Neighboring Group Participation by Pyridine Ring. 3. Synthesis and Solvolysis of 5,8-Dihydro- and 5,6,7,8-Tetrahydro-5,8-methanoquinoline Derivatives[1]

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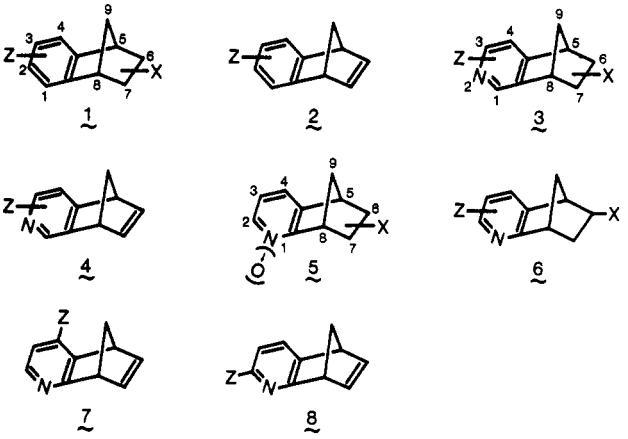
Introduction of a propionaldehyde function into the 3-exo position of 5-*exo*-(benzyloxy)bicyclo[2.2.1]heptan-2-one (**11**) followed by construction of a pyridine ring fused with the bicyclo[2.2.1]heptane ring gave 5,8-dihydro- and 5,6,7,8-tetrahydro-5,8-methanoquinolines, from which their *N*-oxides and aryl-substituted derivatives (**5–8**) were derived. Solvolysis rates for 5,6,7,8-tetrahydro-5,8-methanoquinolin-6-*exo*(and 7-*exo*)-yl arenesulfonates and the aryl-substituted derivatives (**6**) were determined in 50% aqueous *tert*-butyl alcohol to compare with the rates previously reported for the corresponding benzonorbornyl (**1**) and 5,6,7,8-tetrahydro-5,8-methanoisoquinolinyl arenesulfonates (**3**), the molecules of isosteric configuration. When the relative rate for benzonorbornen-6-*exo*-yl arenesulfonate is considered to be unity, those for the 2-CH_3O, H(parent), and 2-Cl substituted 5,6,7,8-tetrahydro-5,8-methanoquinolin-6-*exo*-yl arenesulfonates at 50 °C are 2.46, 5.4×10^{-3}, and 8.13×10^{-4}, respectively, and that for *N*-oxide of the 2-H(parent) 6-exo-yl arenesulfonate is 4.4×10^{-6}. Plots of logarithmic relative rates for the 6-exo-yl arenesulfonates against those for the 2-substituted benzonorbornen-6-*exo*-yl arenesulfonates or 3-substituted 5,6,7,8-tetrahydro-5,8-methanoisoquinolin-7-*exo*-yl arenesulfonates gave straight lines without detectable deviation from the slope of unity. The relative rates for the 2-H(parent) 7-*exo*-arenesulfonate and its *N*-oxide are 1.4×10^{-4} and 1.6×10^{-5}, respectively. Effects of the aryl substituents, the *N*-oxides, and the pyridine ring nitrogen on solvolysis rates are discussed.

Work by our group on the synthesis and solvolytic reactivity of benzonorbornene derivatives **1**[2,3] and those by Paquette's group on the synthesis and triplet-sensitized photorearrangement of benzonorbornadiene derivatives **2**[4] were recently extended to a related aza-heterocyclic system, 5,6,7,8-tetrahydro(and 5,8-dihydro)-5,8-methanoisoquinolines **3** and **4**.[5-7] As an extention of such work, we undertook the synthesis of previously unknown ring derivatives 5,6,7,8-tetrahydro(and 5,8-dihydro)-5,8-methanoquinolines **5–8** in order to investigate their solvolytic reactivities and triplet-sensitized photorearrangements.

For each of the reactions, we tried to explain the results from the benzo system and the two kinds of pyridino systems on a theoretical basis as in previous studies.[2,4-7]

Chart I



Results

Syntheses of Ring Systems (Scheme I). Treatment of 5-*exo*-acetoxybicyclo[2.2.1]heptan-2-one (**9**), prepared by the reported method,[8] with sodium methoxide in methanol gave the hydrolysis product **10**, which was transformed into 5-*exo*-(benzyloxy)[2.2.1]heptan-2-one (**11**) to protect the 5-*exo*-hydroxy group. An allyl group was introduced into the 3-exo position by treatment of **11** with a strong base, lithium diisopropylamide, followed by reaction with allyl bromide. The ketone **12** thus obtained was converted into the ketal **13**, which was oxidized by ozone to provide the aldehyde **14**. Wittig reaction of **14** with (methoxymethylene)triphenylphosphorane afforded the vinyl methyl ether **15**, which was treated with acid to achieve hydrolysis of the vinyl ether group and the 3-ketal moiety. The aldehyde–ketone thus obtained was led to the dioxime without isolation. On heating under reflux in acetic acid, the dioxime was converted into 6-*exo*-(benzyloxy)-5,6,7,8-tetrahydro-5,8-methanoquinoline (**16**), which was treated with boron tribromide to give the corresponding 6-exo alcohol **17**. Formation of the 6,7-double bond to derive 5,8-dihydro-5,8-methanoquinoline (**19**) was achieved with conversion of **17** into 6-chloro-5,6,7,8-tetrahydro-5,8-methanoquinoline (**18**) followed by elimination of hydrochloric acid by the action of a base, potassium *tert*-butoxide.

Syntheses of Aryl-Substituted Derivatives (Scheme II). The 6-chloro derivative **18** was converted into the *N*-oxide **20**, which was treated with phosphorous oxychloride to afford a mixture of the 4,6-*exo*- and 4,6-*endo*-dichloro compounds (**21** and **22**). The dichloro compound **22** was led to the *N*-oxide **23**, which was treated with methoxide in methanol to provide the 4-methoxy *N*-oxide **24**. Removal of the *N*-oxide function to obtain 6-chloro-4-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (**25**) was carried out by treating **24** with phosphorus trichloride.

(1) The numbering in this paper is the same as that used in the previous paper[6] and shown in Chart I. For convenience the effects of aryl substituents were discussed on the basis of the benzo and pyridino systems in Chart I.

(2) (a) Tanida, H.; Ishitobi, H.; Irie, T.; Tsushima, T. *J. Am. Chem. Soc.* **1969**, *91*, 4512. (b) Tanida, H.; Irie, T.; Tsushima, T. *Ibid.* **1970**, *92*, 3404 and references cited therein.

(3) Reviews for the carbonium ion reactions of benzonorbornene derivatives: (a) le Noble, W. J. *Highlights of Organic Chemistry*; Marcel Dekker: New York, 1974; Chapter 20. (b) Schleyer, P. v. R.; Fry, J. L.; Bollinger, J. M. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 27.

(4) (a) Paquette, L. A.; Bay, E. *J. Am. Chem. Soc.* **1984**, *106*, 6693 and the previous papers cited therein. (b) Paquette, L. A.; Varadarajan, A.; Bay, E. *Ibid.* **1984**, *106*, 6702. (c) Paquette, L. A.; Varadarajan, A.; Burke, L. D. *Ibid.* **1986**, *108*, 8032.

(5) Tanida, H.; Irie, T.; Hayashi, Y. *J. Org. Chem.* **1984**, *49*, 2527.

(6) Tanida, H.; Irie, T.; Hayashi, Y. *J. Org. Chem.* **1985**, *50*, 821.

(7) Paquette, L. A.; Coghlan, M. J.; Cottrell, C. E.; Irie, T.; Tanida, H. *J. Org. Chem.* **1986**, *51*, 696.

(8) Meinwald, J.; Crandall, J. K. *J. Am. Chem. Soc.* **1966**, *88*, 1292.

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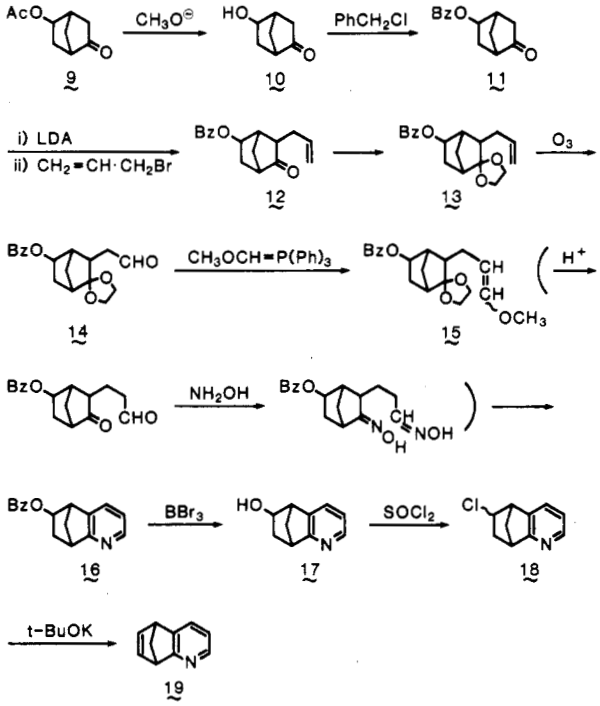
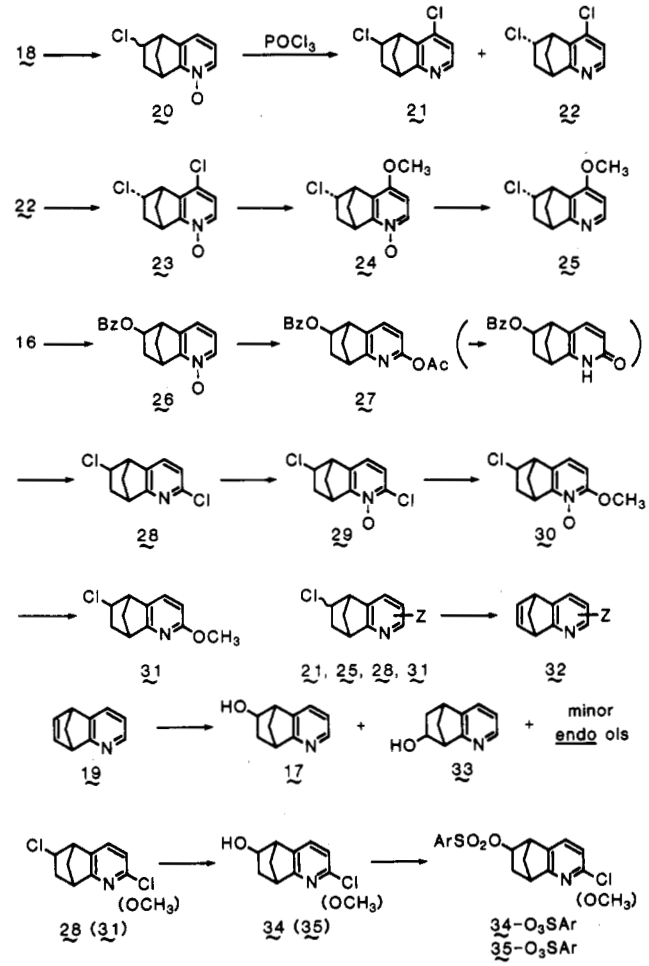
Scheme I. Synthesis of Ring Systems



Scheme II. Aryl-Substituted Derivatives



6-*exo*-(Benzyloxy)-5,6,7,8-tetrahydro-5,8-methanoquinoline *N*-oxide (**26**) obtained from **16** was treated with warm acetic anhydride, leading to 6-*exo*-(benzyloxy)-2-acetoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (**27**). Hydrolysis of **27** followed by treatment with phosphorous oxychloride gave 2,6-*exo*-dichloro-5,6,7,8-tetrahydro-5,8-methanoquinoline (**28**) which was led to the *N*-oxide **29**. Treatment of **29** with methoxide in methanol gave the 6-*exo*-chloro-2-methoxy derivative **30**, which was deoxygenated by phosphorous trichloride yielding 6-*exo*-chloro-2-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (**31**). As for the aryl-unsubstituted compound **18**, elimination of hydrogen chloride was carried out for the aryl-substituted compounds **21**, **25**, **28**, and **31** by treatment with potassium *tert*-butoxide to obtain, respectively, 4-chloro-, 4-methoxy-, 2-chloro-, and 2-methoxy-5,6-dihydro-5,8-methanoquinoline (**32**), which were used for the study of substituent effects on the photorearrangements in a previous study.[9]

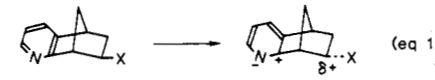
Preparations of Arenesulfonates for Solvolyses. Hydroboration of the parent 5,8-dihydro-5,8-methanoquinoline (**19**) with diborane–dimethyl sulfide complex was found to be not regiospecific and gave mainly a mixture of the 6-exo and 7-exo alcohols **17** and **33** with small amounts of the 6-endo and 7-endo alcohols. The 7-exo alcohols **33** were separated from the aforementioned **17** and the minor endo alcohols. After characterization, **33** was converted into the arenesulfonates for solvolysis studies. The 2-substituted 6-exo-chlorides (**28** and **31**) were solvolyzed in aqueous acetone in the presence of sodium bicarbonate leading to the corresponding 6-exo alcohols **34** and **35** which were esterified to obtain the arenesulfonates (**34**-O_3SAr and **35**-O_3SAr).

Rates of Solvolysis. Under the conditions described in the previous paper,[5,6] solvolyses were carried out in 50% (v/v) aqueous *tert*-butyl alcohol maintaining a constant pH of 7.5 during the reaction, and the rate data are summarized in Tables I and II. As the amounts of samples for solvolyses were limited because of a lengthy synthesis route, rate measurements needed to be done under ordinary conditions and by a simple procedure. Thus, the alcohols in the present study were converted into three different arenesulfonates; *p*-toluenesulfonate, *p*-nitrobenzenesulfonate, and pentafluorobenzenesulfonate. The relative rates at 50 °C in Tables I and II are based on assigning the rate of unity for unsubstituted benzonorbornen-6-*exo*-yl tosylate. The conversion factors among the arenesulfonates were determined as described in previous papers[5,6] and are presented as footnotes in Table I.

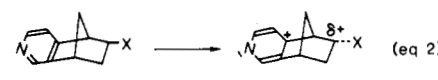
Solvolysis Products. Products from the 5,6,7,8-tetrahydro-5,8-methanoisoquinoline system (**3**) were precisely examined.[5] As products from the **3**, **5**, and **6** systems were similar, detailed investigations were not done.

Discussion

Significant influence of π-electron density of the aryl carbon at the ring-juncture β to the reacting cationic center was observed in the solvolyses of previous ring derivatives (**1** and **3**). The present results agree with this. The electronegative character of pyridine nitrogen is known to cause a positive charge at the ring carbon α and γ to the nitrogen, as pictured in the pyridine moieties in eq 1 and 2, but only a minor positive charge at the β carbon.



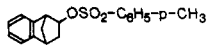
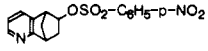
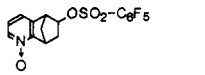
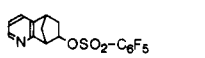
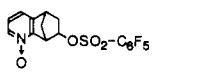
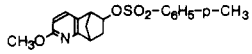
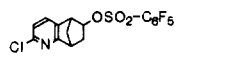
(eq 1)



(eq 2)

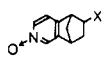
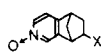
(9) Paquette, L. A.; Burke, L. D.; Irie, T.; Tanida, H. *J. Org. Chem.* **1987**, *52*, 3246.

Table I. Rates of Solvolysis in 50% (v/v) Aqueous *tert*-Butyl Alcohol

material[a]	temp, °C	k_1, s^{-1}	k_{rel} at 50 °C[b]
	50	6.82×10^{-4} [c]	1
	30	5.26×10^{-5} [c]	
	50	2.87×10^{-4}	5.4×10^{-3}
	30	1.84×10^{-5}	
	80	2.96×10^{-4}	
	60	3.21×10^{-5}	
	50	9.98×10^{-6} (calcd)	4.4×10^{-6}
	70	3.26×10^{-4}	1.4×10^{-4}
	50	1.74×10^{-5}	
	50	5.13×10^{-4}	
	30	3.58×10^{-5}	1.6×10^{-5}
	50	1.68×10^{-3}	2.46
	30	1.44×10^{-4}	
	50	1.85×10^{-3}	8.13×10^{-4}
	30	1.50×10^{-4}	

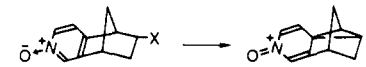
[a] *exo*-Arenesulfonates. [b] As shown in Table II of ref 5 and Table II of ref 6, conversion factors are 77.4 between *p*-nitrobenzenesulfonate and tosylate, 43.4 between pentafluorobenzenesulfonate and *p*-nitrobenzenesulfonate. [c] Table II or ref 5 or Table II of ref 6.

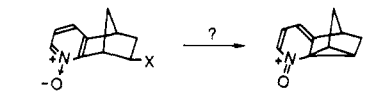
Table II. Relative Solvolysis Rates in 50% (v/v) Aqueous *tert*-Butyl Alcohol and Substituent Constants

material[a]	pyridine N rel to X[b]	Z	k_{rel}, 50 °C	$\sigma_{c,d}$
		*p*-CH_3O	130	−0.268
		p-CH_3	5	−0.170
		H	1	0
		p-Cl	0.15	0.227
	meta	*p*-CH_3O	1.53	0.352
		p-CH_3	4.39×10^{-2}	0.45
		H	5.9×10^{-3}	0.62
		p-Cl	8.53×10^{-4}	0.847
	para		1.8×10^{-5}	0.93
	meta	*p*-CH_3O	2.46	0.352
		H	5.4×10^{-3}	0.62
		p-Cl	8.13×10^{-4}	0.847
	ortho		1.4×10^{-4}	0.81
	para		5.1×10^{-4}	1.35
	meta		5.1×10^{-6}	1.48
	meta		4.4×10^{-6}	1.48
	ortho		1.6×10^{-5}	
	meta	o-CH_3O	0.52	

[a] X = *exo*-arenesulfonate. [b] The location of nitrogen atom in pyridine is indicated relative to the aryl ring-juncture carbon β to the reaction center. [c] Treatments of substituent effects by $\rho\sigma$ were presented in note 12. The σ and σ^+ constants for the substituent Z were cited from Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979. [d] The σ constants for the nitrogen atom in pyridine determined by Jaffe were used for the present pyridino system. The additivity in σ for Z and the nitrogen was assumed. Refer to Jaffe, H. H.; Jones, H. L. *Advances in Heterocyclic Chemistry*; Katritzsky, A. R., Ed.; Academic Press: New York, 1964; Vol. 3, p 209.

Therefore, in arenesulfonates such as those in eq 1 and 2, the reacting cationic center would be greatly disturbed by a positive charge at the carbon α or γ to the nitrogen. We call these arenesulfonates homoortho or homopara derivatives, relative to the ring nitrogen. The same name is used for the aryl-substituted arenesulfonates; for example, the arenesulfonates in eq 3 and 5 are homopara derivatives with respect to the *N*-oxide and methoxy substituents. Thus, the homoortho 7-arenesulfonate (the fourth compound in Table I) gave a relative rate, k_{rel}, of 1.4×10^{-4}, while the homometa 6-arenesulfonate (the second compound) showed a faster rate, k_{rel} of 5.4×10^{-3}.


(eq 3)


(eq 4)

In the previous **3** system, conversion of the homopara arenesulfonate (eq 2) into its *N*-oxide (eq 3) resulted in rate enhancement as shown by the change of relative rates from 1.8×10^{-5} to 5.1×10^{-4} in Table II, while that of the homometa arenesulfonate (the second compound, H for Z, in Table II) into its *N*-oxide (the seventh compound) resulted in a substantial rate depression as shown by the relative rates, 5.9×10^{-3} and 5.1×10^{-6}. Therefore, an electron-donating effect by the *N*-oxide function for the homopara reaction center (eq 3) and a strong electronegative effect for the homometa reaction center were suggested.[5] In the present system, as shown in Table I, the homoortho *N*-oxide arenesulfonate exhibits a rate 0.11 times slower than the homoortho arenesulfonate (1.6×10^{-5} vs. 1.4×10^{-4} in k_{rel} of the fifth and fourth compounds in Table I), but the homometa *N*-oxide arenesulfonate reacts 8.1×10^{-3} times more slowly than the homometa arenesulfonate (4.4×10^{-6} vs. 5.4×10^{-3} in k_{rel} of the third and second compounds). Although an electronegative effect of the *N*-oxide substituent is definite for the present homometa system, an electron-donating effect by the *N*-oxide appears not to be a major factor in the homoortho solvolysis (eq 4). However, the higher rate of the homoortho compared to that of the homometa *N*-oxide arenesulfonate (1.6×10^{-5} vs. 4.4×10^{-6} in k_{rel}) would suggest some contribution of an electron-donating effect by the *N*-oxide.

The effects of substituents on the pyridine ring on solvolysis rates were significantly large. The electron-donating methoxy substituent in the homopara 6-arene-

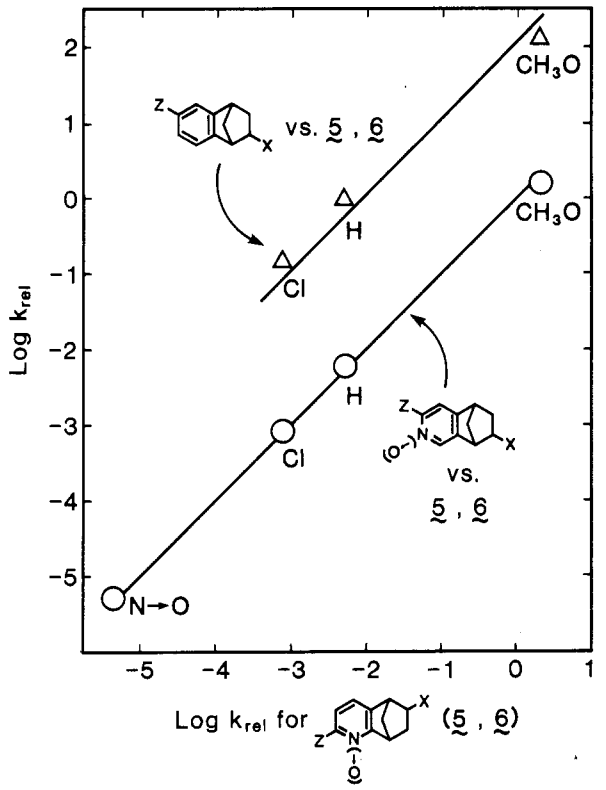
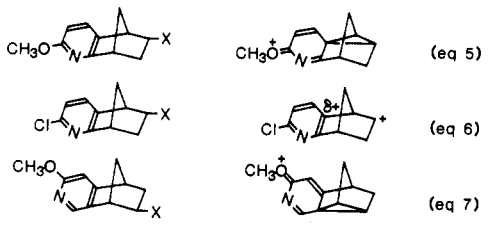


Figure 1. Correlation between logarithmic relative rates for 2-substituted 5,6,7,8-tetrahydro-5,8-methanoquinolin-6-*exo*-yl arenesulfonates and the *N*-oxide (**5** and **6**) and those for 2-substituted benzonorbornen-6-*exo*-yl arenesulfonates (**1**) or 3-substituted 5,6,7,8-tetrahydro-5,8-methanoisoquinolin-7-*exo*-yl arenesulfonates and the *N*-oxide (**3**) with the straight lines of unity slope.

sulfonate raises the rate by a factor of 456 in Table I (2.46 vs. 5.4×10^{-3}) (eq 5). The chloro substituent lowers the



rate by a factor of 0.15 (8.13×10^{-4} vs. 5.4×10^{-3}) (eq 6). We have noted that the rate effects of methoxy and chloro substituents in the present and previous 5,6,7,8-tetrahydro-5,8-methanoisoquinoline and benzonorbornene systems are all of the same order of magnitude. The magnitude of substituent effects is thus nearly independent of the presence or absence of the pyridine ring nitrogen and its position (α or β to the ring junction). The logarithms of relative rates for the present quinolin-6-*exo*-yl arenesulfonates (**5** and **6**) were plotted against the benzonorbornen-*exo*-yl arenesulfonates (**1**) or the isoquinolin-7-*exo*-yl arenesulfonates (**3**) (Figure 1). The relative positions between the aryl substituents and the reaction center are the same (homopara) in the three series of arenesulfonates and, also, those between the pyridine ring nitrogen and the reaction center are the same (homometa) in the quinolinyl and the isoquinolinyl arenesulfonates. Both plots gave straight lines without detectable derivation from the slope of unity. Thus, the lines suggest that the rate variation in solvolyses of the three series of arenesulfonates can be discussed on the same theoretical basis. Also, they afford strong supporting evidence for the concept that replacement of a CH group in benzene by a nitrogen atom (from benzene to pyridine) can be treated as substitution and substituent effects including the nitrogen atom as a substituent are additive. This concept was originally proposed by Jaffe.[10,11]

The importance of participation effects was demonstrated in solvolyses of the benzonorbornene derivatives[2,3] as well as the isosteric pyridino derivatives, 5,6,7,8-tetrahydro-5,8-methanoisoquinolines in previous studies[5,6] and 5,6,7,8-tetrahydro-5,8-methanoquinolines in the present work. The aryl substituent effects on the solvolyses of benzonorbornenes[2a] were related to the electrophilic side-chain reactions and thereby to the electrophilic substitutions of benzene derivatives, for example, by applying the Hammett–Brown ρ–σ^+ relationship. Similarly, the results from the 5,6,7,8-tetrahydro-5,8-methanoisoquinolines and -quinolines will be related to the corresponding reactions of pyridine derivatives,[12] where quantitative experimental data are not yet sufficient.

Experimental Section

Melting points were taken in capillary tubes and are corrected. ^{1}H NMR spectra were determined with a Varian EM390 NMR spectrometer with tetramethylsilane as an internal standard, and infrared spectra were obtained with a Hitachi 260-10 spectrophotometer. HPLC analyses were carried out with a system composed of a Waters 6000-A pump, a UVIDEC-100UV detector, and a Reodyne 7120 injector.

5-*exo*-Hydroxybicyclo[2.2.1]heptan-2-one (10). A solution prepared by dissolving 25 mg of sodium metal and 5.32 g of 5-*exo*-acetoxybicyclo[2.2.1]heptan-2-one (**9**)[8] in 50 mL of methanol was gradually concentrated by distilling off methanol under normal pressure and then under reduced pressure to leave a residue, which was extracted with ether. The ether solution was filtered, concentrated, and subjected to azeotropic dehydration with benzene. The residual solid showed mp 132–133 °C, identical with that previously reported for this compound prepared by another method.[14]

5-*exo*-(Benzyloxy)bicyclo[2.2.1]heptan-2-one (11). A solution of 4.00 g of **10** in 80 mL of tetrahydrofuran was stirred under a nitrogen atmosphere as 1.67 g of 50% sodium hydride was added portionwise accompanied gas evolution over 15 min. To this solution were added 4.41 g of benzyl chloride and 0.12 g of tetra-*n*-butylammonium iodide. The mixture was stirred under reflux for 3 h until the materials disappeared, concentrated under reduced pressure, and extracted with ether after the addition of ice water. The ether layer was washed with brine, dried, and evaporated. Treatment of the residue with Lobar-column chromatography using a 5:1 mixture solvent of benzene and ethyl

(10) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.
(11) Jaffe, H. H.; Jones, H. L. *Advances in Heterocyclic Chemistry*; Katritzsky, A. R., Ed.; Academic Press: New York, 1964; Vol. 3, p 209.
(12) The **1**, **3**, **5**, and **6** systems were subjected to ρ–σ treatment, assuming additivity of the substituents. The σ constants for the methoxy, methyl, and chloro substituents proposed for benzene derivatives[13] were used with those for the pyridine nitrogen and *N*-oxide proposed by Jaffe[10,11] on the basis of alkaline hydrolyses of the three (α, β, and γ) ethyl pyridinecarboxylates and pK of the *N*-oxides of two (β and γ) pyridinecarboxylic acids. A straight line was obtained by plotting the logarithms of relative rates against σ. The eight compounds fit on the line. The upper deviations from the line were the six compounds which are the homopara methoxy derivatives in all three systems and the homopara methyl derivatives in the **1** and **3** systems (slight deviations), as usually observed in the reactions of benzene derivatives defined by σ^+, and also, the aryl-unsubstituted homopara *N*-oxide arenesulfonate in the **3** system. The lower deviations were due to the aryl-unsubstituted 5,6,7,8-tetrahydro-5,8-methanoquinolin-6-*exo*-yl and 5,6,7,8-tetrahydro-5,8-methanoquinolin-7-*exo*-yl arenesulfonates. Clearly, the deviations result from cases in which the aryl substituents and the ring nitrogen can conjugate with the reaction sites. A satisfactorily straight line was obtained at the ρ value of −3.40 by plotting the rate data from the aryl-substituted **1**, **3**, and **6** derivatives (eleven compounds) against σ^+. In these compounds, the nitrogen atoms are located at the homopara positions, not strongly interacting with the reaction centers.
(13) Footnote c in Table II.
(14) Krieger, H. *Chem. Abstr.* **1963**, *58*, 7979b.

acetate afforded 5.39 g of an oily product: ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 6 H, at C_3, C_6, and C_7), 2.56 and 2.8 (m, 2 H, bridgeheads), 3.73 (m, 1 H, at C_5 endo), 4.50 (s, 2 H, PhCH_2-), and 7.32 (s, 5 H, phenyl); IR ($CHCl_3$) 1744 cm^{-1} (C=O).

5-*exo*-(Benzyloxy)-3-*exo*-allylbicyclo[2.2.1]heptan-2-one (12). A solution of lithium diisopropylamide (LDA) was prepared from 2.52 g of diisopropylamine in 10 mL of tetrahydrofuran and 15.6 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane. To this LDA solution was added at −78 °C a solution of 5.39 g of **11** in 15 mL of tetrahydrofuran, and the mixture was left standing for 5 min at −30 °C and cooled to −78 °C. Allyl bromide (3.32 g) was added to the mixture, which was slowly warmed to room temperature. The mixture was concentrated under reduced pressure, leaving a residue, to which ice water was added. The water mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was washed with brine, dried, and evaporated, leaving 6.26 g of oily residue **12**: ^{1}H NMR ($CDCl_3$) δ 1.5–2.6 (m, 9 H, at C_3, C_6, and C_7, bridgeheads, CH_2=CHCH_2), 3.7 (m, 1 H, at C_5 endo), 4.5 (s, 2 H, PhCH_2), 4.95, and 5.1 (m, 2 H, CH_2=CHCH$_2$-), 5.55–6.0 (m, 1 H, CH_2CHCH_2), and 7.3 (s, 5 H, phenyl).

5-*exo*-(Benzyloxy)-3-*exo*-allylbicyclo[2.2.1]heptan-2-one Ethylene Ketal (13). The reaction was conducted by a standard procedure[15] with a mixture of 6.26 g of **12** in 100 mL of toluene, 15.2 g of ethylene glycol, and a trace of *p*-toluenesulfonic acid, giving 6.26 g of an oil: ^{1}H NMR ($CDCl_3$) δ 1.2–2.5 (m, 9 H, at C_3, C_6, and C_7, bridgeheads, CH_2=CHCH_2-), 3.59 (m, 1 H, at C_5 endo), 3.8 (m, 4 H, ethylene ketal), 4.44 (s, 2 H, PhCH_2O-), 4.9 and 5.05 (m, 2 H, CH_2=CHCH$_2$-), 5.5–6.0 (m, 1 H, CH_2=CHCH$_2$-), and 7.3 (s, 5 H, phenyl).

Ozone Oxidation of 13. Ozone was absorbed at −78 °C by a solution of 6.26 g of **13** in 300 mL of dichloromethane. The usual workup gave a crude ketone which was subjected to Lobar-column chromatography using a 10:1 mixture solvent of benzene and ethyl acetate to obtain 4.58 g of an oil, **14**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.8 (m, 9 H, at C_3, C_6, and C_7, bridgeheads, -CH_2CHO), 3.6–3.85 (overlapping m, 5 H, at C_5 endo and ethylene ketal), 4.45 (s, 2 H, PhCH_2O-), 7.3 (s, 5 H, phenyl), and 9.72 (t, 1 H, CHO).

Condensation of 14 with (Methoxymethylene)triphenylphosphorane. To a suspension of 10.38 g of triphenyl(methoxymethyl)phosphonium chloride in 100 mL of tetrahydrofuran was added 19 mL of a 1.6 M hexane solution of *n*-butyllithium at −30 °C with stirring under a nitrogen atmosphere. The mixture was left standing at 0 °C for 10 min and cooled to −78 °C. To this ylide solution was added 4.58 g of the aldehyde (**14**) in 50 mL of tetrahydrofuran and the reaction mixture was slowly warmed to room temperature and concentrated under reduced pressure. The residue was extracted with ether after addition of water. The ether solution was washed with brine, dried, and evaporated. Treatment of the residue with Lobar-column chromatography afforded 2.53 g of the product **15**: ^{1}H NMR ($CDCl_3$) δ 1.2–2.2 (m, 9 H, at C_3, C_6, and C_7, bridgeheads, -CH_2CH=CH$\sim$OCH$_3$), 3.5–3.6 (overlapping m, 4 H, at C_5 endo, OCH$_3$), 3.82 (m, 4 H, ethylene ketal), 4.2–4.8 (m, 1 H, -CH$_2$CH=CH$\sim$OCH$_3$), 4.45 (s, 2 H, PhCH_2O-), 5.85 and 6.3 (m, 1 H, -CH$_2$CH=C$H\sim$OCH$_3$), and 7.3 (s, 5 H, phenyl).

6-*exo*-(Benzyloxy)-5,6,7,8-tetrahydro-5,8-methanoquinoline (16). For hydrolysis, a mixture of 0.75 g of **15**, 15 mL of methanol, and 10 mL of water containing 1 drop of concentrated hydrochloric acid was treated under reflux for 30 min. Usual workup gave 0.7 g of an oil, which was subjected to the following reaction without purification.

To a stirred mixture of 3.55 mg of hydroxylamine hydrochloride in 20 mL of methanol and 288 mg of potassium hydroxide powder was added 0.7 g of the above-obtained oil in 10 mL of methanol at room temperature. The mixture was stirred for 30 min and then concentrated under reduced pressure by distilling off the methanol. The residue was extracted with dichloromethane. The dichloromethane layer was dried and evaporated, leaving 0.49 g of the dioxime as an oil. A solution of 0.49 g of this oil in 10 mL of acetic acid was warmed under reflux with stirring for 16 h. The mixture was concentrated under reduced pressure, leaving a residue, which was made alkaline by adding aqueous sodium hydroxide prior to extraction with ether. The ether solution was dried and evaporated, leaving a residue, which was subjected to Lobar-column chromatography using an ethyl acetate solvent to obtain 0.18 g of an oil product, **16**: ^{1}H NMR ($CDCl_3$) δ 1.8–2.2 (m, 4 H, at C_7 and C_9), 3.33 and 3.45 (m, 2 H, bridgeheads), 3.65 (m, 1 H, at C_6 endo), 4.54 (s, 2 H, PhCH_2O-), 6.9 (q, 1 H, at C_3), 7.3 (overlapping, 6 H, at C_4 and phenyl), and 8.13 (q, 1 H at C_2).

Picrate: mp 181–182 °C (methanol–ether). Anal. Calcd for $C_{23}H_{20}N_4O_8$: C, 57.50; H, 4.20; N, 11.66. Found: C, 57.35; H, 4.18; N, 11.65.

6-*exo*-Hydroxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (17). To a solution of 5.36 g of **16** in 150 mL of dichloromethane was added 35 mL of a solution containing 45.94 g of boron tribromide in 100 mL of dichloromethane, and the mixture was left standing for 10 min and then evaporated under reduced pressure. The remaining residue was dissolved in dilute hydrochloric acid and methanol, forming a clear solution. The solution was concentrated under reduced pressure, made alkaline by addition of aqueous sodium carbonate, and extracted with ether. Evaporation of ether followed by treatment with column chromatography using an ethyl acetate solvent afforded 3.08 g (89.6%) of **17**, mp 102.5–103.5 °C (dichloromethane–hexane): ^{1}H NMR ($CDCl_3$) δ 1.7–2.3 (m, 4 H, at C_7 and C_9), 3.4 (m, 2 H, bridgeheads), 4.0 (m, 1 H, at C_6 endo), 6.9 (q, 1 H, at C_3), 7.35 (q, 1 H, at C_4), and 8.12 (q, 1 H, at C_2). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.58; H, 6.68; N, 8.80.

6-Chloro-5,6,7,8-tetrahydro-5,8-methanoquinoline (18). A mixture of 3.08 g of **17** in 150 mL of benzene, 6.82 g of thionyl chloride, and 2 drops of pyridine was warmed under reflux for 2 h. Concentration under reduced pressure left a residue, which was made alkaline by addition of aqueous sodium carbonate and extracted with ether. The ether solution was washed with water, dried, and evaporated, leaving 2.88 g (83.9%) of **18** as a mixture of the endo and exo chloro compounds.

General Dehydrohalogenation Procedure with 6-Chloro-5,6,7,8-tetrahydro-5,8-methanoquinoline. 5,8-Dihydro-5,8-methanoquinoline (19). The procedure reported for 5,8-dihydro-5,8-methanoisoquinoline was employed,[5] except for the use of a higher reaction temperature. To a solution of 2.0 g of **18** in 20 mL of dimethyl sulfoxide was added 2.50 g of potassium *tert*-butoxide, and the mixture was stirred for 1 h at 80 °C prior to being poured into ice water. The product was extracted with *n*-pentane, and the pentane solution was dried and distilled under vacuum to obtain a pure sample (1.54 g) of **19**, bp 80 °C (2 mmHg): ^{1}H NMR ($CDCl_3$) δ 2.4 (m, 2 H, at C_9), 3.85 (m, 2 H, bridgeheads), 6.7 (q, 1 H, at C_3), 6.8 (m, 2 H, olefin), 7.34 (q, 1 H, at C_4), and 7.99 (q, 1 H, at C_2).

Picrate: mp 147.5–149 °C (methanol–ether). Anal. Calcd for $C_{16}H_{12}N_4O_7$: C, 51.62; H, 3.25; N, 15.05. Found: C, 51.69; H, 3.31; N, 15.00.

4,6-*exo*- and 4,6-*endo*-Dichloro-5,6,7,8-tetrahydro-5,8-methanoquinoline (21 and 22). The *N*-oxide **20** was obtained by treatment of 613 mg of **18** with *m*-chloroperbenzoic acid in dichloromethane. To a solution of **20** in 20 mL of chloroform was added 10 mL of phosphorous oxychloride. The mixture was warmed under reflux overnight and concentrated under reduced pressure, leaving a residue to which aqueous sodium carbonate was added. The product was extracted with dichloromethane, and the dichloromethane solution was dried and evaporated, leavig a residue which was subjected to Lobar-column chromatography using a 1:1 mixture solvent of ethyl acetate–*n*-hexane. This gave a mixture of 133 mg of 4,6-*endo*-dichloro compound **22** and 196 mg of 4,6-*exo*-dichloro compound **21** with 123 mg of the *N*-oxide **20**.

For endo **22**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.1 (m, 3 H, at C_7 endo and C_9), 2.65 (m, 1 H, at C_7 exo), 3.48 (m, 1 H, at C_8), 3.88 (m, 1 H, at C_5), 4.6 (m, 1 H, at C_6 exo), 7.1 (d, 1 H, at C_3), and 8.18 (d, 1 H, at C_2).

For exo **21**: ^{1}H NMR ($CDCl_3$) δ 1.9–2.5 (m, 4 H, at C_7 and C_9), 3.50 (m, 1 H, at C_8), 3.78 (m, 1 H, at C_5), 3.9 (m, 1 H, at C_6 endo), 7.0 (d, 1 H, at C_3), and 8.23 (d, 1 H, at C_2).

The *N*-Oxide 23. By a similar procedure, 309 mg of 4,6-*endo*-dichloro compound **22** was led to 310 mg of **23**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.2 (m, 3 H, at C_7endo and C_9), 2.7 (m, 1 H, at C_7exo), 3.9 (m, 1 H, at C_5), 4.05 (m, 1 H, at C_8), 4.65 (m, 1 H, at C_6exo), 7.1 (d, 1 H, at C_3), and 7.98 (d, 1 H, at C_2).

(15) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*: John Wiley & Sons: New York, 1967; p 376.

6-*endo*-Chloro-4-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline *N*-Oxide (24). To a solution of 154 mg of sodium metal in 20 mL of methanol was added 310 mg of **23**, and the mixture was warmed under reflux overnight. The mixture was evaporated under reduced pressure prior to being added to water. The product was extracted with dichloromethane and the organic phase was dried and evaporated, leaving 278 mg of **24**: ^{1}H NMR ($CDCl_3$) δ 1.4–2.1 (m, 3 H, at C_7endo and C_9), 2.6 (m, 1 H, at C_7exo), 3.9 (s, 3 H, OCH_3), 3.9 and 4.0 (m, 2 H, bridgeheads), 4.6 (m, 1 H, at C_6exo), 6.65 (d, 1 H, at C_3), and 8.0 (d, 1 H, at C_2).

6-*endo*-Chloro-4-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (25). A mixture of 278 mg of **24**, 0.5 mL of phosphorous trichloride, and 10 mL of chloroform was warmed under reflux for 2 h and then concentrated under reduced pressure, leaving a residue to which aqueous sodium carbonate was added. The product was extracted with ether and the ether solution was dried and evaporated, leaving a residue, which was purified by silica gel chromatography using an ethyl acetate solvent to get 226 mg of **25**: ^{1}H NMR ($CDCl_3$) δ 1.25–2.1 (m, 3 H, at C_7endo and C_9), 2.6 (m, 1 H, at C_7exo), 3.4 (m, 1 H, at C_8), 3.89 (overlapping m, 4 H, at C_5, and OCH_3), 4.6 (m, 1 H, at C_6exo), 6.65 (d, 1 H, at C_3), and 8.2 (d, 1 H, at C_2).

6-(Benzyloxy)-5,6,7,8-tetrahydro-5,8-methanoquinoline *N*-Oxide (26). To a stirred solution of 4.86 g of **16** in 80 mL of dichloromethane was added an equivalent mole of *m*-chloroperbenzoic acid at 0 °C. The mixture was left overnight in a refrigerator, washed with aqueous sodium carbonate, dried, and evaporated, leaving 4.9 g of a viscous oil: ^{1}H NMR ($CDCl_3$) δ 1.85–2.25 (m, 4 H, at C_7 and C_9), 3.5 (m, 1 H, at C_5), 3.68 (m, 1 H, at C_6endo), 3.95 (m, 1 H, at C_8), 4.55 (s, 2 H, PhCH_2O-), 7.0 (q, 1 H, at C_3), 7.25–7.35 (overlapping 6 H, at C_4 and phenyl), and 7.93 (q, 1 H, at C_2).

6-*exo*-(Benzyloxy)-2-acetoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (27). A solution of 4.9 g of **26** in 45 mL of acetic anhydride was warmed under reflux for 3 days and concentrated under reduced pressure, leaving a residue, which was treated with aqueous sodium carbonate and accommodated into ethyl acetate. The ethyl acetate solution was dried and evaporated, leaving a residue, which was subjected to Lobar-column chromatography using a 1:1 mixture solvent of ethyl acetate and *n*-hexane to get 2.67 g of **27**, mp 86–87 °C (ether–*n*-hexane), with 1.60 g of the deoxygenated **16**: ^{1}H NMR ($CDCl_3$) δ 1.75–2.2 (m, 4 H, at C_7 and C_9), 2.27 (s, 3 H, OAc), 3.32 (m, 1 H, at C_8), 3.49 (m, 1 H, at C_5), 3.66 (m, 1 H, at C_6endo), 4.55 (s, 2 H, PhCH_2O-), 6.69 (d, 1 H, at C_3), 7.35 (s, 5 H, phenyl), and 7.43 (d, 1 H, at C_4). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.86; H, 6.27; N, 4.66.

2,6-*exo*-Dichloro-5,6,7,8-tetrahydro-5,8-methanoquinoline (28). A mixture of 2.56 g of **27** in 20 mL of methanol and 0.5 g of sodium hydroxide in 5 mL of water was stirred for 10 min and concentrated under reduced pressure, leaving a residue, to which dilute hydrochloric acid was added. This aqueous solution was concentrated under reduced pressure, leaving a residue, which was extracted with chloroform. The chloroform solution was dried and evaporated. The residue was, without purification, dissolved in 20 mL of phosphorous oxychloride, and the mixture was heated overnight at 190 °C in a sealed tube and then distilled to remove excess phosphorous oxychloride under reduced pressure. The residue was treated with aqueous sodium carbonate and extracted with ether. Solvent removal and purification of the residue by Lobar-column chromatography (elution with benzene) gave 1.55 g of **28**, mp 65–66 °C (*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.9–2.4 (m, 4 H, at C_7 and C_9), 3.4 (m, 1 H, at C_8), 3.52 (m, 1 H, at C_5), 3.86 (m, 1 H, at C_6endo), 7.03 (d, 1 H, at C_3), and 7.43 (d, 1 H, at C_4). Anal. Calcd for $C_{10}H_9NCl_2$: C, 56.10; H, 4.24; N, 6.54; Cl, 33.12. Found: C, 56.20; H, 4.39; N, 6.68; Cl, 33.19.

The *N*-oxide **29** was obtained by treatment of 654 mg of **28** with *m*-chloroperbenzoic acid in dichloromethane in a yield of 504 mg, mp 140.5–141 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.95–2.4 (m, 4 H, at C_7 and C_9), 3.6 (m, 1 H, at C_5), 3.9 (m, 1 H, at C_6endo), 4.1 (m, 1 H, at C_8), 7.06 (d, 1 H, at C_3), and 7.26 (d, 1 H, at C_4). Anal. Calcd for $C_{10}H_9NOCl_2$: C, 52.20; H, 3.94; N, 6.09; Cl, 30.82. Found: C, 52.02; H, 3.97; N, 5.96; Cl, 30.45.

6-*exo*-Chloro-2-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline *N*-Oxide (30). To a sodium methoxide solution, prepared by dissolving 378 mg of sodium metal in 20 mL of methanol, was added 470 mg of **29**, and the mixture was warmed under reflux for 2 h. Evaporation of the methanol followed by addition of water separated an organic product, which was extracted with dichloromethane. The dichloromethane solution was dried and evaporated, leaving 375 mg of **30**: ^{1}H NMR ($CDCl_3$) δ 1.95–2.4 (m, 4 H, at C_7 and C_9), 3.53 (m, 1 H, at C_5), 3.85 (m, 1 H, at C_6endo), 4.1 (m, 1 H, at C_8), 6.58 (d, 1 H, at C_3), and 7.1 (d, 1 H, at C_4).

6-*exo*-Chloro-2-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (31). A mixture of 375 mg of **30**, 0.7 mL of phosphorous trichloride, and 15 mL of chloroform was warmed under reflux for 2 h. The mixture was concentrated under reduced pressure, leaving a residue, which was extracted with ether after addition of aqueous sodium carbonate. Solvent removal and purification of the residue by Lobar-column chromatography (elution with a 2:1 mixture solvent of ethyl acetate and *n*-hexane) gave 307 mg of **31**: ^{1}H NMR ($CDCl_3$) δ 1.9–2.3 (m, 4 H, at C_7 and C_9), 3.33 (m, 1 H, at C_8), 3.45 (m, 1 H, at C_5), 3.8 (m, 1 H, at C_6endo), 3.9 (s, 3 H, OCH_3), 6.4 (d, 1 H, at C_3), and 7.33 (d, 1 H, at C_4).

7-*exo*-Hydroxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (33). To a solution of 548 mg of the diene **19** in 20 mL of dichloromethane was added 11.5 mL of a 1 M solution of diborane–dimethyl sulfide complex at 0 °C with stirring under a nitrogen atmosphere, and the mixture was stirred for 2 h. To the mixture were added 10 mL of ethanol with gas evolution, 3 mL of 3 N aqueous sodium hydroxide, and then 3 mL of 30% hydrogen peroxide. After being warmed under reflux for 30 min, the mixture was acidified with dilute aqueous hydrochloric acid and distilled under reduced pressure to remove dichloromethane and ethanol. The aqueous residue was made alkaline with aqueous sodium carbonate and extracted with dichloromethane. After drying, distillation of the dichloromethane gave a residue composed of four isomeric alcohols as described in the text. Treatment of the residue by Lobar-column chromatography using a 1:1 mixture solvent of ethyl acetate and acetone isolated the alcohols: 247 mg of the 6-exo alcohol **17**, 192 mg of the 7-exo alcohol **33**, and very small amounts of the 6-endo alcohol and the 7-endo alcohol, mp 126–127 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.75–2.35 (m, 4 H, at C_6 and C_9), 3.42 (m, 2 H, bridgeheads), 4.22 (m, 1 H, at C_7endo), 6.95 (q, 1 H, at C_3), 7.4 (q, 1 H, at C_4), and 8.14 (q, 1 H, at C_2). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.45; H, 6.86; N, 8.87.

6-*exo*-*p*-Nitrobenzenesulfonate (17-O_3SAr). A mixture of 32 mg of **17**, 48 mg of *p*-nitrobenzenesulfonyl chloride and 0.2 mL of pyridine was left standing overnight in a refrigerator. The usual workup gave 65 mg of the sulfonate, mp 145–145.5 °C: ^{1}H NMR ($CDCl_3$) δ 1.7–2.2 (m, 2 H, at C_7 and C_9), 3.4 (m, 1 H, at C_8), 3.62 (m, 1 H, at C_5), 4.7 (m, 1 H, at C_6endo), 6.97 (q, 1 H, at C_3), 7.45 (q, 1 H, at C_4), 8.12 and 8.41 (2 sets of doublet, 4 H, aromatic), and 8.15 (q, 1 H, at C_2). Anal. Calcd for $C_{16}H_{14}N_2O_5S$: C, 55.48; H, 4.07; N, 8.09; S, 9.26. Found: C, 55.47; H, 4.13; N, 7.98; S, 9.01.

***N*-Oxide of the 6-*exo*-Pentafluorobenzenesulfonate.** To a solution of 121 mg of **17** in 5 mL of tetrahydrofuran was added 0.94 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane at 0 °C with stirring under a nitrogen atmosphere, and the mixture was stirred for 20 min at 0 °C. Pentafluorobenzenesulfonyl chloride (300 mg) was added to the mixture, which was then stirred for 10 min prior to being poured into ice water and extracted with ether. The ether solution was dried and evaporated, leaving a residue, which was treated for purification with preparative layer chromatography using a 1:1 mixture solvent of *n*-hexane and ethyl acetate. The oil (114 mg) obtained was dissolved in dichloromethane and to this solution was added 94 mg of 80% *m*-chloroperbenzoic acid. The mixture was left standing for 1 h, then washed with aqueous sodium carbonate, dried, and evaporated, affording an oil: ^{1}H NMR ($CDCl_3$) δ 2.15 (m, 4 H, at C_7 and C_9), 3.8 (m, 1 H, at C_5), 4.05 (m, 1 H, at C_8), 4.89 (m, 1 H, at C_6endo), 6.9–7.2 (overlapping m, 2 H, at C_3 and C_4), and 7.98 (q, 1 H, at C_2).

7-*exo*-Pentafluorobenzenesulfonate (33-O_3SAr). By a similar procedure, the reaction was carried out with a solution of 113 mg of **33** in 5 mL of tetrahydrofuran, 0.88 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane, and 280 mg of pentafluorobenzenesulfonyl chloride. The workup yielded 85 mg of an oil: ^{1}H NMR ($CDCl_3$) δ 2.2 (m, 4 H, at C_6 and C_9), 3.5 (m, 1

H, at C_5), 3.6 (m, 1 H, at C_8), 4.9 (m, 1 H, at C_7endo), 7.0 (q, 1 H, at C_3), 7.4 (q, 1 H, at C_4), and 8.22 (q, 1 H, at C_2).

***N*-Oxide of the 7-*exo*-Pentafluorobenzenesulfonate.** Treatment of 30 mg of **33**-O_3SAr in 5 mL of dichloromethane with 25 mg of 80% *m*-chloroperbenzoic acid followed by the usual workup gave 32 mg of an oil: ^{1}H NMR ($CDCl_3$) δ 2.2 (m, 4 H, at C_6 and C_9), 3.54 (m, 1 H, at C_5), 4.1 (m, 1 H, at C_8), 4.95 (m, 1 H, at C_7endo), 7.05 (overlapping m, 2 H, at C_3 and C_4), and 7.9 (q, 1 H, at C_2).

2-Chloro-6-*exo*-hydroxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (34). A mixture of 112 mg of **28** and 53 mg of sodium bicarbonate in 4 mL of 50% aqueous acetone was heated overnight at 170 °C in a sealed tube. The mixture was concentrated by distilling off acetone under reduced pressure, leaving a residue, which was extracted with ether. Solvent removal and purification of the residue by Lobar-column chromatography (elution with ethyl acetate) gave 82 mg of **34** as crystals, mp 157.5–158.5 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.5–2.3 (m, 4 H, at C_7 and C_9), 2.6 (s, 1 H, OH), 3.3 (m, 2 H, bridgeheads), 4.0 (m, 1 H, at C_6endo), 7.0 (d, 1 H, at C_3), and 7.4 (d, 1 H, at C_4). Anal. Calcd for $C_{10}H_{10}NOCl$: C, 61.39; H, 5.15; N, 7.16; Cl, 18.12. Found: C, 61.46; H, 5.18; N, 7.21; Cl, 18.29.

2-Chloro-6-*exo*-pentafluorobenzenesulfonate (34-O_3SAr) was prepared from **34** as described above; mp 122–123.5 °C (ether–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 2.0–2.3 (m, 4 H, at C_7 and C_9), 3.43 (m, 1 H, at C_8), 3.72 (m, 1 H, at C_5), 4.82 (m, 1 H, at C_6endo), 7.05 (d, 1 H, at C_3), and 7.50 (d, 1 H, at C_4). Anal. Calcd for $C_{16}H_9NO_3ClF_5S$: C, 45.13; H, 2.13; N, 3.29; Cl, 8.33; F, 22.31; S, 7.53. Found: C, 45.04; H, 2.48; N, 3.27; Cl, 8.61; F, 21.86; S, 7.58.

6-*exo*-Hydroxy-2-methoxy-5,6,7,8-tetrahydro-5,8-methanoquinoline (35). A mixture of 105 mg of **31** and 51 mg of sodium bicarbonate in 6 mL of 50% aqueous acetone was warmed under reflux overnight. The workup as described above gave 90 mg of **35** as crystals, mp 109–110 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4 H, at C_7 and C_9), 3.15–3.3 (m, 2 H, bridgeheads), 3.9 (overlapping 4 H, at C_6endo and OCH_3), 6.36 (d, 1 H, at C_3), and 7.30 (d, 1 H, at C_4). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.20; H, 6.89; N, 7.30.

2-Methoxy 6-*exo*-tosylate 35-O_3SAr was prepared according to the usual manner: crystals, mp 141.5–142.5 °C (dichloromethane–*n*-hexane): ^{1}H NMR ($CDCl_3$) δ 1.7–2.2 (m, 4 H, at C_7 and C_9), 2.43 (s, 3 H, CH_3), 3.23 (m, 1 H, at C_8), 3.43 (m, 1 H, at C_5), 3.86 (s, 3 H, OCH_3), 4.5 (m, 1 H, at C_6endo), 6.36 (d, 1 H, at C_3), 7.3 (d, 1 H, at C_4), and 7.3 and 7.74 (2 sets of d, 4 H, aromatic). Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; S, 9.28. Found: C, 62.44; H, 5.68; N, 3.96; S, 9.02.

Kinetic Materials. In the compounds synthesized for solvolyses, elementary analyses were carried out with crystalline derivatives. Oily solvolysis materials were either purified by preparative thick-layer chromatography or shown to be single compounds by thin-layer chromatography. As described in the Experimental Section of our previous work,[6] kinetic measurements showed no difference in rate constants within experimental error between analytically pure material and material purified by chromatography. Analyses by HPLC also indicated no meaningful difference between the materials.

Kinetic Measurements. Rates were determined at pH 7.5 in 50% (v/v) aqueous *tert*-butyl alcohol by using a pH stat, as described in the previous paper.[5,6]

Registry No. **9**, 5257-38-5; **10**, 58029-22-4; **11**, 110354-77-3; **12**, 110354-78-4; **13**, 110354-79-5; **14**, 110354-80-8; **15**, 110354-81-9; **16**, 110354-82-0; **17**, 110354-83-1; **17** (6-*exo*-*p*-nitrobenzenesulfonate), 110354-98-8; **17** (6-*exo*-*p*-nitrobenzenesulfonate) *N*-oxide, 110354-99-9; *endo*-**18**, 110354-84-2; *exo*-**18**, 110415-86-6; **19**, 108744-29-2; **19**-, 110354-87-5; **20**, 110354-85-3; **21**, 110354-86-4; **22**, 110415-87-7; **23**, 110354-88-6; **24**, 110354-89-7; **25**, 110354-90-0; **26**, 110354-91-1; **27**, 110354-92-2; **28**, 110354-93-3; **29**, 110354-94-4; **30**, 110354-95-5; **31**, 110354-96-6; **33**, 110354-97-7; **33** (7-*exo*-pentafluorobenzenesulfonate), 110355-00-5; **33** (7-*exo*-pentafluorobenzenesulfonate) *N*-oxide, 110355-01-6; **34**, 110355-02-7; **34** (6-*exo*-pentafluorobenzenesulfonate), 110355-03-8; **35**, 110355-04-9; **35** (6-*exo*-tosylate), 110355-05-0; $H_3COCH{=}PPh_3$, 20763-19-3; $H_2C{=}CHCH_2Br$, 106-95-6.

Sigmatropic Rearrangements of Deprotonated Allyl Phenylacetates in the Gas Phase

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The ion $C_6H_5C^-HCO_2CH_2CH{=}CH_2$ undergoes competitive losses of C_3H_5OH and CO_2 on collisional activation. The loss of C_3H_5OH proceeds through ion complex $[C_3H_5O^-(C_6H_5CH{=}C{=}O)]$ yielding $C_6H_5C{\equiv}CO^-$ and C_3H_5OH. This reaction occurs *without* prior ester equilibration $C_6H_5C^-HC(O)O^*C_3H_5 \rightleftarrows C_6H_5C^-HC(O^*)OC_3H_5$. The elimination of CO_2 follows rearrangement $C_6H_5C^-HCO_2C_3H_5 \rightarrow C_6H_5(C_3H_5)CHCO_2^-$. The rearrangement occurs through *both* six- and four-center transition states with the six-center (Claisen) rearrangement predominating.

Introduction

Deprotonated allyl ethers can undergo Wittig, oxy-Cope, or Claisen rearrangements in the gas phase.[1,2] In particular, the diallyl ether ion rearranges first by 1,2- and 1,4-Wittig rearrangements followed by an anionic oxy-Cope rearrangement (eq 1 and 2).[2] This has led us to consider the possibility of similar six-center rearrangements of allyl esters. For example, do deprotonated allyl esters undergo oxygen equilibration by the process shown in eq 3 and the ester to carboxylate ion rearrangement shown in eq 4? Such systems have been studied in the condensed phase. Although no reaction analogous to that shown in eq 3 has been reported, neutral allyl esters undergo "oxygen equilibration" by an analogous [3,3] sigmatropic reaction

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