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Aggregation and Alkylation of the Cesium Enolate of 2-*p*-Biphenylylcyclohexanone[1]

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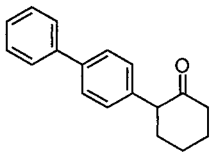
The cesium enolate of 2-biphenylylcyclohexanone (CsBPCH), generated by deprotonation of 2-biphenylylcyclohexanone with diphenylmethylcesium, is shown to be a mixture of monomer and dimer in THF, with a dimerization constant of 1.9×10^3 M^{-1}. The ion pair acidity corresponds to p$K = 19.30 \pm 0.05$. Even in the presence of excess dimer, only monomeric CsBPCH is found to react with methyl tosylate (MeOTs), methyl *p*-bromobenzenesulfonate (MeOBs), hexyl tosylate (HexOTs), hexyl bromide (HexBr) and *p-tert*-butylbenzyl chloride (BBCl). The relative reactivities of these alkylating reagents toward monomeric CsBPCH are BBCl, 1.00; MeOTs, 1.21; MeOBs 6.7; HexBr, 0.10; HexOTs, 0.050. $CsBPh_4$ has essentially no effect on the rates.

Introduction

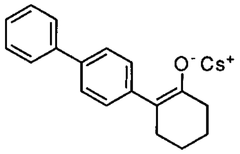
The alkylation of ketones is an important procedure for forming carbon−carbon bonds, especially in ethereal solvents such as THF. Recent studies have concentrated on regioselective reactions of ketones.[2] The counterion and the solvent,[3] as well as other factors, all might have a significant influence on the regioselectivity of the deprotonation of ketones. Recent reports from this laboratory have described the aggregation and reactivity of CsPhIBP, the cesium enolate of *p*-phenylisobutyrophenone,[4] and the lithium enolates of *p*-phenylisobutyrophenone (LiPhIBP)[4] and *p*-phenylsulfonylisobutyrophenone (LiSIBP).[5,6] In both of these cases, the enolate group is not directly conjugated to the aromatic ring. The cesium enolate of 2-phenylcyclohexanone (CsPCH) does involve such conjugation; it has been shown recently to form monomers and dimers in dilute THF solution, and again, alkylation reactions of the monomer dominate.[7] The present paper concerns the cesium enolate (CsBPCH) of 2-*p*-biphenylylcyclohexanone (BPCH), in which conjugation is more extensive than in CsPCH. As a result of the conjugation of the enolate oxygen with the aromatic ring, this enolate is less basic than the others; consequently, we considered it important to determine its tendency to aggregate and the role of any such aggregates in reactivity. A related study of the corresponding lithium enolate, LiBPCH, is being submitted separately.[8] BPCH involves tertiary and secondary enolic protons; we note, for example, that 2-methylcyclohexanone is frequently used as an example in discussions of enolate ion stability.[9,10]

Results and Discussion

Spectra and Aggregation of CsBPCH. The cesium enolate of 2-*p*-biphenylylcyclohexanone (CsBPCH) was generated by deprotonation of the ketone (BPCH) with diphenylmethylcesium (CsDPM). The deprotonation was monitored by using biphenylyldiphenylmethane (BDPM) as an end point indicator; BDPM is much less acidic than the BPCH, and its anion is brightly colored. The conjugated enolate was obtained directly by deprotonation of the ketone with a cesium base. This behavior differs from that for deprotonation with a lithium base; in that case, the unconjugated enolate is formed preferentially and more slowly converts to the conjugated lithium enolate in the presence of ketone.[8] In the present case, the unconjugated cesium enolate is probably also formed but converts so rapidly to the conjugated enolate that it is never detected.



BPCH



CsBPCH

UV spectra of CsBPCH were obtained by deconvoluting the spectral mixture of CsBPCH and CsBDPM, and a series of UV spectra of CsBPCH at different concentrations were then obtained by dilution with THF. The λ_{max} of CsBPCH was found to vary with concentration, from 404.0 nm in more concentrated solutions to 413.0 nm in dilute solution. These changes are shown in Table S1 and Figure S1 (Supporting Information). When all the spectra are normalized to a common concentration, an isosbestic point appears at 404.0 nm, as shown in Figure S2 (Supporting Information). The extinction coefficient at

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(1) Carbon Acidity. 108.

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(10) *Carbon−Carbon Bond Formation*; Caine, D., Ed.; Plenum: New York, 1988.

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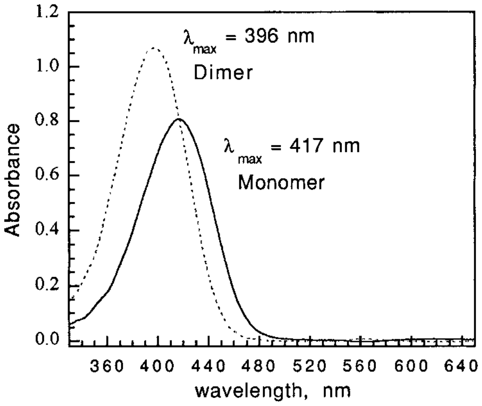

Figure 1. Spectra of monomer and dimer from SVD.

the isosbestic point is more useful than the extinction coefficient at λ_{max}, because it keeps the same value during the change of concentration and wavelength. The extinction coefficient at 404.0 nm obtained by a plot of the absorbance divided by path length vs the formal concentration of the enolate, denoted as {CsBPCH}, is 24 800 (Figure S3, Supporting Information).

The existence of an isosbestic point implies that there are two principal components with different spectra, whose relative concentrations change with a change in the formal concentration of CsBPCH. The spectra featured in Table S1 (Supporting Information) for two runs were digitized at 0.5 nm intervals and subjected to singular value decomposition (SVD) as in our previous analyses.[4,11,12] This procedure gave spectra of two components characterized as monomer and dimer with λ_{max} 417.0, 399.0 and 416.0, 396.5 nm, respectively, for the two series of measurements. The two sets of monomer and dimer spectra were used to analyze each of the composite spectra into the two components. The concentration of monomer present in each solution is also given in Table S1 (Supporting Information). We have shown recently that SVD can contain systematic errors,[4,12] and we further checked the data by plotting λ_{max} against the fraction monomer in solution. The two sets of data give linear correlations that are remarkably similar (Figure S4, Supporting Information). We take the average value of the λ_{max} as monomer, 417 nm, and as dimer, 396 nm, for the spectra shown in Figure 1.

The equilibrium constant between monomer and dimer, $K_{1,2}$, is defined by eqs 1−3 in which {CsBPCH} is the formal enolate concentration.

$$2\ \text{Monomer} = \text{Dimer} \tag{1}$$

$$K_{1,2} = [\text{Dimer}]/[\text{Monomer}]^2 \tag{2}$$

$$[\text{Monomer}] + 2[\text{Dimer}] = \{\text{CsBPCH}\} \tag{3}$$

A plot of [Dimer] vs [Monomer]^2 (Figure S5 from the data in Table S1, Supporting Information) gives an excellent straight line with $K_{1,2} = 2495 \pm 9\ \text{M}^{-1}$. From our past experience, the precision is higher than the accuracy (vide infra).

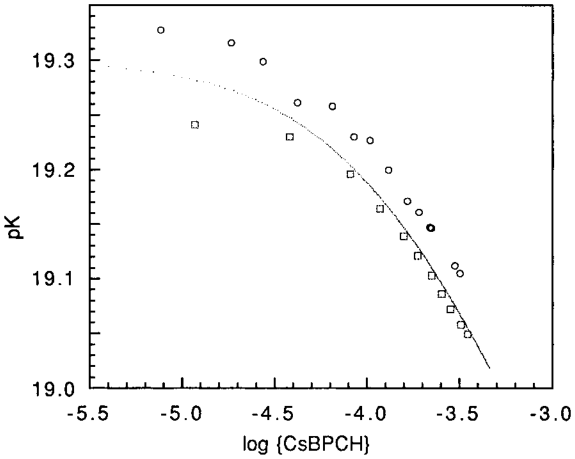

Figure 2. Small points show the calculated pK for $K_{1,2} = 1900$ M^{-1} and pK_o = 19.30. Squares are experimental pK vs DMAPhFl as indicator; circles are vs BiphFl as indicator.

Ion Pair Acidity. The ion pair acidity is defined by eq 4 relative to an appropriate indicator in the proton-transfer equilibrium, eq 5. The indicator ion pair scale for cesium salts in THF was published earlier.[13]

$$\text{p}K(\text{RH}) - \text{p}K(\text{Ind-H}) = -\log K \tag{4}$$

$$\text{RH} + \text{Ind}^- \text{Cs}^+ \overset{K}{\rightleftharpoons} \text{R}^-\text{Cs}^+ + \text{Ind-H} \tag{5}$$

The cesium ion pair acidity of BPCH was measured against the indicators 9-dimethylaminophenylfluorene (9-DMAPhFl, λ_{max} = 376 nm, ϵ_{max} = 28 700, pK = 19.28) and 9-biphenylylfluorene (9-BpFl, λ_{max} = 455 nm, ϵ_{max} = 29 400, pK_a = 17.72).[13] The equilibrium 5 is defined for the monomer; any aggregation reduces the concentration of the monomer below the formal concentration of the substrate and reduces the apparent pK of the substrate. It is this combination of the proton-transfer equilibrium with the aggregation equilibrium that we refer to as *coupled equilibria*.

For the pK measurements using 9-DMAPhFl as indicator, the concentrations of CsBPCH, CsDMAPhFl, BPCH, and DMAPhFl, the equilibrium constant K_{ob}, and the calculated pK are listed in Table S2 (Supporting Information). As shown in Figure 2, the experimental pK reaches an asymptote in dilute solutions and is lower at higher concentrations of the enolate. As shown previously, a plot of K_{ob} vs {enolate}/K_{ob} is linear for a monomer−dimer equilibrium with an intercept equal to K_o and a slope equal to $2K_{1,2}K_o{}^2$.[11] Such a plot is shown in Figure S6 (Supporting Information) and gives K_o = 0.99 (pK_o = 19.28) and $K_{1,2}$ = 1732 M^{-1}.

A similar set of runs was done with 9-biphenylylfluorene to give the data shown in Table S3. The variation of pK with enolate concentration is similar to that determined with the other indicator (Figure 2). A plot of K_{ob} vs {enolate}/K_{ob} gives a linear correlation (Figure S7, Supporting Information) from which K_o = 0.024 (pK_o = 19.33) and $K_{1,2}$ = 1886 M^{-1}. The two determinations are mutually consistent and give an average pK for the monomeric enolate as 19.30 with an estimated error of about ±0.05 pK units. The two $K_{1,2}$ values agree well with each other but differ significantly from that derived by

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(11) Krom, J. A.; Petty, J. T.; Streitwieser, A. *J. Am. Chem. Soc.* **1993**, *115*, 8024−30.

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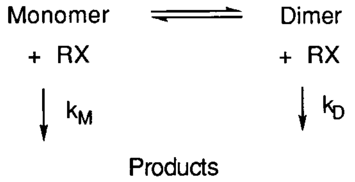
SVD. The values derived from the pK measurements are probably more accurate, and we take as the best value $K_{1,2} = (1.9 \pm 0.2) \times 10^3$ M^{-1}. Figure 2 also shows the pK as a function of log{CsBPCH} calculated using this value of $K_{1,2}$ and pK_o = 19.30; the difference from experiment is of the order of hundredths of a pK unit and less than the estimated experimental error. For comparison, for the cesium enolate of 2-phenylcyclohexanone (CsPCH), $K_{1,2}$ is 1.8×10^3 M^{-1}.[7] The two equilibrium constants are the same within experimental error, and the additional conjugation in CsBPCH has little effect on $K_{1,2}$.

Temperature Effects. To measure the effect of temperature on aggregation, a series of spectra were taken on a set of nine solutions ranging in concentration from 1.4×10^{-4} to 9.1×10^{-4} M. Data at the highest concentration was not used because its absorbance values were above 2. Spectra were taken on each solution at 5° intervals from 25 to 0 °C. The results are summarized in Table S4 (Supporting Information). The spectra changed very little over this range. The isosbestic point remained at 404.0 nm, and the extinction coefficient, corrected for the density change in the THF, increased by less than 4%. SVD was applied to each set of temperature results and gave consistent results; $\lambda_{\max}$ of the monomer varied from 415.0 to 417.5 nm, and that for the dimer ranged from 396.0 to 398.0 nm. The resulting monomer and dimer spectra were used to analyze each solution for the two components, and plots of [dimer] vs [monomer]^2 gave good linear correlations. The resulting $K_{1,2}$ values are summarized in Table S4 (Supporting Information). The value at 25 °C, 2209 M^{-1}, is slightly lower than that obtained from the more extensive spectral study above but is actually closer to the value obtained from the acidity equilibria. For self-consistency, only the values obtained from the temperature study, which showed a decrease of 13% over a 25 °C range, were used to compute the thermodynamic properties, $\Delta H° = 0.67 \pm 0.46$ kcal mol^{-1} and $\Delta S° = 17.5 \pm 1.6$ eu. The errors are given as the standard deviations of the temperature coefficients and do not include possibly substantial systematic errors. Nevertheless, these results reflect the small temperature effects on the spectra and indicate that the dimerization process is slightly endothermic. The entropy term shows that this dimerization is entropy-driven, undoubtedly from loss of solvation of Cs$^+$ on dimerization. The numbers differ little from those of the corresponding lithium enolate, LiBPCH,[8] and show that solvation even of the large cesium cation is important in THF. Finally, taking $K_{1,2} = 1900$ M^{-1} as the best value at 25 °C, the temperature effect measured above was applied to this value to obtain the best values of $K_{1,2}$ at the other temperatures. These values are listed in the final column of Table S4 (Supporting Information) and were used below to calculate monomer concentrations at various temperatures.

Alkylation Reactions. The information above on aggregation equilibria was combined with kinetic studies of alkylation reactions to determine the relative roles of monomer and aggregate in such reactions. In the kinetic studies, a large excess of alkyl sulfonate or halide was added to the enolate solution, and the decrease in enolate absorbance was followed for about 10% reaction. Under these conditions, the initial slopes are linear and when divided by the extinction coefficient become −d{CsBPCH}/d*t*. The time unit used is the second. Alkylations of CsBPCH were carried out with methyl tosylate (MeOTs), methyl *p*-bromobenzenesulfonate (MeOBs), hexyl tosylate (HexOTs), hexyl bromide (HexBr), and *p*-*tert*-butylbenzyl chloride (BBCl). The kinetic data are given in Tables S5−10 (Supporting Information).

Four sets of runs with MeOTs are summarized in Table S5. In the first set, 11 runs at a fixed concentration of CsBPCH = 5.28×10^{-4} M and [MeOTs] varying from 4×10^{-3} to 2×10^{-2} M give a plot of log rate vs log[MeOTs] that is linear with a slope of 1.06 ± 0.04 showing, as expected, that the reaction is first order in alkylating agent. For several of the other compounds also, the CsBPCH concentration was held constant and that of the alkylating agent was varied. In all cases, a plot of log rate vs log[RX] was linear with a slope close to unity, showing that all of these alkylation reactions are first order in [RX]. A comparable plot for two sets of runs with [MeOTs] constant at 0.0105 M and {CsBPCH} varying from 8.0×10^{-5} to 7.4×10^{-4} M is also linear but with a slope of 0.63, indicating that the monomer and dimer present in these mixtures react at different rates. Similar results were obtained for the other alkyl halides and sulfonates studied. We have shown previously that such kinetics can be analyzed conveniently by dividing the total reaction in eq 6 by [Dimer] to give eq 7,[5] a linear equation in which the slope gives k_M and the intercept is k_D.



$$\text{Rate} = k_M[\text{Monomer}][\text{RX}] + k_D[\text{Dimer}][\text{RX}] \quad (6)$$

$$\text{Rate}/[\text{RX}][\text{Dimer}] = k_M[\text{Monomer}]/[\text{Dimer}] + k_D \quad (7)$$

The concentrations of enolate, {CsBPCH}, were converted to the corresponding concentrations of monomer and dimer using $K_{1,2} = 1900$ M^{-1}. The corresponding plot for the data in Table S5 gives a negative intercept of −0.13 and a slope of 0.54 (Figure S8, Supporting Information). For this plot, we deleted data for [Monomer]/[Dimer] greater than 3. The results indicate that the monomer is more reactive than the dimer. Accordingly, the rate should be first order in [Monomer]. Figure 3 shows that a plot of the initial rate divided by [MeOTs] is linear with a slope through the origin of $k_M = 0.46 \pm 0.01$ M^{-1} s^{-1}. This plot includes the data of run set 4, in which dilute solutions of CsBPCH (down to 1×10^{-5} M, in which the enolate is almost all monomer), were run in 1 cm rather than 1 mm cells; nevertheless, the results of this run are consistent with the others.

Similar results were obtained for other alkyl halides. In all cases, the intercept was slightly negative. We take these results to mean that in all cases the rate constant for the dimer is effectively zero and that the negative intercepts are an indication of small systematic errors. In all cases, plots of rate/[RX] vs [monomer] are linear; the slopes are k_2 (Figures S9−12, Supporting Information). The derived second-order rate constants are listed in Table 1.

Rates with MeOTs were also run at 5° intervals down to 0 °C, with the results summarized in Table S6 (Supporting Information). The initial slopes for absorbance

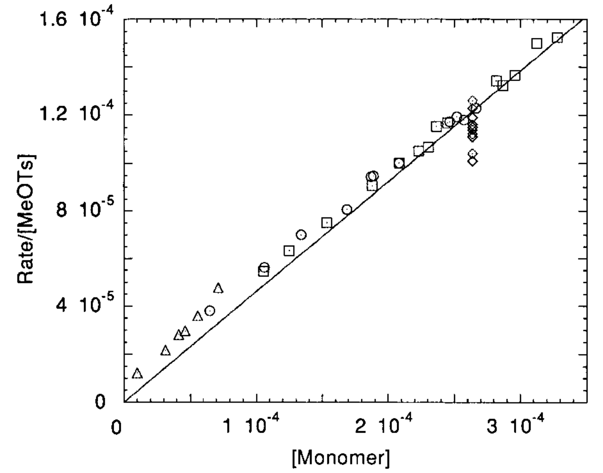


Figure 3. A plot of initial rate/[MeOTs] vs [Monomer]. The line shown uses all of the points and has a slope of 0.460 ± 0.005. Diamonds are run 1, squares are run 2, circles are run 3, and triangles are run 4 in Table S5.

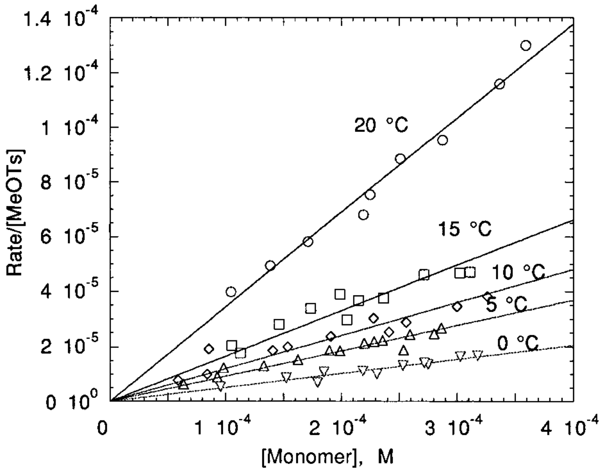


Figure 4. Rates of reaction of MeOTs with CsBPCH monomer at several temperatures. The slopes of the lines shown are 20°, 0.345 ± 0.006, 15°, 0.165 ± 0.005; 10°, 0.120 ± 0.005; 5°, 0.0924 ± 0.002; 0°, 0.0513 ± 0.00146 M^{-1} s^{-1}.

Table 1. Second-Order Rate Constants for Reaction of Monomeric CsBPCH with Alkyl Halides and Sulfonates in THF at 25 °C

RX	k_2, M^{-1} s^{-1}
methyl tosylate (MeOTs)	0.46
methyl brosylate (MeOBs)	2.56
p-tert-butylbenzyl chloride (BBCl)	0.38
hexyl bromide (HexBr)	0.039
hexyl tosylate (HexOTs)	0.019

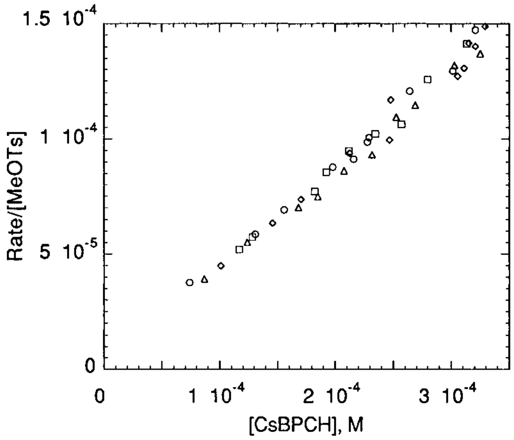


Figure 5. Rates of reaction of 0.010 55 M MeOTs with monomeric CsBPCH in the presence of varying amounts of $CsBPh_4$. Lines through the origin that give the rate constants as slopes are not shown for clarity but are summarized as follows: circles, $[CsBPh_4] = 6.87 \times 10^{-5}$ M, $k_2 = 0.443 \pm 0.005$ M^{-1} s^{-1}; squares, $[CsBPh_4] = 1.50 \times 10^{-4}$ M, $k_2 = 0.440 \pm 0.005$ M^{-1} s^{-1}; diamonds, $[CsBPh_4] = 5.58 \times 10^{-4}$ M, $k_2 = 0.436 \pm 0.006$ M^{-1} s^{-1}; triangles, $[CsBPh_4] = 5.99 \times 10^{-3}$ M, $k_2 = 0.423 \pm 0.004$ M^{-1} s^{-1}.

changes were converted to $-d\{CsBPCH\}/dt$ using the extinction coefficients in Table S4 (Supporting Information), and concentrations were corrected for density changes in THF. Plots of the rates divided by [MeOTs] vs [Monomer] (calculated from the "corrected" $K_{1,2}$ values in Table S4) are shown in Figure 4. The data give excellent straight lines from which the second-order rate constants are given as the slopes. The resulting rate constants (summarized in Figure 4) give a good linear plot of $\ln k_2$ vs $1/T$ (Figure S13, Supporting Information) from which $\Delta H^{\ddagger} = 13.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14.9$ eu. These numbers appear to be of reasonable magnitude; for example, less extensive results with the cesium enolate of *p*-phenylisobutyrophenone, CsPhIBP, gave $\Delta H^{\ddagger} = 10.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17$ eu.[4]

CsPhIBP monomer ($pK = 25.1$) is both more basic than CsBPCH ($pK = 19.3$) and more reactive toward MeOTs (relative rate = 32) at 25 °C, but these numbers correspond to a Brønsted β-value of only 0.26. The corresponding relative rate for BBCl is 8.4, and this Brønsted β-value is even lower at 0.16. A comparison with CsPCH is perhaps more meaningful because the steric environment at the enolate center is the same for both. CsPCH is more basic by $\Delta pK = 0.5$ p*K* units and more reactive toward BBCl by a factor of 1.44; $\Delta \log k_2 = -0.16$ and the corresponding Brønsted β-value is 0.3. The low β-values probably arise because the ion pair distance effectively increases in the displacement reaction transition state; thus, the effect of changing conjugation is diluted by this effect of charge separation. This effect is even stronger for the corresponding lithium enolates where the less conjugated and more basic enolate is *less* reactive in alkylation.[8]

MeOBs is 5.6-fold more reactive than MeOTs toward CsBPCH in THF; for comparison, the relative solvolysis rate of MeOBs and MeOTs in ethanol at 70 °C is 3.4.[14] Few data are available for other comparisons in the literature, but Zook and Rellahan[15] report that benzyl chloride is 8.8 times as reactive as ethyl bromide toward the sodium enolate of butyrophenone in ether, a number of similar magnitude to our rate ratio for BBCl/HexBr in THF of 10.

To test the role of free ions, several kinetic runs with MeOTs were carried out in the presence of cesium tetraphenylborate. If free ions are involved in equilibria that would produce free cesium cations, the presence of $CsBPh_4$ would be expected to reverse these equilibria and lead to lower rates. In fact, as the data summarized in Table S11 (Supporting Information) and Figure 5 show, $CsBPh_4$ has little effect on the rate of reaction. Free ions

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(14) Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *75*, 2700.

(15) Zook, H. D.; Rellahan, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 881–6.

are clearly not involved in these reactions; that is, these alkylations are ion pair displacement reactions. This result leads to a further inference. The cesium enolates correspond to ion pair p*K*'s (referred to cesium salts of delocalized indicators) that are only slightly smaller (~1−2 units) than the ionic p*K*'s of the ketones in DMSO.[7] Accordingly, the dissociation constant of CsBPCH to free ions in THF should be only correspondingly lower than that of the indicator salts, or of the order of 10^{-10} M.[13] Thus, a solution of 10^{-4} M CsBPCH, the magnitude used in many of the kinetics experiments, would contain on the order of 0.1% free ions. Because free ions are not importantly involved in the alkylation reactions, the free enolate anions cannot be orders of magnitude more reactive than the monomer cesium enolate ion pairs.

Preparative scale reactions were carried out with BBCl, MeOTs, and HexBr, and the products were separated by chromatography and identified. Only the products of C-alkylation at the tertiary enolic position could be found; in particular, no products of O-alkylation or reaction at the secondary (unconjugated) enolate position could be detected. This result contrasts with that of the more basic CsPhIBP, which gave products of both C- and O-alkylation.[4]

Conclusion

The cesium enolate of BPCH, CsBPCH, is generated directly in THF by reaction of the ketone with a cesium base. Its UV−vis spectrum varies with concentration and shows an isobestic point at 404.0 nm with an extinction coefficient of 24 800. Singular value decomposition analyses and coupled equilibria with proton-transfer reactions of indicators show that CsBPCH is a mixture of monomer and dimer ion pairs at concentrations from 10^{-5} to 10^{-3} M, with $K_{1,2} = 1.9 \times 10^3$ M^{-1} and $\lambda_{max} = 417$ and 396 nm, respectively. Alkylation reactions (relative rate) with *p-tert*-butylbenzyl chloride, BBCl (1.00), MeOTs (1.21), MeOBs (6.7), hexyl tosylate (0.050), and hexyl bromide (0.10) are first order in alkylating agent and first order in the enolate monomer; that is, the monomer has a substantially higher rate constant than the dimer. Preparative scale reactions of CsBPCH with MeOTs, TBBCl, and hexyl bromide showed only products of C-alkylation at the conjugated enol position, for example, 2-alkyl-2-biphenylylcyclohexanones. Although the monomer is clearly more reactive than the dimer, probably by at least an order of magnitude, no further limit on this ratio can be set. One limitation in the use of UV spectra, as in this study, results from the high extinction coefficient of the conjugated enolate, which requires dilute solutions for accurate spectrometry even with the use of 1 mm cells. Such dilute solutions contain substantial amounts of monomer that dominate the smaller contribution to reaction of the dimer.

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Supporting Information Available: Experimental Section, Tables S1−11, figures S1−13. This material is available free of charge via the Internet at http://pubs.acs.org.

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