(CCl_4) showed a singlet for the *tert*-butyl protons at δ 0.92 from Me_4Si.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.56; H, 13.08.

2-*tert*-Butyl-2-*endo*-camphenilol. This alcohol was prepared by the addition of camphenilone (3,3-dimethyl-2-norbornanone) to *tert*-butyllithium at −78° following the procedure described in the literature.[18] Distillation gave the desired alcohol (93% yield), bp 92–93° (2 mm). VPC analysis (15% Carbowax 20M on Chromosorb W) indicated about 98% purity. Further purification by preparative VPC (20% Carbowax 20M on Chromosorb W) resulted in a solid, mp 33.5–34.5°. NMR spectrum ($CDCl_3$) showed a singlet for the *tert*-butyl hydrogens at δ 1.08 from Me_4Si. Ir spectrum (melt) showed weak absorption at 2.75 μ (sharp).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.75; H, 12.46.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates were prepared via the lithium alkoxides in tetrahydrofuran similar to the procedure described in the literature,[19] except that, before work-up, an equal volume of diethyl ether was added to the reaction mixture. After washing with cold 5% aqueous sodium bicarbonate, the ethereal layer was dried over anhydrous magnesium sulfate. Good to excellent yields of the *p*-nitrobenzoates were obtained. Physical properties are listed in Table II.

Acknowledgment. The authors thank Dr. Jerry D. Buhler for samples of 1-*tert*-butyl-1-cyclohexanol and 3-*tert*-butyl-3-nortricyclanol, Dr. Gary Lynch for a sample of 1-*tert*-butyl-1-cyclopentanol, and Dr. Bruce A Carlson for samples of 9-*tert*-butyl-9-bicyclo[3.3.1]nonanol and bicyclo-[3.3.1]nonan-9-one.

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Solvolysis of 1-(*p*-Cyclopropylphenyl)- and 1-(*p*-Isopropylphenyl)-1-arylethyl Chlorides. Test of the Tool of Increasing Electron Demand to Systems with Relatively Small Electronic Response[1]

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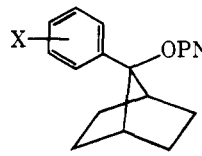
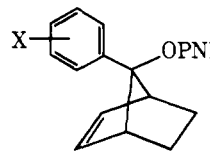
Contribution from the Richard B. Wetherill Laboratory of Purdue University, West Lafayette, Indiana 47907. *Received November 23, 1974*

Abstract: 1-(*p*-Cyclopropylphenyl)-1-arylethyl chlorides and 1-(*p*-isopropylphenyl)-1-arylethyl chlorides were synthesized and their rates of solvolysis in 97.5% aqueous acetone determined in order to establish whether there is, in this highly stabilized cationic system, a detectable difference in the relative abilities of a cyclopropyl and isopropyl group to contribute to the stabilized electron-deficient center. The relative rates of solvolysis of cyclopropyl derivatives compared with the corresponding isopropyl compounds for the usual range of substituents in the aryl group are as follows: *p*-CH_3O, 1.1; *p*-H, 2.8; *p*-CF_3, 8.5; 3,5-$(CF_3)_2$, 13.5. This modest increase in rate is in accordance with the greater ability of the cyclopropyl moiety over isopropyl to react to increasing electron demand by supplying electron density to stabilize the electron-deficient center. The cyclopropyl compounds yield a ρ^+ value of −2.24 as compared with −2.91 for the isopropyl derivatives. It is concluded that the tool of increasing electron demand is quite sensitive, capable of detecting even modest electronic contributions in systems where the electronic demand and supply are relatively small.

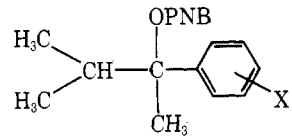
The tool of increasing electron demand has been used to detect π or σ contributions in various systems. For example, Gassman and Fentiman have shown that the ability of the π electrons in 7-aryl-*anti*-7-norbornenyl derivatives (**2**) to stabilize the carbonium center increases as the electron demand is increased.[3] Thus, the relative rates of **2** increase from 3.4 for *p*-anisyl to over 10^5 for 3,5-bis(trifluoromethyl)phenyl, compared with the corresponding 7-aryl-7-nor-

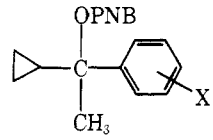




X	1	2
p-CH_3O	1.0	3.4
p-H	1.0	41.5
p-CF_3	1.0	34,500
3,5-$(CF_3)_2$	1.0	255,000

bornyl derivatives (**1**). Similarly, π participation has been detected in the 6-methoxybenzonorbornenyl system[4] and in the 5-methyl-2-norbornenyl system[5] by the application of this tool. Major σ contributions to the electron-deficient center have been revealed by this tool in the cyclopropylcarbinyl system.[6] The rate of solvolysis of the cyclopropyl derivative (**4**) increases enormously as compared with the isopropyl derivative (**3**). However, attempts to confirm the

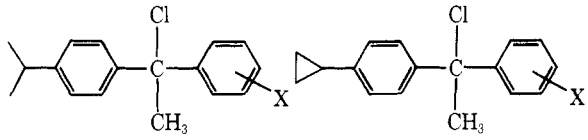




X	3	4
p-CH_3O	1.0	505
p-H	1.0	25,300
p-CF_3	1.0	285,000
3,5-$(CF_3)_2$	1.0	1,210,000

often postulated σ participation in the 2-norbornyl system[7] have failed.[8,9]

The exo:endo rate ratio in norbornyl is ~300. It has been questioned whether the tool of increasing electron demand would respond to a system with such a relatively low electronic response.[10] Hence it was considered desirable to test the tool in a system where the electron response would be relatively small. Accordingly, we undertook to synthesize and to determine the rates of solvolysis of the 1-(*p*-cyclopropylphenyl)-1-arylethyl chlorides (**6**) and 1-(*p*-isopropylphenyl)-1-arylethyl chlorides (**5**).



5

a, X = *p*-CH_3O
b, X = *p*-H
c, X = *p*-CF_3
d, X = 3,5-$(CF_3)_2$

6

a, X = *p*-CH_3O
b, X = *p*-H
c, X = *p*-CF_3
d, X = 3,5-$(CF_3)_2$

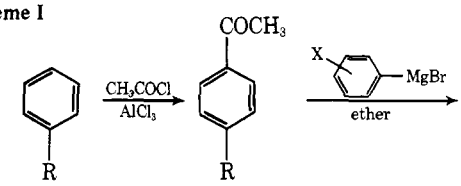
The diarylmethylcarbonium ion is a highly stable one. Consequently, the cationic center should make little demand on the *p*-isopropyl and *p*-cyclopropyl substituent for further stabilization. The question was whether the modest changes in electron demand of the cationic center resulting from the introduction of the usual range of substituents in the second aryl group could result in detectable changes in the electronic contribution from the para substituents in the first aromatic group.

Results and Discussion

The tertiary chlorides (**5a–d** and **6a–d**) were synthesized according to the general scheme outlined in Scheme I.

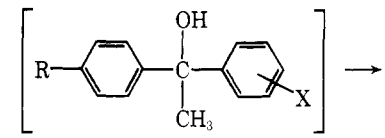
Cyclopropylbenzene was treated with acetyl chloride and aluminum chloride in chloroform at −5 to −10° to yield *p*-

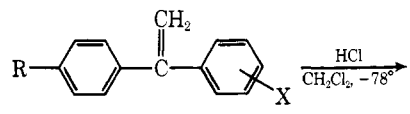
Scheme I



R = cyclopropyl or isopropyl

7





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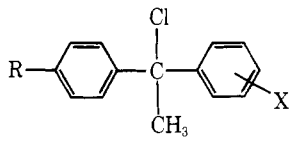
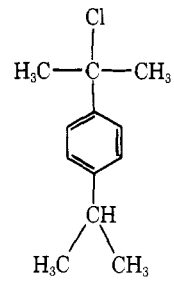


5 and **6**

cyclopropylacetophenone[11] (**7**, R = cyclopropyl). The reaction of the appropriate Grignard reagent with the ketone gave the tertiary alcohols which were thermally dehydrated to the olefins (**8**, R = cyclopropyl). Hydrochlorination of the olefins in methylene chloride at −78° gave the tertiary chlorides.[12,13] Isopropylbenzene was acetylated using acetyl chloride and aluminum chloride in carbon disulfide[14] to yield *p*-isopropylacetophenone (**7**, R = isopropyl), and then the same sequence of steps was followed.

The rates of solvolysis of the tertiary chlorides were determined in 97.5% acetone-water. The kinetic data and thermodynamic parameters are summarized in Table I.

The results reveal that, with increasing electron demand at the cationic center, the rate of solvolysis of the cyclopropyl derivative (**6**) increases moderately when compared to the isopropyl derivative (**5**) (Table II). The enhanced ability of a *p*-cyclopropyl ring to supply electrons to an electron-deficient center (**9**, **10**) is well documented.[15] There is



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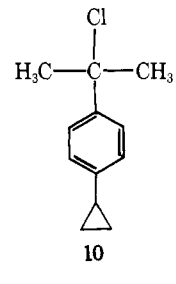


10

rel rate:	1.0	6.6

ample evidence to show that the stabilization of the electron-deficient center by the cyclopropyl ring in the tertiary cumyl system is due to an interaction between the cyclopropyl ring and the adjacent p orbital of the benzene ring via the "bisected geometry".[16,17] The stabilization provided by the cyclopropyl ring becomes more effective as the carbonium ion center is made more electron demanding (compare relative rates for **4**/**3** and for **6**/**5**).

The solvolysis data show excellent linear correlation with the σ^+ values.[18] The cyclopropyl derivatives (**6**) yield a ρ^+ value of −2.24 (correlation coefficient 0.999), and the isopropyl derivatives (**5**) yield one of −2.91 (correlation coeffi-

Table I. Rates of Solvolysis of 1-(*p*-Cyclopropylphenyl)-1-arylethyl Chlorides and 1-(*p*-Isopropylphenyl)-1-arylethyl Chlorides in 97.5% Acetone

Tertiary chloride	Substituent	Rate constant, 10^5k_1, sec^{-1} T_1	T_1	25°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
6a	*p*-CH_3O			57,500[a]		
5a	*p*-CH_3O			51,300[a]		
6b	*p*-H	3.19 (−25°)	66 (0°)	821[b]	16.3	−15.3
5b	*p*-H	19.5 (0°)		296	17.0	−13.0
6c	*p*-CF_3	2.4 (0°)		38.8	17.4	−15.7
5c	*p*-CF_3	0.26 (0°)		4.59	18.0	−15.9
6d	3,5-$(CF_3)_2$	55.2 (50°)		3.75	20.0	−11.7
5d	3,5-$(CF_3)_2$	4.8 (50°)		0.278	21.2	−12.8

[a] Calculated from σ^+ vs. log k plot for other derivatives. [b] Extrapolated from the data at lower temperatures.

Table II. Relative Effect of R = Cyclopropyl and R = Isopropyl in the Solvolysis of *p*-$RC_6H_4CCl(CH_3)(C_6H_4X)Cl$ with Increasing Electron Demand as X is Varied

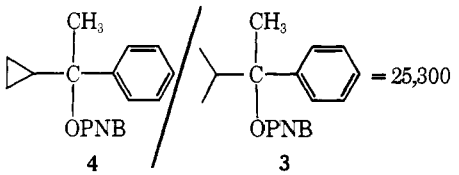
Substituent	Rel rate 6/5
p-CH_3O	1.1
p-H	2.8
p-CF_3	8.5
3,5-$(CF_3)_2$	13.5

cient 1.000). This again establishes that the stabilizing effect of the cyclopropyl group varies linearly with the electron demand of the incipient carbonium ion.

The products produced in the solvolysis of **5** and **6** were analyzed by NMR. The results are listed below in Table III.

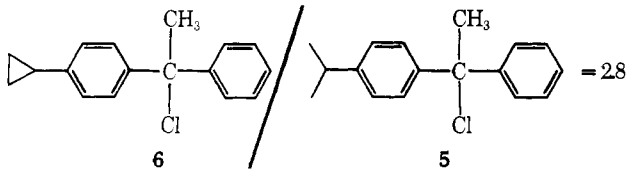
Conclusion

In **3** and **4**, the cyclopropyl group enhances the rate of the unsubstituted derivative (X = *p*-H) by a factor of 25,300.



4 3

The effect of the cyclopropyl group is greatly diminished in **5** and **6**, to approximately 0.01% of this value. Yet the tool of increasing electron demand gives an unambiguous response in both systems. Thus, $\rho^+ = -4.76$ for **3** and -2.78 for **4** ($\Delta\rho^+ = 1.98$). Similarly, $\rho^+ = -2.91$ for **5** and -2.24 for **6** ($\Delta\rho^+ = 0.67$).



6 5

The exo/endo rate ratio in 2-anisyl-2-norbornyl is 284.[8] Consequently, the effect here is approximately 100-fold larger than that observed in **6/5**. If this exo/endo rate ratio owes its origin to a stereospecific electronic contribution from the C1-C6 bonding pair in the exo derivative, the tool of increasing electronic demand should reveal increasing electronic contributions and increasing exo/endo rate ratios with increasing electronic demand, reflected in changing values for ρ^+.

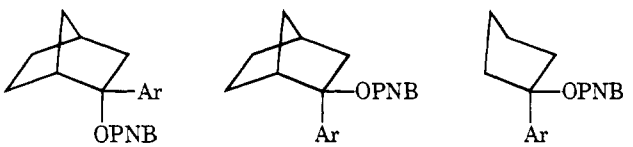
Such changes are observed in **1** and **2**, **3** and **4**, and **5** and **6**, as well as in other systems,[4,5] but are not detectable in 2-norbornyl (**11**, **12**). Indeed, ρ^+ for the 1-arylcyclopentyl derivative[9] (**13**) is indistinguishable from the values for **11** and **12**.

The conclusion indicated is that σ participation is not involved in the high exo:endo rate ratios in the 2-aryl-2-norbornyl derivatives.

Table III. Products of Solvolysis of 1-(*p*-Cyclopropylphenyl)-1-arylethyl Chlorides and 1-(*p*-Isopropylphenyl)-1-arylethyl Chlorides in 97.5% Acetone

Tertiary chloride	Olefin,[a] %	Tertiary alcohol,[a] %
6b	64	36
5b	65	35
6c	63	37
5c	58	42
6d	59	41
5d	57	43

[a] The accuracy limit is ±3%.



11 12 13

ρ^+: −3.75 −3.83 −3.82

Experimental Section

Melting points (uncorrected) were taken on a Thomas-Hoover capillary melting-point apparatus. Infrared spectra were recorded on a Perkin-Elmer 137 instrument. NMR spectra were measured on a Varian T-60 instrument. Isopropylbenzene and cyclopropylbenzene were commercially available (Chemical Samples Co.).

***p*-Cyclopropylacetophenone.** The acetylation of cyclopropylbenzene (14.7 g, 0.125 mol) with acetyl chloride (9.9 g, 0.125 mol) and aluminum chloride (16.68 g, 0.125 mol) in chloroform (100 ml) at −5 to −10° yielded *p*-cyclopropylacetophenone[11] in 64% yield, mp 35–36° (lit.[11] mp 35–36°).

***p*-Isopropylacetophenone** was prepared by the acetylation of isopropylbenzene[14] in 80% yield, bp 104° (2 mm).

General Procedure for the Preparation of Olefins. The following procedure is representative for the preparation of olefins (**8**, R = cyclopropyl, isopropyl). The Grignard reagent was prepared from the appropriate bromobenzene (62.5 mmol) and magnesium (0.0625 g-atom) in ether (50 ml). To the cooled (ice) Grignard reagent was added dropwise a solution of the ketone (50 mmol) in ether (25 ml). The mixture was stirred at 0° for 30 min and allowed to reach room temperature. The reaction mixture was refluxed for 2 hr and then decomposed with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer extracted twice with 30-ml portions of ether. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of solvent and distillation in the presence of a drop of acid gave the olefins. They were crystallized from petroleum ether. Properties and analyses of the olefins prepared in this study are summarized in Table IV.

Hydrochlorination of Olefins. The procedure described by Brown and Liu was used.[13] The olefin (20 mmol) was dissolved in methylene chloride (10 ml) and then treated with hydrogen chloride at −78° in a hydrochlorinator[12] until the estimated amount of hydrogen chloride had been absorbed. After the reaction, the flask was immediately attached to a vacuum line at about 0.5 mmHg to

Table IV. Analysis and Properties of Olefins[a]

Olefin (8)	Mp, °C, or bp, °C (mm)	Yield[b] %	Analysis					
			Calcd %			Found %		
			C	H	F	C	H	F
R = cyclopropyl, X = *p*-OCH_3	113–114	82	86.37	7.23		85.67	7.37	
R = isopropyl, X = *p*-OCH_3	44–45	80	85.7	8.00		85.80	7.78	
R = cyclopropyl, X = *p*-H	53–54	80	92.69	7.31		92.53	7.46	
R = isopropyl, X = *p*-H	110 (0.4 mm)[c]	85	91.86	8.16		92.03	8.19	
R = cyclopropyl, X = *p*-CF_3	99–100	81	74.99	5.23	19.77	74.79	5.50	19.59
R = isopropyl, X = *p*-CF_3	34–35	76	74.47	5.89	19.63	74.73	5.81	19.42
R = cyclopropyl, X = 3,5-$(CF_3)_2$	32–33	75	64.04	3.96	32.00	64.27	4.05	31.97
R = isopropyl, X = 3,5-$(CF_3)_2$	106–108 (0.4 mm)	75	63.69	4.50	31.82	63.67	4.71	32.10

[a] All olefins gave spectral data consistent with the structure. [b] Yields are based on the starting ketone. [c] Literature bp 122–123° (0.1 mm): F. Bergman and J. Szmuskowicz, *J. Am. Chem. Soc.*, **70**, 2748 (1948).

remove the excess hydrogen chloride and solvent. No attempt was made to purify the tertiary chlorides as they were known to be quite unstable,[14] and they were used directly for kinetic measurements.

Kinetic Procedure. The kinetic procedure was similar to that previously described.[14] Acetone [97.5% (v/v)] was prepared and standardized by running the rate of *p*-isopropyl-*tert*-cumyl chloride whose rate had already been established in this solvent.[11] The solvent was brought to the reaction temperature. Approximately 0.5 ml of tertiary chloride was added and mixed thoroughly. Five-milliliter aliquots were removed with fast delivery pipets at appropriate intervals of time and run into 100 ml of cold (0°) dry acetone, and the free acid was titrated with 0.02 *N* sodium hydroxide using a mixed indicator consisting of Methyl Red and Bromocresol Green. The infinity titers were determined after 10 half-lives. The rate for the *p*-methoxy compounds was too fast to measure even at 0°.

Product Analysis. The tertiary chlorides were solvolyzed in 97.5% acetone containing sodium bicarbonate. The acetone was removed using an aspirator. The hydrolysis products were extracted with ether and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the products were analyzed by NMR. The results are summarized in Table III.

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