of ion pair unpairing. However, the stereochemical outcome resulting from the internal-return pathway was not significantly altered by nonpolar solvent when **8** was treated with triethyloxonium tetrafluoroborate in CH_2Cl_2.[19]

A remaining question is to determine which species—a nitrogen-separated or a simple ion pair—is responsible for the reaction's stereochemistry. Moss, in a series of elegant papers on the solvolytic chemistry of *sec*-alkanediazotates, has argued that nitrogen-separated ion pairs play the key role in the stereochemistry of diazotic acid reactions.[14,40,49] Although the significance of this species cannot be unequivocally ruled out, the solvolysis of 1-phenylethyl chloride in water affords 1-phenylethanol with 17.5% net inversion,[50] a value extremely close to that in Table I for the hydrolysis of **6**. As discussed above, even with a primary alkyl group, i.e., optically active **10**, the products from deamination of the amine and solvolysis of the corresponding benzoate ester show virtually the same stereochemistry.[24] Again, we suggest that stereochemical control is exerted after nitrogen extrusion at the ion pair level.

A final point may be made as to whether the ionization of 1-phenylethanediazotic acid to a nitrogen-separated ion pair is a two-step[51] or concerted process.[10] The rapid exchange of ^{18}O label at near neutral pH implies a nonconcerted process, despite the stability of the 1-phenylethyl cation. In basic media the rate of C–N and N–O bond cleavage may be fortuitously similar, as evidenced by the yield of conservation product. However, this is not formally a concerted reaction that does not proceed via an intermediate with a potential energy well.[52,53]

Acknowledgment. This investigation was supported by the National Cancer Institute, National Institutes of Health (Grant CA29088). We are thankful to Drs. Michael Gross and Frank Crow of the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln, which is supported under the National Science Foundation Regional Instrumentation Facilities Program, and to Dr. Phillip Issenberg and Steve Miller for mass spectroscopic analyses.

Registry No. 1, 89017-33-4; **2**, 89017-34-5; **3**, 53198-41-7; **4**, 19935-85-4; **5**, 87549-57-3; **6**, 33290-13-0; **7**, 107-10-8; **8**, 30237-04-8; ^{18}O, 14797-71-8; N_3^-, 14343-69-2; NaN_3, 26628-22-8; (+)-$PhC(OCH_3)(CF_3)C(O)Cl$, 20445-33-4; (*R*,*R*)-$PhC(OCH_3)(CF_3)C(O)OCH(CH_3)Ph$, 39532-30-4; (*R*,*S*)-$PhC(OCH_3)(CF_3)C(O)OCH(CH_3)Ph$, 61184-95-0; (*R*,*R*)-$PhC(OCH_3)(CF_3)C(O)^{18}OCH(CH_3)Ph$, 89017-35-6; (*R*,*S*)-$PhC(OCH_3)(CF_3)C(O)^{18}OCH(CH_3)Ph$, 89017-36-7; 1-phenylethanol, 98-85-1; nitrosylpentacyanoferrate(III), 14636-58-9; 1-propanol-^{18}O, 89017-37-8; 2-propanol-^{18}O, 73569-91-2.

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Reactivity of Free Cyclopentadienone in Cycloaddition Reactions

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Contribution from the Departamento de Quîmica Orgânica, Colegio Universitario de Castellôn, Universidad de Valencia, Castellôn de la Plana, Spain. *Received July 5, 1983. Revised Manuscript Received November 4, 1983*

Abstract: Reactions of polymer-generated free cyclopentadienone with several dienes and dienophiles are studied, giving yields and rate constants for each one. A new method for lifetime measurements of transient species is also described, showing its application to the elusive ketone.

Studies of cyclopentadienone (II) have been recently carried out by our group using the three-phase test.[1] The elusive ketone was generated from an insoluble polymer-bound precursor (I) and trapped by a second solid phase by using Diels–Alder reactions (Scheme I).

Thus, the ability of cyclopentadienone to react as a diene or as a dienophile in Diels–Alder reactions has been demonstrated. Consequently, the next step in the study of the reactivity of cyclopentadienone was to know how the nature and structure of trapping agents could influence the rate and yield of their pericyclic reactions with the ketone. It was also interesting to study the lifetime of free cyclopentadienone in the absence of any trapping agent.

Results and Discussion

Radioassay provides a convenient method for monitoring reactions on solid phases. Thus, cyclobutadiene[2] and metaphosphate[3] transfers were determined by using radioassay procedures. In this way, tritiation of polymeric precursor I was accomplished as shown in Scheme II. According to Korach,[4] 1,3-cyclopentadiene gave the monoepoxide VI, from which diol VII was formed by reaction with tritiated water. Dehydration of VII, followed by a keto–enol tautomerism, gave tritiated cyclopentenone which was brominated with NBS and then bounded to the solid phase as described.[1]

Radioassay of solid phase I indicated its functionalization degree; 4.5 mequiv/g of the cyclopentenone moiety was found to be polymer bound.

Dienophiles. Besides the previously[1] used polymeric monoester of acetylenedicarboxylic acid (IV), four solid-phase reagents have been tested by us as dienophilic trapping agents for cyclopentadienone: the polymeric monoester of maleic acid (VIII), the N-resin maleimide (IX), the polymeric crotonic ester (X), and the polymeric ester of 4-carboxy-2′,4′-dihydroxyazobenzene (XI).

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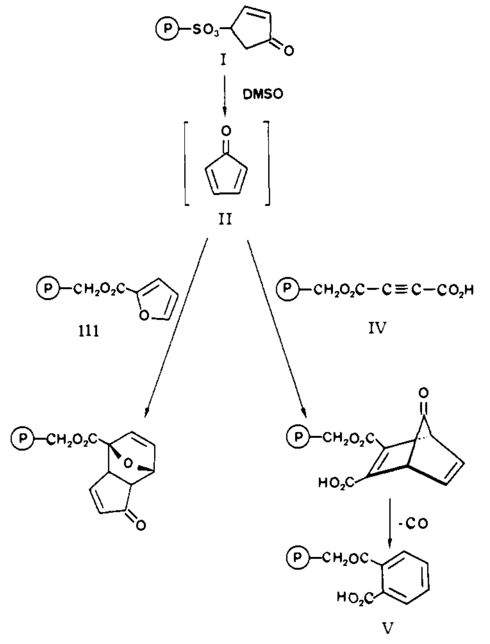
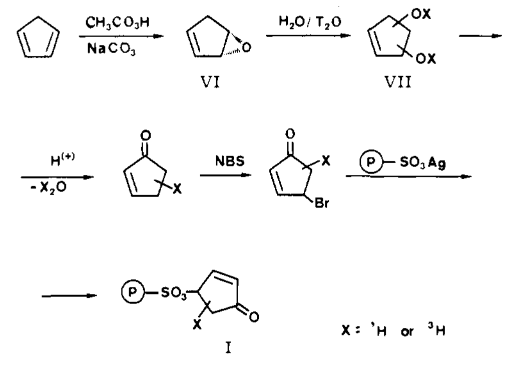
Table I. Experimental Rates for Dimerization and Pericyclic Reactions of Free Cyclopentadienone in Me_2SO at 100 °C

trapping resin (mg)	mg of I	% trapping after 48 h	$k_1 \times 10^6$, s^{-1}	$k_2 \times 10^4$, $mequiv^{-1}\ s^{-1}$	$k_3 \times 10^2$, $mequiv^{-1}\ s^{-1}$
	Dienophiles				
IV, Ⓟ -$CH_2O_2C{-}C{\equiv}C{-}CO_2H$ (200)	200	16.8	5.02	1.21	1.303
VIII, Ⓟ -$CH_2O_2C{-}HC{=}CH{-}CO_2H{-}CO_2H$ (200)	200	10.35	4.80	0.602	1.312
IX, Ⓟ -$CH_2{-}(NC_4H_2O_2)$ (200)	150	5.87	4.69	0.023	1.300
X, Ⓟ -$CH_2O_2C{-}HC{=}CH{-}CH_3$ (200)	200	51.00	4.71	6.74	1.314
XI, Ⓟ -$O_2C{-}C_6H_4{-}N{=}N{-}C_6H_2(OH)_2$ (200)	200	21.38	5.06	1.42	1.316
	Dienes				
III, Ⓟ -$CH_2O_2C{-}C_4H_3O$ (300)	200	1.75	4.81	0.087	1.302
XIII, Ⓟ -$CH_2{-}CO_2{-}HC{=}CH{-}HC{=}CH_2$ (200)	200	71.67	4.90	15.46	1.303

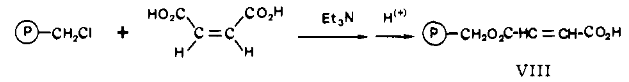
Scheme I



Scheme II

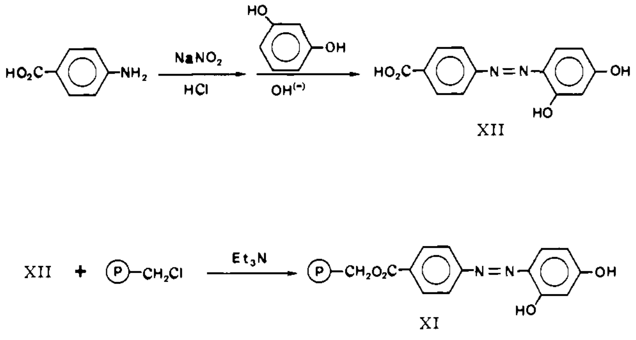


Scheme III

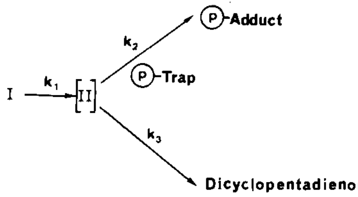


Two of these compounds have been prepared formerly by us: IX[2] and X.[5] The polymeric monoester of maleic acid (VIII) was prepared by treatment of chloromethylated 2% cross-linked (microreticular) Merrifield's resin with maleic acid and triethylamine (Scheme III). Titration of VIII was accomplished against NaOH. Thus, the functionalization value was established in 2.53 mequiv/g.

Scheme IV



Scheme V



In XI, the dienophilic group was not a multiple C–C bond but an azo group. Synthesis of XI was carried out as indicated in Scheme IV. 4-Carboxy-2′,4′-dihydroxyazobenzene was prepared by coupling diazonium salt from 4-aminobenzoic acid with resorcinol. The polymeric ester of XII (XI) was formed in the usual way. Combustion analysis indicated 1.2 mequiv of the azo group/g of XI.

The three-phase reaction of tritiated precursor I with these dienophiles was accomplished as shown in Scheme I. The relative trapping and dimerization of the cyclopentadienone released were quantitatively indicated by the radioassay of polymers and solution. Transfer to the four dienophilic polymers occurred at 100 °C, and the structure of the resulting adducts was established through cleaving from respective resins. Data from these experiments after 48 h are given in Table I. Trapping by dienophilic polymers and dimerization are always competitive. From this, we can deduce the kinetic equations:

$$k_1A = k_1A_0 \exp(-k_1t) = k_2[\mathrm{II}][\mathrm{P{-}trap}] + k_3[\mathrm{II}]^2 = (-\mathrm{d}[\mathrm{P{-}trap}]/\mathrm{d}t + 2\,\mathrm{d}[\mathrm{dimer}]/\mathrm{d}t) \quad (1)$$

where A_0 is the initial concentration of reactive groups in I, and A is the concentration of such groups after a time t. We consider that dicyclopentadienone is obtained only by dimerization of II, excluding a hypothetic reaction of just-released cyclopentadienone with polymer-bound precursor (in this case, new terms should be added to the equation).

Equation 1 and the radioassay data enabled us to determine rate constants as shown in the table. As expected, k_1 values are all similar and so are k_3 values. Coherence of the given results confirms the kinetic hypothesis leading to eq 1. The fact that the electron withdrawing groups in dienophiles decrease k_2 is due to the carbonyl group of cyclopentadienone; thus, the best dienophilic trapping agent among the ones tested is X: its reactivity is ten

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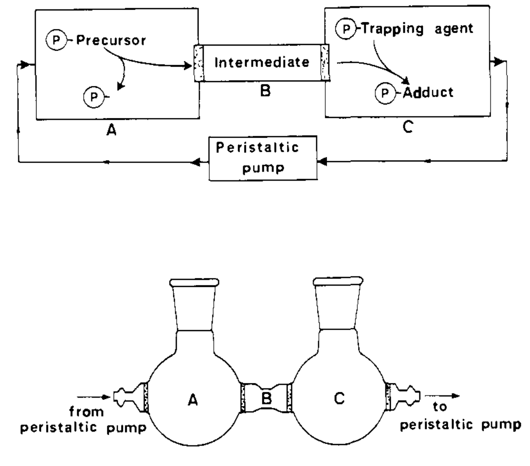

Figure 1. Diagram of the polyphasic dynamic reactor (PDR).

times the one of the polymeric monoester of maleic acid (VIII). The change from double to triple bond carries an increase in reactivity: k_2 for reagent IV is two times higher than that for reagent VIII.

Trapping with polymeric meleimide (IX) shows a poor yield (less than 6%), and the respective rate constant is the lowest one. This is in contrast with the behavior of nonpolymeric maleimides, which have been reported to be good dienophilic agents. We must notice that the steric hindrance in the resin makes endo addition difficult.

Azo trapping agent XI appears to be as reactive as acetylenic resin and quite less reactive than crotonic ester X.

Dienes. Two dienic solid phases, which were prepared formerly by us, have been tested: the cyclic diene, the polymeric ester of 2-furancarboxylic acid[1] (III), and the acyclic one, the buta-1,3-dien-1-ol polymeric ester[5] (XIII). Three-phase reactions were carried out with these dienic polymers and tritiated precursor I, and radioassay enabled us to determine rate constants according to eq 1. Results are given in Table I.

We can observe that the cyclic diene, which seems likely to have the characteristics of a good reagent for Diels–Alder cycloadditions, shows a low yield of trapping. This effect of low yield might be caused by the steric factors related to polymeric bulk as well as by the electronic effect of the electron-withdrawing ester group. Acyclic diene XIII, on the other hand, reacts with cyclopentadienone faster than any tested dienophile.

Lifetime Determination. As the "three-phase test" is reminiscent of the Paneth one[7] for organic free radicals, we always considered that such a test also could be appropriate for measurements of lifetimes through separation of the resins to increasing distances.[8] We now report the use of the three-phase test for lifetime determination of cyclopentadienone through separation of the resins to a constant distance and introduction of a variable flow of the liquid phase.

For that, cyclopentadienone was generated from polymeric precursor I by reaction with Me_2SO[1] in vessel "A" of a "polyphasic dynamic reactor" (PDR) (Figure 1). A second solid phase, the trapping agent polymeric monoester of acetylenedicarboxylic acid (IV), lay in vessel "C" attached to "A" by conduit "B". The reagent solution flowed inside PDR from A to C through B and outside from C to A through an adjustable peristaltic pump. Connections in PDR are made of porous plates, which ensure that only the liquid phase flows, while solid phases remain in their respective places. Thus, the detection of an adduct in the solid phase in C must occur through a polymer-free intermediate of a lifetime higher than run-time through conduit B. This run-time can be adjusted by the peristaltic pump. In our experience, it was varied from 3 to 15 s. Transfer between the two polymers was detected, yielding the polymeric phthalic monoester V (its appearance was monitored by IR), only for run-times shorter than 13.3 ± 0.5 s. Thus, the cyclopentadienone lifetime under those conditions must be stated in this value. In fact, the time of the diffusion of the intermediate to the surface of the precursor polymer bead and the time of diffusion to the inside of the trapping polymer bead should be added. Nevertheless, both timings are of the order of some tenths of a second[9] and can be included in the method's error.

The lifetime of cyclopentadienone, so obtained, shows a close conformity with the value deduced by Baron and Brown[10] from their experiences on the microwave spectra of this specie.

Conclusions

Cyclopentadienone acts as a diene in Diels–Alder reactions with a variety of dienophiles. The best yields in such reactions correspond to reverse electronic demand of these cycloadditions. Anyway, the reactivity of that ketone increases when it acts as a dienophile facing simple dienes such as 1,3-butadiene.

We have shown that cyclopentadienone in a solution of Me_2SO has a lifetime of about 13 s in the absence of dienes, dienophiles, or nucleophiles. The polyphasic dynamic reactor (PDR) based on the three-phase test, proves to be an important tool in determining the lifetime of reactive intermediates, with an error shorter than 1 s.

We have also demonstrated that, as has been suggested,[11] the polymer can alter the reactivity of cycloaddition reactions, making some cyclic dienes and dienophiles less reactive than acyclic ones.

Experimental Section

General methods including the radioassay have been described for manipulating the polymers and multiphase systems.[2,3,8]

Tritiated Polymeric Tosylcyclopentenone. Tritiated cyclopentenone was prepared according to Korach[4] with use of tritiated water (activity 1.3 μCi/mL) for the hydrolysis of epoxide VI. A solution of that cyclopenten-2-one (0.528 g) in 10 mL of carbon tetrachloride was treated with 1.728 g of NBS and a catalytic amount of benzoyl peroxide. The solution was stirred at 100 °C for 1 h, and the mixture was then chilled and filtered. The liquid was extracted twice with 10-mL portions of a cold aqueous solution of 25% $Na_2S_2O_3$, and then the organic phase was evaporated to dryness at reduced pressure. The residue, tritiated 4-bromocyclopentenone[6] (activity 0.71×10^{-2} μCi/mmol), reacted with chlorosulfonated macroreticular resin as described,[1] giving tritiated I. Radioassay indicated 4.5 mequiv of ketone/g of resin.

Preparation and Characterization of Polymer-Bound Trapping Agents. Five trapping agents have been described in previous papers: III[1], IV[1], IX[2], X[5] and XIII.[5]

Polymeric Monoester of Maleic Acid (VIII). Chloromethylated resin (1 g, 1.06 mequiv) was suspended in 50 mL of xylene containing 1.22 g of maleic acid and 10 mL of Et_3N and heated and stirred at 110–120 °C for 70 h. After being washed with xylene, dioxane, and ether, the resin was acidified (HCl in aqueous dioxane) and washed again with water, acetone, and ether to give VIII. IR: 3300, 1730, 1700, 1260, 1160 cm^{-1}. Titration indicated 2.53 mequiv of CO_2H/g.

Polymeric Ester of 4-Carboxy-2′,4′-dihydroxyazobenzene (XI). *p*-Aminobenzoic acid hydrochloride (36 mequiv) was converted into its diazonium salt by standard procedures. A chilled solution of 3.85 g (35 mequiv) of resorcinol and 7 g of NaOH in 25 mL of water was added dropwide to the stirred solution of that diazonium salt at 0 °C. After 1 h of stirring at 0 °C, the mixture was acidified and then filtered. The filtrate was washed exhaustively with water to give XII (80% yield). IR: 3400, 3000, 1700, 1600, 1470, 1230 cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.87. Found, C, 60.48; H, 3.95.

A suspension of chloromethylated resin (1 g, 1.06 mequiv) in 40 mL of dioxane was treated with 2.71 g of XII and 5 mL of Et_3N at 104 °C for 22 h. After having been washed with water, dioxane, acetone, and ethanol, the resin showed IR 3400, 1720, 1600, 1400, 1150, 1100 cm^{-1}. Samples of XI treated with NaOH in dioxane/water (1/1) under reflux released 1.2 mequiv of the sodium salt of XII/g of resin.

Three-Phase Tests. Cyclopentadienone Transfer from Polymeric Tosylcyclopentenone. All cyclopentadienone transfer were carried out as follows (data are given in Table I): A suspension of radioactive I and

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the corresponding trapping agent was heated at 100 °C in Me_2SO for 0.25, 0.50, 1, 2, 4, 10, 20, and 48 h, respectively. Each time, both solid phases (precursor and trapping) were separated, washed, and radioassayed and so was the liquid phase. Thus, we were able to draw plots of $\ln A_0/A$ against t (eq 1) to deduce directly k_1, its value being very similar in all cases. As we already knew simultaneous concentrations of ketone moiety in trapping resin and in solution, we calculated k_2 and k_3. As expected, k_3 is also similar in every instance, whereas k_2 is dependent on the trapping agent.

Polyphasic Dynamic Reactor (PDR). Two 25-mL round-bottomed flasks A and C (Figure 1) are connected by means of a 15 mm long tube B with an internal diameter of 6 mm. Outside, both flasks are also connected by an adjustable peristaltic pump, which regulates the flow rate in the whole system. In the top of each flask, a reflux condenser can be installed. Every flask connection is made by sintered-glass plates.

Calibration of the PDR can be easily done by using a coloring matter which allows the liquid running through conduit B to be seen. In this way, we were able to draw plots of the run-time against the flow.

Lifetime Measurements. In a series of experiments, a suspension of polymeric precursor I (0.1 g) in Me_2SO was heated and stirred at 100 °C in vessel A of the PDR. Trapping agent IV (0.1 g) was also stirred in vessel C. Reagent solution flowed from A to C through B. The run-time through this conduit was adjusted by the peristaltic pump at 3.0, 4.2, 5.3, 6.0, 8.1, 9.1, 10.2, 11.3, 12.6, 13.8, and 15 s, respectively. Each time, resin in vessel C was filtered, washed, and analyzed by hydrolysis and IR. We realized that cyclopentadienone was not trapped by IV for run-times of 13.8 or 15 s. Instead, adducts between IV and the ketone appeared when we experimented with the other run-times. Consequently, cyclopentadienone must have a lifetime between 12.6 and 13.8 s under these conditions.

Registry No. III, 611-13-2; IV, 42507-71-1; VIII, 3052-50-4; IX, 930-88-1; X, 18707-60-3; XI, 88855-00-9; XIII, 1515-76-0; cyclopentadienone, 13177-38-3.

General Base Catalysis, Isotope Effects, Activation Parameters, and the Mechanism of Removal of the Hydrogen-Bonded Proton from Protonated 1,8-Bis(diethylamino)-2,7-dimethoxynaphthalene

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Contribution from the Department of Chemistry, King's College London, Strand, London WC2R 2LS. *Received October 3, 1983*

Abstract: The equilibrium between 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene and the intramolecularly hydrogen-bonded protonated amine in the presence of phenol buffers is established very slowly in 70% $Me_2SO–H_2O$ (v/v) with half-lives in the range of minutes. Evidence is presented to show that deprotonation of the protonated amine occurs through a non-hydrogen-bonded open form from which the proton is removed by base. The rate of the overall reaction is reduced because the non-hydrogen-bonded species is present as a low-concentration intermediate and because proton removal from this intermediate is sterically hindered. These factors are of roughly similar importance. The conclusion is also reached that strain in the amine and the presence of the intramolecular hydrogen bond in the protonated amine contribute about equally to the unusually high basicity of 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene, $pK_a = 16.3$.

In recent years a number of proton transfers involving oxygen and nitrogen acids and bases have been found which do not fit into the classification described by Eigen[1] as normal proton-transfer behavior and observed[1,2] for most oxygen and nitrogen acids. Although this classification is of immense value in making predictions about proton transfers, particularly with reference to these reactions as steps in multistep mechanisms,[3] it is the exceptions to this classification which are perhaps, now, of more interest. Unusual acid–base systems for which proton transfer is exceptionally slow and basicity is high include the [1.1.1]-cryptand[4] and 1,6-diazabicyclo[4.4.4]tetradecane.[5] Several other examples of nitrogen bases which show high basicity but for which the kinetics of proton transfer have not yet been studied in detail are also known.[6] Our interest in this area has concerned the unusual acid–base properties of diaminonaphthalenes,[7] and in this paper we describe our studies with 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene.

1,8-Bis(diethylamino)-2,7-dimethoxynaphthalene ($pK_a = 16.3$)[8] shows unusually high basicity for an aromatic amine. Thus in the protonated amine the proton is very tightly bound and requires strongly basic conditions for its removal. In suitable $Me_2SO–H_2O$ mixtures containing hydroxide ion, proton removal from the protonated amine is thermodynamically favorable but the reaction occurs very slowly and can be followed by using a conventional UV spectrophotometer, for example $t_{1/2} = 22$ s in 50% $Me_2SO–H_2O$ (v/v) in the presence of 0.1 mol dm^{-3} sodium hydroxide.[8] 1,8-Bis(dimethylamino)-2,7-dimethoxynaphthalene is also strongly basic ($pK_a = 16.1$),[8] but proton removal from the protonated amine is more rapid, for example, $t_{1/2} = 15$ ms with 0.1 mol dm^{-3} sodium hydroxide in 60% $Me_2SO–H_2O$ (v/v). Previous papers on 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene have dealt with the hydroxide ion catalyzed proton transfer. In the present paper we are concerned with general base catalysis, isotope effects, and activation parameters. General base catalysis of the reaction of

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