221 (M^+, 1), 164 (100), 149 (16), 141 (18), 121 (36). Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.27; H, 8.44; N, 6.09.

Irradiation of *N*-Formyl-*N*-methylcrotonamide (62). A solution of **62** (406 mg) in 25 mL of acetonitrile was irradiated for 6 h. After the usual workup it was found that the products consisted of mixtures both of **62** and cis isomer **63** (195 mg, **62**/**63** ratio of 65/35) and of *N*-methylcrotonamide **64** and cis isomer **65** (63 mg, **64**/**65** ratio of 60/40 estimated by GLC). Compound **64** was identical with an authentic sample prepared from crotonyl chloride and methylamine.

Registry No. 1, 64090-28-4; **2**, 70264-96-9; **3**, 71099-10-0; **4**, 70265-06-4; **5**, 71098-99-2; **6**, 4630-82-4; **7**, 6642-30-4; **8**, 71099-00-8; **11**, 75598-53-7; **12**, 71099-06-4; **13**, 75598-54-8; **14**, 71099-01-9; **15**, 71099-04-2; **16**, 75598-55-9; **17**, 70265-03-1; **18**, 7741-81-3; **19**, 75558-44-0; **20**, 75558-45-1; **21**, 74651-58-4; **22**, 75558-46-2; **23**, 74651-59-5; **24**, 75558-47-3; **25**, 75558-48-4; **26**, 71131-99-2; **27**, 71099-05-3; **28**, 71099-09-7; **29**, 70264-97-0; **30**, 18853-50-4; **31**, 71099-07-5; **32**, 71099-03-1; **33**, 71099-08-6; **34**, 75558-49-5; **35**, 75558-50-8; **36**, 75558-51-9; **37**, 75558-52-0; **38**, 75558-53-1; **39**, 75558-54-2; **40**, 75558-55-3; **41**, 75558-56-4; **42**, 1121-07-9; **43**, 26491-47-4; **44**, 75578-66-4; **45**, 74255-23-5; **46**, 74255-24-6; **47**, 74255-30-4; **48**, 74255-26-8; **49**, 74255-31-5; **50**, 74255-27-9; **51**, 74255-32-6; **52**, 74255-28-0; **53**, 74255-33-7; **54**, 75558-57-5; **55**, 75558-58-6; **56**, 75558-59-7; **57**, 75558-60-0; **58**, 74255-29-1; **59**, 74255-34-8; **60**, 75578-67-5; **61**, 75558-61-1; **62**, 75558-62-2; **63**, 75558-63-3; **64**, 1189-03-3; **65**, 70265-04-2.

Photoinitiated Radical-Forming Reactions of 2-Quinolinecarbonitrile At 77 and 331 K

Tullio Caronna, Sergio Morrocchi,[1] and Bruno M. Vittimberga*[2]

Chemistry Department, University of Rhode Island, Kingston, Rhode Island 02881

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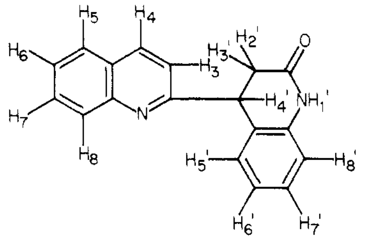
The photoinitiated dimerization of 2-quinolinecarbonitrile (1) in HCl-acidified 2-propanol/water (4:1) has been studied at 77 and 331 K at 250, 300 and 350 nm in unsensitized and benzophenone- and biphenyl-sensitized reactions. One principal product, a dimer lactam (5), is formed at all wavelengths through a triplet state of 1. ESR spectra taken in ethanol at 77 K show a signal for ethyl radical which is formed by a biphotonic process with 1 in acid solution. A mechanism is proposed for the reaction at 331 K which involves an electron transfer from 2-propanol to an upper triplet state of 1.

The photochemistry of 2-quinolinecarbonitrile (1) in HCl-acidified and unacidified alcohols has been the subject of a number of investigations.[3] These reactions generally lead to hydroxyalkylation of the 2-position with the replacement of the cyano group.[4] A second product, a triazapentaphene, is also isolated from reactions run in neutral alcohol. The benzophenone-photosensitized reaction of 1 in ethanol has been reported to yield only the pentaphene in a $T_1(\pi\pi^*)$ reaction.[5]

A few years ago we reported that when a solution of 4-pyridinecarbonitrile (2) and benzophenone in 1 M sulfuric acid in aqueous 2-propanol was irradiated at 350 nm, an electron-transfer–substitution reaction occurred, resulting in the formation of diphenyl(4-pyridyl)carbinol (3) and 4-benzhydrylpyridine (4) as major products.[6] We were surprised to find that when 2-quinolinecarbonitrile was used in this reaction, strikingly different results were obtained from those previously reported with 2-propanol alone.[4]

The reaction mixtures were prepared as described above for 2 by using hydrochloric acid instead of sulfuric acid and a ratio of alcohol to water of 4:1. The mixtures were deaerated by three successive freeze–vacuum–thaw cycles and the irradiations carried out under nitrogen in a Model RPR-100 Rayonet photochemical reactor at 350 nm. One major product (mp 248–249 dec) was isolated along with starting material.[7] The product was assigned structure 5 on the basis of the following data: IR (Nujol) 3030 (NH), 1680 (C═O, lactam), 1591, 831, 773, 747 cm^{-1}, no cyanide band is present; NMR (100 MHz, Me_2SO) δ 10.12 (s, 1 NH_1'), 8.34 (d, 1, H_8, J = 8.4 Hz), 7.97 (d, 1, H_4, J = 8.4 Hz), 7.72 (m, 3, H_5, H_6, H_7), 7.46 (d, 1, H_3, J = 8.4 Hz), 7.17 (d, 2, H_6', H_7', J = 7.0 Hz), 6.96 (d, 2, H_5', H_8', J = 7.0 Hz).



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Decoupling experiments ($CDCl_3$) confirmed that H_2', H_3', and H_4' comprise an ABX system of which the AB part appears as a pair of doublets centered at δ 2.92 and 3.11 ($J_{H_2',H_3'}$ = 16 Hz) further split into four doublets by coupling with H_4' [$J_{H_2'H_4'}$(cis) = 6 Hz, $J_{H_3'H_4'}$(trans) = 7 Hz].

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[1] Visiting Professor on leave from the Istituto di Chimica, Politecnico di Milano, Milan, Italy.

[2] To whom correspondence should be addressed.

[3] For a review of the photochemical reactions of six-membered-ring aromatic monoazaheterocycles with hydrogen containing solvents, see A. Lablache-Combier, "Elêments de Photochemie Avancée", P. Courtot, Ed., Hermann, Paris, 1972, p 289. See also the references therein.

[4] N. Hata, I. Ono, S. Matono, and H. Hirose, *Bull. Chem. Soc. Jpn.*, **46**, 942 (1973).

[5] N. Hata and R. Ohtsuka, *Chem. Lett.*, 1107 (1975).

[6] B. M. Vittimberga, F. Minisci, and S. Morrocchi, *J. Am. Chem. Soc.*, **97**, 4397 (1975).

[7] In reactions in which a small amount of 2-quinolinecarbonitrile was used (150 mg) with a relatively long irradiation time, a low yield of a second product was formed which eluted from a silica gel column with chloroform and melted at 193.5–195.5 °C. An infrared spectrum showed an OH peak but no CN peak, while the NMR spectrum showed only $C-CH_3$ and aromatic C–H.

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Table I. Photoreaction of 2-Quinolinecarbonitrile

sensitizer (E_T, kcal/mol)	λ, nm	t, h	% 5[a]
benzophenone (69)	350	12	41
none	350	11	7.5
none	300	10	12
biphenyl (65)	250	10	30
none	250	10	9.3

[a] Yields are based on starting material used. They would be essentially quantitative if based on the amount of starting material converted.

The X part appears as a coincidental triplet at δ 4.66. The usual band at approximately δ 8.8 for the hydrogen in the 2-position of the quinoline ring system is absent in the spectrum of 5.

An ultraviolet spectrum of a mixture of quinaldine and acetanilide taken in 2-propanol was essentially the same as that of 5 in the range 230–330 nm. Mass spectroscopy indicates a molecular weight of 274 (calcd mol wt 274). ^{13}C NMR analysis shows an 18-line spectrum with the carbonyl line at 169.27 ppm and the methylene at 43.68 ppm relative to Me_4Si. Thin-layer chromatography also indicated the presence of a highly fluorescent, polar product which could not be isolated in sufficient quantity to be studied. Analysis by gas chromatography showed that a substantial quantity of acetone was also formed in the reaction, though accurate yield data were not obtained.

The reaction of 1 with benzophenone could proceed by either of two paths: energy transfer from the triplet state of benzophenone to the triplet state of 1 or hydrogen atom abstraction from the solvent by the $T_1(n\pi^*)$ state of benzophenone followed by chemical sensitization of 1. Since the difference in energy between the lowest triplet states of 2-quinolinecarbonitrile (E_T = 59 kcal/mol)[4] and benzophenone (E_T = 69 kcal/mol) would be expected to fall in the range 5–10 kcal in acid solution, energy transfer should occur at a diffusion-controlled rate.[8,9]

In order to eliminate the possibility of electron or hydrogen atom exchange, we also used biphenyl as a sensitizer. The data obtained at three different wavelengths are shown in Table I.

In the reaction using benzophenone at 350 nm, essentially all the ketone is recovered unchanged, and no benzopinacol could be detected. If diphenyl ketyl were formed, the rate of bimolecular coupling should be fast enough to compete with chemical sensitization of 1 by the ketyl. From these results, it may be concluded that both benzophenone and biphenyl serve as photosensitizers in this reaction and that the triplet state is the photoreactive state leading to 5.

In order to determine whether or not for HCl-acidified 2-quinolinecarbonitrile the initial rate of appearance of radicals (v_0) is related to the incident light intensity, I, by the equation $v_0 = kI^n$, we undertook an ESR study in which a 10^{-3} molar solution of 1 in 10^{-2} molar HCl in absolute ethenol was irradiated at 77 K. The irradiations were carried out by using a 10-W xenon–mercury lamp focused on the cavity of the ESR instrument. A signal was immediately observed at 3277 G which rapidly intensified with time. Surprisingly, an analysis showed this signal to be that of ethyl radical ($CH_3CH_3\cdot$) rather than the expected radical of 2-quinolinecarbonitrile. The concentration of radicals was plotted as a function of time, t, by using three different light intensities and v_0 determined at t = 0 (Figure 1). A plot of log v_0 vs. log I gave a straight line with n = 1.6 (r = 0.99) (Figure 2). From this value of n, it may be concluded that the formation of the ethyl radical in this reaction proceeds by a biphotonic process.[10,11]

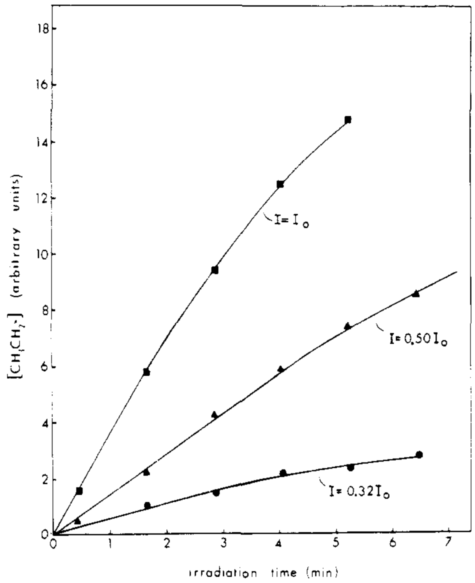

Figure 1. Plot of ethyl radical concentration for $I = I_0$ (■), $0.50I_0$ (▲), and $0.32I_0$ (●) vs. irradiation time in minutes.

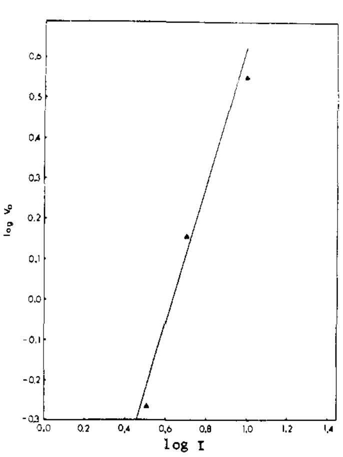

Figure 2. Plot of the logarithm of the initial rate of ethyl radical formation (v_0) vs. the logarithm of the light intensities (I).

Though there is an indication of a small signal at the center of that of the ethyl radical which could be attributed to the 2-quinolincarbonitryl radical, this assignment could not be confirmed.

Lablache-Combier et al.[10] previously reported that the photoreaction of quinoline in methanol acidified with HCl also proceeds by a biphotonic process at 113 K and suggested a mechanism in which an electron is transferred from methanol to an upper triplet state of quinoline.

The question arises as to whether or not a biphotonic reaction of 1 to form a dimer lactam could also occur at 331 K. In this regard, an attempt was made to do the ESR study at a higher temperature, but without success. As the melt temperature of the ethanol was reached, the signal

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[8] S. L. Murov, "Handbook of Photochemistry", Dekker, New York, 1973, p 62.

[9] By use of the rate constants for reaction in pure 2-propanol, it can be estimated that energy transfer should be favored by roughly a factor of 25 over hydrogen atom abstraction. This value was calculated by assuming a diffusion-controlled T–T energy tranfer and $K_d = 3.2 \times 10^9$ L mol^{-1} s^{-1} for 25 °C and a rate constant for hydrogen abstraction $k_r = 1.28 \times 10^6$ L mol^{-1} s^{-1}. See G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967), for the procedure used.

[10] A. Castellano, J. P. Catteau, and A. Lablache-Combier, *Tetrahedron*, **31**, 2255 (1975), and references therein.

[11] In a similar experiment using quinoline under neutral conditions, ethyl radical formed in a monophotonic reaction, n = 1.15.

Scheme I

$$2\text{-CNQ}[S_0] \xrightarrow{h\nu} 2\text{-CNQ}[S_1] \tag{1}$$

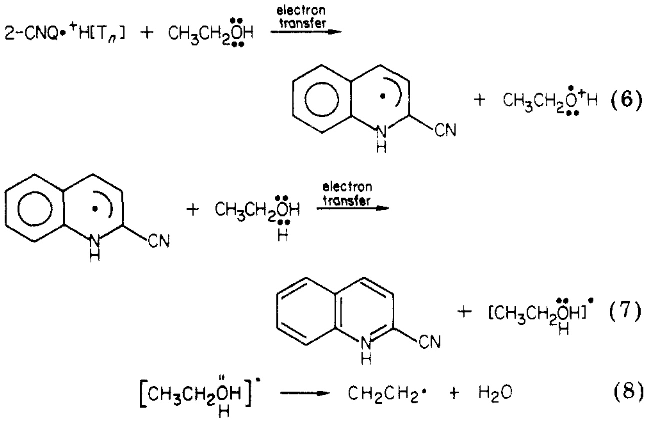
$$2\text{-CNQ}[S_1] \rightarrow 2\text{-CNQ}[T_1] \tag{2}$$

$$2\text{-CNQ}[T_1] \xrightarrow{h\nu} 2\text{-CNQ}[T_n] \tag{3}$$

$$2\text{-CNQ}[T_n] + \text{R-}\ddot{O}^+H_2 \rightarrow 2\text{-CNQ}[S_0] + [\text{R-}\ddot{O}^+H_2][T_1] \tag{4}$$

$$CH_3CH_2OH + [\text{R-}\ddot{O}^+H_2][T_1] \rightarrow \text{R}\cdot + H_3O^+ + CH_3\dot{C}HOH \text{ (not detected)} \tag{5}$$

Scheme II



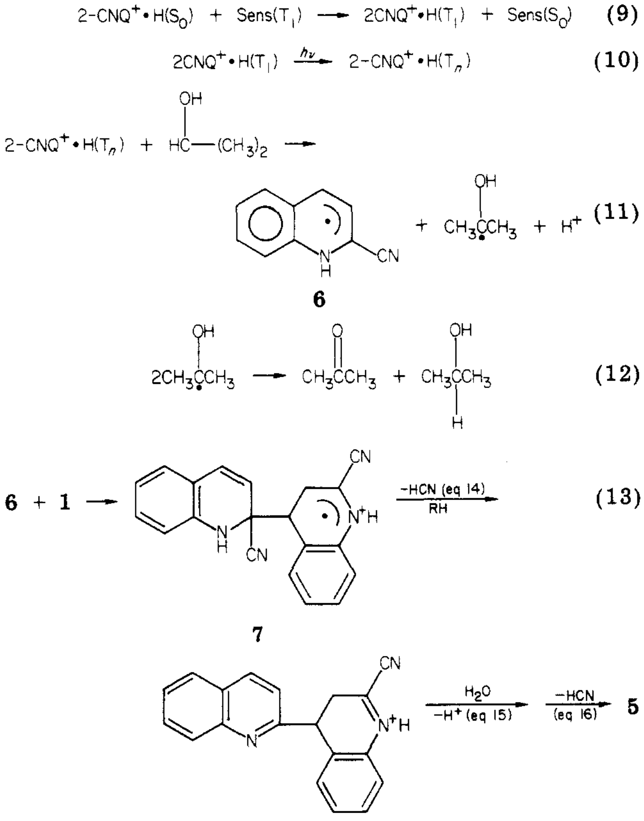
disappeared. When benzophenone was used at 77 K, a strong band which had its origin in benzophenone was the only observable signal.

We propose that the photon dependence of ethyl radical formation reflects the photochemistry of the nitrogen base. There are two different biphotonic mechanisms, however, that could lead to ethyl radical formation at 77 K. One of these is by energy transfer from a doubly excited state of the nitrogen base as shown in Scheme I and the other by electron transfer to the σ^* state of the C–O bond as shown in Scheme II. When the reaction at 77 K was repeated on a macro scale, starting material was isolated (85%) along with some hydrolysis product. No other products were detected. At 77 K an electron could also be transferred to an unprotonated alcohol molecule as is the case with unacidified solutions. This transfer would lead to a radical anion which should decompose immediately to ethyl radical and hydroxyl ion. Both of the mechanistic catagories shown in Schemes I and II have been reported in the literature.[12,13]

Through the lifetime of the 2-quinolinecarbonitrile $[T_1]$ state could be decreased through bimolecular quenching by impurities, the decrease in absolute alcohol is not likely to be significant.

With regard to the probability of bimolecular reaction from the T_2 state, the normal internal conversion rate for T_2 states falls in the range 10^{11}–10^{10} L mol^{-1} s^{-1}. If the T_2–T_1 energy gap of 2-quinolinecarbonitrile is sufficiently large so that Franck–Condon factors slow down the rate of $T_2 \rightarrow T_1$ internal conversion, then intermolecular reaction from T_2 with alcohol would be possible. Moreover, the nπ^* state of six-membered monoazaaromatic compounds is the state that is generally involved in hydrogen atom abstraction.[10] In acidic solutions, both the S_1 and T_1 states of **1** should be $\pi\pi^*$,[14] though because of the small energy gap between the $S_1(n,\pi^*)$ and $S_1(\pi,\pi^*)$ states, vibronic interactions could cause some degree of mixing. Hydrogen atom abstractions from the $T_1(\pi\pi^*)$ state should occur with a very low probability, allowing other mechanisms to become important. In this case, we suggest that an electron is transferred from 2-propanol to a protonated upper excited state of **1** (eq 11). The radical **6** then attacks a ground-state 2-quinolinecarbonitrile molecule in the 4-position as previously described for the reaction of other radicals with this molecule.[15]

Scheme III



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The mechanism for the photosensitized reaction is shown in Scheme III.

In an attempt to determine the likelihood of singlet-state involvement in the formation of the radical **6** the reaction of **1** at 300 nm was repeated under nonacidic conditions without benzophenone. If the $S_1(n,\pi^*)$ state is involved, **5** should form without triplet sensitizer.[16] This was not found to be the case; nearly all (>94%) of **1** was recovered unchanged.

In a previous publication, Hata and Ohtsuka[5] had reported that irradiation of **1** and benzophenone in 2-propanol yielded only a pentaphene in a $T_1(\pi,\pi^*)$ reaction. When we repeated this reaction using a 4:1 mixture of 2-propanol/H_2O, most of the **1** was converted to two principal products. Both of these compounds contain cyano bands in the infrared spectrum, though neither yielded **5** when treated with either acid or base in aqueous

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[12] S. Siegel and H. Judeikis, *U.S. Gov. Res. Rep.*, **39**(21), 28 (1964); *Chem. Abstr.*, **62**, 3566 (1965).

[13] S. Siegel and K. Eisenthal, *U.S. Gov. Res. Rep.*, **39**(21), 160 (1964); *Chem. Abstr.*, **62**, 3566 (1965).

[14] F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Am. Chem. Soc.*, **92**, 2745 (1970).

[15] T. Caronna, G. Fronza, F. Minisci, and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, 2035 (1972).

[16] When 2-quinolinecarbonitrile was irradiated in 5:2 benzene/2-propanol at 300 nm under nonacidic conditions, the starting material was recovered in an amount greater than 96%. These less polar conditions should have increased the possibility of attaining an initial $S_1(n\pi^*)$ state.

2-propanol, indicating that they were not precursors of **5**. The triplet state is again the photoreactive state, though the reaction takes a different course from that in acid solution. In the absence of alternate reaction paths, acetone ketyl has a sufficiently long half-life to undergo disproportionation.[17]

We do not know, at this time, why our results differ so much from those previously published. It is clear, however, that solvation plays an important role. We are now studying the mechanism further and hope to report on these results at a later time.

Experimental Section

Melting points are corrected and were determined on a Thomas-Hoover Unimelt melting point apparatus. The NMR spectra were recorded on a Varian XL-100 spectrometer at 100 MHz and a Varian CFT 20 spectrometer at 80 MHz using tetramethylsilane as an internal standard. IR spectra were determined on a Beckman Acculab 4 spectrophotometer, and UV spectra were measured on a Cary Model 15 spectrophotometer. All solvents used in this study were spectroscopic grade except in certain large-scale irradiations in which "Baker Analyzed" reagent grade 2-propanol from the J. T. Baker Chemical Co. was used. The spectroscopic grade benzene was obtained from Matheson Coleman and Bell and the 2-propanol from the Mallinckrodt Chemical Co. The benzophenone used was certified reagent grade (mp 47.5–48.1 °C) obtained from the Fisher Scientific Co. The elemental analysis of **5** was performed by Micro Analysis, Inc., Wilmington, DE.

ESR Spectrometry. All ESR measurements were made with a Varian E Line EPR spectrometer using an E101 microwave bridge and a V-770 power control. The spectra were run at 3277 G with a 100-kHz modulation frequency.

All samples were irradiated with a Schoeffel Instrument Corp. xenon–mercury lamp, Model 4800A, having a 10-W output focused through two quartz lenses on the cavity of the ESR spectrometer. Nitrogen was bubbled through each sample for 15 min prior to irradiation which was carried out at 77 K with solutions of 10^{-3} M 2-quinolinecarbonitrile in 10^{-2} M HCl in absolute ethanol.

Each run was made by taking spectra on a time scale of 60 s with a time lapse between spectra of 12 s. By use of neutral filters, runs were made at three light intensities, I_0, $0.501I_0$, and $0.32I_0$. Line widths and shapes were the same in every spectrum so that relative radical concentrations were determined by measuring peak heights at maximum amplitude.

Synthesis of 2-Quinolinecarbonitrile. 2-Quinolinecarbonitrile was prepared in two steps. First, 1-benzoyl-2-cyano-1,2-dihydroquinoline was prepared from quinoline, potassium cyanide, and benzoyl chloride by the method of Reissert.[18] Then the dihydroquinoline was converted to 2-quinolinecarbonitrile by treatment with phosphorus pentachloride according to the method of Kaufmann and Dändliker.[19] The final product was purified first by chromatography on silica gel and then by recrystallization from ligroin. The overall yield was approximately 50%.

Irradiation of 2-Quinolinecarbonitrile with Benzophenone in Acidic Aqueous 2-Propanol. A typical large-scale reaction mixture was prepared from 3.0 g (0.019 M) of 2-quinolinecarbonitrile, 5.0 g (0.027 M) of benzophenone, 2.3 cm^3 of 37% analytical grade hydrochloric acid (0.028 M), 80 cm^3 2-propanol, and 20 cm^3 of water.

The mixture to be irradiated was placed in a quartz reaction tube for irradiations carried out at 250 nm and in Pyrex tubes for irradiations carried out at 300 and 350 nm. The mixtures were subjected to three freeze–vacuum–thaw cycles and the irradiations carried out under nitrogen in a Model RPR-100 Rayonet photochemical reactor. The reaction mixtures, which were light yellow-orange at the end of the irradiation period, were made strongly basic with 6 N sodium hydroxide solution and after the addition of 10 mL of water were thorughly extracted with chloroform (3 × 20 mL). The combined extracts were dried over anhydrous magnesium sulfate, and the drying agent was removed by filtration and the solvent by evaporation at reduced pressure. Addition of benzene to the residue caused most of the dimer to crystallize. The product was isolated by filtration, and the filtrate was subjected to chromatography on silica gel using mixtures of benzene, chloroform, and methanol in increasing polarity. In this way, benzophenone, unreacted 2-quinolinecarbonitrile, and additional dimer could be isolated in that order. Essentially a quantitative recovery of benzophenone was obtained in all reactions.

Anal. Calcd for dimer **5**, $C_{18}H_{14}N_2O$ (mol wt 274.3): C, 78.80; H, 5.15; N, 10.21. Found: C, 78.58; H, 5.18; N, 10.40.

The data in Table I were obtained with 0.30 g of 2-quinolinecarbonitrile and proportionately reduced quantities of the other components as described above. In the biphenyl experiment, 400 mg of biphenyl was used instead of benzophenone with 9 mL of 2-propanol and 1 mL of water.

The yields in Table I are based on the amount of starting material used. They would be essentially quantitative if they were based on the amount of starting material converted.

Experiments which used 0.150 g of 2-quinolinecarbonitrile gave higher yields of dimer product (68%) and, in addition, a low yield (8 mg) of a second product which eluted from a silica gel column with chloroform and melted at 193.5–195.5 °C. An infrared spectrum showed an OH peak but no CN peak, while the NMR spectrum showed only C–CH$_3$ and aromatic C–H.

Irradiation of 2-Quinolinecarbonitrile in Benzene/2-Propanol at 300 nm. A solution of 0.150 g of 2-quinolinecarbonitrile in 10 mL of benzene and 4 mL of 2-propanol was placed in a Pyrex reaction tube and subjected to three freeze–vacuum–thaw cycles. The tube was then irradiated under nitrogen for 8 h at 300 nm. At the end of this time, the top of the solution was yellow and the bottom purple. After being allowed to stand overnight, the whole solution became light orange. Evaporation of this solution to dryness under vacuum gave a crystalline solid with a light orange tint. An infrared spectrum (KBr) was identical with that of 2-quinolinecarbonitrile. The recovery was essentially quantitative.

Irradiation of 2-Quinolinecarbonitrile with Benzophenone in Aqueous 2-Propanol (1:4) at 350 nm under Neutral Conditions. A solution prepared with 0.150 g of 2-quinolinecarbonitrile (9.73 × 10^{-4} M), 0.280 g of benzophenone (1.50 × 10^{-3} M), and 10 mL of a 4:1 solution of 2-propanol/water was placed in a Pyrex reaction tube and subjected to three freeze–vacuum–thaw cycles. Irradiation was carried out under nitrogen for 8 h at 350 nm. At the end of this time, the mixture was dark purple. Then 2 drops of 6 N sodium hydroxide were added followed by 10 mL of water, and the mixture extracted thoroughly with chlorform. The combined extracts were dried with anhydrous magnesium sulfate, and the drying agent and solvent were removed as usual, leaving a red oil as a residue. Column chromatography on silica gel gave 0.041 g of 2-quinolinecarbonitrile, 0.235 g of benzophenone, 0.057 g of a compound that eluted from the column with chloroform, and 0.034 g of another compound that eluted with chloroform–methanol (5:1). Both of these compounds contained strong C≡N bonds at 2265 cm^{-1} with no carbonyl peak in the infrared spectrum. On treatment with 6 N HCl in 4:1 2-propanol/H$_2$O neither of these compounds yielded dimer **5**.

Irradiation of 2-Quinolinecarbonitrile in Acidic Ethanol Solution at 77 K. A solution was prepared containing 0.075 g of 2-quinolinecarbonitrile in 5 mL of absolute ethanol and 0.3 mL of 37% analytical grade hydrochloric acid. Nitrogen was bubbled into the sample for a period of 30 min, and then the solution was frozen in liquid nitrogen in a transparent Pyrex Dewar. Irradiation was carried out at 300 nm through the Dewar in a Rayonet Photochemical Reactor for a period of 6 h. At the end of ths time, the frozen sample had a light yellow tint. The sample was kept frozen in the dark for a period of 1.25 h, and it was thawed, and 3 mL of distilled water was added. The mixture was then made basic with 10% sodium hydroxide solution and extracted several times with 15 mL of chloroform. The combined extracts were dried, and the solvent was removed as usual, leaving a residual

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[17] Acetone ketyl does not dimerize very readily to form pinacol. For examples of reactions involving this ketyl, see: S. G. Cohen, S. Aktipis, and H. Rubinstein, *Photochem. Photobiol.*, **10**, 45 (1969); S. A. Weiner, *J. Am. Chem. Soc.*, **93**, 425 (1971); F. A. Lamb and B. M. Vittimberga, *J. Org. Chem.*, **38**, 3520 (1973).

[18] A. Reissert, *Chem. Ber.*, **38**, 1610 (1905).

[19] A. Kaufmann and P. Dändliker, *Chem. Ber.*, **46**, 2927 (1913).

oil with a yellow tint that crystallized immediately (69 mg). Infrared analysis showed this sample to be essentially all starting material (85% recovery). Column chromatography of the entire sample on silica gel separated 4 mg of a carbonyl compound which had an infrared spectrum similar to that of the corresponding amide of 2-quinolinecarbontrile.

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Solvolyses of Secondary Sulfonates in Aqueous Ethanol and Acetone. Nonlinear *mY* Relationships due to Leaving Group and Medium Effects

T. William Bentley,*[1a] Christine T. Bowen,[1a] Herbert C. Brown,*[1b] and Frank J. Chloupek[1b,c]

Department of Chemistry, University College of Swansea, Swansea SA2 8PP, Wales, U.K., and the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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Solvolytic rate constants for secondary mesylates and tosylates in aqueous ethanol and in aqueous acetone are correlated with Winstein–Grunwald Y values. Curvature of these plots is greatest for tosylates in aqueous ethanol, especially for 2-adamantyl. Because mesylates show little or no curvature, it is argued that the results cannot be explained by mechanistic changes but by solvation effects of the leaving group in the mixed solvents. The parameter, m, measuring response to solvent ionizing power varies from 0.68 for isopropyl to 1.21 for 2-adamantyl mesylate in aqueous acetone at 25 °C. An alternative solvent ionizing power parameter for tosylates, Y_{OTs}, and the solvent nucleophilicity parameter, N_{OTs}, are evaluated for 20% ethanol/water, 20% acetone/water, and 40% acetone/water. It is proposed that solvolyses of substrates having the same (or very similar) leaving group should be compared if reliable mechanistic information (e.g., nucleophilic solvation effects) is required. The tendency for "dispersion" of correlation lines for various binary mixed solvents appears to be due to both leaving-group effects and to variations in solvent nucleophilicity. By helping to account for curvature and dispersion in mY correlations, this work supports recent work in which mechanistic information was deduced from similar correlations.

The relative rates of solvolyses of primary, secondary, and tertiary substrates are markedly dependent on solvent.[2] Recent studies of the dependence of solvent on the solvolytic reactivity of secondary substrates have provided important new insights into the mechanisms of these reactions.[3-5] Solvolysis rates of both secondary[3-5] and tertiary[6] tosylates can be correlated by two-parameter linear free energy relationships based on 2-adamantyl tosylate (I, R = p-$CH_3C_6H_4$) as a model compound for a scale of solvent ionizing power designated Y_{OTs}.[3b] This solvent scale now appears to be much more suitable for tosylates than the usual Y scale based on *tert*-butyl chloride, but the reasons for the inadequacies of Y values require further investigation.

The Y scale of solvent ionizing power is based on solvolyses of *tert*-butyl chloride [$m = 1$ at 25 °C, eq 1, where

$$\log (k/k_0)_{\mathrm{RX}} = mY \qquad (1)$$

k/k_0 is the rate of solvolysis in any solvent (k) relative to the rate of solvolysis in 80% v/v ethanol/water (k_0)] and was introduced in 1978 to correlate other S_N1-like solvolyses.[7a] Subsequently it was discovered that even S_N2 solvolyses of primary arenesulfonates in aqueous ethanol mixtures correlated quite well with Y values.[8,9] This now appears to be at least partly because mixtures of ethanol and water have similar nucleophilicities.[3b,10] During the course of our earlier work,[3a] we were surprised to find that solvolyses of secondary tosylates in the full range of aqueous ethanol mixtures did not correlate well with Y values. While good linear correlations were found for a range of solvents from ethanol to 50% v/v ethanol/water, there was upward curvature between data points for 50% v/v ethanol/water and pure water.[11] Because curvature of free-energy relationships is often associated with mechanistic changes,[12] we investigated this phenomenon in more detail.

Hydrolysis rate constants for many alkyl halides and methyl, ethyl, and isopropyl sulfonates have been determined in water[13] and in alcohol–water, acetone–water, and

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