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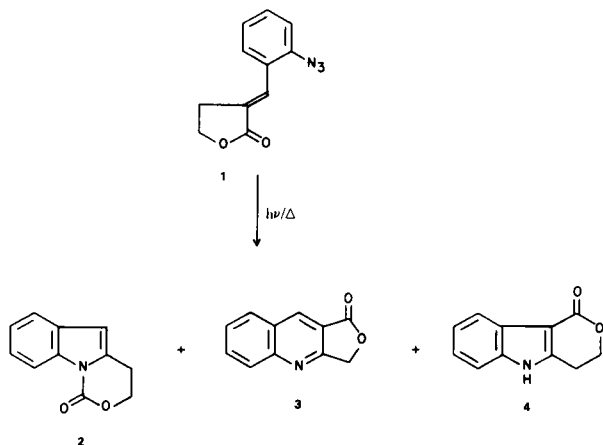
The thermolysis and/or photolysis of 3-(2-azidophenylmethylene)-4,5-dihydro-2-(3*H*)furanone offers a preparatively useful way towards the synthesis of indoles and quinolines. This method is superior over previously published methods which afforded these heterocycles in poor yields by the deoxygenative cyclization of 3-(2-nitrophenylmethylene)-4,5-dihydro-2-(3*H*)furanones.

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Sir:

Due to the high incidence of desirable pharmacological and physiological properties in indoles and quinolines as well as their occurrence as part of many alkaloids, novel synthetic methods to afford these heterocycles are desirable. We found that both thermolysis and photolysis of 3-(2-azidophenylmethylene)-4,5-dihydro-2-(3*H*)furanone (**1**) offers a potentially useful way to generate these heterocycles from readily available starting materials.

When irradiated in diluted benzene solution, **1** lost one molecule of nitrogen and rearranged to give indoles, **2** (11%, m.p. 101-103°, diethyl ether-pentane) and **4** (21%, m.p. 252-253°, ethyl acetate-chloroform) and quinoline, **3** (6.5%, m.p. 217.5-218.5°, methanol, lit. (3) m.p. 218-219°). Similarly, the thermolysis of **1** in cumene afforded **2** (12%), **3** (22%), and **4** (3.5%) in slightly different product ratios. The products could be obtained readily by preparative lc of the product mixture with 1% methanol in chloroform as eluent.



The starting azide was prepared from the corresponding known amine (**4**) by diazotization and treatment with sodium azide following a general procedure by Smith and Brown (5). The product was recrystallized from methanol (m.p. 130.5-131°) in the dark to give **1** as pale yellow needles (*Anal.* Calcd. for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.16; H, 4.00; N, 19.60).

The structures of products **2**, **3**, and **4** were assigned on the basis of analytical (6) (**2**: *Anal.* Calcd. for

$C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.50; H, 4.81; N, 7.40. **4**: *Anal.* Calcd. for $C_{11}H_9NO_2$. Found: C, 70.26; H, 4.79; N, 7.26); nmr (δ , TMS: **2** (deuteriochloroform): 3.15 (dt, CH_2 , $J = 6$ Hz, $J' = 1$ Hz); 4.50 (t, CH_2 , $J = 6$ Hz); 6.35 (broadened singlet, CH); 7.15-7.55 (m, 3H); 8.05-8.30 (ddd, 1H, $J = 8$ Hz, $J' = 3$ Hz, $J'' = 1$ Hz); **3** (deuteriochloroform): 5.5 (s, CH_2); 7.55-8.3 (m, 4H); 8.8 (s, 1H); **4** (perdeuterioacetone): 3.20 (t, CH_2 , $J = 6$ Hz); 4.60 (t, CH_2 , $J = 6$ Hz); 7.10-7.6 (m, 3H); 8.0 (dd, 1H, $J = 6$ Hz, $J' = 3$ Hz); 11.15 (very broad, NH, exchangeable with deuterium oxide); ir ($C=O$, cm^{-1} : **2**: 1735; **3**: 1755; **4**: 1700); ms data (m/e : **2**: 187 (m^+), 143 (base), 115; **4**: 187 (m^+ , base), 157, 129).

The reactions, having not been optimized, gave total product yields of 38%. These results are excellent when compared with work we (7) and other groups (8) have done with various aromatically substituted 3-(2-nitrophenylmethylene)-4,5-dihydro-2-(3*H*)furanones and triethyl phosphite. Preliminary studies of the mechanism of the reaction reported in Scheme 1 provides good evidence that it proceeds *via* the nitrene derived of **1**. However, this mechanism is not in agreement with an earlier published one involving the same nitrene as intermediate in the phosphite deoxygenative cyclization of 3-(2-nitrophenylmethylene)-4,5-dihydro-2-(3*H*)furanones leading to a larger number of compounds including a type **2** compound (**8**). This latter method produced at least six component mixtures and total yields averaging 10% for compounds structurally similar or identical to **2**, **3** and **4**. Although the synthesis of **3** can be effected more efficiently from 2,4-(3*H*,5*H*)furandione and 2-aminobenzaldehyde (**3**), the photolytic production of **2** and **4** from **1** offers a preparatively useful method for the synthesis of these not so readily available indoles. We are currently exploring the generality of the reaction in Scheme 1.

REFERENCES AND NOTES

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