(14) Prepared analagously to *n*-butyl nitrite: W. A. Noyes, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 108.
(15) Prepared in 64% yield from 1-chloro-3-iodopropane.
(16) A convenient modification of the procedure of ref 6.
(17) The reagent obtained employing a shorter reaction time affords a lower yield of **6**. Presumably this is due to *n*-butylcadmium chloride.
(18) Addition of **1a** to an excess of the cadmium reagent gave **6**, too.
(19) A sample of impure **7** detonated during VPC analysis (injector temperature 180 °C) destroying a syringe.
(20) Impure **10** rapidly decomposed at 100 °C on contact with air.

Basic Methanolysis of Benzoylmethylaminopyridines and Their *N*-Oxide and Methyl Quaternary Derivatives

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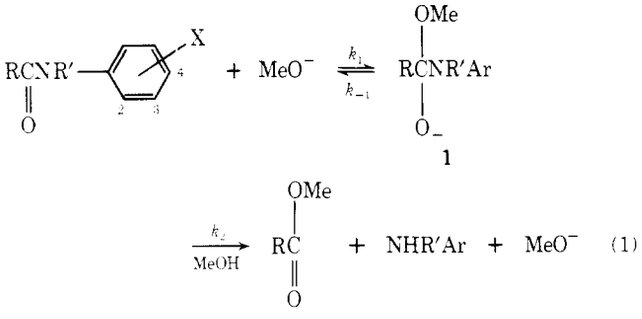
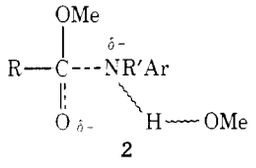
Rate data for the basic methanolysis of PhCON(Me) derivatives of pyridine, pyridine *N*-oxide, and 1-methylpyridinium iodide are reported. Positional reactivities are 4 ≫ 2 > 3 (pyridine), 4 > 3 > 2 (*N*-oxide), and 4 ≫ 3 (methylpyridinium). The heterocycles are also considered as substituted *N*-aryl-*N*-methylbenzamides; when combined with published data, these results yield a linear Hammett plot (ρ = 3.2). Mechanistic implications of this finding are discussed.

The effect of substituents on the rate of basic hydrolysis and methanolysis of anilides (eq 1) is most interesting since



(1)

all types of Hammett plots are possible, depending on the particular structure and reaction conditions. Thus linear,[1] curved,[2] and intersecting straight line[3] plots have been obtained, depending on the mechanisms or mechanism change. Of particular interest is the possibility of change from rate-determining breakdown of **1** (mechanism A, solvent assisted C–N cleavage via transition state **2** with Hammett $\rho \approx 3$[1,2]) to

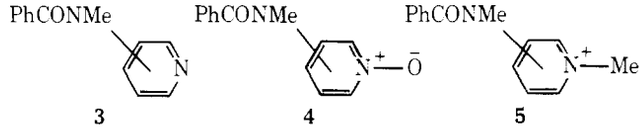


2

rate-determining formation of 1 (mechanism B, $\rho \approx 1.3$[4]) for strongly electron-withdrawing aryl substituents. This mechanism change should be accompanied by a decrease in slope of a Hammett plot.

In the case of *N*-aryl-*N*-methylbenzamides (R = Ph; R′ = Me) the current knowledge seems best fitted by invoking mechanism A for all substituents studied, except 4-nitro where reaction is by mechanism B.[5] The necessity for a strong resonance withdrawing effect for mechanism B is suggested by the observation that the 3,5-dinitro-substituted compound probably reacts by mechanism A, though the total withdrawing effect (σ = 1.42) is greater than that of the 4-nitro (σ^- = 1.26). To probe further into this possible change we decided to extend the range of electron-withdrawing substituents by considering pyridine derivatives with the aza function being regarded as an aromatic substituent.

We have previously noted[6] the similarity in effects of the 4-nitro and 4-aza groups in the methanolysis of *N*-arylacetamides. In this paper we report on the reactivities of the heterocyclic entities **3, 4,** and **5**.[7] Though the Hammett equation



3 **4** **5**

is not generally applicable to ortho substituents, we have included 2-substituted compounds so as to compare reactivity of a complete series with their behavior in basic ester hydrolysis (BEh) and nucleophilic displacement of ring halogen (S_NAr) reactions. This latter reaction, also powerfully aided by electron-withdrawing substituents, provides the substituent effect data for aza functions[8] with which the correlation of the methanolysis results can be attempted. It is apparent from $\sigma^-_{4N^+Me}$ = 2.32 that we are indeed dealing with strong electron-withdrawing substituents.

Results and Discussion

Reactions were followed spectrophotometrically by either standard UV or stopped flow procedures. The species monitored are indicated in the tables. Pseudo-first-order rate constants were obtained at a series of methoxide concentrations and second-order rate constants, k_e, were obtained from k_ψ/[MeO⁻] or from a plot of k_ψ vs. [MeO⁻].

Rate constants at 100 °C were required for comparison with other arylbenzamide results. These were generally obtained by substantial extrapolation from Arrhenius plots.

The 2-methylazonium compound alone showed anomalous behavior in that addition of base produced an immediate UV spectral change, followed by a much slower change. This latter change gave a first-order plot but with nonreproducible results. An NMR investigation showed that more than one organic species was formed in the initial reaction and subsequent spectral changes were complex. The reaction was not investigated further.

Salt effects, generally unimportant in these reactions,[2] were noted in reactions of the other methylazonium isomers. It appeared that both ionic strength and specific salt effects were occurring since a certain minimum concentration of lithium perchlorate was needed before a linear k_ψ vs. [MeO⁻] plot

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Table I. Rate Data for the Basic Methanolysis of *N*-Methyl-*N*-Pyridinylbenzamides, 3, at 373 K[a]

Aza position	Registry no.	[MeO⁻], M	Anal. λ, nm	10^2k_e, $M^{-1}s^{-1}$
2	65052-85-9	0.008–0.016	305[b]	6.84
3	65442-07-1	0.02–0.04	315[b]	3.08
4	65052-87-1	0.002–0.004	252[b]	115

[a] No $LiClO_4$ present. [b] Product formation.

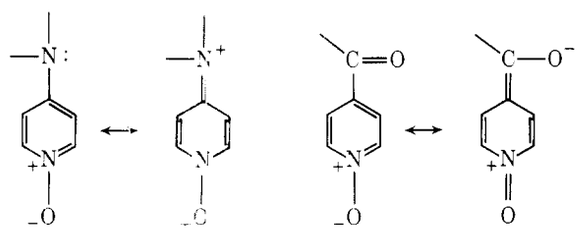
passing through the origin was obtained. Above this concentration (greater for the 3-methylazonium), good k_e values were obtained which decreased as the salt concentration was increased. For comparison with results for other substrates, values of k_e at zero ionic strength were estimated.

Aza 3. The rate constants in Table I show that positional reactivity is in the order 4 ≫ 2 > 3, as for S_NAr[8] and BEh[9] reactions. The substituent exerts its standard combination of resonance and inductive effects.

Aza Oxide 4. For the 3 and 4 isomers $k_\psi/[MeO^-]$ was constant. For the 2 isomer, a plot of k_ψ vs. [MeO⁻] was linear with a small positive intercept. This indicates that some reaction with methanol occurs, though the reason for such behavior is not clear.

Rate constants at 100 °C, and activation parameters, are listed in Table II. The amide reactions are characterized by a lower activation enthalpy but less favorable entropy than the corresponding S_NAr reaction. The reactivity order (4 > 3 > 2) may be compared with those for S_NAr[8] (4 > 2 > 3) and BEh[9] (2 ≈ 3 > 4) reactions.

A resonance withdrawing effect of the aza oxide must make a significant contribution to the overall electronic effect to obtain the order 4 > 3. Interaction of the developing charge on the exocyclic nitrogen with the ring determines reactivity and this is enhanced from the 4 position (**7**). Essentially the same activation occurs in the S_NAr reaction. In the BEh reaction, the reverse reactivity order seems best interpreted in terms of a rate-retarding resonance donation from the 4-aza oxide to the carbonyl group (**8**). The original interpretation[9]



7 **8**

was that the reactivity order was determined by the inductive effect, though the resonance donation possibility was recognized.

The low reactivity of the 2-aza oxide requires that an additional effect operates, probably of a steric nature though its origin is not clear. It presumably cannot arise from hindrance to methoxide attack on the carbonyl group as this should be more pronounced in the ester where the carbonyl group is closer to the pyridine ring.

Methylazonium 5. Reactions of the 4 isomer were carried out at various temperatures and three ionic strengths (curvature in a plot of k_ψ vs. [MeO⁻] was observed at $\mu \leq 0.05$). A value of 1×10^4 M^{-1} s^{-1} for k_e^{373} at $\mu = 0$ was estimated from the effect of $\mu^{1/2}$ on log k_e^{373} (obtained by temperature extrapolation). Since salt effects obey the Debye–Hückel equation only in dilute solution, this estimate is somewhat imprecise but any likely error does not affect the conclusions drawn below. For the 3 isomer, an ionic strength of 0.4 was

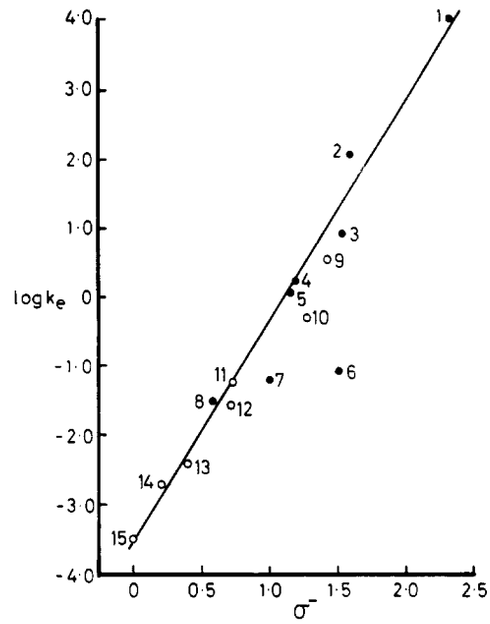


Figure 1. Hammett plot for methanolysis of *N*-aryl-*N*-methylbenzamides: (●), this work, (1) 4-N⁺Me, (2) 3-N⁺Me, (3) 4-N⁺O⁻, (4) 3-N⁺O⁻, (5) 4-N, (6) 2-N⁺O⁻, (7) 2-N, (8) 3-N; (○) data from ref 5, (9) 3,5-$(NO_2)_2$, (10) 4-NO_2, (11) 3-NO_2, (12) 4-CO_2Me, (13) 3-Br, (14) 4-Br, (15) H.

necessary to obtain a linear k_ψ vs. [MeO⁻] plot. Reactions in more concentrated salt solutions were not carried out and the k_e value at $\mu = 0$ (116 M^{-1} s^{-1}) was obtained by assuming that the ionic strength effect on rate was the same for the 3 and 4 isomers. As mentioned earlier, rate data were not obtained for the 2 isomer.

The reactivity order 4 ≫ 3 is also found in the S_NAr[8] and BEh[10] reactions and represents activation by inductive and resonance withdrawing effects.

Hammett Correlation. The rate data obtained in this work, together with published values,[1] make possible correlation of a reactivity range of 10^7 for the basic methanolysis of *N*-aryl-*N*-methylbenzamides. The Hammett plot is shown in Figure 1 (σ values for aza functions are those from S_NAr reactivity[8]). Considering the range of reactivities, uncertainties in some σ values, large temperature extrapolations to get some k_e^{373} values, and salt effects, the correlation is remarkably good. The lower reactivity of the 2-aza oxide has been commented on. The point for the 2-aza compound also lies off the plot. Since proximity effects would be expected to be different in the amide and S_NAr reactions, this deviation is not surprising.

The important point to emerge is that the plot is clearly linear with $\rho = 3.2$. Thus, in spite of an appreciable increase in substituent electron withdrawing power, there is no sign of downward curvature in the plot beyond the point for the 4-nitro substituent. The conclusion is therefore that the mechanism remains the same throughout, i.e., rate-determining breakdown of 1 (mechanism A). This seems entirely reasonable as the basic pK_a of *N*-methyl-4-pyridinimine is ca. 15,[11] i.e., it is only when one gets to the 4-methylazonium substituent that the leaving amine group has a basicity approaching that of methoxide. Thus, with less electron-withdrawing substituents, the amine is a poorer leaving group than methoxide (at least from an electronic viewpoint) and $k_{-1} > k_2$, the requirement for mechanism A.

The 4-nitro-substituted compound remains the anomaly. Though the deviation of the point from the Hammett correlation line is not gross, other evidence suggests that for this compound $k_2 \geq k_{-1}$ and mechanism B operates. We have

Table II. Rate Data for the Basic Methanolysis of *N*-Methyl-*N*-pyridinylbenzamide *N'*-Oxides, 4[a]

Aza oxide position	Registry no.	[MeO⁻], M	Anal. λ, nm	T, K	10^2k_e, M^{-1} s^{-1}	$10^2k_e^{373}$, M^{-1} s^{-1}
2	65442-08-2	0.004–0.04	328[b]	344	1.16[c,d]	8.67[e]
		0.01–0.04		354	2.43[c,f]	
		0.01–0.04		364	4.81[c,g]	
3	65442-09-3	0.01–0.02	399[b]	288.7	0.70	175[h]
		0.01–0.02		299	1.60	
		0.01–0.02		307	3.00	
4	65442-10-6	0.004–0.02	290[b]	283.7	4.91	829[i]
		0.004–0.02		289	7.20	
		0.004–0.01		295.7	12.7	

[a] No $LiClO_4$ present. [b] Product formation. [c] From plot of k_ψ vs. [MeO⁻]. [d] Intercept at [MeO⁻] = 0, 3×10^{-5} s^{-1}. [e] $\Delta H^{\ddagger}_{298}$ = 17.1 kcal; $\Delta S^{\ddagger}_{298}$ = −18 cal mol^{-1} K^{-1}. [f] Intercept = 5×10^{-5} s^{-1}. [g] Intercept = 1.1×10^{-4} s^{-1}. [h] $\Delta H^{\ddagger}_{298}$ = 13.4 kcal; $\Delta S^{\ddagger}_{298}$ = −22 cal mol^{-1} K^{-1}. [i] $\Delta H^{\ddagger}_{298}$ = 11.4 kcal; $\Delta S^{\ddagger}_{298}$ = −24 cal mol^{-1} K^{-1}.

Table III. Rate Data for the Basic Methanolysis[a] of Benzoylmethylamino-1-methylpyridinium Iodides, 5

Isomer	Registry no.	T, K	k_e,[b] M^{-1} s^{-1}	k_e^{373}, M^{-1} s^{-1}
4[c]	65442-11-7	285.5	32.6[d]	4590[e]
		297.4	72.7[d]	
		305.2	129[d]	
		286.5	17.2[f]	2220[g]
		298	37.3[f]	
		308	74.6[f]	
		288	14.5[h]	1880[i]
		297.4	28.4[h]	
		309	62.6[h]	
3[j]	65442-12-8	291.6	0.145[h]	21.8[k]
		304	0.369[h]	
		312	0.657[h]	

[a] [MeO⁻] = 0.01–0.07 M. [b] $k_e = k_\psi/[MeO^-]$. [c] Reactant disappearance at λ 305 nm followed. [d] $\mu = 0.1(LiClO_4)$. [e] $\Delta H^{\ddagger}_{298}$ = 11.4 kcal; $\Delta S^{\ddagger}$ = −12 cal mol^{-1} K^{-1}. [f] μ = 0.25. [g] $\Delta H^{\ddagger}_{298}$ = 11.4 kcal; $\Delta S^{\ddagger}_{298}$ = −13 cal mol^{-1} K^{-1}. [h] μ = 0.4. [i] $\Delta H^{\ddagger}_{298}$ = 11.6 kcal; $\Delta S^{\ddagger}_{298}$ = −13 cal mol^{-1} K^{-1}. [j] Product formation at λ 350 nm followed. [k] $\Delta H^{\ddagger}_{298}$ = 12.7 kcal; $\Delta S^{\ddagger}_{298}$ = −19 cal mol^{-1} K^{-1}.

previously[5] proposed an explanation involving steric and electronic effects for the apparently enhanced leaving group ability of this amine and can now comment further.

Steric compression exists in the tetrahedral intermediate from an NMe anilide relative to the situation for an NH anilide. While mechanism A is generally followed in both classes of compounds, this steric effect produces a difference in mechanism detail, evidenced by major activation parameter differences,[5] for example, irrespective of the nature of the aryl substituent. The strain in an NMe intermediate is relieved more by loss of amine (k_2) than by loss of methoxide (k_{-1}). Thus, k_{-1}/k_2(NMe) < k_{-1}/k_2(NH), but only for the 4-nitro substituent in the NMe series (in methanol) is the effect sufficient to tip the balance such that $k_{-1} > k_2$ and mechanism B operates. We previously concluded that the reason was that this steric compression was most severe where through conjugation between the exocyclic nitrogen and a para ring substituent is a major factor in the substituent's effect and coplanarity of the NMe group and ring is thereby required.

It seems that the change in substituent effect from aza to quaternized aza (N^+–O^- or N^+–Me) is very much due to an increased inductive effect while the resonance effect is relatively little altered.[12] Thus the planarity requirement for through conjugation is not critical, the steric effect of the methyl is not significantly increased, and, even in these highly reactive compounds, the leaving group ability is not increased sufficiently to produce a mechanism change. It can therefore be deduced that, in this reaction in methanol, a further example of mechanism B requires a substituent with either a total electron-withdrawing effect even greater than that provided by the methylazonium group or a resonance component of σ^- greater than that of the nitro group.

Experimental Section

For product analysis studies, 1-methyl-2-methylaminopyridinium iodide, mp 164–166 °C (lit.[13] mp 159–160 °C), 1-methyl-3-methylaminopyridinium iodide, mp 162–163 °C (Anal. Calcd for $C_7H_{11}IN_2$: C, 33.6; H, 4.4; N, 11.2. Found: C, 33.55; H, 4.5; N, 11.0), were prepared by reaction of the appropriate aminopyridine with methyl iodide in ethanol.

Aza 3. The isomeric *N*-methyl-*N*-pyridinylbenzamides were prepared by benzoylation of the corresponding methylaminopyridines.[14]

Methylazonium 5. Quaternization of the appropriate **3** with methyl iodide in ethanol gave 1-methyl-3-(benzoylmethylamino)pyridiniumiodide, mp 165–166 °C (EtOH) (Anal. Calcd for $C_{14}H_{15}IN_2O$: C, 47.5; H, 4.2; N, 7.9. Found: C, 47.5; H, 4.2; N, 7.6), and 1-methyl-4-(benzoylmethylamino)pyridinium iodide, mp 118–121 °C (EtOH) (Anal. Found: C, 47.2; H, 4.55; N, 7.6). The 2 isomer was initially obtained as a viscous oil. This was washed three times with ethanol in a dry ice–acetone bath. The residue slowly crystallized and gave 1-methyl-2-(benzoylmethylamino)pyridinium iodide, mp 170–173 °C, after recrystallization from ethanol. (Anal. Found: C, 47.4; H, 4.35; N, 7.7).

Aza Oxide 4. 2-Methylaminopyridine 1-oxide, mp 102–104 °C (benzene–ether) (lit.[15] mp 103–105 °C), was prepared by reaction of the pyridine with 1 mol of *m*-chloroperbenzoic acid in acetone at room temperature. The 1-oxide crystallized when the solvent was evaporated and ether was added. Benzoylation[16] gave the amide, mp 150–151 °C (lit.[16] mp 152–153 °C).

N-Methyl-*N*-(3-pyridinyl)benzamide *N'*-oxide, mp 178–180 °C (Anal. Calcd for $C_{13}H_{12}N_2O_2$: M, 228.08980. Found: M, 228.09136, by high-resolution mass spectrometry) was prepared by oxidation of the benzamide with *m*-chloroperbenzoic acid in acetone (2 h reflux) as for the amine above. The 4 isomer, mp 149–150 °C (lit. mp[16] 144–145 °C), was prepared similarly.

Kinetics. Rate measurements were carried out in methanol, with varying concentrations of methoxide, under pseudo-first-order conditions.[1] Where applicable, constant salt concentration was maintained with anhydrous lithium perchlorate. Reactions were carried out at least in duplicate and the individual values agreed within 4%.[17] The 3- and 4-methylaminopyridine 1-oxides were not prepared but in all other cases where kinetics were followed, infinity spectra agreed with those of authentic product mixtures.

Stock solutions of the methylazonium compounds, **5**, were made up in acidified methanol (2 drops of 2 M HCl to 50 mL of solvent) and reactions of the 4 isomer were followed by stopped flow kinetics, with k_ψ being calculated from six to nine $t_{1/2}$ measurements. All other reactions were followed by conventional UV monitoring. With the 3 isomer of **5**, where $t_{1/2} \approx 30$ s, it was necessary to preequilibrate separate solutions of amide and methoxide. These were then efficiently mixed within 5 s in the thermostated cell and subsequent reaction was followed.

Registry No.—1-Methyl-3-methylaminopyridinium iodide, 65442-13-9; 1-methyl-4-methylaminopyridinium iodide, 59435-96-0;

1-methyl-2-(benzoylmethylamino)pyridinium iodide, 65442-14-0; 2-methylaminopyridine 1-oxide, 54818-70-1.

References and Notes

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A Novel Intramolecular Homologation of a Phthalimide Group. 1,5,8-Trioxobenz[*f*]indolizidine[1a]

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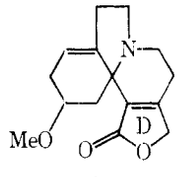
The Reformatsky reaction between ethyl bromoacetate and 1-acetoxy-4-phthalimido-2-butanone (**4**) produces in modest yield β-acetoxy-β-(2-phthalimidoethyl)butyrolactone (**10**), a product of normal addition to the ketone carbonyl, and in low yield a second compound, which arises from transformation of the phthalimide group. The latter product is shown to be 1,5,8-trioxobenz[*f*]indolizidine (**13**), a material which is of synthetic interest because of its structural relationship to the phenanthroindolizidine and Amaryllidaceae alkaloids. The precursor to ketone **4**, 1-diazo-4-phthalimido-2-butanone (**7**), was found to give **13** directly in preparatively acceptable yield via a novel rearrangement of its derived ketocarbene (**17**).

We are presently investigating a synthetic approach to the ring system of cocculolidine (**1**),[2] a member of the D-ring lactone subgroup of the Erythrina group of alkaloids. This approach requires the as yet unknown aminobutenolide **2**, and our immediate synthetic goal was the amine-protected lactone **3**.



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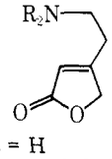
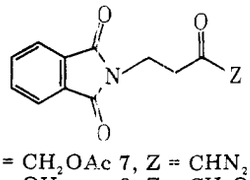
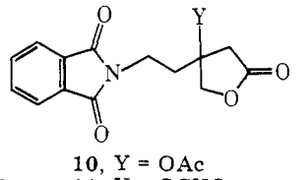


2, R = H
3, R = *o*-phthaloyl

The key step in an initial sequence designed to produce **3** was the Reformatsky reaction between ethyl bromoacetate and 1-acetoxy-4-phthalimido-2-butanone (**4**). This ketone was



4, Z = CH_2OAc
5, Z = OH
6, Z = Cl
7, Z = CHN_2
8, Z = CH_2OCHO
9, Z = CH_2Cl



10, Y = OAc
11, Y = OCHO
12, Y = OH

readily prepared in four steps from β-alanine (3-aminopropionic acid) via intermediates **5**, **6**, and **7**, respectively.

The major product of the Reformatsky reaction was the acetoxylactone **10**, which was formed in modest yield (20%) and presumably arose from normal addition to the ketone followed by transesterification and cyclization. This reaction also produced a second, highly colored, product "A" in lower yield (5%), whose elemental analysis indicated an empirical formula of $C_{12}H_9NO_3$ and whose spectral data indicated that it was not derived from normal addition to the starting ketone. The structure of this product was assigned on the basis of the following.

The ^1H NMR spectrum of the ketone **4** shows a typical A_2X_2 pattern for the adjacent methylene groups: a pair of two-proton triplets at δ 2.9 and 4.1. (J = 8 Hz). The spectrum of A shows these signals unchanged, implying that the NCH_2CH_2CO grouping remains intact in the product. In contrast, the singlets due to the acetate methyl group [δ 2.2 (3 H)] and the 1-methylene group [δ 4.7 (2 H)] in the starting material are absent in the product. In addition, the aromatic protons in **4** show the compact, symmetrical multiplet [δ 7.8 (4 H)] which is typical of N-substituted phthalimides, whereas in A a complex signal [δ 7.6–8.2 (4 H)] appears, suggesting a loss of symmetry in the substitution pattern of the aromatic ring. The only remaining peak in the spectrum of A is a broadened singlet [δ 6.5 (1 H)] which disappears on addition of D_2O.

The transformation of the phthalimide group and loss of ester functionality are both immediately evident from the IR spectrum: the peaks of the starting material **4** at 1715 (strong) and 1780 cm^{-1} (moderate), characteristic of phthalimides, and at 1750 cm^{-1} (OAc) are absent in A. Somewhat surprising is that A also lacks the absorption of **4** at 1730 cm^{-1} due to the simple ketone group. Instead, the product exhibits a strong peak at 1685 cm^{-1}, moderately strong peaks at 1700 and 1675 cm^{-1}, and a very strong band at 1630 cm^{-1}. The spectrum of A shows additionally a broad peak at 3240 cm^{-1}, which correlates with the singlet at δ 6.5 in the NMR spectrum.

Consideration of mechanistic possibilities in view of the above data leads to the benzindolizidine **13** as the structure of A.

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