

Photocyclization of Benzanilides to Phenanthridones with Elimination of the *ortho*-Methoxy-group

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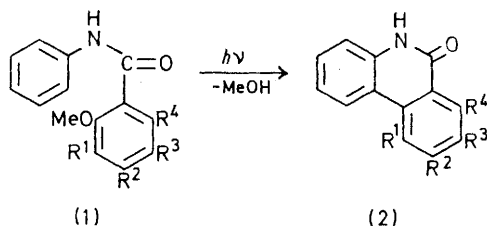
Summary Benzanilides with an *ortho*-methoxy-group on the benzoyl ring undergo efficient nonoxidative photocyclization to give phenanthridones by elimination of methanol.

ALTHOUGH the oxidative photocyclization of *cis*-stilbenes to phenanthrenes has been studied extensively,¹ only limited

information is available on the related reactions of anilides.^{2a,b} We have recently reported that certain heterocyclic anilides are readily photo-cyclized to condensed quinolones.^{2b} During a study of the photoreactions of amides and imides,^{2c} we examined the effect of irradiation on the *ortho*-methoxy-substituted benzanilide (**1a**).[†] The expected phenanthridone (**2**; R¹ = R² = R³ = H; R⁴ = OMe) was not detected

[†] Irradiation was performed in benzene EtOH (9:1) with a 100 W high-pressure mercury lamp for 6 h. All new compounds gave satisfactory analytical results and had spectral properties (u.v., i.r., n.m.r., mass) consistent with the structures assigned.

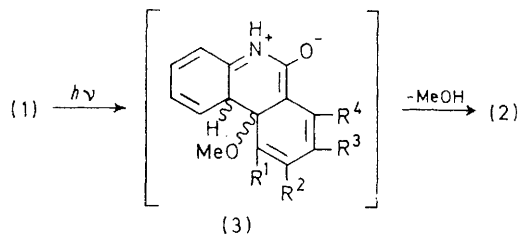
and instead, the unsubstituted parent phenanthridone (**2a**) was isolated in 8% yield. Likewise, (**1b—f**) afforded the phenanthridones (**2b—f**), respectively, in fair yield. None of the 'normally' cyclized products retaining the initial *ortho*-methoxy-group were detected.



	Yield (%)
a ; R ¹ = R ² = R ³ = R ⁴ = H	8
b ; R ¹ = OMe; R ² = R ³ = R ⁴ = H ..	80
c ; R ¹ = R ³ = R ⁴ = H; R ² = OMe ..	50
d ; R ¹ = R ² = R ⁴ = H; R ³ = OMe ..	37
e ; R ¹ = R ² = R ³ = H; R ⁴ = OMe ..	45
f ; R ¹ = R ⁴ = H; R ² = R ³ = OMe ..	64

In the photocyclization of stilbene analogues, several examples of the elimination of the *ortho*-group such as methyl and halogen have been reported.³ However, irradiation of *o*-methoxystilbene gave only traces of

phenanthrene, which could not be isolated in quantity even in a preparative experiment.^{3b} This photocyclization of (**1**) to (**2**) with expulsion of the *ortho*-methoxy-group thus may be characteristic of the anilide system.



Since degassed solutions of (**1b**) smoothly gave (**2b**) and the formation of methanol during the reaction was confirmed by identification as its *p*-nitrobenzoate, the reaction may proceed by a nonoxidative mechanism in which the intermediate dihydrophenanthrene analogue (**3**) undergoes thermal elimination of methanol to give (**2**).

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¹ E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.

² (a) B. S. Thyagarajan, N. Kharasch, H. B. Lewis and W. Wolf, *Chem. Comm.*, 1967, 614; (b) Y. Kanaoka and K. Itoh, *Synthesis*, 1972, 36; and papers cited therein; (c) Y. Kanaoka, H. Migita, K. Koyama, Y. Sato, N. Nakai, and T. Mizoguchi, *Tetrahedron Letters*, 1973, 1193; and papers cited there.

³ (a) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163, and papers cited therein; (b) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.