# Photochemical Synthesis of 1*H*-1,2-Benzodiazepines from *N*-Iminoquinolinium Ylide Dimers

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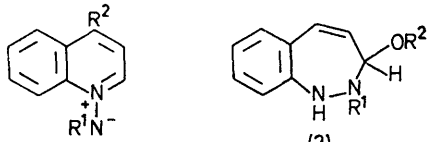
*Summary* Photolysis of the *N*-iminoquinolinium ylide dimers (**3**) affords 1*H*-1,2-benzodiazepines (**5**) in moderate yields.

THE photolysis of *N*-iminopyridinium ylides to give 1*H*-1,2-diazepines is a general heterocyclic photoisomerization reaction[1,2] but the analogous *N*-imino-quinolinium ylides

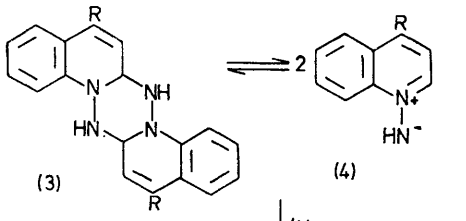
(**1**, $R^1$ = Ac, $CO_2Et$, COPh, or $SO_2Ph$, $R^2$ = H)[3,4] and -isoquinolinium[3–5] ylides undergo rearrangement to 2-aminoquinoline and 1-aminoisoquinoline derivatives respectively



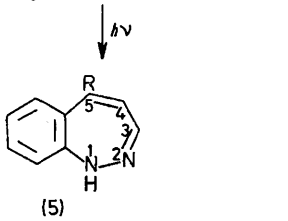
(1)



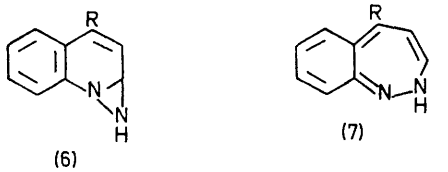
(2)
$R^1$ = Ac, $R^2$ = Me
$R^1$ = $CO_2Et$, $R^2$ = Et



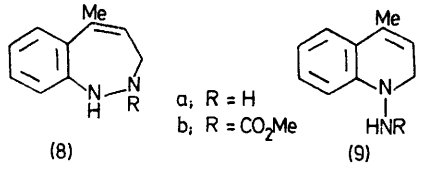
(3) (4)



(5)
a; R = H
b; R = Me



(6) (7)



(8) (9)

as well as products of N–N fragmentation of the parent heterocycles. Ring-expansion products have not been obtained except in two isolated cases which have yielded the alcohol adducts (**2**).[3] We report that photolysis of the *N*-iminoquinolinium dimers (**3**) affords the previously unknown, fully unsaturated 1*H*-1,2-benzodiazepines (**5**).

Irradiation (400 W high-pressure Hg lamp; Pyrex) of the dimers (**4a**) and (**4b**)[6] in $CH_2Cl_2$ or $Me_2CO$ solution gave, besides 2-aminoquinolines (10—15%) and quinolines (10%), the benzodiazepines (**5a**) and (**5b**) (30—40%):† (**5a**) m.p. 63—64°; ν (KBr) 3270, 1640, 1620, and 1595 $cm^{-1}$; $\lambda_{max}$ (EtOH) 250 nm (ε 17,000); δ ($CCl_4$) 5·78 (1H, dd, 4-H), 6·54 (1H, d, 3-H), 6·60 (1H, d, 5-H), 6·6 br (1H, NH), and 6·4—7·2 (4H, m, Ar-H); (**5b**) m.p. 63·5—64°; ν (KBr) 3290, 1638, 1620, and 1592 $cm^{-1}$; $\lambda_{max}$ (EtOH) 246 nm (ε 16,000); δ($CCl_4$) 2·12 br (3H, 5-Me), 5·89 (1H, m, 4-H), 6·42 br (1H, NH), 6·86 (1H, d, 3-H), and 6·6—7·25 (4H, m, Ar-H). These spectral data are consistent with the proposed structures and eliminate tautomeric 2*H*-, 3*H*-, and 5*H*-1,2-benzodiazepines. These structures were confirmed by the following chemical studies.

$LiAlH_4$ reduction of (**5b**) afforded in quantitative yield the 2,3-dihydro-derivative (**8a**)‡ m.p. 75—76°; ν (KBr) 3230 (NH) $cm^{-1}$. Furthermore, $NaBH_4$ reduction of (**5b**) in the presence of methyl chloroformate[7] gave the benzodiazepine (**8b**):§ m.p. 63—64°; ν (KBr) 3280 and 3310 (NH), 1700 (CO) $cm^{-1}$. Structures (**9a**) and (**9b**) for the respective products of $LiAlH_4$ and $NaBH_4$–$ClCO_2Me$ treatment of (**5b**) were eliminated by independent synthesis as follows. $NaBH_4$ reduction of the hydroiodides of (**1**, $R^1$ = H, $R^2$ = Me) and (**1**, $R^1$ = $CO_2Me$, $R^2$ = Me) gave (**9a**) and (**9b**) which were different (n.m.r., u.v., and mass spectra) from the compounds assigned structures (**8a**) and (**8b**). Catalytic reduction (Pd–C) of (**5a**) and (**5b**) gave quinoline and 4-methylquinoline respectively. This result can be explained by N–N bond fission followed by cyclization and deamination.

The formation of the diazepines (**5**) from the dimers (**3**) may proceed by equilibration to the ylides (**4**) followed by isomerization and cycloreversion (**4**) → (**6**) → (**7**) as previously suggested for the *N*-iminopyridinium ylides.[1] The *o*-quinonoid intermediates (**7**) would then tautomerize to the products (**5**). Direct formation of the diaziridines (**6**) from the dimers (**3**) possibly *via* diradical intermediates is also possible. For *N*-acyliminoquinolinium ylides, proton transfer would not be possible from the 2-acyl intermediates from (**7**); furthermore, N–N bond weakening would be expected in the *N*-acyl-diaziridine from (**6**). Both factors may contribute towards the formation of 2-acylaminoquinolines as the major products in these photoreactions.[3,4]

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† Satisfactory elemental analyses were obtained for all new compounds. N.m.r. spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with $D_2O$.

‡Compound (**8a**) was also obtained by $NaBH_4$ reduction of (**5b**) in MeOH.

§ Compound (**8b**) was also prepared by treatment of (**8a**) with NaH–$ClCO_2Me$ in tetrahydrofuran at 0—5°.

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