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PHOTOCYCLOADDITIONS OF ELECTRON POOR OLEFINS TO 2-ARYL-1-PYRROLINIUM SALTS[1]

Patrick S. Mariano[2,*] and Andrea Leone-Bay
Department of Chemistry, University of Maryland, College Park, MD 20742

Photocycloadditions of the electron poor olefins, acrylonitrile and methyl acrylate to a series of *para*-substituted 2-phenyl-1-pyrrolinium perchlorates have been explored as part of studies designed to test new synthetic methods.

Studies in our laboratory[3] have uncovered interesting olefin photoadditions to iminium salts occuring through electron-transfer or 2+2-cycloaddition pathways. Additions of electron poor olefins to 2-phenyl-1-pyrrolinium perchlorate (1H→3H) appear to involve initial 2+2-cycloaddition across the C-1 C-2 π-bond of the aromatic ring (1H→2H) followed by ring expansion and aromatization.[3b] This reaction appears potentially applicable to the synthesis of spirocyclic amines, exemplified by the proposed route to serratinine[4] 4 outlined retrosynthetically in Chart 1. The success of this approach would depend upon the effect of aromatic ring substitution, needed for spiroannulation and A-ring functional group introduction, on photoaddition. In order to investigate this point, we have studied photocycloadditions of electron poor olefins and a series of 2-*p*-substituted-phenyl pyrrolinium perchlorates 1.

The 1-pyrroline precursors of 1F, 1Cl, 1CH_3, 1Br and 1OCH_3,[5] were prepared by use of the method of Bielawski[6] involving addition of the corresponding aryl lithium to N-vinylpyrrolidone followed by hydrolysis. Irradiations[7] were conducted on methanolic acrylonitrile or methyl acrylate solutions (1 M) of the salts (*ca*. 10^{-3} *M*), formed *in situ* from the pyrrolines and 70% $HClO_4$. Crude photolysates were neutralized, concentrated, and products purified by molecular distillation and/or chromatography. Yields of the benzospirocyclic amines produced are recorded in Table 1.[9] Product structures were assigned on the basis of spectroscopic data and comparisons with that for the known parent amines, 3CN-H and 3CO_2CH_3-H.[3b] Chemical correlations of 3CN-Cl and 3CN-Br with 3CN-H ($LiAlH_4$ THF, 60°C, 12h-reduction to identical mixtures of the stereoisomeric diamines 6) provided unambiguous structural assignments to these materials.

The results indicate that additions of electron poor olefins to photo-excited 2-aryl-1-pyrrolinium perchlorates, proceeding by initial 2+2 cycloaddition to the aromatic ring, serve as useful methods for construction of the reasonably complex benzospirocyclic amines. An exception to this generality was found in studies of the 2-anisyl-1-pyrrolinium salt, 1OCH_3. The spirocyclic amines obtained by cycloaddition to *p*-alkoxy substituted salts would be ideal precursors to the phenoxides 5, useful in spiro-annulation procedures (Chart 1). Irradiation of methanolic solutions of 1OCH_3 and acrylonitrile leads to generation of an abnormal photoadduct 7. Spectroscopic data indicate that this material is a 1:1 adduct containing a *p*-disubstituted aromatic ring and a 1,2,2-trisubstituted pyrrolidine unit and suggest that it possesses the bicyclic azetidine structure, 7. The characteristic ABM pattern observed in the ^{1}H-NMR spectrum[10] is that expected for a conformationally fixed $CH_2CH(NR_2)CN$ moiety.

These results demonstrate that the p-methoxy substituent has altered the chemical selectivity for 2+2 cycloaddition to the pyrrolinium salts. This phenomenon along with the regiochemistry for both C=N and C=C additions require brief comment. Although 2+2 olefin-aromatic ring photocycloadditions occur in a number of other systems[11], additions to C=N π-bonds are less common.[11a,12] The results of Cantrell[11a] and Margaretha[12c], involving competitive C=C and C=N cycloadditions of olefins to benzonitrile and α,β-unsaturated imines, respectively, are particularly relevant. The data currently available does not rule out non-concerted mechanisms for these processes. However, it is instructive to analyze the chemo- and regioselectivities of these processes from the viewpoint of FMO theory.[13] The effect of substituents on the C=N vs. C=C selectivities may arise from influences on pyrrolinium salt HOMO' and LUMO' coefficients and/or energies. CNDO/2 calculations (Table 2) show that the imine N-1 and C-2 coefficients are greater than those for C-1 and C-2 of the aromatic ring in the LUMO' and smaller in the HOMO' orbitals of the substituted salts. Thus FMO theory yields the prediction that cycloaddition to the C=N π-bonds would be preferred if LUMO (acrylonitrile)-LUMO' (pyrrolinium salt) interactions are controlling. Indeed, these calculations also show that the LUMO' and HOMO' energies of the p-OCH_3 system are higher than those for the unsubstituted salts. These differences are in a direction expected if the source of the substituent effect is in LUMO-LUMO' vs. HOMO-HOMO' control.[14] It should be mentioned that this reasoning affords a correct prediction of the regiochemistry for cycloaddition to the C=N bond.

Cycloaddition to the aromatic C=C π-bond would be preferred when pyrrolinium salt HOMO' orbital interactions predominate. In order to rationalize the regiochemistry observed for these processes, it is necessary to suggest that the HOMO' orbital of the salt interacts more strongly with the lowest energy bonding π orbital of acrylonitrile, ψ_1. Thus, if 2+2 cycloadditions to the aromatic ring are concerted, the regiochemistry is subject to acrylonitrile subjacent orbital control, an unusual occurrence in excited state cycloaddition processes.[15] This could arise when orbital energies of the excited addend are lowered significantly by the presence of electron withdrawing groups or, as in this case, a positive charge. This as well as other aspects of the excited state chemistry of 2-aryl-1-pyrrolinium salts are under current study.

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5. All new compounds gave satisfactory spectroscopic data and elemental analysis or high resolution mass spec derived molecular formula.
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7. (a) Photolyses were conducted in a preparative apparatus on N_2 purged solutions; (b) UV maxima for the salts were $1CH_3$ 278nm, 1F 268nm, 1Cl 276nm, 1Br 280nm and $1OCH_3$ 308nm.
8. TLC was performed on silica gel and HPLC on a Whatman Partisil ODS column.
9. Stereoisomeric mixtures were obtained in all cases except $1CH_3 \rightarrow 3CN\text{-}CH_3$.
10. Spectroscopic properties of 7: IR (liq film) 2240cm^{-1}, ^{1}H-NMR ($CDCl_3$)δ 7.30 (d, J=9.0Hz, 2H), 6.91 (d, J=9.0Hz, 2H), 4.34 (dd, J=10,6Hz, 1H), 3.76 (brs, 2H), 3.68 (S, 3H), 2.59 (dd, J=18,10Hz, 1H), 2.33 (dd, J=18,6Hz, 1H), 1.98 (m, 2H), 0.80 (brs, 2H); ^{13}C-NMR ($CDCl_3$) 173.2(s), 159.2(s), 128.3(d), 121.0(s), 114.3(d), 76.9(s), 60.8(q), 39.3(d), 55.2, 38.0, 33.5 and 22.4 (t); Mass Spec, m/e 228.1258 ($C_{14}H_{16}N_2O$ requires 228.1263), 213 ($-CH_3$). 200 ($-CH_2{=}CH$), 146, 121.
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14. It is difficult to compare orbital energies of the pyrrolinium salts with those of acrylonitrile since the degree of ion association and solvent stabilization of the cation should have a large effect on these values for the positively charged system.
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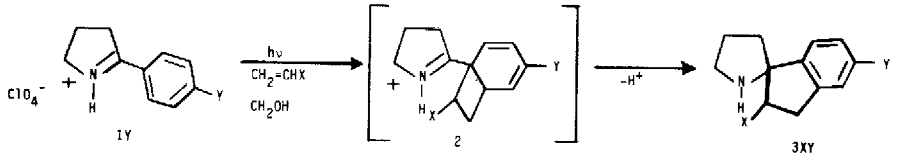

Chart 1.

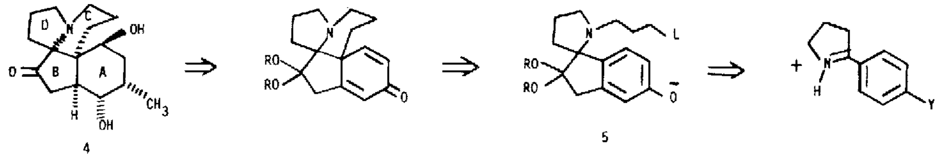

Table 1. Photocycloadditions to 2-Aryl-1-Pyrrolinium Salts.

Pyrrolinium Perchlorate	Olefin	Product	Purification Method[a]	Yield
1CH$_3$	CH$_2$=CHCN	3CN-CH	MD-TLC	18%
1CH$_3$	CH$_2$=CHCO$_2$CH$_3$	3CO$_2$CH$_3$-CH$_3$	MD	25%
1F	CH$_2$=CHCN	3CN-F	MD-TLC	20%
1F	CH$_2$=CHCO$_2$CH$_3$	3CO$_2$CH$_3$-F	MD	40%
1Cl	CH$_2$=CHCN	3CN-Cl	MD	50%
1Br	CH$_2$=CHCN	3CN-Br	MD	5%
1OCH	CH$_2$=CHCN	7	MD-HPLC	29%

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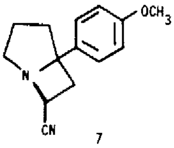
a) MD = molecular distillation



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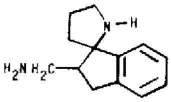

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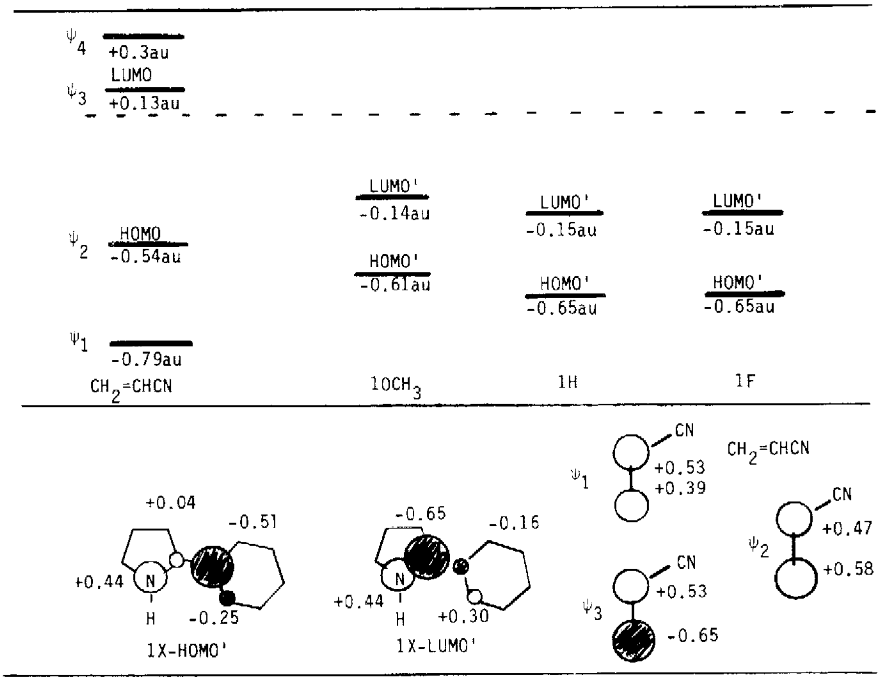
Table 2.



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