Preparation of 2-Oxazolones.—The appropriate benzoin (2.0 g), urethan (3.0 g), and polyphosphoric acid (10 g) were heated with stirring at 160° for 2 hr and then poured into water. The solid was crystallized from a suitable solvent (see Table III).

Acknowledgment.—H. G. thanks the South African Council for Scientific and Industrial Research for a bursary. The authors thank Mr. F. D. Wayne for some of the experimental work.

The Synthesis of the Pyrido[2,1-*a*]isoindole System by an Intramolecular Photochemical Cyclization[1,2]

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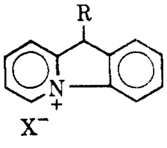
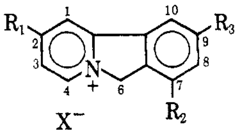
Received March 3, 1967

Aqueous solutions of 2-bromo-N-benzylpyridinium salts (IV), on irradiation with ultraviolet light, cyclize intramolecularly to afford pyrido[2,1-*a*]isoindolium salts (II). The cyclization failed only if a nitro group was present on the benzyl ring of the salt (IV). Pyrido[2,1-*a*]isoindolium bromide may be obtained in lower yield by irradiating N-(2′-bromobenzyl)pyridinium bromide (V). Treatment of pyrido[2,1-*a*]isoindolium salts (II) with carbonate ion led to the unstable and light-sensitive pyrido[2,1-*a*]isoindoles (III) of interest as examples of a pseudo-aromatic system.

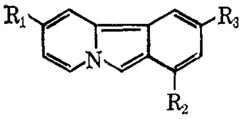
Although at the time this work was undertaken several samples of the related pyrido[1,2-*a*]indolium salts (I) were known,[3] the literature afforded no examples of pyrido[2,1-*a*]isoindolium salts (II).[4] This system (II) was of interest since it was expected to behave as a "super fluorene," the methylene protons being more acidic (owing to the adjacent, positively charged nitrogen atom) than those of fluorene. On basification of the salt, it would be expected that the corresponding pyrido[2,1-*a*]insoindole (III) would be obtained. Irradiation of certain halogenated aromatic molecules with ultraviolet light brings about homolytic cleavage of the carbon–halogen bond and cyclization. An example is the formation of phenanthrene derivatives from iodostilbenes.[5] A similar cyclization, though not photochemical, is the synthesis of dibenzothiophene from the reaction of phenyl *o*-bromophenyl sulfide, methyl magnesium iodide, and colbaltous chloride.[6]



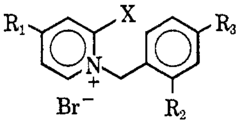
I



II



III



IV

It was decided to attempt the synthesis of pyrido[2,1-*a*]isoindolium salts by irradiation of appropriate N-benzyl-2-bromopyridinium salts (IV, X = Br). When an aqueous solution of N-benzyl-2-bromopyridinium bromide (IV, $R_1 = R_2 = R_3 = H$; X = Br)[7] was irradiated with an ultraviolet source, a change in the ultraviolet spectrum of the salt (IV, $R_1 = R_2 = R_3 = H$; X = Br) occurred and a spectrum of the type expected[8] for an azoniafluorene derivative was observed. After irradiation had continued for 5 hr, the reaction mixture afforded a salt (50% yield) which had all the characteristics of the expected pyrido[2,1-*a*]isoindolium bromide (II, $R_1 = R_2 = R_3 = H$; X = Br). The structure was confirmed by elemental analysis and nmr spectrum. The ease with which the cyclization occurred was surprising in view of the participation of the nonbonding electrons of the bromine atom in the conjugated system of the pyridinium ring.[9] No evidence was found to suggest that any dimerization had occurred as did in the case of N-substituted pyridones[10] and aminopyridines.[11]

When the pyridoisoindolium salt (II, $R_1 = R_2 = R_3 = H$) was treated with aqueous sodium carbonate, a vivid yellow-green solid precipitated. The structure of this product, which was obtained in quantitative yield, was proven to be pyrido[2,1-*a*]isoindole (III, $R_1 = R_2 = R_3 = H$) by elemental analysis and by its nmr spectrum which shows the presence of aromatic protons only, in the range σ (ppm) 8.97–7.27. This molecule (III, $R_1 = R_2 = R_3 = H$) is interesting in that it has a peripheral conjugated ring system. Further, if the cross-links are regarded as producing relatively small perturbations so that the Hückel $4n + 2$ π electron rule[12] may be applied,[13] the molecule (III, $R_1 = R_2 = R_3 = H$) has 14 π electrons (including the pair from the nitrogen) and should have some aromatic character. It can thus be considered somewhat analogous to 14-annulene. The nmr spectrum of the molecule (III, $R_1 = R_2 = R_3 = H$) does, in fact, by the

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(1) This work was described in a preliminary communication: A. Fozard and C. K. Bradsher, *Tetrahedron Letters*, 3341 (1966).

(2) This research was supported by a grant (CA-05509) from the National Cancer Institute of the National Institutes of Health.

(3) R. Robinson and J. E. Saxton, *J. Chem. Soc.*, 976 (1952).

(4) Subsequent to completion of this work, but prior to its publication, the synthesis of 7,9-dinitropyrido[2,1-*a*]isoindole and some derivatives was described by W. Augstein, Doctoral Dissertation, Giessen, 1966, p 28.

(5) S. M. Kupchan and H. C. Wormer, *J. Org. Chem.*, **30**, 3792 (1965).

(6) M. Tecco, *Chem. Commun.*, 555 (1965).

(7) B. R. Baker and F. J. McEvoy, *J. Org. Chem.*, **20**, 118 (1955).

(8) The new spectrum showed a marked similarity to that of fluorene. See R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, No. 311.

(9) A long wavelength band of the ultraviolet spectrum of the quaternary salt (IV, $R_1 = R_2 = R_3 = H$; X = Br) is shifted 20 mμ to longer wavelengths compared with that of N-benzylpyridinium bromide. This would suggest some participation of nonbonding electrons from the bromine atom in resonance of the pyridinium system with consequent strengthening of the C–Br bond.

(10) L. A. Paquette and E. Stomp, *J. Am. Chem. Soc.*, **85**, 765 (1963).

(11) E. C. Taylor and R. O. Kan, *ibid.*, **85**, 776 (1963).

(12) E. Hückel, *Z. Physik.*, **70**, 204 (1931); **76**, 628 (1932).

(13) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 288.

TABLE I

ELECTRONIC SPECTRA OF PYRIDO[2,1-*a*]ISOINDOLIUM BROMIDES (II) AND OF PYRIDO[2,1-*a*]ISOINDOLES (III)

				Absorption maxima,[a] mμ (log ε)	
Compd	R_1	R_2	R_3	Bromide salts (II)[b]	Indolizine bases (III)[c]
a				256 (4.14), 313 (4.02)	255 (4.61), 308 (3.65), 321 sh (3.62), 334 (3.76), 395 (3.85)
b		Br		258 (4.07), 312 (4.10)	248 (4.43), 270 sh (3.93), 288 sh (3.56), 354 (3.84), 370 (3.90), 396 (3.10), 425 (3.04), 450 (2.74)
c		CH_3		257 (4.10), 313 (4.06)	250,[d] 326, 346 sh, 366, 420 sh
d			Br	255 (4.24), 312 (4.01)	240 (4.31), 268 sh (4.11), 284 sh (3.97), 405 sh (3.83), 423 (3.97)
e			$(CH_3)_2CH$	257 (4.19), 316 (4.01)	250 (4.39), 330 sh (3.52), 350 sh (3.51), 364 (3.54), 405 sh (3.47), 424 (3.57)
f	CH_3			250 (4.10), 256 (4.13), 308 (4.09)	250 (4.25), 356 sh (3.39), 368 (3.43), 408 sh (3.46), 423 (3.60)

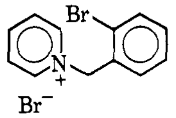
[a] Absorptions below 220 mμ have not been recorded. [b] In water. [c] Freshly prepared solutions in 95% ethanol. The bases decompose in solution. [d] This base was too unstable to permit measurement of the log extinction coefficient. The base was not obtained in a state of analytical purity.

position and narrow range of the proton spectrum, suggest the presence of an aromatic ring current.

Pyrido[2,1-*a*]isoindole (III, $R_1 = R_2 = R_3 = H$) was relatively stable when kept under nitrogen and away from light. Prolonged exposure to sunlight or artificial light caused decomposition. Heating in solvents also had the same effect. The compound (III, $R_1 = R_2 = R_3 = H$) could, however, be crystallized from ethanol with difficulty. On addition of hydrobromic acid to the pyridoisoindole protonation occurred on position 6 to give again pyrido[2,1-*a*]isoindolium bromide (II, $R_1 = R_2 = R_3 = H$; X = Br). The ultraviolet and visible spectral data for the new pyridoisoindolium salts and the corresponding pyridoisoindoles are recorded in Table I.

Most of the irradiation experiments were carried out in water and were continued until the relative intensities of the ultraviolet absorption maxima indicated that reaction was virtually complete. The dark solution which resulted from the irradiation of aqueous N-benzyl-2-bromopyridinium bromide for 5 hr afforded only a 50% yield of pyridoisoindolium salt (II, $R_1 = R_2 = R_3 = H$). By carrying out the irradiation in 10% hydrobromic acid, the darkening was avoided and a higher yield (75%) of the salt (II, $R_1 = R_2 = R_3 = H$; X = Br) was obtained, even though the reaction time was slightly longer (8 hr). It is likely that the darkening of the aqueous reaction was due to some formation of the pyridoisoindole (III, $R_1 = R_2 = R_3 = H$), which then decomposed on further irradiation. When an attempt was made to carry out the irradiation procedure in ethanol, the ultraviolet spectrum of the solution indicated that cyclization had occurred, but decomposition was so extensive that no pure material could be isolated.

Irradiation of the salt obtained by reaction of 2-chloropyridine with benzyl bromide likewise gave pyrido[2,1-*a*]isindolium bromide in about the same yield. Unfortunately the intermediate salt was not pure N-benzyl-2-chloropyridinium bromide (IV, $R_1 = R_2 = R_3 = H$; X = Cl) but appeared to be a mixture, probably due to exchange of the chlorine at the 2 position of the salt with the bromide anion.[14] When the 2-fluoropyridinium compound (IV, $R_1 = R_2 = R_3 = H$; X = F) was irradiated in water, a white solid was precipitated. This was found to be the dimer of N-benzyl-2-pyridone by its unambiguous synthesis from N-benzyl-2-pyridone using the method described by Paquette.[10] It seems likely that the fluoropyridinium salt (IV, $R_1 = R_2 = R_3 = H$; X = F) first undergoes nucleophilic substitution by the solvent to afford the pyridone which subsequently dimerizes. An attempt to cyclize N-(2′-bromobenzyl)pyridinium bromide (V)[15] was successful, but the rate of cyclization was considerably slower than that of the 2-bromopyridinium salt (IV, $R_1 = R_2 = R_3 = H$; X = Br), 24-hr irradiation giving only a 38% yield of the indolizine (III, $R_1 = R_2 = R_3 = H$). The unsubstituted salt[16] (IV, $R_1 = R_2 = R_3 = H$; X = H) failed to undergo cyclization even after prolonged irradiation.



V

Several derivatives of the pyrido[2,1-*a*]isoindolium system (III, $R_1 = R_2 = R_3 = H$) have been prepared (Table II) by irradiation of suitable 2-bromopyridinium salts (IV, X = Br) (Table III). One of the more interesting cyclizations is that of the dibromo compound (IV, $R_1 = R_3 = H$; R_2 = X = Br) in which cyclization could theoretically, occur in either of two directions. However, on irradiation, exclusive photolysis of the bromine on the pyridinium ring occurred, affording 7-bromopyrido[2,1-*a*]isoindolium bromide (II, $R_1 = R_3 = H$; R_2 = Br). The structure of this compound was confirmed by the characteristic doublet of the α-pyridinium proton (C_4) at δ 9.31 in the nmr spectrum and by the ultraviolet spectrum. The pyridoisoindoles (Table IV) were all prepared by the addition of aqueous sodium carbonate solution to the corresponding pyridoisoindolium salts (II). The stability of the bases varied, the unsubstituted compound (III, $R_1 = R_2 = R_3 = H$) and the bromopyridoisoindole (III, $R_1 = R_2 = R_3 = H$; R_3 = Br) were reasonably stable, but the others were less stable and could not be purified. The least stable, the 7-methyl compound (III, $R_1 = R_3 = H$; $R_2 = CH_3$), decomposed at temperatures above 40° and turned black in a few hours on exposure to light.

Notable exceptions to the general nature of cyclization were 2-bromopyridinium salts containing a nitro

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[14] *Cf.* B. R. Baker and F. J. McEvoy, *J. Org. Chem.*, **20**, 118 (1955).

[15] F. Kröhnke and I. Vogt, *Chem. Ber.*, **85**, 368 (1952).

[16] J. Willems and J. Nys, *Bull. Soc. Chim. Belges*, **66**, 502 (1957).

TABLE II

PYRIDO[2,1-*a*]ISOINDOLIUM BROMIDES (II, X = Br)

Compd	R_1	R_2	R_3	Irradiation, hr	Yield,[a] %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IIa	H	H	H	5	50[b]	207.5–209.5	$C_{12}H_{10}BrN \cdot 0.5H_2O$	56.06	4.32	5.44	56.53	4.38	5.44
IIb	H	Br	H	3	66	275 dec[c]	$C_{12}H_9Br_2N$	44.07	2.78	4.28	44.29	2.80	4.25
IIc	H	CH_3	H	7	44	202–204[d]	$C_{13}H_{12}BrN \cdot 0.5H_2O$	57.55	4.83	5.16	57.15	4.84	5.18
IId	H	H	Br	3.5	67	265–266 dec[e]	$C_{12}H_9Br_2N$	44.07	2.78	4.28	44.31	2.79	4.74
IIe	H	H	$CH(CH_3)_2$	4	35	138–140[c]	$C_{15}H_{16}BrN \cdot 0.5H_2O$	60.22	5.72	4.68	60.38	5.69	4.52
IIf	CH_3	H	H	10	60	255[d]	$C_{13}H_{12}BrN \cdot 0.75H_2O$	56.64	4.94	5.08	56.46	4.96	4.99

[a] The reaction was carried out in water. [b] The yield was 75% when irradiation was carried out in 10% hydrobromic acid. [c] Purplish needles from ethanol. [d] Tan microcrystalline solid from ethanol–ethyl acetate. [e] Small, tan needles from ethanol.

TABLE III

N-BENZYLPYRIDINIUM BROMIDES

Compd	R	R_2	R_3	X	Quaternization time, days	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IVa	H	H	H	F	5.5	14	161–162[a]	$C_{12}H_{11}BrFN$	53.75	4.14	5.19	54.00	4.53	5.23
IVb	H	Br	H	Br	3	20	150–151[b]	$C_{12}H_{10}Br_3N$	35.33	2.47	3.43	35.40	2.47	3.40
IVc	H	CH_3	H	Br	4	86	147–148[c]	$C_{13}H_{13}Br_2N$	45.41	3.82	4.08	45.47	3.76	4.13
IVd	H	H	Br	Br	1.5	78	169.5–171[b]	$C_{12}H_{10}Br_3N$	35.33	2.47	3.43	35.11	2.43	3.50
IVe	H	H	$CH(CH_3)_2$	Br	3	53	172[a]	$C_{15}H_{17}Br_2N$	48.58	4.62	3.78	48.72	4.59	3.70
IVf	CH_3	H	H	Br	6	60	153[c]	$C_{13}H_{13}Br_2N \cdot 0.5H_2O$	44.35	4.01	3.98	44.20	3.97	4.01
IVg	H	H	NO_2	Br	1.5	75	171[a]	$C_{12}H_{10}Br_2N_2O_2$	38.53	2.70	7.48	38.92	2.84	7.44
IVh	H	Cl	NO_2	Br	2	10	145–146[c]	$C_{12}H_9Br_2ClN_2O_2$	35.28	2.23	6.86	35.40	2.22	6.91

[a] Colorless needles from ethanol–ethyl acetate. [b] Colorless microcrystalline solid from ethanol. [c] Colorless microcrystalline solid from ethanol–ethyl acetate.

TABLE IV

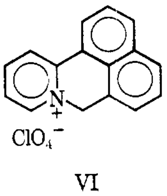
PYRIDO[2,1-*a*]ISOINDOLES

Compd	R_1	R_2	R_3	Dec pt, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IIIa	H	H	H	225[a,b]	$C_{12}H_9N$	86.12	5.45	8.37	85.94	5.17	8.24
IIIb	H	Br	H	90[c,d]	$C_{12}H_8BrN$	58.55	3.28	5.69	57.86	3.24	5.61
IIIc	H	H	Br	157[e]	$C_{12}H_8BrN$	58.55	3.28	5.69	58.08	3.27	5.51
IIId	H	H	$CH(CH_3)_2$	. . .[c,d]	$C_{15}H_{15}N \cdot 0.5H_2O$	82.51	7.37	6.41	82.50	6.71	6.51
IIIe	CH_3	H	H	100[c–e]	$C_{13}H_{11}N \cdot {}^1/_3H_2O$	83.39	6.29	7.50	82.82	5.89	7.82

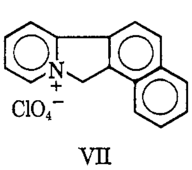
[a] Starts to decompose over 200°. [b] Yellow-green needles from ethanol. [c] Yellow solid. [d] Analysis was done on unpurified material dried overnight at 0.1 mm and room temperature. [e] Yellow plates from ether.

group (IV, $R_1 = R_2 = H$; $R_3 = NO_2$; X = Br; and $R_1 = H$; $R_2 = Cl$; $R_3 = NO_2$; X = Br) in the phenyl ring. No indication of cyclization was observed when these salts were irradiated for 24 hr, and the starting material was recovered unchanged at the end of this period.[17] Although the cyclization reaction is probably a free-radical reaction, the results suggest that the cyclization may not be so simple as previously described examples of cyclization by photochemical dehydrohalogenation.

2-Bromo-N-(1′-naphthylmethyl)pyridinium bromide, irradiated, showed a change in its ultraviolet spectrum, a long wavelength absorption maximum appearing at 375 mμ. A yellow crystalline perchlorate was obtained from the reaction mixture. In this case, two positions are available for cyclization so that the product could have structure VI or VII. Elemental analysis of the product confirmed that cyclization had occurred, but the actual structure could not be assigned from nmr, ultraviolet, or infrared spectra.



VI



VII

Experimental Section

Analyses were carried out by Janssen Pharmaceutica, Beerse, Belgium. Melting points are taken on a Hoover melting point apparatus and are uncorrected. Ultraviolet spectra (Table I) were determined on a Beckman DB spectrophotometer and nmr spectra were determined on a Varian A-60 instrument using tetramethylsilane as a external standard.

Preparation of Quaternary Salts (IV and V). *E.g.*, **N-Benzyl-2-bromopyridinium Bromide (IV, $R_1 = R_2 = R_3 = H$; X = Br).**—2-Bromopyridine (7.9 g, 0.05 mole) and α-bromotoluene (8.3 g, 0.05 mole) in sulfolane (10 ml) were kept at 45° for 4 days. A white solid which precipitated during this period was suspended in ether and collected. It was recrystallized from ethanol–ethyl acetate to afford 12.4 g of colorless needles, mp 158–160° (lit.[7] mp 156–157°).

Irradiation of Quaternary Salts. *E.g.*, **N-Benzyl-2-bromopyridinium Bromide (IV, $R_1 = R_2 = R_3 = H$; X = Br).**—The quaternary salt (2.0 g) in water (430 ml) was irradiated with a water-cooled 450-w Hanovia ultraviolet source equipped with a Pyrex filter. The ultraviolet spectrum of samples taken during the irradiation showed a shift from the 278-mμ absorption maximum of the starting material to two absorption maxima at 256 and 313 mμ. The change was complete at the end of 5 hr. The dark green solution was then evaporated to small volume and treated with decolorizing charcoal (0.5 g). After filtering, the solution was evaporated to dryness, and the residue was dissolved in the minimum quantity of ethanol and precipitated by careful

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[17] A restudy of the effect of irradiation on 2-bromo-N-methylpyridinium bromide revealed that the salt does indeed undergo photolysis (*cf.* ref 1), although the products were not identified.

addition of ethyl acetate to afford 0.8 g (50%) of benz[*a*]indolizinium bromide (II, $R_1 = R_2 = R_3 = H$; X = Br) as the hemihydrate. The product had mp 207.5–209.5° after one recrystallization from absolute ethanol: nmr (CF_3COOH), δ 6.06 (s, 2, CH_2) and >7.5 (m, 8, aromatic).

When 10% hydrobromic acid was used as the solvent in the irradiation, the use of decolorizing charcoal was unnecessary and 1.18 g (75%) of the indolizinium salt (II, $R_1 = R_2 = R_3 = H$; X = Br) was isolated after an irradiation period of 8 hr.

Preparation of Bases. *E.g.*, **Pyrido[2,1-*a*]isoindole (III, $R_1 = R_2 = R_3 = H$).**—Pyrido[2,1-*a*]isoindolium bromide (1.0 g) dissolved in water (5 ml) was treated with saturated aqueous sodium carbonate solution until no further precipitation occurred. The precipitate was collected and dried under vacuum at room temperature to afford 0.73 g (100%) of a yellow solid. This could be recrystallized, with difficulty, from ethanol as yellow-green needles, mp 225° (charring above 205°). The product could also be purified by sublimation at 110° under reduced pressure.

The base (III, $R_1 = R_2 = R_3 = H$) dissolved when treated with 10% hydrobromic acid to give a solution which had the same ultraviolet spectrum as pyrido[2,1-*a*]isoindolium bromide (II, $R_1 = R_2 = R_3 = H$; X = Br). This solution was evaporated to dryness, the residue was dissolved in a minimum quantity of ethanol, and ethyl acetate was added to precipitate the salt (II, $R_1 = R_2 = R_3 = H$; X = Br).

Irradiation of N-benzyl-2-fluoropyridinium Bromide (IV, $R_1 = R_2 = R_3 = H$; X = F).—The quaternary salt (1.5 g) in water (430 ml) was irradiated, as previously described, for 6 hr. During this period, the dimer of N-benzyl-2-pyridone was precipitated. The precipitate was collected (0.3 g, 20%) and recrystallized from dimethyl formamide–ethanol to afford colorless plates, mp 215–216°, ν_{max}^{Nujol} 1670 cm^{-1} (amide C=O).

Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 76.80; H, 5.99; N, 7.56. Found: C, 77.16; H, 6.05; N, 7.68.

Dimerization of N-Benzyl-2-pyridone.[10]—N-Benzyl-2-pyridone (2.0 g, obtained by addition of saturated aqueous sodium carbonate solution to an aqueous solution of N-benzyl-2-bromopyridinium bromide) in 95% ethanol (430 ml) was irradiated for 2 days. The dimer which precipitated (0.6 g, 30%) was collected and recrystallized from dimethylformamide–ethanol to yield colorless plates, mp 215–218°. This product had identical physical and spectral characteristics with those of the product from irradiation of the 2-fluoropyridinium salt (IV, $R_1 = R_2 = R_3 = H$; X = F). The nmr spectrum of the dimer in trifluoroacetic acid showed four olefinic protons as two sets of multiplets centered at 403 and 376 cps. These had exactly the same splitting pattern as those of the dimer of N-methyl-2-pyridone.[10]

2-Bromo-N-(1′-naphthylmethyl)pyridinium Bromide.—2-Bromopyridine (7.9 g) and 1-bromomethylnaphthalene (11.1 g) in sulfolane (15 ml) were heated at 45° for 18 hr. The precipitated solid was suspended in ether, collected, and then recrystallized from ethanol–ethyl acetate to afford 12.1 g (65%) of colorless plates, mp 158.5°, $\lambda_{max}^{95\%\ EtOH}$ 278 mμ (log ϵ 4.11).

Anal. Calcd for $C_{16}H_{13}Br_2N$: C, 50.68; H, 3.46; N, 3.69. Found: C, 50.87; H, 3.46; N, 3.78.

Irradiation of 2-Bromo-N-(1′-naphthylmethyl)pyridinium Bromide.—The quaternary salt (2.0 g) in water (430 ml) was irradiated for 7 hr, during which the solution's ultraviolet spectrum showed a shift from a single maximum at 278 mμ to maxima at 272 and 375 mμ. Aqueous perchloric acid (25%) was then added to precipitate a crude perchlorate (1.05 g). After two recrystallizations from acetonitrile–ethanol, a product (VI or VII) was obtained (0.4 g, 18%), as yellow-green rhombs, mp 178–180.5°, $\lambda_{max}^{95\%\ EtOH}$ 272 and 375 mμ (log ϵ 3.92 and 3.92).

Anal. Calcd for $C_{16}H_{12}ClNO_4 \cdot 0.5H_2O$: C, 53.15; H, 3.60; N, 3.34. Found: C, 52.95; H, 3.71; N, 3.22.

The nmr spectrum of this compound in trifluoroacetic acid, showed a collection of protons between δ 8.77 and 7.45, weight of 10 (aromatic protons), and a singlet at 6.06, weight of 2 (methylene protons).

Registry No.—IIa, 13160-91-3; IIb, 13160-95-7; IIc, 13584-39-9; IId, 13584-40-2; IIe, 13584-41-3; IIf, 13584-42-4; IIIa, 245-30-7; IIIb, 13584-44-6; IIIc, 13584-45-7; IIId, 13584-46-8; IIIe, 13584-47-9; IVa, 13612-72-1; IVb, 13160-94-6; IVc, 13612-74-3; IVd, 13612-75-4; IVe, 13639-79-7; IVf, 13639-80-0; IVg, 13612-76-5; IVh, 13639-81-1; VI, 13612-77-6; VII, 13584-48-0; 2-bromo-N-(1′-naphthylmethyl)pyridinium bromide, 13584-49-1; dimer of N-benzyl-2-pyridone, 13573-31-4.

Pyrolysis Products of Cycloalkano[*a*]pyrroles

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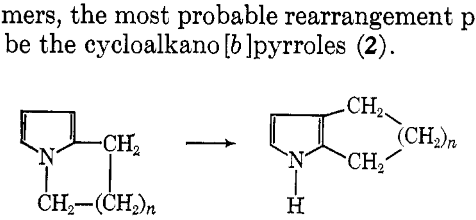
Received March 30, 1967

A reinvestigation of the pyrolysis of cycloheptano- and cyclohexano[*a*]pyrrole has shown that the major rearrangement products at 600° are the corresponding cycloalkano[*b*]pyrroles rather than those previously reported. Cyclopentano[*a*]pyrrole at 600° yields only 9% of the cyclopentano[*b*]pyrrole. At 650° cyclopentano-[*a*]pyrrole produces primarily the isomeric 2- and 3-methylpyrroles, pyridine, 2-ethylpyridine, and 2-vinylpyridine.

Since the pyrolysis of N-substituted pyrroles, where the substituent is alkyl,[1] benzyl,[2,3] and phenyl,[4] invariably leads to the production of a mixture of 2 and 3 isomers and since the presence of a 3-substituted pyrrole had not been reported in the pyrolysis products of cycloalkano[*a*]pyrroles,[5] we decided to reinvestigate the pyrolysis of these compounds. In addition, two of the structures proposed for some of the products, *i.e.*, 9-azabicyclo[4.2.1]nona-1,3,5-triene and 10-azabicyclo-[5.2.1]deca-1,3,5-triene, were highly strained and therefore open to question. In view of the facile formation of 3 isomers, the most probable rearrangement products should be the cycloalkano[*b*]pyrroles (**2**).



1 **2**

a, $n = 1$
b, $n = 2$
c, $n = 3$

The cycloalkano[*a*]pyrroles were pyrolyzed at several temperatures and the product compositions were determined. The results, given in Table I, confirm the

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[3] J. M. Patterson and L. T. Burka, *J. Am. Chem. Soc.*, **88**, 3671 (1966).

[4] J. M. Patterson, unpublished results.

[5] J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, **27**, 1652 (1962).