

TEMPERATURE DEPENDENT SOLVENT EFFECTS IN PHOTOCHEMISTRY OF 1-PHENYLPENTAN-1-ONES

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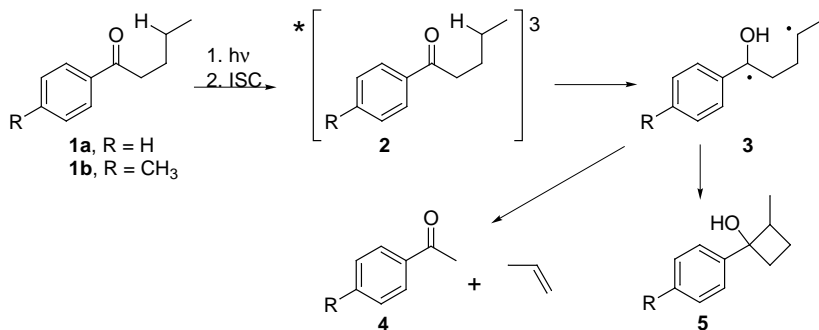
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Dedicated to Professor Milan Kratochvíl on the occasion of his 75th birthday.

Temperature dependent solvent effects have been investigated on the Norrish Type II reaction of 1-phenylpentan-1-one and its *p*-methyl derivative. Efficiencies of the photoreaction were studied in terms of solvent polarity and base addition as a function of temperature. Such a small structure change as the *p*-methyl substitution in 1-phenylpentan-1-one altered the temperature dependent photoreactivity in presence of weak bases. The experimental results suggest that the hydrogen bonding between the Type II biradical intermediate OH group and the solvent is weaker for 1-(4-methylphenyl)pentan-1-one than that for 1-phenylpentan-1-one at 20 °C but the interactions probably vanish in both cases at 80 °C. **Key words:** Photochemistry; Solvent effects; Ketones; Norrish Type II reaction; Valerophenone.

Structure and solvent effects on photoreactivity of alkyl aryl ketones have been extensively studied over four decades¹. Alkyl phenyl ketones with hydrogen on γ -carbon react upon irradiation on their alkyl chains according to Norrish Type II reaction² *via* the triplet state to produce the triplet 1,4-biradicals, which intersystem cross to the short lived singlet biradicals¹ that can cleave, cyclize (Yang cyclization)³, or disproportionate back to the starting ketone (Scheme 1). Scaiano's group provided temperature studies of 1-phenylpentan-1-one and its *p*-methoxy derivative in nonpolar solvents⁴ and Wagner studied temperature effects on photochemistry of molecules, in which two different phenyl ketones are attached to a flexible tether⁵. Zepp and his coworkers showed that going from 20 to 30 °C, the triplet reactivity of 1-phenylpentan-1-one in water increased⁶. There has been, however, no detailed study of temperature effects on the phenyl ketone triplet lifetime in polar and protic solvents yet.

We have recently studied a simultaneous effect of both ultraviolet and microwave irradiation on valerophenone photoreactivity as part of our program on *microwave photochemistry*⁷ and one of us also demonstrated an application of Norrish Type II reaction in intramolecular triplet energy transfer studies⁸. Now we wish to report additional results from our investigations on photoreactivity of 1-phenylpentan-1-one (valerophenone, **1a**) and 1-(4-methylphenyl)pentan-1-one (4-methylvalerophenone, **1b**) as a function of temperature, wavelength, and solvent properties.



SCHEME 1

EXPERIMENTAL

Equipment

¹H and ¹³C NMR spectra were obtained for solutions in CDCl₃ on an Avance Bruker DRX 500. Chemical shifts are given in ppm (δ -scale), coupling constants *J* in Hz. Gas chromatography was accomplished on a Shimadzu GC-17A apparatus and on a GC/mass system TRIO 1000 (FISONS Instruments). UV spectra were obtained on a Shimadzu UV-1601 instrument with matched 1.0 cm quartz cells and temperature dependent absorption spectra were measured on a Cary 50 equipped with the Fibre Optic dip probe and Cary Win software.

Chemicals and Solvents

1-Phenylpentan-1-one (**1a**) was obtained from Aldrich Chemical Co. and was purified by distillation under reduced pressure. 1-(4-Methylphenyl)pentan-1-one (**1b**) was synthesized from *p*-methylbenzotrile and butylmagnesium bromide according to the Wagner's procedure⁹ and was purified by distillation under reduced pressure. Hexadecane (99+%) from Schuchardt was used as received. Reagent grade benzene was washed with sulfuric acid until further portions remained colourless, then washed with water, dried, and distilled over P₂O₅, b.p. 80 °C. Reagent grade cyclohexane was worked up with sulfuric acid in the same way as benzene a then distilled over CaH₂, b.p. 81 °C. Acetonitrile (analytical grade) was dried and distilled over CaCl₂, b.p. 80–81 °C. Ethanol (analytical grade) was dried and distilled over sodium, b.p. 78 °C. Pyridine from Aldrich (99+%) was distilled before the use.

1-(4-Methylphenyl)pentan-1-one. M.p. 19–20 °C. ^1H NMR (500 MHz, CDCl_3): 0.95 (t, $J = 7.3$, 3 H); 1.41 (m, 2 H); 1.71 (m, 2 H); 2.40 (s, 3 H); 2.92 (t, $J = 7.5$, 2 H); 7.24 (d, $J = 8.1$, 2 H); 7.85 (d, $J = 8.1$, 2 H). ^{13}C NMR (125 MHz, CDCl_3): 13.79, 21.42, 22.39, 26.52, 38.08, 128.08, 129.10, 134.57, 143.43, 200.15.

Irradiation Procedures

All solutions were prepared directly by weighing the desired material into volumetric flasks or by dilution of stock solutions. Solution mixtures (3 ml) of both **1a** and **1b** of the same concentration in 13×100 mm Simax (Pyrex equivalent) tubes were degassed by bubbling the solutions with argon for 15 min. Magnetically stirred samples were irradiated in tubes equipped with a condenser. All photochemical experiments were accomplished under argon at 20 °C or at boil (≈ 80 °C; for all solvents used), using a conventional medium-pressure mercury lamp (400 W, Conrad-Hanovia) with 2 mm thick Simax filter (>280 nm) or 5 mm thick solution filters¹⁰. The solution cut-off filter for >313 nm was prepared by dissolving NaBr (400 g) and $\text{Hg}(\text{NO}_3)_2$ (1 g) in water (1 000 ml) and the filter for >366 nm by dissolving NaBr (650 g) and $\text{Pb}(\text{NO}_3)_2$ (3 g) in water (1 000 ml). Photoreaction conversions in all experiments were always kept below 20%. Time of irradiation experiments was usually 1 h.

Analysis of the Irradiated Samples

The only photoproducts followed for all reactants in this work were acetophenones (**4**) and cyclobutanols (**5**). Formation of a minor photoproduct ($<2\%$ yield, assuming the same GC response factor as valerophenone) was also observed and was believed to be 1-arylcyclopentanol as described elsewhere⁶. Identification of acetophenones and starting valerophenones, isolated by flash chromatography, was based on ^1H NMR, ^{13}C NMR, and on GC comparisons with authentic samples (Aldrich). Cyclobutanols were identified as described in the literature using GC and GC/mass instruments^{6,11}. The photoproducts are stable under all GC conditions used. For comparison, $4 \cdot 10^{-4}$ M solution valerophenone in acetone was irradiated using Simax-filtered radiation from Hg lamp until the reaction reached the first half-time. The products were analyzed by GC/mass spectrometry and the results were successfully compared to those described in the literature⁶. The same analysis was accomplished for 4-methylvalerophenone. Concentrations of the photoproducts were calculated from peak integrations of data obtained with flame ionization detection, assuming that the cyclobutanols had the same response as valerophenones.

Each sample was analyzed three times; in case that the values differed by more than 5% the measurement was repeated. Samples were analyzed by GC with response factors for products, starting ketones, and hexadecane as internal standard. The reaction efficiencies are not corrected on molar absorption coefficients. Since the coefficients of both ketones in all solvents were independent on temperature the calculations of reaction efficiency are not affected as discussed in the following chapter. Molar absorption coefficients of both **1a** and **1b** for three wavelengths are listed in Table I.

We tested the stability of cyclobutanols in boiling solvents. The reaction mixtures after the irradiation at 20 °C were heated to 80 °C for 4 h (four times as long as an average photochemical experiment) and re-analyzed. Concentrations of the photoproducts remained unchanged in all cases.

TABLE I
Molar absorption coefficients of valerophenone (**1a**) and 4-methylvalerophenone (**1b**)

λ , nm	ϵ^a (1a)			ϵ^a (1b)		
	benzene	ethanol	acetonitrile	benzene	ethanol	acetonitrile
280	908.2 ^b	990.2	891.3	764.9 ^b	1 687.4	1 091.2
313	55.2	69.3	60.3	60.6	106.2	84.7
366	4.0			3.8		

^a Molar absorption coefficients in $l \text{ mol}^{-1} \text{ cm}^{-1}$. ^b In cyclohexane.

TABLE II
Solvent and wavelength effects on the photolysis of **1a** and **1b** mixtures^a

T, °C	Wavelength, nm	Solvent	F/C ^b		R ^c
			1a	1b	
20	>280	benzene	4.05	5.11	1.22
80			4.16	5.14	1.03
20	>313		4.03	4.60	1.25
80			4.06	4.66	1.10
20	>366		3.79	4.59	1.23
80			4.07	4.89	1.07
20	>280		acetonitrile	4.50	5.87
81		5.10		6.82	1.08
20	>313	4.44		5.87	2.33
81			4.89	7.06	1.21
20	>280	ethanol	6.00	5.65	1.93
79			6.15	7.73	1.40
20	>313		6.04	7.59	1.93
79			6.65	7.66	1.59

^a The ketone concentrations were 0.01 mol l^{-1} . The reproducibility for each measurement was $\pm 5\%$. ^b The Type II fragmentation/cyclization ratio for both **1a** and **1b**. ^c Photochemical efficiency ratios $R = ([\mathbf{4a}] + [\mathbf{5a}]/[\mathbf{4b}] + [\mathbf{5b}])$; not corrected on ϵ values.

RESULTS AND DISCUSSION

We investigated the Norrish Type II (Scheme 1) reactivity of two phenyl ketones, valerophenone (**1a**) and 4-methylvalerophenone (**1b**), as a function of temperature, wavelength, and solvent properties. Equimolar mixtures of both ketones were irradiated and chemical yields of photoproducts were obtained; such experimental arrangement guaranteed identical photochemical conditions for both compounds. Type II cleavage to acetophenone (**4a**, R = H), 4-methylacetophenone (**4b**, R = CH₃), respectively, and cyclization to two isomeric 2-methyl-1-phenylcyclobutan-1-ols and its *p*-methyl derivatives (**5a** and **5b**, respectively) were the dominant pathways for the photoreaction of both valerophenones under all experimental conditions. Acetophenones were, as expected, major detectable photoproducts¹. We have not directly measured the quantum yields because of technical difficulties in experiments with boiling solutions.

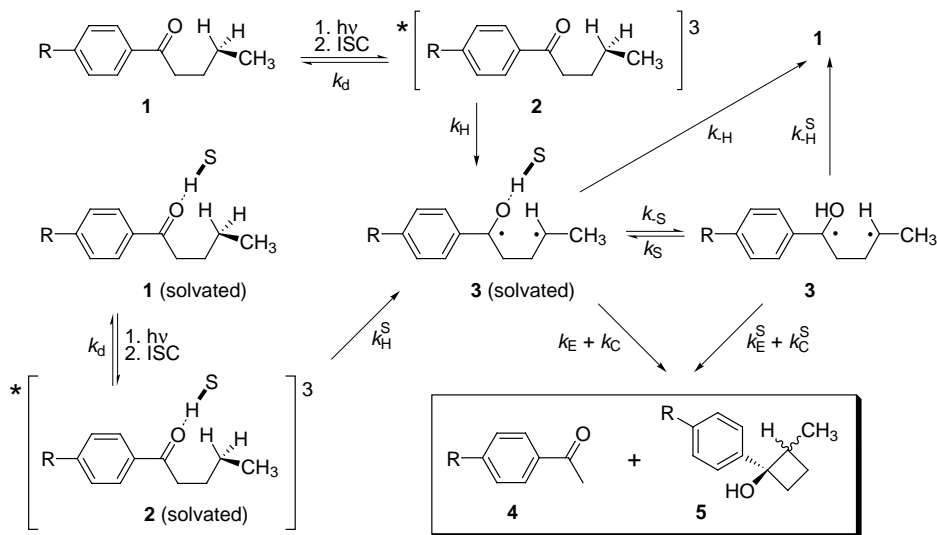
Table II displays the data from irradiation of equimolar ketone mixtures at different temperatures, wavelengths, and in three different solvents. The fragmentation/cyclization ratio was monitored for both **1a** and **1b**. The ratio of photoproduct concentrations ($[4a] + [5a]/[4b] + [5b]$) from the same experiment is the photochemical efficiency ratio. The results from irradiation experiments, in which pyridine or water as Lewis base additives were added into the mixtures are shown in Table III.

Solvent and temperature effects on the photoreaction efficiency of alkyl phenyl ketones and photoproduct formation depend on several factors that relate to the nature of the lowest triplet as well as interactions of the biradical intermediate with the solvent. Scheme 2 exemplifies the Norrish Type II reaction and possible solvent effects on the course of this reaction. In the following discussion, we will consider (i) hydrogen bonding capabilities of the carbonyl group with the solvent, (ii) hydrogen bonding capabilities of the biradical OH group with the solvent – (k_S and k_{-S}), and (iii) competition between cleavage and cyclization (k_E or k_C).

Type of the Excitation

It is well known that alkyl phenyl ketones have the lowest n, π^* and π, π^* excited states close in energy and vibronically coupled¹². An electron-releasing substituent such as *p*-methyl group in the aromatic ring stabilizes the π, π^* triplet. This effect also occurs in the presence of a solvent with higher permittivity and better hydrogen-bonding abilities (**1** (solvated) and **2** (solvated); Scheme 2) causing slower hydrogen atom abstraction (k_H^S). Such

stabilization has been evidenced by red shifts of the $\pi\text{-}\pi^*$ electronic transitions^{12a}. At the same time, the n,π^* transition is increased in energy because the lowest n,π^* state is less polar than the ground state⁶.



SCHEME 2

We measured the solvent shifts in water and ethanol for ketones **1a** and **1b** as well as for 1-(4-methoxyphenyl)pentan-1-one (4-methoxyvalerophenone) as a function of temperature. The 4-methoxy derivative displayed the largest effect and so it is included to this discussion even if it was not used in the photochemistry experiments. The UV spectrum of 4-methoxyvalerophenone in water showed a blue shift when going from 20 to 80 °C. The observed 4 nm shift corresponds to 2.1 kcal mol⁻¹ (valerophenone S⁻¹L_a transition in water is lowered by approximately 8 nm compared with nonpolar solvents), which may cause larger n,π^* population. This may be explained by the weakening (but not breaking of) the hydrogen bonding with the carbonyl group resulting in an increase of the hydrogen abstraction rate constant. 4-Methylvalerophenone exhibited only 2 nm shift and there was practically no change in absorption spectrum of **1a**, obviously thanks to the lack of a strongly electron donating group in conjugation with the carbonyl group. We observed the same effect also in ethanol but much weaker. No temperature dependent shift of the n,π^* transition band in all compounds have been detected. Those characteristics would have little effect on the data showed in Tables II and III, however, such tempera-

ture dependence expresses trends further discussed in the following chapter.

Biradical Solvation

Earlier studies showed that the Type II cleavage and cyclization quantum yields reach nearly unity in water or other highly polar solvents, in contrast to much lower quantum yields in nonpolar organic solvents^{1,6,13}. The quantum yield in water was found essentially temperature- and wavelength-independent when the n, π^* absorption band was irradiated^{6,13}. Basic polar solvents slow the disproportionation of biradicals (k_{-H} , Scheme 2) which means that enhancing biradical lifetime raises the overall quantum yield. Scheme 2 depicts a different reaction pathway of either not solvated or solvated biradical (**3**). We assume an equilibrium between those intermediates, which certainly depends on both solvent and biradical properties.

Quantum yields of the Type II reaction of alkyl phenyl ketones (Scheme 2) are given by the following equations¹:

TABLE III
Effect of addition of a base on the Type II reaction of **1a** and **1b** mixtures^a at wavelength >313 nm

T, °C	Solvent	F/C ^b		R ^c
		1a	1b	
20	benzene + pyridine ^d	7.02	8.06	1.21
boil		5.47	6.38	1.19
20	ethanol + pyridine ^d	6.90	7.90	1.62
boil		6.81	7.18	1.44
20	acetonitrile + pyridine ^d	5.12	6.04	1.34
boil		4.96	6.09	1.23
20	acetonitrile + water ^e	4.32	4.41	1.92
boil		4.45	5.41	1.25

^a The ketone concentrations were 0.01 mol l⁻¹. The reproducibility for each measurement was $\pm 5\%$. ^b The Type II fragmentation/cyclization ratio for both **1a** and **1b**. ^c Photochemical efficiency ratios $R = ([4a] + [5a])/[4b] + [5b]$; not corrected on ϵ values. ^d 0.5 M

$$\Phi_{II} = \Phi_{ISC} \Phi_R P_p \quad (1)$$

$$\Phi_{ISC} = 1 \text{ (alkyl phenyl ketones)} \quad (2)$$

$$\Phi_R = k_H / (k_H + k_d) \quad (3)$$

$$P_p = (k_E + k_C) / (k_E + k_C + k_{-H}) = (k_E + k_C) \tau_{BR} = k_p \tau_{BR} \quad (4)$$

where Φ_{II} , Φ_{ISC} , and Φ_R are quantum yields of the Type II reaction, the intersystem crossing from singlet to triplet, and the product formation, respectively. P_p is the probability that the biradical will collapse into products and τ_{BR} is the biradical lifetime. The value k_d refers to the excited state decay other than hydrogen abstraction. Similarly, the probability for the solvated biradical can be expressed by Eq. (5).

$$P_p^S = (k_E^S + k_C^S) / (k_E^S + k_C^S + k_{-H}^S) \quad (5)$$

Thus, our goal was to add some more information to this well-known photochemical subject to reveal how *p*-methyl substitution in valerophenone affects temperature dependent solvation. We have not measured quantum yields, however, employment of a mixture of two valerophenones (**1a**, **1b**), where same photochemical condition for both compounds were anticipated, brought an interesting insight into their photoreactivity. When we assume that triplet energy transfer is negligible at 0.01 M concentration⁸ and $k_H \gg k_d$ (ref.¹) the quantum yield ratio for those two ketones can be expressed using Eqs (1)–(4) as:

$$\begin{aligned} \Phi_{II}(\mathbf{1a}) / \Phi_{II}(\mathbf{1b}) &= P_p(\mathbf{1a}) / P_p(\mathbf{1b}) = [k_p(\mathbf{1a}) \tau_{BR}(\mathbf{1b})] / [k_p(\mathbf{1a}) \tau_{BR}(\mathbf{1b})] \approx \\ &\approx ([\mathbf{4a}] + [\mathbf{5a}] / [\mathbf{4b}] + [\mathbf{5b}]) = R \quad (6) \end{aligned}$$

where R is the conversion (photochemical efficiency) ratio proportional to the quantum yield ratio.

Table II shows temperature studies of the mixture in various solvents. In all examples the R ratio dropped when temperature was raised. The difference was found to be quite small in benzene but large in polar acetonitrile and ethanol. Wavelength was found to have only negligible effect on R . All solvents were purposely chosen to boil at temperature very close to 80 °C for easier comparison (R_{20} is assigned for the photochemistry at 20 °C and R_{80} at 80 °C). Wagner⁵ as well as Scaiano⁴ in their temperature studies reasoned that in *p*-substituted phenyl ketones with an electron-donating group, upper (reactive) n,π^* triplet is reached from the lower-lying π,π^* level and the gap between both states is reflected as an increase in the activation energy. In other words, n,π^* triplets are thermally populated from lower π,π^* levels. The fact that R_{20} was always larger than R_{80} in our results is then in accord with their results.

The ratio R_{20}/R_{80} , for a corresponding solvent, concentration, and wavelength, is defined in Eq. (7):

$$R_{20}/R_{80} \approx [\Phi_{II}(\mathbf{1a})/\Phi_{II}(\mathbf{1b})]_{20}/[\Phi_{II}(\mathbf{1a})/\Phi_{II}(\mathbf{1b})]_{80}, \quad (7)$$

in which R_{20}/R_{80} ratio, calculated from Eq. (6), is proportional to the quantum yield ratio. The starting ketones (**1a** and **1b**) did not have same molar absorption coefficients (ϵ) in all solvents used (Table I) but these coefficients were temperature-independent. Since it was difficult to obtain precise coefficients in the mixtures with pyridine and the calculations using Eq. (7) are not affected by the corrections on ϵ , only uncorrected values R are listed in Tables II and III.

Table II clearly depicts that the R_{20}/R_{80} ratio is highest in polar acetonitrile, lower in ethanol, but negligible in benzene (we obtained similar results in cyclohexane; not shown). In addition, Table III lists results from experiments in which more basic compounds (pyridine, water) were added into ketone mixtures, which caused dramatic changes in values of the ratio. The ratios R_{20}/R_{80} , also displayed in Fig. 1, reflect a relation of the ratio magnitude with basicity of the solvent used (pyridine, $pK_{\text{aBH}^+} = 5.2$; water, $pK_{\text{aBH}^+} = -1.7$; ethanol, $pK_{\text{aBH}^+} = -1.9$; acetonitrile, $pK_{\text{aBH}^+} = -12.0$). It is obvious from the Eq. (6) that k_p and τ_{BR} are the only relevant values that can affect the ratio. Scaiano measured biradical lifetimes in various solvents and found that increasing solvent polarity results in longer τ_{BR} (ref.^{3c}). It is also known that methyl substitution in phenyl ketones enhances P_p (refs^{1,13}).

We assume that methyl substitution in **1b** enhances P_p but OH group in the biradical is less acidic than that in **1a**; thus, the hydrogen bonding to a base is weaker. Scheme 3 shows a ring-substituent effect in the biradical, which is best visualized by the valence bond representation^{1h}. An electron-donating group definitely lowers the probability of the radical-cation form. Steenken measured basicity of various radical cations which was found dramatically higher than in that of non-ionized compounds (e.g., pK_a of $[\text{Ph-OH}]^{+\bullet}$ is ≈ 2 , which is about 8 orders of magnitude higher than that of phenol)¹⁴.



SCHEME 3

Our data suggest that the hydrogen bonding between the biradical OH group and the solvent is very specific and temperature dependent. We propose the following:

1. High values of R_{20}/R_{80} ratios reflect weaker interactions of the **1b** biradical (biradical formed from **1a** is more acidic) with weaker bases (ethanol, acetonitrile) at 20 °C but interactions in both derivatives vanish at 80 °C. Thus, weaker biradical interactions mean suppression of P_p (ref.^{1b}) (larger k_{-H}) resulting in a larger R_{20}/R_{80} ratio (Eq. (6)).

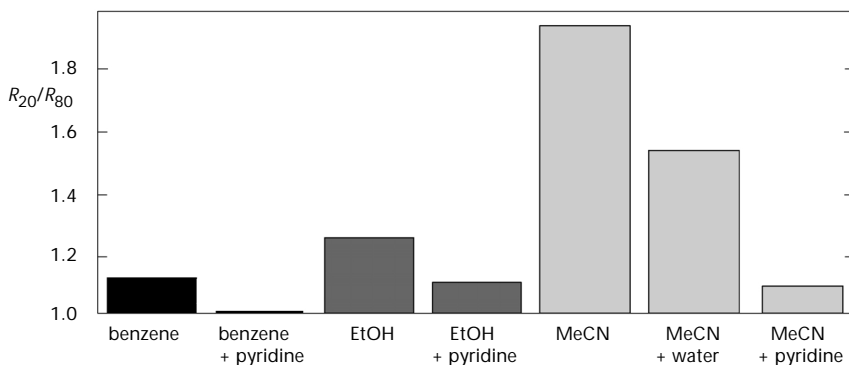


FIG. 1

Temperature-dependent solvent effect on photochemistry of 1-phenylpentan-1-ones at 313 nm. The R_{20}/R_{80} ratios were calculated from Tables II and III

2. The R_{20}/R_{80} ratio is close to unity when a much stronger base – pyridine – was used: it interacts either not selectively (pyridine is a too strong base) or both ketone biradicals retain hydrogen bonding even at 80 °C. Such observation resembles the behavior of ketones in nonpolar solvents, *i.e.*, in the absence of biradical solvation.

Thus, we probably observed an unexpected behaviour of the Type II biradical in which such a small structure change, as the *p*-methyl substitution, alter solvent effect in presence of weak bases. A weak interaction (hydrogen bonding) between solvent and the Type II intermediate is obviously reduced at a higher temperature. This is an example of hydrogen-bonding weakening with increasing temperature similar to those reported in the previous part of the discussion as well as in the literature¹⁵. The selectivity was lost when a stronger base was used.

The fact that the fragmentation/cyclization (F/C) ratio often increased with temperature (Table II) probably reflects changed conformational factors in the course of reaction.

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