Table II. Relative Rate[a] and Absorptions of **2a**

Irradiated light (nm)	Rel rate[b]	λ_{max} of **2a** (log ϵ)[c]
233	39.1	233 (3.95)
259	8.3	
273	18.1	273 (3.27)
285	8.3	
312	5.3	
339	1.7	
372	2.6	372 (4.17)
392	1.0	
433	0.0	433 (2.20)

[a] Photolysis of solutions in a quartz cell with a 2-kW xenon-arc lamp. [b] Initial slope from plots of [**2a**] against time, [**2a**] determined spectrophotometrically. Reaction rates are normalized to overcome fluctuations in light intensity. [c] In cyclohexane.

the excited thione compound **2*** might interact with the tin–tin bond, followed by abstraction of sulfur to produce the *S,S*-carbene, which dimerized to **1**, presumably by attack to another carbene molecule or thione **2.**

Other advantages of the present one-step synthesis, in addition to those mentioned in the introduction, include the convenience and safety of the procedure, and the ease of isolating the products, **1**, with high purity. We are continuing our investigations of the application of the present method. It is noteworthy that the desulfurization proceeds only under irradiation. The development of other useful processes involving the reaction of distannane with excited organosulfur compounds may be expected.

References and Notes

(1) J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948–949 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125–1132 (1973); for reviews see A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 7, 232–240 (1974).

(2) Recently, Moses and Chambers reported the method involving the electrochemical process: P. R. Moses and J. Q. Chambers, *J. Am. Chem. Soc.*, **96**, 945–946 (1974).

(3) Y. Ueno and M. Okawara, *Chem. Lett.*, 1135–1138 (1974); Y. Ueno, Y. Masuyama, and M. Okawara, *ibid.*, 603–606 (1975); Y. Ueno, A. Nakayama, and M. Okawara, *Synthesis*, 277–278 (1975).

(4) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453–1454 (1970).

(5) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258–2268 (1971), and references cited therein; J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553–2556 (1973).

(6) Desulfurizative dimerization of thione **2** with trivalent phosphorus compounds has been successful only when a strong electron withdrawing group, such as COOMe, CF_3, CN, etc., is attached to the 4- or 5-positions in thione **2**; H. D. Hartzler, *J. Am. Chem. Soc.*, **92**, 1412–1413 (1970), **95**, 4379–4387 (1973).

(7) H. Shirai, Y. Sato, and M. Niwa, *Yakugaku Zasshi*, **90**, 59–63 (1970); *Chem. Abstr.*, **72**, 90593 (1970).

(8) For example, see R. D. Chambers, H. C. Clark, and C. J. Willis, *Chem. Ind. (London)*, 76–77 (1960).

(9) R. C. Poller, "The Chemistry of Organotin Compounds", Logos Press, London, England, 1970, pp 137–144.

Y. Ueno,* A. Nakayama, M. Okawara

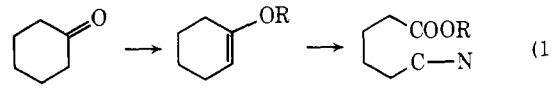
Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Ookayama, Meguro, Tokyo, 152, Japan

Received June 28, 1976

Cleavage of Carbon–Carbon Bonds. Copper(II)-Induced Oxygenolysis of *o*-Quinones, Catechols, and Phenols

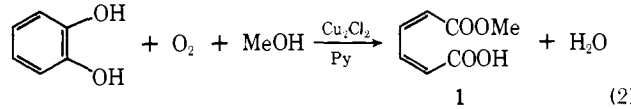
Sir:

Our interest in new synthetic approaches to caprolactam led us to explore carbon–carbon bond cleavage of various cyclic C_6-systems. We recently reported on a successful development of the nitrosolysis reaction—a carbon–carbon bond cleavage effected through nitrosation with a simultaneous introduction of a terminal carbon–nitrogen bond (eq 1).[1]



(1)

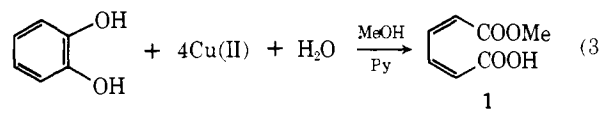
The remarkable ability of certain oxygenases to catalyze oxidative carbon–carbon bond cleavage of various aromatic substrates, most notably of phenols and catechols, is well known.[2] It is also recognized that a similar carbon–carbon bond cleavage of certain catechols can be effected with molecular oxygen and various transition metal ions.[3] The carbon–carbon bond cleavage of benzil to benzoic acid with molecular oxygen in the presence of certain copper(I) complexes was investigated by Kinoshita[4] more than 20 years ago, and very recently it has been claimed that the carbon–carbon bond cleavage of catechol to the *cis,cis*-muconic acid monomethyl ester, **1**, was achieved by oxidation with molecular oxygen activated by a particular copper(I)/pyridine/methanol system (eq 2).[5]



1 (2)

For reasons mentioned in the opening sentence, we too have investigated the carbon–carbon bond cleavage of catechol and of phenol in the presence of various transition metal ions and molecular oxygen. While we will present a full account of our work in this area in the near future, we would like to comment here on the role of the oxygen in the oxidative cleavage of catechol to *cis,cis*-muconic acid monoalkyl esters in the presence of copper(II).[5]

We have demonstrated that catechol reacts with cupric methoxy chloride in pyridine containing methanol and water *under anaerobic conditions* to give the *cis,cis*-muconic acid monomethyl ester (eq 3, Cu(II) = CuClOMe). Cupric methoxy chloride is a stable light yellow-green solid which readily reacts with atmospheric moisture. Hay, Endres, and their coworkers reported that cupric methoxy chloride reacts with pyridine to give a deep green complex, PyCuClOMe (I), which according to them exists as a dimer.[6] The pyridine cupric methoxy chloride complex I appears more stable and consequently it is more convenient to use than the cupric methoxy chloride itself (eq 3, Cu(II) = PyCuClOMe). The following experimental procedure is representative.

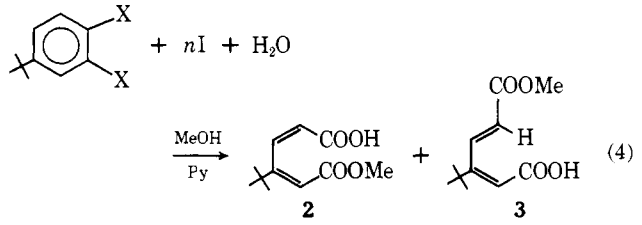


1 (3)

A three-neck flask equipped with a mechanical stirrer, and an addition funnel, protected with an inert gas atmosphere, was charged with solid I (6.26 g, 30 mmol), and a solution of methanol (0.3 ml) and water (0.27 g, ca. 15 mmol), in pyridine (60 ml). The green suspension was then freeze–pump–thaw degassed under nitrogen or argon. A similarly degassed solution of catechol (0.55 g, 5 mmol) in pyridine (10 ml) and methanol (0.5 ml) was added dropwise from the addition funnel at room temperature with stirring under anaerobic conditions. After complete addition (15–30 min) the reaction mixture was stirred an additional 15 min and then evaporated. The yellow-brown solid residue was hydrolyzed with dilute hydrochloric acid in the presence of chloroform under the inert atmosphere. Drying and evaporation of the chloroform solution afforded the *cis,cis*-muconic acid monomethyl ester, mp 80–80.5 °C, in an 80–85% yield.

While we think that the discussion of the mechanism of this carbon–carbon bond cleavage effected by the copper(II) sys-

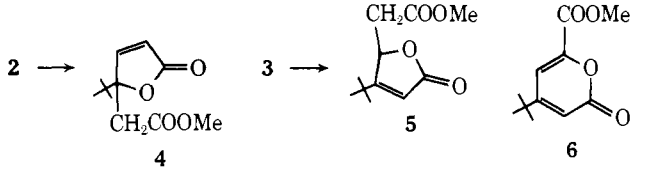
tem would be premature at this time, a few additional observations may put these considerations in proper perspective. The conversion of catechol to *cis,cis*-muconic acid monomethyl ester is a four-electron oxidation. It is possible that catechol is first converted in a two-electron oxidation to *o*-benzoquinone, and subsequently transformed to the observed monomethyl ester. Since 4-*tert*-butyl-1,2-benzoquinone[7] is considerably easier to handle than the *o*-benzoquinone itself, we used the *tert*-butyl derivatives to test the above hypothesis. Thus, the reaction of 4-*tert*-butylcatechol (0.83 g, 5 mmol) with I (6.26 g, 30 mmol) in pyridine/methanol/water solution as above, under anaerobic conditions, followed by a similar workup as before, gave a mixture of the corresponding isomeric 3- and 4-*tert*-butylmuconic acid monomethyl esters **2** (55%) and **3** (40%) (eq 4, X = OH, n = 4).[8,9] Upon attempted chromatography on silica gel both acid esters were converted to the corresponding ester lactones **4** and **5**.[10] Essentially the same results were obtained when the reaction was carried out with 4-*tert*-butyl-1,2-benzoquinone (0.82 g, 5 mmol) and I (3.14 g, 15 mmol) as above (eq 4, X = O, n = 2).



(4)

2 **3**

While the anaerobic oxidation of catechol itself, as above but under anhydrous conditions, gave predominantly a polymeric material, the anaerobic oxidation of either 4-*tert*-butylcatechol or 4-*tert*-butyl-*o*-benzoquinone in the absence of added water, followed by exaporation of the solvents, gave a brown solid. Acid hydrolysis of this solid in chloroform gave crystalline material **6**, mp 84–85.5 °C, analyzing for $C_{11}H_{14}O_4$. The spectroscopic evidence suggested that the **6** is the 6-carbomethoxy-4-*tert*-butyloxacyclohexa-3,5-diene-2-one.[11]

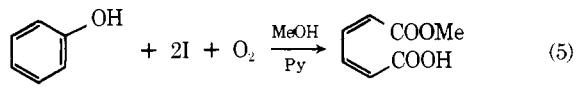


4 **5** **6**

The same cleavage reaction of the catechols and 4-*tert*-butyl-1,2-benzoquinone (10 mmol) can be carried out with I (20 mmol) under similar reaction conditions as above but in the presence of oxygen. Alternatively, the reaction can be carried out with copper(II) reagent generated either by reaction of oxygen with cuprous chloride in pyridine containing ca. 5 equiv of methanol, ethanol, *n*-butyl alcohol, or isopropyl alcohol,[5,12,13] or by a reaction of oxygen with cuprous chloride in pyridine followed by addition of an alcohol. In either case, the addition of catechol solution in a similar solvent mixture as above resulted in consumption of an equivalent amount of oxygen. After the complete reaction a similar workup procedure gave the corresponding *cis,cis*-muconic acid monoalkyl esters:[8] R = Me, mp 80–80.5 °C, 82%; Et, mp 101–102 °C, 63%; *n*-Bu, mp 54.5–56 °C, 76%; $(Me)_2CH$, mp 51–71 °C (mixture of double bond isomers) 26% yield, respectively.

Finally, we would like to report that our preliminary experiments indicated that oxidation of phenol with I in the presence of oxygen as described above in the catechol oxidation, gave the *cis,cis*-muconic acid monomethyl ester **1** in 60–70% yield (eq 5).

The above experiments clearly demonstrate that the oxidative carbon–carbon bond cleavage in catechol is effected by



(5)

1

the particular copper(II) system used. Evidently, one of the two new oxygen atoms introduced into the product **1**, originated directly from the copper(II) reagent in a form of the methoxy group, and the second one, in a form of the hydroxy group, came from the water provided externally. Thus, contrary to previously proposed mechanisms,[2,5] it now appears that the role of oxygen in these transformations is to reoxidize the copper(I) generated in the course of the reaction between catechol and the copper(II) oxidizing reagent present initially.[14] Consequently, the conclusion that cuprous chloride in pyridine is a good system for activating molecular oxygen, and hence that it can be used as the nonenzymatic model reaction for pyrocatechase[5] must be taken *con granulo salis*. We suggest that the above conclusion about the role of oxygen in our system, may be relevant to enzymatic reactions as well and may provide an alternative explanation to previous hypotheses involving activation of molecular oxygen.[2,5]

It is clear that molecular oxygen is an efficient reagent for converting copper(I) to copper(II) under very mild conditions.[15] Thus, certain copper(II) systems, and possibly some other transition metal ions, in combination with oxygen may provide highly efficient catalytic systems for this kind of carbon–carbon bond cleavage reaction.

After this manuscript was submitted to the Editor, we learned that Tsuji also found that phenol can be cleaved to *cis,cis*-muconic acid monomethyl ester (J. Tsuji and H. Takayanagi, *Tetrahedron Lett.*, 1365 (1976)). However, the authors still presume that cuprous chloride in pyridine/methanol is an efficient system for activation of molecular oxygen and, hence, that the reaction represents a good nonenzymatic model reaction for pyrocatechase.

References and Notes

(1) (a) M. M. Rogić, J. Vitrone, and M. D. Swerdloff, *J. Am. Chem. Soc.*, **97**, 3848 (1975); (b) M. M. Rogić, J. Vitrone, and M. D. Swerdloff *J. Am. Chem. Soc.*, in press; (c) M. M. Rogić, K. P. Klein, J. M. Balquist, and B. C. Oxenrider, *J. Org. Chem.*, **41**, 482 (1976).

(2) Cf. for example G. A. Hamilton in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1974, p 405, and references therein.

(3) R. R. Grinstead, *Biochemistry*, **3**, 1308 (1964).

(4) K. Kinoshita, *Bull. Chem. Soc. Jpn.*, **32**, 777, 780, 783 (1959); (b) K. Kinoshita, *J. Chem. Soc. Jpn., Pure Chem. Sect.*, **75**, 48 (1954).

(5) J. Tsuji and H. Takayanagi, *J. Am. Chem. Soc.*, **96**, 7349 (1974); (b) J. Tsuji, H. Takayanagi, and I. Sakai, *Tetrahedron Lett.*, 1245 (1975).

(6) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); (b) A. S. Hay, *J. Polym. Chem.*, **58**, 581 (1962); (c) G. F. Endres and J. Kwiatek, *Ibid.*, **58**, 593 (1962); (d) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, *28*, 1300 (1963); (e) A. S. Hay and G. F. Endres, *Polym. Lett.*, **3**, 887 (1965); (f) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

(7) V. Balogh, M. Fetizon, and M. Golfier, *J. Org. Chem.*, **36**, 1339 (1971).

(8) All new compounds gave satisfactory elemental analysis.

(9) The 60-MHz NMR spectrum of the crude product clearly revealed two major components, **2** (ca. 55%) ($CDCl_3$) δ 10.97 (bs, CO_2H, 1 H), 6.83 (dd, J_{45} = 13 Hz; $J_{24} \sim 2$ Hz, CH=CHCOOH, 1 H), 5.97 (d, J_{45} = 13 Hz, C=-CHCOOH, 1 H), 5.82 (d, $J_{24} \sim 2$ Hz, C=$CH$$CO_2$Me, 1 H), 3.63 (s, OCH_3, 3 H), 1.13 (s, $C(CH_3)_3$, 9 H); and **3** (ca. 40%) ($CDCl_3$) δ 10.97 (bs, CO_2H, 1 H), 7.57 (dd, J_{23} = 16.8 Hz, $J_{35} \sim 1.5$ Hz, CH=CCOOMe, 1 H), 5.87 (d, J_{23} = 16.8 Hz, CH=$CH$$CO_2$Me, 1 H) 5.82 (d, $J_{35} \sim 1.5$ Hz, C=$CH$$CO_2$H, 1 H), 3.77 (s, OCH_3, 3 H), 1.13 (s, $C(CH_3)_3$, 9 H).

(10) 5-Carbomethoxymethyl-5-*tert*-butyloxacyclopent-3-ene-2-one (**4**) 100-MHz NMR ($CDCl_3$) δ 7.58 (d, J_{34} = 5.9 Hz, CH=CHCOO, 1 H), 6.10 (d, J_{34} = 5.9 Hz, CH=CHCOO, 1 H) 3.64 (s, OCH_3, 3 H), 2.95 (q, CH_2COOMe, 2 H), 1.01 (s, $C(CH_3)_3$, 9 H); ir (neat) 3140, 1780–1730, 610 cm^{-1}; mass spectrum C.I. (methane) MH^+ at *m/e* 213. 5-Carbomethoxymethyl-4-*tert*-butyloxacyclopent-3-ene-2-one, **5**, 60-MHz NMR ($CDCl_3$) δ 5.91 (d, $J_{35} \sim$ 1.7 Hz, C=CHCO–, 1 H), 5.46 (ddd, J_{ac} = 9.2 Hz, J_{bc} = 3.2 Hz, $J_{3c} \cong$ 1.7 Hz, O$CH_cCH_aH_b$–, 1 H), 3.77 (s, OCH_3, 3 H), 3.08 (dd, J_{bc} = 3.2 Hz, J_{ab} = 16.0 Hz, $CH_cCH_aH_b$–, 1 H), 2.54 (dd, J_{ab} = 16.0 Hz, J_{ac} = 9.2 Hz, $CH_cCH_aH_b$–, 1 H), 1.26 (s, $C(CH_3)_3$, 9 H); ir (neat) 1780–1740, 1630 cm^{-1}; mass spectrum: C.I. (methane) MH^+ at *m/e* 213.

(11) 6-Carbomethoxy-4-*tert*-butyloxacyclohexa-3,5-diene-2-one, **6**, 100-MHz NMR ($CDCl_3$) δ 7.21 (d, J = 1.8 Hz, –CH=C–O–, 1 H), 6.42 (d, J = 1.8 Hz, C=CHCO–, 1 H), 3.97 (s, OCH_3, 3 H), 1.27 (s, $C(CH_3)_3$, g H); ir (neat) 3130, 1760–1720, 1645 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71.

Found: C, 62.79; H. 6.56.

(12) Numerous others have investigated the reaction of cuprous chloride with oxygen in various solvents; for a more recent study see C. E. Kramer, G. Davies, and R. W. Slaven, *J. Chem. Soc., Chem. Commun.*, 606 (1975).

(13) Davies and his co-workers[12] suggested the presence of a copper(I) peroxide complex in pyridine solution.

(14) As early as in 1937 F. Kubowitz, *Biochem. Z.*, **292**, 221 (1937); **299**, 32 (1939), proposed that in oxidation of catechol to *o*-benzoquinone catalyzed by copper oxidases, the function of oxygen was to regenerate copper(I) -enzyme to copper(II)-enzyme, which was the actual oxidizing reagent. Similar conclusion was reached by Hay, Endres, and their co-workers[6] who felt that in the catalytic oxidative polymerization of phenols the function of oxygen was the same and that in their reaction too the copper(II) was the true oxidizing reagent.

(15) Wacker process for conversion of ethylene and oxygen into acetaldehyde is an example; for details see G. Szonyi, *Adv. Chem. Ser.* **No. 70**, 53 (1968).

Milorad M. Rogić,* Timothy R. Demmin, Willis B. Hammond

Chemical Research Center, Allied Chemical Corporation
Morristown, New Jersey 07960

Received May 24, 1976

Bridging Regioselectivity in Triplet-Sensitized Di-π-methane Photorearrangements of Ortho-Substituted Benzonorbornadienes. A Case for the Importance of Benzene HOMO and LUMO Polarization

Sir:

We have recently delineated the striking regioselectivity observed in the triplet-sensitized di-π-methane rearrangements of donor and acceptor meta-substituted benzonorbornadienes (**1**)[1] and developed a simple MO model which accounts for the preferential benzo-vinyl bonding, which operates in *opposite directions*.[2] At the level presented, the model would predict no selectivity in rearrangements of ortho-substituted benzonorbornadienes. Yet, as summarized in Figure 1 and Table I, this substitution pattern can exert large directive effects, although they are now in the *same direction*. Double resonance studies and experimental determination of LIS values established the major products to be **3** in several cases. That all such benzonorbornadienes (except X = F) adopt the same triplet bonding preference was confirmed additionally by chemical methods and ^{13}C NMR spectroscopy. All photoproducts showed no inclination for further reaction under the conditions employed.

These results can be accounted for by further elaboration of our model,[2] taking into account the polarization of frontier orbitals caused by donor or acceptor substituents.[3] As indicated in Figure 2,[4] the influence of a donor group (e.g., amino, as an extreme) is to split the degeneracy of the highest occupied molecular orbitals (HOMO's) and lowest unoccupied molecular orbitals (LUMO's) of benzene. The donor orbital (n) conjugatively interacts most with the symmetric (b_1 in C_{2v}) HOMO and to a lesser extent with the symmetric (b_1*) LUMO. In addition to these changes in energy, the substituent causes a mixing of b_1 orbitals. The sign and magnitude of mixing of ψ_1, ψ_4, and ψ_6 into the HOMO can be numerically calculated by perturbation theory as demonstrated by Libit and Hoffmann,[3] but can be qualitatively determined by the following simple rules: (1) the extent of mixing of an orbital (ψ_n) into the HOMO (or any orbital, ψ_i) is inversely dependent on both the difference in energy between the HOMO and ψ_n, and the difference in energy between the HOMO and the perturbing orbital; (2) a low-lying perturbing orbital will cause the HOMO (or any other orbital, ψ_i, lying higher in energy than the perturbing orbital) to mix in all lower lying orbitals in a bonding fashion, and to mix in all higher lying orbitals in an antibonding fashion; (3) a high-lying perturbing orbital will cause the HOMO (or any other orbital, ψ_i, lying lower in energy than the perturbing orbital) to mix in all lower lying orbitals in an antibonding fashion, and to mix in all higher lying orbitals in a bonding fashion. "Bonding" or "antibonding" is determined at the site of substitution.

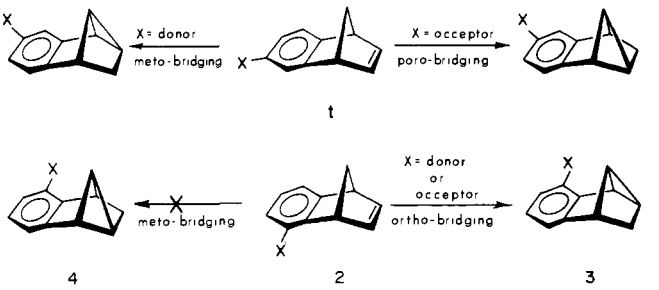


Figure 1. Regiochemistry of triplet-sensitized di-π-methane rearrangements of benzonorbornadienes.

Table I. Product Distribution Data for Triplet-Sensitized Irradiation of **2**[b]

X	3, %	4, %	X	3, %	4, %
$-NO_2$	>99		$-OCH_3$	89.3	10.7
$-COCH_3$	>99		$-NH_2$	82.6	17.4
$-CN$	96	4	$-CH_3$[a]	70	30
			$-F$	50	50

[a] J. R. Edman, *J. Am. Chem. Soc.*, **91**, 7103 (1969). [b] Dilute C_6H_6 solutions, Pyrex, 3500-Å radiation with acetophenone present.

Returning to the benzene case, the following generalizations may be made on the basis of these rules: For all perturbing donor orbitals whose energies lie below that of ψ_3 (the HOMO), ψ_3 will be polarized by mixing in ψ_1 in a bonding fashion and some of ψ_4 in an antibonding fashion at the site of attachment of D. That is, ψ_3 becomes $\psi_3' = \psi_3 + \psi_1 - \psi_4 - D$ (D having been mixed in first order), where coefficients of mixing have been omitted for clarity. The mixing in of ψ_1 will cause the HOMO ipso and ortho coefficients to be increased, while the meta and para will be decreased; mixing in of ψ_4 decreases the ipso and meta coefficients and increases the ortho and para coefficients. Since ψ_4 has large ipso and para coefficients, the effect on these coefficients is largest. As shown in Figure 2, the strong donor amino group gives HOMO (ψ_3') coefficients in the order para > ipso $\gtrsim$ ortho > meta. As pointed out by Zimmerman, the benzyl anion represents the extreme of donor substitution.[5] In general, as the donor strength increases, the ortho/meta coefficient ratio increases from 1 toward ∞, and the para/ortho ratio decreases from 2 to 1. The SLUMO (ψ_4') of donor-substituted benzene is polarized by a similar mechanism, but to the opposite extent and in the opposite direction.

An acceptor group will generally have not only a low-lying vacant orbital, but will have a weak donor orbital also. The vacant orbitals of acceptor-substituted aromatics will be important in both reaactions with nucleophiles and in photochemical reactions. The influence of vacant acceptor orbitals, whose energies lie above ψ_4 and ψ_5 of benzene, on the LUMO (ψ_4) of benzene is the mirror image of the influence of a donor orbital on the filled orbitals. Thus, ψ_4 is lowered most by strong acceptors, and coefficient magnitudes are para > ipso $\gtrsim$ ortho > meta, as represented in Figure 2 by the nitrobenzene orbitals. For this molecule, the SHOMO (ψ_3') polarization is dominated by the nitro acceptor orbital, but this will vary depending on the energy of the acceptor filled orbital.

Turning to the photochemical phenomena in question, in the meta-substituted cases discussed in our previous communication, the fact that the b_1* orbital contributed more to the