

garded as being formed by donation of π -electron density from a filled orbital on C(α) to an empty orbital on Ta.

We note that M-C(α)-C(β) angles are frequently increased from their ideal sp^3 value both in transition metal alkyls and perfluoroalkyls.⁶ The observation of an extremely obtuse Ta-C(1)-C(2) angle in the Ta(η^5 -C₅H₅)₂(CHCMe₃)Cl molecule, whether it be due principally to steric or electronic effects,^{7,8} is possibly relevant to the olefin metathesis reaction (which is believed to proceed via reaction of an olefin with an alkylidene ligand to give a metallocyclobutane complex),⁹ insofar as it shows that the M-C(α)-C(β) backbone can easily distort in order to accommodate or react with other ligands at the metal.

Finally we should stress that, in the general case, alkylidene ligands are expected to rotate easily, since a π orbital (of appropriate energy) orthogonal to that forming the π bond in the ground state will normally be available; bis(cyclopentadienyl) systems are exceptions.⁵

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References and Notes

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- (7) In Ta(η^5 -C₅H₅)₂(CH₂)(CH₃) (ref 2), the H-C(methylene)-H angle is 107 (9)°; the average Ta-C(methylene)-H angle is therefore 126.5°. The esd's on these angles are, however, large. In W(CO)₅(CPh₂) (ref 8), the W-C(α)-C(β) angles within the two independent molecules range from 120.7 (11) to 126.1 (11)°, averaging 124.0°. C-C angles at the W-bonded atoms have values of 112.3 (13) and 110.7 (15)°, averaging 111.5°. There, therefore appears to be a general tendency toward large M-C(α)-C(β) angles in alkylidene systems.
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Alkali Metal Cation Catalysis of a Photochemical Reaction

Sir:

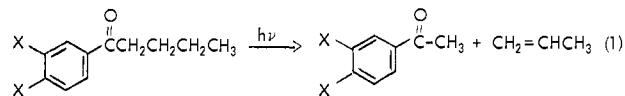
The binding of alkali metal cations to crown ethers is a well-known phenomenon.¹ Numerous novel effects arising from this complexation have been intensively investigated since the pioneering studies of Pedersen in 1967.² Included among these effects are UV spectral changes^{1a} and perturbations of the fluorescence and phosphorescence efficiencies³ of aromatic chromophores attached to the cyclic polyethers. As part of a

Table I. Effect of Methoxy Ring Substituents on the Photoelimination Quantum Yield of Valerophenone in Benzene

Ketone	ϕ	Ref
Valerophenone	0.33	6
4-Methoxyvalerophenone	0.10	6
3-Methoxyvalerophenone	0.014	6
3,4-Dimethoxyvalerophenone	0.0039	This work

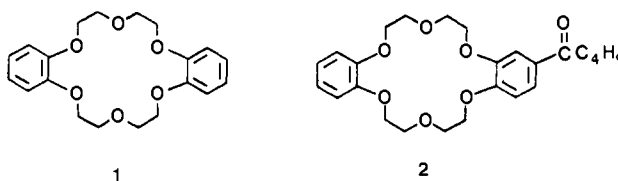
series of studies involving highly specific effects of molecular association on photochemical reactions we have been seeking to identify other potential systems which exhibit selective catalysis. Thus it was of interest to determine whether cation binding might be capable of exerting an influence on photochemical reactions of suitably functionalized crown ethers. We report here encouraging results from our studies involving the valeroyl substituted dibenzo-18-crown-6 (**2**).

We selected the 3,4-dialkoxyvalerophenone photochemical system for the following reasons. The type II photoelimination reaction of aryl alkyl ketones has been intensely investigated and is rather well understood.⁴ The reaction is known to occur from the triplet n, π^* excited state of the aromatic ketone to produce a 1,4-hydroxy biradical intermediate which (a) disproportionates back to the original ketone, (b) closes to form cyclobutanols, or (c) fragments to an olefin and the enol of the corresponding methyl ketone (eq 1). The introduction of



electron-releasing ring substituents, such as methoxy, results in a pronounced decrease in the quantum efficiency for the photoelimination process as seen in Table I. The effect is predominantly due to inversion of the lowest lying triplet excited state from n, π^* to π, π^* .⁵ When polar hydroxylic solvents are used for the reactions at least two effects occur.⁶ Solvation of the 1,4-hydroxy biradical intermediate retards the disproportionation reaction thereby maximizing the efficiency of product formation. At the same time, however, polar solvents facilitate the inversion of the n, π^* and π, π^* excited states. The net effect is to increase the disparity in type II efficiencies between valerophenone ($\phi = 1.0$ in methanol)⁶ and 3,4-dimethoxyvalerophenone ($\phi = 7.5 \times 10^{-4}$ in methanol).

Dibenzo-18-crown-6 (**1**) is known to have a high affinity for complexation with alkali metal salts and particularly for those of potassium.¹ For example the equilibrium constants for complex formation between **1** and sodium chloride and between **1** and potassium chloride in methanol are 14 500 and 37 000 M⁻¹, respectively.⁷



We have measured (spectrophotometrically) the corresponding equilibrium constants for **2** with sodium acetate and potassium acetate in methanol and found them to be 7200 and 36 000 M⁻¹, respectively.⁸ Thus the functionalized dibenzo-18-crown-6 (**2**) retains a high affinity for complexation with potassium ion and, to a lesser extent, other alkali metal salts.

Crown ether **2** was prepared by treating **1** with an equimolar amount of valeric acid in polyphosphoric acid at ~65 °C for 6 h. Purification yielded off-white platelets (mp 123–124 °C).⁹

Deoxygenated methanolic solutions of the crown in the

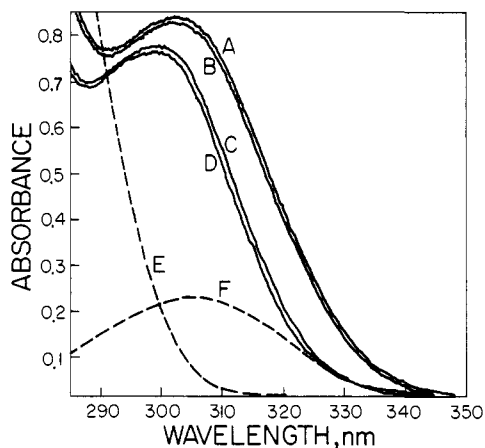


Figure 1. Absorption spectra in methanol of crown **2** in the presence and absence of added salts: A, crown **2**; B, crown **2** and LiCl; C, crown **2** and NaCl; D, crown **2** and KCl. Curves E and F are the spectra of 4-methoxyacetophenone and 3-methoxyacetophenone for comparison. The concentration of ketone (or crown) was 1.0×10^{-4} M in all cases, and the concentration of added salt was 5×10^{-3} M.

Table II. Effects of Alkali Metal Salts on the Photoelimination Quantum Yields of Valerophenone Derivatives in Methanol

Ketone ^a	Salt ^b	ϕ_{rel} ^c	λ_{max} , nm (ϵ) ^d
Crown 2		1	303 (8300)
Crown 2	LiOAc	1.4	303 (8200)
Crown 2	LiCl	1.2	303 (8200)
Crown 2	NaOAc	5.0	300 (7700)
Crown 2	NaCl	4.3	300 (7700)
Crown 2	KOAc	8.8	299 (7600)
Crown 2	KCl	10.8	299 (7600)
3,4-Dimethoxyvalerophenone		1.2	
3,4-Dimethoxyvalerophenone	KOAc	1.0	
3,4-Dimethoxyvalerophenone	KCl	1.1	

^a Deoxygenated solutions containing 1.0×10^{-3} M ketone were photolyzed with 313-nm light in a conventional merry-go-round apparatus. ^b 1.0×10^{-3} M. ^c Relative quantum yields for the formation of propene; conversions were <10%; the conversion of valerophenone to acetophenone and propene ($\phi = 0.33$) in benzene was used as an actinometer. ^d As described in Figure 1.

presence and absence of equimolar quantities of various alkali metal salts were photolyzed using conventional procedures. We found it convenient to analyze for the formation of propene (eq 1) by gas chromatography.¹⁰ The results of these studies are presented in Table II. Control experiments for 3,4-dimethoxyvalerophenone studied in the presence and absence of potassium salts are also included. The presence of sodium salts enhances the efficiency of photoelimination by a factor of 5 and that of potassium salts by a factor of 10. The corresponding lithium salts exhibit only a small increase. The potassium salts, as expected, have no effect on the corresponding photochemistry of 3,4-dimethoxyvalerophenone. Furthermore we have found that UV spectral shifts for crown **2** parallel the photochemical effects (Figure 1 and Table II). Both the shift to shorter wavelength and the reduction in extinction coefficient are in the direction expected if complexation reduced the electronic interaction of the "alkoxy" substituents with the aryl ketone chromophore (spectra of the mono alkoxy ketones are included for comparison).

In principle, it should be possible to ascertain whether the "catalytic" effect of complexation serves to increase the hydrogen abstraction rate constant (k_r) or to decrease the competing radiationless decay (k_d) of the excited state, or both. Measurement of the excited-state lifetime, $(k_r + k_d)^{-1}$, by conventional triplet quenching experiments should yield a larger value for the excited-state lifetime if the effect involves

decrease in k_d or a smaller (perhaps imperceptibly so) value if the effect is to increase k_r . These experiments have unfortunately been very problematic, and we have been unable to draw definitive conclusion. In addition to considerable scatter in the Stern-Vollmer plots, no more than 50% (in the case of crown **2** complexed with potassium acetate) or 70% (in the case of crown **2** alone) of the photochemistry is quenchable with high concentrations (~ 2 M) of typical triplet quenchers such as 1,3-pentadiene.¹¹ The latter observation implies that a portion of the observed photochemistry occurs from the singlet state.

In conclusion, we have observed a substantial "catalytic" effect of alkali metal cations on the efficiency of a photochemical reaction. It is moderately specific for potassium ion. Studies are in progress to assess the potential magnitude and specificity of the effect.

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- (8) Under the conditions described for the photochemical experiments, 50% of the crown is complexed with KOAc and 47% of the crown is complexed with NaOAc.
- (9) Spectral data and elemental analysis are consistent with the proposed structure.
- (10) Photolyses were carried out in sealed Pyrex tubes and were analyzed immediately upon opening. The reliability and reproducibility of the propene analysis were exhaustively tested using valerophenone and 3,4-dimethoxyvalerophenone. The efficiencies for production of propene were found to be identical with those for production of the corresponding methyl ketones.
- (11) It should be noted that identical complications with quenching are also observed with 3,4-dimethoxyvalerophenone and do not arise from features of the crown per se.

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Preparation and Rearrangements of Some 8,8-Dimethylhomotropylium Cations¹

Sir:

While the migration of C₈ and its attendant substituents around the periphery of the "seven-membered" ring of a homotropylium cation can be induced photochemically,² no comparable thermal rearrangement has yet been detected.³ The barrier of such a thermally initiated rearrangement is expected to be dependent on the substitution pattern at the migrating carbon.⁴ Indeed, on the basis of molecular orbital calculations, Hehre has suggested that, in contrast to the unsubstituted ion, circumambulatory rearrangements of the 8,8-dimethylhomotropylium cation should be facile.⁵ We report here the preparation of several 8,8-dimethyl substituted homotropylium cations and show that these species undergo a variety of molecular rearrangements, including circumambulation.

The dimethylhomotropone **1**, prepared by the procedure of Franck-Neumann,⁶ was dissolved in FSO₃H at -78 °C to give the cation **2**. Irradiation of **2** (-70 °C, $\lambda > 360$ nm) caused it