Anal. Calcd. for $C_{14}H_{28}N_2OS$: S, 11.77; N, 10.28. Found: S, 11.45, 11.23; N, 10.50, 10.52.

***t*-Butyloxamide.**—To a mixture of 0.12 mole of *t*-butyl alcohol in 30 ml. of acetic acid was added 0.11 mole of 96% sulfuric acid at 5°, and 0.10 mole of 1-cyanoformamide in 20 ml. of acetic acid. After 4 hr. at 25°, the wine-red mixture was poured onto ice and extracted with ether to give 62% yield of *t*-butyloxamide. It was soluble in hot acetonitrile (1 g./3 ml.), ethanol and benzene, slightly soluble in hot ether, water and hexane; m.p. 141–142°, subliming at 80° at reduced pressure.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 50.28; H, 8.50; N, 19.43.

***t*-Octyloxamide** was prepared similarly from diisobutylene in 55% yield. It was soluble in cold acetonitrile, 2B alcohol, ethylene dichloride, benzene, ether, hot hexane (1 g./4 ml.), and slightly soluble in hot water; m.p. 85–86°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 59.96; H, 10.06; N, 13.99. Found: C, 60.23; H, 10.20; N, 13.96.

Aminolysis of 1-Cyanoformamide.—A mixture of 0.10 mole of 1-cyanoformamide and 0.11 mole of butylamine in 50 ml of dry ether was stirred at 5°. Silver platelets were observed, and then a color change to yellow and brown. After the addition of 10 ml. of water the two-phase mixture was stirred for 1.5 hours, at 5–25°. Concentration at reduced pressure gave a tarry residue. It was triturated with ether, decolorized with charcoal and recrystallized from ethylene dichloride and benzene to give white crystals of **butylurea** in 28% yield, identified by its m.p. 97.5–98°, infrared spectrum and analysis. Authentic butylurea melts at 96°[36]; the expected product, butyloxamide, melts at 197–198°.[37]

Anal. Calcd. for $C_5H_{12}N_2O$: C, 51.69; H, 10.42; N, 24.12. Found: C, 51.69; H, 10.22; N, 23.52.

A mixture of 0.050 mole of 1-cyanoformamide, 0.055 mole of dodecylamine hydrochloride, 0.055 mole of sodium hydroxide, 0.10 mole of water and 15 ml. of methanol was refluxed 7 hours, neutralized and filtered. Repeated recrystallization of the brown solid from ethanol and ethylene dichloride gave white crystals of **dodecylurea**, m.p. 100–102°.

Anal. Calcd. for $C_{13}H_{28}N_2O$: C, 68.37; H, 12.46; N, 12.27. Found: C, 67.46, 67.74; H, 12.15, 12.29; N, 12.12, 12.17.

Authentic dodecylurea[38] had m.p. 102–103.5°, mixed m.p. 101–103°. The infrared spectra were identical.

Acknowledgment.—We wish to thank C. B. Shaffer for toxicity data, N. Colthup for assistance in interpreting infrared spectra, and M. Sabia and D. J. Wilson for assistance with the pressure experiments.

(36) T. L. Davis and K. C. Blanchard, THIS JOURNAL, **51**, 1790 (1929).

(37) J. Reiger, *Monatsh. Chem.*, **9**, 603 (1888).

(38) J. G. Erickson, THIS JOURNAL, **76**, 3977 (1954).

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

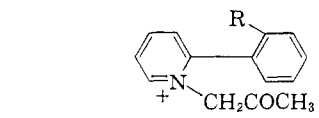
Aromatic Cyclodehydration. XXXIX.[1,2] The Morphanthridizinium Ion—A New Heterocyclic System

BY K. B. MOSER[3] AND C. K. BRADSHER

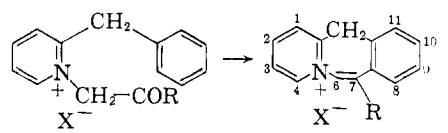
RECEIVED OCTOBER 17, 1958

The synthesis and proof of structure of a derivative of a new heterocyclic system, the 7-methylmorphanthridizinium ion, have been described. Three other substituted morphanthridizinium salts have been prepared and characterized.

The success[1,4] met with in the cyclization of 1-acetonyl-2-arylpyridinium salts (I) to yield benzo[a]quinolizinium salts, raised the question whether 1-acetonyl-2-benzylpyridines (III) would undergo a similar cyclization to yield a new heterocyclic system (IV) with a seven-membered ring. Since the



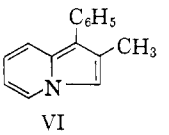
I, R = H; II, R = CH_3



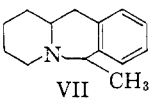
III, R = CH_3 IV, R = CH_3 V, R = C_6H_5

central ring of IV is not aromatic by Dewar's[5] definition, there was some doubt whether it would withstand the long hours of refluxing with mineral acid needed for cyclization.

Benzylpyridine reacted readily with iodoacetone, and the resulting quaternary iodide (III, X = I) was converted to the chloride, and refluxed for 5 days with 48% hydrobromic acid. The product, isolated as the perchlorate, had the composition expected for the new heterocyclic derivative (IV, X = ClO_4). All of our observations would have been accounted for if the product were really the hydroperchlorate of the known[6] 1-phenyl-2-methylpyrrocoline (VI), a base known to be formed when 1-acetonyl-2-benzylpyridinium salts are treated with



VI



VII

sodium bicarbonate. We prepared the pyrrocoline VI and found that its hydroperchlorate differs both in melting point and ultraviolet absorption from the product obtained in the acid cyclization.

Further evidence that the acid cyclization product had the structure IV was afforded by perman-

(1) For the preceding communication in this series, see THIS JOURNAL, **81**, 1941 (1959).

(2) This research was supported in part by a research grant (NSF-G2364) of the National Science Foundation.

(3) Monsanto Chemical Co. Research Fellow, 1957–1958.

(4) C. K. Bradsher and L. E. Beavers, THIS JOURNAL, **77**, 453 (1955).

(5) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949, p. 160.

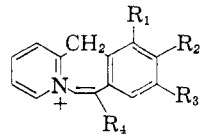
(6) A. E. Tschitschibabin, *Forts. Teerfarbenfabrikation*, **16B**, 2651 (1931).

ganate oxidation, which produced a 20% yield of phthalic anhydride. Reduction of the new salt (IV) over platinum oxide catalyst resulted in the uptake of the expected[7] four moles of hydrogen, yielding what is believed to be VII. As would be predicted from the formula VII, the perchloric acid salt prepared from the reduction product appeared to be a mixture of diastereoisomers. From this mixture only the higher melting form was isolated in a pure condition. Distillation of the crude base VII gave a distillate which boiled in a narrow temperature range and showed the expected molecular weight. On the basis of these observations one can eliminate the possibility that the acid-catalyzed reaction has given rise to some type of bimolecular condensation product, and can accept with confidence formula IV as being correct. Because of the relation of IV to morphanthridine,[8] the name morphanthridizinium[9] is proposed for the new aromatic nucleus.

Table I summarizes the results of our experiments aimed at the synthesis of substituted morphanthridizinium salts.

TABLE I

SYNTHESIS OF MORPHANTHRIDIZINIUM SALTS



	R_1	R_2	R_3	R_4	Yield quatern., %	Time, hr.	Cyclization agent	Yield, %
IV	H	H	H	CH_3	80	119	HBr	75
V	H	H	H	C_6H_5	66	156	HBr	0[a]
VIII	H	OCH_3	OCH_3	CH_3	68	1.5	HCl	82
IX	H	OCH_3	OCH_3	C_6H_5	84	2.5	HCl	51
X	CH_3	H	H	CH_3	35	116	HBr	78

[a] Starting material was recovered (92%).

It will be noted that refluxing 1-phenacyl-2-benzylpyridinium chloride with hydrobromic acid produces no isolable 7-phenylmorphanthridizinium salt (V). This reflects the low order of activity previously observed[3,10] for phenyl ketones in related cyclizations. Where there is a methoxyl group present in an activating position, as in VIII and IX, cyclization is quite rapid even with a phenyl ketone.

In the cyclization of 1-acetonyl-2-tolylpyridinium salts[1] it was observed that the *ortho* isomer II afforded very poor yields of the benzo[α]quinolizinium salt. This was attributed to the interference offered by the *o*-methyl group to the achievement of the coplanarity necessary for cyclization. It is interesting that in X, where no such steric problem is to be expected, the presence of an *o*-methyl group appears to have little effect on the ease of cyclization.

Because of the ready availability of 2-benzylpyridine, as well as its benzologs and heterocyclic analogs, the new synthesis should provide a route to many new and interesting compounds.

Experimental[11]

Spectroscopy.—All ultraviolet spectra were determined in 95% ethanol solution using the Warren Spectracord recording spectrophotometer and 1-cm. matched silica cells.

1-Acetonyl-2-benzylpyridinium Iodide (III).—To 6 g. of cold 2-benzylpyridine 6.52 g. of iodoacetone was added, and the mixture allowed to stand for three days in the refrigerator. The crystalline mass was dissolved in water (Norite) and the filtered solution was concentrated *in vacuo*. The residue was crystallized from ethanol–ether as a light yellow product, m.p. 167–171°, yield 10.1 g. (80%). An analytical sample crystallized from methanol–ethyl acetate as colorless needles, m.p. 169.5–171°.

Anal. Calcd. for $C_{15}H_{16}INO$: C, 51.00; H, 4.57; N, 3.97. Found: C, 50.92; H, 5.01; N, 3.90.

The perchlorate, prepared from an aqueous solution of the iodide, crystallized from ethanol as colorless rhombs, m.p. 140.5–141°.

Anal. Calcd. for $C_{15}H_{16}ClNO_5 \cdot {}^1/_2C_2H_6O$: C, 55.10; H, 5.49; N, 4.02. Found: C, 55.14; H, 5.77; N, 4.28.

7-Methylmorphanthridizinium Perchlorate (IV, X = ClO_4).—A solution of 3.5 g. of 1-acetonyl-2-benzylpyridinium iodide in 40 ml. of water containing a few drops of hydrochloric acid was stirred for 1.5 hours with freshly prepared and thoroughly washed silver chloride from 4.5 g. of silver nitrate. The silver halide was filtered off and the filtrate evaporated under reduced pressure leaving the chloride as a colorless gum. The gum was dissolved in 25 ml. of 48% hydrobromic acid and cyclized by refluxing it for 119 hours. The acid was evaporated under reduced pressure and the dark residue was dissolved in hot distilled water. Addition of 7 ml. of 72% perchloric acid to the hot solution produced an oil which crystallized on cooling and stirring. The crude product was recrystallized from ethanol–water as a tan crystalline solid, m.p. 153–157°, yield 2.30 g. (75%). The analytical sample was obtained from methanol–ether as light tan irregular crystals, m.p. 156.5–158°, λ_{max} (log ε) 312 mμ (3.88), λ_{min} 260 (3.55).

Anal. Calcd. for $C_{15}H_{14}ClNO_4$: C, 58.54; H, 4.59; N, 4.55. Found: C, 58.76; H, 4.68; N, 4.63.

In another experiment the **picrate** was prepared from the crude bromide. It crystallized as yellow needles from ethanol, m.p. 200.5–202.5°.

Anal. Calcd. for $C_{21}H_{16}N_4O_7 \cdot {}^1/_2C_2H_6O$: C, 57.52; H, 4.17; N, 12.20. Found: C, 57.47; H, 3.79; N, 12.10.

1-Phenyl-2-methylpyrrocoline[3] (VI). Hydroperchlorate.—Two grams of 1-acetonyl-2-benzylpyridinium iodide was converted to the chloride as in the preparation of IV and the crude chloride refluxed with 50 ml. of saturated sodium bicarbonate solution for a half-hour. The reaction mixture was steam distilled and since the distillate did not solidify[12] it was extracted with ether. The base which remained after concentration of the ethereal solution was dissolved in dilute hydrochloric acid and converted to the perchlorate by addition of perchloric acid. This afforded 1.2 g. (69%) of green crystalline product, m.p. 165.5–168°. The analytical sample was obtained by recrystallization first from acetone–ether (Norite) and again from ethanol–ether, as cream-colored needles, m.p. 167–168.5°; λ_{max} (log ε), 240(4.47), 286(3.89), 310(3.98) and 356 mμ(3.54); λ_{min}, 260(3.71), 292(3.88) and 330 mμ(3.49).

Anal. Calcd. for $C_{15}H_{14}ClNO_4$: C, 58.54; H, 4.59; N, 4.55. Found:[13] C, 58.42; H, 5.03; N, 4.55.

(7) The preferential reduction of rings having a common quaternary nitrogen may be seen in the case of acridizinium bromide; C. K. Bradsher and L. E. Beavers, THIS JOURNAL, **77**, 4812 (1955).

(8) Morphanthridine is 11-dibenz[b,e]azepin; R. Scholl and J. Muller, *Ber.*, **64B**, 640 (1931).

(9) This parallels the usage in the cases of quinoline–quinolizinium and acridine–acridizinium. In each example one can think of the ring nitrogen atom being exchanged with the adjacent bridgehead carbon atom. The terminal -ne of the base is dropped and the ending -izinium added to indicate the quaternary aromatic ion.

(10) C. K. Bradsher and F. A. Vingiello, THIS JOURNAL, **71**, 1434 (1949).

(11) Except as noted all analyses were done by Galbraith Laboratories, Knoxville, Tenn. The melting points were taken on the Fisher–Johns apparatus and (like the boiling points) are uncorrected.

(12) Tschitschibabin (ref. 6) reported that the base was a low-melting solid, m.p. 20–23°. No yields or analyses were reported, nor were any physical constants for derivatives given.

(13) The sample exploded during the carbon–hydrogen analysis.

Oxidation of 7-Methylmorphanthridizinium (IV) Perchlorate.—A solution containing 0.75 g. of the perchlorate of IV (m.p. 156–158.5°) in 25 ml. of hot water was stirred on the steam-bath while 10 g. of potassium permanganate in 150 ml. of water was added slowly. Addition of permanganate was interrupted occasionally to permit addition of 20% sodium hydroxide solution (total 45 ml.). The reaction was continued for 91 hours. After removal of the manganese dioxide the acidified solution was extracted with ether in a continuous liquid–liquid extractor. Evaporation of the ether extracts and sublimation of the residue yielded 58 mg. of white crystals, m.p. 128–131°. This substance did not depress the melting point of an authentic sample of phthalic anhydride and gave an identical infrared absorption spectrum.

5-Methylbenzo[d]-1-azabicyclo[5.4.0]undecane (VII) Hydroperchlorate.—To a solution containing 998 mg. of 7-methylmorphanthridizinium (IV) perchlorate in 100 ml. of methanol, 44 mg. of platinum oxide was added and hydrogenation carried out at room temperature and atmospheric pressure until the uptake of hydrogen had apparently ceased, 325 ml. (97.6% theoretical for reduction of four double bonds). The solution was filtered, concentrated and ether added yielding 409 mg. (40%) of colorless crystals, m.p. 120–180°. Repeated recrystallization from methanol–ether gave a pure sample of the higher melting racemic mixture as colorless needles, m.p. 253–255°.

Anal. Calcd. for $C_{15}H_{22}ClNO_4$: C, 57.05; H, 7.02; N, 4.44. Found: C, 57.37; H, 6.88; N, 4.66.

In a reduction similar to the previous one the crude reduction product in methanol was made alkaline with methanolic sodium hydroxide and the mixture poured into water. The resulting mixture was extracted with ether. The combined ethereal extracts were washed and dried (magnesium sulfate) and the ether evaporated. Distillation of the residue yielded 1.39 g. (59%) of a colorless mobile liquid, b.p. 137° (4 mm.). The analytical sample, b.p. 141.5° (6 mm.), did not give very satisfactory results in a carbon and hydrogen analysis, but a molecular weight determination gave approximately the expected value.

Anal. Calcd. for $C_{15}H_{21}N$ (215.3): C, 83.66; H, 9.83. Found: C, 82.86; H, 9.67; mol. wt., 222 (ebulliometric, in acetone).

A sample of the distilled base was converted to the hydroperchlorate, m.p. 100–160°. The infrared absorption spectrum of this salt was almost identical with that of the analytical sample of the high melting racemic form of the hydroperchlorate, m.p. 253–255°.

2-Pyridyl-3,4-dimethoxyphenylcarbinol does not appear to have been recognized previously as a solid. Our preparation, b.p. 200–205° (2 mm.) [lit.[14] 180–185° (1 mm.), 205–210° (5 mm.)], solidified and the analytical sample from benzene–hexane gave colorless crystals, m.p. 92–93.5°.

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.40; H, 6.29; N, 5.84.

1-Acetonyl-2-(3,4-dimethoxybenzyl)-pyridinium Iodide.—To 1.55 g. of 2-(3,4-dimethoxybenzyl)-pyridine,[15] cooled in an ice-bath, 1.25 g. of iodoacetone was added and the mixture allowed to stand in the refrigerator for 24 hours. The gum which formed was crystallized from ethanol–ether as yellow crystals, m.p. 178–181.5°, yield 1.90 g. (68%). The analytical sample afforded yellow plates from methanol–ether, m.p. 179–181.5°.

Anal. Calcd. for $C_{17}H_{20}INO_3 \cdot {}^1/_4H_2O$: C, 48.87; H, 4.95; N, 3.35. Found: C, 48.93; H, 4.67; N, 3.26.

9,10-Dimethoxy-7-methylmorphanthridizinium (VIII) Chloride.—The conversion of 1.17 g. of the 1-acetonyl-2-(3,4-dimethoxybenzyl)-pyridinium iodide to the corresponding chloride was carried out as usual by the use of silver chloride. The crude quaternary chloride was cyclized by refluxing it for 1.5 hours with concentrated hydrochloric acid. The acid was removed *in vacuo* and the residue crystallized from methanol–ether as a fine yellow powder, m.p. 263–267°, yield 744 mg. (82%). The analytical sample, crystallized from methanol–ether, appeared to be hydrated, m.p. 268–270°; λ_{max} 224, 256 and 364 mμ; λ_{min} 242 and 315 mμ.

Anal. Calcd. for $C_{17}H_{18}ClNO_2 \cdot {}^1/_2H_2O$: C, 65.27; H, 6.12; N, 4.48. Found:[16] C, 65.06; H, 6.11; N, 4.30.

1-Phenacyl-2-(3,4-dimethoxybenzyl)-pyridinium Bromide.—A mixture of 4.20 g. of 2-(3,4-dimethoxybenzyl)-pyridine and 3.65 g. of phenacyl bromide was warmed on the steam-bath until solution occurred and a precipitate began to form. The mixture was placed in the refrigerator for 20 hours, and then recrystallized from ethanol–ether. The product, 6.6 g. (84%), consisted of light yellow plates, m.p. 198.5–201°. The analytical sample was obtained from ethanol–ether as light yellow plates, m.p. 200–203°.

Anal. Calcd. for $C_{22}H_{22}BrNO_3$: C, 61.69; H, 5.18; N, 3.27. Found: C, 61.82; H, 4.98; N, 3.29.

9,10-Dimethoxy-7-phenylmorphanthridizinium (IX) Perchlorate.—The cyclization of 6.6 g. of 1-phenacyl-2-(3,4-dimethoxybenzyl)-pyridinium bromide in 110 ml. of concentrated hydrochloric acid was carried out by refluxing the mixture for 2.5 hours. After removal of the hydrochloric acid *in vacuo* the product was precipitated as the perchlorate by addition of perchloric acid. The perchlorate was twice crystallized from methanol–ether, m.p. 219–223°, yield 3.35 g. (51%). Further recrystallization afforded an analytical sample as yellow crystals, m.p. 222.5–225°, λ_{max} 367 mμ (shoulders at 232, 257, 279 and 315 mμ), λ_{min} 340 mμ.

Anal. Calcd. for $C_{22}H_{20}ClNO_6$: C, 61.47; H, 4.69; N, 3.26. Found: C, 61.16; H, 4.75; N, 3.34.

2-Pyridyl-2-tolylcarbinol.—A Grignard reagent was prepared from 30.6 g. of 2-bromotoluene and to it was added slowly an ether solution containing 18.2 g. of pyridine-2-aldehyde. The mixture was stirred for 2.5 hours and decomposed by addition of dilute hydrochloric acid. The acid layer was separated and the ether layer washed with more dilute hydrochloric acid. The combined acid solutions were neutralized with ammonia gas and the resultant oil taken up in methylene chloride. The methylene chloride solution was dried and concentrated and the residue distilled. The product was obtained as a viscous yellow oil, b.p. 151–152.5° (2.5 mm.), yield 21.5 g. (64%). The oil crystallized on standing and an analytical sample was obtained as colorless cubes from dilute methanol, m.p. 60–60.5°.

Anal. Calcd. for $C_{13}H_{13}NO$: C, 78.36; H, 6.57; N, 7.03. Found: C, 78.23; H, 6.67; N, 7.14.

2-(2-Methylbenzyl)-pyridine.[17]—To a solution of 22.0 g. of 2-pyridyl-2-tolylcarbinol in 100 ml. of methylene chloride, 10 ml. of thionyl chloride was added dropwise with stirring. During the addition the temperature was kept below 20°. The reaction was then stirred at room temperature for three hours, cooled, and 100 ml. of 20% sodium hydroxide solution added dropwise at such a rate that the temperature did not exceed 30°. The layers were separated and the aqueous layer extracted once with methylene chloride. The combined methylene extracts were concentrated *in vacuo* and the red-violet residue dissolved in 100 ml. of acetic acid. The acid solution was vigorously stirred and heated on the steam-bath while 12 g. of zinc dust was added over the period of an hour. After the mixture had been heated for an additional five hours it was filtered and the acetic acid removed *in vacuo*. The residue was treated with a mixture of methylene chloride and 20% sodium hydroxide and the methylene chloride layer washed, dried and concentrated. Distillation of the residue afforded 14.7 g. (73%) of liquid, b.p. 128–134°. A middle fraction, b.p. 130–130.5°, was redistilled for analysis.

Anal. Calcd. for $C_{13}H_{13}N$: C, 85.21; H, 7.15. Found: C, 85.26; H, 7.06.

1-Acetonyl-2-(2-methylbenzyl)-pyridinium Perchlorate.—The quaternization of 2-(2-methylbenzyl)-pyridine (5.0 g.) was carried out in the usual way and the product crystallized from ethanol–ether. The yield of crude iodide suitable for further reactions was 4.5 g. (45%), m.p. 121–124°.

For analytical purposes the *perchlorate* was prepared. Recrystallization from methanol–ether gave colorless needles, m.p. 129–131°.

Anal. Calcd. for $C_{16}H_{18}ClNO_5$: C, 56.56; H, 5.34. Found:[16] C, 56.55; H, 5.51.

(14) N. Sperber, D. Papa, E. Schwenk and M. Sherlock, THIS JOURNAL, **71**, 887 (1949).

(15) N. Sugiomoto, *J. Pharm. Soc. Japan*, **76**, 1045 (1956).

(16) Analysis by Drs. Weiler and Strauss, Oxford, England.

(17) *Cf.* N. Sperber, E. Schwenk and M. Sherlock, THIS JOURNAL, **73**, 3856 (1951).

7,11-Dimethylmorphanthridizinium (X) Perchlorate.—The conversion of 3.5 g. of the crude 1-acetonyl-2-(2-methylbenzyl)-pyridinium iodide to the chloride and cyclization of the chloride by refluxing it for 116 hours in 48% hydrobromic acid was carried out in the case of the simpler homolog III. The product, isolated as the perchlorate, was recrystallized from methanol–ether as tan irregular crystals, m.p. 230–234°, yield 2.4 g. (78%). The analytical sample was crystallized from methanol–ether, m.p. 234.5–236°; λ_{max} (log ϵ), 229(4.19), 275(3.72) and 315 mμ(3.81); λ_{min} 260(3.55) and 286 mμ(3.61).

Anal. Calcd. for $C_{16}H_{16}ClNO_4$: C, 59.72; H, 5.01; N, 4.35. Found:[16] C, 59.57; H, 5.24; N, 4.22.

1-Phenacyl-2-benzylpyridinium bromide was prepared in the usual way starting with 6 g. of benzylpyridine and 7.06 g. of phenacyl bromide. The product formed colorless crystals, m.p. 191–195°, from ethanol–ethyl acetate, yield 8.55 g. (66%). The analytical sample was crystallized from ethanol–ether, m.p. 193.5–195.5°.

Anal. Calcd. for $C_{20}H_{18}BrNO$: C, 65.23; H, 4.93; N, 3.80. Found: C, 65.20; H, 4.99; N, 3.69.

Attempted Cyclization of 1-Phenacyl-2-benzylpyridinium Bromide. (a) **In Hydrobromic Acid.**—When 3.75 g. of the phenacyl salt was refluxed in 48% hydrobromic acid for 156 hours, 3.45 g. (92%) of the starting material, m.p. and m.m.p. 191–193°, was recovered.

(b) **In Polyphosphoric Acid.**—Five grams of the phenacyl salt was heated for 11 hours at 170° with 48.7 g. of polyphosphoric acid. The cooled mixture was diluted with ice and water and 72% perchloric added. The precipitate crystallized from methanol as tan crystals, m.p. 223–229°, yield 2.7 g. The analytical sample melted at 225–230°, λ_{max} 262 mμ, λ_{min} 238 mμ.[18] The infrared spectrum showed no peak in the 6.83 region.

Anal. Calcd. for $C_{20}H_{16}NClO_4$: C, 64.95; H, 4.36; N, 3.79. Found:[16] C, 64.59; H, 4.39; N, 3.49.

(18) Although this compound shows the approximate composition expected for 7-phenylmorphanthridizinium perchlorate, the ultraviolet absorption spectrum gives no evidence of the conjugation characteristic of the morphanthridizinium system. On this basis, the polyphosphoric acid reaction product is to be regarded as a compound of unknown structure.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Aromatic Cyclodehydration. XL.[1,2] meso-Substituted Acridizinium Derivatives

BY C. K. BRADSHER AND T. W. G. SOLOMONS[2]

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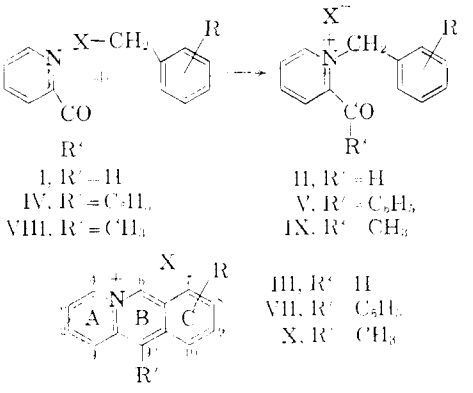
The cyclodehydration in liquid hydrogen fluoride of the 1-benzyl salts obtained from 2-benzoyl- and 2-acetylpyridine has afforded the first acridizinium salts having substituents at position 11. In the same way, the salt obtained by quaternization of 2-benzoylpyridine with 1-phenylethyl bromide cyclized to yield a 6-methyl-11-phenylacridizinium derivative, in which both *meso* positions are occupied.

In earlier papers[3,4] it was shown that acridizinium derivatives (III) with substituents in the remote (C) ring may be produced by the cyclization of the quaternary salts (II) obtained by the reaction of substituted benzyl halides with picolinic aldehyde (I).



As yet no general methods have been described for the synthesis of acridizinium derivatives with substituents in the central (B) ring. An obvious method for the introduction of alkyl and aryl substituents at position 11 in ring B would be to replace picolinic aldehyde (I) in the synthesis by a 2-pyridyl ketone. It was found that quaternization of 2-benzoylpyridine (IV) could be effected using a variety of benzyl halides, but cyclization of the salt (V) in boiling hydrobromic acid gave very poor results. Since liquid hydrogen fluoride had been used to bring about the cyclization of certain organic acids and ketones[5] it seemed worthwhile to investigate its utility in the acridizinium ion synthesis.

Although liquid hydrogen fluoride did cause the cyclization of 1-benzyl-2-formylpyridinium bromide, the yield and the quality of the product (III) were both inferior to that observed when boiling (48%) hydrobromic acid was used. It was gratifying to discover that the hydrogen fluoride medium does effect the cyclization of 1-benzyl-2-benzoylpyridinium salts in yields up to 90%, affording the desired 11-phenylacridizinium salts (VII).

Of the five benzoylpyridinium salts (V) studied, only that from *p*-methoxybenzyl bromide deserves particular mention. This compound fails to cyclize under the usual conditions, probably because the positions available are unactivated and *meta* to a methoxyl group.[6] The benzyl-2-benzoylpyridinium salts as a group are only moderately difficult to obtain in a state of analytical purity. This is in contrast to the behavior of the salts (II) derived

(1) For the preceding communication of this series see THIS JOURNAL, **81**, 2547 (1959).

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(3) C. K. Bradsher and L. E. Beavers, THIS JOURNAL, **77**, 4812 (1955).

(4) C. K. Bradsher and J. H. Jones, *ibid.*, **79**, 6033 (1957).

(5) *Cf.* W. S. Johnson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 157; W. S. Johnson, C. A. Erickson and J. Ackerman, THIS JOURNAL, **74**, 225 (1952).

(6) For a partial bibliography concerning the inhibition of cyclization *meta* to a methoxyl group see C. K. Bradsher, F. C. Brown and P. H. Leake, THIS JOURNAL, **79**, 1471 (1957), ref. 10.