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.

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[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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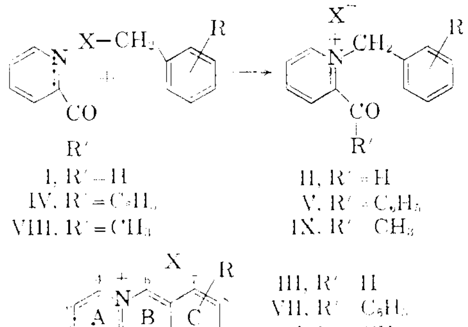
The cyclodehydration in liquid hydrogen fluoride of the 1-benzyl salts obtained from 2-benzoyl- and 2-acetylpyridine has afforded the first acridizinium salts having substituents at position 11. In the same way, the salt obtained by quaternization of 2-benzoylpyridine with 1-phenylethyl bromide cyclized 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).



I, R′ = H
IV, R′ = C_6H_5
VIII, R′ = CH_3

II, R′ = H
V, R′ = C_6H_5
IX, R′ = CH_3

III, R′ = H
VII, R′ = C_6H_5
X, R′ = CH_3

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

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[1] For the preceding communication of this series see This Journal, **81**, 2547 (1959).

[2] This investigation was supported by a research grant (NSF-G2364) from the National Foundation. Abstracted in part from a dissertation to be submitted by T. W. G. Solomons in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

[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.

TABLE I

11-PHENYLACRIDIZINIUM SALTS VII

R	Yield,[a] %	M.p.,[b] °C. Perchlorate	Picrate
H	77[c]	247–249	213–215
8-OCH_3	41[d]	189–191	255–257
9-CH_3	34[e]	249.5–251	.....
7-CH_3	53	189–191	.....

[a] The yield is for the perchlorate salt. [b] Melting points of analytical samples. [c] Yield on quaternization 86%, cyclization 90%. [d] In one run in which the product was isolated as the picrate the yield was 57%. [e] Yield on quaternization 61%, on cyclization 56.5%.

from picolinic aldehyde, none of which has yet been obtained in a pure state.

An attempt to use 2-acetylpyridine (VIII) as a starting material for the synthesis of 11-methylacridizinium salts (X) has met with very limited success. Quaternization with benzyl bromide proved difficult and only a 3% over-all yield of 11-methylacridizinium perchlorate could be obtained.

Quaternization of 2-benzoylpyridine with 1-phenylethyl bromide, followed by cyclization of the crude salt, gave a low yield (8%) of 6-methyl-11-phenylacridizinium perchlorate. This is the first example of an acridizinium salt in which both of the *meso* positions are substituted.

Experimental[7]

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

1-Benzyl-2-benzoylpyridinium Perchlorate (V, R = H).—A solution containing 1.83 g. of 2-benzoylpyridine, 2.0 g. of benzyl bromide and 1 ml. of dimethylformamide was allowed to stand at room temperature for two weeks. The yellow oil which was formed was triturated with a small quantity of ethyl acetate. The small colorless crystals were collected and washed with ethyl acetate. The dry product believed to be 1-benzyl-2-benzoylpyridinium bromide, 3.05 g. (86%), m.p. 121–123°, was not purified further, but used directly in the cyclization experiments.

The perchlorate was prepared by addition of perchloric acid to an aqueous solution of the bromide, and crystallization from ethanol as colorless rectangular plates, m.p. 154–155°.

Anal. Calcd. for $C_{19}H_{16}ClNO_5$: C, 61.05; H, 4.32; N, 3.75. Found: C, 61.06; H, 4.64; N, 3.77.

11-Phenylacridizinium Salts (VII, R = H).—One gram of the crystalline 1-benzyl-2-benzoylpyridinium bromide was placed in a polyethylene bottle and to this was added approximately 200 ml. of liquid hydrogen fluoride. The mixture was allowed to stand at room temperature until all the hydrogen fluoride had evaporated and then the bottle was rinsed with 40 ml. of water and 5 ml. of methanol. To the combined and filtered rinsings 2 ml. of 70% perchloric acid was added, and the light yellow crystals of the **perchlorate** which formed were collected and washed with a little water. The yield was 0.90 g., 89.5%, 77% over-all, m.p. 246–248°. The analytical sample prepared by crystallization from ethanol consisted of clusters of yellow needles and melted at 247–249°, λ_{max} (log ϵ), 245 (4.52), 365 (3.99), 383 (3.98), 404 mμ (3.91); λ_{min}, 317 (3.20), 375 (3.90) and 393 mμ (3.78).

Anal. Calcd. for $C_{19}H_{14}ClNO_4$: C, 64.13; H, 3.96; N, 3.94. Found: C, 63.84; H, 3.91; N, 3.83.

The picrate formed yellow leaflets from ethanol, m.p. 213–215°.

Anal. Calcd. for $C_{25}H_{16}N_4O_7$: C, 61.98; H, 3.33; N, 11.57. Found: C, 61.85; H, 3.33; N, 11.56.

1-(3-Methoxybenzyl)-2-benzoylpyridinium Bromide (V, R = 3-OCH$_3$).—A mixture containing 1.83 g. of 2-benzoylpyridine, 2.01 g. of *m*-methoxybenzyl bromide and 1.0 ml. of dimethylformamide was heated on the steam-bath for 12 hours[8] and allowed to stand at room temperature for three days.

The ether-insoluble gum which formed could not be crystallized so it was dissolved in enough methanol to make a total volume of 10 ml. One milliliter of this solution was converted to the picrate by addition of alcoholic picric acid, yield 0.36 g. (68%), m.p. 154–156°. The analytical sample was obtained from ethanol as clusters of yellow needles, m.p. 158–160°.

Anal. Calcd. for $C_{26}H_{20}N_4O_8$: C, 58.65; H, 3.79; N, 10.52. Found: C, 58.56; H, 3.65; N, 10.57.

8-Methoxy-11-phenylacridizinium Perchlorate (VII, R = 8-OCH$_3$).—The remaining nine-tenths of the methanolic solution of the crude bromide (V, R = 3-OCH$_3$) was placed in a polyethylene bottle and the methanol removed on the steam-bath. By use of a magnetic stirrer with a Teflon coated bar the residue was stirred as approximately 25 ml. of liquid hydrogen fluoride was added. After the hydrogen fluoride had evaporated the residue was dissolved in water, the solution filtered and the perchlorate salt precipitated by addition of perchloric acid. Crystallized from ethanol it afforded 1.42 g. (41% over-all) of yellow crystals, m.p. 186.5–188°. The analytical sample consisted of tiny yellow needles, m.p. 189–191°; λ_{max} (log ϵ), 259 (4.46), 298 (4.23), 344 (3.81), 363 (4.04), 400 (3.75), 420 mμ (3.73); λ_{min}, 287 (4.20), 335 (3.72), 350 (3.78), 385 (3.64), 410 (3.71).

Anal. Calcd. for $C_{20}H_{16}ClNO_5$: C, 62.26; H, 4.18; N, 3.63. Found: C, 62.70; H, 3.89; N, 3.52.

The picrate was prepared in ethanol and was obtained as a deep yellow powder from acetonitrile, m.p. 255–257°.

Anal. Calcd. for $C_{26}H_{18}N_4O_8 \cdot {}^1/_2H_2O$: C, 59.66; H, 3.66; N, 10.70. Found:[9] C, 59.77; H, 3.93; N, 10.65.

1-(4-Methylbenzyl)-2-benzoylpyridinium Picrate (V R = 4-CH$_3$).—The quaternization of 3.43 g. of 2-benzoylpyridine with 3.47 g. of *p*-methylbenzyl bromide in 1 ml. of dimethylformamide was allowed to continue for 20 days at 10°. The ether-washed oil was dissolved in enough ethanol to make exactly 15 ml. of solution.

Exactly one-tenth of the solution was converted to the picrate yielding 0.59 g. (61%) of yellow crystals, m.p. 128–130°. The analytical sample crystallized from ethanol as clusters of yellow needles, m.p. 129–130°.

Anal. Calcd. for $C_{26}H_{20}N_4O_8$: C, 60.46; H, 3.90; N, 10.77. Found: C, 60.65; H, 3.60; N, 10.77.

9-Methyl-11-phenylacridizinium Perchlorate (VII, R = 9-CH$_3$).—The remainder of the ethanol solution of the bromide (V, R = 4-CH$_3$) was concentrated and the residue cyclized by allowing it to stand with 75 ml. of liquid hydrogen fluoride. The residue was converted to the perchlorate in the usual way affording 2.4 g. (34.5% over-all) of a pale yellow powder, m.p. 230°, resolidifies and melts at 247–250°. The analytical sample was obtained from ethanol as thin yellow plates, m.p. 249.5–251°; λ_{max} (log ϵ), 247 (4.61), 382 (4.15), 403 mμ (3.96); λ_{min}, 317 (3.15), 395 mμ (3.94).

Anal. Calcd. for $C_{20}H_{16}ClNO_4$: C, 64.95; H, 4.36; N, 3.79. Found: C, 64.73; H, 4.33; N, 3.54.

7-Methyl-11-phenylacridizinium Perchlorate (VII, R = 7-CH$_3$).—Quaternization of 1.83 g. of 2-benzoylpyridine by 1.85 g. of *o*-methylbenzyl bromide was carried out at 10° for 19 days. The crude yellow oil was washed with ether and cyclized in 60 ml. of hydrogen fluoride in the usual way. The perchlorate was isolated as a light yellow powder, m.p. 188–190°, yield 1.95 g. (53% over-all). The analytical sample crystallized from ethanol as small yellow needles, m.p. 189–191°; λ_{max} (log ϵ), 252 (4.59), 371 (4.00), 391 (4.00), 412 (3.97); λ_{min}, 321 (3.20), 381 (3.92), 402 mμ (3.88).

Anal. Calcd. for $C_{20}H_{16}ClNO_4$: C, 64.95; H, 4.36; N, 3.79. Found: C, 65.05; H, 4.49; N, 3.70.

Attempted Cyclization of Crude 1-(4-Methoxybenzyl)-2-benzoylpyridinium Bromide (V, R = 4-OCH$_3$).—The

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[7] All melting points were determined on the Fisher-Johns block and are not corrected. Except as noted all analyses were by Galbraith Laboratories, Knoxville, Tenn.

[8] Quaternization at room temperature is to be preferred since cyclization of a salt quaternized for two weeks at room temperature afforded a 57% over-all yield of the acridizinium derivative V as compared with 41% by the method here reported.

[9] Analysis by Drs. Weiler & Strauss, Oxford, England.

quaternization of 1.83 g. of 2-benzoylpyridine with 2.01 g. of *p*-methoxybenzyl bromide[10] was carried out in six days at room temperature. To the crude salt 60 ml. of hydrogen fluoride was added and allowed to evaporate slowly in the usual way. The residue was dissolved in water and exactly one-half of the solution was converted to the reineckate by addition of ammonium reineckate. The rose-colored precipitate was washed with ethanol and ether, m.p. 158–159°, yield 1.12 g. (36%). The melting point of the analytical sample (recrystallized from ethanol and ether) was unchanged.

A sample of **1-(4-methoxybenzyl)-2-benzoylpyridinium reineckate** prepared from the bromide gave the identical melting point, mixed melting point and infrared spectra.

Anal. Calcd. for $C_{24}H_{24}CrN_7O_2S_4$: C, 46.21; H, 3.88; N, 15.72. Found: C, 46.31; H, 3.83; N, 16.09.

11-Methylacridizinium Perchlorate (X, R = H).—The quaternization of 1.21 g. of 2-acetylpyridine with 1.71 g. of benzyl bromide in the presence of 1 ml. of dimethylformamide was carried out in a 4-oz. polyethylene bottle at 10° for 23 days. Ether was added to precipitate the salt (as an oil) and the ether decanted. To the small quantity of oil obtained, 60 ml. of liquid hydrogen fluoride was added and cyclization and isolation carried out as usual. The perchlorate was obtained from ethanol as blunt orange-brown needles, m.p. 239–241°, yield 0.10 g. (3%). The analytical sample melted at 243–244.5°; λ_{max} (log ϵ): 243 (4.61), 250 (4.60), 365 (4.04), 382 (4.11), 402 (4.00); λ_{min}, 247 (4.58), 313 (3.08), 372 (3.93), 391 mμ (3.82).

Anal. Calcd. for $C_{14}H_{12}ClNO_4$: C, 57.25; H, 4.12; N, 4.77. Found: C, 57.54; H, 3.86; N, 4.80.

6-Methyl-11-phenylacridizinium Perchlorate.—Quaternization of 1.83 g. of 2-benzoylpyridine by 1.85 g. of α-bromoethylbenzene in 1.0 ml. of dimethylformamide was carried out at 10° for 222 days. The crude orange oil which formed was washed with ether and cyclized in 100 ml. of hydrogen fluoride in the usual way. After all the hydrogen fluoride had evaporated the residue was taken up in water and filtered. The addition of perchloric acid to the filtrate gave a light yellow precipitate which after separation and crystallization from ethanol, consisted of large yellow irregular crystals, m.p. 218.5–220°, yield 0.32 g. (8.6%). The analytical sample melted from 222–223°; λ_{max} (log ϵ), 249 (4.65), 370 (4.11), 389 (4.09), 410 mμ (4.05); λ_{min}, 318 (3.24), 379 (3.98), 400 (3.90).

Anal. Calcd. for $C_{20}H_{16}ClNO_4$: C, 64.95; H, 4.36; N, 3.79. Found: C, 65.19; H, 4.32; N, 3.71.

DURHAM, N. C

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(10) A. Lapworth and J. B. Shoesmith, *J. Chem. Soc.*, **121**, 1397 (1922).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE EASTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Chain Transfer Constants of Vinyl Esters with Toluene[1]

BY C. F. THOMPSON,[2] W. S. PORT AND L. P. WITNAUER

RECEIVED NOVEMBER 6, 1958

Weight average molecular weights have been used to determine chain transfer constants of three vinyl esters with toluene. It has been shown that polyvinyl acetate prepared in varying amounts of toluene has a constant molecular weight distribution $M_w/M_n = K$, leading to a linear relation between $1/P_w$ and (S)/(M). The transfer constant obtained from this relation has been designated C_S', and differs only slightly from the true transfer constant. It has the advantage of being more easily measured in many cases. The vinyl esters have similar reactivities, regardless of the length of the acyl chain, although increased chain transfer to monomer is observed with increasing chain length.

An earlier report on the copolymer reactivity ratios of a number of vinyl esters has shown that all have similar reactivities, regardless of the nature of the acyl portion of the molecule.[3] In the present work, the chain transfer of vinyl acetate, vinyl pelargonate and vinyl stearate with toluene has been studied, the monomers being chosen for the wide variance in the length of the acyl chain. These monomers have been polymerized in the presence of varying amounts of toluene at three temperatures, and activation energy differences and frequency factor ratios have been calculated from the temperature dependence of the chain transfer constants. A new method for evaluating transfer constants by means of weight average molecular weights has been used and found to be theoretically and experimentally justified.

Chain transfer constants are determined by means of the expression

$$1/P_n = C_M + C_S \frac{(S)}{(M)} + C_I \frac{(I)}{(M)} + \frac{k_t R_p}{k_p^2 (M)^2} \quad (1)$$

where P_n is the number average degree of polymerization, R_p is the rate of polymerization, and (S), (M) and (I) are the concentrations of solvent, monomer and initiator. The transfer constants C_M, C_S and C_I represent the ratios of the rate constants for transfer to the rate constant for propagation; *i.e.*, $C_S = k_{Tr,S}/k_p$.[4,5]

This expression may be simplified by the proper choice of experimental conditions. The term involving the initiator transfer constant may be reduced to zero by using azobisisobutyronitrile, which does not undergo transfer.[5] Furthermore in polymerizations initiated bimolecularly, the steady state treatment yields for the last term $(k_i k_t)^{1/2}(I)^{1/2}/k_p(M)^{1/2}$ which may be held constant over a series of polymerizations by maintaining a constant (I)/(M) ratio. Since the term C_M is constant by nature, the simplified expression results

$$1/P_n = C_S \frac{(S)}{(M)} + 1/P_0 \quad (2)$$

By plotting the reciprocal degree of polymerization

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(1) This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.

(2) The paper is based on portions of a thesis submitted by C. F. Thompson to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Reprint requests should be addressed to Polymer Research, 107 Noyes Laboratory, University of Illinois, Urbana, Ill.

(3) C. S. Marvel and W. G. DePierri, *J. Polymer Sci.*, **27**, 39 (1958).

(4) (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) S. Basu, J. Sen and S. R. Palit, *Proc. Roy. Soc.* (*London*), **A214**, 247 (1952); (c) B. Baysal and A. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

(5) S. R. Palit and S. K. Das, *Proc. Roy. Soc.* (*London*), **A226**, 82 (1954).