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ORGANIC PHOTOCHEMICAL REACTIONS—V[1]
PHOTOREARRANGEMENT OF ANTHRANILS INTO AZEPINES

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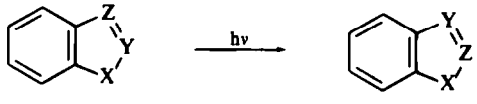
Abstract—The photolysis of anthranils (III) led to ring enlargement with the formation of 3-acyl-2-methoxy-3*H*-azepines (IV). The reaction in ether containing water or amines yielded the corresponding 2-oxo- or 2-amino-3*H*-azepines (V or VII). On the other hand, photolysis of some 7-substituted 3-phenylanthranils (IX and XIII) gave the corresponding 9-acridanone derivatives (X and XIV). A hypothetical scheme (anthranil → nitrene → azirene → azepine) similar to that proposed by Huisgen and Appl for the analogous ring enlargement of phenylazide is applicable to the anthranil rearrangement. By UV and IR spectroscopic methods, the last step was proved to involve a dark reaction of an intermediate (probably azirene species) with protic solvents.

THE photochemical rearrangement in some benzazole ring systems (I → II), e.g. the 1,2-benzisoxazole (I; X = O, Y = N, Z = CH) rearrangement to benzoxazole (II; X = O, Y = N, Z = CH), prompted us to investigate the photolysis of 2,1-benzisoxazoles (anthranils) (III) as compared with 1,2-benzisoxazoles.



I II

X = O, Y = N, Z = CH[2]
X = NH, Y = N, Z = CH[3]
X = S, Y = N, Z = C—OH[4]

The photolysis of anthranils involves a new rearrangement to the corresponding 3-acyl-3H-azepines (IV, V and VII).

Photolysis of 7-unsubstituted anthranils (III)

Irradiation of 5-chloro-3-phenylanthranil (IIIa)[5] in methanol using high pressure mercury arc lamp was followed by UV absorption spectroscopy and a carbonyl compound (IVa; 69·6%) was obtained. The spectral (UV, IR and NMR) and analytical data of IVa are all consistent with the structure of 3-benzoyl-5-chloro-2-methoxy-3*H*-azepine as shown in Tables 1, 2 and 3. Its mass spectrum showed a fragment ion peak at *m/e* 156 (M^+-C_6H_5CO), which gave further support for the presence of a benzoyl group. As the alternative 2*H*-azepine structure (IVa') cannot be excluded, compound IVa was hydrolysed to a lactam (Va), which was also obtained on irradiation of IIIa in aqueous THF. Its NMR spectrum is shown in Table 2. When deuterium

TABLE 1. PHOTOLYSIS OF ANTHRANILS

Anthranil	Reaction solvent[a]	Product (Azepine)	Yield (%)	Recryst. solvent[b]	m.p. (b.p./mmHg)	UV (MeOH) mμ (log ε)	IR[c] cm^{-1}
IIIa[5]	MeOH	IVa	69·6	IPE	83·5–84·5	247 (4·30)	1612, 1687 (N)
IIIb[6]	MeOH	IVb	61·6	n-hex	65–66	246 (4·21)	1613, 1690 (N)
		VI[11]	0·7				
IIIc	MeOH	IVc	69·0	MeOH	93·5–95·5	247 (4·28)	1614, 1693 (N)
IIId[7]	MeOH	IVd	64·0	—	115–116/13	259 (3·71)	1613, 1715 (F)
IIIe[8]	MeOH	IVe	11·3	—	70–80/6	264 (3·72)	1615, 1723 (F)
IIIf[9]	MeOH	IVf	3·1	—	100/2	258 (3·71)	1624, 1725 (F)
IIIg	MeOH	IVg	78·3	IPE	73	272 (4·25)	1621, 1684 (N)
IIIh[10]	MeOH	IVh	72·7	—	160/0·3	261 (4·16)	1613, 1669 (F)
IIIa[5]	THF	Va	38·6	Bz.	174–175 (dec.)	247 (4·26) 252 (4·50) 340 (4·12)	1623, 1655, 1683, 3170 (N)
		VIII	0·8	EtOH	199–202 (dec.)		1617, 1645 (N)
IIIb[6]	THF	Vb	60·8	Bz.	166–168	246 (4·24)	1631, 1655, 1690 3065, 3185 (N)
IIId[7]	Ether	Vd	41·4	MeOH-IPE	132–133·5	255 (3·66)	1629, 1655, 1718, 3220 (N)
IIIa[5]	BA-Ether	VIIi	18·6	MeOH-H_2O	105–107	248 (4·10) 297 (3·75)	1627, 1668 3230 (N)
IIIa[5]	AN-Ether	VIIj	41·5	MeOH	129–131	247 (4·29) 311 (4·13)	1674, 3270 (N)
IIIa[5]	DA-Ether	VIIk	32·6	MeOH	131–132	237 (4·29) 310 (4·00)	1604, 1681 (N)
IIId[7]	AN-Ether	VIII	9·4	MeOH	128·5–130·5	305 (4·18)	1615, 1703 3200, 3240 (N)

[a] BA = *n*-butylamine, AN = aniline, DA = diethylamine.
[b] IPE = isopropyl ether, n-hex. = n-hexane, Bz. = benzene.
[c] N = Nujol mull. F = neat film.

TABLE 2. NMR SPECTRAL PARAMETERS FOR AZEPINES

Compound	Solvent	τ-Values[a] H-3	H-4	H-5	H-6	H-7	OMe	COR_1	NH	J, Hz
IVa	$CDCl_3$	6·60	3·65	—	4·03	3·12	6·88	2·1–2·3 2·8–2·6	—	$J_{3,4}$ = 6·0, $J_{3,6}$ = 0·4 $J_{4,6}$ = 1·4, $J_{4,7}$ = 0·6 $J_{6,7}$ = 8·5
IVb	$CDCl_3$	6·30	3·5–4·2			2·90	6·42	2·0–2·2 2·4–2·7	—	$J_{6,7}$ = 8·0
IVc	$CDCl_3$	6·20	3·95	3·57	—	2·72	6·38	2·0–2·2 2·3–2·6	—	$J_{3,4}$ = 5·5, $J_{3,5}$ = 1·0 $J_{4,5}$ = 9·5, $J_{4,7}$ = 0·5 $J_{5,7}$ = 1·5
IVd	$CDCl_3$	7·02	3·7–4·4			3·00	6·60	8·15	—	$J_{3,4}$ = 6·0, $J_{6,7}$ = 7·5
IVe	$CDCl_3$	7·32	4·68	3·90	—	2·83	6·72	0·83	—	$J_{3,4}$ = 6·5, $J_{4,5}$ = 9·5 $J_{4,7}$ = 0·7
IVf	C_6D_6	7·03	3·8–4·8			3·10	6·63	0·83	—	$J_{3,4}$ = 7·0, $J_{6,7}$ = 8·0
IVg	C_6D_6	6·45	2·8–4·2				6·70	?	—	?
IVh	C_6D_6	6·58	2·8–4·2				6·77	?	—	?
Va	$(CD_3)_2SO$	5·37	3·87	—	4·17	3·57	—	1·9–2·2 2·3–2·7	−0·4	$J_{3,4}$ = 6·5, $J_{4,6}$ = 1·0 $J_{6,7}$ = 9·0, J_{NH-7} = ~0·5
Vb	$CDCl_3$	5·66	3·5–4·3				—	1·9–2·2 2·4–2·7	0·7	$J_{3,4}$ = 4·0
Vd	$CDCl_3$	6·45	3·5–4·5				—	7·70	1·67	$J_{3,4}$ = 6·0
VIIi	$CDCl_3$	6·43	4·70	—	4·17	2·83	—	6·72 8·62 9·05	3·83	$J_{3,4}$ = 7·0, $J_{4,6}$ = 1·0 $J_{6,7}$ = 8·0
VIIj	C_6D_6	6·82	4·92	—	4·05	?	—	2·2–2·5 2·7–3·1	0·92	$J_{3,4}$ = 7·0, $J_{6,7}$ = 8·0
VIII	$(CD_3)_2SO$	5·45	4·2–4·7			3·60	—	8·05	0·90	$J_{3,4}$ = 9·0, $J_{5,7}$ = 6·0 $J_{6,7}$ = 9·0

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

TABLE 3. ANALYSIS OF AZEPINES

Compound	Empirical formula	Found % C	Found % H	Found % N	Calcd % C	Calcd % H	Calcd % N
IVa	$C_{14}H_{12}NO_2Cl$	64·39	4·68	5·29	64·23	4·62	5·34
IVb	$C_{14}H_{13}NO_2$	74·23	5·71	6·29	73·99	5·77	6·16
IVc	$C_{14}H_{12}NO_2Cl$	64·28	4·74	5·15	64·23	4·62	5·34
IVd	$C_9H_{11}NO_2$	65·44	6·83	8·82	65·44	6·71	8·48
IVe	$C_8H_8NO_2Cl$	51·87	4·39	7·42	51·75	4·31	7·54
IVf	$C_8H_9NO_2$	63·56	6·00	9·27	63·66	6·09	8·74
IVg	$C_{12}H_{11}NO_3$	66·32	5·18	6·35	66·35	5·10	6·45
IVh	$C_{12}H_{11}NO_2S$	61·76	4·76	5·72	61·80	4·75	6·01
Va	$C_{13}H_{10}NO_2Cl$	62·94	4·03	5·62	63·03	4·04	5·65
Vb	$C_{13}H_{11}NO_2$	72·63	5·30	6·19	73·22	5·20	6·57
Vd	$C_8H_9NO_2$	63·62	5·99	9·18	63·56	6·00	9·27
VIIi	$C_{17}H_{19}N_2OCl$	67·44	6·31	9·24	67·43	6·32	9·25
VIIj	$C_{19}H_{15}N_2OCl$	70·73	4·74	8·62	70·73	4·68	8·67
VIIk	$C_{17}H_{19}N_2OCl$	67·32	6·42	9·07	67·43	6·32	9·25
VIII	$C_{14}H_{14}N_2O$	74·39	6·21	12·38	74·31	6·24	12·38

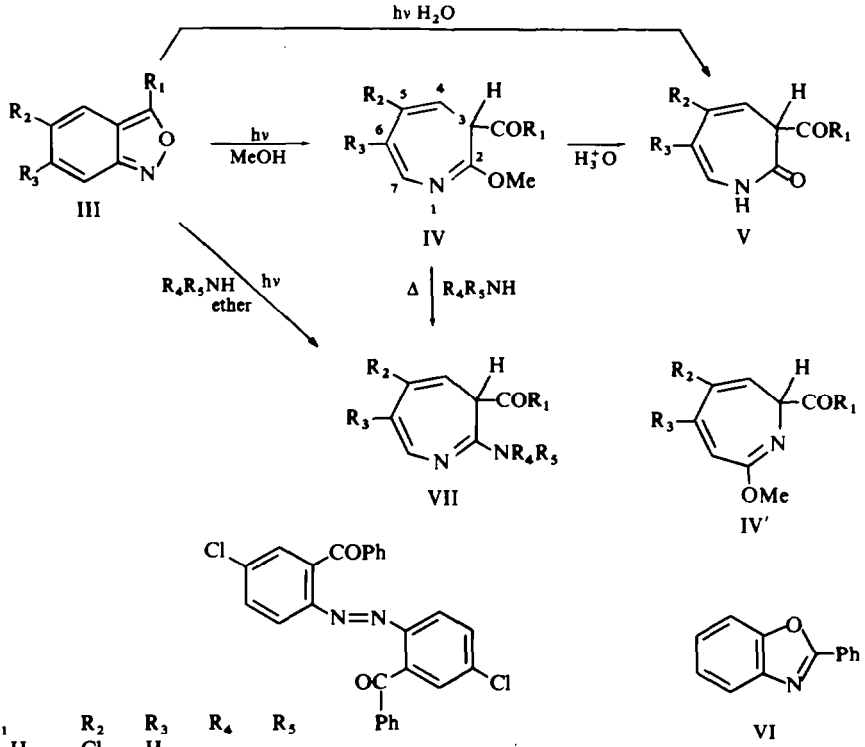
oxide was added, the NH proton signal disappeared and a broad signal at τ 3·57 turned into a simple doublet, which supports only the structure Va and is incompatible with a 7-oxo-2*H*-azepine derivative. Accordingly, the compound from which the lactam was derived must be IVa and IVa'.

Similarly, 3-phenyl,[6] 6-chloro-3-phenyl, 3-methyl,[7] 6-chloro,[8] unsubstituted,[9] 3-(2-furyl) and 3-(2-thienyl)[10] (IIIb–h) anthranils yielded 2-methoxy-3*H*-azepines (IVb–h). The physical data of these compounds are listed in Tables 1, 2 and 3, and are in accord with the assigned structures. The photolysis of IIIb into IVb was accompanied by the I → II type rearrangement which gave 2-phenylbenzoxazole (VI).[11] In aqueous THF or in hydrous ether, photolysis of IIIa, b and d gave 2-oxo-3*H*-azepine derivatives (Va, b and d). Irradiation of III in ether containing primary of secondary amines gave 2-(substituted amino)-3*H*-azepines (VIIi—l), one of which VIIj was also obtained from the corresponding 2-methoxy derivative IVa by treatment with aniline. Photolysis of IIIa in THF gave an orange-red azo compound (VIII; 0·8%) besides the azepine Va (38·6%). Formulation of VIII as 2,2'-dibenzoyl-4,4'-dichloroazobenzene was established by the analytical and spectral data (Experimental).

Photolysis of some 7-substituted 3-phenylanthranils

Substituents on the 7-position of the anthranil ring produced a marked effect on the photolysis. Irradiation of 7-methoxy-3-phenylanthranil (IXa) gave 4-methoxy-9-acridanone (Xa)[12] in 6·3% yield. Similar photolysis with 7-chloro-3-phenylanthranil (IXb) gave 4-chloro-9-acridanone (Xb; 0·2%) and an inseparable mixture of 7-chloro-2-phenylbenzoxazole (XI) and an azepine-like compound (XII). Hydrolysis of the mixture made it possible to separate XI from the other component (XII') derived from XII (probably a lactam analogous to V). The structure XI was confirmed by the catalytic hydrogenation to VI and a comparison of dipole moments* XI and VI (2·65 D and 1·31 D).[13]

* In benzene solution at 25°.



	R_1	R_2	R_3	R_4	R_5
a	C_6H_5	Cl	H		
b	C_6H_5	H	H		
c	C_6H_5	H	Cl		
d	CH_3	H	H		
e	H	H	Cl		
f	H	H	H		
g	2-furyl	H	H		
h	2-thienyl	H	H		
i	C_6H_5	Cl	H	H	n-C_4H_9
j	C_6H_5	Cl	H	H	C_6H_5
k	C_6H_5	Cl	H	C_2H_5	C_2H_5
l	CH_3	H	H	H	C_6H_5

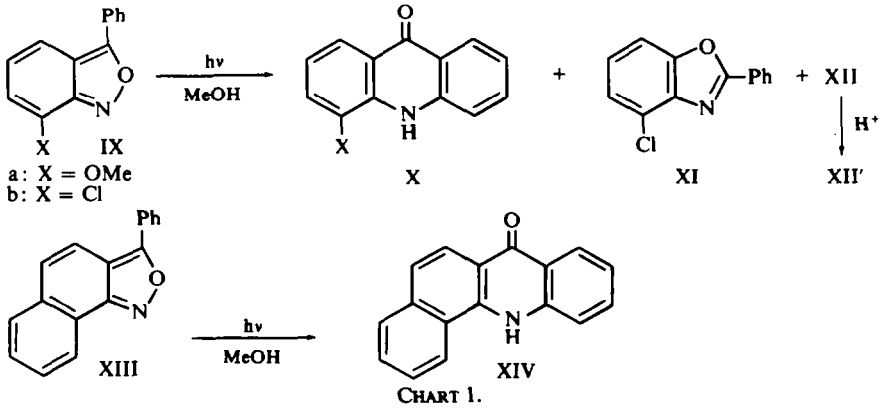


CHART 1.

Irradiation of 3-phenyl-naphth[1,2-*c*]isoxazole (XII) in methanol gave benz[*c*]-acridanone[12] (XIV) in 19·2% yield.

As shown in the above examples, substituents at the 7-position of the anthranil ring strongly inhibit the rearrangement of anthranils into azepine derivatives.

Mechanistic study

The photolysis or pyrolysis of phenyl azide in the presence of primary or secondary amines leads to ring enlargement with formation of 2-(substituted amino)-3*H* azepines.[14] The hypothetical scheme for the thermal rearrangement of phenyl azide (azide → nitrene → azirene → azepine) proposed by Huisgen and Appl[14] provides an important clue to the mechanism of the anthranil rearrangement. Thus the hypothetical scheme for the photolysis of anthranils, as shown in Chart 2, is proposed.

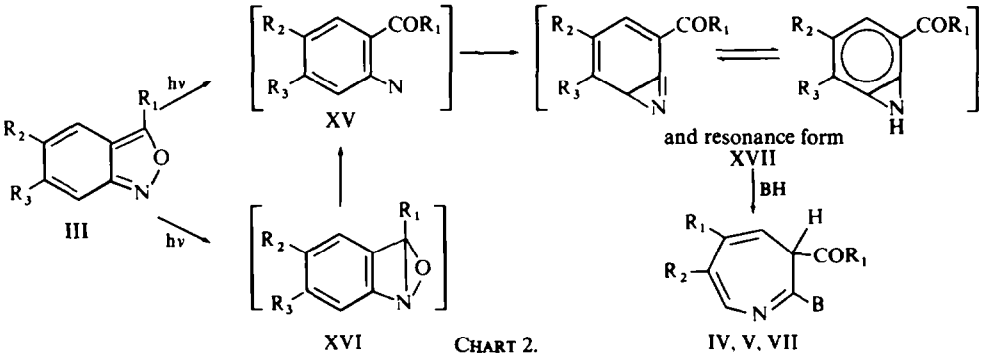


CHART 2.

The photolytic or thermal N—O bond fission of III would produce a nitrene intermediate (XV) which then undergoes ring enlargement to the azepine derivative (IV, V, VII) through an azirene species (XVII) similar to the simple phenyl nitrene rearrangement. The initial step, however, may alternatively involve an oxaziran intermediate (XVI) whose ring cleavage to the nitrene (XV) seems likely.* In the case of 7-substituted 3-phenylanthranils, the nitrene (XV) would undergo intramolecular cyclization to an acridanone derivative such as X and XIV interacting with the α-position of the phenyl group (R_1) (C—H insertion or hydrogen abstraction followed by radical coupling). The formation of the azo compound (VIII) mentioned provides further evidence for the nitrene intermediate.[16]

To gain further support for the hypothetic scheme, IIIb was irradiated (>300 μm) in cyclohexane. The UV absorption curve varied as shown in Fig. 1 (a → b → c) (isobestic point at 262 mμ). The absorption curve-c of the solution changed into the curve-f *via* d and e (isobestic point at 283 mμ) upon addition of ethanol in the dark (Fig. 2). The curve-f was similar to that of IVb obtained by photolysis of IIIb in ethanol. When a 0·2% solution of IIIb in methylene dichloride was irradiated at room temperature, an absorption curve similar to c was obtained. Addition of methanol to the solution in the dark gave IVb in 83·3% yield (46·5% as pure crystals). A irradiated solution of IIIb in methylene dichloride using IR cell (at room temperature) displayed absorption bands at 3423, 1644 and 1606 cm^{-1} (Fig. 3).

* For references see the reports.[15]

From these results, the photoproduct of III in an aprotic solvent seems to be an azirene species (XVII) (corresponding to the absorption curve-c in Fig. 1 and the IR spectrum in Fig. 3), which would readily undergo rearrangement to the final products (IV, V, VII) by addition of protic solvents in the dark.

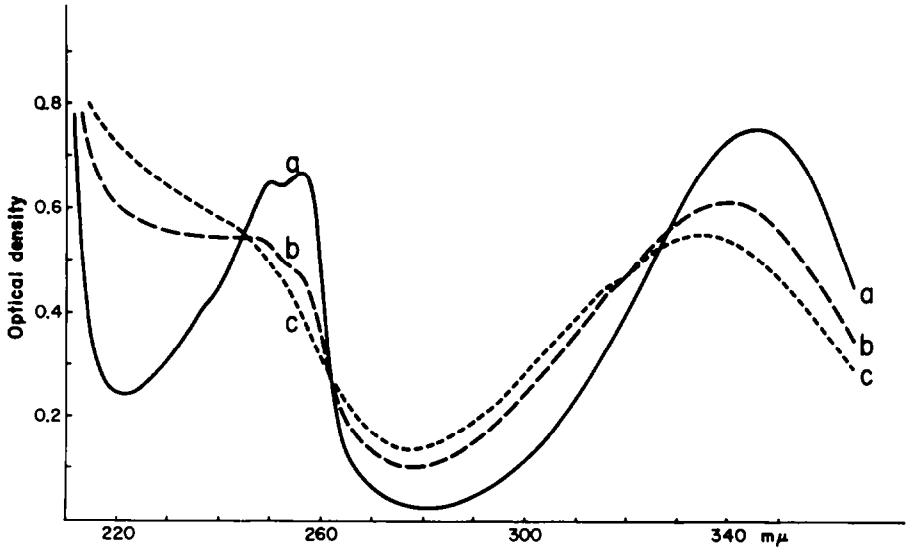


FIG. 1 UV spectral change by irradiation of IIIb (curve-a) in cyclohexane.

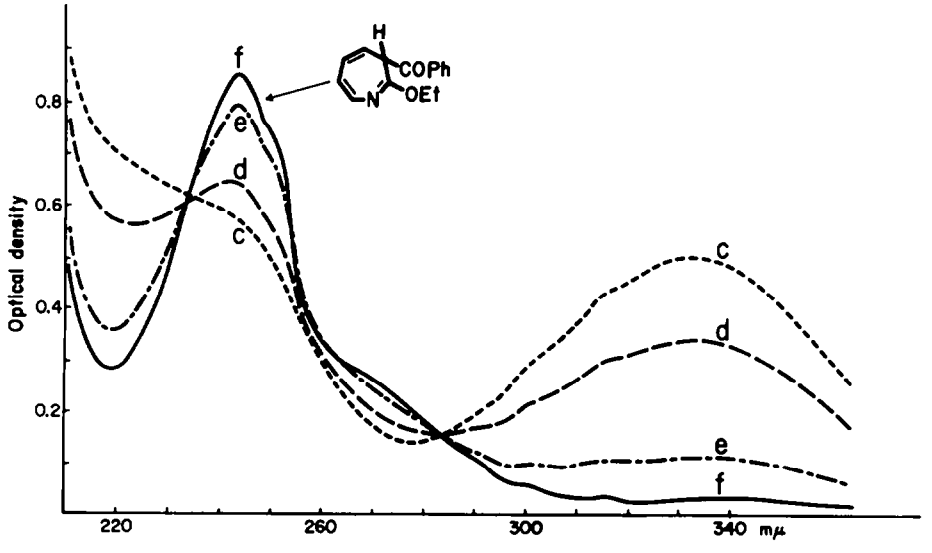


FIG. 2 UV spectral change by the addition of ethanol to curve-c in the dark.

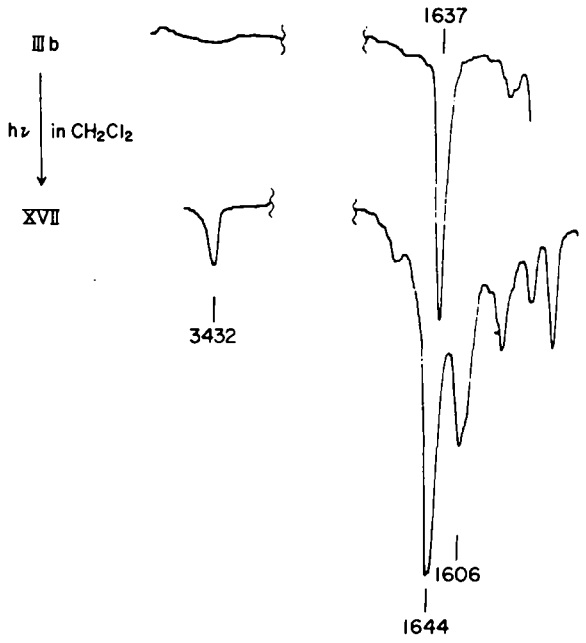


FIG. 3 Infrared spectra of the amino, carbonyl and double bond regions of IIIb before and after irradiation (> 300 mμ) at room temperature (CH_2Cl_2 soln).

EXPERIMENTAL

General procedure of photolysis. The reaction was run with a 450W high pressure Hg arc lamp with a pyrex filter. During irradiation a steady stream of argon was bubbled through the soln. Adequate cooling with water was provided to maintain the soln at room temp. Progress of the reaction was followed by UV spectroscopy and TLC. The crude photomixture was isolated by removal of solvent under vacuum on a water bath followed by chromatography on neutral alumina (activity IV) column.

Formation of IVa–h

Starting materials (g)		Solvent (MeOH) ml	Irradiation time hr	Product
IIIa[5]	(2)	300	4	IVa
IIIb[6]	(1)	100	1	IVb, VI[11]
IIIc	(2)	200	1	IVc
IIId[7]	(3)	300	7	IVd
IIIe[8]	(2)	200	14	IVe
IIIf	(6·1)	400	24	IVf
IIIg	(0·65)	65	1	IVg
IIIh[10]	(1)	100	1	IVh

Formation of Va, b, d *and* VIII

Starting material (g)		Solvent (ml)	Irradiation time hr	Product
IIIa[5]	(2)	THF (400)	3	Va, VIII
IIIb[6]	(2)	THF (400)	2	Vb
IIId[7]	(2)	Et_2O (350)	14	Vd

Formation of VIIi–l

Starting material (g)		Solvent (ml)	Amine (g)	Irradiation time hr	Product
IIIa[5]	(2)	Et_2O (200)	n-$BuNH_2$ (2)	2	VIIi
IIIa[5]	(1)	Et_2O (100)	$PhNH_2$ (1)	1·5	VIIj
IIIa[5]	(5)	Et_2O (380)	Et_2NH (5)	2	VIIk
IIId[7]	(2)	Et_2O (400)	$PhNH_2$ (2)	2	VIIl

Formation of 2-phenylbenzoxazole[11] (VI) *from* IIIb[6]

After irradiation of IIIb[6] in MeOH, crude IVb was obtained as a distillate (b.p. 122°/0·22 mmHg). A soln of 2·0 g of the crude IVb in 30 ml MeOH and 1 ml 6 N HCl was heated under reflux for 5 min. After addition of water, the soln was extracted with excess ether. The residue from the soln was crystallized from benzene to give 315 mg (16·7%) of Vb. This was identified with Vb derived from IIIa[5] (photolysis in THF) by comparison of their IR spectra.

The filtrate was chromatographed on preparative thin-layer plates (alumina, solvent; benzene) to give VI[11] (13 mg, 0·7%). This compound was indentical with an authentic sample[11] by comparison of their IR spectra.

6-*Chloro*-3-*phenylanthranil* (IIIc). IIIc was prepared from *m*-chloronitrobenzene and phenylacetonitrile according to the general method of Davis and Pizzini,[5] m.p. 111–113° (recrystallization from MeOH). (Found: C, 68·10; H, 3·61; N, 5·98. $C_{13}H_8NOCl$ requires: C, 67·97; H, 3·49; N, 6·10%).

3-(2-*Furyl*)*anthranil* (IIIg). 2-Nitrophenyl 2-furylketone was prepared from *o*-nitrobenzoyl chloride furan according to the method of Morton and Bannerman,[17] m.p. 87–89° (recrystallization from benzene-cyclohexane). (Found: C,61·13; H, 3·16; N, 6·15. $C_{11}H_7NO_4$ requires: C, 60·83; H, 3·25; N, 6·45%).

IIIg was prepared from 2-nitrophenyl 2-furylketone according to the method of Morton and Bannerman,[17] m.p. 63° (recrystallization from n-hexane-benzene). (Found: C, 71·23; H, 3·79; N, 7·38. $C_{11}H_7NO_2$ requires: C, 71·35; H, 3·81; N, 7·56%).

*Formation of 3-benzoyl-5-chloro-2-anilino-*3H*-azepine* (VIIj) *from 3-benzoyl-5-chloro-2-methoxy-*3H*-azepine* (IVa)

A mixture of 216 mg of IVa and 102 mg of aniline was heated for 4 hr at 120°. After cooling, the residue was crystallized from MeOH to give 29 mg of VIIj, m.p. 128·5–129·5°. The filtrate was chromatographed on alumina to give VIIj, 115 mg and IVa, 99 mg. Recrystallization of VIIj from n-hexane gave 71 mg, m.p. 129–131°. This was identical with VIIj derived from IIIa[5] (photolysis in ether-aniline) by comparison of their IR spectra.

Formation of 2,2'-dibenzoyl-4,4'-dichloroazobenzene (VIII)

A soln of 2·0 g of IIIa[5] in 400 ml THF was irradiated for 3 hr. The solvent was evaporated and the residue was washed with CH_2Cl_2 to give Va (300 mg). The filtrate was chromatographed on alumina. Elution with benzene gave VIII as orange-red plates [8 mg, 0·8%, m.p. 199–202° (dec) after recrystallization from CH_2Cl_2-MeOH]. (Found: C, 67·75; H, 3·55; N, 5·83. $C_{26}H_{16}N_2O_2Cl_2$ requires: C, 67·99; H, 3·51; N, 6·10%). Mass spectrum of VIII, *m/e* 458 (molecular in M), ratio M:M + 2 = 3:2; strong peaks appeared at *m/e* 423, 425 (3:1) (M − Cl, M + 2 − Cl, m* = 391); 395, 397 (3:1) (423 − N_2, 425 − N_2, m* = 343); 353, 355 (3:2) (M − COPh, M + 2 − COPh, m* = 271); 325, 327 (3:1) (353 − N_2, 355 − N_2); 318, 320 (3:1) (353 − Cl, 355 − Cl, m* = 286); 105 (COPh). Elution with CH_2Cl_2-MeOH (10:1) gave Va (550 mg). Recrystallization of the product from benzene gave 830 mg (38·6%) of colorless prisms [m.p. 174–175° (dec)].

Photolysis of 7-methoxy-3-phenylanthranil (IXa)

A soln of 2·0 g of IXa in 200 ml MeOH was irradiated for 11 hr. The solvent was evaporated and the residue was chromatographed on alumina. Elution with benzene gave IXa (697 mg, 34·9%). Elution with CH_2Cl_2 gave Xa[12] (126 mg, 6·3%, m.p. 287–288° after crystallization from CH_2Cl_2-isopropylether). This material was identical with an authentic sample prepared by the method of Ullmann[12] by comparison of their IR spectra.

Photolysis of 7-chloro-3-phenylanthranil (IXb)

A soln of 9·1 g of IXb in 910 ml MeOH was irradiated for 8 hr. The solvent was evaporated, and the residue was crystallized from MeOH to give 5·8 g (65·7%) of unchanged starting material. The filtrate was chromatographed on alumina and elution with pet. ether gave a mixture (950 mg) of IXb, XI and XII, and unchanged IXb (346 mg, 3·8%). Further elution with pet. ether–ether (1:1)-benzene gave Xb[12] (17 mg, 0·2%, m.p. 300°, recrystallization from CH_2Cl_2-MeOH). This material was identical with an authentic sample prepared by the method of Ullmann[12] by comparison of their IR spectra. A soln of the above mixture (IXb, XI and XII, 950 mg) in 6 N HCl (1 ml) and EtOH (8 ml) was refluxed for 15 min. After addition of water, the product was extracted with CH_2Cl_2. After evaporation of CH_2Cl_2, the residue was chromatographed on silica gel. Elution with benzene–pet. ether (1:1) gave XI (102 mg, 1·1%, colorless needles, m.p. 111° after recrystallization from isopropyl ether). (Found: C, 68·05; H, 3·43; N, 6·01. $C_{13}H_8NOCl$ requires: C, 67·98; H, 3·51; N, 6·10%). Elution with benzene:pet. ether (1:1) gave IXb (116 mg) and further elution with CH_2Cl_2 gave XII' as colorless needles (52 mg, m.p. 155° after recrystallization from cyclohexane). (Found: C, 63·37; H, 4·26; N, 5·72. $C_{13}H_{10}NO_2Cl$ requires: C, 63·04; H, 4·07; N, 5·66%).

Catalytic hydrogenation of 3-phenyl-7-chlorobenzoxazole (XI)

A soln of 20 mg of XI in 10 ml MeOH and 0·2 ml sat. NH_3-MeOH was shaken in H_2 atmosphere over Pd-C until the calculated volume of H_2 had been absorbed. After removal of the catalyst, the filtrate was evaporated and the residue was extracted with ether. Evaporation of ether gave VI[11] (12 mg). This was identical with an authentic sample[11] by comparison of their IR spectra.

Photolysis of 3-phenyl-naphth[1,2-c]*isoxazole* (XIII)

According to the general method of Davis and Pizzini,[5] XIII was obtained from 1-nitronaphthalene and phenylacetonitrile as violet scales, 6·6 g (16·1%), m.p. 129–131°, (Found: C, 83·01; H, 4·45; N, 5·70. $C_{17}H_{11}NO$ requires: C, 83·24; H, 4·52; N, 5·71%). A soln of 200 mg of XIII in 70 ml of MeOH was irradiated for 8 hr through quartz vessel. The solvent was evaporated and the residue was chromatographed on alumina and elution with benzene gave XIII; 57 mg (28·5%). Elution with $CHCl_3$—$CHCl_3$—MeOH (10:1) gave XIV,[12] 38 mg (19·0%, m.p. >250°, after washing with CH_2Cl_2). This was identical with an authentic sample[12] by comparison of their IR spectra.

Photolysis of 3-phenylanthranil[6] (IIIb) *in methylene dichloride*

A soln of 1·0 g of IIIb in 500 ml CH_2Cl_2 was irradiated for 1·5 hr. After irradiation, 50 ml MeOH was added to the soln in the dark. The soln was allowed to stand for overnight at room temp in the dark. The solvent was evaporated and the residue was chromatographed to give 948 mg of pale yellow crystals, IVb, (83·3%). Recrystallization from MeOH gave colorless prisms, m.p. 65–66°, 541 mg (46·5%). This was identical with IVb derived from IIIb[6] (photolysis in MeOH) by comparison of their IR spectra.

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