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# PHOTOCHEMISTRY OF HOST-GUEST COMPLEX I, PHOTOCHEMICAL REACTION OF ALKYL ARYL KETONES WITH 18-CROWN-6

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Knowledge of cyclic polyethers, crown ethers, is rapidly accumulating.[1-6] The chemistry of cyclic polyethers, however, is mostly concerned of the relation between the structure and complexation ability, the catalytic behavior by the complexation of cation, and the solubilization of inorganic reagent in organic solvents. We are studying the effect of the complexation on the reactivity of the cyclic polyether itself, and in this paper we like to report the photochemical reaction of alkyl aryl ketones with 18-crown-6.

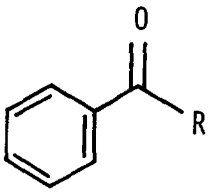
External irradiation (450w high pressure Hg lamp, $N_2$ atmosphere, Pyrex vessel) of a 1:1 mixture of acetophenone and 18-crown-6 ($5X10^{-2}M$) in benzene for 15-20 hr precipitated pinacol (IIa). Separation of the soluble fraction by repeated preparative TLC ($SiO_2/CHCl_3$-EtOAc-MeOH, 60:35:5) gave a cross coupling product (IIIa) in 9% yield beside the recovered starting materials. IIIa, viscous oil, mass m/e=385($M^+$+1), 384($M^+$), 369($M^+-CH_3$), 367($M^+$-OH), 263($M^+-C(CH_3)(OH)C_6H_5$). IR($CCl_4$) 3470, 1110 cm$^{-1}$. NMR($CDCl_3$) $\delta$=1.45 and 1.51 (3H, s), 3.31-3.90 (crown ether), 7.3 (5H, m). Irradiation of 3-cyano-1-phenyl-1-propanone (Ib) under the same conditions and the same work up gave a cross coupling product (IIIb) in 17-20% yield beside a pinacol (IIb) and the starting materials. IIIb, viscous oil, mass m/e=424($M^+$+1), 423($M^+$), 406($M^+$-OH), 369($M^+-CH_2CH_2CN$), 263($M^+-C(OH)(C_6H_5)-CH_2CH_2CN$). IR($CCl_4$) 3480, 2210, 1105 cm$^{-1}$. NMR($CCl_4$) $\delta$=1.60-2.70 (4H, m), 3.60-3.80 (crown ether), 7.50 (5H, m).

The structures of the adducts (IIIa and IIIb) are evident from the spectral data. The mass spectra of these adducts show molecular peaks and the peaks due to the loss of each group attached to the benzylic carbon. The fragment peak at m/e=263 decomposes to a series of fragments by the stepwise loss of $-CH_2CH_2O-$ group which is characteristic to 18-crown-6.[7)] Though the adducts IIIa and IIIb were homogeneous in TLC analyses, they showed two peaks in HPLC (Bondapack-$C_{18}$/Corasil, $CH_3OH-H_2O$). The NMR spectrum of IIIa shows twin peaks at 1.45 and 1.51 ppm (total 3H). This fact suggests that the cross-coupling gives erythro and threo isomers.

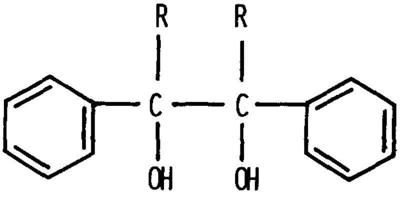
Prolonged placement of IIIb on silica gel plate or the treatment with dil-HCl converted it into a lactone IV, though 3-cyano-1-phenyl-1-propanol could be converted into a γ-lactone only slowly under the same conditions. IV, viscous oil, mass m/e=425($M^+$+1), 424($M^+$), IR($CCl_4$) 1772,1105 $cm^{-1}$, NMR($CDCl_3$) $\delta$=1.10-1.93(4H, m), 3.17-4.30(crown ether), 7.4(5H, m).

Nitriles are known to form host-guest complexes with crown ethers,[8)] and the difference in yields of the cross-coupling products, IIIa (9%) and IIIb (17-20%), must be due to the complexation. This is in accordance with the fact that irradiation of Ib ($5X10^{-2}$M) in benzene containing dioxane ($1.5X10^{-1}$M) did not give the isolable amount of the coupling product between Ib and dioxane but gave only pinacol IIb. p-Cyanoacetophenone gave a 1:1 adduct with 18-crown-6 in less than 7% under the same reaction conditions. The low yield of the adduct may be attributable to (a) the small tendency of complex formation between the aromatic nitrile and the crown ether due to steric hindrance, or (b) the unfavorable geometry of the complex for the cross coupling.

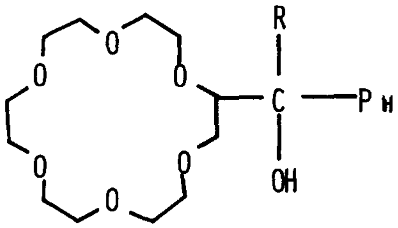
Irradiation of methyl 4-oxo-4-phenylbutanoate (Ic) and 4-oxo-4-phenylbutanoic acid (Id) in the presence of 18-crown-6 for 40 hr, in the same manner but using benzene/t-butanol (2:1) as a solvent, gave adducts IIIc and IIId which were converted into lactone IV in 10% yield from Ic and 12% yield from Id. Potassium 4-oxo-4-phenylbutanoate (Ie) gave lactone IV in 21% yield by a similar treatment after neutralization by HCl. The stimulation effect on the cross coupling by the formation of host-guest complex must be operative in the photochemistry of Ie. Without the addition of crown ether, Ie does not dissolve up to $5X10^{-2}M$ in the solvent system used for the reaction, and therefore the complex formation with potassium ion is evident. In organic solvents the carboxylate ion of Ie can not be free from the restraint of the potassium ion complexed with the crown ether, and these ions must be in "loose ion pair".9) This loose ion pair must be a real entity to enter the photo-coupling and therefore it is reasonable to attribute the difference in reactivity of Ic, Id, and Ie to this "loose ion pair effect".



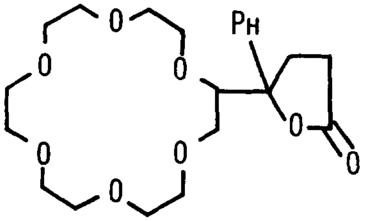
IA - IE



IIA - IID



IIIA - IIID



IV

A : R = $CH_3$ B : R = $CH_2CH_2CN$ C : R = $CH_2CH_2COOCH_3$

D : R = $CH_2CH_2COOH$ E : R = $CH_2CH_2COO^-$, $K^+$

Excitation of an alkyl aryl ketone must produce a triplet $n\pi^*$ state10) which abstracts a hydrogen from 18-crown-6. The ketyl radical and 18-crown-6-yl radical thus formed are held together more tightly than a simple radical pair, and they collapse into the 1:1 cross-coupling product. These results demonstrate a unique aspect of 18-crown-6 in photochemical reaction and this property may offer a useful method to introduce a functional group to cyclic polyethers.

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