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PHOTO-OXIDATIVE DEGRADATION OF N-SUBSTITUTED ALDIMINES

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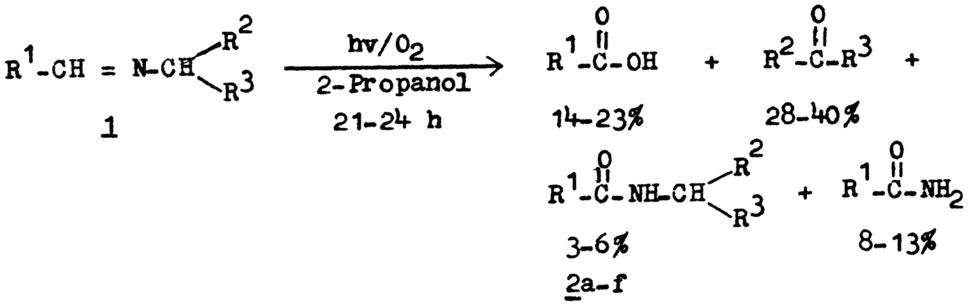
Photo-oxidation of several N-substituted aldimines (**1**) gave carboxylic acids, N-diarylmethyl benzamides (**2**), ketones and benzamides; compound **2** was a precursor for ketone and amide. A tentative mechanistic route for the formation of products has been suggested.

Photo-oxidation of benzophenoneimines to benzophenones and benzaldehyde N-aryl or alkylimines to amides and carboxylic acids has been reported$^{1)}$. In the present paper we describe the isolation of N-diarylmethylbenzamides and ketones besides the expected products, carboxylic acids and benzamides, from the photo-oxidation of several N-substituted aldimines which suggests a different mechanistic route for this reaction than observed earlier$^{1)}$.

A solution of benzaldehyde N-benzhydrylimine (**1a**, 0.50 g) in 2-propanol (50 ml) was irradiated in a stream of oxygen with uv light from 2537 Å lamps in a Rayonet reactor. Monitoring by uv spectroscopy indicated the disappearance of absorption at 250 nm (λmax of **1a**) in 22 h. Four such runs were combined. Evaporation of the solvent under reduced pressure and extraction of the ethereal solution of the residual matter with sodium bicarbonate solution gave 0.43 g (21%) of benzoic acid on acidification. The organic layer was subjected to column chromatography over neutral alumina to give 0.75 g (39%) of benzophenone, 0.08 g (4%) of N-benzhydrylbenzamide and 0.25 g (13%) of benzamide$^{2)}$. No reaction occurred on refluxing the solution of **1a** in dark for 22 h showing that the above reaction is truly photochemical. Similar results were obtained on irradiation (21-24 h) of other benzaldehyde N-alkylimines (**1b** - **f**).

Irradiation of a solution of N-benzhydrylbenzamide (**2a**, 0.30 g) in 2-propanol (80 ml) under the same conditions as described above (three such runs were combined) gave 0.15 g (17%) of benzamide and 0.36 g (40%) of benzophenone separated by column chromatography and identified by comparison with authentic samples$^{2)}$. These results suggest that benzamides and benzophenones are formed from imines **1a** through N-diarylmethylbenzamides **2**.

On the basis of above observations the photo-oxidation of substituted aldimines can be illustrated as follows:



Imines 1	R^1	R^2	R^3
a	C_6H_5	C_6H_5	C_6H_5
b	C_6H_5	C_6H_5	$C_6H_4CH_3$-p
c	$C_6H_4OCH_3$-p	C_6H_5	C_6H_5
d	$C_6H_4CH_3$-p	C_6H_5	C_6H_5
e	C_6H_4Cl-o	C_6H_5	C_6H_5
f	C_6H_5	$C_6H_4CH_3$-p	$C_6H_4CH_3$-p

The photo-oxidation of imines 1 proceeds more readily in 2-propanol than in either methanol or cyclohexane indicating that the solvent with a better hydrogen-donating power is more effective. A similar solvent effect has been observed in the photoreduction of substituted imines$^{3)}$. Benzaldehyde N-tritylimine does not undergo any change on irradiation for 45 h under the same conditions as described above. This observation further supports the view that the initial step, hydrogen abstraction by the ground state imine from ketyl radical obtained from solvent, is common in photoreduction$^{1,3)}$ as well as in photo-oxidation. The yields of the photoproducts increase in presence of acetophenone$^{4)}$ while methylene blue$^{5)}$ is ineffective suggesting that ground state oxygen, and not the excited singlet oxygen, is involved in these reactions$^{1)}$. Further studies are in progress.

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