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Structural Effects in Solvolytic Reactions. 24. Solvolysis of 1-Cycloalkyl-1-aryl-1-ethyl *p*-Nitrobenzoates. Effect of α -Cycloalkyl Groups in Stabilizing an Electron-Deficient Center as Revealed by the Tool of Increasing Electron Demand

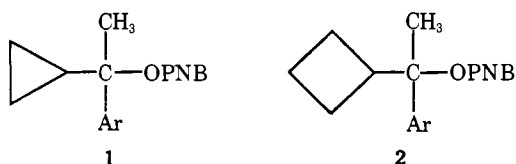
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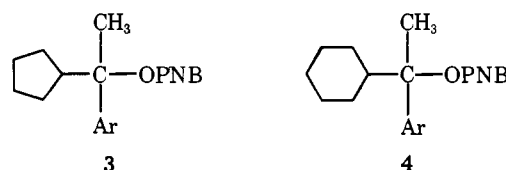
Abstract: Representative 1-cycloalkyl-1-aryl-1-ethyl *p*-nitrobenzoates of the type $(\overline{\text{C}}\text{H}_2)_{n-1}\text{CH}-\text{C}(\text{Ar})(\text{CH}_3)\text{OPNB}$ containing appropriate substituents in the aryl ring were synthesized and their rates of solvolysis determined in 80% aqueous acetone. The earlier work on the solvolysis of 1-cyclopropyl-1-aryl-1-ethyl *p*-nitrobenzoates ($n = 3$) and 1-cyclobutyl-1-aryl-1-ethyl *p*-nitrobenzoates ($n = 4$), utilizing the tool of increasing electron demand, clearly indicated major stabilization of the cationic center by π -electronic conjugation from the cyclopropyl group and modest σ stabilization from the cyclobutyl group. The ρ^+ values realized in the various systems examined are cyclopropyl ($n = 3$), -2.78 ; cyclobutyl ($n = 4$), -3.94 ; cyclopentyl ($n = 5$), -4.48 ; cyclohexyl ($n = 6$), -4.71 ; Δ^1 -cyclohexenyl, -2.35 ; and Δ^2 -cyclohexenyl, -4.83 . The large negative ρ^+ observed by applying the tool of increasing electron demand to the solvolysis of cyclopentyl and cyclohexyl derivatives indicates that any enhanced stabilization of the cationic center by these groups, as compared to simple aliphatic groups, is borderline for cyclopentyl and not significant for cyclohexyl. Major π -electronic contributions from the allylic double bond are observed in the solvolysis of the 1-(Δ^1 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates. The homoallylic double bond in the 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl system does not reveal any significant participation. Indeed, 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl derivatives (*p*-CH₃O, *p*-H, *p*-CF₃) solvolyze slower than the saturated derivatives, presumably a result of the inductive effect of the double bond. However, with the 3,5-(CF₃)₂ derivative, there occurs an increase in the relative rate and a break in the log k - σ^+ plot, indicative of some kind of participation. The possibility of π participation in the 1-(Δ^3 -cyclohexenyl)-1-aryl-1-ethyl system was also explored.

The tool of increasing electron demand offers major promise in evaluating objectively neighboring group effects.² Participation, both π ^{3,4} and σ ,⁵ could be detected with this tool in representative systems where such participation is significant. The Hammett-Brown relationship enables one to vary the electron demand at a developing cationic center over a wide range, while maintaining the steric effects around that center essentially constant.⁶ We recently applied this tool to the study of the effect of ring size on the stabilization of developing carbocations on one of the ring members.⁷ Ring systems ranging in size from cyclopropyl to cyclooctyl were explored. The ρ^+ values observed in these systems could be accounted for quite reasonably in terms of the I-strain concept.⁸

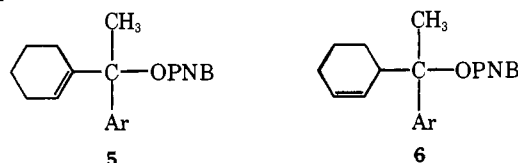
It seemed desirable to extend the study to the effect of α -cycloalkyl groups in stabilizing the cationic center, as measured by ρ^+ . Earlier studies on 1-cyclopropyl-1-aryl-1-ethyl (**1**)⁹ and 1-cyclobutyl-1-aryl-1-ethyl (**2**) systems¹⁰ indicated that such



α -cycloalkyl groups are capable of affording considerable stabilization to the carbonium ion center. Therefore, we wanted to extend this tool to the study of the related cyclopentyl (**3**)



and cyclohexyl (**4**) systems, where the stabilization of the carbonium ion center, if any, must be attributed to σ -electronic contributions from the ring system. We also wanted to examine the effect of a double bond in such a ring system, α and β to the carbonium ion center. Accordingly, we synthesized 1-(Δ^1 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates (**5**), containing an allylic double bond, and 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates (**6**), containing a homoallylic double



bond, and studied their rates of solvolysis. The possibility of participation in 1-(Δ^3 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates (**7**) was also briefly explored.

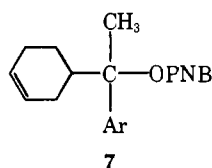
Results

Synthesis. The tertiary alcohols corresponding to systems **3**, **4**, and **5** were obtained by the addition of the appropriate aryl

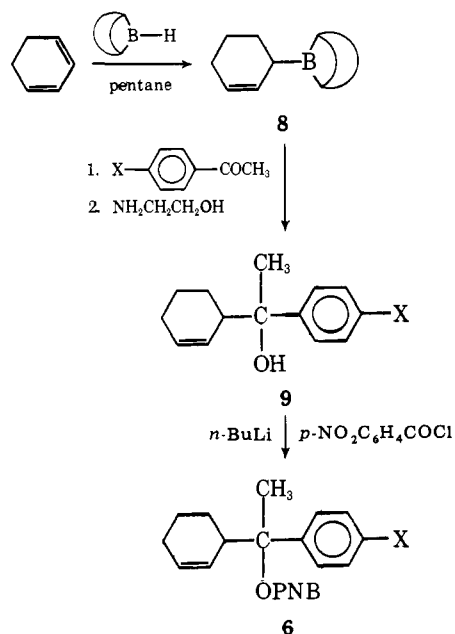
Table I. Rate Data on the Solvolysis of Tertiary *p*-Nitrobenzoates in 80% Aqueous Acetone

System	Substituent in aryl	$10^6 k_1 \text{ s}^{-1}$			ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu
		T_1 , °C	T_2 , °C	25 °C ^b		
3	<i>p</i> -CH ₃ O			113.0 ^a		
	<i>p</i> -H	329 (100)	24.2 (75)	0.035	26.4	-4.2
	<i>p</i> -CF ₃	40.0 (125)	2.79 (100)	6.50×10^{-5}	30.7	-1.7
	3,5-(CF ₃) ₂	31.6 (150)	2.30 (125)	7.97×10^{-7}	34.5	1.8
4	<i>p</i> -CH ₃ O			97.1 ^a		
	<i>p</i> -H	213 (100)	14.9 (75)	0.0191	26.9	-3.7
	<i>p</i> -CF ₃	245 (150)	21.9 (125)	2.43×10^{-5}	31.7	-0.6
	3,5-(CF ₃) ₂	132 (175)	12.6 (150)	2.71×10^{-7}	34.8	0.7
5	<i>p</i> -CH ₃ O			8100 ^a		
	<i>p</i> -H			123.4		
	<i>p</i> -CF ₃	759 (75)	70.0 (50)	4.33	20.1	-13.6
	3,5-(CF ₃) ₂	69.9 (75)	6.69 (50)	0.431	20.4	-19.2
6	<i>p</i> -CH ₃ O			26.2		
	<i>p</i> -H	58.4 (100)	3.83 (75)	4.17×10^{-3}	27.6	-4.5
	<i>p</i> -CF ₃	81.1 (150)	6.76 (125)	5.06×10^{-6}	32.7	-0.6
	3,5-(CF ₃) ₂	134 (175)	12.8 (150)	2.77×10^{-7}	34.8	0.7
7	3,5-(CF ₃) ₂	59.6 (175)	5.69 (150)	1.23×10^{-7}	34.8	-0.8

^a Calculated by multiplying the rate of benzoate by a factor of 20.8.¹³ ^b Extrapolated from data at higher temperatures.



Grignard reagents to the corresponding ketone. 1-(Δ^2 -Cyclohexenyl)-1-aryl-1-ethanols (**9**, X = *p*-CH₃O, *p*-H, *p*-CF₃) were synthesized by the allylboration of 1,3-cyclohexadiene with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by treatment of the allylborane (**8**) with the appropriate acetophenones.¹¹



The 3,5-(CF₃)₂ derivative (**9**, X = 3,5-(CF₃)₂) was obtained by the addition of the corresponding Grignard reagent to Δ^2 -cyclohexenyl methyl ketone. 1-(Δ^3 -Cyclohexenyl)-1-(3,5-bistrifluoromethylphenyl)-1-ethanol was prepared by the addition of the Grignard reagent to Δ^3 -cyclohexenyl methyl ketone. The conversion of tertiary alcohols into *p*-nitrobenzoates was effected by treating their lithium salts with *p*-nitrobenzoyl chloride.¹² The properties of the *p*-nitrobenzoates are summarized in the Experimental Section.

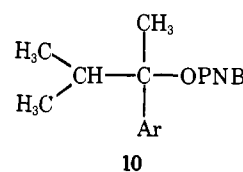
Rates of Solvolysis. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone by the ti-

trimetric method. The rate constants of the *p*-nitrobenzoates of some of the highly reactive *p*-methoxy derivatives were obtained by determining the rate for the benzoates and multiplying the rate constant by a factor of 20.8.¹³ The pertinent rate data are summarized in Table I.

Discussion

The tool of increasing electron demand³ provides a relatively objective probe for the presence of either π or σ participation or π or σ conjugation as significant factors in solvolysis. Consequently, we have been applying it to representative systems¹⁴ in order to establish a consistent understanding of the place of these factors in solvolytic behavior.

That a cyclopropyl group is far more responsive to providing electronic contributions ($\pi\sigma$) than the isopropyl group (σ) to the increasing electron demand of the cationic center is revealed by comparing the rates of 2-aryl-3-methyl-2-butyl *p*-nitrobenzoates (**10**) with 1-cyclopropyl-1-aryl-1-ethyl *p*-nitrobenzoates (**1**).⁹



Aryl substituent	10 Rel rate (25 °C)	1 Rel rate (25 °C)
<i>p</i> -CH ₃ O	1.00	505
<i>p</i> -H	1.00	25 300
<i>p</i> -CF ₃	1.00	285 000
3,5-(CF ₃) ₂	1.00	1 210 000

We have shown that this $\pi\sigma$ -electron supply can be considerably increased by methyl substituents and decreased by chlorine substituents in the cyclopropane moiety.⁹

Recently it was established that increasing the electron demand at the carbonium ion center results in small increases in rates of solvolysis for 1-cyclobutyl-1-aryl-1-ethyl *p*-nitrobenzoates (**2**) as compared with the corresponding isopropyl derivatives (**10**).¹⁰

Aryl substituent	10 Rel rate (25 °C)	2 Rel rate (25 °C)
<i>p</i> -CH ₃ O	1.00	1.0
<i>p</i> -H	1.00	5.7
<i>p</i> -CF ₃	1.00	9.0
3,5-(CF ₃) ₂	1.00	17.6

The rate increases must reflect increases in electron supply by

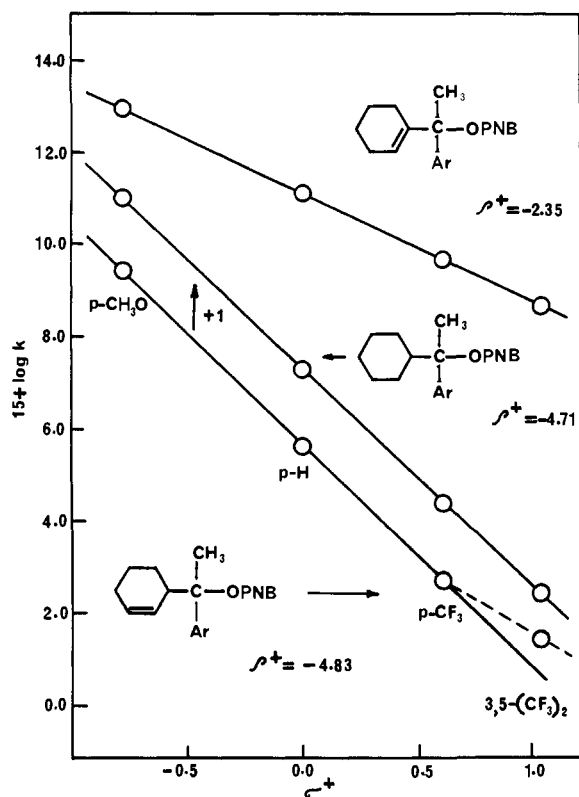


Figure 1. Log k - σ^+ plots for 1-cyclohexyl-1-aryl-1-ethyl, 1-(Δ^1 -cyclohexenyl)-1-aryl-1-ethyl, and 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C. (The data points for 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates are displaced down by one unit to minimize overlap.)

the cyclobutyl group under the increasing electron demand of the cationic center.

The data presented in Table I reveal that cyclopentyl may be a borderline case, a transition point between the enhanced contributions of cyclopropyl and cyclobutyl and the standard contributions of cyclohexyl and aliphatic groups such as methyl and isopropyl.

Aryl substituent	10	3	4
		Rel rate (25 °C)	
<i>p</i> -CH ₃ O	1.0	1.73	1.48
<i>p</i> -H	1.0	3.68	2.00
<i>p</i> -CF ₃	1.0	4.77	1.78
3,5-(CF ₃) ₂	1.0	5.57	1.90

Thus, an α cyclopentyl or cyclohexyl group is very similar to isopropyl in its ability to stabilize an adjacent electron-deficient center.

On the other hand, an allylic double bond in the ring system has an enormous effect. The rate of solvolysis of 1-(Δ^1 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoates (5) is tremendously increased over the saturated analogue (4) on increasing the electron demand at the cationic center.

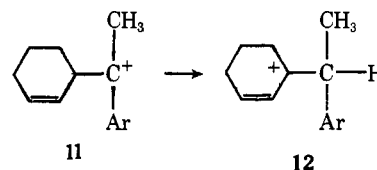
Aryl substituent	4	5	6
		Rel rate (25 °C)	
<i>p</i> -CH ₃ O	1.0	83.4	0.27
<i>p</i> -H	1.0	6460	0.22
<i>p</i> -CF ₃	1.0	178 200	0.21
3,5-(CF ₃) ₂	1.0	1 592 000	1.02

Hence, the solvolysis of these derivatives proceeds with major π -electronic stabilization from the allylic bond.

In 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl *p*-nitrobenzoate, where the double bond is homoallylic, no participation is observed with the first three derivatives (*p*-CH₃O, *p*-H, *p*-CF₃). In fact, these derivatives solvolyze four to five times slower than

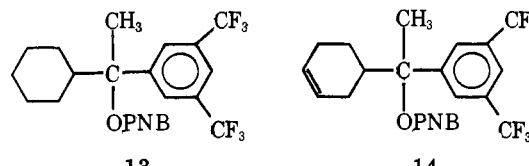
the corresponding saturated derivatives, presumably owing to the inductive rate-retarding effect of the double bond.^{15,16}

The 3,5-(CF₃)₂ derivative (6, X = 3,5-(CF₃)₂) shows a modest rate enhancement, the rate of solvolysis being quite comparable with the saturated derivative. The log k - σ^+ plot (Figure 1) reveals a definite break, indicating the inception of participation of some kind. Such participation could be π , similar to that recently postulated by Lambert and Featherman for the solvolysis in trifluoroacetic acid of the cyclohexen-4-yl tosylates.¹⁷ Alternatively, the participation may involve the transfer of the allylic hydrogen to the developing cationic center (11), producing a stabilized allylic cation (12). Unfor-



tunately, the solvolytic products proved to be complex and did not permit a conclusion to be drawn as to these two possible interpretations.

The double bond in the 1-(Δ^3 -cyclohexenyl)-1-aryl-1-ethyl system (7) should be even more favorable for π participation, if such participation is involved. Accordingly, we synthesized 1-(Δ^3 -cyclohexenyl)-1-(3,5-bistrifluoromethylphenyl)-1-ethyl *p*-nitrobenzoate (14) and studied its solvolysis. However, this



Rel rate (25 °C) 1.00

0.45

derivative did not show any rate enhancement over the saturated derivative (13). Accordingly, we conclude that 1-(Δ^3 -cyclohexenyl)-1-aryl-1-ethyl derivatives (7) solvolyze without significant participation. It appears probable therefore that the enhanced rate for the 3,5-(CF₃)₂ derivative of the Δ^2 -cyclohexenyl system (6, X = 3,5-(CF₃)₂) is the result of a rearrangement to the related allylic cation.

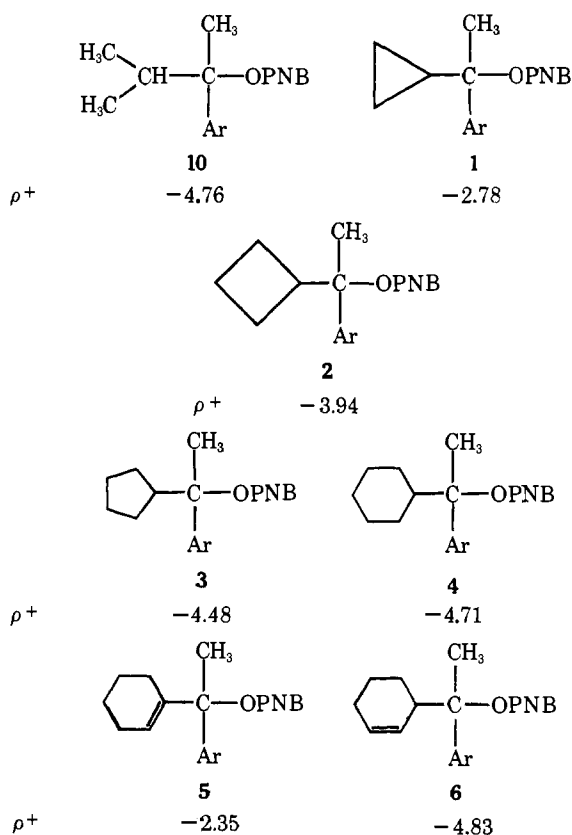
The log k - σ^+ treatment of the solvolysis data gave excellent linear plots in all cases (Figure 1), with the one exception just discussed. The solvolysis of 1-cyclopropyl-1-aryl-1-ethyl *p*-nitrobenzoates yielded a value of ρ^+ of -2.78 ,⁹ considerably more positive than for the isopropyl derivatives ($\rho^+ = -4.76$), suggesting major stabilization of the cationic center with increasing electron demand. The 1-cyclobutyl-1-aryl-1-ethyl system gave a ρ^+ value of -3.94 .¹⁰ The change in ρ^+ compared to the isopropyl derivatives ($\Delta\rho^+ = 0.82$) is a consequence of neighboring group stabilization. The 1-cyclopentyl-1-aryl-1-ethyl system (3) appears to be a borderline case, as is shown by the slightly more positive value of ρ^+ compared with the isopropyl and cyclohexyl systems. The 1-cyclohexyl-1-aryl-1-ethyl system yields a value of ρ^+ of -4.71 , similar to the isopropyl derivatives, indicating no significant electronic stabilization. The ρ^+ realized in 1-(Δ^1 -cyclohexenyl)-1-aryl-1-ethyl derivatives (5), -2.35 , is consistent with major electronic conjugation from the allylic double bond. It is interesting to note that the ρ^+ for the 1-(Δ^2 -cyclohexenyl)-1-aryl-1-ethyl system (6, omitting the 3,5-(CF₃)₂ derivative) is more negative than the ρ^+ for the saturated system suggesting the absence of participation (correlation coefficient for the log k - σ^+ plots is 0.999–1.000 in all of the cases).

Conclusion

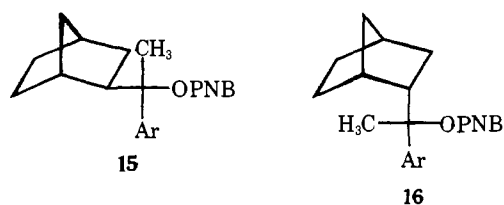
The present study of the tool of increasing electron demand establishes that the major $\pi\sigma$ -electronic contributions by the

Table II. Properties of *p*-Nitrobenzoates

System	Substituent in aryl	Yield, %	Mp, °C	Molecular formula	Anal.							
					Calcd				Found			
					C	H	N	F	C	H	N	F
3	<i>p</i> -H	78	115–116	C ₂₀ H ₂₁ NO ₄	70.77	6.25	4.12		68.89	5.90	3.54	
	<i>p</i> -CF ₃	81	138.5–139	C ₂₁ H ₂₀ F ₃ NO ₄	61.90	4.96	3.44	13.99	62.15	5.18	3.31	13.79
	3,5-(CF ₃) ₂	77	109–110	C ₂₂ H ₁₉ F ₆ NO ₄	55.59	4.02	2.94	23.98	55.79	4.10	2.84	23.90
4	<i>p</i> -CH ₃ O ^a	71	104–105	C ₂₂ H ₂₅ O ₃	78.07	7.74			77.78	7.89		
	<i>p</i> -H	81	138.5–139.5	C ₂₁ H ₂₃ NO ₄	71.36	6.55	3.96		71.28	6.48	3.92	
	<i>p</i> -CF ₃	78	145–145.5	C ₂₂ H ₂₂ F ₃ NO ₄	62.69	5.26	3.32	13.52	62.80	5.36	3.29	13.48
	3,5-(CF ₃) ₂	68	150.5–151	C ₂₃ H ₂₁ F ₆ NO ₄	56.43	4.32	2.86	23.29	56.33	4.28	2.89	23.24
5	<i>p</i> -H	40	105–106 dec	C ₂₁ H ₂₁ NO ₄	71.77	5.98	3.98		72.01	6.03	3.80	
	<i>p</i> -CF ₃	45	112–113	C ₂₂ H ₂₀ F ₃ NO ₄	63.0	4.77	3.34	13.60	63.18	4.82	3.20	13.70
	3,5-(CF ₃) ₂	48	101–102	C ₂₃ H ₁₉ F ₆ NO ₄	56.67	3.90	2.87	23.4	56.69	4.01	2.7	23.5
6	<i>p</i> -CH ₃ O	58	115–116	C ₂₂ H ₂₃ NO ₅	69.29	6.03	3.67		69.51	6.19	3.39	
	<i>p</i> -H	68	114–115	C ₂₁ H ₂₁ NO ₄	71.77	5.98	3.98		72.06	6.07	3.69	
	<i>p</i> -CF ₃	75	142–143	C ₂₂ H ₂₀ F ₃ NO ₄	63.0	4.77	3.34	13.60	62.83	4.94	3.10	13.52
	3,5-(CF ₃) ₂	62	159–160	C ₂₃ H ₁₉ F ₆ NO ₄	56.67	3.90	2.87	23.4	56.93	4.18	2.88	23.61
7	3,5-(CF ₃) ₂	64	142–143	C ₂₃ H ₁₉ F ₆ NO ₄	56.67	3.90	2.87	23.4	56.91	4.20	2.81	23.52

^a Benzoate.

cyclopropyl ring diminish greatly with the cyclobutyl ring, and become borderline with the cyclopentyl ring. With cyclohexyl, the effect becomes comparable with those realized with such aliphatic groups as methyl and isopropyl. The introduction of a double bond in the cyclohexyl ring in the allylic position has a major effect. We are now applying this approach to *exo*- and *endo*-norbornyl (15, 16).¹⁸ Will the developing charge at the



α position reveal a significant difference in the electronic contributions of the two structures?

Experimental Section

Preparation of 1-Cyclopentyl-1-aryl-, 1-Cyclohexyl-1-aryl-, and 1-(Δ^1 -Cyclohexenyl)-1-aryl-1-ethanols. These alcohols were prepared by the addition of the appropriate aryl Grignard reagents to the cycloalkyl methyl ketones. The tertiary alcohols were converted into *p*-nitrobenzoates without further purification.

Synthesis of 1-(Δ^2 -Cyclohexenyl)-1-aryl-1-ethanols. These alcohols (6, *p*-CH₃O, *p*-H, *p*-CF₃) were prepared by the addition of the appropriate aryl methyl ketones to the allylborane obtained by the allylboration of 1,3-cyclohexadiene with 9-BBN.¹¹ The following procedure is representative. To an oven-dried, flamed-out, nitrogen-flushed, 200-mL flask fitted with a magnetic stirring bar and septum inlet and topped with a connecting tube leading to a mercury bubbler was added a solution of 9-BBN in pentane (0.54 M, 60 mL, 32.4 mmol), followed by 1,3-cyclohexadiene (3.2 g, 40 mmol). The reaction mixture was stirred overnight and then acetophenone (3.36 g, 28 mmol) was added. The mixture was stirred for 2 h at room temperature and then worked up by the usual transesterification procedure with ethanolamine.¹¹ Excellent yields (80–85%) were realized in all the three cases.

Δ^2 -Cyclohexenyl Methyl Ketone. This compound was synthesized from Δ^1 -cyclohexenyl methyl ketone via the enol acetate following the literature procedure.^{19,20}

1-(Δ^2 -Cyclohexenyl)-1-(3,5-bis(trifluoromethyl)phenyl)-1-ethanol. Addition of Δ^2 -cyclohexenyl methyl ketone to the Grignard reagent prepared from magnesium and 3,5-bis(trifluoromethyl)bromobenzene in ether yielded the tertiary alcohol in 85% yield, bp 119–121 °C (0.2 mm).

Δ^3 -Cyclohexenyl methyl ketone was prepared by treating 3-cyclohexene-1-carbonitrile with methylmagnesium iodide in ether²¹ (67% yield), bp 80–84 °C (15 mm) [lit.²² bp 184–185 °C (747 mm)].

1-(Δ^3 -Cyclohexenyl)-1-(3,5-bis(trifluoromethyl)phenyl)-1-ethanol. This alcohol was prepared by the addition of Δ^3 -cyclohexenyl methyl ketone to 3,5-bis(trifluoromethyl)phenylmagnesium bromide in 78% yield, bp 123–124 °C (0.4 mm).

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates of the tertiary alcohols were prepared by treating the lithio derivatives with *p*-nitrobenzoyl chloride in THF.¹² The properties of the *p*-nitrobenzoates are summarized in Table II.

Rates of Solvolysis. The rates of solvolysis of the *p*-nitrobenzoates were determined in 80% aqueous acetone.¹² The rate constants are reproducible to $\pm 1\%$.

Products of Solvolysis. The products of solvolysis of a representative (phenyl) *p*-nitrobenzoate in each series were determined at the temperature of the kinetic measurement in buffered 80% aqueous acetone. 1-Cyclopentyl-1-phenyl-1-ethyl *p*-nitrobenzoate and 1-(Δ^1 -cyclohexenyl)-1-phenyl-1-ethyl *p*-nitrobenzoate gave only the tertiary alcohol. 1-Cyclohexyl-1-phenyl-1-ethyl *p*-nitrobenzoate yielded the tertiary alcohol (97%) and olefin (3%). Solvolysis of 1-(Δ^2 -cyclohexenyl)-1-phenyl-1-ethyl *p*-nitrobenzoate gave 45% of the tertiary alcohol and 55% of unidentified olefinic compounds.

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Synthesis and Reactions of Some New Sulfur Transfer Reagents¹

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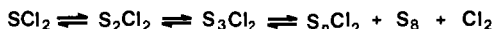
Abstract: Six new azole sulfur transfer reagents have been prepared from their trimethylsilyl derivatives and S_xCl_2 ($x = 1, 2$). The reactions of these reagents are different from those of SCl_2 or the corresponding phthalimide reagent with thiols, amines, and alcohols. A possible mechanism is discussed. Of particular interest is the facile, high-yield formation of sultines **21** and **22** with the monosulfur azole reagent, *N,N'*-thiobisbenzimidazole (**6a**).

Introduction

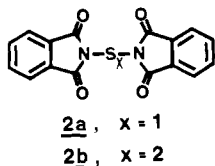
Sulfur di- and monochloride (**1a,b**) have been known since the late 1800s² and employed as valuable synthetic reagents



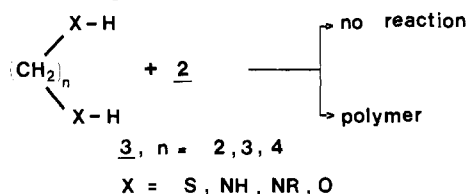
for a wide range of purposes. Possessing two leaving groups, they allow the formation of both ring and special polymer chains under the appropriate conditions. However, several features considerably limit the utility and effectiveness of these reagents: they are both liquids of a disagreeable odor and are unstable due to disproportionation.³ Even a minimal procedure involves one or more distillations prior to use.⁴



The crystalline, phthalimide-blocked sulfur-transfer analogs (**2a,b**) have been investigated in our⁵ and other labo-



ratories.⁶ While they possess several improved features compared with the sulfur halides, we have observed that a number of bifunctional reagents **3**, when treated with **2**, either formed



intractable polymers or simply did not react. It appears that in the case of the phthalimide group a price in reactivity is paid for the increased shelf stability over sulfur halides **1**.

The importance of this type of reagent in synthesis has led to the present work of trying to find a workable compromise between these two properties. We report here the synthesis and some properties of a series of new sulfur-transfer reagents with nitrogen heterocycles as a leaving group.

Results

The initial approach taken to synthesize compounds **4-8** was

