A *Meta*-Photo-Fries Reaction

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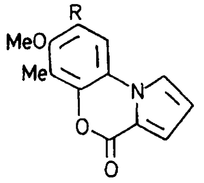
Summary The first useful '*meta*' photo-Fries reaction has been applied to the preparation of a highly substituted tricyclic structure potentially useful in mitomycin synthesis.

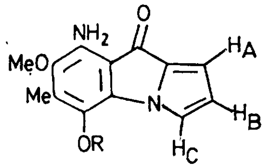
THE photo-Fries rearrangement of phenyl esters to yield *ortho*-acylated phenols is well studied and understood as a radical-pair reaction.[1] The photolysis of benzolactones has rarely been examined and in only one case has an acylation of the aromatic ring been observed, in 0·8% overall yield.[2] In our studies of mitomycin synthesis,[3] the aminolactone (**3**) became available *via* careful reduction of the nitrolactone (**2**).†‡ Irradiation of (**3**) in tetrahydrofuran (THF) with a sun-lamp through plate glass with a continuous purge of oxygen-free nitrogen afforded a 57% yield of a red, crystalline isomer which was assigned structure (**4a**).‡ That it was (**4**) and not (**5**) which could have arisen from the spiro-intermediate (A) was determined by an n.m.r. study of (**4b**) [prepared in quantitative yield by treatment of (**4a**) with Me_2SO_4] using the shift reagent $Eu(fod)_3$. Other than the NH_2 which shifted the most (9·8 p.p.m./mol/mol), the pyrrole H_A had the largest shift (4·2 p.p.m./mol/mol).

We believe that a radical such as (B) is an intermediate in this first useful example of a '*meta*' Fries reaction since a hydrogen-donating solvent such as THF is required in our work and, similarly, alcohols with α-hydrogens are necessary in the photosolvolyses of dihydrocoumarins studied by Gutsche.[2b]

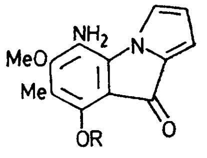
Financial support from the National Cancer Institute is gratefully acknowledged.



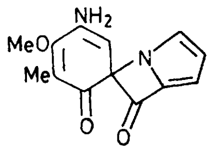
(1) R = H
(2) R = NO_2
(3) R = NH_2



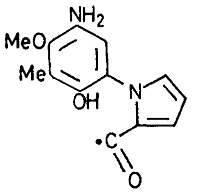
(4)
a; R = H
b; R = Me



(5)



(A)



(B)

(*Received*, 19*th August* 1974; *Com.* 1075.)

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† Prepared from (**1**) by treatment with HNO_3–H_2SO_4 followed by H_2–Pd–C; (**1**) was prepared from 2,6-dimethoxytoluene by treatment, sequentially, with $TiCl_4$–HcCl; NH_2OH,HCl; CF_3CO_2H; $AlCl_3$; *conc.* HCl; and methyl 2,5-dimethoxytetrahydrofuran-2-carboxylate.

‡ Satisfactory elemental analyses were obtained.

[1] (a) W. Adam, J. Arce de Sanabia, and H. Fischer, *J. Org. Chem.*, 1973, **38**, 2571; (b) D. Bellus, *Adv. Photochem.*, **1971**, **8**, **109**.

[2] (a) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015; (b) C. D. Gutsche and B. A. M. Oude-Alink, *J. Amer. Chem. Soc.*, 1968, **90**, 5855; (c) J. C. Andersen and C. B. Reese, *J. Chem. Soc.*, 1963, 1781.

[3] For recent bibliographies, see H. W. Moore, and P. Germeraad, *J. Org. Chem.*, 1974, **39**, 774; G. J. Siuta, R. W. Franck, and R. J. Kempton, *ibid.*, in the press.