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Photochemical Reactions of 3,3-Bis(dialkylamino)acrylophenones and 3-Dibenzylaminopropiolophenone

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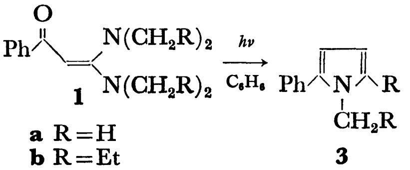
Synopsis. The photolysis of 3,3-bis(dialkylamino)acrylophenones **1a**, **b**, and **c** gave the **3a**, **b**, and **c** pyrroles respectively. 3-Dibenzylaminopropiolophenone (**2**) reacted with water upon irradiation to give *N,N*-dibenzylbenzoylacetamide (**5**), whereas the addition of acetic acid to **2** proceeded without irradiation.

Recently, we reported the photochemical cyclization of 3-dialkylaminoacrylophenones.[1] This paper will be concerned with the photochemical reactions of 3,3-bis(dialkylamino)acrylophenones (**1a**, **b**, and **c**) and 3-dibenzylaminopropiolophenone (**2**).

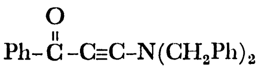
The **1a**, **b**, and **c** ketones were prepared by the condensation of 3,3-dichloroacrylophenone (**4**) with the corresponding secondary amines according to the method in the literature.[2] On the other hand, the reaction of **4** with dibenzylamine yielded the ynaminoketone **2**.

The irradiation of **1a**, **b**, and **c** in benzene by means of a high-pressure mercury lamp gave the **3a**(trace), **3b**(25%) and **3c**(8%) pyrroles respectively. The structures of the pyrroles were confirmed by direct comparison (IR, NMR, tlc) with samples obtained in the photochemical reactions of 3-dialkylaminoacrylophenones.[1] These reactions also proceeded in *n*-hexane, but did not proceed in methanol or acetonitrile. The mechanism of these reactions is not clear at present.



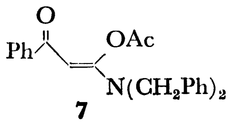
a R=H
b R=Et
c R=*n*-Pr

The ynaminoketone **2** was inert toward photolysis in dry benzene, whereas the irradiation of **2** in benzene containing water yielded *N,N*-dibenzylbenzoylacetamide (**5**). The structure of **5** was confirmed by an unequivocal synthesis from ethyl benzoylacetate and dibenzylamine. The formation of **5** can be easily explained in terms of the addition of water, followed by ketonization. The reaction did not take place in the dark. On the other hand, the addition of acetic acid to **2** proceeded without irradiation[3,4] to give an adduct **7**.



$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}C{\equiv}C{-}N(CH_2Ph)_2}$

2



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Experimental

All the melting points are uncorrected. An Ushio 450 W high-pressure mercury lamp was used as an irradiation source.

3-Dibenzylaminopropiolophenone (2). To dibenzylamine (25 g), 3,3-dichloroacrylophenone (3.5 g) was added, drop by drop. The temperature rose to 74 °C and then slowly fell to room temperature. After the addition of dry ether (50 ml), the mixture was refluxed for 24 hr and then stirred at room temperature for an additional 24 hr. The mixture was filtered to remove the dibenzylamine hydrochlororide, and the filtrate was evaporated *in vacuo*. On the addition of a small amount of petroleum ether to the residue, a crystalline solid was deposited; this was later recrystallized from benzene–petroleum ether to give 2.6 g of **2**; mp 109—110 °C; IR (KBr) 2300, 1610, 1570 cm^{-1}; UV $\lambda_{\mathrm{max}}^{\mathrm{EtOH}}$ 254 (ε, 10500), 323 nm (16000); NMR (CDCl$_3$) δ 4.32 (s, 4H, CH$_2$), 7.20—7.45 (m, 13H, aromatic), 7.50—7.73 (m, 2H, aromatic).

Found: C, 84.83; H, 5.88; N, 4.34%. Calcd for $\mathrm{C_{23}H_{19}NO}$: C, 84.89; H, 5.89; N, 4.30%.

General Procedure for the Photochemical Reaction of 1a, b, and c. A solution of **1** (200 mg) in benzene (70 ml) was irradiated in a Pyrex vessel under nitrogen for 30—50 hr. After the removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene yielded **3**.

N,N-*Dibenzylbenzoylacetamide (5).* A solution of **2** (100 mg) in benzene (50 ml) containing a small amount of water was irradiated in a Pyrex vessel under nitrogen for 30 hr. After the removal of the solvent, the residue was chromatographed on silica gel (benzene–ethyl acetate 2: 1) to give 80 mg of **5**; mp 79—80 °C; IR (KBr) 1690, 1630, 1570 cm^{-1}.

Found: C, 80.18; H, 6.43; N, 4.08%. Calcd for $\mathrm{C_{23}H_{21}NO_2}$: C, 80.44; H, 6.16; N, 4.08%.

The amide **5** was also prepared by heating a solution of ethyl benzoylacetate (6.1 g) and dibenzylamine (5.7 g) in xylene (7.5 ml) to 140 °C (yield, 79%).

3-Dibenzylamino-3-acetoxyacrylophenone (6). A solution of **2** (200 mg) and acetic acid (1 ml) in benzene (10 ml) was stirred for 2 hr at room temperature. After the removal of the solvent, the residue was chromatographed on silica gel (benzene–ethyl acetate 20: 1) to give 225 mg of **6**; mp 72—73 °C; IR (KBr) 1770, 1650, 1610 cm^{-1}; NMR (CDCl$_3$) δ 2.32 (s, 3H, CH$_3$), 4.55 (d, 4H, CH$_2$), 6.43 (s, 1H, olefinic), 6.80—7.80 (m, 15H, aromatic).

Found: C, 78.09; H, 5.99; N, 3.73%. Calcd for $\mathrm{C_{25}H_{23}NO_3}$: C, 77.90; H, 6.01; N, 3.63%.

References

1) a) H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N. Sugiyama, *Chem. Commun.*, **1972**, 775; b) H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N, Sugiyama, *J. Chem. Soc. Perkin I*, **1975**, 298.

2) R. L. Soulen, Ph. D. Thesis, Kansas State University (1960).

3) The ynaminoketone **2** also reacted with ethanol (by irradiation, ~20%) and diethylamine (without irradiation, ~90%) to give the corresponding adducts. However, these adducts were viscous oils, and their complete purification was not achieved.

4) Ground-state addition reactions of ynaminoketones have been reported; A. Niederhauser, A. Frey, and M. Neuenschwander, *Helv. Chim. Acta*, **56**, 944 (1973); M. Neuenschwander and P. Bigler, *ibid.*, **56**, 959 (1973); A. Niederhauser, G. Bart, and M. Neuenschwander, *ibid.*, **56**, 2427 (1973).