When $C_i = 4 \times 10^{-2}$ M, the dependence of k_2/k_H on R* is shown in Figure 1.

Since the thioether 4 was isolated in 49% yield in DMSO and 87% yield in MeCN, we could derive from Figure 1 that $k_2/k_H = 38$ M^{-1} in DMSO and 440 M^{-1} in MeCN. The former value is almost identical with the value determined by Parker et al.[4] and Savéant et al.[3b] in DMSO (k_2/k_H = 40 M^{-1}) (Table I) whereas the latter differs by a factor of 29 from the value proposed by Savéant et al. ($k_2/k_H = 15$ M^{-1}), assuming that k_1 was the same in DMSO and MeCN. Our results suggest that the cleavage rate of 1-BrNaph$^{\bullet-}$ would be higher in MeCN than in DMSO, as in the case of 1-INaph$^{\bullet-}$ radical anion,[3a] and so the moderate yield of 4 (32%) obtained in MeCN in the absence of mediator would result from the side reaction (7). In Table I, we have also indicated the absolute k_2 values derived from the k_H values proposed by Saveant et al.[3a] and Parker et al.[4] In MeCN, the k_2 value derived from Saveant's data exceeds the limiting diffusion-controlled value ($k_d = 2 \times 10^{10}$ M^{-1} s^{-1}), suggesting that the rate of hydrogen abstraction is at least five times slower ($k_H \leq 4.6 \times 10^7$ s^{-1}) than the proposed value. The same remark probably holds in DMSO. Finally, a comparison of the k_2 values in MeCN and DMSO show that the nucleophilic attack of PhS$^-$ toward the 1-Naph$^\bullet$ radical is 26 or 13 times faster in MeCN than in DMSO, depending on the data provided by Saveant et al.[3a] or Parker et al.[4] (Table I).

These latter results are consistent with those previously obtained for the 9-Antr$^\bullet$/PhE$^-$ couples and confirm the unfavorable influence of DMSO as far as the PhE$^-$ nucleophiles are involved. This influence cannot be explained from thermodynamic considerations such as the donor number values (DN) of the solvents (DN = 29.8 for DMSO and 14.1 for MeCN).[11] Indeed, such data suggest that decomposition of the unstable ArX$^{\bullet-}$ radical anion is more rapid in DMSO than in MeCN,[3a] due to a stronger solvatation in DMSO of the generated Ar$^\bullet$ radical, which thus becomes less electrophilic and therefore less inclined to nucleophilic attacks. Thus, k_1 should increase and k_2 decrease in DMSO, which is not compatible with the experimental results observed in the case of 1-BrNaph. Therefore, a kinetic effect of the solvent upon the activation barrier has to be considered. A stabilization of the transition state or a decrease of the solvent reorganization energy can be involved if the ArX$^{\bullet-}$ cleavage and the ArNu$^{\bullet-}$ formation are considered as intramolecular dissociative and associative electron transfers.[12-15]

Experimental Section

Analytical-grade MeCN and DMSO were purchased from SDS. Acetonitrile was carefully dried on neutral alumina. The starting materials were of commercial origin. Pure thioether 4 was obtained by column chromatography (Kieselgel with CH_2Cl_2/hexane = 5/95 as eluant) of the crude product isolated after electrolysis of 1-bromonaphthalene in MeCN (yield 68%). β-Phenylcinnamonitrile was prepared by cathodic reduction of benzophenone in MeCN.[10]

An Amel 552 potentiostat (output voltage 200 V at full load) and a Tacussel IG5-N integrator were used in coulometry and preparative electrolysis. All the potentials referred to the aqueous saturated calomel electrode (SCE). The electrochemical synthesis of 4 was carried out in a H-type cell, the three compartments of which were separated by ion-exchange membranes Ionax MA 3475 (anodic side) and MC 3470 (cathodic side). The cathode was a graphite cloth of cylindrical shape and the anode a Pt grid. The cathodic solution (100 mL) was stirred mechanically and deaerated with argon prior to and during electrolysis. Helium was the gas vector of a Shimatzu GC 14A chromatograph equipped with a CR 6A detector (25 m × 0.25 mm capillary column DB1). The temperature of the injector and detector (FID) was 300 °C. The temperature of the column was changed from 80 to 250 °C (5 °C per min) then maintained at 250 °C.

Electrochemical Synthesis of 4 in MeCN. After a preelectrolysis of the solvent containing Bu_4NPF_6 (0.1 M) in order to suppress any electroactive impurities, PhSSPh (2 mmol; 2×10^{-2} M) was introduced and reduced to PhS$^-$. The potential had to be changed from −1.0 to −2.05 V, whereas the faradaic current dropped from 90 mA (initial value) to a negligible value, after consumption of 390 C (4 mmol of electrons). The electrolysis was interrupted, and 1-bromonaphthalene (4 mmol) together with benzophenone (1 mmol) were added and reduced at −1.7 V. The faradaic current dropped from 24 mA (initial value) to 13 mA after consumption of 155 C (1.60 mmol of electrons). Finally the potential was changed from −1.7 to 0 V in order to oxidize the benzophenone radical anions and the PhS$^-$ anions in excess. The electrolysis was stopped after consumption of 213 C (2.81 mmol of electrons). The cathodic solution was diluted with water, and the electrolysis products were extracted with diethyl ether. After the solution was dried and the ether removed, the crude product was purified on a Soxhlet with diethyl ether in order to suppress any traces of supporting electrolyte. The ethereal solution was dried, ether was removed, and the crude product was dried under vacuum at room temperature for 1 day. A sample of the crude product (1.147 g) was analyzed by GC with phthalonitrile as internal standard and compared to a reference mixture containing β-phenylcinnamonitrile in addition to the expected compounds. Thus, the crude product was a mixture of naphthalene (17.3 mg; 0.146 mmol), 1-BrNaph (257.4 mg; 1.243 mmol), 4 (566.4 mg; 2.396 mmol), PhSSPh (116.5 mg; 0.534 mmol), benzophenone (38.5 mg; 0.211 mmol), and β-phenylcinnamonitrile (100.0 mg; 0.49 mmol).

Electrochemical Synthesis of 4 in DMSO. The preceding experiment was repeated in DMSO. After a preelectrolysis then generation of PhS$^-$ (4 mmol), the indirect reduction of 1-BrNaph (4 mmol) by benzophenone (1 mmol) was carried out at −1.65 V. The faradaic current dropped from 26 mA (initial value) to 5 mA after consumption of 270 C (2.87 mmol of electrons). The anodic step consumed 168 C (1.75 mmol of electrons). From a sample of the crude product (0.822 g) which was isolated as previously, a GC determination indicated that the crude product was a mixture of naphthalene (167 mg; 1.415 mmol), 1-BrNaph (37.5 mg; 0.181 mmol), PhSSPh (94.2 mg; 0.431 mmol), 4 (446.1 mg; 1.888 mmol), and benzophenone (88.5 mg; 0.485 mmol).

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Correlation of the Rates of Solvolysis of the Benzyldiphenylsulfonium Ion[1]

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As an aid to assessing the extent of nucleophilic participation by the solvent at the transition state for solvolytic displacement reactions, several scales of solvent nucleophilicity[2] for use within the extended Grunwald-

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Winstein equation (1)[3] are currently available. In the equation, k is the specific rate of solvolysis of RX in a given

$$\log (k/k_0)_{RX} = lN + mY \quad (1)$$

solvent of nucleophilicity N and ionizing power Y and k_0 is the specific rate of solvolysis of RX in 80% ethanol. The l and m values are measures of the sensitivity of the solvolysis of RX to changes in solvent nucleophilicity and ionizing power, respectively. The equation is intended for use with initially neutral substrates, from which an anion is displaced during the substitution process.

For initially positive substrates (RX^+) of the type that lose a neutral molecule during the substitution process, there is a dispersal rather than a development of charge[4,5] and, also, the solvation of the leaving group is not an important factor.[6] The first term of eq 1 now dominates, and indeed, the second term can be omitted[6] to give eq 2.

$$\log (k/k_0)_{RX^+} = lN \quad (2)$$

There are very strong indications[7,8] that the originally developed N_{OTs} scale[9] (eq 3), based on methyl p-toluene-

$$N_{OTs} = \log (k/k_0)_{MeOTs} - 0.3Y_{OTs} \quad (3)$$

sulfonate solvolysis, is set up using an erroneous sensitivity toward the solvent ionizing power scale (Y_{OTs}, based on 2-adamantyl p-toluenesulfonate solvolysis[9,10]), and it was suggested[8] that it should be modified to what can be termed the N'_{OTs} scale (eq 4).

$$N'_{OTs} = \log (k/k_0)_{MeOTs} - 0.55\ Y_{OTs} \quad (4)$$

In our laboratories, we have preferred to develop scales of solvent nucleophilicity by use of eq 2. Scales have been developed based upon the solvolyses of the triethyloxonium ion ($N_{Et_3O^+}$)[5,11] and the S-methyldibenzothiophenium ion (N_T).[8] The $N_{Et_3O^+}$ scale has been used to correlate the rates of solvolysis of several other R–X$^+$ substrates, including the methyldiphenylsulfonium ion.[12] Several p-toluenesulfonate esters have been correlated by use of eq 1, employing the $N_{Et_3O^+}$ scale in conjunction with the Y_{OTs} scale.[7,13,14]

In this paper, the correlation of the specific rates of solvolysis of the benzyldiphenylsulfonium ion in terms of eq 2 is compared to the previously carried out[13,14] correlation of the rates of solvolysis of benzyl p-toluenesulfonate in terms of eq 1. Attempts to extend to derivatives with substituents within the aromatic ring of the benzyl group[14] were thwarted in the present study; only the parent ion was obtained as a solid trifluoromethanesulfonate salt. The attempted preparation of four derivatives led repeatedly to unstable oils of insufficient purity.

Table I. Specific Rates of Solvolysis (k) at 25.0 °C of Benzyldiphenylsulfonium Trifluoromethanesulfonate[a] in Organic and Aqueous Organic Solvents and Solvent Nucleophilicity Values

solvent[b,c]	10^5k,[d] s^{-1}	N_T[e]	$N_{Et_3O^+}$[f]	N_{OTs}[g]	N'_{OTs}[e]
100% EtOH	92.7 ± 1.1	0.37	0.55	0.06	0.43
80% EtOH	52.5 ± 0.7	0.00	0.00	0.00	0.00
60% EtOH	31.2 ± 1.1	−0.39	−0.35	−0.08	−0.31
100% MeOH	125 ± 2	0.17	0.64	−0.04	0.19
97% TFE	0.174 ± 0.007	−3.30	−2.28	−2.79	−3.25
80% TFE	0.736 ± 0.040	−2.19[h]	−1.44	−1.63	−2.12[h]
50% TFE	1.68 ● 0.06	−1.73	−1.05	−0.93	−1.47
CH_3CO_2H	1.67 ± 0.17	−1.78	−1.42	−2.35	−2.06
HCO_2H	0.475 ± 0.020	−2.44	−1.71	−2.35	−3.11
95% Me_2CO	8.70 ± 0.24	−0.49	−0.23		
60T-40E	9.10 ± 0.22	−0.94	−0.42	−1.01	−1.06

[a] Substrate concentration of ca. 0.005 M. [b] With water as other component, except for the TFE–EtOH (T–E) mixture. [c] On a volume–volume basis, at 25 °C, except for the TFE–H_2O mixtures, which are on a weight–weight basis. [d] With associated standard deviations. [e] Values from ref 8. [f] Values from refs 5 and 11 (first columns of Table I). [g] Values from ref 15. [h] Interpolated value.

Table II. Correlation of the Specific Rates of Solvolysis of the Benzyldiphenylsulfonium Ion at 25.0 °C with Solvent Nucleophilicity (N) Values[a,b]

scale	n[c]	l	c	r[d]
N_T	11	0.80 ± 0.05	−0.03 ± 0.17	0.986
$N_{Et_3O^+}$	11	1.01 ± 0.07	−0.25 ± 0.21	0.979
N_{OTs}	10[e]	0.87 ± 0.12	0.00 ± 0.39	0.935
N'_{OTs}	10[e]	0.74 ± 0.05	0.00 ± 0.21	0.983

[a] By use of $\log k/k_o = lN + c$, where c is a constant term and the other symbols are defined in the text. [b] By use of k, k_o, and N values from Table I. [c] Number of solvents. [d] Correlation coefficient. [e] The N_{OTs} and N'_{OTs} values are not available for 95% acetone.

Results

A study was made, at 25.0 °C, in four pure solvents (ethanol, methanol, acetic acid, and formic acid), in six aqueous organic solvents (mixtures of water with ethanol, 2,2,2-trifluoroethanol, and acetone), and in a 2,2,2-trifluoroethanol (TFE)–ethanol mixture. All runs were performed, at least, in duplicate, and average values of the integrated first-order rate coefficients from all runs are reported in Table I, together with solvent nucleophilicity values from the literature.

Discussion

The 11 specific rate values were correlated, using eq 2, against four scales of solvent nucleophilicity (data from Table I). The scales included two developed from R–X$^+$ substrates, $N_{Et_3O^+}$[5,11] and N_T[8] scales, and two based on methyl p-toluenesulfonate solvolysis, evaluated using either eq 3 to give N_{OTs} values[9,15] or eq 4 to give N'_{OTs} values.[8] The N_{OTs} and N'_{OTs} scales do not have available a value for 95% acetone, and correlations using these scales are based on only 10 solvents. The slopes (l values), intercepts, and correlation coefficients are presented in Table II.

The l values obtained from use of N_T, N_{OTs}, and N'_{OTs} values were all close to 0.80, but the standard deviations and correlation coefficients were inferior when N_{OTs} values were used, consistent with the recent claim[8] that N'_{OTs} values are to be prefered over N_{OTs} values, especially for correlations involving other than a p-toluenesulfonate leaving group. As is to be expected for a scale based upon attack at ethyl rather than methyl, a higher l value of 1.01

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was obtained with $N_{Et_3O^+}$ values. If one applies the previously proposed[5] scaling factor of 0.83, the value is reduced to 0.84, in good agreement with the other estimates.

The good correlations observed are of interest since it has recently been claimed[16,17] that, for unimolecular solvolyses (k_c processes) of arylalkyl chlorides, dispersions observed in plots against Y_{Cl} values (based on 1-adamantyl chloride solvolysis) are associated with differences in solvation between aromatic rings and alkyl groups. These arguments do not seem to apply to correlations against nucleophilicity; within the present substrate, there are three aromatic rings and good correlations are obtained against solvent nucleophilicity scales developed from a study involving attack at methyl or ethyl groups. This would seem to give indirect support to the claims that these effects manifest themselves primarily at the incipient carbocation of a k_c process transition state.[16,17] Further, in the recently reported[14] study of a series of benzylic *p*-toluenesulfonates, the transition-state structure for attack by solvent (k_s process) varied appreciably with substituent, as reflected in large *l* and low *m* values with a *p*-NO_2 substituent and low *l* and large *m* values for a *p*-Me substituent. However, the correlation coefficients showed only random variation rather than the gradual reduction in value one might have expected[16,17] to accompany increasing contributions from the mY_{OTs} term (with the Y_{OTs} scale based on solvolysis of an adamantyl *p*-toluenesulfonate). It appears that either the dispersion effects are important only for pure or nearly pure k_c processes or, less likely, there was a fortuitous cancelling of dispersion affects associated with the particular 11 solvents chosen for these studies. It is probable that, for k_s processes involving benzylic derivatives, the original *Y* scales,[15] based on solvolysis of adamantyl derivatives, are preferable and only for pure or nearly pure k_c processes should the new scales based on tertiary benzylic derivatives[16] or *p*-methoxybenzyl chloride[17] be used.

Correlations against $N_{Et_3O^+}$ values of the specific rates of solvolysis of the methyldiphenylsulfonium ion ($MeSPh_2^+$) led to an *l* value of 0.99,[12] virtually identical with the presently obtained value for the benzyldiphenylsulfonium ion ($BzSPh_2^+$) at a 25 °C lower temperature. From a study of the ethanolysis of $MeSPh_2^+$ at several temperatures,[12] an extrapolated specific rate at 25.0 °C of 6.1×10^{-8} s^{-1} is found to be lower than the value for $BzSPh_2^+$ by a factor of 1.5×10^4. For the corresponding *p*-toluenesulfonates, a value for the ethanolysis of MeOTs at 25.0 °C of 4.1×10^{-7} s^{-1}, obtained by extrapolation of data of Robertson,[18] is only lower than the value for BzOTs[14] by a factor of 131. The *l* values for solvolysis are of magnitudes for BzOTs of 0.77 (using $N_{Et_3O^+}$ values) and 0.50 (using either[7] N_{OTs} or N'_{OTs} values), obtained[14] by use of eq 1 (with Y_{OTs} values), and for $BzSPh_2^+$ of 1.01 ($N_{Et_3O^+}$ values) and 0.74 (N'_{OTs} values), obtained by use of eq 2. In the presence of strong solvation of a leaving anion, both the BzX/MeX rate ratio and the sensitivity of BzX to variations in solvent nucleophilicity (*l* values) are lower than when X leaves as a neutral molecule, a situation where nucleophilic attack at the α-carbon is the overwhelming rate-determining factor and, therefore, sensitivities toward changes in nucleophilicity are magnified.

Other comparisons that can be made by use of the previously discussed specific rates of ethanolysis involve leaving-group effects. A value of 0.15 for the $MeSPh_2^+$/MeOTs ratio can be compared to a value of 17 for the $BzSPh_2^+$/BzOTs ratio. By use of data for specific rates of solvolysis of BzOTs at 25.0 °C from the literature[19] and $BzSPh_2^+$ values from Table I, values for the $BzSPh_2^+$/BzOTs ratio are found to be reduced to 1.62 in 80% EtOH and 0.32 in 60% EtOH. The inversions of the $BzSPh_2^+$/BzOTs ratio, either by replacing the benzyl group by methyl or by varying the composition of an aqueous ethanol mixture, illustrate very clearly that scales of leaving-group abilities, such as from reaction in methanol of methoxide ion with a series of methyl derivatives,[20] would be of only limited applicability, especially when both anionic and neutral leaving groups are included in the listing.

The finding of an appreciable sensitivity toward solvent nucleophilicity in the solvolysis of $BzSPh_2^+$ is consistent with the earlier claim by Friedberger and Thornton[21] of an S_N2 mechanism for the hydrolysis of the benzyldimethylsulfonium ion ($BzSMe_2^+$). However, their claim that the S_N2 mechanism also applies to the hydrolysis of the (*p*-methoxybenzyl)dimethylsulfonium ion is inconsistent with a subsequent finding for the solvolyses of this ion of essentially zero sensitivity to changes in solvent nucleophilicity, coupled with an observation of common molecule rate depression in 95% acetone.[22] Harris and Raber[23] have previously suggested that the similarity in the sulfur kinetic isotope effect observed[21] for the hydrolyses of the parent $BzSMe_2^+$ and its *p*-methoxy derivative is due not to mechanistic similarity but to failure of the probe to respond to changes in mechanism.

Experimental Section

Materials. The purifications of acetic acid,[24] acetone,[25] ethanol,[25] formic acid,[26] methanol,[25] and 2,2,2-trifluoroethanol[27] were as previously described. Benzyl bromide (Aldrich), diphenyl sulfide (Aldrich), and silver trifluoromethanesulfonate (Aldrich) were used without further purification.

Benzyldiphenylsulfonium Trifluoromethanesulfonate. Benzyl bromide (1.63 mL, 13.7 mmol) and diphenyl sulfide (2.4 mL, 14.5 mmol) were added to nitromethane (2 mL). The mixture was cooled within an ice bath and stirred for 30 min. Then, silver trifluoromethanesulfonate (3.52g, 13.7 mmol) dissolved in nitromethane (21 mL) was added dropwise over a period of 10 min. Acetonitrile (20 mL) was added and the mixture stirred for 30 min. Filtration and evaporation of the solvent under vacuum led to a brown viscous liquid that became a paste at ice bath temperature. Addition of pentane to the paste, followed by filtration and washing of the precipitate with small portions of pentane, led to white crystals: 3.39 g (58.1%); mp 100–102 °C; IR (KBr disk) 3020, 2920, 1585, 1500, 1450, 1400, 1250, 1030, 680 cm^{-1}; ^1H NMR (CD_3CN) δ 5.32 (s, 2 H), 7.2–7.5 (m, 5 H), 7.6–7.9 (m, 10 H). Anal. Calcd for $C_{20}H_{17}F_3O_3S_2$: C, 56.37; H, 4.02. Found: C, 55.97; H, 4.07. The salt decomposed within a few days. Attempts to prepare derivatives with *p*-methyl, *p*-chloro, *p*-bromo, or *p*-nitro substituents within the benzyl group led only to oils,

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which underwent fairly rapid decomposition.

Kinetic Procedures. Each run was carried out by the removal at appropriate time intervals of 5-mL portions from 50 mL of a solution initially ca. 5×10^{-3} M in freshly prepared substrate. Infinity titers (V_∞) were taken after 10 half-lives. For runs in 97 and 80% TFE, the time to V_∞ was reduced by addition of a 5-mL portion to 10 or 5 mL of ethanol and allowing the solution to stand for 4 days before addition of acetone and titration in the usual manner. The titration procedures for runs in acetic and formic acids and the calculation of the first-order solvolytic rate coefficients were as previously described.[5] For experiments in other solvents, the 5-mL portions were added to 15 mL of cooled acetone (solid CO_2), containing Lacmoid (resorcinol blue) as indicator, and titration was against a standardized solution of NaOMe in MeOH.

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3,4-Benzodiazocine Derivatives from *N*-Aminonoscapinium Chloride

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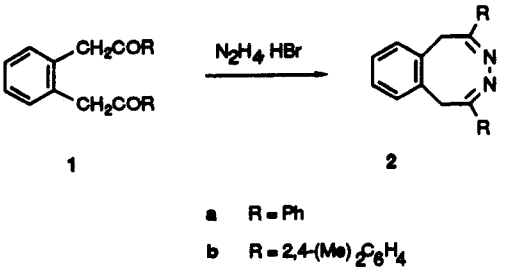
Only a few 3,4-benzodiazocines have been reported in the literature so far.[1] Allinger and Youngdale[2] prepared the first 3,4-benzodiazocine derivatives (1,6-dihydro-3,4-benzodiazocines **2a** and **2b**, respectively) from the corresponding *o*-phenylenediacyl compounds **1a** and **1b**, respectively, by treatment with hydrazine hydrobromide (Scheme I).

Heine et al.[3] treated *o*-phenylenediacetyl chloride (**3**) with 3,3-pentamethylenediaziridine to obtain diaziridine **4**. Isomerization and rearrangement of **4** gave the 3,4-benzodiazocine-2,5-dione **5** (Scheme II).

Reported here is a simple, efficient, and direct route to 3,4-benzodiazocine derivatives from *N*-aminonoscapinium chloride (**7**). N-Amination of noscapine (**6**) with chloramine has been described by Grace.[4] We prepared *N*-aminonoscapinium chloride from noscapine by using either *O*-(2,4-dinitrophenyl)hydroxylamine (DNPH)[5,6] or *O*-(diphenylphosphinyl)hydroxylamine (DPH)[7,8] as N-amination reagent. Hofmann degradation of **7** with diluted NaOH yielded *N*-aminonornarceine (**8**). Heating compound **8** to 140–150 °C gave the yellow lactam **9**, while treatment of **8** with absolute EtOH/HCl afforded the isomeric red enone **10** (Scheme III).

Since both compounds (**9** and **10**) were available only in low yields by the methods described, we sought for a more efficient route for the synthesis of such 3,4-benzodiazocine structures. Instead of amphoteric **8**, we wanted to prepare first the *N*-aminonornarceine ethyl ester (**11**) analogously to the formation of *N*-benzylnornarceine ethyl ester from *N*-benzylnoscapinium bromide with EtOH/Et_3N.[9] Refluxing **7** in EtOH/Et_3N afforded the desired

Scheme I

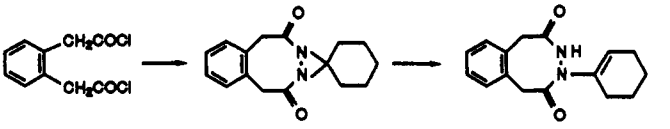


1 2

a R = Ph

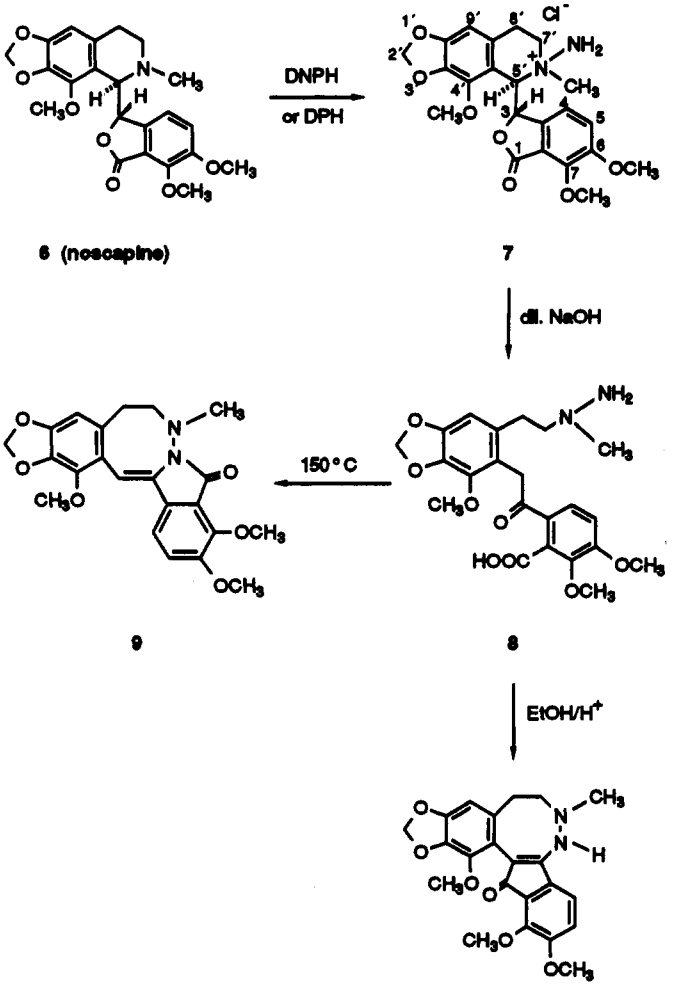
b R = 2,4-(Me)$_2$C$_6$H$_3$

Scheme II



3 4 5

Scheme III



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(10) A diastereomeric mixture was obtained: TLC (AcOEt/EtOH 3:2): R_f 0.2 and 0.1, respectively; ^{1}H NMR showed two sets of signals: intensity I/II 2:1 (Table I).

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