Photorearrangement of Anthranils into Azepines

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RECENTLY there have been described many examples of photo-induced rearrangements of five-membered-ring heterocyclic compounds. Our interest in the photochemical behaviour of indazoles[1] and benzisoxazoles (1,2-benzisoxazoles)[2] led us to examine the photochemistry of anthranils (2,1-benzisoxazoles).

Irradiation of 6-chloro-3-phenylanthranil (Ia)[3] in methanol through Pyrex gave a carbonyl compound (IIa) (69·6%), $C_{14}H_{12}NO_2Cl$ (M^+ 261), m.p. 83·5—84·5°, λ_{max} (MeOH) 247 mμ (log ϵ 4·30); ν_{max} (Nujol) 1687, 1612 cm.$^{-1}$. In the mass spectrum of (IIa), the fragment ion peak at m/e 156 corresponds to $M^+ - C_7H_5O$, which suggests the presence of a benzoyl group. These data and the n.m.r. spectrum of (IIa) shown in the Table are consistent with the structure of 3-benzoyl-5-chloro-2-methoxy-3*H*-azepine. However, the alternative 2*H*-azepine structure (IIa′) could not be ruled out. In order to decide between the two alternatives, the following reaction was carried out.

Hydrolysis of (IIa) with aqueous ethanol

TABLE

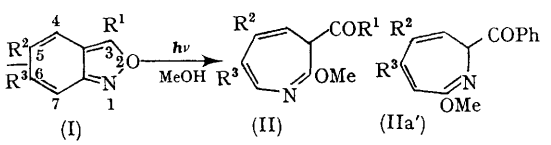
N.m.r. spectral parameters[a] *of the compounds* (IIa–c) *in* C_6D_6; (III) $(CD_3)_2SO$

Compounds	Chemical shifts (τ) (multiplicities)								Spin–spin couplings (c./sec.)
	H_a	H_b	H_c	H_d	H_e	OMe	COR	NH	
(IIa)	6·60 (dd)	3·65 (dq)	—	4·03 (dq)	3·12 (dd)	6·88 (s)	2·1—2·3 (2H, m)	—	J_{Ha-Hb} 6·0; J_{Ha-Hd} 0·4
							2·8—3·1 (3H, m)	—	J_{Hb-Hd} 1·4; J_{Hb-He} 0·6 J_{Hd-He} 8·5
(IIb)	7·02 (bd)	3·7—4·4 (m)			3·00 (bd)	6·60 (s)	8·15 (s)	—	J_{Ha-Hb} 6·0; J_{Hd-He} 7·5
(IIc)	7·32 (bd)	4·68 (qd)	3·90 (bd)	—	2·83 (bd)	6·72 (s)	0·83 (bs)	—	J_{Ha-Hb} 6·5; J_{Hb-Hc} 9·5 J_{Hb-He} 0·7
(III)	5·37 (d)	3·87 (dd)	—	4·17 (bd)	3·57 (bdd)	—	1·9—2·2 (2H, m)	−0·4 (b)	J_{Ha-Hb} 6·5; J_{Hb-Hd} 1·0
							2·3—2·7 (3H, m)		J_{Hd-He} 9·0; J_{NH-He} ~5

b = broad, d = doublet, dd = a doublet of doublets, dq = a doublet of quartets, m = multiplet, qd = a quartet of doublets, s = singlet.

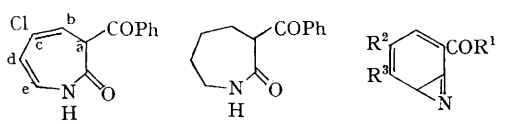
[a] The spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as internal standard. The coupling constants for (IIa) were determined by proton spin–decoupling experiments at 100 Mc./sec. with a Varian HA-100 spectrometer using a Hewlett–Packard HP-200ABR audio-oscillator in a frequency sweep and Me_4Si-locked mode operation.

afforded an amide (III), $C_{13}H_{10}NO_2Cl$, m.p. 174—175° (decomp.), λ_{max} (MeOH) 247 mμ (log ε 4·26); ν_{max} (Nujol) 3170, 1683, 1655, 1621 cm.$^{-1}$. The n.m.r. spectral data of (III) are given in the Table. In the spectrum, upon addition of deuterium oxide, the NH proton signal disappeared and a broad doublet of doublets signal at τ 3·57 turned into a simple doublet. These data support the partial arrangement :CH·NHCO rather than ·NHCO·CH:. Accordingly, the structure from which the amide was derived should be (IIa) and not (IIa′).



(I) (II) (IIa′)

a; R^1=Ph, R^2=Cl, R^3=H
b; R^1=Me, R^2=R^3=H
c; R^1=H, R^2=H, R^3=Cl



(III) (IV) (V)

Catalytic hydrogenation of (III) in methanol with palladium–charcoal in the presence of sodium acetate gave a hexahydro-amide (IV), $C_{13}H_{15}NO_2$, m.p. 186—188°, ν_{max} (Nujol) 3205, 1684, 1653 cm.$^{-1}$; no methyl signal in the n.m.r. spectrum.

From these data, the structures of 3-benzoyl-5-chloro-2-oxo-3*H*-azepine and its dechlorohexahydro-derivative were assigned to (III) and (IV), respectively.

Under similar conditions, 3-methylanthranil (Ib)[4] and 6-chloroanthranil (Ic)[5] were converted into azepine derivatives: $C_9H_{11}NO_2$ (M^+ 165) (IIb) (42·2%) [b.p. 117—118°/11 mm., λ_{max} (MeOH) 259 mμ (log ε 3·71);[6] ν_{max} (neat) 1715, 1613 cm.$^{-1}$] and $C_8H_8NO_2Cl$ (M^+ 185) (IIc) (11·3%) [b.p. 78°/6 mm., λ_{max} (MeOH) 264 mμ (log ε 3·72); ν_{max} (neat) 2800, 2690, 1723, 1615 cm.$^{-1}$]. In the mass spectra of (IIb) and (IIc), the fragment ion peaks at *m/e* 122 (corresponds to $M^+ - C_2H_3O$) and *m/e* 156 (corresponds to M^+ —CHO) suggest the presence of acetyl and formyl groups, respectively. The n.m.r. spectral data of (IIb) and (IIc) are in good agreement with the assigned structures (Table).

A possible mechanism for the photorearrangement of anthranils involves initial N–O bond cleavage followed by ring closure to the resonance-stabilized azirine intermediate (V),[7] which undergoes ring expansion and addition of methanol to yield the azepine (II). Studies are in progress to further elucidate the scope and the mechanism of the reaction. Satisfactory analytical data for the structural assignments of the new compounds were obtained.

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