounter complex. Gijzeman et al.[6] assumed that intersystem crossing within the singlet complex was insignificant with respect to spin-allowed dissociative processes. This assumption is not necessarily valid and we have considered the possibility that the inefficient production of $^1\Delta_g$ which we have observed is in fact a result of such an intersystem crossing. In this event it is possible that the efficiency of intersystem crossing within the singlet encounter complex reflects that within the free sensitizer singlet; i.e., S_Δ should decrease with an increase in ϕ_{isc}. The data in Table II clearly show this to be the case. It would therefore appear that the factors which influence sensitizer intersystem crossing efficiencies may also influence the mode of decay of the corresponding singlet encounter complexes with oxygen. Further studies on this hypothesis are proceeding.

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(31) A referee points out that Garner and Wilkinson's data for $O_2^*(^1\Delta_g)$ yields sensitized by naphthalene and benzophenone are 1.05 and 0.56, respectively, different from the values of 0.5 and 0.4 found by us. He comments that the discrepancies may arise from insufficiently precise literature data for triplet–triplet extinction coefficients either for the sensitizers used by us or β-carotene used by Garner and Wilkinson. We agree with this observation but emphasize that, in both works, the ketone-derived yield was lower.

Carbon Acidity. 56. Equilibrium Acidities of 4-Methyl-, 4-Ethyl-, and 4-Isopropylbiphenyls with Cesium Cyclohexylamide[1]

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Abstract: *p*-Methylbiphenyl whose pK_{CsCHA} was reported previously to be 38.7 has been found to be incompletely converted to carbanion by cesium cyclohexylamide (CsCHA). The extinction coefficient for *p*-biphenylmethylcesium in CHA has been determined and the revised pK_{CsCHA} is 38.95. The same procedure applied to *p*-ethylbiphenyl and *p*-isopropylbiphenyl gives pK_{CsCHA} values of 38.8 and 38.6, respectively (all values statistically corrected). *p*-Methylbiphenyl had been used as an indicator for thiophene and methyldithiane and to provide an extrapolated acidity for toluene. The revised pK_{CsCHA} values are 38.2, 37.8, and 41.2, respectively.

p-Methylbiphenyl (pMB) occupies an important place in the scale of equilibrium hydrocarbon acidities. Its pK measurement[3] with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA), pK_{CsCHA}, represents the least acidic hydrocarbon whose equilibrium acidity is measured directly. As such, it is an important indicator that has been used for acidity measurements of some heterocyclic molecules (e.g., thiophene[4] and methyldithiane[5]). It forms a vital point in the Brønsted correlation of kinetic acidities with lithium cyclohexylamide[6] to provide an extrapolated pK_{CsCHA} of toluene. pMB is an indicator for that crucial region of the acidity scale accessible in the CsCHA system that lies beyond the observable realm of the Me_2SO system. We now report that our previous measurement of the pK_{CsCHA} of this compound is in error because of an unrecognized solvent-leveling effect. pMB is sufficiently close to solvent CHA in equilibrium acidity with the CsCHA base that it is incompletely converted to its cesium salt. We report corrected values together with the equilibrium

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Table I. Acidities of *p*-Alkylbiphenyls

Para substituent	Cesium salt		K	
	λ_{max}	ϵ	(eq 1)	pK_{CsCHA}[a]
Methyl	470	39200	68.8	38.95
Ethyl	482	33400	60	38.8
Isopropyl	493.5	17000	57	38.6

[a] Statistically corrected; per hydrogen.

constant for reaction 1. Similar measurements have also been made for *p*-ethylbiphenyl and *p*-isopropylbiphenyl in order to assess the effect of methyl substituents in these relatively nonacidic aromatic systems.

$$RH + C_6H_{11}NH^-Cs^+ \overset{K}{\rightleftharpoons} R^-Cs^+ + C_6H_{11}NH_2 \quad (1)$$

For a series of solutions with varying concentrations of initial pMB and added CsCHA, the absorbance was measured at 470 nm, the λ_{max} of the cesium salt of pMB (CsMB). The total base present at equilibrium, $[CsCHA]_e + [CsMB]_e$, was determined by addition of excess fluorene, a much more acidic hydrocarbon. To determine K_{eq} and the extinction coefficient ϵ we use the following procedure. We define an experimental extinction coefficient, ϵ_{exp}, as

$$\epsilon_{exp} = Abs/[RH]_0 l \quad (2)$$

where Abs is the experimental absorbance at 470 nm in a cell of length l of a solution containing the added hydrocarbon $[RH]_0$ and for which the added CsCHA is present in excess; e.g., $[CsCHA]_0 > [RH]_0$. For sufficiently acidic hydrocarbons $\epsilon_{exp} = \epsilon$. By a straightforward derivation it can be shown that

$$\epsilon = \left(1 + \frac{1}{K_{eq}[CsCHA]_e}\right)\epsilon_{exp} \quad (3)$$

where $[CsCHA]_e$ is now the value at equilibrium. For increasingly large concentrations of CsCHA the second term in parentheses in eq 3 becomes an ever smaller correction factor. Rearranging gives

$$\epsilon_{exp} = \epsilon - \frac{1}{K_{eq}} \cdot \frac{\epsilon_{exp}}{(CsCHA)_{eq}} \quad (4)$$

In an iterative procedure we calculate starting values of $[CsCHA]_{eq}$ for each solution and plot ϵ_{exp} vs. $\epsilon_{exp}/[CsCHA]_{eq}$. The intercept gives a first value of ϵ and the slope gives $1/K_{eq}$. From these we calculate the next approximations to ϵ and $1/K_{eq}$ and continue to self-consistency.

For points with excess hydrocarbon, i.e., $[RH]_0 > [CsCHA]_0$, the similar relationship, eq 5, holds.

$$\epsilon_{exp} = \epsilon - \frac{1}{K_{eq}} \cdot \frac{\epsilon_{exp}}{[RH]_{eq}} \quad (5)$$

The final iteration for pMB is shown in Figure 1. The extrapolated extinction coefficient of 39 200 is substantially higher than the value 21 400 reported previously.[2] Using the new value in the equilibrium studies of Chang[3] gives pK_{CsCHA} of 38.95 (per hydrogen) for pMB, 0.22 units higher than the previous value. The difference is relatively small because the logarithm is involved. Furthermore, we may note that the reference indicator used for determining the acidity of pMB, bis-2,4-dimethylphenylmethane has a pK_{CsCHA} sufficiently low (36.3) that the solvent acidity does not complicate the determination of its pK.

The new value changes slightly the value extrapolated for toluene from a Brønsted correlation of tritium exchange rates with LiCHA and pK_{CsCHA}.[6] The new value for toluene is 41.2, 0.3 units higher than the old value; the difference is of the order of the experimental error in the extrapolation.

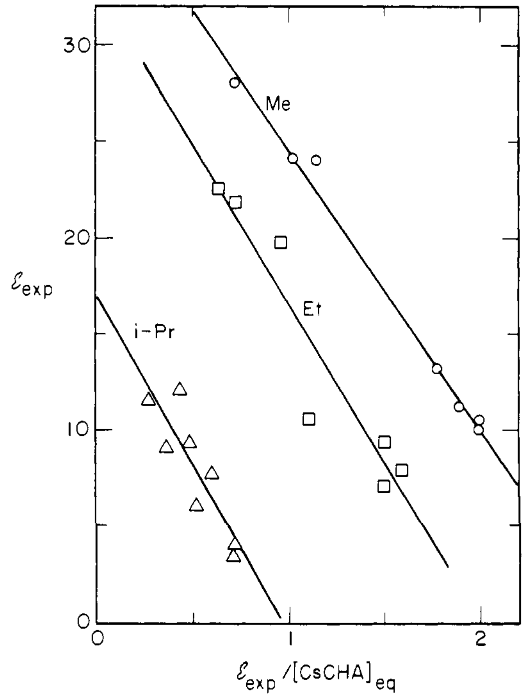

Figure 1. Plots of ϵ_{exp} vs. $\epsilon_{exp}/[CsCHA]_{eq}$ according to eq 4 for *p*-methyl-, *p*-ethyl-, and *p*-isopropylbiphenyl. The least-squares lines with standard deviations and correlation coefficients, r, follow (where $y = \epsilon_{exp}$ and $x = \epsilon_{exp}/[CsCHA]_{eq}$): methyl, $y = (39236 \pm 971) - (14538 \pm 612)x$, $r = 0.995$; ethyl, $y = (33431 \pm 2733) - (16770 \pm 2259)x$, $r = 0.95$; isopropyl, $y = (17020 \pm 2020) - (17592 \pm 3730)x$, $r = 0.87$.

pMB was used as the indicator for determining the pK_{CsCHA} of thiophene.[4] In the "single indicator" method used in this determination the concentration of cesium thiophenide is obtained from the decrease in absorbance resulting when thiophene is added to a mixture of pMB and its cesium salt. In correcting the previous results we note that for indicator and thiophene concentrations much higher than the total base concentration the changes associated with the indicator pMB pK and extinction coefficient cancel each other. The only significant change is that associated with the presence of CsCHA in solution. The corrected pK_{CsCHA} (per hydrogen) for thiophene is 38.18. Note that this value is slightly *lower* than the previously reported value of 38.42. Similar corrections apply to the pK_{CsCHA} values communicated previously for methyl- and ethyldithiane;[5] the revised values of 37.8 and 38.4, respectively, will be discussed in the full paper in preparation. The changes in all of the revised values are small and none of the conclusions drawn from the earlier results is altered.

The equilibrium constant for pMB in reaction 1 as derived from the slope in Figure 1 is 68.8 ± 2.9 M^{-1} for $K = [RCs]/[RH][CsCHA]$. This result can be expressed as a solvent acidity pK_{CsCHA} of 40.3 for cyclohexylamine in which the solvent concentration has not been included; that is, a small amount of an indicator having this pK_{CsCHA} would be half-converted to its cesium salt by 1 M CsCHA. If the solvent concentration is considered in the usual way, the statistically corrected pK_{CsCHA} for CHA in CHA is 41.6.

Mixtures of CsCHA with *p*-ethylbiphenyl and with *p*-isopropylbiphenyl were also studied in CHA in the same manner as was pMB. The results are included in Figure 1. These solutions were difficult to work with and the results show more scatter than for pMB; however, as summarized in Table I the results show reasonable trends. On a statistically corrected basis the more highly substituted groups are slightly more acidic than methyl. The differences are similar to those for fluorene and 9-methylfluorene both in CHA[8] and in

Me$_2$SO[9,10] or aqueous Me$_2$SO.[11] Since these differences remain so constant for hydrocarbons over a broad pK range, it seems likely that they would apply as well to the simple phenyl compounds; accordingly, using the pK_{CsCHA} for toluene derived above we deduce the following statistically corrected pK_{CsCHA} values: ethylbenzene, 40.9; cumene, 40.7. In these values methyl substitution has the effect of slightly increasing the acidity. We note that in kinetic acidities of these compounds, for example in exchange reactions with lithium cyclohexylamide, methyl substitution generally decreases reactivity.[12] The difference may involve steric hindrance effects in kinetic acidity or an effectively greater electron-donating effect of alkyl substituents in the pyramidal transition state.[13]

Finally, we recall that the pK_{CsCHA} values cited pertain to an equilibrium between cesium salts in cyclohexylamine where they are probably present as contact ion pairs. Absolute values are assigned for convenience by reference to a series of indicator carbon acids having delocalized carbanions. The relative acidities of these delocalized reference systems are approximately solvent independent and at the lower end have been related to aqueous solutions.[14] Within these limits the pK_{CsCHA} values for delocalized carbanions such as the *p*-alkylbiphenyls and toluenes may be expected to approximate values for the dilute aqueous standard state.

Experimental Section

Materials. 4-Methylbiphenyl (Aldrich) (pMB) was purified by column chromatography (silica gel, hexane) and sublimed, mp 47–48 °C. 4-Ethylbiphenyl was prepared by Wolff–Kishner reduction of *p*-acetylbiphenyl[15] but purified by column chromatography on silica gel (hexane eluent) followed by sublimation: mp 33–34.5 °C (lit.[16] mp 32–34 °C). 4-Isopropylbiphenyl was prepared by reaction of *p*-acetylbiphenyl with methylmagnesium iodide to give 2-(*p*-biphenylyl)-2-propanol[17] followed by hydrogenolysis in methanol over Pd/C and a few drops of perchloric acid. The product was chromatographed on silica gel (hexane eluent). The product is liquid at room temperature but crystallizes when chilled (lit.[18] mp 11 °C): NMR (CCl$_4$) δ 1.29 (6 H, t), 2.94 (1 H, sept), 7.1–7.65 (4 H, m).

Equilibrium Measurements. With normal techniques, difficulty was experienced in obtaining stable solutions of the cesium salts of the alkylbiphenyls especially in the presence of excess hydrocarbon. Addition of a few drops of stock CsCHA solution would give an initial color for the carbanion which would fade within seconds; addition of fluorene at this point showed by the color of fluorenylcesium produced that active base was still present. Extensive use of a Vacuum Atmospheres recirculating glovebox with an argon atmosphere ameliorated this problem. Solid hydrocarbons were weighed in a small tube and dissolved in CHA. The solution was transferred into a cell modified but similar to that described previously.[4] Quantitative transfer was monitored by testing the tubes and syringes with CsCHA solution for carbanion color. CHA was added followed by stock CsCHA solution. Two drops of the latter were added first to ensure the development of stable color. Additional CsCHA was then added until the desired color intensity was obtained. The spectrum was recorded at least twice at 15-min intervals to check color stability. Excess fluorene was then added from a stock solution and the spectrum was recorded. Even with all precautions a few runs gave spurious results and were discarded. The procedure with isopropylbiphenyl was modified because it is liquid at room temperature. A stock solution was made in CHA on a vacuum line and was used for the equilibrium studies.

The total base concentration was found from the absorbance of fluorenylcesium at $\lambda_{\max}$ 472 nm using ϵ 1200 and correcting for the change in volume in adding the fluorene stock solution. The CsCHA concentration at equilibrium was found from the equation $[\mathrm{CsCHA}]_{\mathrm{e}} = B_{\mathrm{T}} - A/l\cdot\epsilon_{\mathrm{i}}$, where B_{T} is the total base as determined by fluorene, A is the experimental absorbance in a cell of length l, and ϵ_{i} is the extinction used in the ith iteration. Hydrocarbon concentrations used were of the order of 10^{-3} M and B_{T} varied from 5×10^{-3} to 5×10^{-2} M. In several cases the hydrocarbon concentration was in excess over CsCHA and eq 5 was used in place of eq 4 for the experimental points summarized in Figure 1. Spectral measurements were determined on a Cary 118 spectrometer and pertain to approximately room temperature.

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