Transannular Formation of 1,10-Dimethoxy-4-azatricyclo[6,2,2,$0^{4,8}$]dodeca-9,11-dien-3-one

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Summary Photolysis of *N*-chloroacetyl-3,4-dimethoxyphenylpropylamine (**1**) gave the eight-membered lactam (**2**) and the novel aza-azulene derivatives (**4** and **5**); the nine-membered lactam (**9**) was synthesized similarly from *N*-chloroacetyl-3,4-dimethoxyphenylbutylamine (**8**).

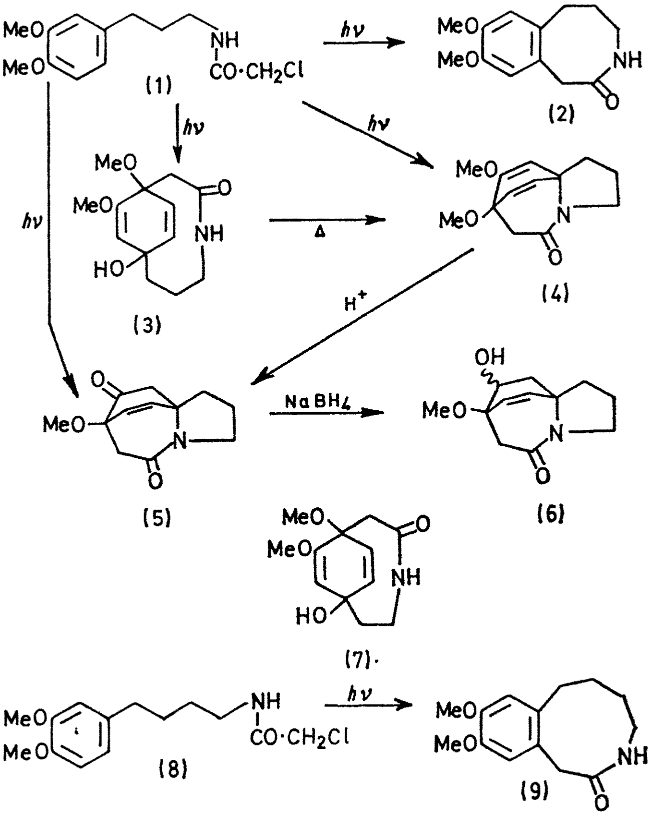
Photolysis of the homologue (**1**) may again proceed by electron-transfer from the aromatic chromophore to the carbon–chlorine bond[1,4] to yield (**2**) and (**3**); the latter is transformed into the tricycles (**4**) and (**5**) by secondary thermal reactions.

THE photocyclizations of *N*-chloroacetylphenethylamines[1] have now been extended to the propylamine (**1**) and butylamine (**8**) homologues.

When an aqueous ethanolic solution of (**1**) was irradiated with a high-pressure mercury lamp (100 W) under nitrogen for 3 h, the benzazocinone (**2**) (8%), m.p. 215°, was isolated. The structure of (**2**) was confirmed by analogy with that of 7,8-dimethoxy-4,5-dihydro-1*H*-[3]benzazepin-2(3*H*)-one[2] by mass and n.m.r. spectroscopy [*m/e*, 235 (M^+), 218, and 165; δ ($CDCl_3$) 6·84 (1H, s), 6·60 (1H, s), 6·25 (1H broad), 3·86 (3H, s), 3·84 (3H, s), 3·20—3·64 (4H, m), 2·76—3·02 (2H, m), and 1·60—2·10 p.p.m. (2H, m)].

Another crystalline product, m.p. 122—124°, isolated by chromatography (silica-gel), has a carbonyl group (1730 cm^{-1}) in addition to the original amide (1625 cm^{-1}) and no NH absorption in the i.r. spectrum. This compound must be a ketone because it forms a 2,4-dinitrophenylhydrazone and is easily reduced to the alcohol (**6**) by $NaBH_4$ in methanol. In the u.v. spectrum no maximum above 220 nm is observed. The composition of (**5**) was determined by mass spectrometry [221 (M^+), 205, 178, and 163, $C_{12}H_{15}NO_3$ indicates loss of HCl and CH_2 from (**1**)]. The n.m.r. spectrum [δ ($CDCl_3$) 6·32 (2H, s), 3·46—3·77 (2H, m), 3·37 (3H, s), 2·72 (2H, s), 2·63 (2H, s), and 1·75—2·44 p.p.m. (4H, m)], shows two vinyl protons and one methoxy-group. The structure of the dione (**5**) is suggested by mechanistic considerations and was confirmed by the isolation of the intermediates (**3**) and (**4**).

In the presence of $NaHCO_3$ photolysis of (**1**) gave (**2**) (8%) and (**4**) (18%), extractable into ethyl acetate, and (**3**) (6%) which remained in the aqueous layer. The bicyclo-[6,2,2]dodecadienone (**3**) has chemical and spectral properties similar to those of the [5,2,2]-analogue (**7**),[3] though the mass spectrum of (**3**) is identical with that of (**4**), indicative of the easy pyrolysis of (**3**) to (**4**). On a small scale, this transannular dehydrative cyclization can be brought about easily and quantitatively by brief heating at 200°. N.m.r. data, δ 6·30 (2H, s) and 4·96 (1H, s), (both vinyl protons) and 3·61 and 3·39 (both MeO) and the mass spectrum, 235 (M^+), 220, and 204 (base), support the structure of the novel tricyclic aza-azulene derivative as 1,10-dimethoxy-4-azatricyclo[6,2,2,$0^{4,8}$]dodeca-9,11-dien-3-one (**4**), m.p. 138—139°. This enol-ether was easily hydrolysed to the ketone (**5**) by dilute acid.



Photolysis of the phenylbutylamine (**8**) under the same conditions gave the benzazoninone (**9**) (13%), a nine-membered lactam, m.p. 178—179° [*m/e*, 249 (M^+), 232, and 165; δ ($CDCl_3$) 6·95 (1H, s), 6·58 (1H, s), 6·40br (1H), 3·83 (6H, s), 3·60 (2H, s), 3·20—3·55 (2H, m), 2·55—2·86 (2H, m), and 1·30—1·77 (4H, m)].

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