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A facile preparation of ethanolamines by direct irradiation of some carbonyl compounds in *N*,*N*-dimethylaniline

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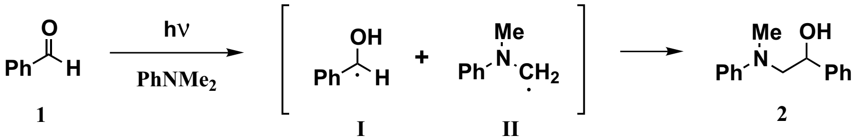
Abstract—Direct irradiation of some carbonyl compounds in *N*,*N*-dimethylaniline, without solvent, with 300 nm UV light afforded ethanolamines as the major product in moderate yields. © 2001 Elsevier Science Ltd. All rights reserved.

The photochemistry of carbonyl compounds with amines is of particular interest since it is an efficient process for the synthesis of diols or other types of reductive products.[1–5] Photoreduction of benzophenone by amines involves abstraction of hydrogen and leads to benzpinacol.[1,2] In the case of the photochemical reactions of benzaldehyde with amines in methanol, ethanolamine[6,7] is produced in poor yield.[3] Recently, we found that direct irradiation of some carbonyl compounds in amines, without using other solvents, overcome a serious problem in these reactions, i.e. low chemical yields of photoproducts and the formation of many kinds of products.

Irradiation of benzaldehyde **1** (0.1 mL, 1 mmol) in *N*,*N*-dimethylaniline (DMA, $PhNMe_2$, 10 mL) with 300 nm UV light (Rayonet Photochemical Reactor, Model RPR-208) in the atmosphere of nitrogen gas for 24 h resulted in ethanolamine **2** in 79% yield with % conformeric excess 46, as shown in Scheme 1 and Table 1. When **1** (1 mmol) and DMA (2 mL, 16 mmol) were irradiated in methanol (10 mL), the chemical yield of **2** decreased to 25%. The photoreaction of **1** (1 mmol) and DMA (1 mmol) in methanol (10 mL) for 24 h afforded **2** only in 8% yield. The photoproduct was isolated by flash column chromatography (silica gel, 230–400 mesh) using *n*-hexane and ethyl acetate as the eluent. As is clearly seen, irradiation of carbonyl compounds in aromatic amines, without using other solvents, can prevent the prevalent reaction, e.g. photoreduction of carbonyl compounds by amines. The formation of ethanolamine **2** can be easily interpreted by the intermolecular H-abstraction which leads to radical intermediates **I** and **II**, as shown in Scheme 1. Some aldehydes, such as 1-naphthaldehyde **3**, vanillin **5** and *t*-cinnamaldehyde **7**, were also irradiated in DMA to give the corresponding ethanolamines such as **4**, **6** and **8**, respectively (Table 1).

In contrast, photoreactions of 2-dimethylaminopyridine **9** with aldehydes, such as benzaldehyde **1**, resulted in the formation of not only ethanolamine **10** (47%) but also its oxidized products as α-aminoketone (21%). Ethanolamines isolated here were found to be the mixtures of conformers except for **4** which has diagnostic peaks at δ 3.48 (CH_2, d) and 5.60 (CH, t) in ^1H NMR ($CDCl_3$). The carbon signals of CH_2 and CH group were observed at δ 62.00 and 71.70, respectively.

Some ketones were also investigated in which ethanolamines were produced as the major products



Scheme 1.

Keywords: carbonyl compound; *N*,*N*-dimethylaniline; ethanolamine.

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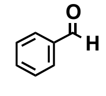
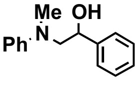
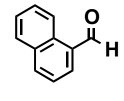
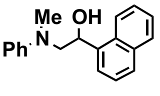
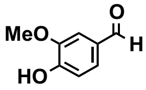
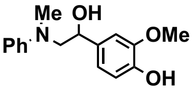
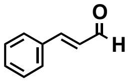
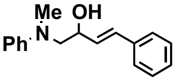
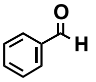
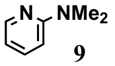
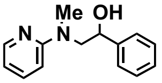
Table 1. Formation of ethanolamines by direct irradiation of aldehydes (1 mmol) in amines (10 mL) with 300 nm UV light for 24 h

Aldehyde		Amine	Ethanolamine			
			Structure		% ce*	% Yield
1		$PhNMe_2$	2		46	79
3		$PhNMe_2$	4		100	66
5		$PhNMe_2$	6		26	71
7		$PhNMe_2$	8		12	73
1		 9	10		48	47

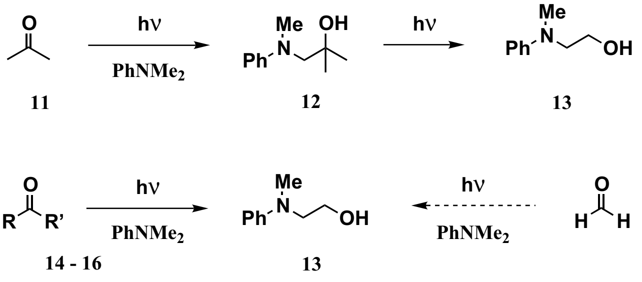
*: % conformeric excess.

(Scheme 2). When irradiated acetone **11** (1 mmol) in DMA (10 mL) for 24 h, ethanolamine **12** was produced in 21% yield (Scheme 2). Prolonged irradiation of **12** for 72 h gave rise to *N*-methyl-*N*-phenylethanolamine **13** in 3% yield. ^{1}H NMR spectrum ($CDCl_3$) shows peaks at δ 7.20–6.65 (5H), 3.75 (2H, t), 3.40 (2H, t), 2.90 (3H, s). Molecular ion peak was observed at m/e 151 in mass spectrum (EI). In order to confirm the formation of **13**, simple carbonyl compounds (1 mmol) such as acetophenone **14** (R = Ph, R′ = Me), benzophenone **15** (R = R′ = Ph), and ethyl acetate **16** (R = Me, R′ = OEt) were irradiated in DMA (10 mL) for 24 h to yield the same compound **13**, in 57, 59 and 42% yields, respectively, in one pot. It is interesting to note that *N*-methyl-*N*-phenylethanolamine **13** can be produced from direct irradiation of **14**–**16** without using troublesome gas, i.e. formaldehyde.

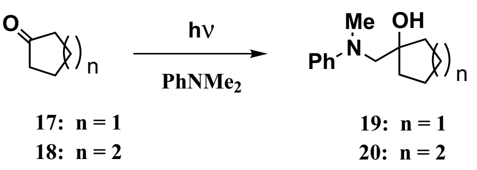
The photoreactions of cyclic ketones, such as cyclopentanone **17** and cyclohexanone **18**, in DMA also afforded the same type of ethanolamines **19** and **20** in 39 and 38% yield, respectively (Scheme 3). ^{1}H NMR spectrum ($CDCl_3$) of **19** showed three diagnostic peaks at δ 3.40 (NCH_2), 2.99 (NCH_3) and 1.97 (OH). A molecular ion peak was also observed at m/e 205 in EI mass spectrum.

In a similar manner, a reductive photoadduct **22** as ethanolamine was also isolated in 11% yield, when anthraquinone **21** (1 mmol) was irradiated in DMA (10 mL) for 24 h (Scheme 4). Three peaks were observed at δ 3.58 (NCH_2), 2.99 (NCH_3) and 6.60 (OH) in ^{1}H NMR spectrum ($CDCl_3$) of **22**. On the other hand, photoreaction of tetrachloro-1,4-benzoquinone **23** (1 mmol) with DMA (10 mL) for 24 h gave 4-(dimethylamino)benzaldehyde **25** (50%) and ethanolamine **26** (10%) which was derived from DMA and **25**. Irradiation of **24** in DMA also afforded **25** (45%) and **26** (37%).

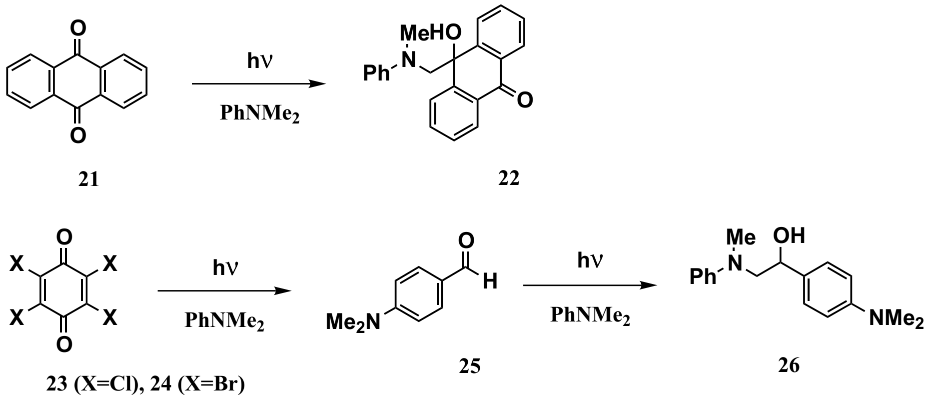
In the case of 1,4-benzoquinone, 1,4-naphthoquinone and 1,2-naphthoquinone, different type of products, i.e. *N*-methyl-*N*-phenylaminoquinones were produced as the major product when irradiated in DMA. In summary, we found that various ethanolamines can be prepared easily by direct irradiation of some carbonyl



Scheme 2.



Scheme 3.



Scheme 4.

compounds, such as aldehydes, ketones and anthraquinone, in aromatic amines without using other solvents.

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References

1. Cohen, S. G.; Parola, A.; Parsons, Jr., G. H. *Chem. Rev.* **1973**, *73*, 141.
2. Cohen, S. G.; Stein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6542.
3. Kessar, S. V.; Mankotia, A. K. S.; Scaiano, J. C.; Barra, M.; Gebicki, J.; Huben, K. *J. Am. Chem. Soc.* **1996**, *118*, 4361.
4. Groth, T.; Grotli, M.; Lubell, W. D.; Miranda, L. P.; Meldal, M. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4258.
5. Miyasaka, H.; Kiri, M.; Morita, K.; Mataga, N.; Tanimoto, Y. *Bull. Chem. Soc. Jpn* **1995**, *68*, 1569.
6. Hendrix, M.; Alper, P. B.; Priestley, E. S.; Wong, C.-H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 95.
7. Matsumura, Y.; Ohishi, T.; Sonoda, C.; Maki, T.; Watanabe, M. *Tetrahedron* **1997**, *53*, 4579.