methoxybenzylhydroxylamine, 55606-48-9; *N*-*o*-nitrobenzylhydroxylamine, 37558-77-3; *N*-*o*-chlorobenzylhydroxylamine, 55606-45-6; *N*-*o*-methoxybenzylhydroxylamine, 55606-46-7; α-bromotoluene, 100-39-0; α-chlorotoluene, 100-44-7; *p*-nitro-α-bromotoluene, 100-11-8; *N*-benzylhydroxylamine, 622-30-0; *p*-methylbenzyl chloride, 104-82-5; *N*-bromosuccinimide, 128-08-5; phenyliodoso acetate, 3240-34-4; mercuric oxide, 21908-53-2; iodine, 7553-56-2; ceric ammonium nitrate, 16774-21-3.

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Photochromism of Quinolylhydrazones. III.[1] The Mechanism of Isomerization of the Photocolored α-Quinolylimino-(*Z*)-hydrazone to the α-Quinolylamino-(*E*)-hydrazone

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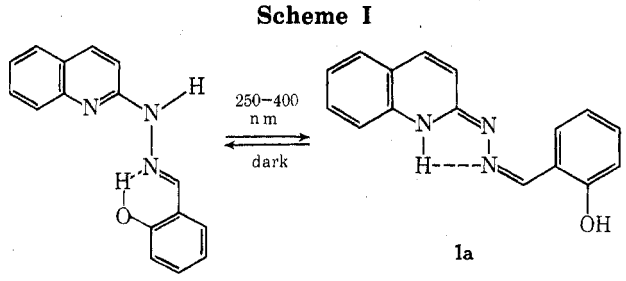
The kinetics and mechanism of the thermal decay of the photocolored form **1a** of salicylaldehyde 2-quinolylhydrazone (**1**) are reported. Two isomerization reactions, viz., α-imino- to α-aminoquinoline and $Z \rightarrow E$ hydrazone, are involved. The first conversion occurs via an intramolecular transfer of the phenolic hydrogen to the α-imino group. This is deduced on the basis of medium effect, concentration effect, and base inhibition studies. The decay of the 8-nitro colored form **2a** confirms this and implicates the quinoline NH as the source of the phenolic hydrogen of the uncolored form. The overall deuterium isotope effect of 1.84 denotes the non-rate-determining nature of the participation of the OH and NH. Since plots of the logarithm of the decay rate constant k vs. solvent Z or E_T (30) values show linear relationship and large negative $\Delta S^{\ddagger}$ values accompany the decay process, a rotation mechanism is postulated for the $Z \rightarrow E$ hydrazone isomerization. Also, acid catalysis substantiates the mechanistic scheme proposed for the decay process.

The photochromic phenomena of anils[2] and hydrazones[3] are generally observed only in a solid matrix. The instability of these colored forms in solution is typified by the *N*-salicylidene anil in the trans-quinonoid structure,[4] which showed a half-life of 1 msec at 30° in ethanol.[5a] The transient hydrazone photocolored species remains elusive. By contrast, the photochromism of salicylaldehyde 2-quinolylhydrazone (**1**) has been shown as follows (Scheme I).[1]

Scheme I



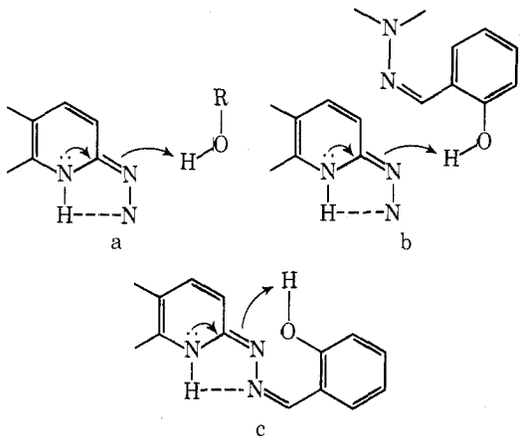
1 **1a**

The quinolylhydrazone **1** in ethanol is readily converted to the colored form **1a** when irradiated in the uv region of 250–400 nm at room temperature. This colored species has shown remarkable stability in both protic and aprotic solvents at room temperature. The availability and stability of **1a** thus afforded us an opportunity to investigate the relatively unexplored isomerization of α-heterocyclic imines and *Z* hydrazones. While *E,Z* isomerizations of the azomethine double bond in aldimines[5] and ketimines[6] have been the subjects of intensive studies, there is as yet no reported mechanism for the interconversions of hydrazones. This article details the kinetics and mechanisms of these isomerizations. The sequence of events reported herein also represents the first elucidated thermal decay process of the hydrazone photochromism.

Results and Discussion

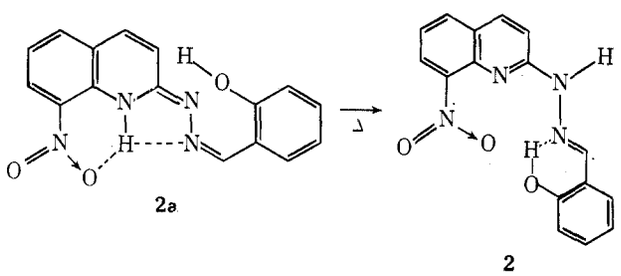
Intramolecular Hydrogen Transfer. In the isomerization of **1a** to **1**, involving imine → amine and $Z \rightarrow E$ hydrazone conversions, one or more hydrogen transfer steps must intervene. They may occur inter- or intramolecularly as shown in Scheme II. Scheme IIa supposes a hydrogen transfer between **1a** and a protic solvent. That this is not generally applicable is shown by (1) the instant conversion of **1a** to **1** when the colored form is heated to its melting point at 152° in an evacuated sealed tube, and (2) the decay constant of **1a** to **1** at 25° in an aprotic medium such as dimethyl sulfoxide (1.2×10^{-6} sec^{-1}) is similar to that in ethanol (3.0×10^{-6} sec^{-1}). Scheme IIb assumes intermolecular transfer between adjacent molecules of **1a**. Such a mechanism should be facilitated by increasing concentrations of **1a**. However, when the decay of **1a** was followed in ethanol at 25°, varying the concentration of **1a** from 4×10^{-5} *M* to 20×10^{-5} *M* caused only negligible change in the first-order rate constant (k, 10^{-6} sec^{-1}, 2.11 and 2.0, respectively). A corollary observation was made in methylcyclohexane, a solvent which facilitates aggregation of solute molecules. In this case, the decay constant k (10^{-6} sec^{-1}, 25°) actually decreased from 2.56 at 0.5×10^{-5} *M* to 1.25 at

Scheme II



ten times the concentration. While the concentration effect is insignificant, indicating the inoperation of Scheme IIb, the addition of 1 equiv of pyridine suppressed the rate of decay of **1a** in benzene (5.13×10^{-5} *M*, 25°) by a factor of 50. These rate data are therefore suggestive of the free phenolic proton being involved in an intramolecular protonation of the α-imine (cf. Scheme IIc). Further elucidation of the role of the phenolic proton was derived from the isomerization of the 8-nitro colored form **2a**. A KBr pellet of **2a** (1% by weight) was heated at 100° and monitored by ir spectroscopy. The sharp band at 3295 cm^{-1}, assignable only to the stretching mode of the unchelated phenolic OH, diminished gradually in intensity with a concomitant increase of a new sharp band at 3345 cm^{-1} for the exocyclic amino hydrogen of the uncolored form **2**. These assignments are firm since the quinoline NH in **2a** and the phenol OH in **2** are strongly chelated and should appear as broad, indistinct bands.[7] Furthermore, this 8-nitro photochromic pair also lends insight into the participation of the quinoline N hydrogen of the colored form in the decay process. Thus, the presence of the 8-nitro group in **2a** retarded the rate of decay by a factor of 5 compared to that of the parent colored form **1a** in ethanol at 79°. This may be attributed to the intramolecular chelation of the quinoline N hydrogen in **2a**, thus inhibiting its transfer to the adjacent hydrazone nitrogen which would labilize the carbon nitrogen double bond (Scheme III). Evidence of such internal

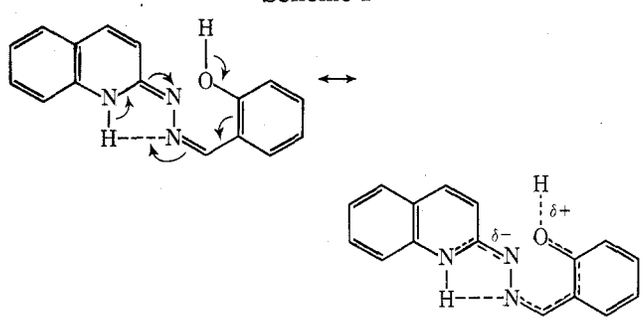
Scheme III



chelation is that the ν(asym,sym)[8] of the 8-nitro group in **2** at 1530 and 1352 cm^{-1}, respectively, are reduced to a weak band at 1530 cm^{-1} in **2a**.

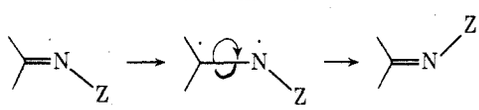
The net effects of these two intramolecular hydrogen transfers during the isomerization of the colored to the uncolored form are that (1) the α-amino hydrogen of **1** is derived from the phenolic proton of **1a** and (2) the ring N hydrogen of **1a** becomes the salicylidene hydrogen of **1**. It appears that specific isotope effect on the rate of decay of the colored form **1a** would detail the rate-determining nature of these steps. Specifically deuterated colored form **1a**, e.g., NH, OD, or ND, OH, could not be secured owing to deuterium scrambling even in aprotic solvents. In their place was prepared the N,O-dideuterated derivative of **1a**. By treating the 83% N,N,N′-trideuterated α-quinolylhydrazine with the 82% O-deuterated salicylaldehyde in benzene, a 70% N,O-dideuterated derivative of **1** was prepared, which, upon irradiation at 365 nm, was converted to **1a**. The percentage deuteration was made by ^1H NMR analysis. The decay rate constant k (10^{-3} min^{-1}, 56°) of the 70% O,N-dideuterated colored form in cyclohexane at 7.6×10^{-5} *M* was 7.54 ± 1.08 compared to 9.69 ± 0.88 for the undeuterated **1a** under the same conditions. These rate data translate to an overall kinetic isotope effect of 1.84. This is far short of the primary deuterium isotope effect of 9 for the tautomerization involving ND or 11 involving OD deduced by Hine.[9] Plausible interpretations of such weak isotope effect are (1) these hydrogen transfer steps are not rate determining, implying that the $Z \rightarrow E$ hydrazone isomerization is, and (2) the O–H and N–H bonds in **1a** are already stretched prior to the transfer steps (Scheme IV).

Scheme IV

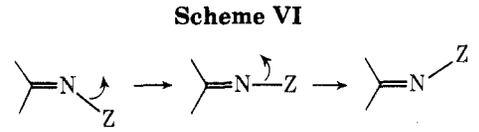


Rotation of the *Z* Hydrazone. In addition to the intramolecular hydrogen transfer steps deduced above, the salicylaldehyde hydrazone azomethine double bond must undergo $Z \rightarrow E$ isomerization to complete the decay of the colored form. Three potential mechanisms for such isomerization are shown as follows (Schemes V–VII).[10] Scheme V

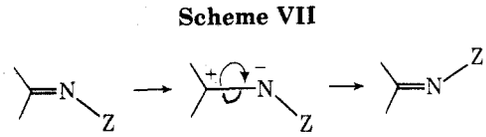
Scheme V



Scheme VI



Scheme VII



involves homolytic cleavage of the carbon–nitrogen double bond and closely parallels the rotational trans ⇄ cis isomerization of alkenes or azo compounds. This mechanism is usually dismissed because of the large activation energy involved in alkene isomerization ranging from 36 to 60 kcal mol^{-1} while that of azo compounds is even higher.[10] Scheme VI, the so-called "lateral shift" or inversion mechanism, is related to the inversion known for amino compounds.[11] The inversion mechanism is the preferred one to account for the low activation energy observed for aldimines and ketimines.[10] The third mechanism, Scheme VII,

Table I
Kinetic and Activation Parameters for the Decay of 1a at 25° [a]

Solvent	$k \times 10^7$, sec	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal mol^{-1}
1 Ethanol	30.20 (±0.0)	12.15 (±1.3)	−42.2 (±4.5)	24.7
2 Dimethyl sulfoxide	12.10 (±2.7)	5.9 (±1.8)	−62.8 (±5.2)	24.6
3 Methylcyclohexane	10.85 (±3.6)	9.0 (±1.6)	−53.1 (±4.9)	24.8
4 Dimethylformamide	6.8 (±0.6)	15.5 (±1.2)	−33.0 (±3.1)	25.3
5 Hexamethylphosphoramide	3.1 (±0.7)	17.1 (±1.1)	−28.5 (±2.9)	25.6
6 Dioxane	2.7 (±0.6)	14.6 (±1.3)	−37.5 (±1.6)	25.8
7 Toluene	2.4 (±0.1)	15.4 (±0.4)	−34.0 (±1.2)	25.5
8 *tert*-Butylbenzene	2.1 (±0.4)	10.9 (±0.9)	−49.9 (±2.7)	25.8
9 Benzene	1.1 (±0.0)	15.7 (±2.6)	−35.6 (±4.1)	26.3

[a] From a computer-assisted least-square routine. The concentration of 1a was ~4.3×10^{-5} M for all solvents.

known as rotation, involves polarization of the carbon–nitrogen double bond.[11] Unlike the nonionic inversion in Scheme VI, the rotation mechanism is particularly susceptible to solvent effects.[11] We therefore undertook a study of the kinetics and activation energies of the isomerization of **1a** as a function of the solvent medium.

Table I summarizes the first-order rate constants k, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ obtained in nine different solvents of various types (i.e., protic, aprotic–dipolar, nonpolar, and aromatic). Attempts to correlate the solvent effect with rate in terms of the dielectric constant of the solvent resulted in a random distribution of points. This in itself does not indicate a nonpolar reaction, since Wiberg[12] has shown that the dielectric constant may not be useful in describing the solvent effect on a dipolar species. Furthermore, Frost and Pearson[13] contended that the correlation of rate with gross dielectric constant is very misleading, since the interaction of an ion or dipole with a nonpolar solvent is much greater than would be expected, this being particularly true of aromatic solvents, which are sometimes good for ionic reactions despite their low dielectric constant. Thus, other solvent polarity parameters, e.g., the Z values compiled by Kosower[14] and the E_T (30) proposed by Dimroth,[15] were employed. The Z values arise from the sensitivity of the charge transfer band of 1-alkylpyridinium iodides to solvent polarity.[14] The E_T (30) is based on solvent effect on the charge transfer transition energy of the pyridinium phenol betaines.[15] Both of the Z and E_T (30) vs. log k plots for the decay of the colored form **1a** in these solvents at 25° give a linear relationship as shown in Figure 1. This linear correlation is indicative of a polar transition state for the rate-determining step, implicating the rotation scheme VII for the $Z \rightarrow E$ hydrazone isomerization.

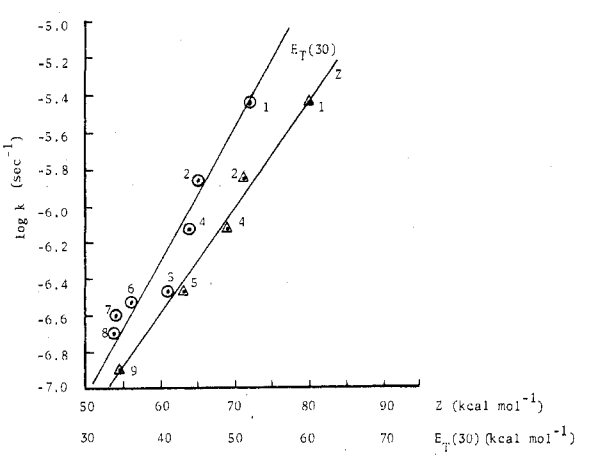


Figure 1. Plots of log k vs. solvent polarity parameters [Z,[14] E_T (30)[15]] for the decay of **1a**. Numbers refer to solvent systems in Table I. [No Z or E_T (30) values are reported for methylcyclohexane (solvent 3)].

Further inspection of Table I reveals a uniformly high negative entropy of activation for the decay reaction regardless of solvent types. This large negative $\Delta S^{\ddagger}$ is consonant with the polar rotation mechanism as depicted in Scheme VII. The substantial variation (29–63 eu) of the negative $\Delta S^{\ddagger}$ in the various solvents is worthy of note. According to Leffler,[16] large variations in $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ do not necessarily indicate a change in mechanism as long as there is a linear relationship between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ from one solvent to the next. The linear relationship, known as the compensation law or the isokinetic relationship, is indeed observed as shown in Figure 2.

Comparison of these decay data with those reported for the $Z \rightarrow E$ isomerization of salicylaldehydephenylhydrazone[17] and *N*-salicylideneaniline[5a] is shown in Table II. It is seen that the rate constant and the activation energies for the α-quinolylimino-(*Z*)-hydrazone (**1a**) are quite comparable to those for the phenylhydrazone. However, the aniline anil, which isomerized about 100,000 times faster with one-third of the $\Delta S^{\ddagger}$ loss, is in a class by itself. Since anils

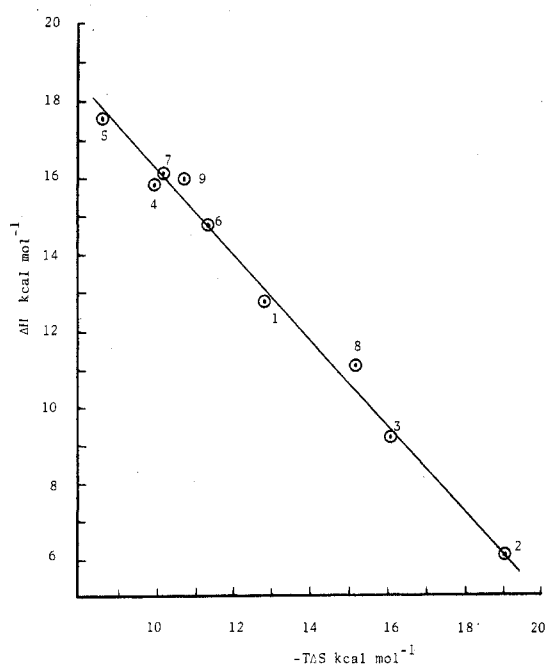


Figure 2. Isokinetic plot for the decay of **1a** in nine solvent systems. Numbers refer to solvent systems in Table I.

Table II
Comparison of Kinetic and Activation Parameters of $Z \rightarrow E$ Isomerization

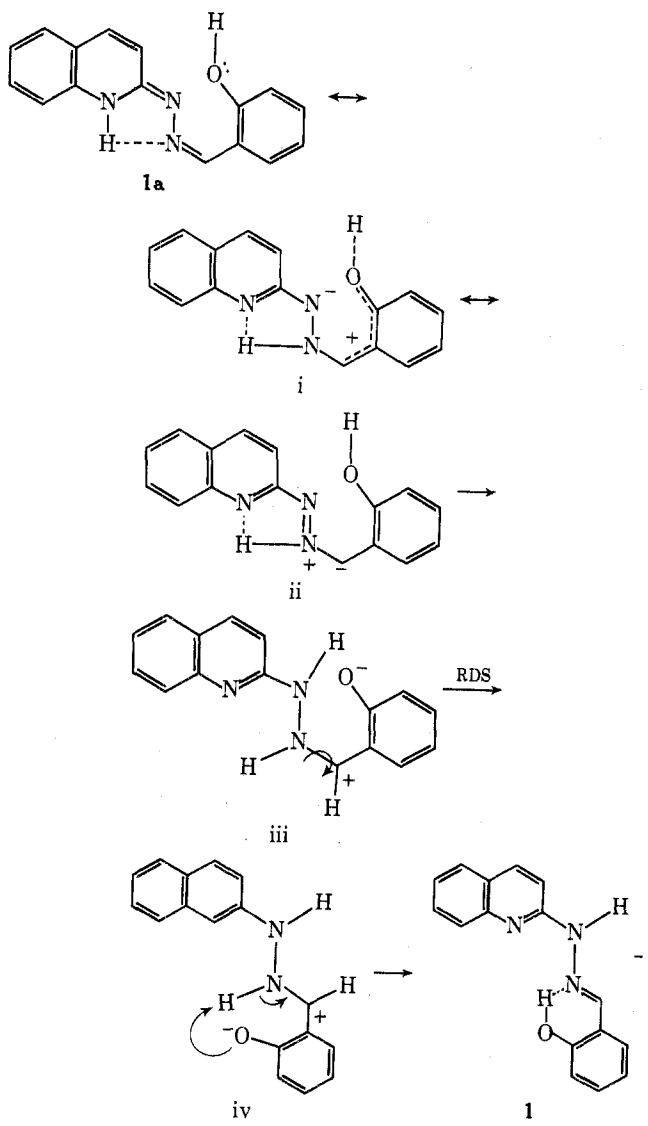
Compd	Solvent	k, sec^{-1} (°C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
1a	Ethanol	3.7×10^{-6} (32)	12	−42	25
Salicylaldehyde-phenylhydrazone[a]	Ethanol–cyclohexane (3:1)	1.15×10^{-5} (37)	14	−34	24
N-Salicylidene-aniline[b]	Ethanol	1.67 (30)	14	−11	17

[a] Reference 17. [b] Reference 5a.

have been shown to undergo $Z \rightarrow E$ isomerization by inversion (Scheme VI),[5c] it appears most likely that the $Z \rightarrow E$ isomerization of **1a** and the phenylhydrazone proceeds via rotation (Scheme VII).

Decay Mechanism of the Colored Form 1a. Given the two intramolecular hydrogen transfers and the rotation mechanism of the *Z* hydrazone, the sequence of events can be arranged as shown in Scheme VIII. Thus, electron delocalization in **1a** affords the mesomeric forms i and ii. These dipolar structures allow the transfer of the quinoline N hydrogen to the *Z*-hydrazone nitrogen to form iii, thereby facilitating its rotational isomerization to iv. It then follows that the intramolecular migration of the phenolic proton to the α-imino nitrogen should precede the hydrazone double bond rotation. The reverse order would necessitate a most awkward intramolecular hydrogen rearrangement. The acid catalysis provides credence to this reaction sequence. Thus, the presence of 0.8 equiv of acetic acid in a 1×10^{-4} *M* solution of **1a** in ethanol at 32° increased the decay rate by a factor of 5. The probable site of protonation in **1a** is the α-imino nitrogen. The added proton source therefore obviates the need of the phenolic hydrogen transfer via the strained seven-membered ring to the α-imino nitrogen.

Scheme VIII



Experimental Section[18]

Salicylaldehyde 2-Quinolylhydrazone (1). A mixture of 1.59 g (10 mmol) of 2-hydrazinoquinoline (Eastman, recrystallized) and 1.22 g (10 mmol) of salicylaldehyde in 150 ml of 95% ethanol was refluxed for 5 hr. The solution was concentrated, the crystalline precipitate was collected, and recrystallized twice from ethanol, yielding 1.44 g (55%) of **1**: mp 203°; uv λ_{max} (EtOH) (log ε) 358 nm (4.387), 310 s (4.230), and 237 (4.406); NMR (Me_2SO-d_6) δ 11.10 (s, 2), 8.50 (s, 1), and 8.27–6.82 (m, 10).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.98, H, 4.98; N, 15.96. Found: C, 73.36; H, 5.11; N, 16.13.

Colored Form 1a. A solution of 0.1 g (0.4 mmol) of salicylaldehyde 2-quinolylhydrazone (**1**) in 125 ml of 95% ethanol was irradiated with a Sylvania Black Lamp Blue (366 nm) for 14 days. The solution was evaporated to dryness, the residue was dissolved in 25 ml of ether, and the latter was chromatographed on silica gel G preparative plates of 1 mm in thickness with chloroform as eluent. The uv fluorescent band nearest to the solvent was eluted with ether, and 0.09 g (90%) of the orange-colored form **1a** was isolated: mp 152°; uv λ_{max} (EtOH) (log ε) 400 nm (4.220), 298 (4.176), 289 (4.204), and 247 (4.344); NMR ($CDCl_3$) δ 11.30 (s, 1) and 7.99–6.65 (m, 12).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.98; N, 15.96. Found: C, 72.89; H, 5.07; N, 15.73.

Salicylaldehyde 2-(8-Nitro)quinolylhydrazone (2). A mixture of 2.04 g (10 mmol) of 2-hydrazine-8-nitroquinoline (prepared from 2-chloro-8-nitroquinoline[19]) and 1.22 g (10 mmol) of salicylaldehyde in 150 ml of 2-propanol was refluxed for 5 hr. The solution was concentrated, and the crystalline precipitate was recrystallized twice from 2-propanol, giving 1.85 g (60%) of **2**: mp 204–206°; uv λ_{max} (EtOH) (log ε) 440 s nm (3.878), 370 (4.182), 335 (4.279), 302 (4.369), and 240 (4.450); NMR (Me_2SO-d_6) δ 12.02 (s, 1), 10.78 (s, 1), 8.77 (s, 1), and 8.53–6.93 (m, 9).

Anal. Calcd for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 61.90; H, 3.76; N, 18.07.

Colored Form 2a. A solution of 0.1 g (0.3 mmol) of **2** in 125 ml of an acetone–water (9:1) mixture was irradiated with a Sylvania Black Lamp Blue (366 nm) for 14 days. Upon standing and slow evaporation, 0.06 g (60%) of the colored form **2a** was obtained as red crystal: mp 206–208°; uv λ_{max} (EtOH) (log ε) 442 nm (4.164), 358 s (4.021), 295 (4.415), and 238 (4.433).

Anal. Calcd for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 62.32; H, 4.21; N, 17.94.

Kinetic Measurements. The rate studies were carried out in 1-cm quartz cuvettes which could be sealed with ground glass stoppers. The temperatures employed in the study were varied from room temperature to some temperature below the boiling point of the solvent employed by means of a constant-temperature bath. The absorbance of the colored species was determined in the various solvents using a Cary 14 spectrophotometer at zero time and at regular intervals after being placed in the constant-temperature bath. In all cases, four readings were made for each sample, and at least three different temperatures were used for each solvent sys-

tem. The first-order rate constant, k, was obtained from the straight line plot of log A vs. time. The thermodynamic values, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$, as well as the rate constant, $k_{25°}$, were determined by standard methods.[20] The activation parameters were determined by a computer-assisted least-square curve fit of plots of log k vs. $1/T$. Standard deviations were obtained from the equation

$$S = \sum [(X_i - X)^2/n - 1]^{1/2}$$

N,O-Dideuterated Derivative of 1a and the Isotope Effect. A mixture of 34.5 g (283 mmol) of salicylaldehyde and 11.0 g (611 mmol) of D_2O (99.8% D) in 25 ml of anhydrous dioxane was heated at reflux for 12 hr followed by distillation to remove the solvents. The process was repeated and the salicylaldehyde-*O*-*d* was distilled, bp 63° (3 mm), 82% deuteration by NMR integration of the residual OH resonance: (neat) δ 11.07 s (0.18 H), 9.7 s (1 H), 7.3 m (2 H), 6.8 m (2 H).

A mixture of 0.69 g (4 mmol) of 2-hydrazinoquinoline and 10 g (556 mmol) of D_2O (99.8% D) in 25 ml of anhydrous dioxane was refluxed under a dry nitrogen atmosphere for 72 hr. The solvent was removed by distillation and the process was repeated. The resulting N,N,N′-trideuterated 2-hydrazinoquinoline was recrystallized from ligroin, 83% deuteration by NMR integration: ($CDCl_3$) δ 7.78–6.62 m (6 H), 4.87 s (0.5 H).

A mixture of 0.123 g (1 mmol) of salicylaldehyde-*O*-*d* and 0.162 g (1 mmol) of N,N,N′-trideuterated 2-quinolylhydrazine in 5 ml of anhydrous benzene was heated at reflux for 4 hr. The solution was concentrated and the crystalline precipitate was collected and recrystallized twice from benzene to yield the N,O-dideuterated **1**, 70% deuteration, determined by NMR: (Me_2SO-d_6) δ 11.1 broad s (0.6 H), 8.5 s (1 H), 8.27–6.82 (10 H).

The uncolored, N,O-dideuterated salicylaldehyde-2-quinolylhydrazone (1) (2 mg) was placed in a 100-ml volumetric flask and dissolved in distilled, dried cyclohexane. The resulting solution was irradiated to the photostationary state. The absorbance at 400 nm was recorded on a Cary 14 spectrophotometer and samples of the solution were placed in a constant-temperature bath maintained at 56° for various lengths of time, with the absorbance being recorded periodically. From a plot of log A vs. time the rate constant k_D was determined to be $7.54 \pm 1.08 \times 10^{-3}$ min^{-1}. The entire process was repeated for the undeuterated 1 and the rate constant k_H was found to be $9.69 \pm 0.88 \times 10^{-3}$ min.$^{-1}$ The ratio k_H/k_D was found to be 1.84 after correction for the percentage deuterium in the sample by dividing by 0.70.

Acknowledgments. The decay data of **1a** in ethanol are taken from the Ph.D. Thesis of F. N. Bruscato, University of Louisville, 1969.

Registry No.—**1**, 55637-44-0; **1a**, 55570-67-7; **2**, 55570-68-8; **2a**, 55605-91-9; 2-hydrazinoquinoline, 15793-77-8; salicylaldehyde, 90-02-8; 2-hydrazino-8-nitroquinoline, 55570-69-9.

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Large-Scale Synthesis of Diammonium Acetyl Phosphate[1]

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A detailed procedure for the large-scale synthesis of diammonium acetyl phosphate (1) is presented. Ketene is used to acylate 100% phosphoric acid in ethyl acetate at −10°, and the resulting mixture of mono- and polyacetyl phosphoric acids converted to 1 by treatment with anhydrous ammonia in ethyl acetate–methanol at −10°. The product is obtained as an easily filtered, crystalline solid in ca. 90% yield and ca. 90% purity.

One limitation to the use of enzymatic catalysis in large-scale organic synthesis has been the expense of many of the common cofactors. As part of an effort to devise techniques that would make enzymatically catalyzed reactions requiring adenosine triphosphate (ATP) useful in practical synthesis, we have developed the reaction sequence outlined in eq 1 and 2 as a method for regenerating ATP from AMP and/or ADP.[2]

$$\text{ATP} + \text{AMP} \underset{\text{kinase}}{\overset{\text{adenylate}}{\rightleftharpoons}} 2\text{ADP} \quad (1)$$

$$2\text{ADP} + 2\text{AcP} \xrightarrow[\text{kinase}]{\text{acetate}} 2\text{ATP} + 2\text{Ac} \quad (2)$$

ADP is produced from ATP and AMP by phosphoryl transfer catalyzed by adenylate kinase. ADP is converted to ATP by reaction with acetyl phosphate (AcP) catalyzed by acetate kinase. Acetyl phosphate, the ultimate phosphorylating agent in this sequence, had been synthesized previously from phosphoric acid by acylation with acetyl chloride,[3] ketene,[4] isopropenyl acetate,[5] and acetic anhydride,[6,7] and isolated as the lithium or silver salts.[8] All of these procedures contain difficult work-up and isolation sequences. None are suitable for the preparation of acetyl phosphate in large quantity. Here we report a synthesis of diammonium acetyl phosphate from phosphoric acid, ke-