Tetrahedron. Vol. 25, pp. 1125 to 1136. Pergamon Press 1969. Printed in Great Britain

PHOTOCHEMICAL REACTION OF BENZOPYRIDINES WITH ALKANOIC ACIDS

NOVEL REDUCTIVE ALKYLATION OF ACRIDINE, QUINOLINE AND ISOQUINOLINE UNDER DECARBOXYLATION

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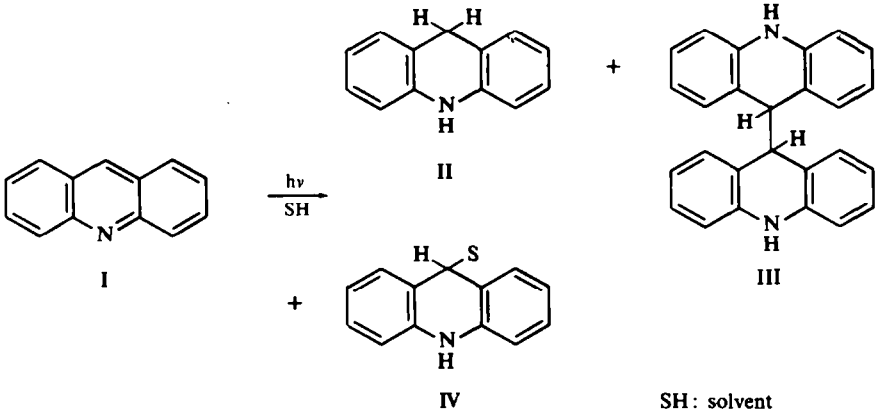
(*Received in Japan* 3 *October* 1968, *Received in the UK for publication* 14 *October* 1968)

Abstract—Photoreaction of acridine with aliphatic carboxylic acids results in decarboxylation and formation of 9-alkylacridans. Irradiation of δ-(9-acridyl)valeric acid or ε-(9-acridyl)caproic acid yields spiro compounds, 9,9-tetramethylene- and 9,9-pentamethyleneacridan, respectively. Extention of the reaction to quinoline as a substrate gives rise to 2- and 4-alkylquinolines and 4-alkyl-1,2,3,4-tetrahydroquinolines. Similar treatment of isoquinoline gives 1-alkylisoquinolines. The mechanistic implication of the photoalkylation is discussed in terms of the acid-base equilibrium between carboxylic acid and the photoexcited nitrogen heterocycle.

PHOTOCHEMICAL behaviour of acridine (I) has recently been investigated in various solvents including alcohols, ethers, aliphatic and aromatic hydrocarbons.[1] The ability of the triplet state(s) to abstract H atoms from the solvents brings about three types of radical reaction yielding acridan (II), 9,9'-diacridan (III) and the coupling products IV. We have examined the photochemical reaction of I in the presence of a variety of alkanecarboxylic acid and found a novel reductive alkylation instead of such a radical process.



Irradiation of an equimolar mixture of acridine (I) and carboxylic acids (0·25M each) in benzene solution caused evolution of carbon dioxide and afforded 9-alkylacridans (V) in yields summarized in Table 1.†

TABLE 1. REDUCTIVE ALKYLATION OF ACRIDINE[a]

Carboxylic acid	Reaction time, hr	Conversion %	Product yield, %[b] V	III
MeCOOH[c]	18	88	tr	22
EtCOOH[d]	20	80	31	17
n-BuCOOH	15	85	55	8
sec-BuCOOH	6	80	67	7
t-BuCOOH	4	80	60	tr
$PhCH_2COOH$	2	79	72	10
Ph_2CHCH_2COOH	4	73	57	10
PhCH(Me)COOH	2	90	68	10

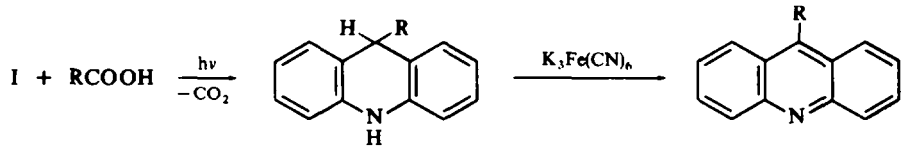
[a] All the photolyses were conducted under the condition A (see Experimental).

[b] Isolation yield calculated on the basis of consumed acridine.

[c] 9-Methylacridine (VIa; 12%) and acridan (II; 5%) were isolated.

[d] 9-Ethylacridine (VIb; 5%) and II (tr) were obtained.

The reductive dimer III was isolated as a byproduct, but usually no appreciable quantity of II was obtained. All the photoproducts were isolated by silica gel chromatography and the structures were determined by spectroscopic data (Table 2) as well as



V

a: R = Me
b: R = Et
c: R = n-Bu
d: R = sec-Bu

VI

e: R = t-Bu
f: R = $PhCH_2$
g: R = Ph_2CHCH_2
h: R = PhCHMe

elemental analyses. Further proof was secured by quantitative conversion into the corresponding alkylacridines (VI) upon treatment with aqueous potassium ferricyanide. As summarized in Table 1, carboxylic acids having larger alkyl groups generally gave favourable results. It was notable that acetic acid gave 9-methylacridine (VIa; 12% yield) and acridan (II; 5%), the expected product Va being obtained only in a trace amount. Propionic acid also gave the acridine derivative VIb in a 5% yield. These alkylation products would probably be ascribed to thermal acid-catalysed disproportionation between unchanged acridine (I) and the primary photoproducts,

† The photoreactions herein recorded occurred in excess carboxylic acid as a solvent as well. The presence of benzene is not prerequisite to the reaction.

TABLE 2. PHYSICAL PROPERTIES OF ALKYLATION PRODUCTS OF ACRIDINES

Compound	M.p., °C (lit.)	UV max, nm[a] (log ε)	NMR, δ in ppm[b]	M.p. of VI, °C (lit.)
Va	123–124 (122–124[c])	—	1·31 (3, d, J = 7 Hz, Me), 3·98 (1, q, J = 7 Hz, C(9)H)	117–118 (117–118[d])
Vb	110–111 (112[e])	279 (4·20)	0·75 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1·3–1·9 (2, m, $C\underline{H}_2Me$), 3·87 (1, t, J = 7 Hz, C(9)H)	110–112 (112–113[f])
Vc	100–101 (101–103[c])	276 (4·27)	0·75 (3, t, J = 6 Hz, Me), 0·9–1·8 (6, m, CH_2), 3·85 (1, t, J = 7 Hz, C(9)H)	42–44 (42–45[c])
Vd	141 (140–141[c])	280 (4·23)	0·65–0·90 (6, t and d, Me), 1·2–1·8 (3, m, $C\underline{H}(Me)C\underline{H}_2Me$), 3·87 (1, d, J = 7 Hz, C(9)H)	oil (oil[c])
Ve	189–192 dec	275 (4·18)	0·83 (9, s, t-Bu), 3·61 (1, s, C(9)H)	138–139
Vf	196–198 (198–200[c])	277 (4·04)	2·82 (2, d, J = 7 Hz, $PhC\underline{H}_2$), 4·15 (1, d, J = 7 Hz, C(9)H)	173 (175[c])
Vg	glassy oil	276 (4·13)	2·28 (2, dd, $C\underline{H}_2CH\langle$), 3·6–4·1 (2, m, benzylic)	155–156
Vh	113–114	278 (4·21)	1·12 (3, d, J = 7 Hz, $\rangle CHC\underline{H}_3$), 2·6–3·3 (1, m, $\rangle C\underline{H}Me$), 4·04 (1, d, J = 6 Hz, C(9)H)	oil
VIIa	125–126 (125–126[g])	280 (4·19)	1·53 (6, s, Me)	— —
VIIb	91–92	278 (4·30)	0·59 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1·61 (3, s, C(9)Me), 1·82 (2, q, J = 7 Hz, $C\underline{H}_2Me$)	—
VIIc	89–90 (90–91[g])	281 (4·28)	0·62 (6, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1·92 (4, q, J = 7 Hz, $C\underline{H}_2Me$)	—

[a] Taken in n-hexane soln.

[b] Measured in 10% $CDCl_3$ soln using TMS as an internal standard. All compounds listed gave a broad singlet due to NH proton around δ 5·90 ppm and an 8-proton multiplet between δ 6·5 and 7·3 ppm. The multiplicity of signals is indicated in abbreviated form: s for singlet, d for doublet, t for triplet, q for quartet, h for heptet, and m for multiplet.

[c] E. Hayashi, S. Ohsumi and T. Maeda, *Yakugaku Zasshi* **78**, 967 (1958).

[d] O. Blum, *Ber. Dtsch. Chem. Ges.* **62**, 881 (1929).

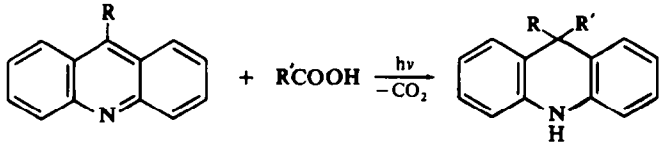
[e] T. D. Perrine, *J. Org. Chem.* **25**, 1516 (1960).

[f] W. Koenigs, *Ber. Dtsch. Chem. Ges.* **32**, 3599 (1899).

[g] W. L. Semon and D. Craig, *J. Am. Chem. Soc.* **58**, 1278 (1936).

9-alkylacridans. This is supported by a control experiment: a solution of I, 9-ethylacridan (Vb) and acetic acid (0·1, 0·1, 0·2M, each) in benzene was allowed to stand overnight at room temperature in the dark to produce a mixture of I, Vb, 9-ethylacridine (VIb) and acridan (II; ca. 5:4:6:5 ratio).

Irradiation of 9-alkylacridines VI in the presence of appropriate carboxylic acids serves as a convenient method for synthesis of 9,9-dialkylated acridans VII. This is exemplified by the reaction of 9-methylacridine (VIa) with acetic acid giving 9,9-dimethylacridan (VIIa) in a 51% yield. Similarly propionic acid with 9-methyl- or 9-ethylacridine (VIa, b) afforded 9-ethyl-9-methyl- and 9,9-diethylacridan (VIIb and VIIc) in 76 and 65% yields, respectively. The structural evidences are given in Table 2.

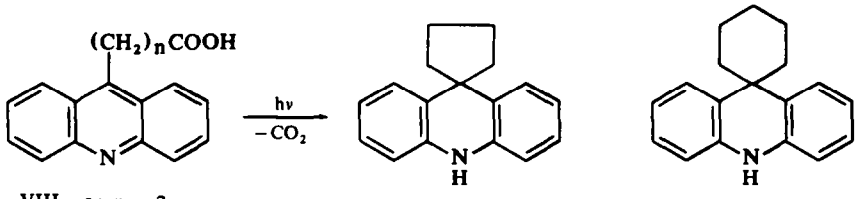


VI

VII

a: R = R' = Me
b: R = Me, R' = Et
c: R = R' = Et

This type of reductive alkylation was successfully applied to an intramolecular reaction to give hitherto unknown spiro compounds. Irradiation of δ-(9-acridyl)-valeric acid (VIIIb) in pyridine solution† followed by chromatographic separation gave 9,9-tetramethyleneacridan (IX), m.p. 102–103°, in a 10% yield, and ε-(9-acridyl)-caproic acid (VIIIc) afforded 9,9-pentamethyleneacridan (X), m.p. 125–127°, in a 7% yield. The spiro structures IX and X were supported by spectral data.‡§ The



VIII a: n = 2
b: n = 4
c: n = 5
d: n = 8

IX

X

† Pyridine is a suitable solvent for the photoreaction of benzene-insoluble carboxylic acids VIIIa–d, as it is not affected under the reaction conditions herein recorded.

‡ Compound IX exhibited IR absorption (Nujol) at 3400 cm^{-1} characteristic of NH bond, and UV maximum (n-hexane) at 280 nm (log ε 4·18), as this was the case with 9,9-dialkylacridan derivatives (Table 2). The NMR spectrum ($CDCl_3$, TMS) showed a broad singlet due to the secondary amine proton at δ 6·00, a symmetrical multiplet at 1·6–2·3 (methylenes), and a multiplet at 6·5–7·4 ppm (aromatics) all in the expected ratio.

§ Compound X showed IR band at 3400 cm^{-1} and UV maximum at 272 nm (log ε 4·13). The NMR signals appeared at δ 2·50 (1, broad s, NH), 1·7–2·3 (10, m, methylenes) and 6·5–7·5 ppm (8, m, aromatics).

mass spectra of IX and X displayed a striking similarity as shown in Figs 1 and 2. Notably the ease of the cyclization depends on the length of the methylene chain of the carboxylic acid, and β-(9-acridyl)propionic acid (VIIIa) or ω-(9-acridyl)pelargonic acid (VIIId) failed to form the corresponding spiro compounds.

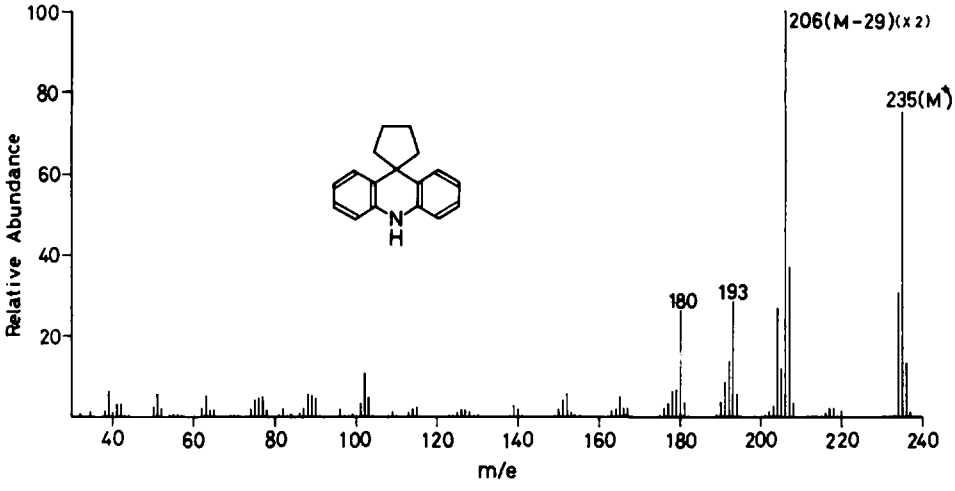


FIG. 1 Mass spectrum of 9,9-tetramethyleneacridan (IX).

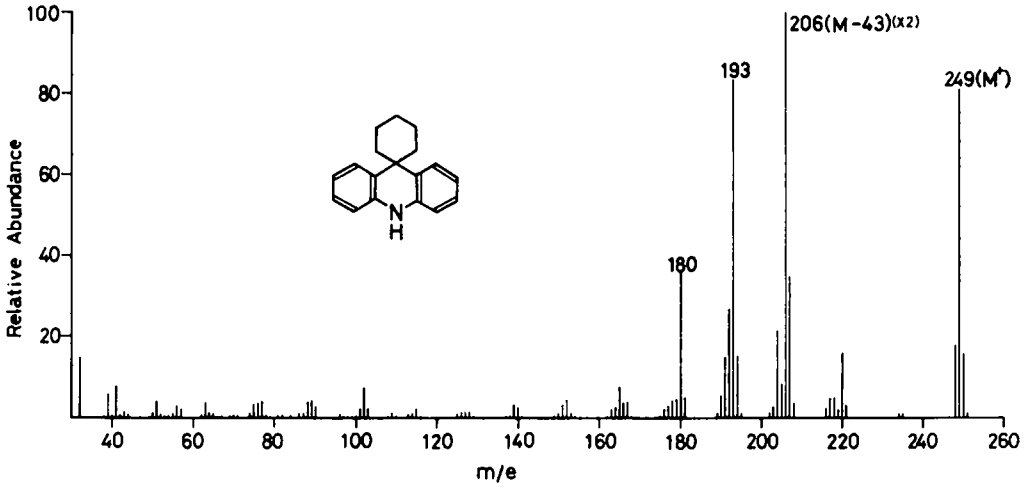


FIG. 2 Mass spectrum of 9,9-pentamethyleneacridan (X).

Photoreactions of quinoline (XI) as a substrate have previously been found to involve either dimerization[2] or coupling reaction with solvents proceeding through radicals.[3] Upon irradiation under the conditions as described above, XI was alkylated at the 2- and 4-positions.[4] In this case, however, marked disproportionation[5] and/or

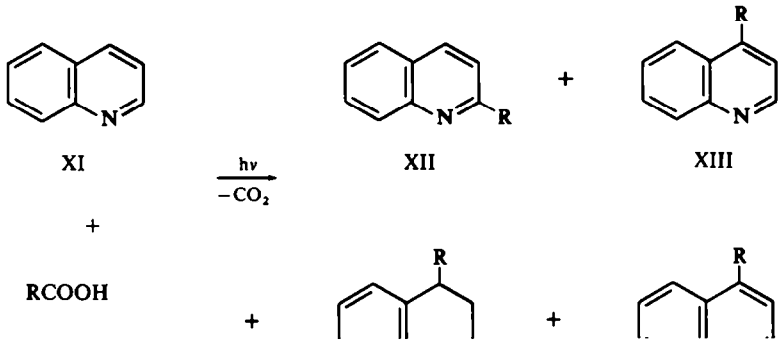


TABLE 5. NMR SPECTRA OF 4-ALKYL-1,2,3,4-TETRAHYDROQUINOLINES[a]

Compound[b]	Chemical shift, δ in ppm
XIVb	0·98 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1·3–2·1 (4, m, $C\underline{H}_2Me$ and $C(3)H_2$), 2·4–2·8 (1, m, C(4)H), 3·27 (2, t, J = 7 Hz, $C(2)H_2$)[c], 3·58 (1, 2, NH), 6·4–7·2 (4, m, aromatic)
XIVc	0·86 and 0·98 (6, two d, J = 7 Hz, Me), 1·6–2·3 (3, m, $C(3)H_2$ and $C\underline{H}Me_2$), 2·3–2·7 (1, m, C(4)H), 3·25 (2, t, J = 7 Hz, $C(2)H_2$), 3·57 (1, s, NH), 6·3–7·2 (4, m, aromatic)
XIVd	0·96 (6, d, J = 6 Hz, Me), 1·4–2·4 (5, m, $C\underline{H}_2C\underline{H}\langle$ and $C(3)H_2$), 2·6–2·9 (1, m, C(4)H), 3·3–3·5 (3, m, NH and $C(2)H_2$), 6·4–7·2 (4, m, aromatic)
XIVe	0·6–1·1 (6, t and d, Me), 1·0–2·1 (5, m, $C(3)H_2$ and $C\underline{H}(Me)C\underline{H}_2Me$), 2·4–2·9 (1, m, C(4)H), 3·23 (2, t, J = 7 Hz, $C(2)H_2$), 3·66 (1, s, NH), 6·3–7·1 (4, m, aromatic)

[a] Taken in 10% $CDCl_3$ soln using TMS as an internal standard. For abbreviation of signal multiplicity see footnote *b* of Table 2.
[b] All compounds were oily.
[c] Singlet on irradiation at the $C(3)H_2$.

TABLE 6. PHOTOCHEMICAL ALKYLATION OF ISOQUINOLINE[a]

Carboxylic acid	Reaction time, hr	Conversion,[b] %	Yield of XVII[b,c] %
MeCOOH	24	50	10
EtCOOH	15	60	20
i-PrCOOH	19	75	20

[a] Irradiations were carried out under the condition B (Experimental).
[b] Determined by GLPC.
[c] Based on consumed isoquinoline.

Benzoic acid, chloroacetic acid, cyanoacetic acid or ethyl acetate as well as sodium acetate were found not to serve as the attacking reagent of the nitrogen heterocycles. Pyridine, benzimidazole, benzthiazole and indole did not undergo such a type of alkylation.

TABLE 4. PROPERTIES OF ALKYLATED QUINOLINES AND ISOQUINOLINES

Compound[a]	NMR, δ in ppm[b]	M.p. of picrate °C (lit.)
XIIa[c]	2·64 (3, s, Me), 7·1–8·3 (6, m, aromatic)	
XIIb	1·37 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2·93 (2, q, J = 7 Hz, $C\underline{H}_2Me$), 7·1–8·1 (6, m, aromatic)	148 (148[d])
XIIc	1·42 (6, d, J = 7 Hz, Me), 2·9–3·5 (1, h, $C\underline{H}Me_2$), 7·1–8·3 (6, m, aromatic)	155–157 (155–157[e])
XIId	0·95 (6, d, J = 6 Hz, Me), 1·9–2·5 (1, m, —CH<), 2·75 (2, d, J = 7 Hz, CH_2), 6·9–8·1 (6, m, aromatic)	162–163 (162[f])
XIIe	0·85 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1·33 (3, d, J = 7 Hz, >$CHC\underline{H}_3$), 1·5–2·1 (2, m, >$CHC\underline{H}_2Me$), 2·6–3·2 (1, m, CH(Me)Et, 7·0–8·1 (6, m, aromatic)	163–164 (163·5–164·5[g])
XIIf	1·45 (9, s, t-Bu), 7·3–8·2 (6, m, aromatic)	171–172·5[h]
XIIIa[c]	2·61 (3, s, Me), 7·0–8·2 (5, m, aromatic), 8·62 (1, d, J = 5 Hz, C(2)H)	—
XVa[i,j]	2·50 and 2·56 (6, two s, Me), 6·90 (1, s, C(3)H), 7·3–8·1 (4, m, aromatic)	—
XVb	1·38 (6, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2·80 and 3·02 (4, two q, J = 7 Hz, $C\underline{H}_2Me$), 7·00 (1, s, C(3)H), 7·3–8·1 (4, m, aromatic)	174–175
XVc	1·47 and 1·49 (12, two d, J = 7 Hz, Me), 2·8–4·0 (2, m, $C\underline{H}Me_2$), 6·74 (1, s, C(3)H), 6·8–8·2 (4, m, aromatic)	156–158
XVIIa[i,k]	2·88 (1, s, Me), 7·2–8·4 (6, m, aromatic)	228–230 dec (230–232[l])
XVIIb	1·42 (3, t, J = 7 Hz, $CH_2C\underline{H}_3$), 3·25 (2, q, J = 7 Hz, $C\underline{H}_2Me$), 7·3–8·5 (6, m, aromatic)	208 dec (208–209 dec[m])
XVIIc	1·43 (6, d, J = 7 Hz, Me), 3·6–4·2 (1, h, $C\underline{H}Me_2$), 7·3–8·5 (6, m, aromatic)	219–220 dec

[a] All compounds listed did not crystallize.

[b] Spectra were taken in 10% CCl_4 soln using TMS as an internal standard. Patterns arising from aromatic protons of XIIa–e are characteristic of 2-alkylquinolines, cf. A. Albert and G. Catterall, *J. Chem. Soc.* (C), 1533 (1967). Abbreviation of signal multiplicity is as shown in footnote *b* of Table 2.

[c] Identified by comparison with the commercial sample.

[d] F. L. Warren, *J. Chem. Soc.* 1366 (1936).

[e] W. Koenigs, *Ber. Dtsch. Chem. Ges.* **32**, 226 (1899).

[f] O. Doebner, *Liebigs Ann.* **242**, 265 (1887).

[g] F. W. Bergstrom, *J. Am. Chem. Soc.* **53**, 4075 (1931).

[h] Elemental analyses indicated that this was not a simple 1 :1 complex.

[i] Compared with the authentic specimen.

[j] W. R. Vaughan, *Org. Syn.* Coll. Vol. III, 329 (1955).

[k] H. Nozaki, Y. Yamamoto and R. Noyori, *Tetrahedron Letters* 1123 (1966).

[l] W. H. Mills and J. L. B. Smith, *J. Chem. Soc.* **121**, 2724 (1922).

[m] E. Späth, E. Berger and W. Kuntara, *Ber. Dtsch. Chem. Ges.* **63**, 134 (1930).

XVI

XVII a: R = Me
b: R = Et
c: R = i-Pr

TABLE 5. NMR SPECTRA OF 4-ALKYL-1,2,3,4-TETRAHYDROQUINOLINES[a]

Compound[b]	Chemical shift, δ in ppm
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XIVc	0·86 and 0·98 (6, two d, J = 7 Hz, Me), 1·6–2·3 (3, m, $C(3)H_2$ and $C\underline{H}Me_2$), 2·3–2·7 (1, m, C(4)H), 3·25 (2, t, J = 7 Hz, $C(2)H_2$), 3·57 (1, s, NH), 6·3–7·2 (4, m, aromatic)
XIVd	0·96 (6, d, J = 6 Hz, Me), 1·4–2·4 (5, m, $C\underline{H}_2C\underline{H}\langle$ and $C(3)H_2$), 2·6–2·9 (1, m, C(4)H), 3·3–3·5 (3, m, NH and $C(2)H_2$), 6·4–7·2 (4, m, aromatic)
XIVe	0·6–1·1 (6, t and d, Me), 1·0–2·1 (5, m, $C(3)H_2$ and $C\underline{H}(Me)C\underline{H}_2Me$), 2·4–2·9 (1, m, C(4)H), 3·23 (2, t, J = 7 Hz, $C(2)H_2$), 3·66 (1, s, NH), 6·3–7·1 (4, m, aromatic)

[a] Taken in 10% $CDCl_3$ soln using TMS as an internal standard. For abbreviation of signal multiplicity see footnote *b* of Table 2.
[b] All compounds were oily.
[c] Singlet on irradiation at the $C(3)H_2$.

TABLE 6. PHOTOCHEMICAL ALKYLATION OF ISOQUINOLINE[a]

Carboxylic acid	Reaction time, hr	Conversion,[b] %	Yield of XVII[b,c] %
MeCOOH	24	50	10
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[a] Irradiations were carried out under the condition B (Experimental).
[b] Determined by GLPC.
[c] Based on consumed isoquinoline.

Benzoic acid, chloroacetic acid, cyanoacetic acid or ethyl acetate as well as sodium acetate were found not to serve as the attacking reagent of the nitrogen heterocycles. Pyridine, benzimidazole, benzthiazole and indole did not undergo such a type of alkylation.

Mechanistic approach

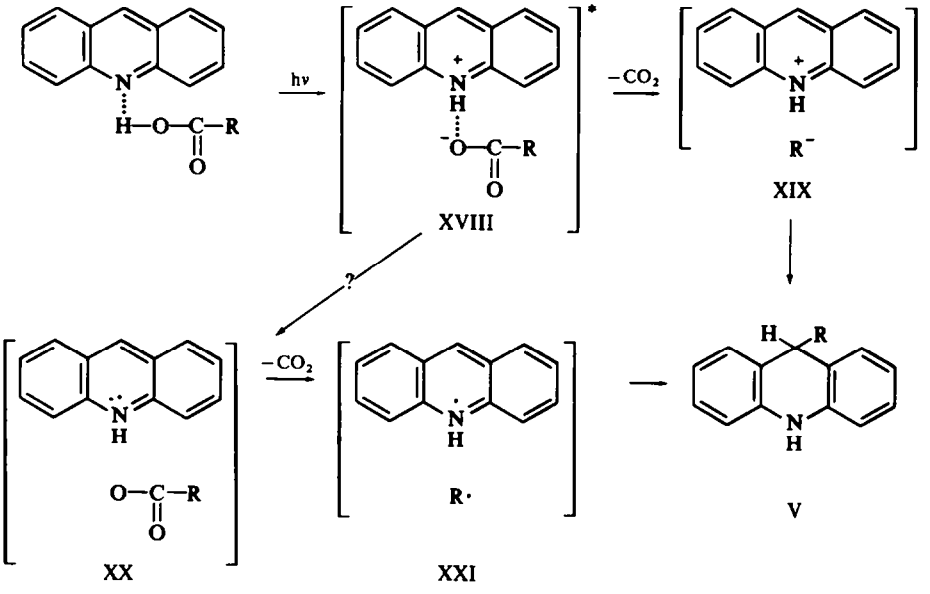
First it should be pointed out that the successful introduction of t-butyl group by means of pivalic acid excludes the possibility of previously proposed radical mechanism[3] which assumes an initial abstraction of α-H atom of carboxylic acids. Although further investigations should be required to elucidate the details of the specific photoalkylation, the foregoing findings would fundamentally be interpreted in terms of the acid-base equilibrium.

Acridine (I) in the ground state is a rather weak base p*Ka* 5·5),[7] and I and a carboxylic acid are held together merely through H-bonding. As previously recognized, however, I shows marked enhancement of the basicity in the first excited singlet state

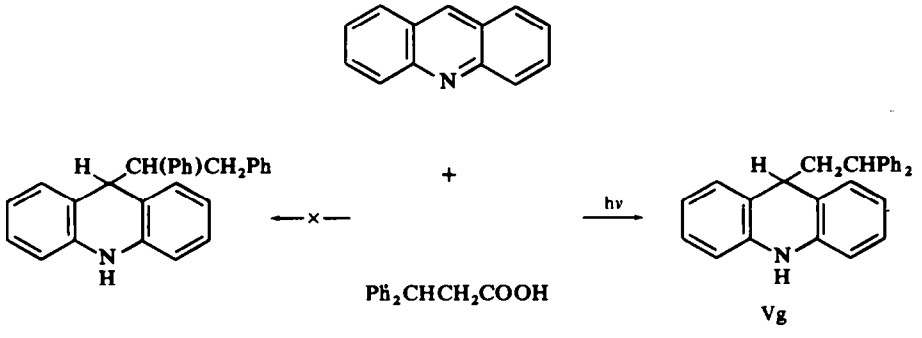
TABLE 7. ELEMENTAL ANALYSES OF NEW COMPOUNDS

Compound	Formula	Required, %			Found, %		
		C	H	N	C	H	N
9-t-*Butylacridan* (Va)	$C_{17}H_{19}N$	86·0	8·1	5·9	85·6	7·9	6·0
9-α-*Phenethylacridan* (Vh)	$C_{21}H_{19}N$	88·4	6·7	4·9	88·2	6·9	4·9
9-(β,β-*Diphenylethyl)acridine* (VIg)	$C_{27}H_{21}N$	90·2	5·9	3·9	89·8	5·8	4·0
9-*Ethyl*-9-*methylacridan* (VIIb)	$C_{16}H_{17}N$	86·1	7·7	6·3	85·9	7·7	6·3
2-t-*Butylquinoline* (XIIf)	$C_{13}H_{15}N$	84·3	8·2	7·6	84·7	8·1	7·3
2,4-*Diethylquinoline* (XVb) *picrate*	$C_{19}H_{18}N_4O_7$	55·1	4·4	13·5	55·2	4·4	13·3
2,4-*Diisopropylquinoline* (XVc) *picrate*	$C_{21}H_{22}N_4O_7$	57·0	5·0	12·7	56·5	5·0	12·0
4-*Ethyl*-1,2,3,4-*tetrahydroquinoline* (XIVb)	$C_{11}H_{15}N$	81·9	9·4	8·7	82·6	9·1	8·8
4-*Isopropyl*-1,2,3,4-*tetrahydroquinoline* (XIVc)	$C_{12}H_{17}N$	82·2	9·8	8·0	82·4	9·7	8·2
4-*Isobutyl*-1,2,3,4-*tetrahydroquinoline* (XIVd)	$C_{13}H_{19}N$	82·5	10·1	7·4	82·0	9·9	6·8
4-sec-*Butyl*-1,2,3,4-*tetrahydroquinoline* (XIVe)	$C_{13}H_{19}N$	82·5	10·1	7·4	82·3	10·0	7·2
1-*Isopropylisoquinoline* (XVIIc) *picrate*	$C_{18}H_{10}N_4O_7$	54·0	4·0	14·0	53·8	4·1	13·7

(p*Ka* 10·6).[7]† Upon irradiation I (probably in the π,π^* singlet state[8]) is capable of capturing OH proton from the carboxylic acid to form an excited complex of acridinium and carboxylate ion (XVIII). Subsequent decarboxylation produces



an ion pair XIX, whose combination yields reductive alkylation product V. An alternative might be a process involving electron transfer at the stage of XVIII to form XX, decarboxylation to yield a radical pair XXI§ and final combination to V. The choice is difficult at present, but we are tempted to prefer the ionic pathway on the basis of following findings. The use of β,β-diphenylpropionic acid as the alkylating agent afforded 9-(β,β-diphenylethyl)acridan (Vg) as the sole alkylation product.



† Acridine in the lowest triplet state has a p*Ka* of 5·6 (cf. Ref. 7).

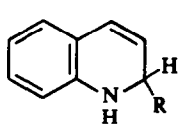
‡ Observation of fluorescence arising from complex XVIII (R = Me) has been recorded. See Ref. 9.

§ Decarboxylation of carboxylate ions *via* electron transfer has been well-documented. See Ref. 10.

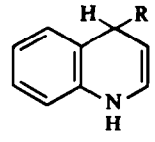
There was no sign of Ph migration in the side chain which would be expected for β,β-diphenylethyl radical.[11] Photoreaction of I with (−)-hydratropic acid ($[\alpha]_D^{20}$ −69·6°, *c* 1·98. $CHCl_3$)[12] followed by careful workup gave 9-α-phenethylacridan (Vh) which was optically active ($[\alpha]_D^{20}$ +1·3°, *c* 3·00, $CHCl_3$). Although the configuration and optical purity of the product are not known yet, the result would indicate that the intermediary ion pair XIX is tightly bound together. However, these results could be interpreted as well by assuming an "intimate" radical pair XXI or fast radical combination.†

Formation of 9,9′-diacridan (III) as the byproduct could be accounted for by assuming previously proposed n,π* triplet acridine as the reactive species.[14] In fact, the photoreaction of I with pivalic acid lacking of labile α-H atom gave the reductive dimer III only in a trace amount.

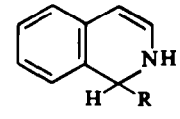
Although the nature of excited states of quinoline (XI) and isoquinoline (XVI) does not seem to have been well-defined,‡ the observed reactivities would be explained in a similar manner. The primary products would very probably be the corresponding alkyldihydrobenzopyridines XXII–XXIV, which have not been isolated possibly due to the lability under the reaction[5] and/or the workup conditions.[6] The question remains to be elucidated why 2-alkylquinolines and 4-alkyl-1,2,3,4-tetrahydroquinolines are formed mainly and the reverse is not the case. The fact that the introduction of t-butyl group to quinoline occurred exclusively at the 2-position might be attributed to the steric interaction with the *peri* hydrogen.



XXII



XXIII



XXIV

EXPERIMENTAL

All m.ps are corrected. NMR spectrum were taken on JEOLCO C-60-H spectrometer. Mass spectra were operated on Hitachi RMU-6 spectrometer at an ionizing voltage of 80 eV and a probe temp of 200°. GLPC analyses and purifications were performed on an Apiezon L (30%) column using He as a carrier gas.

A. *Photochemical reaction of acridine* (I) *with carboxylic acids.* A soln of I (1·79 g, 10 mmoles) and an appropriate alkanoic acid (10 mmoles) in benzene (40 ml) was placed in a Pyrex tube (2·5 × 18 cm), degassed, covered with N_2, and irradiated with a 200W high-press Hg lamp externally from a distance of 3 cm at room temp. After pptd III was removed by filtration, the benzene soln was concentrated *in vacuo* to afford crystalline mass, which consisted mainly of V. Purification by silica gel chromatography (benzene as an eluant) gave the analytical sample, the homogeneity being confirmed on TLC (silica gel, benzene). IR and mass spectra supported the assigned structure. Yields and physical properties are summarized in Tables 1 and 2, respectively. The caution was exercised that the workup of the reaction product using optically active hydratropic acid was effected below 40°.

Oxidation of V to VI was performed according to the method of Hayashi *et al.* (cf. footnote *c* of Table 2).

B. *Photochemical reactions of quinoline* (XI) *and isoquinoline* (XVI) *with carboxylic acids.* A benzene soln (20 ml) of XI or XVI (1·29 g, 10 mmoles) and a carboxylic acid (10 mmoles) was irradiated in a quartz tube (1·5 × 18 cm) under the conditions as described above. The resulting photolysate was treated with

† Retention of configuration of radicals has been recorded in the reaction of hydratropoyl chloride and sodium peroxide (cf. Ref. 13).

‡ Increase of basicity of quinoline in the excited singlet has been recorded. See Ref. 15.

dil $NaHCO_3$ aq, washed, dried (Na_2SO_4) and concentrated to give a brownish oily mixture. After simple distillation, the volatile fraction was subjected to preparative GLPC and/or silica gel chromatography to afford respective alkylated products in a pure state. The results are summarized in Tables 3 and 6. IR and UV as well as mass spectra were consistent with the structure assigned. M.ps of the picrates and NMR data are shown in Tables 4 and 5.

Irradiation in a Pyrex vessel gave practically the same results, though the reaction proceeded rather sluggishly.

C. *Photolysis of* ω-(9-*acridyl*)*carboxylic acids* (VIII). Carboxylic acids VIIIa–d were prepared from diphenylamine and the corresponding dibasic acids according to the published method.[16] A soln of VIII (18 mmoles) in pyridine (500 ml) placed in an immersion-well apparatus fitted with a Pyrex filter was irradiated under N_2 atmosphere by means of a 200W high-press Hg arc at room temp for 2 days. After removal of the solvent pyridine, the reaction mixture was triturated with benzene repeatedly. Combined benzene solns were concentrated *in vacuo*. Silica gel chromatography using benzene as an eluant afforded crystalline spiro compounds IX or X rather in low yields. In these runs, considerable amount of starting materials were recovered unchanged.

Results of elemental analyses for new compounds are comprised in Table 7. Oily 9-(β,β-*diphenylethyl*)-*acridin* (Vg) was analysed after converting to crystalline VIg. 2,4-*Diethylquinoline* (XVb), 2,4-*diisopropyl*-*quinoline* (XVc) and 1-*isopropylisoquinoline* (XVIIc) which turned dark on standing were analysed as the picrates. Elemental compositions of spiro compounds, 9,9-*tetramethyleneacridan* (IX) and 9,9-*pentamethyl*-*eneacridan* (X) were determined on the basis of mass spectroscopy: IX, $(M^+ + 1)/M^+$ 0·19 ($C_{17}H_{17}N$ requires: 0·19) and X, $(M^+ + 1)/M^+$ 0·20 ($C_{18}H_{19}N$ requires: 0·20).

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