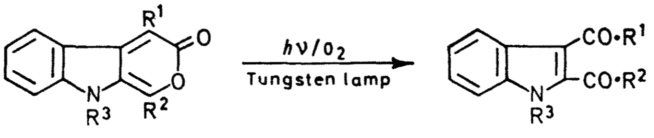
Photo-oxygenation of Substituted Pyrano[3,4-*b*]indol-3(9*H*)-ones

By J. ROKACH,* D. MCNEILL, and C. S. ROONEY
(*Merck Frosst Laboratories*, 16711 *Trans-Canada Highway, Kirkland, Quebec, Canada*)

Summary A photo-oxygenation reaction of indolopyrones is reported which provides access to novel indole 2,3-dicarbonyl derivatives, and 2-hydroxyalkylindole-3-acetic acid derivatives.

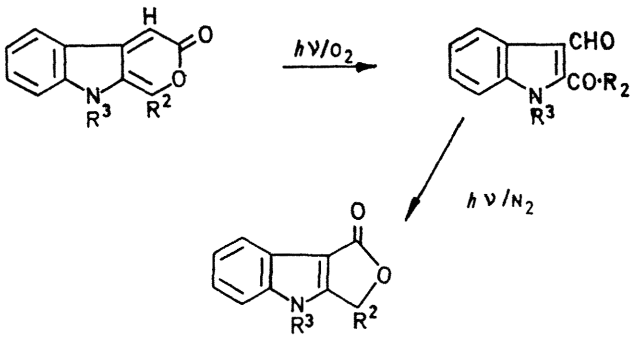
THE photochemistry of α-pyrones has received limited attention. Recent publications have described the ring opening,[1] intramolecular cyclization,[2] and the photodimerization.[3] We report here the preliminary work on the photo-oxygenation of some closely related tricyclic pyrone derivatives; namely substituted pyrano[3,4-*b*]indol-3(9*H*)-ones.

When substituted pyrano[3,4-*b*]indol-3(9*H*)-ones were irradiated in solution with a tungsten lamp in the presence of oxygen, high yields (70—97%) of indole 2,3-dicarbonyl derivatives were obtained. The reaction is represented as follows:



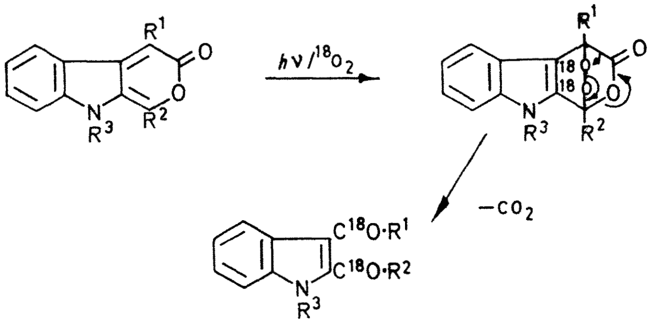
	R^1	R^2	R^3
(1)	H	Me	H
(2)	H	Et	H
(3)	H	Pr	H
(4)	H	Ph	H
(5)	Me	Me	H
(6)	Me	Et	H
(7)	H	Me	Me
(8)	H	Et	Me

When R^1 = H and the irradiation was carried out with a u.v. lamp in the presence of oxygen for a short length of time, a mixture of keto-aldehyde and a new compound, a lactone was formed. On longer irradiation only the lactone was isolated. When the keto-aldehyde was irradiated under nitrogen the lactone was formed in high yields (70—95%). The whole sequence is best described as follows:



The lactone formation from the keto-aldehyde derivative is similar to an analogous process described recently for *o*-phthalaldehyde.[4] The high yield of the photochemical reactions makes the new class of reactive indole dicarbonyl derivatives and lactones easily available.

The dicarbonyl derivatives are probably formed through a peroxide intermediate which then loses CO_2. When $^{18}O_2$ (90 atom %) was used as a source of oxygen, the products, checked by mass spectrometry, showed an $^{18}O_2$ content of 82—84 atom %. This result strongly supports the intermediacy of a peroxide:



We thank Dr. J. Atkinson for helpful discussions and suggestions.

(*Received, June 2nd,* 1971; *Com.* 885.)

---

[1] (a) P. de Mayo, *Adv. Org. Chem.*, 1960, **2**, 314; (b) W. H. Pirkle and L. H. McKendry, *J. Amer. Chem. Soc.*, 1969, **91**, 1179.
[2] E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, 1964, **86**, 950.
[3] (a) P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 1964, 84; (b) W. H. Pirkle and L. H. McKendry, *Tetrahedron Letters*, 1968, 5279.
[4] (a) J. Kagan, *Tetrahedron Letters*, 1966, 6097; (b) S. P. Pappas and J. E. Blackwell, jun., *ibid.*, 1968, 3337.