

REACTION OF AZOXYANISOLE WITH OXALYL CHLORIDE:  
USE OF PHOTOELECTRON SPECTROSCOPY IN SEEKING NEW REACTIONS

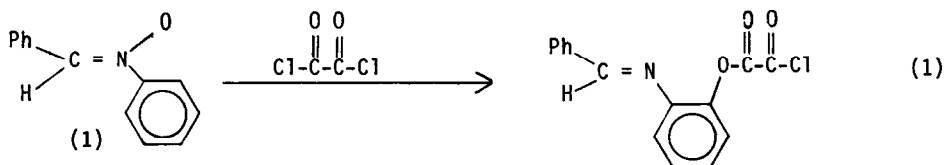
Garo Horozoglu Armen, Carlos Braunstein, Mitchell I. Weinstein and  
A. David Baker\*

Department of Chemistry, City University of New York, Queens College,  
Flushing, N.Y. 11367

Azoxyanisole, but not azoxybenzene, reacts readily with oxalyl chloride to give the corresponding orth-substituted azocompound. The differences in reactivity are discussed in terms of different HOMO energies, measured by PES.

According to frontier orbital treatments, the HOMO of a reactant may be an important factor in determining reactivity. The experimental parameter most closely related to an orbital energy is an ionization potential; within the framework of Koopmans' theorem the two may be equated<sup>1</sup>. Thus, techniques such as photoelectron spectroscopy which provide an experimental measure of ionization potentials, can be expected to have potential for providing insights into various aspects of reactivity. Previous studies from this and other laboratories confirm this potential<sup>2</sup>.

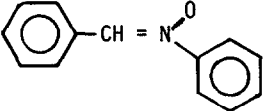
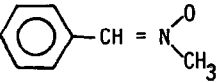
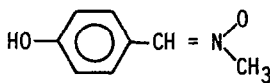
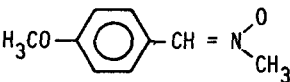
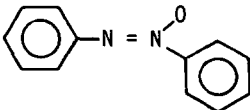
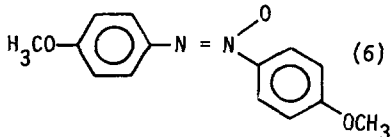
For some time now we have been interested in reactions of nitrones and azoxy compounds as well as in the general area of photoelectron spectroscopy; in this paper we describe an attempt to use photoelectron spectroscopy (PES) to probe effects of substituents on these systems with a view to modifying structure to give new kinds of reactions. For nitrones, two kinds of reactions have been of interest in our work, viz. (1) 1,3 dipolar cycloadditions<sup>3</sup>, and (2) ortho-substitution reactions of N-aryl nitrones in reaction with certain acid and acyl halides or other reagents<sup>4</sup>; one example of which is the reaction of  $\alpha$ ,N-diphenylnitron (1) with oxalyl chloride:



While nitrones undergo these two kinds of reaction with relative ease, azoxy compounds are

essentially inert, e.g. it was not until 1973 that the first report of a 1,3-dipolar cycloaddition reaction of an azoxy compound (benzo[c]cinnoline-N-oxide with dimethylacetylenedicarboxylate) was made<sup>5</sup>. On comparison of a nitron with a corresponding azoxy compound, the diminished reactivity of the latter in cycloaddition and other similar reactions can be understood qualitatively in terms of the replacement of the methine group in the nitron by the more electronegative nitrogen atom in an azoxy compound. This replacement will tend to stabilize the orbitals of an azoxy compound relative to the corresponding nitron. Quantitatively such stabilization can be measured by PES; e.g. comparison of the spectra of  $\alpha$ ,N-diphenyl nitron and of azoxybenzene show the first ionization potential (I.P.) of the latter to exceed that of the former by ca. 0.8 eV (entries 1 and 5 in Table)

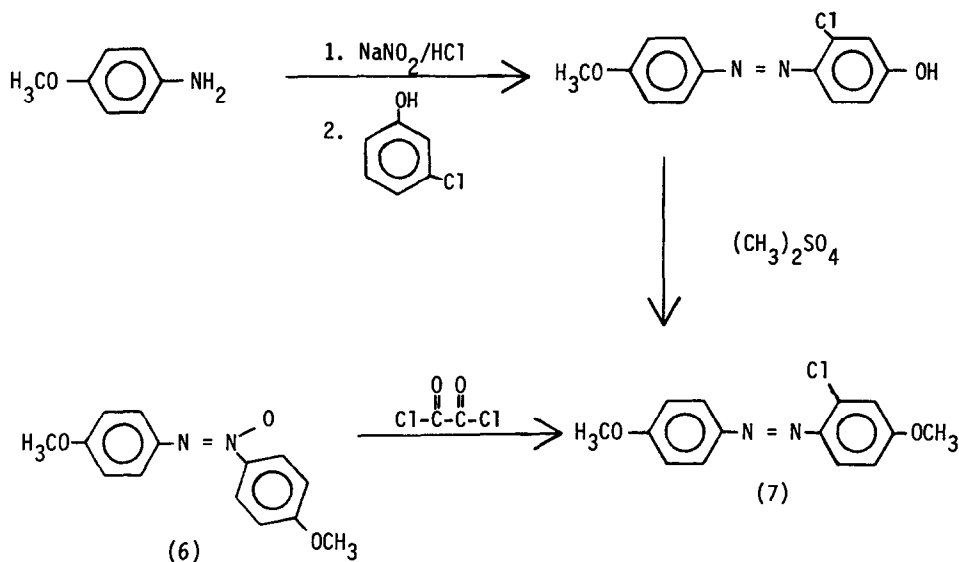
TABLE  
Ionization Potentials of Selected Nitrons and  
Azoxycompounds

Compound		Ionization Potential (eV) <sup>*</sup>
	(1)	7.75
	(2)	8.01
	(3)	7.76
	(4)	7.60
	(5)	8.55
	(6)	8.00

\*measured with a modified Perkin Elmer  
PS16 photoelectron spectrometer

The first IP of phenyl 1,3-dipoles relates to the HOMO orbital ( $\pi 4b_1$ ) which is localized partly on the oxygen atom<sup>6</sup>. Entries 3 and 4 in the Table show that significant lowering of the IP (i.e. raising of the HOMO energy) can be achieved by the introduction of a para -OH or -OCH<sub>3</sub> substituent in the phenyl ring. For azoxy compounds, it is therefore to be expected that a corresponding HOMO destabilization should be observed if appropriate -OH or -OCH<sub>3</sub> groups are introduced. Our objective in this work was to verify this prediction, and to find out if enhanced reactivity might accompany such raising of HOMO energy.

Entries 5 and 6 in the Table show that the expected HOMO destabilization was observed, so at this point our chemical investigation began. Dichloromethane solutions of azoxybenzene and of anoxyanisole were mixed in separated experiments with oxalyl chloride. Azoxybenzene showed no reaction even after several hours, while a deep red coloration appeared immediately upon addition of the oxalyl chloride to azoxyanisole. Upon work up, an orange product, m.pt. 94-96<sup>o</sup> was isolated. Mass spectrometry of the product showed it contained one chlorine atom per molecule and had a molecular weight of 276 (M+2 at 278). The position of the added chlorine atom was determined by an independent synthesis:



The yield of (7) from (6) was essentially quantitative. Thus the reactivity of azoxybenzene towards oxalyl chloride is dramatically enhanced by the introduction of para -OCH<sub>3</sub> groups. We have also observed increased reactivity towards phosgene, thionyl chloride, and ethyl oxalyl chloride

(azoxybenzene itself is inert to all these reagents). However, we were surprised that oxalyl chloride reacts differently with azoxyanisole than with N-aryl nitrones, giving ortho-chlorination rather than formation of an ortho-chloroglyoxalate (equation 1). Ethyl oxalyl chloride in reaction with (6) also gives some (7), so  $\text{Cl}^-$  may be the chlorinating species. The reason that nitrones do not react similarly with oxalyl chloride is a mystery at this time. Later work will explore this, and the possibility of effecting other novel reactions with azoxy compounds of low ionization potential.

#### Acknowledgements

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#### References and Footnotes

1. For a discussion of Koopmans' theorem and its limitations, see A.D. Baker and C.R. Brundle, in "Electron Spectroscopy - Theory, Techniques, and Applications", Volume 1, p. 45, Academic Press, London (1977).
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