

An Assessment of the Causes of the "Cesium Effect"

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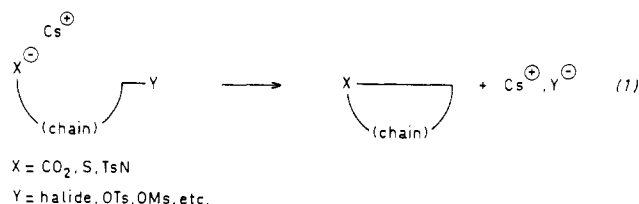
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Cesium alkanoates (chiefly the propionate) have been investigated for their solubility, nucleophilic reactivity, and degree of ion pairing in dimethylformamide (DMF) and, in some cases, dimethyl sulfoxide (DMSO) solutions. ^{133}Cs NMR has been used to establish the degree of ion pairing. From the data obtained it is concluded that the cesium ion is virtually completely solvated and that the carboxylates are essentially free and highly reactive. The consequences of this effect on macrocyclization by means of nucleophilic substitution are discussed.

Introduction

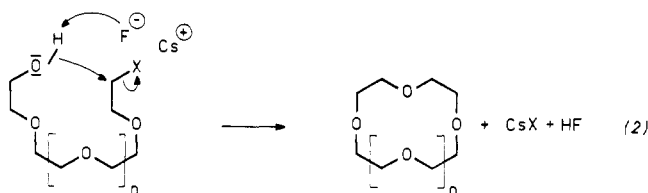
The cesium salts of some weak organic acids are useful for synthetic purposes. These are readily obtained on reaction with cesium carbonate, the most basic of the alkali carbonates of the group I metals.¹ Carboxylic acids,² phenols,³ thiols,⁴ sulfonamides,⁵ some ureas,³ and 1,3-dicarbonyl compounds⁶ are deprotonated to form the corresponding cesium salts. The choice of cesium carbonate rests on practical considerations, particularly the ease of handling and low hygroscopicity relative to the hydroxide.

These cesium salts, usually dissolved in a dipolar aprotic solvent like dimethyl formamide (DMF), exhibit reactivity characteristics that have been dubbed the "cesium effect".^{7,8} This term is used nowadays with reference to either or both of two different synthetic phenomena. As first employed, the term applied to the readiness with which cesium carboxylates dissolved in DMF could be alkylated with alkyl halides.² This approach is used to anchor the carboxylate end of a peptide to be synthesized by the Merrifield method to benzyl chloride entities in a polystyrene polymer.⁷⁻⁹ Cesium carboxylates, (thio)phenolates, thiolates, and amides subsequently have been shown to be well suited for $\text{S}_{\text{N}}2$ displacement on primary and secondary halides, mesylates, and tosylates.^{10,11} Even for racemization prone compounds clean $\text{S}_{\text{N}}2$ inversion can usually be realized. But "cesium effect" refers also to a more spectacular phenomenon. As illustrated schematically in eq 1, many macrocycles, often those with very large rings and relatively apolar chain components, can be obtained by ring closure via an intramolecular anionic $\text{S}_{\text{N}}2$ substitution of an appropriate precursor.^{4,5,12} Inter-



molecular substitution is suppressed relative to the intramolecular process. Extensive synthetic applications of this effect have been made.¹³

A related observation is summarized in eq 2. Very large (20-30-membered) macrocycles with extensive sections composed of polyethylene glycols are formed in remarkably good yields in the presence of cesium fluoride.¹⁴ The



powerful hydrogen bond forming potential of fluoride clearly aids in activating the hydroxyl group as a nucleophile,¹⁵ and the cesium ion, relative to other alkali metal cations, appears to direct the reaction in an intramolecular fashion.

Although these two sorts of "cesium effect" both involve $\text{S}_{\text{N}}2$ nucleophilic substitutions, there are fundamental differences between the types of reactions involved. The effectiveness of intramolecular ring closure is governed by the effective molarity (E.M.), $k_{\text{intra}}/k_{\text{inter}}^{-1}$. For structurally unappended macrocyclic rings with 13 or more members E.M. values of roughly 5×10^{-2} M are typical.¹⁶ However,

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Table I. Solubilities ($\times 10^{-2}$, mol L $^{-1}$) of Alkali Metal Propionates^a

salt	solvent		
	MEK	DMF	DMSO
Cs ⁺ , -O ₂ CC ₂ H ₅	1.02	12.4	>100
Rb ⁺ , -O ₂ CC ₂ H ₅	0.42	3.55	22.6
K ⁺ , -O ₂ CC ₂ H ₅	0.06	0.46	3.87
Na ⁺ , -O ₂ CC ₂ H ₅	0.03	0.25	3.24

^a Measured at 51 °C by a conductometric technique.

Table II. Substitution on Mesylate of 2-Octanol (1) by Propionate Salts^a

cation	yield of 2, % ^b	material balance, % ^c
Na ⁺	76	84
K ⁺	81	81
Rb ⁺	97	97
Cs ⁺	98	98

^a Initial concentration of 1, 7×10^{-2} M; concentration of propionate, 0.27 M; reaction time, 24 h. ^b As determined by ¹H NMR spectroscopy; percentage calculated on the basis of the total amount of 1. ^c Total 1 + 2 after workup divided by initial 1; missing material is octene, which could not be isolated.

that ion pairing can have an effect on macrocyclization has been demonstrated quantitatively for the case of benzocrown ether formation by Mandolini et al.¹⁷ for dilute (about 10^{-2} M) homogeneous solutions in 99% DMSO/1% H₂O.

For the case of cesium reactions experimental complications occur because at synthetically useful concentrations [(1–5) $\times 10^{-2}$ M] reaction mixtures are in some cases not entirely homogenous under synthetic conditions; at practical concentrations the eventual precipitation of cesium halide, tosylate, etc. during the course of reaction will ensure heterogeneity at some stage.

These experimental observations with cesium salts are of demonstrated synthetic usefulness. What lies behind this behavior? Are there special properties attributable to the cesium ion that account for these phenomena?

Results and Discussion

A. Solubility. We have described the synthetic usefulness of cesium propionate as an oxygen nucleophile.^{10a} Solubilities in methyl ethyl ketone (MEK), DMF, and dimethyl sulfoxide (DMSO) are given in Table I. The solubilities were determined from plots of conductivity against concentration of salt and are defined as the inflection points on the curves so obtained. The cesium salts in dipolar aprotic solvents are at least four times more soluble than their rubidium counterparts.

No attempt was made to study quantitatively the effect of structural change in the carboxylate ion solubility. Qualitatively both cesium acetate and cesium benzoate are more soluble than the propionate; the acetate is, however, more hygroscopic.

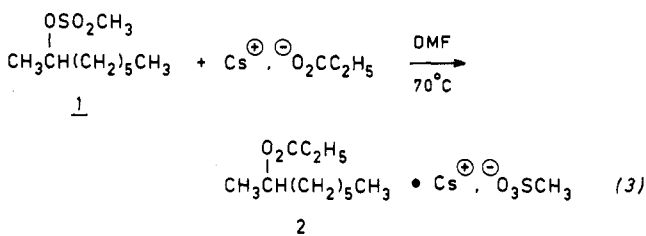
B. Intermolecular Substitution Reactions. The propionates discussed above were allowed to react with the mesylates of several secondary alcohols. The reaction mixtures were worked up as carefully as possible to avoid loss of material and the compositions were determined by ¹H NMR spectroscopy. Yields were determined in duplicate and are accurate to within $\pm 3\%$. Results for sub-

Table III. Substitution on Mesylate of Cyclohexanol (3) by Propionate Salts^a

cation	solvent	yield of 4, % ^b	material balance, % ^c
Na ⁺	MEK	30	84
K ⁺	MEK	43	77
Rb ⁺	MEK	54	78
Cs ⁺	MEK	50	86
Na ⁺	DMF	<i>d</i>	<i>d</i>
K ⁺	DMF	31	80
Rb ⁺	DMF	68	93
Cs ⁺	DMF	98	98
Na ⁺	DMSO	69	95
K ⁺	DMSO	52	52
Rb ⁺	DMSO	70	94
Cs ⁺	DMSO	92	94

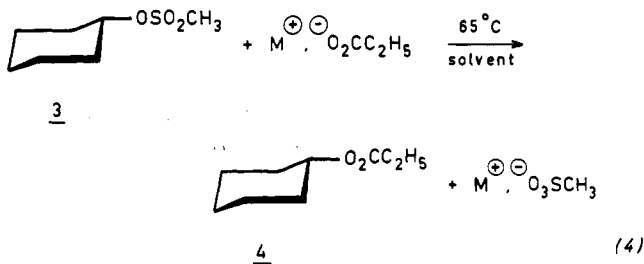
^a Initial concentration of 3, $2.5 \cdot 10^{-2}$ M; concentration of propionate, 0.1 M; temperature, 65 °C; reaction time, 24 h. ^b As determined by ¹H NMR spectroscopy; percentage calculated on the basis of the total amount of 3. ^c Total 3 + 4 after workup divided by initial 1; missing material is cyclohexene, which could not be isolated. ^d No reaction occurs owing to poor solubility of sodium propionate.

stitution on the mesylate of (racemic) 2-octanol (1) (eq 3) in DMF as solvent are given in Table II. Complete in-



version of configuration (S_N2 reaction) occurs on substitution with cesium propionate.^{10a} The balance of the missing material, especially for reactions with sodium and potassium salts, is octene, which evaporated with the DMF during workup. At 70 °C the reaction with cesium propionate was just homogenous, and those with other salts were not.¹⁸

The mesylate of cyclohexanol was also examined in various solvents (eq 4). The problem of solubility was again acute, and in all cases in MEK and for the sodium and potassium propionates in DMF and DMSO, the reaction mixtures were heterogeneous. Missing material is



cyclohexene, which evaporated on removal of the solvents. Results are given in Table III. Isolated product mixtures consisted therefore of 4 and any unreacted 3. It is clear that cesium propionate in DMF or DMSO under these conditions leads to results better than obtained with other salts under otherwise identical concentrations and temperatures.

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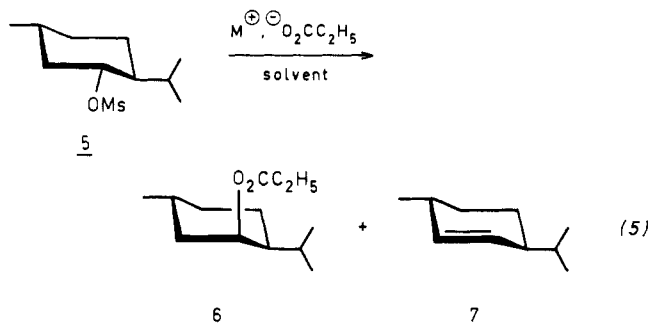
(18) The data given are not kinetic comparisons but synthetic. Systems are compared at identical concentrations, the consequence of which is that some salts only partially dissolve. Even in the case of the cesium salt reactions, the reaction mixture becomes heterogeneous during the course of the conversion owing to precipitation of the cesium salt of the leaving group.

Table IV. Substitution on Mesylate of (-)-Menthol (5) by Propionate Salts^a

cation	solv	yield of 6, % ^b	yield of 7, % ^b	material balance, % ^c
Na ⁺	DMF	14	0	66
K ⁺	DMF	21	12	98
Rb ⁺	DMF	46	27	98
Cs ⁺	DMF	59	29	88
Na ⁺	DMSO	15	8	98
K ⁺	DMSO	25	16	50
Rb ⁺	DMSO	33	26	93
Cs ⁺	DMSO	48	52	98

^aInitial concentration of 5, 5×10^{-2} M; concentration of propionate, 0.2 M; temperature, 82 °C; reaction time, 48 h. ^bAs determined by ¹H NMR spectroscopy; percentage calculated on the basis of the total amount of 5. ^cTotal 5 + 6 + 7 after workup divided by initial 5, the fraction multiplied by 10²; the explanation for the unsatisfactory material balances in DMF for Na⁺ and DMSO for K⁺ is not known.

A more demanding test is substitution of the mesylate of (-)-menthol (5) as shown in eq 5. Mesylate 5 is especially prone to elimination to give Δ²-menthene (7) together with the substitution product, neomenthyl propionate (6).¹⁹



The temperature was raised to 82 °C to achieve better solubility of 5; in MEK no detectable conversion with any of the salts could be obtained. Material balances were less satisfactory in this case for reasons that were not clear. Results are given in Table IV. Again the best overall conversions, although with significant amounts of elimination, were obtained with cesium propionate as nucleophile.

C. Rates of Substitution Reactions. A brief survey of the rates of S_N2 substitutions by alkali metal halides in dipolar aprotic media was done to examine whether significant kinetic differences attributable to a cation effect could be observed. Substitutions were carried out on 2-octyl mesylate (1) (eq 1) by using NMR to monitor the rates. DMSO-*d*₆ could not be used because of subsequent reaction of the 2-octyl halide with this solvent.²⁰ This problem does not exist with DMF-*d*₆, but for reasons of solubility only acetates and benzoates were suitable as nucleophiles. Concentrations were sufficiently low (0.03 M) that all reaction mixtures were homogenous at initiation of the reaction. Significant downward deviations in rates were observed after one half-life. Data are given in Table V. Each rate constant was determined in duplicate; accuracy is estimated to be ±5%. Small amounts of water have an appreciable effect on the rates. At the concentrations used dissociation of the salts into free ions is

Table V. Rates of Nucleophilic Substitution of 2-Octyl Mesylate in DMSO by Alkali Metal Carboxylates^a

nucleophile	10 ³ k ₂ , L mol ⁻¹ s ⁻¹
NaO ₂ CCH ₃	3.38 (0.1% H ₂ O) 4.1 (0.2% H ₂ O)
KO ₂ CCH ₃	4.9 (0.55% H ₂ O)
CsO ₂ CCH ₃	3.5 (0.03% H ₂ O) 6.4 (0.55% H ₂ O)
NaO ₂ CC ₆ H ₅	2.2 (0.3% H ₂ O)
CsO ₂ CC ₆ H ₅	2.3 (0.05% H ₂ O)

^aConditions: 65 °C; solvent, CD₃SOCD₃; initial concentrations, 2-octyl mesylate and metal salt both 2×10^{-2} M; reactions were followed by ¹H NMR for 6–8 h.

probably virtually complete; with other systems over a broader concentration range Mandolini et al.¹⁶ have demonstrated that increased ion pairing leads to decreased reactivity. The failure to follow pure S_N2 kinetics at higher conversions could be indicative of a modest cation effect.²¹

D. Cesium NMR. Cesium ions are readily observable by NMR techniques. The natural abundance of ¹³³Cs is 100% and the sensitivity of the nucleus relative to ¹H is 4.74%.²² Although the nucleus has a spin of 7/2, the natural line width is narrow. The range of chemical shifts is roughly 200 ppm, which means that this parameter is a potentially sensitive probe of the local environment of the cesium ion. Popov^{22,23} has shown that ¹³³Cs NMR is a powerful technique for examination of ion pairing.

Use of the chemical shift as probe of local environment requires, however, the fulfillment of several experimental criteria. ¹³³Cs shifts are very temperature dependent,^{23c} and, owing to dependence of the chemical shift on concentration and shielding ability of the anion,²⁴ in a series of experiments comparable concentrations must be employed. This latter point leads to experimental restrictions because of the limited solubility of many of the salts.

Probably the most spectacular demonstration of the effect of environment on cesium chemical shifts has been given by Popov et al., who demonstrated that in various solvents the ¹³³Cs chemical shift changes rapidly with addition of complexing agents like 18-crown-6, reaching a maximum or minimum at a 1:1 ratio of crown ether to ¹³³Cs.²³ The initially formed 1:1 complex at higher concentrations of crown ether is converted, at least partially, to a 2:1 crown ether/Cs⁺ complex followed by a levelling off as saturation is reached. To check our apparatus and experimental technique the chemical shift of CsB(C₆H₅)₄ in pyridine was measured as a function of 18-crown-6 concentration. Chemical shifts are relative to a solution

(21) The kinetic results are reminiscent of borderline behavior. The rate increases with increasing amounts of water, in other words greater potential for ionization in the solvent, are consistent with a polar transition state. The inversion of configuration known to occur in these reactions can only be explained by an S_N2-like mechanism that does not involve a free carbonium ion. However, the rate-enhancing effect of added water, and, more significantly, of cesium cations could be consistent with initial formation of a tight ion pair not subject to racemization. Were the relatively soft and polarizable cesium ion to participate in the reaction by coordination to incoming nucleophile and/or leaving group this might explain what appears to be a tendency toward borderline behavior.

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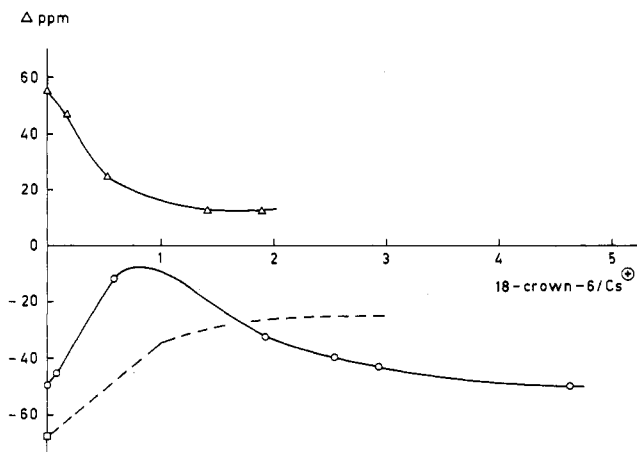


Figure 1. ^{133}Cs chemical shifts as a function of 18-crown-6/ Cs^+ salt ratios: (a) (—○—) $\text{CsB}(\text{C}_6\text{H}_5)_4$ in pyridine; (b) (---△---) $\text{CsO}_2\text{CC}_2\text{H}_5$ in DMSO; (c) (---) $\text{CsB}(\text{C}_6\text{H}_5)_4$ in DMSO. The reference for b is 1 M CsCl in D_2O as external standard. Curve c is from ref 22 and is not on the same absolute scale as b.

Table VI. Concentration Dependence of ^{133}Cs NMR Shifts (at 65 °C)

solv	conc, mol L^{-1}	chem shifts, ^a ppm			
		CsO_2CEt	CsBr	$\text{CsB}(\text{C}_6\text{H}_5)_4$	CsCl
DMSO	1.5×10^{-2}	55.0	55.4	53.1	56.5
	1.0×10^{-3}	55.5	53.2	53.2	53.5
DMF	1.5×10^{-2}	-8.2	-12.0	b	-14.5
	1.0×10^{-3}	-13.8	-15.3	b	b
$\text{C}_5\text{H}_5\text{N}$	1.0×10^{-3}	37.3	b	-49.1	b

^a Chemical shifts relative to 1 M CsCl in D_2O as external standard. ^b Not measurable because of poor solubility.

of 1M CsCl in D_2O . Results are given in Figure 1 together with the literature data.^{23b} For $\text{CsB}(\text{C}_6\text{H}_5)_4$ in pyridine a change of slope at about a 18-crown-6/ Cs^+ ratio of 1 as reported is observed.²² In the same figure the plot is given of the chemical shift of cesium propionate in DMSO (used as dipolar aprotic solvent because of the higher solubility of the cesium salts) as a function of 18-crown-6 concentration together with the literature data²² for the behavior of $\text{Cs}^+ \text{B}(\text{C}_6\text{H}_5)_4$ in the same solvent. Both plots show inflection points at a Cs^+ /18-crown-6 ratio of 1, indicative of 1:1 complex formation.

In Table VI the chemical shifts at different concentrations of various cesium salts including the propionate in DMSO, DMF, and pyridine are given.

Consideration of the data given in Figure 1 and Table VI, coupled with the extensive measurements of Popov et al.,^{23a} who have also investigated cesium octanoate,^{23c} leads to the conclusion that in DMSO there is no measurable effect of ion pairing with propionate, bromide, tetraphenylborate, or chloride as counterions. Solvation of Cs^+ is effective enough that ion-pairing effects are minimal. The data in Table VI suggest that in DMF on the other hand dissociation is not entirely complete as judged from the modest concentration dependence of the chemical shift.

Discussion

The ^{133}Cs NMR experiments indicate that cesium salts, in particular the carboxylates, are nearly or completely dissociated in free ions or solvent separated ion pairs in dipolar aprotic solvents. Solvents like DMSO and DMF solvate cations more effectively than anions.²⁵ Reactive

anions are produced; "naked anion" suggests itself. Although this is an oversimplification, in general terms one can conclude that cation solvation leads to relatively free anions that are the reactive species in the nucleophilic substitution that occurs.

This picture of separated ions differs from a suggestion that was advanced by us some time ago.^{7,12} We speculated, in the absence of ^{133}Cs NMR data, as well as subsequently obtained kinetic evidence,¹⁶ that for the case of cesium carboxylates in particular and other cesium salts in general, that the solvation of cesium ions in DMF would be relatively poor and that the salts would be present chiefly in the form of tight ion pairs. A charge following^{26,27} mechanism for substitution reactions occurring chiefly in the tight ion pairs was advanced. We were led to this supposition chiefly on the basis of an attempt to extrapolate data obtained by Bordwell on the ion pairing of alkali metal benzoates (not cesium) in DMSO as measured by a spectral technique.²⁸ At 25 °C potassium benzoate, for example, has an equilibrium constant for association of 48 in DMSO.²⁸ Similar values have been found for phenoxides in 95% DMSO/1% H_2O .^{16a} At 1.5×10^{-2} M, the highest concentration used for NMR experiments or ring closure reactions,¹² 33% of the ions would be associated, if K_{assoc} is 48. On the basis of such data, for the case of DMF as solvent the decrease in association of the ion pairs expected on change from potassium to cesium was anticipated to be roughly compensated by the lower dielectric constant (37) of DMF compared to DMSO (47). The ^{133}Cs NMR data make clear, however, that these effects do not cancel but rather that cation solvation predominates.

The relative effectiveness of cesium carboxylates, thioates, phenolates, etc. in intermolecular $\text{S}_{\text{N}}2$ substitutions derives then most likely both from the good solubility characteristics, which makes the attainment of concentrations of around 0.3 M possible with concomitant higher rates of reaction, together with a higher degree of dissociation into solvated cations and "free" anions, which have maximum reactivity.

The advantages provided by cesium in macrocyclization reactions can be better understood on the basis of effective molarity, which is the ratio of the rate constants for comparable *intra*- as compared to *intermolecular* reactions, $k_1 k_2^{-1} = \text{E.M.}$ This can be rewritten as eq 6. When the

$$\text{rate}_1[\text{C}] = \text{E.M.} \times \text{rate}_2 \quad (6)$$

concentration [C] is equal to the E.M. the rates of intramolecular ring closure and oligomerization are equal. As the concentration becomes less than the E.M. $\text{rate}_1 > \text{rate}_2$. Mandolini and Galli^{16b} have pointed out that on a first principle basis the yield of macrocyclization should be equal to or greater than 50%, providing that the initial concentration is no higher than the E.M. There can be, however, a pronounced cation effect on macrocyclization.^{12,13,17,27} One probable cause of this is that relatively small changes in the E.M. as, for example, function of cation have significant effects for the results of a synthetic reaction. An increase of the E.M. from 10^{-2} to 1.5×10^{-2} M causes the rate of the intramolecular reaction to become 1.5 times greater at a concentration of

(26) See, for example: Hoffmann, R. W. *Aufklärung von Reaktionsmechanismen*; Georg Thieme Verlag: Stuttgart, 1976; pp 226 ff.

(27) Some other related examples of cation-anion association on chemical reactivity can be found in: (a) Smid, J. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 112. (b) Solovyanov, A. A.; Beletskaya, I. P. *Russ. Chem. Rev. (Engl. Transl.)* 1978, 47, 425. (c) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* 1980, 102, 774.

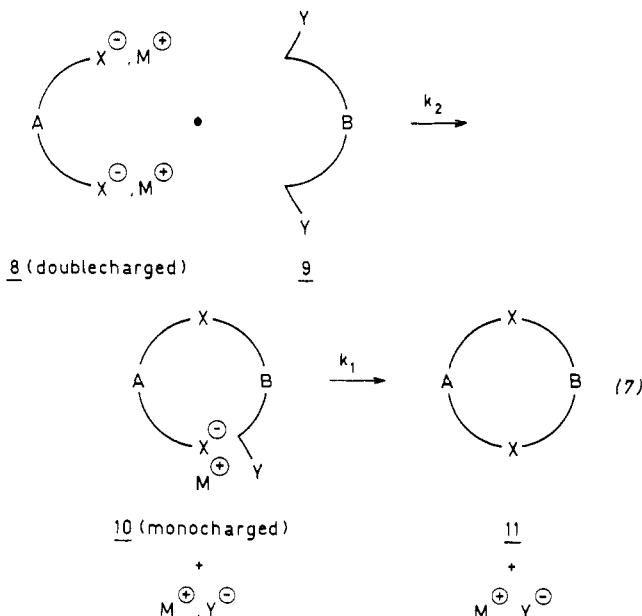
(28) Olmstead, W. N.; Bordwell, F. G. *J. Org. Chem.* 1980, 45, 3299.

(29) See also: Steliou, K.; Poupart, M.-A. *J. Am. Chem. Soc.* 1983, 105, 7130.

(25) See, for example: Alder, R. W.; Baker, R.; Brown, J. M. *Mechanism in Organic Chemistry*, Wiley-Interscience: London, 1971; p 43 and subsequent discussion.

10^{-2} M. If these rate differences were held until completion of reaction the cyclization yield should be raised to 60%. The actual results should be better because of the constantly decreasing concentration during the course of the reaction.

Many macrocyclizations, particularly those in which cesium is used with special success, are also two stage reactions in which two sections are joined convergently in a single-pot reaction as illustrated schematically in eq 7. The key competition that determines the effectiveness



of macrocyclization lies in mono-charged 10, which either cyclizes or oligomerizes. The cation can affect this balance at several points. It is desirable that the solubility of the doubly charged anion 8 be maximal; as a first approximation the reactivity per mole is twice that of the mono-charged ion (one nucleophilic site) 10. The competition for 9 will be more heavily in favor of doubly charged 8, thereby decreasing the chance for oligomerization of 10. Cesium salts contribute positively here because of the higher solubility. Many other doubly charged salts react heterogeneously, owing to limited solubility of the doubly charged anion.

The picture that arises is complex rather than one based on a single and unambiguous effect. We have, however, no reason to be surprised by subtlety in chemistry.

Experimental Section

Solvents were distilled, repeatedly if necessary, and dried prior to use. Chemicals cited without reference were available from stock.¹³ Analyses of the compositions of mixtures obtained from substitution reactions were carried out by ^1H NMR spectroscopy on a Jeol C 60-HL spectrometer. ^{133}Cs measurements were performed on a Nicolet NT-200 apparatus operating at 26.243 MHz; the probe temperature was held at 25 °C.

The preparation of metal propionates was carried out analogously to previously described procedures.^{10a} The respective alkali metal carbonate, M_2CO_3 (M = Na, K, Rb, and Cs) (5 mmol), was dissolved in dry MeOH (40 mL). To this solution was added

propionic acid (10 mL, 9.92 g, 134 mmol) dissolved in dry CH_3OH . The solution was stirred for 30 min, and then the methanol was removed under vacuum. The white powder that remained was collected on a glass filter and was washed repeatedly with ether until no propionic acid could be detected in the washings. The powders so obtained in nearly quantitative yields were stored under nitrogen.

General Procedure for Preparation of Mesylates. The alcohol (5 mmol) was dissolved in dry ether (40 mL) to which triethylamine (2.02 g, 20 mmol) was added. The solution was cooled to -10 °C, and methanesulfonyl chloride (860 mg, 7.5 mmol) dissolved in diethyl ether (10 mL) was added dropwise. After a reaction period of 1 h, the salt, triethylammonium chloride, was filtered off, the filtrate was washed with saturated salt solution, then 0.1 M HCl solution, 10% NaHCO_3 solution, and finally twice with saturated salt solution. The ether layer was dried over MgSO_4 . After filtration and removal of the ether the mesylates, all known compounds, were examined with the aid of ^1H NMR to ensure that they were free of impurities.

General Procedure for Substitutions. The mesylate was dissolved in the appropriate amount of solvent (see Tables II-IV for concentrations). The propionate was then added in solid form. The reaction mixture was stirred vigorously and was brought to reaction temperature and allowed to stand 24 h (48 h for menthol mesylate). No attempt was made to determine alkenes, except for menthene (7), after reaction. The reaction mixtures with sodium and potassium propionates were heterogeneous at start of reaction and remained so. Salt solution was added to the reaction mixture, this aqueous layer was extracted three times with ether, and the ether layer was dried over MgSO_4 . After removal of the ether the reaction mixture was weighed and its composition established by ^1H NMR.

Solubility Determined by Conductance Measurements. This is illustrated with a concrete example, the determination of the solubility of cesium propionate in DMF.

The DMF, which had been distilled, was then dried over a column of Al_2O_3 . The cesium propionate was recrystallized from diethyl ether/ethanol (1:1). Measurements were carried out at 51 °C. A homogeneous solution of cesium propionate was made, and its conductivity was measured by conductometry. Dilution was carried out by addition of small quantities of solvent with the aid of a graduated syringe. The specific conductivity of a 0.167 mol L^{-1} solution of cesium propionate at 51 °C in DMF in $6.1 \cdot 10^{-3}$ $\Omega^{-1} \text{cm}^{-1}$. The conductances at various concentrations were plotted against concentration propionate; the inflection points were taken as the saturation points.

A Philips conductance meter PW9501/01 was used with a cell with a cell constant of 1.59. The cell was mounted in a thermostated bath. The conductances in methyl ethyl ketone were measured with a Wayne-Kerr autobalance universal bridge, B-642.

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Registry No. (\pm)-1, 109716-84-9; (\pm)-2, 109637-84-5; 3, 16156-56-2; 4, 6222-35-1; (-)-5, 61548-81-0; 6, 109716-85-0; 7, 5113-93-9; $\text{CsO}_2\text{CCH}_2\text{CH}_3$, 38869-24-8; $\text{RbO}_2\text{CCH}_2\text{CH}_3$, 19559-54-7; $\text{KO}_2\text{CCH}_2\text{CH}_3$, 327-62-8; $\text{NaO}_2\text{CCH}_2\text{CH}_3$, 137-40-6; NaO_2CCH_3 , 127-09-3; KO_2CCH_3 , 127-08-2; CsO_2CCH_3 , 3396-11-0; $\text{NaO}_2\text{CC}_6\text{H}_5$, 532-32-1; $\text{CsO}_2\text{CC}_6\text{H}_5$, 17265-04-2; Cs, 7440-46-2; Na_2CO_3 , 497-19-8; K_2CO_3 , 584-08-7; Rb_2CO_3 , 584-09-8; Cs_2CO_3 , 534-17-8; $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, 79-09-4; $\text{CsB}(\text{C}_6\text{H}_4)_4$, 18-crown-6 complex, 56688-33-6; $\text{CsO}_2\text{C}_2\text{H}_5$, 18-crown-6 complex, 109637-85-6; CsCl , 18-crown-6 complex, 63889-68-9; CsBr , 7787-69-1; $\text{CsB}(\text{C}_6\text{H}_5)_4$, 3087-82-9; CsCl , 7647-17-8; (\pm)-2-octanol, 4128-31-8; cyclohexanol, 108-93-0; (-)-menthol, 2216-51-5.