Tetrahedron Letters,Vol.24,No.50,pp 5567-5570,1983 0040-4039/83 $3.00 + .00
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INTRAMOLECULAR PHOTOARYLATIONS OF HALOARYLETHYL-β- and -α-ENAMINOKETONES. A CORRECTION AND FURTHER RESULTS

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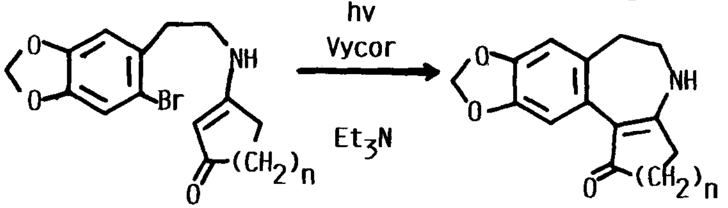
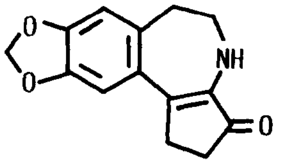
Summary. Continuing studies of haloarylethyl-β- and α-enaminoketone photocyclization reactions have demonstrated that both C- and N-cyclized products are generated.

Photocyclization reactions of appropriately substituted aryl halides with appended enamine, enolate anion, enamide and carbamate moieties have been utilized in approaches to the synthesis of some naturally occuring substances.[1-4] Our recent investigations[5] with the haloarylethyl-β-enaminones, **1** and **2**, uncovered modified photochemical reaction conditions which resulted in high yield production of the tricyclic β-enaminones **3** and **4**. However, one result disclosed in this earlier report[5] concerning the photoconversion of **2** to the α-enaminone product **5** is now demonstrated to be erroneous. We reported earlier[5] that Vycor-filtered irradiation of **2** in p-dioxane leads to products having the C-cyclized β- and α-enaminone skeletons **4** and **5**. Structural assignments were based upon characteristic ^{1}H-NMR, UV and IR data. Owing to the unusual nature of the pathway required for the transformation of **2** to **5** a more thorough study of this reaction was conducted in order to gain additional spectroscopic data and to probe the generality of the mechanistic proposals made previously.[5] These investigations have provided results which show that the minor product arising by irradiation of **2**, pre-



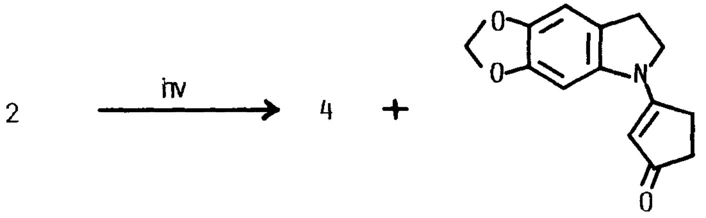
1 (n=2) 3 (n=2)

2 (n=1) 4 (n=1)



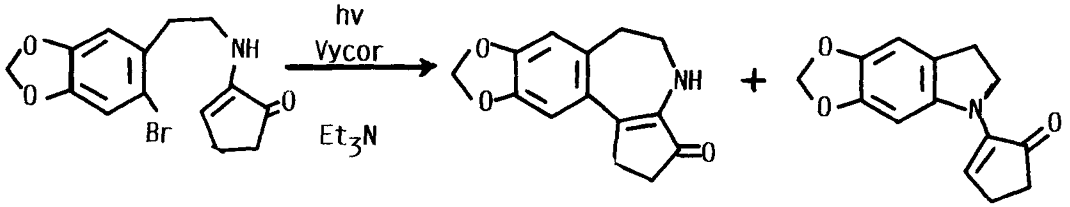
5

viously identified as the α-enaminone 5, is really the N-cyclized product 6.



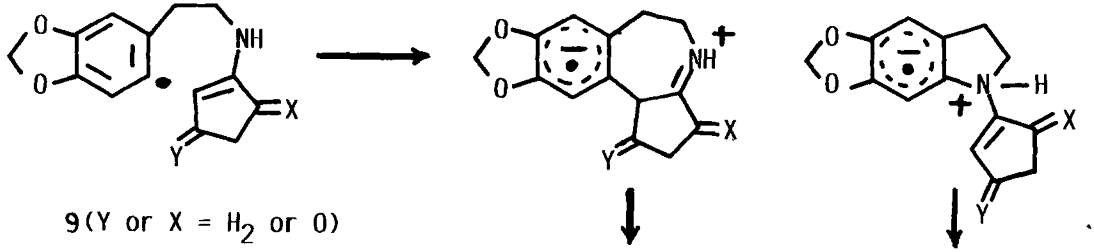
6

Thoughts about the need for this structure revision were stimulated by observations made in photochemical studies with the N-haloarylethyl-α-enaminone 7.[6] Irradiation (Vycor) of 7 in p-dioxane leads to production of two new photoproducts with spectroscopic properties (see Table) different from those of **4** and **6** and perfectly in accord with the C- and N-cyclized α-enaminone structures 5 and **8**. The conflicting nature of these and the previously obtained results was quickly resolved by inspection of key spectroscopic data. Accordingly, the ^{13}C-resonance at 96.3 ppm (CH by INEPT) for the α-vinyl carbon in **6**, the C=O and C=C bands in the IR of **6** at 1655 and 1550 cm^{-1}, respectively, and the D_2O non-exchangeability of the proton-resonance previously assigned as the NH in **5** but in reality corresponding to the α-vinyl proton in **6** all serve to confirm the new structural assignments. Additional support resides in the perfect match of the ^{1}H-NMR data for **6** with those of the known compound prepared earlier by Kibayashi.[2c]



7 5 8

In summary, the current results now clearly demonstrate that Vycor-filtered irradiations of the N-haloarylethyl-β- and α-aminocyclopentenones 2 and 7 lead to smooth and chemoselective generation of C- and N-cyclized products **4** and **6**, and **5** and **8**, respectively, by straightforward mechanistic pathways



9(Y or X = H_2 or O)

4 or 5

6 or 8

involving aryl radical **9** generation and cyclization through bonding at the enamine terminal carbon or nitrogen.[8]

Table. Characteristic Spectroscopic Data for the C-Cyclized (**4** and **5**) and N-cyclized (**6** and **8**) Photoproducts.

Product	^{1}H-NMR (CDCl$_3$) (ppm, rel. TMS)		^{13}C-NMR (CDCl$_3$) (ppm, rel. TMS)		IR (CHCl$_3$) (cm^{-1})			UV (CH$_3$OH) (max., nm)
	$C{=}C\underline{H}$	$N\underline{CH_2}$	$N\underline{C}{=}CH$	$NC{=}\underline{C}H$	$C{=}O$	$C{=}C$		
6	5.30	4.00	170.3	96.3	1655	1550		345
8	6.80	3.90	145.5	94.7	1710	1610		320
	$N\underline{CH_2}$	NH	$N{-}\underline{C}{=}C$	$N{-}C{=}\underline{C}$	NH	$C{=}O$	$C{=}C$	
4	3.78	5.60	173.0	108.9	3415	1660	1585	297
5	3.50	4.50	160.7	140.1	3420	1690	1610	368

Acknowledgment. The financial support for this work by the National Institutes of Health (GM-27251) is greatly appreciated.

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4. Luly, J.; Rapoport, H. *J. Amer. Chem. Soc.*, **1983**, *105*, 2859.
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6. This material was prepared by condensation of the corresponding haloarylethylamine with 1,2-cyclopentandione.

7. All new compounds have satisfactory molecular formulae (high resolution mass spec) and/or elemental compositions (combustion analysis).

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(Received in USA 15 August 1983)