Kinetics Studies of the Pyrolysis Reactions of Ethyl Aroyl(1-aroyl-1,2-dihydro-2-quinolyl)acetates

George F. Palladino and William E. McEwen*

Departments of Chemistry, U.S. Military Academy, West Point, New York 10996 and the University of Massachusetts, Amherst, Massachusetts 01003

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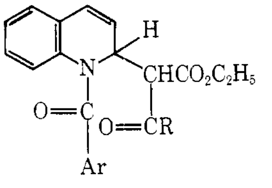
When ethyl benzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1a**) is heated in benzene solution, it is converted to a mixture of quinoline and ethyl *O*-benzoylbenzoylacetate (**2a**). The first-order rate constant at 76.4 °C is 1.95×10^{-6} s^{-1}. The rate is increased about ninefold when the more polar solvent, acetonitrile, is used in place of benzene. Substituent effects are also relatively small, and the presence of either electron-withdrawing or electron-donating substituents on either of the phenyl groups of **1a** causes an increase in the rate of thermolysis. These and other data suggest that spin-paired diradicals are formed as unstable intermediates in these reactions. Only one of the two possible geometrical isomers of **2** has been isolated from each pyrolysis reaction mixture, and, in the case of the thermolysis of ethyl benzoyl(1-*p*-methoxybenzoyl-1,2-dihydro-2-quinolyl)acetate (**1c**), the olefin has been assigned the structure of (*Z*)-ethyl *O*-(*p*-methoxybenzoyl)benzoylacetate, (*Z*)-**2c** (which is thermodynamically more stable than (*E*)-**2c**), on the basis of NMR spectral considerations.

Ethyl benzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1a**) and ethyl aceto(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1b**) have been obtained by the reaction of benzoyl chloride with ethyl benzoylacetate and ethyl acetoacetate, respectively, in quinoline solution.[1] It was also reported that **1a** and **1b** undergo pyrolysis to give quinoline and the *O*-acylated products, **2a** and **2b**, respectively. Whereas the earlier studies were carried out in order to obtain additional evidence about the mechanism of *O*-acylation of β-keto esters in the presence of tertiary amines,[2-8] the present study is concerned mainly with the scope and mechanism of the thermolysis reaction **1** → **2**.



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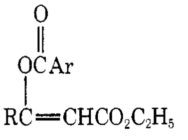
a, R = Ar = C_6H_5
b, R = CH_3; Ar = C_6H_5
c, R = C_6H_5; Ar = *p*-$MeOC_6H_4$
d, R = C_6H_5; Ar = *m*-ClC_6H_4
e, R = *p*-$MeOC_6H_4$; Ar = C_6H_5
f, R = *p*-$NO_2C_6H_4$; Ar = C_6H_5
g, R = C_6H_5; Ar = *p*-MeC_6H_4
h, R = *p*-FC_6H_4; Ar = C_6H_5
i, R = *p*-$NO_2C_6H_4$; Ar = *m*-ClC_6H_4



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Results

Seven new compounds of type **1** (**1c–i**) have been prepared and subjected to thermolysis in refluxing benzene for periods of 6–12 days. In each case, the product **2** was isolated in yields ranging from 41–89%. The rates of thermolysis at 76.4 ± 0.2 °C were also determined, and the results are summarized in Table I.

The rates of thermolysis of **1a** were measured at 76.4 ± 0.1 °C in solvents of different polarities. The solvents, specific rate constants, and dielectric constants, respectively are as follows: benzene, 1.95×10^{-6} s^{-1}, 2.28; *o*-chlorotoluene, 4.22×10^{-6} s^{-1}, 4.45; acetonitrile, 17.1×10^{-6} s^{-1}, 37.5.

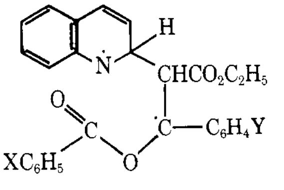
The rates of thermolysis of **1a** in *p*-xylene were measured at three different temperatures, and the results are as follows: 76.4 ± 0.2 °C, 11.3×10^{-6} s^{-1}; 86.4 ± 0.2 °C, 30.2×10^{-6} s^{-1}; 96.4 ± 0.2 °C, 84.6×10^{-6} s^{-1}. From these data, $\Delta H^{\ddagger}$ was calculated to be 26.6 ± 4.0 kcal mol^{-1} and $\Delta S^{\ddagger}$ at 76.4 °C to be −5.97 ± 4.05 cal mol^{-1} deg^{-1}.

Discussion

In a formal sense, the thermolysis of **1** to **2** plus quinoline may be classified as $\pi^2 + \pi^2 + \sigma^2 = \sigma^2 + \sigma^2 + \pi^2$ skeletal rearrangements.[9-11] However, the question remains whether these transformations are fully concerted,[12] involve a considerable degree of charge separation in the transition state, or involve spin-paired diradicals as unstable intermediates.

The possibility that the transition state for the conversion of **1** to **2** plus quinoline is characterized by a large degree of charge separation can be discounted readily. The relatively small change in rate with change in polarity of the solvent, the relatively small substituent effects, and the fact that the presence of either electron-donating or electron-withdrawing substituents in **1** lead to an increase in rate all support this conclusion.

As the massive exchanges between Huisgen[13] and Firestone[14-16] testify, it is a much more difficult matter to distinguish between a concerted process and one in which a spin-paired diradical is formed as an unstable intermediate. The small effects of changes of solvent polarity and of substituents on rate and the negative value of $\Delta S^{\ddagger}$ mentioned under Results are consistent with either mechanism. However, the fact that all of the substituents listed under formula **1**, regardless of whether they are electron withdrawing or electron donating, cause an increase in the rate of pyrolysis is more readily explained by the spin-paired diradical concept than by the assumption of a synchronous process.[17] In particular, the conversion of **1** (R = C_6H_4Y and Ar = C_6H_4X) to **2** via the spin-paired diradical **3** should show a stronger rate-enhancing effect of the substituent Y than that of X.[18] Examination of the data provided in Table I shows that the effect of Y is indeed greater than that of X, although, as expected, X also exerts some influence on the rate. Of course, more conclusive evidence will be required before a final decision about the mechanism can be reached.



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In all of the thermolysis reactions of **1**, only one geometrical

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Table I. Rate Data for the Thermolysis of Compounds of Type 1 at 76.4 ± 0.2 °C

1	$k \times 10^6$, s^{-1} [a]	Rel rate
a]1.95 ± 0.04	1.00	
c	5.32 ± 0.05	2.73
d	17.3 ± 0.40	8.87
e	15.5 ± 0.20	8.21
f	26.2 ± 1.50	13.4
g	2.99 ± 0.02	1.53
h	6.59 ± 0.12	3.38
i	35.0 ± 0.10	17.9

[a] Average deviation based on at least three determinations. As against these average deviation values, the corresponding P.M. values would probably indicate a deviation of about ±5–10%.

isomer of **2** resulted. Ethyl *O*-(*p*-methoxybenzoyl)benzoylacetate (**2c**) was chosen as the model for the determination of the geometry. The product of the thermolysis of **1c** had a mp of 95.0–95.3 °C, and it exhibited a vinyl proton resonance at δ 6.38 in its NMR spectrum. When subjected to irradiation by the procedure of Zechmeister and McNeely,[19] a mercury lamp and a vycor filter being used, the geometrical isomer of mp 109–110 °C was obtained, and it exhibited a vinyl proton resonance at δ 6.06.

A modification of the method of Pascual, Meir, and Simon,[20] which has also been discussed by Jackman and Sternhell,[21] can be used to determine the configurations of the two geometrical isomers of **2c**. The strict use of the additive constants of Pascual, Meir, and Simon[20] indicates that the *Z* isomer (vinylic proton cis to phenyl) would have a value of vinylic proton resonance at δ 0.20 units downfield from that of the *E* isomer. In addition, one can compare cis-to-phenyl and trans-to-phenyl proton shifts in a series of known olefins (the fundamental basis of the method of Pascual, Meir, and Simon[20]) and arrive at the conclusion that the cis-to-phenyl proton should resonate 0.47 ppm downfield relative to a trans-to-phenyl proton. By either rationale, it follows that the compound of mp 95.0–95.3 °C formed directly by the thermolysis of **1c** is (*Z*)-**2c**. This is the thermodynamically more stable isomer, and, by analogy, the more stable isomer of **2** may be assumed to be formed in all of the thermolysis reactions of **1**. It is not unreasonable that this should be so if a spin-paired diradical unstable intermediate is the precursor of the olefin.

As a control experiment, *E*-(**2c**), mp 109–110 °C, was subjected to the conditions of the thermolysis of **1c**, which gave (*Z*)-**2c** exclusively. No isomerization of the less stable (*E*)-**2c** to the more stable (*Z*)-**2c** was observed. Thus, (*Z*)-**2c** was formed directly from **1c** in the thermolysis reaction, and the result is related to the configuration of the transition state.[22]

Experimental Section

General. Melting points were obtained with a Mel-temp apparatus and are uncorrected. Infrared spectra were recorded on a Backmann IR-5, IR-10, or Acculab-2 spectrometer. ^{1}H-NMR spectra were obtained with either a Varian A-60 or a Perkin-Elmer R-12 spectrometer. Chemical shifts are reported as parts per million (δ) vs. Me_4Si as an internal standard in $CDCl_3$ solutions. UV spectra were obtained by use of a Perkin-Elmer Model 202 spectrometer. UV measurements for kinetics studies were obtained with a Cary Model 14 or a Beckmann Model DK2 spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory, University of Massachusetts, Amherst, Mass.

Preparation of Compounds of Type 1. Quinoline (Eastman) was distilled at reduced pressure (bp 63–64 °C at 1 mm) and collected over Drierite. Commercially available substituted benzoyl chlorides were used without further purification and commercially available substituted ethyl benzoylacetates were dried over Drierite and used without further purification.

Ethyl Benzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (1a). The preparation of **1a** was carried out as previously reported.[1,7] Recrystallization of the crude product from absolute ethanol gave material of mp 154–155 °C, somewhat higher than the value previously reported:[7] ^{1}H NMR δ 1.01 (t, 3 H), 3.85 (dq, 2 H), 4.60 (d, 1 H), 6.02 (dd, 1 H), 6.10–7.85 (16 H); IR, carbonyl peaks at 1741, 1690, and 1650 cm^{-1}. Anal. Calcd for $C_{27}H_{23}NO_4$: C, 76.22; H, 5.45; N, 3.29. Found: C, 75.98; H, 5.29; N, 3.36.

Ethyl Benzoyl(1-*p*-methoxybenzoyl-1,2-dihydro-2-quinolyl)acetate (1c). The procedure was the same as for **1a**. Quinoline (129 g, 1.0 mol), ethyl benzoylacetate (96 g, 0.5 mol), and *p*-methoxybenzoyl chloride (85 g, 0.5 mol) gave 111 g (49%) of **1c**: mp 137.1–138.5 °C; ^{1}H NMR δ 1.00 (t, 3 H), 3.75 (s, 3 H), 3.85 (2 H), 4.67 (d, 1 H), 5.90–7.90 (16 H); IR, carbonyl peaks at 1730, 1685, and 1640 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_5$: C, 73.83; H, 5.53; N, 3.08. Found: C, 73.75; H, 5.62; N, 3.07.

Ethyl Benzoyl[1-(3-chlorobenzoyl)-1,3-dihydro-2-quinolyl]acetate (1d). From 59 g (0.5 mol) of quinoline, 42.8 mL (0.25 mol) of ethyl benzoylacetate, and 27.9 mL (0.25 mol) of *m*-chlorobenzoyl chloride there was obtained 74.1 g (64%) of **1d**: mp 141.5–142.8 °C after recrystallization from ethanol; ^{1}H NMR δ 1.04 (t, 3 H), 3.88 (dq, 2 H), 4.60 (d, 1 H), 5.90–7.97 (16 H); IR, carbonyl peaks at 1740, 1690, and 1650 cm^{-1}. Anal. Calcd for $C_{27}H_{22}NO_4Cl$: C, 71.13; H, 4.72; N, 2.98; Cl, 7.55. Found: C, 70.96; H, 4.73; N, 3.00; Cl, 7.60.

Ethyl *p*-Methoxybenzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (1e). From 0.5 mol of quinoline, 0.25 mol of ethyl *p*-methoxybenzoylacetate, and 0.25 mol of benzoyl chloride there was obtained 59.5 g of **1e**: mp 157.7–158.1 °C after recrystallization from ethanol; ^{1}H NMR δ 1.02 (t, 3 H), ca. 3.82 (2 H), 3.89 (s, 3 H), 4.60 (d, 1 H), 5.92–7.92 (16 H); IR, carbonyl peaks at 1740, 1685, and 1650 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_5$: C, 73.83; H, 5.53, N, 3.08. Found: C, 73.73; H, 5.55; N, 2.93.

Ethyl *p*-Nitrobenzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (1f). From 0.1 mol of quinoline, 0.05 mol of ethyl *p*-nitrobenzoylacetate (dissolved in 75 mL of anhydrous ether), and 0.05 mol of benzoyl chloride there was obtained 2.6 g (11%) of **1f** as pale yellow crystals: mp 138.5–140.0 °C after recrystallization from ethanol; ^{1}H NMR δ 1.01 (t, 3 H), 3.86 (dq, 2 H), 4.60 (d, 1 H), 6.02–8.22 (16 H); IR, carbonyl peaks at 1740, 1698, and 1650 cm^{-1}. Anal. Calcd for $C_{27}H_{22}N_2O_6$: C, 68.92; H, 4.71; N, 5.96. Found: C, 68.72; H, 4.57; N, 5.98.

Ethyl Benzoyl(1-*p*-methylbenzoyl-1,2-dihydro-2-quinolyl)acetate (1g). From 0.156 mol of quinoline, 0.078 mol of ethyl benzoylacetate, and 0.078 mol of *p*-toluyl chloride there was obtained 8.47 g (25%) of **1g**: mp 147–148 °C after crystallization from ethanol; ^{1}H NMR δ 1.02 (t, 3 H), 2.3 (s, 3 H), 3.87 (dq, 2 H), 4.62 (d, 1 H), and 5.90–7.85 (16 H); IR, carbonyl peaks at 1730, 1683, and 1640 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NO_4$: C, 76.52; H, 5.73; N, 3.19. Found: C, 76.54; H, 5.64; N, 2.83.

Ethyl *p*-Fluorobenzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (1h). From 0.114 mol of quinoline, 0.057 mol of benzoyl chloride, and 0.057 mol of ethyl *p*-fluorobenzoylacetate there was obtained 9.68 g (38%) of **1h**: mp 169–170 °C after crystallization from ethanol; ^{1}H NMR δ 1.02 (t, 3 H), 3.88 (dq, 2 H), 4.57 (d, 1 H), 5.92–7.90 (16 H); IR, carbonyl peaks at 1725, 1670, and 1635 cm^{-1}. Anal. Calcd for $C_{27}H_{22}NFO_4$: C, 73.12; H, 5.00; F, 4.28; N, 3.16. Found: C, 72.56; H, 5.27; F, 4.20; N, 3.16.

Ethyl *p*-Nitrobenzoyl[1-(*m*-chlorobenzoyl)-1,2-dihydro-2-quinolyl]acetate (1i). From 0.12 mol of quinoline, 0.06 mol of ethyl *p*-nitrobenzoylacetate, and 0.06 mol of *m*-chlorobenzoyl chloride there was obtained 12.25 g (40.3%) of yellow **1i**: mp 132.5–133.5 °C after crystallization from acetone; ^{1}H NMR δ 1.01 (t, 3 H), 3.88 (dq, 2 H), 4.54 (d, 1 H), 5.90–8.30 (15 H); IR, carbonyl peaks at 1730, 1691, and 1648 cm^{-1}. Anal. Calcd for $C_{27}H_{21}N_2O_6Cl$: C, 64.22; H, 4.21; N, 5.55; Cl, 7.03. Found: C, 63.48; H, 4.62; N, 5.78; Cl, 6.66.

Ethyl β-Benzoxycinnamate (2a). A solution of 5.00 g (0.012 mol) of ethyl benzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**2a**) in 2.5 mL of dry benzene was refluxed. The solution gradually turned from colorless to a deep yellow color. After 12 days the reflux was discontinued and 50 mL of ether was added. The ether–benzene layer was extracted thoroughly with cold 10% HCl, cold 10% NaOH, and finally with water. The organic layer was then dried over Drierite and evaporated. The residue was dissolved in hot absolute ethanol and then cooled. A white crystalline solid was collected and identified as ethyl β-benzoxycinnamate by comparison with the physical properties of an authentic sample. The melting point was 85.5–86.5 °C and a mixture melting point test with an authentic sample[5] showed no depression. The IR spectrum was identical with that of the authentic sample.[5] The yield was 2.59 g (72.5%).

Ethyl β-*p*-Anisoxycinnamate (2c). The procedure was the same as for **2a**. From 3.0 g (0.0067 mol) of ethyl benzoyl(1-*p*-methoxybenzoyl-1,2-dihydro-2-quinolyl)acetate (**1c**) there was obtained 1.46 g (67.9%) of **2c**, a white crystalline solid, mp 90–95 °C. Recrystallization from absolute ethanol yielded a sample of mp 95.0–95.3 °C: ^{1}H NMR δ 1.15 (t, 3 H), 3.88 (s, 3 H), 4.12 (q, 2 H), 6.38 (s, 1 H), 6.82–8.30 (m, 9 H); IR, carbonyl peaks at 1715 and 1735 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 70.04; H, 5.48.

Ethyl β-*m*-Chlorobenzoxycinnamate (2d). From 3.0 g (0.0065 mol) of ethyl benzoyl(1-*m*-chlorobenzoyl-1,2-dihydro-2-quinolyl)acetate there was obtained 1.83 g (84.5%) of **2d**, a white crystalline solid, mp 86.5–87.5 °C. Recrystallization from absolute ethanol yielded a sample of mp 86.5–87.5 °C: ^{1}H NMR 1.18 (t, 3 H), 4.18 (q, 2 H), 6.41 (s, 1 H), 7.20–8.18 (m, 9 H); IR, carbonyl peaks at 1750 and 1720 cm^{-1}. Anal. Calcd for $C_{18}H_{15}ClO_4$: C, 65.35; H, 4.57; Cl, 10.73. Found: C, 65.25; H, 4.51; Cl, 10.70.

Ethyl β-Benzoxy-*p*-methoxycinnamate (2e). From 3.9 g (0.0067 mol) of ethyl *p*-anisoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1e**) there was obtained 1.55 g (72.1%) of **2e**, a white crystalline solid, mp 110–112 °C. Recrystallization from absolute ethanol yielded a sample of mp 111.5–112.8 °C: ^{1}H NMR δ 1.12 (t, 3 H), 3.83 (s, 3 H), 4.12 (q, 2 H), 6.28 (s, 1 H), 6.83–8.25 (m, 9 H); IR, carbonyl peaks at 1750 and 1720 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.91; H, 5.72.

Ethyl β-Benzoxy-*p*-nitrocinnamate (2f). From 0.50 g (0.0011 mol) of ethyl 4-nitrobenzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1f**) there was obtained 0.32 g (88.9%) of **2f**, yellow crystalline solid, mp 67.1–68.0 °C. Recrystallization from absolute ethanol yielded a sample of mp 67.1–68.0 °C: ^{1}H NMR δ 1.17 (t, 3 H), 4.18 (q, 2 H), 6.52 (s, 1 H), 7.25–8.50 (m, 9 H); IR, carbonyl peaks at 1749 and 1720 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}NO_6$: C, 63.34; H, 4.46; N, 4.10. Found: C, 63.29; H, 4.62; N, 4.00.

Ethyl β-*p*-Methylbenzoxycinnamate (2g). From 1.5 g (0.0034 mol) of ethyl benzoyl(1-*p*-methylbenzoyl-1,2-dihydro-2-quinolyl)acetate (**1g**) there was obtained 0.74 g (71%) of **2g**, a pale yellow crystalline solid, mp 97.5–99.0 °C. Recrystallization from absolute ethanol yielded material of mp 97.5–99.0 °C: ^{1}H NMR δ 1.12 (t, 3 H), 2.35 (s, 3 H), 4.06 (q, 2 H), 6.30 (s, 1 H), 7.00–8.10 (m, 9 H); IR, carbonyl peaks at 1738 and 1710 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.30; H, 5.79.

Ethyl β-Benzoxy-*p*-fluorocinnamate (2h). From 1.50 g (0.0034 mol) of ethyl 4-fluorobenzoyl(1-benzoyl-1,2-dihydro-2-quinolyl)acetate (**1h**) there was obtained 0.435 g (41%) of **2h**, a white crystalline solid, mp 90.2–91.0 °C. Recrystallization from absolute ethanol gave material of mp 90.2–91.0 °C: ^{1}H NMR δ 1.13 (t, 3 H), 4.13 (q, 2 H), 6.30 (s, 1 H), 6.95–7.32 (m, 9 H); IR, carbonyl peaks at 1738 and 1705 cm^{-1}. Anal. Calcd for $C_{18}H_{15}FO_4$: C, 68.78; H, 4.81; F, 6.05. Found: C, 68.99; H, 5.38; F, 6.17.

Ethyl β-m-Chlorobenzoxy-*p*-nitrocinnamate (2i). From 1.5 g (0.0030 mol) of ethyl 4-nitrobenzoyl[1-(3-chlorobenzoyl)-1,2-dihydro-2-quinolyl]acetate (**1i**) there was obtained 0.655 g (58.5%) of **2i**, a pale yellow crystalline solid, mp 98.5–99.5 °C. Recrystallization from absolute ethanol yielded a sample of mp 98.5–99.5 °C: ^{1}H NMR δ 1.20 (t, 3 H), 4.28 (q, 2 H), 6.48 (s, 1 H), 7.50–8.50 (m, 8 H); IR, carbonyl peaks at 1725 and 1700 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}NClO_6$: C, 57.53; H, 3.76; N, 3.73; Cl, 9.43. Found: C, 57.53; H, 3.82; N, 3.92; Cl, 9.58.

(*E*)-Ethyl β-Anisoxycinnamate. Ethyl β-anisoxycinnamate (1.0 g) from the pyrolysis of **1c** was dissolved in 100 mL of benzene and photolyzed by means of a Hanovia medium pressure mercury lamp having a vycor filter, the lamp being centered in the well of the reaction chamber. The reaction was followed by observing the disappearance of **2c** by use of VPC.

By use of TLC, 50% Skelly F–50% Ether being used as eluent, three spots were observed under UV light, one being the starting material and one trailing the starting material. The benzene was evaporated, and the residue was orange in color and smelled of a ketone. The residue was dissolved in 10 mL of hot ethanol and cooled. There was obtained 0.65 g (65%) of one product only, which melted sharply at 109–110 °C. Its NMR spectrum showed the same integration (9:3:3:2:1) as did the spectrum of the starting material, but the vinylic proton absorption had been shifted from δ 6.38 to 6.06. In all other respects, the NMR spectra were essentially the same.

The assignment of *E* and *Z* configurations was made on the basis of the observed ^{1}H-NMR shift of the vinylic proton according to the method of Pascual, Meir, and Simon[20] and also discussed by Jackman and Sternhell.[21]

Attempts to effect thermal isomerizations of the (*E*) isomer to the (*Z*) isomer were made by two methods. First, a purely thermal isomerization was attempted by refluxing 0.3 g of (*E*)-**2c** in benzene for 4 days. The 0.3 g of starting compound was recovered unchanged by evaporation of the solvent and recrystallization of the residue from ethanol. The product isolated exhibited a mp of 109–110.5 °C, and there was no change in its NMR absorption from that of the starting material, the *E* isomer.

To determine if the quinoline present in the reaction mixture was affecting the product formation, a solution of 0.3 g (0.0092 mol) of (*E*)-**2c** and 0.12 g of quinoline in benzene was refluxed for 6 days. At the end of 6 days the solvent was evaporated and the recovered starting material was purified by recrystallization from hot ethanol. The melting point of the product was 108–109 °C. The NMR spectrum showed no change from that of the starting material. Therefore, exposure to the reaction conditions does not cause conversion of (*E*)-**2c** to (*Z*)-**2c**.

Kinetics Studies

Materials. The preparation of the various 1,2-dihydroquinoline adducts (**1a–i**) has been described previously. Solvent purification was accomplished as follows: Benzene was distilled from sodium and collected over molecular sieves. Prior to kinetics experiments, it was distilled once more and the first 5–10 mL of distillate was discarded. Acetonitrile and *o*-chlorotoluene were distilled prior to use. Xylene was distilled from sodium prior to use.

Procedure. Two procedures were used to determine relative reaction rates.

1. In a 100-mL volumetric flask was placed 1.5–1.8 × 10^{-5} mol of a given 1,2-dihydroquinoline adduct. A given solvent contained in a round-bottom flask, purified as previously described, was placed in a constant temperature bath at 76.4 °C for 30 min. A 100-mL pipette was then used to transfer 100 mL of the solvent (usually benzene) at 76.4 °C into the 100-mL volumetric flask. The volumetric flask was swirled twice and immediately fitted with a rubber septum cap, secured with copper wire, and clamped in the constant temperature bath. Zero time was defined as the instant of complete delivery of the 100 mL of solvent. At 2- to 4-h intervals, a 2.00-mL aliquot was removed by the use of a hypodermic syringe fitted with a 9-in. needle. Quenching was accomplished by discharging the 2.00-mL aliquot into the wall of a 15-mL test tube which was maintained in a 20 °C bath. The UV measurement was taken directly from the aliquot. To check on the accuracy of quenching, samples were left at room temperature for 24 h with no detectable change in spectrum.

2. In a 250-mL volumetric flask was placed 3.3–4.1 × 10^{-5} mol of a given 1,2-dihydroquinoline adduct. The mass was then diluted to the 250-mL mark with a given solvent. The solution was swirled for 5 min and then 4.0-mL aliquots were pipetted into 36-cm lengths of Pyrex tubing which were sealed at one end and were then capped with a rubber stopper. Each 4.0-mL aliquot was placed in a constant temperature bath (76.4, 86.4, 96.4 °C). The zero time was defined as the instant that the tube was delivered into the constant temperature bath. Each tube represented one determination and from 12 to 15 samples were used to evaluate one kinetics run. The samples were quenched by removal from the constant temperature bath and cooling under cold tap water. The UV measurement was taken directly from the aliquot for all samples except **1i**. In the case of **1i** it was necessary to dilute 2.00 mL of benzene.

The rates were determined by following the growth of a quinoline absorption peak at 314 mμm by use of either a Cary Model 15 spectrophotometer or a Beckman Model DK2A spectrophotometer.

A calibration curve was constructed by taking the UV spectra of solutions of known concentrations of stoichiometric quantities of products (quinoline and **2a**) and starting material (**1a**) in benzene at 314 mμm. The plot was found to fit Beer's law.

From the UV spectrum of the aliquot and the calibration curve, the concentration of quinoline at each time, t, could be determined.

Results. For the determination of substituent effects and solvent effects, all kinetics experiments were carried out at 76.4 ± 0.2 °C. To obtain the Arrhenius plot ($\ln k$ vs. $1/t$) additional runs were made at 86.4 ± 0.2 and 96.4 ± 0.2 °C.

Rate data of each kinetics experiment are shown in Table I. The method of least squares was used to derive the average slope of each reaction plot from the raw data.

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Registry No.—**1a,** 56346-06-6; **1c,** 65815-43-2; **1d,** 65815-44-3; **1e,** 65815-45-4; **1f,** 65815-46-5; **1g,** 65815-47-6; **1h,** 65815-48-7; **1i,** 65815-49-8; **2a,** 65847-84-9; (*Z*)-**2c,** 65815-50-1; (*E*)-**2c,** 65815-51-2; **2d,** 65815-52-3; **2e,** 65815-53-4; **2f,** 65815-54-5; **2g,** 65847-83-8; **2h,** 65815-55-6; **2i,** 65815-56-7; quinoline, 91-22-5; ethyl benzoylacetate, 94-02-0; *p*-methoxybenzoyl chloride, 100-07-2; *m*-chlorobenzoyl chloride, 618-46-2; ethyl *p*-methoxybenzoylacetate, 2881-83-6; benzoyl chloride, 98-88-4; ethyl *p*-nitrobenzoylacetate, 838-57-3; *p*-toluyl chloride, 874-60-2; ethyl *p*-fluorobenzoylacetate, 1999-00-4.

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(22) There are two chiral centers in **1**, but we have found no evidence for the formation of two racemates in any of the condensation reactions. Owing to the facile reversibility of condensation in reactions of this type,[6–8] and also owing to the acidity of the hydrogen bonded to one of the chiral carbon atoms, interconversion of diastereomers would occur readily. Thus, it is probable that the thermodynamically more stable racemate is being formed in each of the reactions giving rise to **1**. However, we have no solid evidence which permits us to decide which of the racemates is the more stable in each case. Also, examination of space filling models for each of the possible diastereomers of **1** suggests no obvious explanation for the exclusive formation of (*Z*)-**2** in thermolysis.

Rate of Deprotonation of Phenylnitromethane by Hydroxide Ion in Aqueous Dimethyl Sulfoxide and Aqueous Methanol[1]

Carl D. Slater* and Yau Wai (David) Chan

Department of Chemistry, Memphis State University, Memphis, Tennessee 38152

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The rates of deprotonation of phenylnitromethane by hydroxide ion in aqueous dimethyl sulfoxide and aqueous methanol have been measured at 20, 30, and 40 °C under pseudo-first-order conditions using the stopped-flow technique. The various solvents (vol %) used, the second-order rate constants ($k_2 \times 10^{-2}$ M^{-1} s^{-1}) found at the three temperatures, ΔH^* (kcal/mol), and ΔS^* (cal/mol deg), respectively, are as follows: 20% methanol, 1.54, 2.97, 5.78, 11.4, −9.4; 50% methanol, 2.22, 4.39, 8.44, 11.6, −8.3; 33.3% Me_2SO, 3.22, 6.43, 9.42, 9.2, −15.5; 50% Me_2SO, 13.8, 20.8, 36.9, 8.3, −15.8; and 66.7% Me_2SO, 10.47, 17.03, 24.60, 7.2, −15.6. A plot of $\log k_2$ (25 °C) vs. ΔpK for the aqueous Me_2SO solutions gave a least-squares slope (β) of 0.58 ($r = -0.997$). The Brønsted β coefficient calculated on the basis of the enhanced basicity of hydroxide ion in these mixtures thus agrees closely with that obtained for aqueous solutions by variation in the type and strength of the bases employed. The constancy of the entropy of activation in Me_2SO–water mixtures suggests that solvent reorganization is very similar in each solvent and that the differences in rate can be attributed to the increased strength of the interaction between the solvent and the incipient water molecule.

Interest in proton transfer reactions is promoted by their formal simplicity. The accumulated evidence points to the mechanism shown in eq 1-3, in which charge types are not shown.[2]

$$\text{H–A} + \text{B} \rightarrow \underset{1}{\{\text{A–H} \cdots \text{B}\}} \qquad (1)$$

$$\{\text{A–H} \cdots \text{B}\} \rightarrow \underset{2}{\{\text{A} \cdots \text{H–B}\}} \qquad (2)$$

$$\{\text{A} \cdots \text{H–B}\} \rightarrow \text{A} + \text{H–B} \qquad (3)$$

Species **1** and **2** represent hydrogen-bonded encounter complexes, and reactants and products can be free species or ion pairs.

Carbon acids are expected to behave qualitatively differently than oxygen or nitrogen acids because of the inability of the former to hydrogen bond in the encounter complex. Both carbonyl[3] and nitro compounds[4] have been studied extensively with a view toward defining the structure of the transition state in deprotonation reactions in aqueous solution. Many weaker acids have been studied in nonaqueous

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