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ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES, X[1]

PHOTOLYSES OF SOME *N*-(3-QUINAZOLINIO)-AMIDATES[2]

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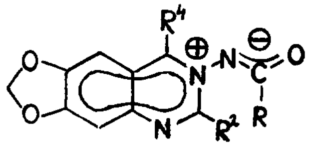
The *N*-(3-quinazolinio)-amidates **1a**-**e** do exist in alcoholic solns as equilibrium mixtures with their alcohol adducts, *e.g.* **2a**-**e**.[3] When an Ar purged ethanolic soln of **1a** was irradiated through Pyrex with a high pressure Hg lamp, four products,[4] **5a** (R'=Et, 26 %, mp. 174-5°), **6a** (30 %, mp. 180°), **7a** (5 %, mp. 126-8°) and ethyl carbamate, were obtained. **6a** and **7a** were identical with authentic samples. The structure assignment of **5a** (R'=Et) is based on the following observations. UV [209 (4.56) ; 220 (4.4), sh; 300 (4.00) in EtOH], IR [KBr; νNH 3300, b, νC=O 1690] and mass spectra [*m/e* 321: (M) 44 %, *m/e* 276: (M − OEt)[5] 100 %, *m/e* 248: (276 − C_2H_4) 15 %, *m/e* 230: (276 − EtOH) 20 %, *m/e* 204: (248 − CO_2) 9 %, *m/e* 189: ($C_{10}H_9N_2O_2$) 28 %, *m/e* 188: (230 − NCO) 16 %] are consistent with the isomeric structures **5a** (R'=Et) and **12**; the latter, however, is ruled out by the PMR spectrum [OEt: δ 1.28, t + 3.6, q, J = 7 Hz; COOEt: 1.35, t + 4.3, q, J = 7 Hz; 2-Me: 2.15, s; OCH_2O: 5.95, s; 5-H + ArH's: 6.35 + 6.4 + 6.7, all s; NH: 7.1, bs in $CDCl_3$; OEt: 1.08, t + ~3.45, m, J = 7 Hz; COOEt: 1.14, t + 4.10, q, J = 7 Hz; 2-Me: 1.96, s; OCH_2O: 6.01, s; 5-H + ArH's: 6.35 + 6.6 + 6.9, all s; NH: 8.8 bs in DMSO-d_6] because there is no H-N-C-H coupling as required by structure **12**, while such a coupling ($J_{H-C(2)-N-H}$ = 5 Hz) is observed in the DMSO-d_6 PMR spectrum of the analogous **5d** (R'=Et). When irradiation of **1a** was performed in benzyl alcohol, **5a** (R'= $PhCH_2$, 4 %, m.p. 90-3°) was formed along with **6a** and ethyl urethane.



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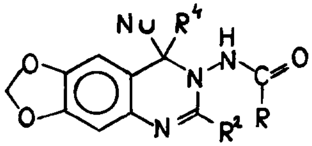
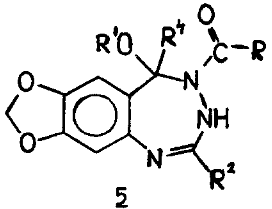


2: Nu = OEt
3: Nu = NR'R"
4: Nu = SCH_2Ph



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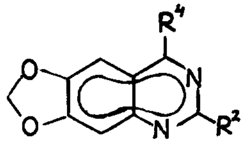

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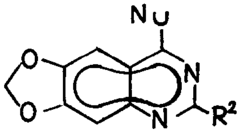
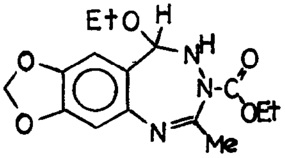


7: Nu = OEt
8: Nu = NHBu
9: Nu = $NHCH_2Ph$
10: Nu = morpholino
11: Nu = SCH_2Ph

1 - 11			
	R^2	R^4	R
a	Me	H	OEt
b	Me	H	OCH_2Ph
c	Me	H	Ph
d	H	H	OEt
e	Me	Me	OEt



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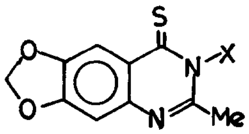
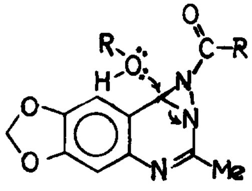


13: X = H
14: X = NH-COOEt



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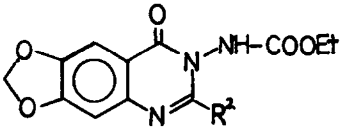

16: R^2 = H
17: R^2 = Me

Irradiations of 1b-d in EtOH furnished the analogous benzotriazepines 5b (R'=Et; 23 %, mp. 176°), 5c (R'=Et; 26 %, mp. 197°) and 5d (R'=Et; 11 %, mp. 122-4°), respectively, whose UV, IR, mass and PMR spectra are in agreement with their assumed structures. Irradiation of 1e, for which the equilibrium with its EtOH adduct is shifted towards the amidate,[3] furnished 6e (86 %, m.p. 181-3°).

When benzylamine or α-toluenethiol were added to $CDCl_3$ solutions of 1c, the signals corresponding to 1c[3] were gradually replaced by those of the adducts **3c** (NRR' = $NHCH_2Ph$; 2-Me: δ 2.25; 4-H: 4.8; OCH_2O: 5.75; ArH's: 6.8 + 7.1)[6] and **4c** (OCH_2O: δ 5.90), respectively.

Irradiation of **1a** in $BuNH_2$, $PhCH_2NH_2$ and morpholine furnished **8a** (70 %, mp. 193°), **9a** (42 %, mp. 199-200°) and **10a** (70 %, m.p. 187°), respectively, whose structures were derived from their IR and mass spectra, and corroborated by comparison with authentic samples. Irradiation of **1e** in $BuNH_2$ furnished **6e** (80 %). Ethyl urethane was obtained as the by-product in all cases.

When **1a** was irradiated in a mixture of $CHCl_3$ and α-toluenethiol, **11a** (4 %, mp. 170-1°), **13** (4 %, mp. 290-2°) and **14** (25 %, mp. 170-1°) were obtained as the major products. **11a** and **13** proved identical with authentic samples, while structure **14** was derived from the mass spectrum [*m/e* 307: (M) 100 %, *m/e* 274: (M $\overset{*}{-}$ SH) 12 %, *m/e* 262: (M $\overset{*}{-}$ EtO) 11 %, *m/e* 235: (M - CO_2 - C_2H_4) 16 %, *m/e* 220 (262 $\overset{*}{-}$ NCO) 20 %, *m/e* 206 (235 $\overset{*}{-}$ 29) 9 %, *m/e* 205: 9 %, *m/e* 187: (220 $\overset{*}{-}$ SH) 17 %], IR [νNH 3240, νC=O 1740 in KBr] and the PMR spectrum [NH: δ 8.1, bs; 5-H: 7.98, s; 8-H: 7.05, s; OCH_2O: 6.18, s; 2-Me: 2.68, s; COOEt: 1.35, t + ~4.3, m, J = 7.3 Hz, in $CDCl_3$] of the product.

The Type **7**-**11** compounds are thought to arise from a Norrish Type II cleavage of the Type **2**-**4** adducts,[7] respectively, while the Type **6** compounds are clearly the acylnitrene elimination products of the amidates **1** themselves, and probably formed through the T_1 states (*c.f.* Ref. 8). The ring enlargement products **5**, on the other hand, are probably formed *via* the S_1 states and the diaziridine intermediates **15**. The formation of **6e** as the only heterocyclic product on photolysis of **1e** in EtOH and $BuNH_2$ reflects the reduced propensity of C-4 of the latter towards being attacked by nucleophiles. **11a**, the primary photolysis product of **5a** formed in the presence of α-toluenethiol is, as shown in a separate experiment, photounstable. Photolysis of its S-CH_2 bond leads to **13**. Formation of **14**, on the other hand, may be rationalized by assuming photolysis of the S-CH_2 bond of **4a** and H abstraction by the resulting heterocyclic radical.

An interesting by-product of the photolysis of **1d** in EtOH is **16** (10 %, m.p. 226°), whose 2-Me derivative **17** (13 %, mp. 160-2°) is one of the products formed on prolonged refluxing of **1a** with $BuNH_2$. The structure of **17** was proven by comparison with an authentic sample, while that of **16** follows from the similarity of its mass, IR, UV and PMR spectra to those of **17**.

References and Notes

1. Part IX: B. Ágai and K. Lempert, submitted for publication
2. Part II of *N*-(3-Quinazolinio)amidates. For Part I, see Ref. 3.
3. J. Fetter, K. Lempert and J. Møller, *Tetrahedron* **31** (1975), accepted for publication
4. All new compounds gave satisfactory microanalyses
5. An asterisk indicates that the decomposition is accompanied by the appropriate metastable peak
6. For the formation of an analogous NH_3 adduct, see Ref. 3.
7. The dihydroderivative **2a** (with H instead of Nu) similarly yields **6a**, when irradiated in EtOH.
8. J. Streith, T.P. Luttringer and M. Nastasi, *J. Org. Chem*. **36**, 2962 (1971)