

energy state, $E_{\bar{\Delta}}(\bar{\Delta} = \bar{a} \text{ to } \bar{k})$, is the arithmetic average of those parameters for the corresponding enantiomers. The relationship of the five averaged theoretical vicinal coupling parameters to those values determined experimentally is depicted graphically in Figure 8.

The magnitudes of the cis vicinal couplings are independent of the algebraic sign of the corresponding ring torsional angle and provide information regarding only the *degree* of ring puckering adjacent to the substituent. The magnitude of $(J_{4,5})_{\bar{\Delta}}$ is highly sensitive to such puckering, and the small magnitude of the experimental value suggests that conformers $e, \bar{e}, f, \bar{f}, g,$ and \bar{g} (bisectional bonding) are sparsely populated. The behavior of $(J_{5,8})_{\bar{\Delta}}$ and $(J_{6,7})_{\bar{\Delta}}$ is less informative because of the relative insensitivity of these parameters to conformational change, and the apparent better fit of these parameters to a less puckered model is accorded little significance.²⁵

The behavior of the trans coupling constants, $(J_{4,6})_{\bar{\Delta}}, (J_{5,7})_{\bar{\Delta}},$ and $(J_{6,8})_{\bar{\Delta}},$ reflects both the magnitude and sign of the corresponding ring torsional angles and is therefore sensitive to any axial or equatorial bonding preference for the methyl substituent. The magnitudes of each of these parameters is consistent with a pseudorotation model involving substantial preference for those conformers ($a, \bar{a}, b, \bar{b}, c, \bar{c}, d,$ and \bar{d}) in which the methyl group is equatorial and appears to rule out any substantial population of those states in which the methyl substituent is either axial or bisectional.

(25) In fact, the small but systematic increase of $J_{6,7}$ with decreasing temperature is in the direction expected for a highly puckered minimum energy conformation.

At a given temperature, the value of each nmr parameter is an average which reflects the conformer distribution at that temperature. As the temperature is decreased, the Boltzmann distribution law favors increased population of the lowest energy pseudorotameric states, *i.e.*, those conformations in which the methyl substituent is equatorially bonded. Each of these vicinal couplings studied here was found to exhibit a systematic temperature dependence in the direction expected from the above model. This dependence is most dramatic in the case of $J_{5,7}$ and $J_{6,8}$, which involve trans coupling between diastereotopic protons and which undergo large temperature changes in opposite directions.

Conclusion

From the above systematic analysis, it has been clearly demonstrated that with the addition of a methyl substituent, the cyclopentane ring can no longer undergo free pseudorotation but is somewhat restricted to those conformations ($a, \bar{a}, b, \bar{b}, c, \bar{c}, d,$ and \bar{d}) in which the substituent is equatorially bonded. This result is in qualitative agreement with the simple prediction based on 1,3-H-H diaxial interactions (Figure 1) and the semiquantitative estimates of Pitzer and Donath³ and Allinger.⁴

Acknowledgment. The author is grateful to the National Science Foundation, which provided financial support for this investigation, and to Professor Ernest Grunwald (Brandeis University) and Dr. W. G. Klemperer (M.I.T.), for helpful discussions.

Effects of Polar Substituents on Photoreduction and Quenching of Aromatic Ketones by Amines. Fluorenone and Substituted Dimethylanilines

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Abstract: Photoreduction of fluorenone by dimethylaniline in benzene leads to the 9-hydroxy-9-fluorenyl radical I and the *N*-methylanilinomethyl radical II, addition of II to the oxygen of ground state fluorenone forming radical III, and combination and cross combination of radicals I and III. Hydrolysis of these products leads to fluorenone pinacol, 97% yield, and to high yields of *N*-methylaniline and formaldehyde. Quantum yields for the photoreduction are at a maximum, ~ 0.8 , with the unsubstituted dimethylaniline and with weak electron donating or withdrawing substituents. Quantum yields decrease with strong electron donating or withdrawing substituents. Very strong electron donation may lead to no photoreduction but to efficient quenching, presumably due to excessive stability of the initially formed charge-transfer complex. Values of k_{ir} , rate constant for charge-transfer interaction of excited fluorenone triplet with the substituted dimethylanilines, have been measured in quenching studies. They vary from $3.2 \times 10^6 M^{-1} \text{sec}^{-1}$ for the *p*-CN compound to $\sim 10^{10} M^{-1} \text{sec}^{-1}$ for the *p*-OEt and *p*-N(CH₃)₂ compounds and lead to a linear plot of $\log k_{ir}$ vs. σ values, σ^+ for the strong electron donating substituents, σ^- for *p*-CN, with $\rho = -1.96$. Photoreductions of Methylene Blue by substituted phenylglycines, of benzophenone by substituted dimethylanilines and benzylamines, and of *p*-aminobenzophenone by dimethylanilines are discussed.

It has been proposed¹⁻³ that photoreduction by amines proceeds *via* rapid charge-transfer type interaction of

(1) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, **72**, 3782 (1968).

(2) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(3) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).

excited acceptor with the *n* electrons of nitrogen, k_{ir} , followed either by spin inversion, charge destruction and quenching, k_e , or hydrogen transfer and electron reorganization, k_h , as indicated for reduction of excited triplet carbonyl compounds in eq 1. Such a mechanism is consistent with low sensitivity of quantum yield

Stokler Isotope, 99.5% D, bromobenzene, Baker reagent grade, *p*-carbethoxy-*N,N*-dimethylaniline, Aldrich, mp 63°, sodium deuteroxide, 40% in D₂O, Merck, Sharp and Dohme of Canada, sulfuric acid-d₂, Merck, Sharp and Dohme of Canada, and *trans*-stilbene, Pilot Chemicals, scintillation grade, mp 124°, were used directly. *p*-Acetamido-*N,N*-dimethylaniline was prepared from *p*-amino-*N,N*-dimethylaniline and acetyl chloride, mp 130°, from water. Benzene, Eastman Spectroquality, was dried by distillation, bp 80°, and stored over P₂O₅ in a desiccator. *p*-Bromo-*N,N*-dimethylaniline, Eastman reagent grade, was sublimed under vacuum, mp 53–54°. *p*-Chloro-*N,N*-dimethylaniline, Adams Chemical, was distilled under vacuum, mp 25°. *m*-Chloro-*N,N*-dimethylaniline, Aldrich, was redistilled, bp 93° (8 mm). *p*-Cyano-*N,N*-dimethylaniline, obtained from Dr. G. A. Davis, was sublimed under vacuum, mp 39–42°. *p*-Dimethylamino-*N,N*-dimethylaniline was prepared by treatment of the hydrochloride (Eastman) with aqueous alkali and extraction with ether. The ether was dried and removed and the product was sublimed under vacuum, mp 50.5–51°. *p*-Ethoxyacetanilide was prepared from acetyl chloride and redistilled *p*-ethoxyaniline (Eastman), mp 134°, from water. *p*-Ethoxy-*N,N*-dimethylaniline, Adams Chemical, was distilled under vacuum, mp 37°. *m*-Ethoxy-*N,N*-dimethylaniline, Adams Chemical, was distilled under vacuum, bp 102° (0.3 mm). *p*-Fluoro-*N,N*-dimethylaniline was prepared from *p*-fluoroaniline (Eastman) and methyl iodide, bp 100° (8 mm). It showed satisfactory ir and nmr spectra. 9-Fluorenone was prepared by lithium aluminum hydride reduction of fluorenone, mp 153–154°, from petroleum ether. 9-Fluorenone, Eastman, was crystallized from petroleum ether, mp 83°. *p*-Methyl-*N,N*-dimethylaniline, Eastman, was distilled before use, bp 81° (15 mm). *p*-Thiomethylaniline, Aldrich, was distilled, bp 100° (2 mm). *p*-Thiomethyl-*N,N*-dimethylaniline was prepared from *p*-thiomethylaniline and methyl iodide, bp 83° (0.03 mm), and showed satisfactory nmr and ir analyses.

Irradiation Procedure. Quantum yields were determined with a ferrioxalate actinometer,²¹ $\phi = 1.14$, at 405 nm on a Bausch and Lomb 38-86-01 monochromator. Solutions of 0.003 *M* fluorenone and 0.01 *M* amine in benzene were degassed in three freeze-thaw cycles and irradiated under Argon in 1-cm square Pyrex tubes fitted with Fisher-Porter Teflon screw tops. In the study of dependence of quantum yield on the concentration of amine, these solutions were used as secondary actinometers; tubes containing 0.003 *M* fluorenone and varying concentrations of amine were irradiated 8 cm from a G. E. H85A3 lamp simultaneously on a rotating wheel. The light was filtered through Corning 7380 filters, except in reduction by *p*-dimethylaminoacetophenone, when Corning 3850 filters were used. The wheel was arranged so that tubes were inserted while the fully warmed lamp was in an opaque chamber beneath, and the lamp could be raised and lowered in ~0.2 sec, allowing irradiation for known intervals with relatively constant intensity. The tubes were cooled by an air blower during irradiation. In studies of effects of stilbene quencher these solutions were used as standards as they and tubes containing varying concentrations of stilbene were irradiated simultaneously on the wheel.

Analysis for residual ketone was made at 405 nm directly in the photolysis tubes on a Beckman D.U. spectrophotometer after measured periods of irradiation. The solutions were not opaque initially at 405 nm and became more transparent as the ketone was reduced. Values of optical density, OD, and times of irradiation, *t*, were used for calculation of quantum yield, ϕ , in accord with eq 2

$$\frac{2.303\text{OD}}{\epsilon_{\text{anal}}} + \sum_{\lambda_i} \frac{\ln(P_{\lambda_i})(1 - e^{-\epsilon_{\lambda_i}l[F]})}{\epsilon_{\lambda_i}l} = \phi I_0 t + C \quad (2)$$

in which λ_i is the *i*th photochemically active wavelength, P_{λ_i} is the fraction of light incident on the system at that wavelength, ϵ_{λ_i} is the base *e* extinction coefficient at λ_i , ϵ_{anal} is extinction coefficient at the analytical wavelength, *l* is the optical pathlength in centimeters, and [F] is the measured concentration of fluorenone. I_0 is the total incident light intensity. A program for this equation was prepared for use in a Wang 700 calculator that calculates the left side of eq 2 for a series of OD's and plots them as a function of time in a least-squares fit, for which the slope is proportional to quantum yield. Relation to the secondary actinometer irradiated at the same wavelength leads to the quantum yields. P_{λ_i} 's were calculated from lamp output data of the manufacturer corrected for filtering. In this system three wavelengths contributed to the photoreduction: 366

nm, $\epsilon = 560 \text{ M}^{-1} \text{ cm}^{-1}$, $P = 0.259$; 405 nm, $\epsilon = 533 \text{ M}^{-1} \text{ cm}^{-1}$, $P = 0.237$; and 435 nm, $\epsilon = 114 \text{ M}^{-1} \text{ cm}^{-1}$, $P = 0.505$. For irradiation in the monochromator a simplified version of eq 2 was used. In our preliminary communication¹⁸ insufficient correction was made for transparency.

Quenching of fluorescence of 0.003 *M* fluorenone by 0.01–0.10 *M* *N,N*-dimethylaniline in benzene was measured at 487 nm on an Aminco spectrofluorimeter, exciting wavelength 405 nm. Quantum yields of photoreduction at these high concentrations of amine were measured as usual on the irradiation wheel.

Products of Photoreduction of Fluorenone by Dimethylaniline.

A solution (23 ml) of 0.100 *M* fluorenone and 0.053 *M* dimethylaniline in benzene was degassed and irradiated under Argon in a 50-ml R.B. flask for 3.5 hr with light from a G.E. H85A3 lamp filtered through a Corning 7380 filter. Analysis of a diluted aliquot at 405 nm indicated consumption of 64.4% of the ketone. The solvent was removed from 20.6 ml under nitrogen, the residue was dissolved in 25 ml of ether, and this solution was shaken with 4 ml of 1 *N* HCl and 4 ml of water. The aqueous extracts were brought to pH 10 with 4 *N* NaOH and extracted with two 10-ml portions of ether. The ether was evaporated, leading to 0.129 g of residue, approximately the theoretical amount of amine. This was treated²² with excess benzenesulfonyl chloride and aqueous KOH and extracted with ether. The ether was washed with acid and analysis by nmr indicated that only unreacted dimethylaniline was removed by the acid treatment. The ether extract was concentrated, leading to the benzenesulfonamide of *N*-methylaniline, 0.147 g, 0.59 mmol, mp 74°, lit.²² 77°, 89% yield based on reduction of 2 mol of fluorenone per mole of amine and the extent of reduction. The original aqueous extract, from which the amines had been removed, was treated with dimedone and made neutral, and the derivative of formaldehyde was collected, 0.137 g, 0.47 mmol, 71% yield, mp 194°, lit.²³ 192°. The original ether extract, from which the amines had been removed, was dried and diluted with hexane, and fluorenone pinacol precipitated and was collected, 0.234 g, 0.65 mmol, 97% yield, mp 184–185°, from ethanol–water, lit.²⁴ 180–182°. The nmr spectrum showed only the pinacol.

Analysis by Ir and Nmr of the Fluorene-Dimethylaniline Reaction.

(i) A benzene solution (4 ml) of 0.10 *M* fluorenone and 0.045 *M* dimethylaniline was degassed in a 1-cm square Pyrex tube and irradiated overnight with the G.E. lamp and 7380 filter. Analysis at 405 nm of a diluted aliquot indicated 82% reduction of the ketone. The infrared spectrum showed a decrease in the carbonyl absorption at 1710 cm^{-1} , a new absorption at 3550 cm^{-1} due to hydroxyl of reduced carbonyl, and no N–H absorption at 3420 cm^{-1} . An aliquot (3 ml) of the unphotolyzed solution was evaporated and the residue was dissolved in 1 ml of CDCl₃ containing tetramethylsilane. The nmr spectrum showed a complex multiplet around δ 7.35 due to aromatic protons of fluorenone and dimethylaniline, an additional small multiplet around δ 6.70 due to aromatic protons of the amine, and a singlet at δ 2.88 due to the methyl groups of the amine. The nmr spectrum of the irradiated material, treated in the same way, showed all the aromatic resonances as a multiplet around δ 7.03 and only a trace of the original methyl singlet at δ 2.88. New singlets appeared at δ 4.40, CH₂ between O and N, and δ 2.68, shifted N–CH₃; resonances due to OH appeared at δ 3.30 and 3.70 which disappeared on shaking with D₂O. The methyl singlet of *N*-methylaniline at δ 2.58 and the 9-OH resonance of fluorenone¹² at δ 5.50 were absent.

(ii) In another experiment the photoreduction was carried out in benzene-*d*₆. The *N*-methyl resonance of dimethylaniline, at δ 2.50, in this solvent nearly disappeared and singlets appeared at δ 4.30, CH₂, and at δ 2.44 and 2.52, N–CH₃. Shaking with D₂SO₄ caused all aliphatic resonances to disappear from the organic layer. Neutralization with NaOD restored the diminished singlet of dimethylaniline at δ 2.50 to the organic layer and a new peak at δ 2.30, due to *N*-methylaniline.

(iii) Aliquots of a solution of 0.10 *M* fluorenone and 0.053 *M* dimethylaniline in benzene were irradiated on the wheel with Corning 7380 filters for 3.84 hr. Analysis at 405 nm of aliquots diluted with benzene indicated 64% reduction of the ketone. Analysis was made for hydroxyl at 3550 cm^{-1} against a calibration curve for

(22) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 332.

(23) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1954, p 332.

(24) M. Gomberg and W. E. Bachman, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

(21) C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

the hydroxyl of authentic fluorenone pinacol, available in the laboratory from previous studies,¹¹ and corresponded to 0.021 *M* pinacol, 65% yield. No appearance of absorption at 3420 cm^{-1} , characteristic of N-H, was observed.

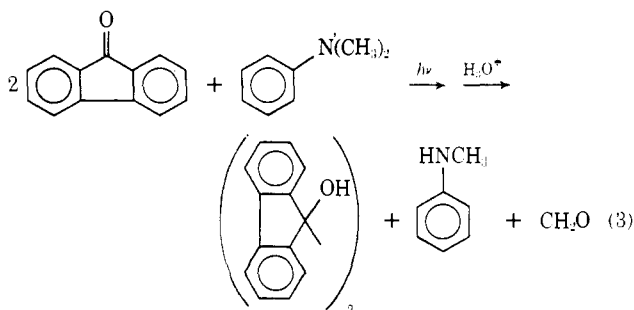
Products of Photoreduction of Fluorenone by Substituted Dimethylanilines. (i) A solution of 0.20 *M* fluorenone and 0.10 *M* *p*-methyl-dimethylaniline in benzene was irradiated overnight. Analysis at 405 nm indicated 60% reduction. The N-methyl resonance at δ 2.55 decreased as a result of the irradiation and appeared in part at δ 2.58 and a new singlet peak appeared at δ 4.30, probably due to CH_2 in an O- CH_2 -N group. No absorption due to the 9-OH of fluorenone was observed.

(ii) A solution of 0.10 *M* fluorenone and 0.034 *M* *p*-ethoxydimethylaniline in benzene was irradiated overnight. Analysis at 405 nm and at 1720 cm^{-1} indicated 54.6 and 56.2% reduction of fluorenone, respectively. An nmr spectrum of the original mixture in CDCl_3 showed the N-methyl singlet at δ 2.80, a methyl triplet centered at δ 1.32, and a methylene quartet around δ 3.90 in addition to the aromatic absorptions. After irradiation virtually no band remained at δ 2.80 and new singlets appeared as before at δ 4.28, 2.76, and 2.69. The triplet appeared as two overlapping triplets; the quartets resonances were diffused.

Aliquots of the photolyzed and original solutions were diluted with ethanol, examined at 405 nm, and subjected to base decomposition. The OD of the original solution was 0.820 and of the photolyzed solution 0.368 before and 0.612 after treatment with base. This corresponds to 74.6% of the original ketone. Reduction of 54.6% of the ketone, leaving 45.6%, would lead after base decomposition to 72.9% ketone if all had been reduced to pinacol type products and to less if any monomolecular or base stable products had been formed. A similar result was obtained in base decomposition of the product of reduction by unsubstituted dimethylaniline.

Results and Discussion

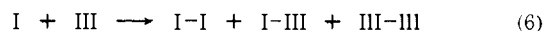
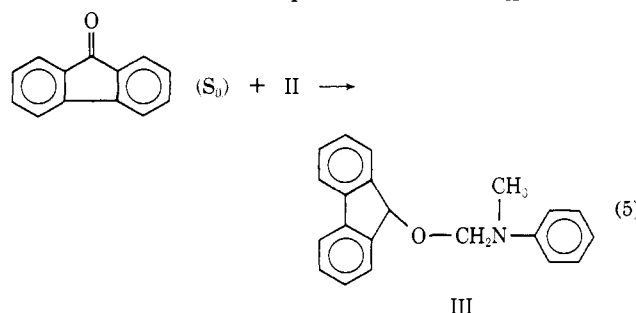
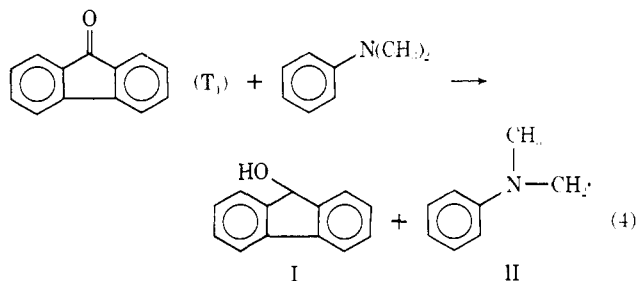
Products. Photoreduction of 0.10 *M* fluorenone by 0.053 *M* *N,N*-dimethylaniline in benzene led, after treatment with aqueous acid, to fluorenone pinacol, 97% yield based on conversion, *N*-methylaniline, as the benzenesulfonamide, 89% yield, and formaldehyde as the dimerone derivative, 71% based on the stoichiometry of eq 3. Nearly quantitative yields of the pinacol were



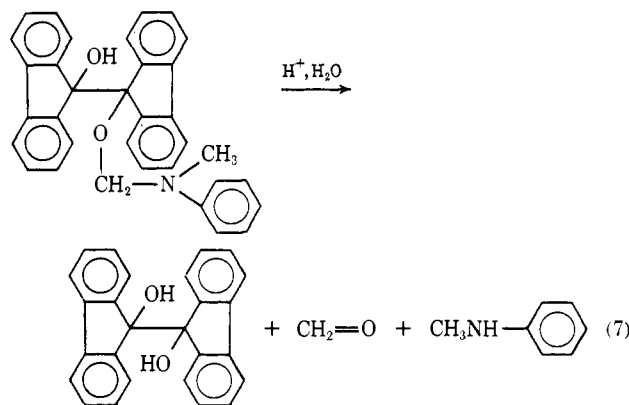
also obtained in similar photoreductions by *p*-methyl-dimethylaniline and *p*-carbethoxydimethylaniline. Irradiation of 0.10 *M* fluorenone and 0.045 *M* dimethylaniline for an extended period led to 82% reduction indicating that 2 mol of ketone may be reduced by 1 mol of amine. That high yields of *N*-methylaniline and formaldehyde are obtained after acid treatment indicates that both reducing groups are derived from one methyl group of one amine molecule. Examination of the photolyzed solution in benzene, before acid treatment, showed that no secondary amine was present, indicated by absence of N-H absorption at 3400 cm^{-1} , and only 65% of the fluorenone consumed could be accounted for in the hydroxyl absorption at 3550 cm^{-1} ; nmr analysis indicated that the methyl singlet of dimethylaniline was greatly reduced and was largely replaced by new singlets. Only after hydrolysis did the methyl

absorption characteristics of *N*-methylaniline appear. Similar nmr results were obtained in photoreductions by *p*-methyl- and *p*-ethoxydimethylanilines.

The results are consistent with the process proceeding largely by abstraction of hydrogen by excited fluorenone from a methyl group of the amine, leading to 9-hydroxy-9-fluorenyl I and the amine derived radical II, addition of the amine derived radical II to ground state fluorenone, leading to an oxygen-substituted 9-fluorenyl radical III, and combination of radicals I and III to pinacol type products I-I, I-III, and III-III, eq 4-6.



The reaction of eq 5 is equivalent to transfer of the second reducing moiety from methyl to a ground state ketone. Hydrolysis of the combination product, indicated for I-III, leads to the observed products, eq 7.



Evidence has been reported indicating that formation of benzpinacol itself, in photoreduction by 2-propanol, proceeds *via* combination of radicals formed after addition of the initially formed ketone and alcohol derived radicals to ground state ketones.²⁵ This mechanism is consistent with the early observation that photoreduction of benzophenone by *o*-chlorobenzhydrol led to benzpinacol, and to *o*-chlorobenzophenone as the sole product from the initial carbinol derived radical.²⁶

(25) G. O. Schenck, W. Meder, and M. Pape, *Proc. U. N. Int. Conf. Peaceful Uses At. Energy*, 2nd, 29, 352 (1958).

(26) W. D. Cohen, *Recl. Trav. Chim. Pays-Bas*, 39, 243 (1920).

Cross coupling products from the initially formed radicals I and II have been reported in photoreduction of fluorenone by triethylamine¹¹ and of benzophenone by dimethylaniline.¹⁶ This reaction is of little importance in the present case, as indicated by the essentially quantitative yield of pinacol by isolation after hydrolysis and of pinacol type products I-I, I-III, III-III, indicated by the base decomposition. Products of type I-II are stable to base.

Quantum Yields. Sixteen meta- and para-substituted dimethylanilines were examined as photoreducing agents for fluorenone in benzene. Quantum yields for photoreduction of 0.003 *M* fluorenone by 0.010 *M* amine are listed in Table III. The quantum yields are

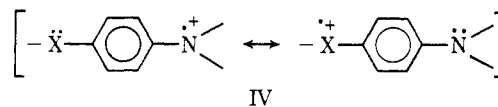
Table III. Photoreduction of 0.003 *M* Fluorenone by 0.01 *M* *m*- or *p*-XC₆H₄N(CH₃)₂ in Benzene

X	ϕ
<i>p</i> -CN	0.11 ± 0.02
<i>p</i> -COCH ₃	0.10 ^a
<i>p</i> -CO ₂ C ₂ H ₅	0.16 ± 0.01
<i>m</i> -Cl	0.27 ± 0.03
<i>p</i> -Br	0.27 ± 0.03
<i>p</i> -Cl	0.37 ± 0.01
<i>m</i> -OC ₂ H ₅	0.47 ± 0.05
<i>p</i> -H	0.59 ± 0.03
<i>p</i> -F	0.76 ± 0.08
<i>p</i> -CH ₃	0.71 ± 0.05
<i>p</i> -OC ₂ H ₅	0.32 ± 0.02
<i>p</i> -SCH ₃	0.30 ^b
<i>p</i> -NHCOCH ₃	0.03 ^b
<i>p</i> -N(CH ₃) ₂	~0 ^b
<i>p</i> -NH ₂	~0 ^b
<i>m</i> -OH	~0 ^b

^a Measured on the irradiation wheel relative to *p*-carboxydimethylaniline. ^b Measured on the wheel relative to dimethylaniline. All other quantum yields were measured by ferrioxalate actinometry.

low, 0.1–0.16, for the anilines with strong electron withdrawing substituents, *p*-CN, *p*-COCH₃, *p*-CO₂C₂H₅, increase as electron withdrawal decreases, and appear to reach a maximum with the unsubstituted compound and the weak electron donors, *p*-F and *p*-CH₃, $\phi = 0.59, 0.76,$ and $0.71,$ respectively, and then decrease with stronger electron donation, *p*-OC₂H₅ and *p*-SCH₃, $\phi = 0.3,$ and become negligible with the very strong electron donor *p*-N(CH₃)₂, $\phi \sim 0.$ The *p*-acetamido group leads to unexpectedly low quantum yield, and the *p*-NH₂ and *m*-OH may quench by reversible hydrogen transfer. The strong electron attracting substituents may result in weak charge transfer interaction at N, enough to lead to electron perturbation and spin inversion and electron return $k_e,$ but not strong enough to facilitate proton transfer $k_h.$ The strong electron donors may lead to extensive charge transfer, forming a complex with stability and long life in which spin inversion and quenching may occur but from which hydrogen transfer would require an activation energy. The optimum in hydrogen transfer appears to occur where the substituent neither stabilizes nor destabilizes the complex excessively and is weakly electron donating.

Para substituents containing heteroatoms attached to the nucleus may show enhanced effects due to resonance interaction within the charge-transfer complex, IV.



Such an effect would be at a maximum in *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, and this compound is not a photoreducing agent but a very efficient quencher. Interaction of this kind may account in part for the very low quantum yield in the case of the *p*-acetamido compound. The *p*-ethoxy group may interact similarly, leading to a more stable complex and lower quantum yield than the *m*-ethoxy group. Analysis by nmr indicates that reduction by *p*-ethoxydimethylaniline occurs at the amino methyl and not at the ethoxyl group. The *m*-ethoxy group, with a low σ value, leads to a moderately high quantum yield. The *m*-chloro substituent, with a higher σ value, leads to a lower quantum yield than the *p*-chloro compound. The *p*-bromo substituent leads to a low quantum yield despite a σ value closer to that of *p*-Cl than to *m*-Cl, and this may result from a heavy atom effect.

It is not entirely appropriate to draw conclusions from quantum yields at a single concentration of amine. Comparison should be made of extrapolated limiting quantum yields, which are proportional to the ratios $k_h/(k_h + k_e)$ characteristic of each amine, and a study of effect of concentration of amine has been carried out for several of the amines. Some results are summarized in Table IV.

Table IV. Photoreduction of 0.003 *M* Fluorenone by *p*-XC₆H₄N(CH₃)₂ in Benzene

		X							
		<i>p</i> -CH ₃		<i>p</i> -H		<i>p</i> -Br		<i>p</i> -CN	
<i>k_d/k_{ir}</i>	ϕ_{lim}	[Am], <i>M</i>	ϕ	[Am], <i>M</i>	ϕ	[Am], <i>M</i>	ϕ	[Am], <i>M</i>	ϕ
		0.101	0.15	0.0493	0.31	0.100	0.19	0.0500	0.11
		0.020	0.52	0.0099	0.59	0.020	0.28	0.0100	0.11
		0.013	0.67	0.0064	0.68	0.013	0.26	0.0067	0.10
		0.010	0.71	0.0049	0.65	0.010	0.27	0.0055	0.090
		0.0080	0.70	0.0039	0.55	0.0080	0.26	0.0050	0.080
		0.0070	0.83	0.0035	0.54	0.0070	0.24	0.0033	0.064
		0.0060	0.88	0.0029	0.57	0.0060	0.25		
		0.0050	0.76	0.0025	0.53	0.0050	0.23		
<i>k_d/k_{ir}</i>	~0			0.0013 <i>M</i>		0.0017 <i>M</i>		0.0054 <i>M</i>	
ϕ_{lim}	~0.8			0.80		0.31		0.18	

The *p*-CN compound has a level quantum yield, 0.11, at high concentration, 0.05–0.01 *M*, which then falls slowly with decreasing concentration. The latter data may be converted to a plot of $1/\phi$ vs. $1/[Am],$ with extrapolated limiting quantum yield $\phi_{lim} = 0.18$ and with the ratio of slope to intercept $k_d/k_{ir} = 0.0054 M,$ the ratio of rate constants of self- and solvent-induced deactivation of the triplet, $k_d,$ to that for interaction of the triplet with the amine. The *p*-bromo, unsubstituted, and *p*-CH₃ compounds show substantially lower quantum yields at the higher concentrations than at intermediate concentrations. This has been observed before in photoreduction of fluorenone by aliphatic amines and is attributed to quenching of the singlet.^{12,13} A few experiments were carried out on quenching of singlet fluorescence of fluorenone by dimethylaniline. The quenching was very efficient, $k_q \sim 6 \times 10^{10} M^{-1} sec^{-1};$ such a high value may indicate that static²⁷ quenching is

(27) A. Weller, *Progr. React. Kinet.*, **1**, 189 (1961).

contributing at the higher concentrations. The data below 0.020 *M* for the *p*-bromodimethylaniline may be treated as were the data for the *p*-CN compound, leading to $k_d/k_{ir} = 0.0017 M$ and $\varphi_{lim} = 0.31$. With unsubstituted dimethylaniline and the *p*-methyl compound, consistent with greater electron availability, lower quantum yields, due apparently to singlet quenching, persist at 0.01 *M* amine and very small effects of further decrease in concentration are observed, indicating high values of k_{ir} . For dimethylaniline the data below 0.0064 *M* lead to $k_d/k_{ir} = 0.0013 M$, $\varphi_{lim} = 0.80$. For *p*-methyl dimethylaniline the slope of the low concentration data is essentially zero, k_d/k_{ir} cannot be evaluated, and the limiting quantum yield appears to be about 0.8. A few similar experiments were done with the *p*-ethoxydimethylaniline; quantum yields were 0.032, 0.037, and 0.035 at 0.010, 0.0067, and 0.0054 *M*, indicating too small a slope to lead to a value of k_d/k_{ir} and a value of φ_{lim} little different from those measured. The limiting quantum yields lead to consideration about the effects of substituents on quantum yields similar to those indicated by the observed quantum yields at 0.01 *M* amine.

In other related studies smaller effects of polar substituents were observed. *p*-Aminobenzophenone, which differs from fluorenone in having high triplet energy and unfavorable reduction potential, also appears to show increasing quantum yield with increasing electron availability from *p*-carbethoxy to *p*-methyl, Table II. However, the effects of the substituents are less pronounced than in the fluorenone-dimethylaniline systems. The benzophenone-benzylamine systems, Table I, show increasing quantum yield as substituents become less electron donating, from *p*-OCH₃ to *p*-Cl. It may be that all three systems show maximum quantum yields around the unsubstituted compounds and that photoreduction is decreased relative to quenching by either strong electron donation or electron withdrawal. It would be of interest to examine the benzophenone-benzylamine systems with strong electron attracting substituents. An extensive study has been reported on photoreduction of Methylene Blue by substituted *N*-phenylglycines in aqueous solution.²⁸ Quantum yields were 0.2–0.3 for many substituents, *m*-OCH₃, H, *o*- and *m*-Cl, *m*-CO₂H, *m*-COCH₃, *p*-CN, and *m*-NO₂; lower quantum yields, 0.01–0.09, were found for *o*-, *m*-, and *p*-Br, possibly due to a heavy atom effect, and for *p*-CH₃ and *p*-NO₂. The *p*-OCH₃ substituent led to no reduction and presumably caused quenching. The polar medium may dampen the effects of polar substituents.

Interaction Rate Constants, k_{ir} , and Quenching. For information as to whether the substituents were acting by their effects on the electron density at the dimethylamino group or by interacting themselves with the excited ketone, the effects of some were examined as substituents in benzene. Bromobenzene, ethoxybenzene, phenyl methyl sulfide, and acetanilide, 0.01 *M*, had no effect on the photoreduction of 0.003 *M* fluorenone by 0.01 *M* *N,N*-dimethylaniline in benzene. Phenyl methyl sulfide, 0.01 *M* in benzene, also caused no photoreduction of fluorenone, although it is both a quencher and photoreducing agent for benzophenone.²⁹ Strangely,

(28) S. Matsumoto, *Bull. Chem. Soc. Jap.*, **35**, 1860, 866 (1962); *ibid.*, **37**, 491, 499 (1964).

it accelerated the photoreduction of fluorenone by *p*-carbethoxydimethylaniline, an effect which may be related to the acceleration by aliphatic mercaptans of photoreduction of benzophenone by 2-butylamine.³⁰ Enhancement in the effects of para substituents may be seen in *p*-ethoxyacetanilide. The individual substituents, in benzene, led to no observed quenching, while the disubstituted benzene was a quencher, $k_q = 1.5 \times 10^7 M^{-1} sec^{-1}$, as measured by its effect on the photoreduction of fluorenone by *p*-carbethoxydimethylaniline. Aniline and phenol, on the other hand, were themselves very effective quenchers for photoreduction of fluorenone by dimethylaniline, $k_q = 2.2 \times 10^9 M^{-1} sec^{-1}$ and 1.5 and $10^9 M^{-1} sec^{-1}$, respectively, and values of k_{ir} were not determined for the dimethylaminoaniline and phenol because of uncertainty in interpretation of the results.

Effects of the substituents on the initial interaction of fluorenone with the dimethylanilines, k_{ir} , were examined (i) by study of the effects of a quencher, stilbene, on photoreduction of 0.003 *M* fluorenone by $\sim 0.01 M$ substituted dimethylaniline and (ii) for dimethylanilines which were ineffective reducing agents, by study of them as quenchers of the photoreduction of fluorenone by dimethylaniline. The dependence of quantum yield on concentration of amine and of added quencher may be indicated as in eq 8. In the absence of added quencher

$$1/\varphi = 1/af + k_d/afk_{ir}[Am] + k_q[Q]/afk_{ir}[Am] \quad (8)$$

the ratio of slope to intercept of a plot of $1/\varphi$ vs. $1/[Am]$ leads to k_d/k_{ir} . In the presence of added quencher the ratio of slope to intercept of a plot of $1/\varphi$ vs. concentration of quencher, $[Q]$, is indicated in eq 9. For *trans*-

$$\text{slope/intercept} = k_q/(k_{ir}[Am] + k_d) \quad (9)$$

stilbene $k_q = 3.6 \times 10^9 M^{-1} sec^{-1}$, and for the photostationary mixture of *cis*- and *trans*-stilbene, $k_q = 1.28 \times 10^9 M^{-1} sec^{-1}$.³¹ For values of $k_{ir} > 1 \times 10^8 M^{-1} sec^{-1}$ when high concentrations, 10^{-3} – $10^{-2} M$, of stilbene were used, the former value was used for k_q . For values of $k_{ir} < 1 \times 10^8 M^{-1} sec^{-1}$, when low concentrations, 10^{-4} – $10^{-3} M$, of stilbene were used, the lower value was used for k_q . *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine and *p*-dimethylaminoacetanilide were examined at 10^{-3} – $10^{-2} M$ as quenchers of photoreduction of fluorenone by dimethylaniline. Values of ratios of slope to intercept were determined experimentally. Values of k_{ir} (or k_q) were calculated from eq 9. For *p*-CN, *p*-Br, and unsubstituted dimethylaniline, values of k_d/k_{ir} are given in Table IV, determined from the effects of amine concentration on quantum yield. For *p*-CH₃ and substituents with electron donating power greater than that of CH₃, values of k_d/k_{ir} are very low and may be neglected. For *p*-Cl and *p*-F the same value of k_d/k_{ir} as that for *p*-Br was taken, 0.0017 *M*, since their slope/intercept ratios are similar in the quenching experiments. For *p*-CO₂C₂H₅, *p*-COCH₃, and *m*-Cl a value of 0.002 *M* was used because of their somewhat higher values of slope/intercept ratios. Values of k_{ir} are not particularly sensitive to the values

(29) J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, **38**, 2001 (1973).

(30) A. W. Rose, Ph.D. Thesis, Brandeis University, Waltham, Mass., 1971.

(31) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

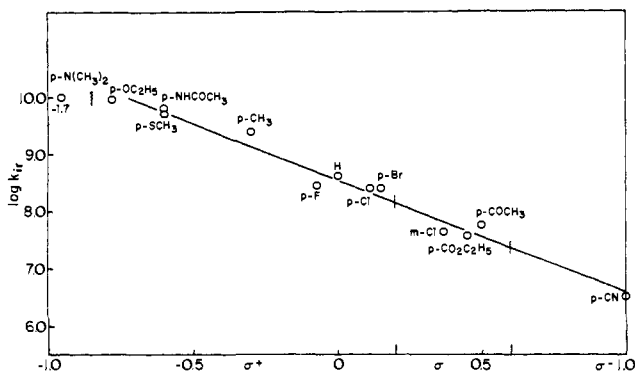


Figure 1. Interaction of fluorenone triplet with substituted dimethylanilines, $\log k_{ir}$ vs. σ , $\rho = -1.95 \pm 0.08$. Correlation coefficient 0.98.

Table V. Interaction of Excited Fluorenone Triplet with *m*- or *p*-XC₆H₄(CH₃)₂ in Benzene

X	Slope/ intercept, ^a M ⁻¹	k_{ir} , M ⁻¹ sec ⁻¹	σ^b	σ^+	σ^-
<i>p</i> -CN	26,500	3.2×10^6	0.67	0.66	1.00
<i>p</i> -COCH ₃	1,875	5.6×10^7	0.50		0.87
<i>p</i> -CO ₂ C ₂ H ₅	2,920	3.7×10^7	0.45	0.48	0.67
<i>m</i> -Cl	2,300	4.4×10^7	0.37	0.40	
<i>p</i> -Cl	1,230	2.5×10^8	0.23	0.11	
<i>p</i> -Br	1,200	2.6×10^8	0.23	0.15	
<i>p</i> -F	1,070 ^c	2.9×10^8	0.06	-0.07	
H	670	4.8×10^8	0	0	0
<i>p</i> -CH ₃	140	2.6×10^9	-0.17	-0.31	
<i>p</i> -SCH ₃	62	5.8×10^9	0	-0.60	
<i>p</i> -OC ₂ H ₅	38	9.5×10^9	-0.24 ^d	-0.78 ^d	
<i>p</i> -NHCOCH ₃	1,050 ^e	6.2×10^9	0	-0.60	
<i>p</i> -N(CH ₃) ₂	2,020 ^e	1.1×10^{10}	-0.83	-1.7	

^a $k_d/(k_{ir}[Am] + k_d/k_{ir})$. ^b Values taken from J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 204 and 211. ^c Value derived from quenching by a single concentration of *trans*-stilbene. ^d Value for OCH₃ used. ^e Values determined by use as a quencher for the reaction of unsubstituted dimethylaniline and fluorenone.

of k_d/k_{ir} chosen in these highly reactive systems. Results are summarized in Table V and Figure 1.

The substituents had marked effects on the interaction rates, values of k_{ir} varying over almost four orders of magnitude from 3.2×10^6 M⁻¹ sec⁻¹ for the *p*-CN compound to 1×10^{10} for the *p*-OC₂H₅ and *p*-N(CH₃)₂ compounds. A plot of $\log k_{ir}$ vs. σ values may be constructed, $\rho = -1.96$, Figure 1. The linear relationship is obtained if σ^+ values are used for the strong electron donors, *p*-OC₂H₅, *p*-SCH₃, *p*-NHCOCH₃, and *p*-CH₃, and for the para halogens, and a σ^- value is used for the strongest electronegative substituent, *p*-CN. Ordinary, σ values seem to be appropriate for the electronegative substituents, *p*-COCH₃, *p*-CO₂C₂H₅, and *m*-Cl. The rate constant cannot respond to electron donation greater than that of *p*-OC₂H₅, which already leads to an almost diffusion-controlled rate, and the *p*-N(CH₃)₂ group, with a much larger negative σ^+ value, leads to essentially the same maximum value of k_{ir} . However, σ values for these substituent, which are rather small, do not reflect the large effects of these electron donating substituents in these interactions. The relevance of σ^+ values strongly supports the development of charge,³²

(32) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

and thus the charge-transfer mechanism for these reactions, and the importance of contributions, is indicated in formula IV. The effects of the para halogens may be accounted for by ordinary σ values nearly as well as by σ^+ values, with little change in ρ . The fit of the σ^- value for *p*-CN may reflect the need to overcome ground state resonance between *p*-CN and N(CH₃)₂ in arriving at the charge-transfer transition state. This seems to be rather unimportant, however, with *p*-COCH₃ and *p*-CO₂C₂H₅, for which ordinary σ values apply.

Quenching constants in a number of other amine systems may also be correlated by the Hammett equation. The rates of quenching of triplet biacetyl by substituted anilines and phenols have been correlated with a combination of σ^+ and σ^- values,³³ $\rho = -0.85$ and -1.15 , respectively. Extension and refinement of the study³⁴ of quenching of fluorenone triplet by substituted anilines indicates that the rate constants may be correlated with σ^+ values for the strong electron donors, σ^- for *p*-CN, similar to the correlation in the substituted dimethylanilines. In this case the value of ρ is lower,³⁵ -0.96 , and the range of rate constants is smaller. Partial transfer of H from N may be involved in quenching by anilines, lowering the dependence on the electron availability. Methylene Blue displays a pattern of reactivity²⁸ toward meta- and para-substituted *N*-monosubstituted anilines, the *N*-phenylglycines, in aqueous solution which is similar to that of fluorenone toward the substituted dimethylanilines in benzene. Methylene Blue has a low triplet energy,³⁶ ~ 34 kcal/mol, and very favorable reduction potential,³⁷ 19 kcal/mol, as compared with the corresponding values for fluorenone, 53.3³⁸ and 31.8 kcal/mol,³⁹ respectively. Values of k_{ir} are about two orders of magnitude less than in the fluorenone-dimethylaniline systems, but they range over nearly four orders of magnitude from 5.8×10^4 M⁻¹ sec⁻¹ for the *p*-cyano compound to 2×10^8 M⁻¹ sec⁻¹ for the *p*-methoxy compound. Here too, the strongest electron donating substituent led to very little photoreduction and its high value of k_{ir} was established by use of it as a quencher. The author used σ and σ^- substituent constants, but again a better correlation is obtained if σ^+ values are used above *p*-halogen, $\rho = -1.46$. In this case the σ^- value fits better for *p*-COCH₃, and even this constant does not appear large enough for *p*-CN.

While it may appear overly empirical to apply σ^+ and σ^- constants, these systems are unusual in that they show both partial development of an α positive charge in resonance interaction with para electron donating heteroatom substituents, for which σ^+ was introduced,³² and reaction at an α heteroatom which is in direct resonance interaction with an unsaturated electron withdrawing substituent, for which σ^- was introduced;⁴⁰

(33) N. J. Turro and T. Lee, *Mol. Photochem.*, **2**, 185 (1970).

(34) G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1971).

(35) G. H. Parsons, Jr., L. T. Mendelson, and S. G. Cohen, unpublished results.

(36) D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *J. Amer. Chem. Soc.*, **89**, 5455 (1967).

(37) M. von Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter and Co., Berlin, 1950, p 309.

(38) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(39) H. Berg and K. Kramarczyk, *Ber. Bunsenges. Phys. Chem.*, **68**, 296 (1964).

(40) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, p 193.

a σ^\pm treatment has been applied similarly before.³³ One might not expect the same sensitivity, ρ , to apply over the whole range. These interactions of excited carbonyl with amines involve partial electron and partial hydrogen transfer in the transition state.⁵ The former may dominate with electron donating and the latter with withdrawing substituents. There may in effect be a

change in mechanism over the range of substituents and the data might alternately be placed on a broken line. However, the considerations relating to applicability of σ^+ and σ^- , above, appear relevant.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission, AT(30-1)2499 and AT(11-1)3118.

The Laser Initiated Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene¹

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Abstract: As part of a program to appraise the photochemical potential of the argon ion laser the photoaddition of *p*-benzoquinone to cyclooctatetraene has been examined. Laser irradiation of these materials in a nonacidic solvent leads to the formation of the 1,4-adduct **5**. When acetic acid is used as the solvent, **5** is not observed. Instead the acid catalyzed rearrangement products, **6** and **7**, are observed as the only products. If the irradiation is conducted in a nonacidic solvent in the presence of oxygen, the peroxide 4'a,10'a-dihydrospiro[2,5-cyclohexadiene-1,3'-cycloocta-*as*-trioxin]-4-one (**11**) is formed in good yield. The structure of **11** was confirmed by a single crystal X-ray study conducted with the 3-bromo derivative **13**. The mechanism of this unusual oxidative photoaddition and the advantages of the laser light source are discussed.

The anaerobic photochemistry of quinones has been studied extensively,² but only recently has the effect of oxygen upon quinone photochemistry begun to be assessed.³ Our attention has been drawn to this area for two reasons. The weak long wavelength n, π^* absorption of most quinones in the 450–500-nm region of the spectrum is well suited for excitation with an argon laser,⁴ thus constituting an ideal system for evaluating the photochemical potential of the argon laser. Furthermore, photooxidations initiated by n, π^* excited carbonyl groups have not been examined in any detail, and in particular a knowledge of quinone photooxidations might be most useful in view of the involvement of quinones in biological oxidations.⁵ Consequently, we have undertaken a general program of study intended to better define the scope and mechanistic nature of quinone-sensitized photooxidations of olefins using an argon ion laser as the exciting source. The *p*-benzoquinone (PBQ)–cyclooctatetraene (COT) system has been examined as a part of this general program, and observed to yield several novel photo-

products. Of these substances only one arises from the reaction of molecular oxygen. The structure of this material has been unequivocally determined by X-ray crystallography, and found to be that of a unique dienone–peroxide. Therefore, while the overall objectives of the general program are still under active investigation, the unusual results observed in the PBQ–COT system are reported at this time.

Results and Discussion

Anaerobic Photochemistry. Argon laser irradiation of PBQ and COT in the absence of oxygen and in a nonacidic solvent such as carbon tetrachloride, benzene, acetone, or methanol affords a single product ($\sim 77\%$). This sensitive substance has apparently been prepared previously using conventional light sources.⁶ However, it may be isolated more readily and in crystalline form from the uncomplicated laser reaction mixture. Elemental analysis and mass spectroscopy, m/e 212 (M^+), indicate that the material is a 1:1 adduct between PBQ and COT. The nmr spectrum of the adduct exhibits two overlapping doublets of doublets, (δ) 2.74 ppm, $J = 8$ Hz (1 H) and 4.67 ppm, $J = 5$ Hz (1 H). These signals had previously been assigned to the oxetane protons in the 1,2-cycloaddition product **1**.⁶ However, these two signals have been shown not to be coupled with each other in a double resonance experiment. Furthermore, in our hands Pd/C hydrogenation of this adduct yielded a phenolic alcohol **2**, mp 136.8–137.2°, which was not the same as the analogous Pd/C hydrogenation product **3**, mp 120–121°, obtained from

(1) E. J. Gardner, R. H. Squire, R. C. Elder, and R. M. Wilson, *J. Amer. Chem. Soc.*, **95**, 1693 (1973).

(2) J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1967).

(3) (a) C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 731 (1969); (b) D. Creed, H. Werbin, and E. T. Strom, *ibid.*, **93**, 502 (1971); (c) S. Fugisawa, S. Kawabata, and R. Kamamoto, *J. Pharm. Soc. Jap.*, **87**, 1451 (1967); (d) M. Ohmae and G. Katsui, *Bitamin*, **35**, 116 (1967); (e) G. Katsui and M. Ohmae, *J. Vitaminol. (Kyoto)*, **12**, 117 (1966).

(4) The n, π^* absorption of *p*-benzoquinone, for example, has $\lambda_{\text{max}}^{\text{hexane}}$ 458 nm (ϵ 21) and 479 (11). A Coherent Radiation Model 53A argon ion laser was used in this work. This laser emits 6 W of power in the following lines: 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2).

(5) R. A. Morton, Ed., "Biochemistry of Quinones," Academic Press, New York, N. Y., 1965; T. P. Singer, "Biological Oxidations," Interscience, New York, N. Y., 1968.

(6) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).