Intramolecular Photochemical Arylation of *N*-Substituted Enaminones: Application to Synthesis of Heterocyclic Compounds

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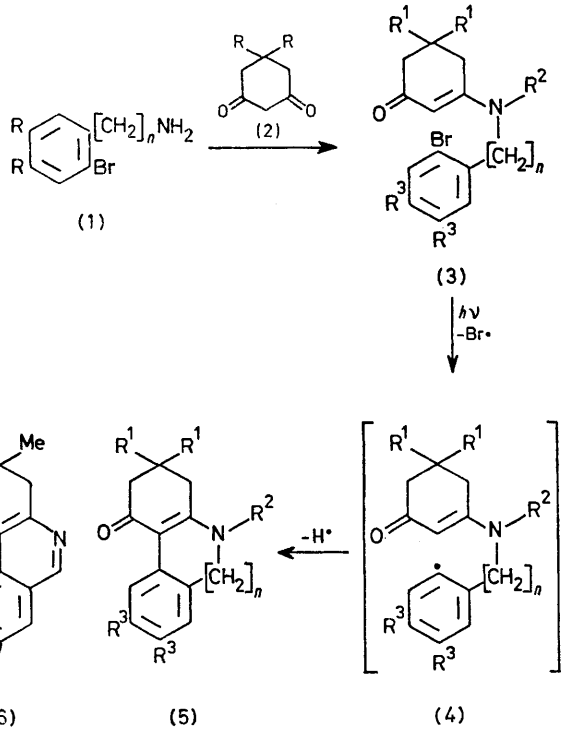
Summary The *N*-(2-bromophenyl)-, *N*-(2-bromobenzyl)-, and *N*-(2-bromophenethyl)-derivatives (**3**) of 3-aminocyclohex-2-enones and 1,2,3,3a,4,5-hexahydro-1-(2-halogeno-4,5-methylenedioxybenzyl)indol-6-ones (**10**) and (**11**)

underwent photochemical cyclisation to yield the five- to seven-membered heterocyclic compounds (**5**) and the 3,3a,4,5-tetrahydropyrrolo[3,2,1-*de*]phenanthridine-1,7-(2*H*)-dione (**13**), respectively.

THE reactions of enaminones have received considerable attention in recent years because of their versatility and potential utility as synthetic intermediates, particularly in heterocyclic chemistry.[1] The enaminone system (>N–C=C–C=O) consists of three functional groups, and shows interesting and sometimes complicated reactivity with the five possible reaction sites. Although examples of the alkylation and acylation of enaminones have been reported, there has been much less work on their arylation. We now report the direct photochemical introduction of aryl groups into the enaminone system leading to a new and general synthesis of heterocyclic compounds with five- to seven-membered rings.



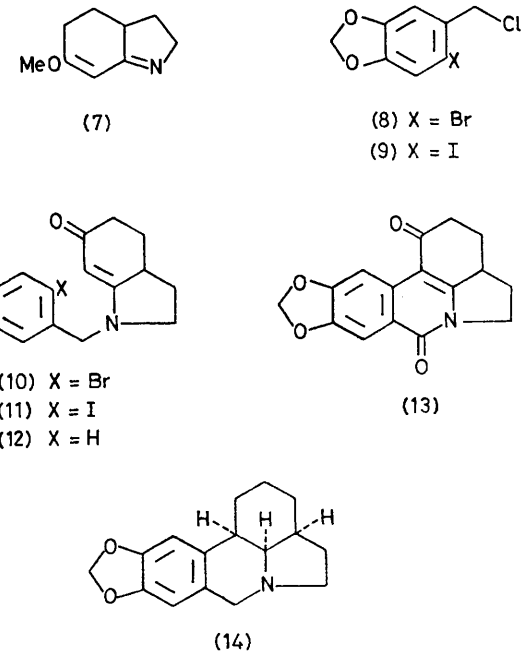
(1) (2) (3) (4) (5) (6)

The required bromoenaminones (**3**)† were readily prepared by condensation of the appropriate primary amines (**1**) with the cyclic β-diketones (**2**; R = H or Me), except for (**3c**) and (**3f**), which were prepared by *N*-alkylation (NaH, EtI, toluene, reflux) of (**3b**) and (**3e**) in 78 and 74% yield, respectively. Irradiation of dioxan–acetonitrile solutions of the bromoenaminones (**3a**—**f**) containing triethylamine in a Pyrex vessel with a high-pressure mercury lamp gave the corresponding cyclised products (**5a**—**f**) (Table). In the case of (**3d**) the photo-product actually isolated was the oxidatively aromatised compound (**6**) rather than (**5d**). These photo-products may arise *via* initial formation of the radical (**4**). The n.m.r. spectra of (**5**) confirm their cyclised structure, since they showed no signals due to vinyl protons [δ 4·7—5·4 in (**3**)].

TABLE. Photocyclisation of (**3**) to (**5**).

	n	R¹	R²	R³	% Yield[a] of (**5**)	M.p./°C
a	0	H	H	H	79	227—228
b	0	Me	H	H	86	209—211
c	0	Me	Et	H	64	c
d	1	Me	H	$-OCH_2O-$	25[b]	175—177
e	2	Me	H	OMe	91	229—230
f	2	Me	Et	OMe	94	c

[a] Based on isolated yields. [b] Yield for the oxidized product (**6**). [c] Liquid; purified by silica gel column chromatography.



(7) (8) X = Br (9) X = I (10) X = Br (11) X = I (12) X = H (13)

(14)

We have applied this method to the synthesis of a naturally occurring compound related to the lycorine alkaloids. The iminoenol ether (**7**),[2] readily prepared by the Birch reduction of 6-methoxyindoline, was heated with the benzyl chloride (**8**) or (**9**) in toluene, affording the desired enaminone (**10**) (55%), m.p. 157—158 °C, or (**11**) (50%), m.p. 173—174 °C, respectively. Irradiation of (**10**) as already described gave the keto-lactam (**13**) (19%), m.p. 252—253 °C, identical in all respects with an authentic sample,[2] along with the photo reduction product (**12**) (28%), m.p. 148—149 °C. Similar irradiation of the iodo-enaminone (**11**) yielded (**13**) (20%) and (**12**) (31%). The keto-lactam (**13**) is a degradation product derived from lycorine[3] or caranine[4] and has been converted into γ-lycorane (**14**) in two steps.[2]

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† Satisfactory analyses and spectral data were obtained for all new compounds.

[1] For review see, J. V. Greenhill, *Chem. Soc. Rev.*, 1977, **16**, 277.
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[4] E. W. Warnhoff and W. C. Wildman, *J. Amer. Chem. Soc.*, 1957, **79**, 2192.