CHEMISTRY LETTERS, pp. 515-516, 1980. © The Chemical Society of Japan 1980

EFFECT OF GUEST CATIONS ON THE PHOTO-SOLVOLYSIS OF 4′-(1-ACETOXY)ETHYLBENZO-15-CROWN-5[1]

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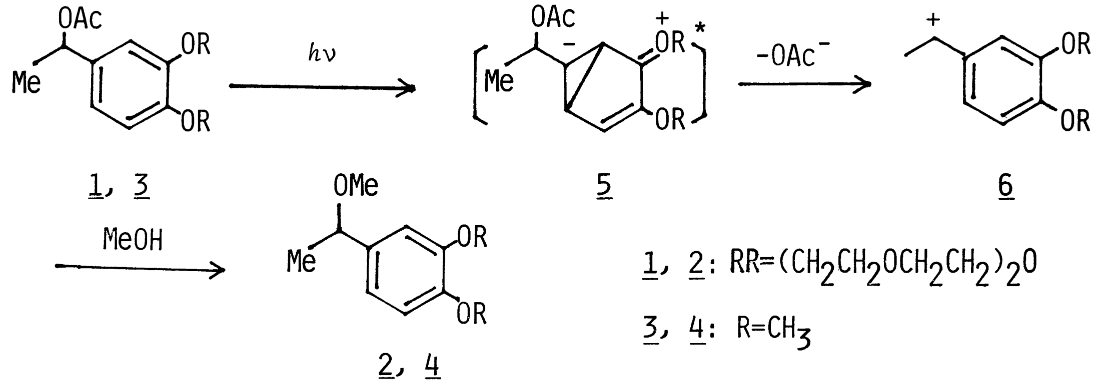
Photo-solvolysis of 4′-(1-acetoxy)ethylbenzo-15-crown-5 (1) in methanol is depressed by the complex formation of the crown ether moiety with alkali metal ions. This effect is accounted for by the destabilization of excited state of 1 and benzyl cation from 1 .

Electronic effect of a substituent on benzene ring is well understood in fundamental organic chemistry. The effect appears at ortho and para positions in ground state whereas it appears at a meta position in excited state.[2,3] Photo-excitation of p-methoxybenzyl acetate causes a radical cleavage to give a p-methoxybenzyl radical whereas the excitation of m-methoxybenzyl acetate causes an ionic cleavage to give a m-methoxybenzyl cation preferentially.[2] In a line of our study on the photochemistry of crown ether derivatives,[1] now we like to report the photochemical behavior of 4′-(1-acetoxy)ethylbenzo-15-crown-5 (1) which has alkoxy groups at positions meta and para to the 1-acetoxyethyl group.

Internal irradiation (a 100w high pressure mercury lamp, under nitrogen) of 4-(1-acetoxy)ethylbenzo-15-crown-5 (1)[4] (900 mg) in 100 ml of dry methanol for 10 h and the separation of the product by preparative TLC (silica gel $CHCl_3$-CH_3OH 20:1) afforded a photo-solvolysis product, 4′-(1-methoxy)ethylbenzo-15-crown-5 (2)[5] in 43 % yield. Similar result was obtained on the irradiation of 4-(1-acetoxy)-ethyl-1,2-dimethoxybenzene (3)[6] affording 4-(1-methoxy)ethyl-1,2-dimethoxybenzene (4)[7] in 49 % yield. The effect of host guest complex formation on the relative quantum yield of the solvolysis product (2) was tested and the results are shown in Fig. 1. No effect was observed by the addition of sodium perchlorate - until 16 equivalents - to the reaction mixture of dimethoxybenzene derivative (3). The observed salt effect for 1 can not be due to perchlorate anion since no effect was seen by the addition of tetramethylammonium perchlorate.



1, 2: $RR=(CH_2CH_2OCH_2CH_2)_2O$

3, 4: $R=CH_3$

Formation constant of the complex between 4'-(1-acetoxy)ethylbenzo-15-crown-5 (1) and metal ions in methanol was determined by Benesi-Hildebrand's method;$^{8)}$ 5.0×10^{2} M^{-1} for $NaClO_4$ and 2.0×10 M^{-1} for $LiClO_4$. Sodium ion fits more comfortably to the cavity of 15-crown-5 than lithium ion. An inflection appears at smaller relative quantum yield ($\Phi_{rel.}$) and smaller salt concentration for sodium salt than for lithium salt, and this difference is expected from the formation constant and the efficiency of electronic interaction between the cation and the crown ether system.

These results are well accounted for by Zimmerman's generalization$^{2)}$ which assigns a structure 5 as an approximate representation of the excited state of m-alkoxybenzyl acetate derivative. The complexation of a metal ion must destabilize the excited state 5 $^{9)}$ and cation 6 , and depresses the ionic cleavage of the acetoxy group to give the substitution product 2 .

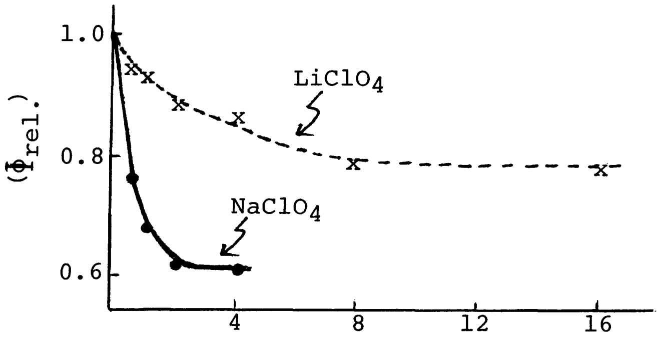


Figure 1. Relative quantum yields of 2 from 1 (9.0×10^{-3}M in MeOH) in the presence of lithium or sodium perchlorate

References and Notes

1) Photochemistry of host guest complex, part IV. For part III see M. Tada, H. Hirano, and A. Suzuki, Bull. Chem. Soc. Jpn., under submission.
2) H. E. Zimmerman and V. R. Sandel, J. Am. Chem. Soc., 85, 915 (1963).
3) H. E. Zimmerman and S. Somasekhara, J. Am. Chem. Soc., 85, 922 (1963).
4) The starting material 1 was prepared by $NaBH_4$ reduction of 4'-acetylbenzo-15-crown-5 followed by acetylation. oil; λ_{max}^{MeOH} 278 nm (2880); IR($CHCl_3$) 1725 and 1255 cm^{-1}; NMR(CCl_4) (δ) 1.43(3H, d, J=7Hz), 1.91(3H, s), 3.52-4.65(16H), 5.57(1H, q, J=7), and 6.57-6.66(3H, m). An adduct with sodium picrate, mp 120-121°C, gave a correct value in elemental analysis.
5) The product 3 , oil; IR(CCl_4) 1502, 1252, and 1130 cm^{-1}; NMR(CCl_4) (δ) 1.31 (3H, d, J=7Hz), 3.08(3H, s), 3.60-4.17(17H), and 6.65-6.76(3H, m). An adduct with sodium picrate gave a correct value in elemental analysis.
6) C. L. Ludwig, B. J. Nist, and J. L. McCarthy, J. Am. Chem. Soc., 86, 1186 (1964).
7) H. L. Hergert, J. Org. Chem., 25, 405 (1960).
8) H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949).
9) Fluorescence maximum of 1 (3.33×10^{-4} M in methanol, excitation at 260 nm) moves from 318 nm to 313 nm by the addition of $NaClO_4$ (3.33×10^{-3} M).

(Received February 16, 1980)