Photorearrangement of 3,4-Benzotropolone

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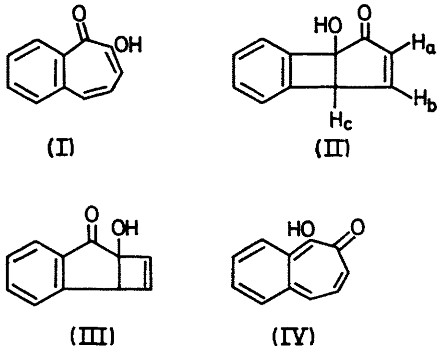
Summary Irradiation of a methanol solution of 3,4-benzotropolone gives rise to a novel type of rearrangement product, 1-hydroxy-6,7-benzobicyclo[3,2,0]hepta-3,6-dien-2-one.

PURPUROGALLIN TETRAMETHYL ETHER, a trimethoxy-derivative of 3,4-benzotropolone methyl ether, undergoes photorearrangement to methyl 6,7,8-trimethoxy 1-naphthoate.[1,2] On the other hand, irradiation of 4′,5′-dimethoxy-3,4-benzotropolone methyl ether gives 1-methoxy-3,4-(4′,5′-dimethoxy) benzobicyclo [3,2,0] hepta-3,6-dien-2-one as a major product.[3] We report a new type of photochemical valence isomerization of 3,4-benzotropolone (I).

Irradiation of a dilute solution of (I) in methanol with Pyrex filtered light resulted in the formation of a crystalline material (II) m.p. 112—113°, in good yield, accompanied by significant amounts of unidentified products. On the basis of elemental analysis and molecular-weight determination (mass spectroscopy), (II) was found to be an isomer, $C_{11}H_8O_2$, of (I). The u.v. spectrum [λ_{max} (MeOH) 227 nm (log ϵ 4·32)] suggested that (II) contained a conjugated enone system. Its n.m.r. spectrum [τ ($CDCl_3$), 2·50—2·95 (4 H, ArH), 2·18 (1 H, dd, J 6·0 and 3·0 Hz, H_b), 3·92 (1 H, d, J 6·0 Hz, H_a), 5·51 (1 H, d, J 3·0 Hz, H_c), and 5·75 (1 H, broad s, O*H*)] provided confirmatory evidence.



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This reaction represents a novel type of photorearrangement of 3,4-benzotropolone and may be explained either by the initial formation of (III) followed by rearrangement to (II), or by a mechanism in which (IV) is postulated as an intermediate.

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[3] E. J. Forbes and J. Griffiths, *J. Chem. Soc.* (*C*), 1966, 2072.