for i at 50 °C[14] and a triflate:tosylate rate ratio of 10[4.76]. This is the measured rate ratio of 1-OTf/1-OTs at 50 °C. See ref 5 and 14 and Table I.

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# Steric Relief Control of Solvolysis Rates of 1-Alkyl-2-adamantyl Substrates. Empirical Force-Field Calculations

Dan Fărcaşiu

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

8-Cyano-4-exo-protoadamantanol (exo-3) isolated from the solvolysis of 1-cyano-2-adamantyl tresylate (1g-OTres) was oxidized to 8-cyano-4-protoadamantanone (4), which was reduced by sodium borohydride to a 5:4 mixture of 8-cyano-4-endo-protoadamantanol (endo-3) and exo-3. No endo-3 was evidenced in the original solvolysis mixture from 1g-OTres, so that solvolysis of 1g-OTres is as stereoselective as the solvolysis of the 1-methyl analogue (1b-OTs). The variation of steric strain in the ionization of 1-alkyl-2-adamantyl substrates (1b-e) was evaluated by force-field calculations. A significant relief of steric strain [Δ(strain)] was found for this process, and it was correlated with the rates of solvolysis ($k$) by the equation: log $k$ = 0.63Δ(strain) − 6.73 ($r$ = 0.9693, SD = 0.271). Thus, the rate increase produced by 1-alkyl substituents in the solvolysis of 2-adamantyl substrates is fully accounted for by the steric strain relief (which can be adjusted for a more refined treatment by a smaller polar effect of 1-substituents), and no other mechanistic assumption is necessary.

Empirical force field calculations[1] have been used to solve various problems in physical organic chemistry.[2] Recent applications permitted estimation of the most stable conformations of known[3] or as yet unsynthesized compounds;[4] calculation of barriers and pathways for conformer interconversions;[5] determination of the most stable member of a (usually large) family of isomeric hydrocarbons;[6] predictions or rationalizations of pathways in carbocationic isomerizations;[6a,7] and hydrogenolysis reactions of strained polycycles.[8] Examples of rationalization of products obtained in cyclizations[9] and in ring enlargements of carbocations[10] can also be noted. A special group of applications consists of the calculations of steric strain variations in reactions involving a change of hybridization at the reaction center and the correlation of reaction rates with the variations in strain energy. Thus, ester hydrolysis[11] and oxidation of secondary alcohols[12] were successfully correlated. The most useful results, however, were obtained for the solvolytic reactions involving carbocations by Schleyer, who pioneered the use of force field calculations for mechanistic studies of chemical reactions.[13]

It is the purpose of this paper to report on the application of this approach to the solvolysis of 1-alkyl-2-adamantyl substrates and to present new experiments in the study of the 1-cyano analogue.[14]

Studies of the solvolysis of the parent (1a) and 1-alkyl-substituted 2-adamantyl bromides (1b-e-Br) and sulfonates (1b-e-OSO₂Ar) have been interpreted to indicate that the ionization of 1b-e is anchimerically assisted ($K_\Delta$ process[15]) and involves σ-bridged ions (2b-e) as intermediates.[16] It was stated that 1b provides a "textbook" example of "nonclassical" ion, . . . "free from the many anomalies of the 2-norbornyl system".[16c] A subsequent investigation of related substrates carrying deactivating substituents (1f,g)[17] led the present writer to question[14] some of the conclusions expressed by previous workers.[16] Such a viewpoint elicited interest[18] as well as criticism.[19] Most of the latter concerned the existence[14] of a relationship between rearrangement and rate enhancement in the solvolysis of 1-substituted 2-adamantyl substrates (1). It was considered[14] that, if the formation of rearranged product is due to bridging, then the measured solvolysis rate is faster than the value expected in the absence of bridging. A precise mathematical relationship between rates and amount of rearrangement for 1 could not be deduced,[20] but in the same solvent and under the same conditions a larger amount of rearranged product possibly reflects a larger acceleration.[14] In other words, if two phenomena (rate enhancement and rearrangement) are produced by the same cause (bridging) they are necessarily related. As this point was also recognized by the previous workers,[21] it needs no further elaboration. One valid observation remained, however: In the solvolysis of the cyano derivative (1g-OTres), a rearranged product, 8-cyanotricyclo[4.3.1.0[3,8]]decan-4-exo-ol (8-cyano-4-exo-protoadamantanol) (exo-3) was formed (38%) along with the starting alcohol (1g-OH).[14] The absence of the



I (X = OH, Br, OTs, OTres)                    2

a  R = R' = H                    e  R = t-Bu , R' = H
b  R = Me , R' = H               f  R = H, R' = COO Me
c  R = Et , R' = H               g  R = H, R' = CN
d  R = i-Pr , R' = H

stereoisomeric *endo*-3 was inferred from the fact that only one peak was observed on GLC on two different columns,[14] but a coincidence in retention time of two isomers could not be ruled out.

In order to remove any uncertainty the preparation of *endo*-3 was undertaken. The rearranged product from solvolysis (*exo*-3)[14] was oxidized with the Jones reagent under mild conditions to give 8-cyano-4-protoadamantanone (4) as the only product. Sodium borohydride reduction of 4 at 0 °C led to a mixture of *endo*-3 and *exo*-3 in about 5:4 ratio. The
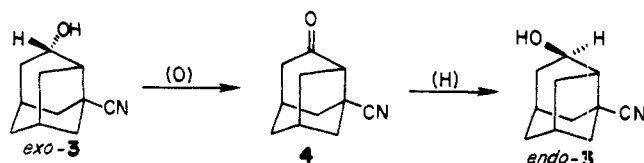


epimers could be separated by GLC, the endo isomer eluting first on a silicone-SE30 column. The same analysis conditions failed to reveal any *endo*-3 in the solvolysis mixture from 1g-OTres.[14] Thus, the rearranged product from 1g-OTres is formed with the same stereospecificity as the rearranged product from 1b-OTs.[16c]

The similar behavior of 1b and 1g substrates could be rationalized either by admitting the intermediacy of σ-bridged ions in both, or by considering that ionization leads to a nonbridged ion in both cases and the rearrangement takes place after ionization.[14] It has been already shown that by accepting the first alternative we are led to the disturbing conclusion that the observed acceleration produced by a 1-methyl group in 1 is too small to reflect any significant stabilization by bridging in 12.[14] In order to accept the second alternative we must identify the origin of the observed rate effect of the 1-methyl substituent. This rate acceleration (the point for 1b-OTres deviates upward by a factor of 13 from the least-squares $\rho^*\sigma^*$ line drawn through the points for 1a-, 1f-, and 1g-OTres[14]) was previously explained by bridging.[16] However, it has been shown that neighboring alkyl substituents exert a magnified steric effect in the solvolysis of rigid, polycyclic substrates.[22] In order to probe the existence of a steric effect upon rates in 1b–e, the variation of strain energy on ionization was calculated for the reaction shown in eq 1. This is, in fact,
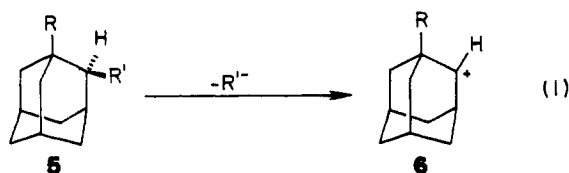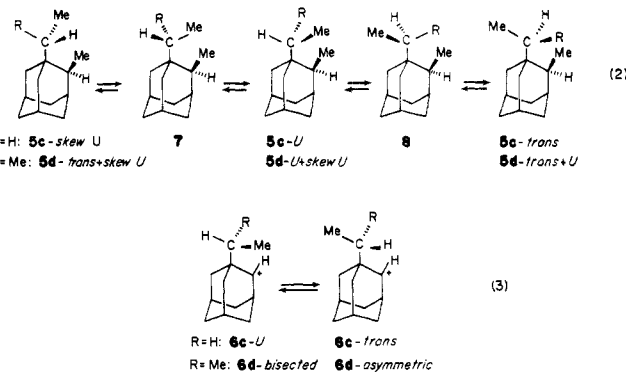


the standard procedure used in previous studies of effects of steric strain upon solvolysis rates.[13]

In formula 5 (eq 1) R' represents the leaving group. Ideally, the force field should include the actual leaving group employed in solvolysis. Recently, attempts have been made to extend the force field calculations to heteroatom-substituted molecules.[23] However, the agreement with the experiment was consistently poorer than that secured for hydrocarbons.[23a,c,24] A more successful approach has been to use the force field for hydrocarbons, either "engrossing" a carbon atom to the size of the heteroatom,[25] or trying to match the heteroatom or group by an isosteric alkyl group.[26a] Most of the previous correlations of solvolysis rates[13] have used hydrogen for the leaving group. This admitted simplification[13c] masked the steric interactions involving the leaving group and was recently criticized.[27] In the case of 2-alkyl-2-adamantyl substrates[13c] the probable result was too high[27] a slope for the line correlating the solvolysis rates with the strain energy variations (Δ (strain)) (vide infra).

Looking for a measure of comparison between the size of a halide or sulfonate and that of an alkyl group, it became clear that conformational energies (*A* values) were not suitable for the following reasons: (1) The *A* values are determined in a flexible system (cyclohexane) which can flatten or pucker to minimize steric interactions; this is not the case with 5. (2) The *A* values vary widely with the solvent, in most cases systematically with the solvent polarity.[28] (3) The equatorial/axial preference of a substituent is significantly influenced by its polarity; the more polar substituents, even when much bulkier, have a larger proportion of axial conformer.[29] (4) The *A* values are largely determined by 1,3-diaxial interactions in the axial conformer. This is constant throughout our reaction series (eq 1), while the 1,2-skew interaction between R and R' increases. The two kinds of interaction do not have a parallel variation.[30]

A better measure of the space requirements of substituents are probably the van der Waals radii. Indeed, correlation of a large number of reaction series has been achieved using steric constants derived from van der Waals radii.[31] On that basis, $CH_3$ (about as large as Cl, but smaller than Br) is an acceptable model for the leaving group, although it is too small to represent a sulfonate ester group. Previously, $CH_3$ has been used to model Br and neopentyl to model $OSO_2Ar$ in a correlation of tosylate/bromide solvolysis rate ratios with Δ(strain) on ionization.[26a] The correlation was only fair, but the goal was probably too ambitious, with the systems investigated varying widely.[26b] More recently, to detect steric acceleration in the solvolysis of cyclooctyl tosylate,[32] $CH_3$ was used to mimic the leaving group. The same approach was adopted in the present work (5, R' = $CH_3$, eq 1). The latest force field developed at Princeton University[2a] was employed.[33] Results of the calculations are shown in Table I. Since there are three possible rotamers each for compounds 5c and 5d (eq 2) and two possible rotamers each for ions 6c and 6d (eq 3), the strain ener-





gies for all these were calculated.[34] The barriers for rotamer interconversions were tested for compound 5c by calculating the strain energies and heats of formation for the eclipsed conformers 7 and 8 (eq 2 and Table I).

The variation of strain energy on ionization (eq 1) is calculated in Table 1 as Δ(strain) = $\Delta H°$(strain 5) − $\Delta H°$(strain 6). Since the barriers for rotamer interconversion are small in comparison with the activation energy of the solvolysis,[16a] the strain relief for the ionization of 5c and 5d was calculated from the strain energies of individual conformers by the approach used previously to evaluate activation energies for reactions in systems with mobile equilibrium in both reactants and products.[35] (Using in calculation the values for the lowest energy conformers,[13c] or the average strain energy for each state, did not alter the correlation significantly.)

Examination of Table I reveals that Δ(strain) increases markedly with the size of the alkyl group at C-1 (R). As intuitively expected, the greatest difference is between H and Me,[36] and between *i*-Pr and *t*-Bu.

For a quantitative correlation, the solvolysis rates measured

**Table I. Strain Energies for Hydrocarbons and Carbocations (eq 1, R' = CH₃) and Solvolysis Rates of 1-Alkyl-2-adamantyl Tosylates**

| structure | registry no. | $\Delta H_f°$, kcal/mol | $\Delta H°$(strain), kcal/mol | $\Delta$(strain)[a] | $\log k$[b] |
|---|---|---|---|---|---|
| **5a** | | $-37.94$[c] | 8.56[c] | $-0.65$ | $-7.620$ |
| **6a** | 21410-12-8 | $-25.08$ | 9.21 | | |
| **5b** | | $-46.05$[c] | 8.64[c] | 0.65 | $-6.078$ |
| **6b** | 67011-20-5 | $-34.49$ | 7.99 | | |
| **5c**-skew U | 29521-81-1 | $-49.28$ | 10.54 | | |
| **5c**-U | | $-47.47$ | 12.35 | | |
| **5c**-*trans* | | $-48.85$ | 10.97 | | |
| **6c**-*trans* | 66966-43-6 | $-38.06$ | 9.55 | 1.17[d] | $-5.564$ |
| **6c**-U | | $-38.03$ | 9.58 | | |
| **5d**-*trans* + skew U | 34529-25-4 | $-52.85$ | 14.05 | | |
| **5d**-U + skew U | | $-51.40$ | 15.50 | | |
| **5d**-*trans* + U | | $-51.04$ | 15.86 | | |
| **6d**-asymmetric | 66966-44-7 | $-43.06$ | 11.63 | 2.55[d] | $-5.089$ |
| **6d**-bisected | | $-42.36$ | 12.33 | | |
| **5e** | 66966-45-8 | $-54.75$ | 20.34 | 5.13 | $-3.668$ |
| **6e** | 66966-46-9 | $-47.67$ | 15.21 | | |
| **7** (R = H)[e] | | $-41.76$ | 18.06 | | |
| **8** (R = H)[f] | | $-45.79$ | 14.95 | | |

[a] Positive value means strain relief on ionization. [b] 80% ethanol, 25 °C.[16a] [c] From E. M. Engler, Ph.D. Thesis, Princeton University, 1973. [d] See text. [e] The actual barrier was found for a dihedral angle C2–C1–C11–C12 = $-4.40°$ (i.e., toward **5c**-U). $\Delta H_f° = -41.68$, $\Delta H°$(strain) = 18.14. [f] Dihedral angle C8–C1–C11–C12 = $-1.30°$. The actual barrier was not established, but it cannot be significantly different in energy.
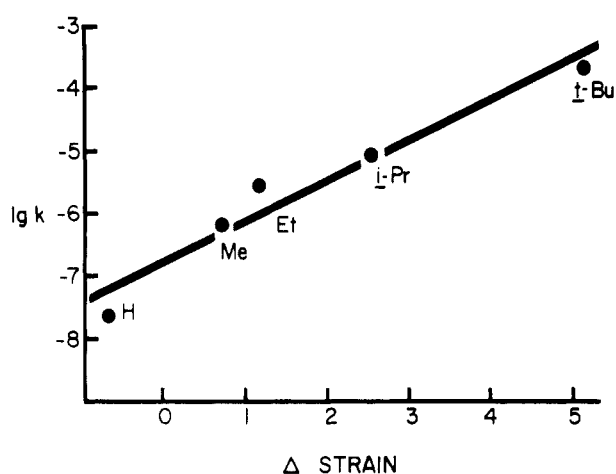


**Figure 1.** Plot of the log of rate constants for the solvolysis (80% ethanol, 25 °C) of 1-alkyl-2-adamantyl tosylates vs. the relief of strain energy calculated for eq 1. The straight line (least-squares fit) is represented by eq 4.

for compounds **1b–e** relative to the parent compound **1a** should be dissected in contributions of the polar and steric effects of $\beta$-alkyl substituents. It has been shown previously that the solvolysis of 2-adamantyl substrates (**1**) has an appreciable sensitivity to polar effects ($\rho^* = -4.09$).[14] However, as a first approximation it was decided to use the *measured* (nondissected) rates. This leads to a calculated sensitivity of rates to steric effects (for a linear relationship[37] that is the slope of the log $k = f(\Delta(\text{strain}))$ plot), which is too high.[27] The data are correlated by eq 4 (represented in Figure 1).

$$\log k = 0.63\Delta(\text{strain}) - 6.73$$

$$r = 0.9693; \text{SD} = 0.271 \qquad (4)$$

Although polar effects were not substracted, the slope of this line is rather low: 0.63 vs. 1.23 for the solvolysis of 2-alkyl-2-adamantyl *p*-nitrobenzoates.[13c] While the difference might indicate a higher sensitivity to steric effects for the latter reaction series, it is more probable that neglecting the steric effects of the leaving group in that study[13c] was re-

sponsible for at least a part of the difference.[27] The slope found for the present reaction series is also smaller than the one found for the acid-catalyzed dehydration of 2-alkyl-2-adamantanols.[27] Possibly, the leaving group steric effect was not fully accounted for by the model chosen in that study either.

The comparatively large effect of a $\beta$-alkyl group (particularly of a $\beta$-methyl group) upon solvolysis rates constituted the central evidence around which the case for a bridged intermediate in the solvolysis of **1b–e** has been built.[16a–c] As it was already pointed out,[14] the stereospecificity of the rearranged product formation does not require $\sigma$ bridging; in fact, stereospecificity was found in polycyclic systems for reactions in which bridging can play no role.[7b,10,38] It is also noteworthy that the total stereoselectivity in the formation of rearranged product in the solvolysis of **1b** is accompanied by an *incomplete* stereoselectivity in the formation of nonrearranged product (**1b-OH**). The predominant retention in the latter case[39] is consistent with the absence of a bridged intermediate since, as noted by Schleyer,[40] retention is expected in limiting solvolysis of polycyclic systems like 2-adamantyl,[41] or even of acyclic tertiary systems.[40]

The central point of the debate[14,16] about the solvolysis of adamantyl (**1a**) and 1-alkyl-2-adamantyl substrates (**1b–e**) has been the contention[16] that introduction of a 1-alkyl group changes the nature of the process from essentially limiting ($k_c$ process[15]) for **1a**[16b,c,40,41b] to anchimerically assisted, involving a bridged ion intermediate (**2b**), for **1b**.[16,42] This was easily rationalized, since a bridged intermediate from **1a** would be a hybrid between two structures differing by about 11 kcal/mol in energy,[16b] while for **2b** the two limiting structures should be nearly equal in energy.[16c] Yet, introduction of a 1-methyl group only insignificantly changes the stereoselectivity for the unrearranged product, from 64–84% retention[16b,41a] to 90% retention.[39] On the other hand, the rearranged product is, in the limits of sensitivity of the GLC analysis, exclusively exo from both **1a** and **1b**. Clearly, the stereospecificity in the formation of protoadamantyl product cannot be invoked as an argument for the intervention of **2b**. The present results indicate that the acceleration produced by $\beta$-alkyl groups in the solvolysis of secondary 2-adamantyl substrates has a steric origin, just as the acceleration produced

by the alkyl groups in the solvolysis of tertiary[43] 2-adamantyl substrates does.[13c,27] Therefore, the conclusion[14] that bridging in the solvolysis of **1b–e** is at best marginal,[44] or more probably absent altogether, unquestionably holds.

## Experimental Section

**General.** The NMR spectra were recorded at 60 MHz (Varian A-60A instrument). High resolution mass spectra were determined at 70 eV (AEI-MS9 instrument), GLC–mass spectra were also done at 70 eV on an E. I. duPont 21-491 instrument. Melting points are uncorrected.

**8-Cyano-4-protoadamantanone (4).** Jones reagent was prepared from 4.575 g of $CrO_3$, 7.247 g of 94% $H_2SO_4$, and 15.20 g of water. 8-Cyano-4-*exo*-protoadamantanol (exo-**3**)[14] (0.0492 g) dissolved in acetone (1 mL) was cooled in an ice water bath and Jones reagent was added dropwise, with magnetic stirring. Each drop was added after the previous one had reacted completely (1–3 min). When the yellow color persisted for more than 10 min (ca. 7 drops were used) methanol was added (3 drops) and the mixture was stirred for 5 min. The solvent was evaporated at room temperature under a stream of nitrogen, then the solid residue was extracted several times with $CH_2Cl_2$. Drying and evaporation of solvent gave a white solid, homogeneous on TLC (4 can be separated from exo-**3**, endo-**3**, and 1-cyano-2-adamantanol on E. Merck silica gel plates, using 4:1 benzene–ethyl acetate as eluent). Yield 0.046 g (93%); mp 206–208.5 °C (from heptane); IR (KBr disk) 2940 (s), 2900, 2870, 2850, 2228, 1713 (vs), 1460, 1400, 1348, 1335, 1285, 1230, 1215, 1165, 1090, 1028, 970, 850, 832 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 1.45–2.30, with peaks at 1.95 and 2.08 (8 H); 2.30–2.83, with a peak at 2.47 (4 H), and 2.88–3.21 (1 H). Anal. Calcd for $C_{11}H_{13}NO$: M, 175.0997. Found: M 175.0991 (by high resolution MS).

**8-Cyano-4-*endo*- (*endo*-3) and 8-Cyano-4-*exo*-protoadamantanol (*exo*-3).** Sodium borohydride (0.010 g) was added to a solution of 4 (0.043 g) in anhydrous methanol (1.5 mL), at 0 °C. The mixture was stirred at 0 °C for 3 h, then for 3 h at room temperature. Acetic acid (2 drops) was added, the solvent was evaporated to dryness at room temperature under a stream of nitrogen, then water (1 drop) was added and the mixture was extracted several times with ether. The GLC of the dried (Na$_2$SO$_4$) solution (3% silicone SE-30, 1.8 m × 3 mm o.d., 120°) indicated a mixture of endo-**3** and exo-**3** (eluted in that order) in ca 5:4 ratio. Evaporation of the solvent left a solid (0.038 g, 87% yield): IR (KBr disk) 3455, 2910, 2860, 2220, 1455, 1035 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 1.15–3.00 (complex, 14 H), 3.93–4.36 (m, 1 H); mass spectra[45] (determined by GLC–MS) for endo-**3** 177 (M$^+$·) (4), 159 (100), 149 (17), 144 (16), 134 (16), 130 (15), 118 (26), 117 (73), 107 (20), 106 (22), 105 (23), 104 (34), 93 (33), 92 (44), 91 (33), 80 (32), 79 (24), 77 (17), 67 (19), 57 (15), 56 (19), 55 (17), 41 (19), 39 (15); MS for exo-**3**[46] 177 (M$^+$·) (1), 159 (91), 144 (19), 118 (35), 117 (100), 106 (15), 105 (28), 104 (43), 93 (27), 92 (40), 91 (26), 81 (18), 80 (34), 79 (20), 67 (16), 57 (19), 56 (20), 41 (25), 39 (17).

**Registry No.**—exo-**3**, 66966-47-0; endo-**3**, 67010-36-0; **4**, 66966-48-1.

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(41) (a) J. A. Bone and M. C. Whiting, *J. Chem. Soc., Chem. Commun.*, 115 (1970); (b) See the discussions and references in: J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Am. Chem. Soc.*, **96**, 4484 (1974).

(42) Thus, it was stated that "unlike the secondary protoadamantyl and 2-adamantyl series, the bridged ion (i.e., **2b**) dominates the chemistry of" **1b** and the tertiary protoadamantyl substrates.[16c]

(43) For the reaction of tertiary substrates,[13c,27] the steric effect observed was also that of β and γ substituents, since the variable substituent was CRR'R'', with R = R' = R'' = H for the "parent" compound.

(44) Following our previous article (ref 14) and the solvolysis study on optically active **1b**, the original workers in the field describe presently this system as involving a weakly bridged ion **2b** (ref 19), in contrast to a model nonclassical ion "which behaves according to textbook expectations", as was stated originally (ref 16c).

(45) With the exception of the parent peak, only the peaks with an intensity (in parentheses) higher than 15% of the intensity of the base peak are listed.

(46) The conditions used for the present GLC–MS experiments (5% silicone SP2250, 3 m × 3 mm o.d., at 170 °C with 30 mL/min He as carrier gas) ensured a more uniform elution of each component from the column (broader, yet well-resolved peaks) than in the previous work.[14] Whenever the relative intensities of fragment ions differ from those reported,[14] it is believed that the present values are more reliable.

# Tautomerism and Dissociation of 4-Arylazo-1-naphthols in Various Solvents[1]

Satoshi Kishimoto,*[2a] Shinya Kitahara,[2a] Osamu Manabe,[2b] and Hachiro Hiyama[2a]

*Osaka Municipal Technical Research Institute, Ogimachi, Kita-ku, Osaka-shi, 530, Japan*

The tautomerism of 4-(4'-substituted-phenylazo)-1-naphthol [azo form (1) vs. hydrazone form (2)] is estimated by means of electronic spectra in various solvents. With electron-donating substituents the azo form is stabilized, while electron-withdrawing ones stabilize **2**. The azo form is stabilized in pyridine, acetone, ethanol, and methanol, while the hydrazone form predominates in chloroform and acetic acid based on the equilibrium in benzene as standard. The equilibrium fits the Yukawa–Tsuno equation, $\log K/K_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+)$, $r$ and $\rho$ values being determined in the solvent system mentioned above. The proton-donating solvent (chloroform) gives a larger $r$ value; the values for the proton-acceptor solvents are smaller than that of benzene, the standard solvent. In polar aprotic solvents such as dimethyl sulfoxide and *N,N*-dimethylformamide 4-(4'-substituted-phenylazo)-1-naphthol is found to be present as a dissociated form.

## Introduction

The physical properties of azo dyestuff (e.g., tone, color) are closely related with the tautomerism of the dyes. 4-(4'-Substituted-phenylazo)-1-naphthols (4-azo dyes) prepared by the coupling reaction of 4-substituted benzenediazonium salts with 1-naphthol are profoundly interesting as fundamental azo compounds. They may have two tautomeric isomers, **1** and **2**, as shown in eq 1. The tautomeric equilibration
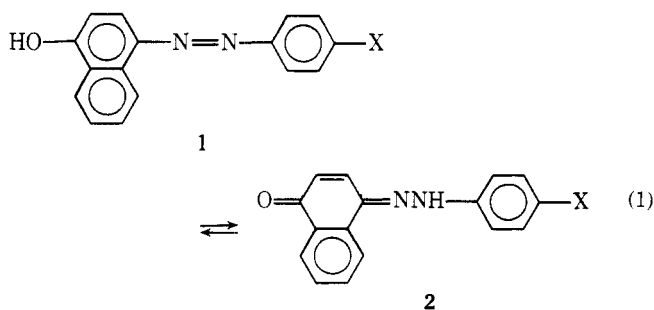


$$X = OCH_3, CH_3, H, Cl, NO_2$$

is found to depend upon their substituents as well as on solvents.[3-5] Every study reported so far has been qualitatively treated. In this paper we wish to describe experimental results

on the tautomerism investigated quantitatively by means of electronic spectra and to discuss the effects of substituents and solvents.

## Experimental Section

**Materials.** The 4-azo dyes[6,7] 1-methoxy-4-phenylazonaphthalene (**3**)[8] and 1,4-naphthoquinone-*N*-methylphenylhydrazone (**4**)[9] were prepared according to the literature.
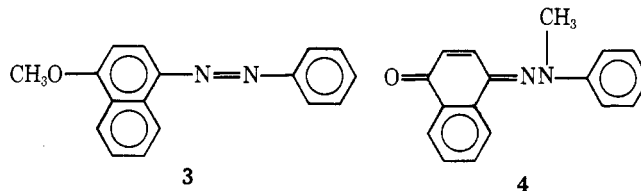


**Methods.** Spectra were taken on a Shimadzu MPS-50L spectrometer in $2 \times 10^{-5}$ M solution with 10-mm cuvettes; Beer's law was shown to be valid at this concentration.

The 1/2 ratios were estimated by assuming that **3** and **4** represent the extreme forms for **1** and **2** and that the spectral shape of **1** and **2** and the ratios of the molecular extinction coefficients of **1** and **2** at the maximum absorptions are constant irrespective of the kinds of substituents when recorded in the same solvent.

## Results and Discussion

Figure 1a exhibits the electronic spectra of 4-(4'-methox-