nitrogens suggests that the technique will be valuable in this field of research. Finally, it has been suggested that the vanadate and oxovanadium(IV) ions may play a role in regulating enzyme activity.[4,10,11] Already ESR has been applied to study the fate of the vanadate ion transported into the human red cell.[4] Here also ENDOR could provide valuable complementary information. It is of interest that information on ligand hfsc's in VO^{2+} complexes can be derived also from modulation effects on electron spin-echo decay curves.[19] Whether or not this method can give access to the detailed information presented here remains to be seen. In any case, the method of analysis used by Dikanov et al.[19] does not lend itself for this purpose.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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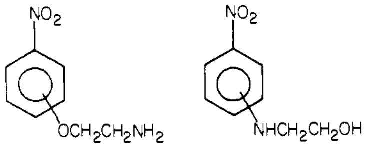
Thermal and Photochemical Smiles Rearrangements of β-(Nitrophenoxy)ethylamines

Sir:

Our interest in aromatic photosubstitution reactions prompted us to search for intramolecular photosubstitutions analogous to the extensively reported intermolecular reactions.[1] Ground-state intramolecular nucleophilic aromatic substitutions are known as Smiles rearrangements or, when carbon nucleophiles are involved, as Truce-Smiles rearrangements.[2] We wish to report that we have successfully synthesized, as prospective Smiles rearrangement precursors, the hydrochlorides of the ortho, meta, and para isomers of β-(nitrophenoxy)ethylamine, I, II, and III, and have examined their thermal and excited-state reactions.

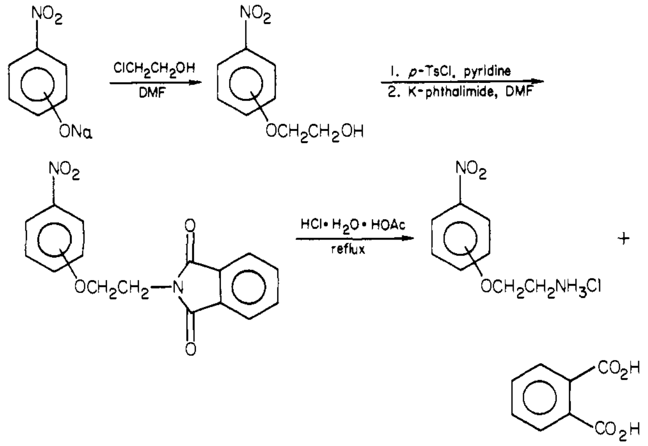


I, ortho
II, meta
III, para

IV, ortho
V, meta
VI, para

The hydrochlorides of I, II, and III were synthesized by the sequence outlined in Scheme I.[3] Hydrochlorides were selected as the synthetic targets because previous attempts to isolate the neutral forms of I and III[4-6] had failed due to their facile rearrangements.[7]

Scheme I



As expected, I and III underwent smooth Smiles rearrangements in aqueous sodium hydroxide to give the corresponding β-(nitroanilino)ethyl alcohols, IV and VI. First-order rate constants for the rearrangements of I and III in aqueous sodium hydroxide (0.01 M) at 33 °C are 1.5×10^{-4} s^{-1} and 4.2×10^{-5} s^{-1}, respectively.[8]

I and III at 0 °C in aqueous sodium hydroxide had half-lives on the order of days. We were able, therefore, to examine the photochemical reactions of I and III with little interference by the thermal reaction by keeping the photolysis temperatures near 0 °C. Photolysis of I (1.6×10^{-4} M) with Pyrex-filtered light from a medium-pressure Hg lamp (1200 W General Electric UA-11) in a cuvette in aqueous sodium hydroxide (0.01 M) at 0-5 °C caused complete loss of reactant absorptions in 2 min and gradual thermal changes in the UV spectrum over 15 min, leading to product absorptions at 335, 300, and 229 nm. Absorption by a thermally reactive intermediate was observed at 287 nm. A scarcely noticeable shoulder absorption appeared in the 400-450-nm range, a region in which the Smiles product IV absorbs strongly (λ_{max} 441 nm (ϵ 6140)); IV was stable thermally and photochemically in the reaction medium. Though we have not isolated the photoproducts, the observations are sufficient to conclude that I does not undergo Smiles rearrangement in the excited state.

Photolysis of III under the same conditions used for I also caused little or no absorption attributable to the Smiles rearrangement product VI (λ_{max} 404 nm (ϵ 13 300)). In this case also, the Smiles product VI was shown to be stable under the irradiation conditions. A preparative photoreaction of III (600 mg) in aqueous 0.04 M Na_2CO_3 (550 mL) was carried out by irradiating the solution for 2 h at 2-18 °C with a 450-W Hanovia immersion lamp. UV spectra of diluted aliquots of the reaction mixture showed that III (λ_{max} 318 nm (ϵ 8000)) had almost completely reacted in this time. Workup was performed by neutralization, extraction with ethyl acetate, and concentration of the extract to a brown oil. Chromatography of a portion of the extracted products (392 mg) on activated alumina (15 g) gave a red solid (67 mg) identified as 3,4-dihydro-6-nitro-2*H*-1,4-benzoxazine (VII, 14%),[9] a yellow solid (55 mg) identified as *N*-(2-hydroxyethyl)-4-nitroaniline (VI, 11%),[7] and a red salt (148 mg), recovered by washing the alumina with water, which was identified as the sodium salt of *N*-(2-hydroxyethyl)-2-hydroxy-5-nitroaniline (VIII, 25%).[10] These substances were identified by spectral and chromatographic comparisons with authentic samples. Additional study revealed that VII is stable under the irradiation conditions and could not be an intermediate in the formation of VIII. The elimination of atmospheric oxygen by flushing the reaction solution

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(8) The kinetics of Smiles rearrangement of III have been reported: Knipe, A. C.; Lound-Keast, J.; Sridhar, N. *J. Chem. Soc., Chem. Commun.* **1976**, 765-6.

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(10) Eckhardt, W. German Patent 928 909; *Chem. Abstr.* **1958**, *52*, 4197f.

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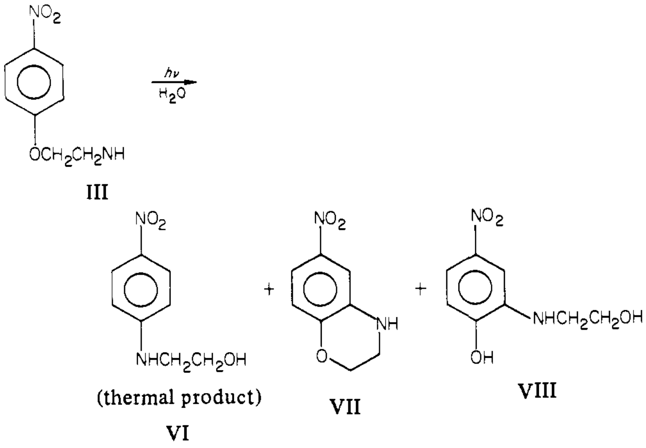
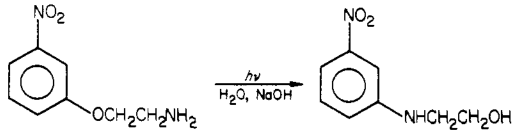


with nitrogen or by vacuum degassing had no influence on the rate of the photoreaction.

The meta isomer II showed no change in its UV spectrum after heating at 99 °C for 15 min in aqueous sodium hydroxide (0.01 M). On photolysis of II (1.1×10^{-4} M) in a cuvette in aqueous sodium hydroxide (0.01 M) at 313 nm or with Pyrex-filtered light from a mercury lamp, λ_{max} at 332 nm ($A = 0.10$) and 274 nm ($A = 0.29$) shifted to 383 nm ($A = 0.11$) and 241 nm ($A = 0.81$), respectively; isosbestic points were observed at 358, 306, 292, 272, and 218 nm. The final UV spectrum was superimposable on that of V at 1.1×10^{-4} M. The preparative reaction was carried out by using 273 mg of the hydrochloride of II in 250 mL of 0.01 M NaOH and irradiating with a 200-W Hanovia immersion lamp for 4 h. Workup was performed by extracting with ether and concentrating the extract to an oily orange solid which was identified as nearly pure V.



II V

The quantum yield for the photo-Smiles rearrangment of II (1.3×10^{-3} M) in aqueous sodium hydroxide (0.01 M) was determined at 313 nm on a merry-go-round apparatus by using degassed valerophenone (0.1 M) in benzene as the actinometer.[11] At less than 10% conversions, the quantum yield is 0.23.

Remarkable contrast to these results is shown by the intermolecular photosubstitutions by amines on 3- and 4-nitroanisoles. Though quantitative efficiency data are not available, Cornelisse and Havinga note[1] that the photodisplacements of methoxide from 4-nitroanisole in water by amines such as methyl-, dimethyl-, or ethylamine to give 4-nitroanilines are clean and efficient reactions.[12] The opportunity for the analogous reaction, if the mechanism involves nucleophilic attack on C-1 of the excited aromatic molecule, is clearly presented by III since it undergoes Smiles rearrangement in the ground state. Such reaction is, however, not seen in the excited state; intramolecular attack at C-2 of III prevails instead. Also, whereas the *intermolecular* substitution on 3-nitroanisole by amines is relatively inefficient among nitroanisole photosubstitution,[1] we observed the *intramolecular* meta photosubstitution of II to be highly efficient.

An attractive explanation for these differences is that, in contrast to the intermolecular reactions, the intramolecular reactions of II and III allow no direct interaction of the nucleophile with the nitro group in the excited state. The strong meta-activating influence of the nitro group in the π,π^* state[13,14] prevails and directs the incoming nucleophile in II and III to a ring carbon atom meta to nitro. Thus, the intermolecular photosubstitutions on 4-nitroanisole may be initiated not by nucleophilic ring attack but by an electron-transfer interaction in an n,π^* state[15] involving the nitro group and the amine. This interaction cannot occur in III. The electron-transfer interaction may lead to quenching as well as to substitution for 4-nitroanisole[13] but largely to quenching for 3-nitroanisole because the odd electron distribution in the anion radical is unfavorable for radical coupling at the ring position bearing the nucleofugic methoxy group.[16] This quenching interaction would be unfavorable in II, the absence of which may enable its efficient photosubstitution.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A research equipment grant from the National Science Foundation for a UV-vis spectrophotometer used in this research is also gratefully acknowledged.

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Natural Abundance $^{13}C-^{13}C$ Coupling Observed via Double-Quantum Coherence

Sir:

We propose a new technique for observing $^{13}C-^{13}C$ spin-spin coupling in the NMR spectra of compounds with ^{13}C in natural abundance. The basic problem is that of identifying the appropriate weak satellite signals in the flanks of strong ^{13}C lines, and the limit is set not so much by the sensitivity or dynamic range of the NMR spectrometer but rather by the presence of a jumble of other weak lines from spinning sidebands, from incomplete proton decoupling, or simply from small amounts of impurities. Investigations of carbon-carbon coupling[1-5] have consequently relied heavily on specific isotopic enrichment, particularly for weak long-range couplings, which are important in conformational studies. The new method filters out the desired ^{13}C satellite signals, suppressing the much stronger signals from molecules with an isolated ^{13}C nucleus, together with any modulation sidebands of the latter.

This discrimination is achieved on the basis of the homonuclear spin-spin coupling J_{C-C}. The idea is to create double-quantum coherence[6-18] in the manner of recent two-dimensional Fourier

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