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Reactions of p-Benzoquinone Diimine Derivatives with N,N-Dimethylanilines

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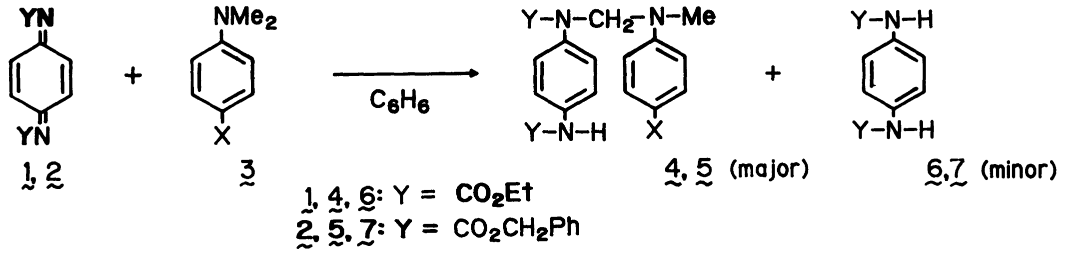
N,N'-Bisalkoxycarbonyl-p-benzoquinone diimine underwent a thermal addition reaction with N,N-dimethylanilines to form an N-C bond between an imino group and an N-methyl group. Upon irradiation the reaction was accerelated. The reaction did not proceed with N-alkyl substituted anilines other than methyl.

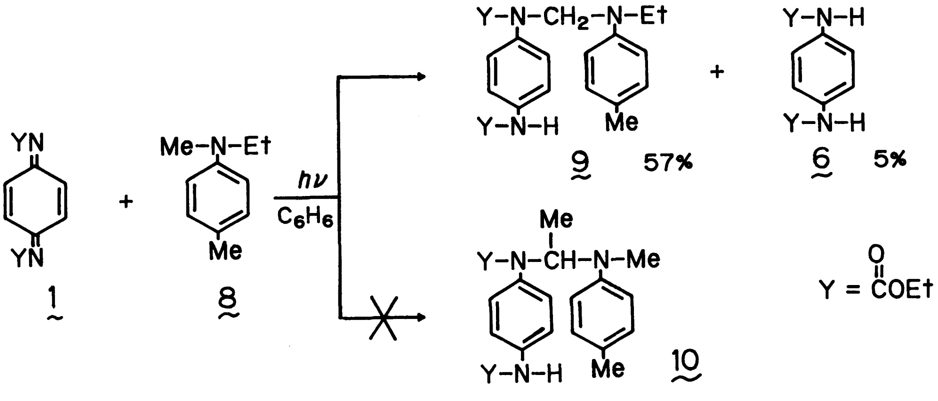
We are interested in the chemistry of p-benzoquinone equivalent in comparison with that of the parent compound. The reaction of p-benzoquinone diimine, one of p-benzoquinone equivalents, has little been investigated so far.[1)] We wish to report here that N,N'-bisalkoxycarbonyl-p-bezoquinone diimines (1 and 2)[2)] abstract a hydrogen atom from an N-methyl group of N,N-dimethylanilines[3)] (3) to give an addition product, N,N'-bisalkoxycarbonyl-N-(N"-methylanilinomethyl)-p-phenylenediamines (4 and 5)[4)] in a good yield with a minor amount of reduced products, N,N-bisalkoxycarbonyl-p-phenylenediamines (6 and 7). The reaction proceeded in the dark, but was accerelated on irradiation.[5)]



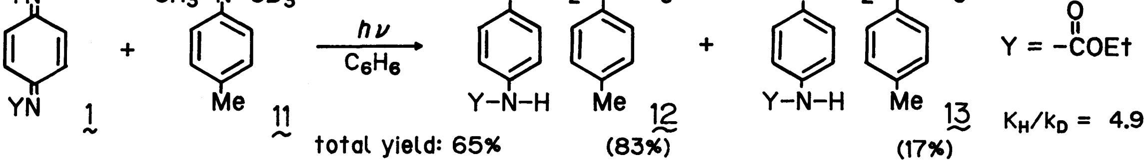
		4a	4b	4c	4d	5a	5b	5c	5d
X		H	Me	OMe	Cl	H	Me	OMe	Cl
mp/°C		108-11	151-2	131-4	122-5	99-101	113-5	115-7	157-9
Yield/%	(thermal)	50	64	82	74	38	76	77	69
	(photolytic)	72	62	33	32	60	70	36	60

When a deep purple brown solution of N,N'-bisethoxycarbonyl-p-benzoquinone diimine (**1**) (0.2 M) and N,N-dimethyl-p-toluidine (**3b**) (0.4 M) in benzene[6] was left standing at room temperature in the dark for 48 h, the solution turned to almost colorless and **4b** was obtained after usual work-up with column chromatography on silica-gel in a yield of 64% along with 5% of **6**. **4b**; ^{1}H NMR (acetone-d_6): δ 1.13 (3H, t, J = 7.0 Hz, $\underset{\sim}{\mathrm{Me}}\mathrm{CH_2}$), 1.24 (3H, t, J = 7.0 Hz, $\underset{\sim}{\mathrm{Me}}\mathrm{CH_2}$), 2.18 (3H, s, MeAr), 2.69 (3H, s, NMe), 4.07 (2H, q, J = 7.0 Hz, $\mathrm{Me}\underset{\sim}{\mathrm{CH_2}}$), 4.14 (2H, q, J = 7.0 Hz, $\mathrm{Me}\underset{\sim}{\mathrm{CH_2}}$), 5.30 (2H, s, $\mathrm{NCH_2N}$), 6.65 and 6.95 (4H, ABq, J = 8.7 Hz, ArH), 7.01 and 7.50 (4H, ABq, J = 8.7 Hz, ArH), 8.63 (1H, br. s, NH). On irradiation of the same solution (10 ml) by using a 300 W high pressure Hg-arc lamp for 1 h through a Pyrex filter, the solution turned to colorless resulting in the formation of **4b** in a yield of 62% along with 3% of **6**.

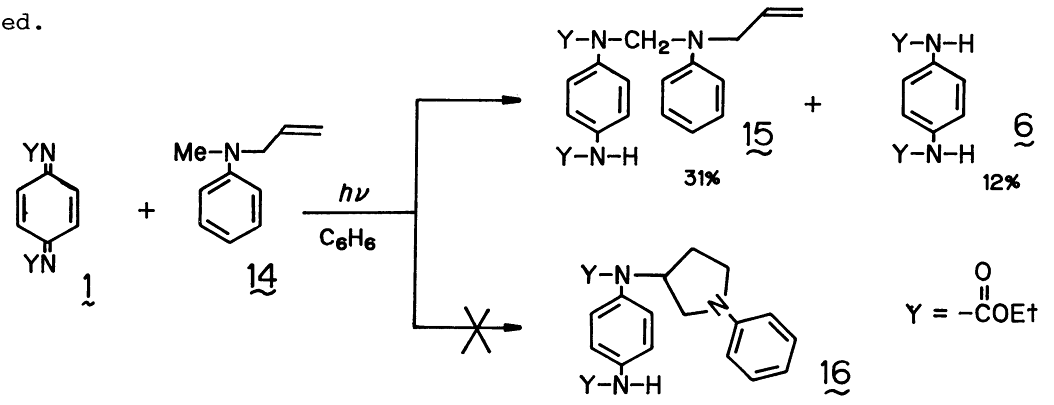
N,N'-Diethyl- and N,N'-dibenzylaniline did not undergo the reaction. The specific hydrogen abstraction from an N-methyl group, but not from an N-ethyl group, was demonstrated by the photolysis of **1** with N-ethyl-N-methyl-p-toluidine (**8**), which gave **9** (57%, mp 148-151 °C) and **6** (5%) with none of **10**.



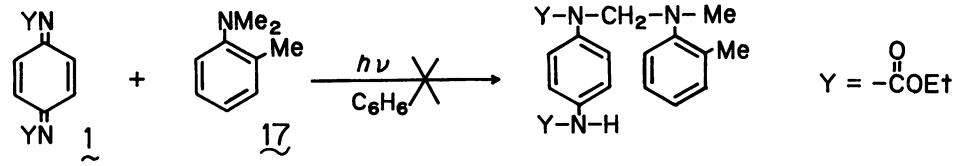
The hydrogen abstraction of **1** occurred predominantly from the N-methyl group of N-methyl-N-[$^2H_3$]-methyl-p-toluidine (**11**) to give a mixture of **12** and **13** in a yield of 65% with the molar ratio of 4.9. The molar ratio was determined with intensities of ^{1}H NMR signals due to CH_2 of **12** and CH_3 of **13**.



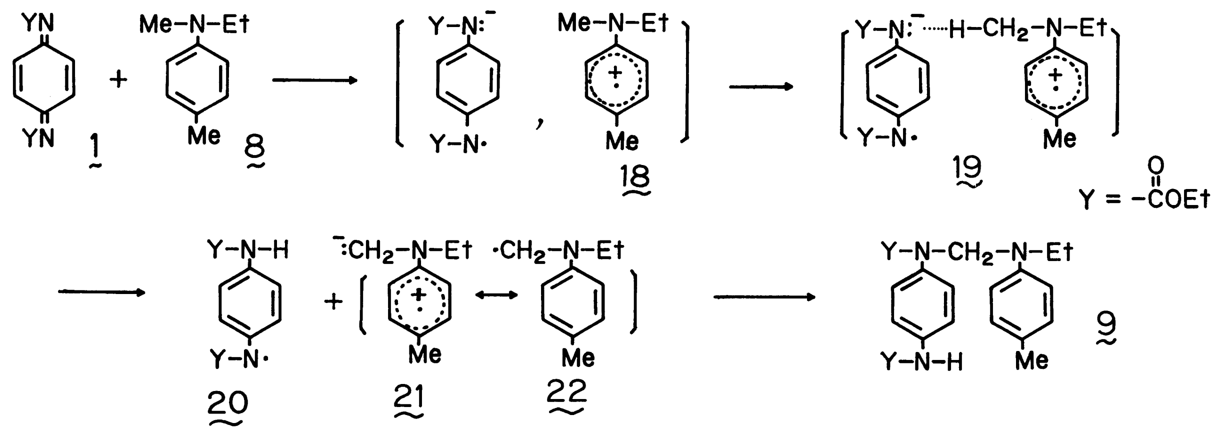
Even in the photochemical reaction with N-allyl-N-methylaniline (14), 1 gave 31% of 15 (mp 120-122 °C) with 12% of 6. The expected cyclized product 16 was not detected.



On the contrary to the facile reaction of 3b, N,N-dimethyl-o-toluidine (17) was insusceptible to the reaction with 1.



These results suggest the following scheme as the most plausible reaction mechanism, exemplified with the reaction of 8. The electon transfer from 8 to 1 could be accerelated on irradiation. The specific reaction at the N-methyl group may be explained in terms of the intervension of a primary carbanion 21,7) more stable than the secondary carbanion. The electron density of the N atom in 18 would be decreased by conjugation of the lone pair orbital of the N atom with π-orbitals of the benzene ring. The electron deficiency at the N atom would facilitate the deprotonation of the N-methyl group. In 17, such conjugation might be prohibited by steric repulsion between the N-methyl and the ortho-methyl group. Consequently the reaction of 1 with 17 does not proceed.



References

1) Syntheses of a series of N,N'-diacyl-p-benzoquinone diimines and related compounds were reported by R. Adams and W. Reifschneider in Bull. Soc. Chim. Fr., 1958, 23, and literatures cited therein: For the photochemistry of N,N'-diacyl-p-benzoquinone diimines and related compounds, see; I. Baxter and D. W. Cameron, J. Chem. Soc., C, 1968,1747; I. Baxter and I. A. Mensah, ibid., 1970, 2604.

2) 2 was prepared by imitating the method for 1, i.e., oxidation of N,N'-bisbenzyloxycarbonyl-p-phenylenediamine (7) with $Pb(OAc)_4$ in boiling 1,2-dichloroethane. Mp 101-103 $^{\circ}$C; Yield 60%.

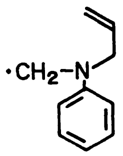
3) For the photo-reduction of carbonyl compounds by N,N-dimethylaniline and related compounds, see: S. G. Cohen, A. Parola, and G. H. Parsons, Jr., Chem. Rev., 73, 141 (1973); J. D. Simon and K. S. Peters, J. Am. Chem. Soc., 103, 6403 (1981); L. E. Manring and K. S. Peters, ibid., 107, 6452 (1985).

4) All new compounds gave satisfactory results in elemental and mass spectroscopic analyses.

5) The reaction was carried out without deaeration. In preliminry studies it gave little effects on the reaction.

6) The use of acetonitrile instead of benzene as solvent had little effects on the thermal reaction, but induced decomposition of 4 and 5 upon irradiation.

7) 9 may be considered to be formed by the radical coupling of 22 with 20. However it is incompatible with the preferential formation of 15 from 14 because the radical intermediate (23), corresponding to 22, should cyclize to another radical intermediate (24), the precursor of 16. The dichotomy may be solved by considereing that the C-H bond would be perpendicular to π-orbitals of the benzene ring in the stage of deprotonation (19) and that the developed carbanion orbital in 21 would retain a similar position until the C-N bond formation.



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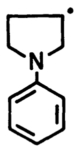

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