Structural Effects in Solvolytic Reactions. 17. Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl *p*-Nitrobenzoates. Evidence for Major Increases in Electron Supply by the Cyclopropyl Group with Increasing Electron Demand at the Cationic Center. Effect of Substituents on the Cyclopropane Ring. σ Conjugation vs. σ Participation[1]

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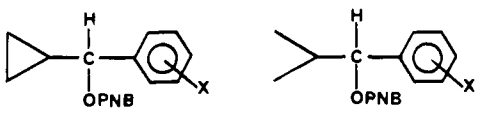
Abstract: The rates of solvolysis in 80% acetone of 1-aryl-1-cyclopropyl-1-ethyl *p*-nitrobenzoates containing representative substituents in the aryl ring (*p*-CH_3O, *p*-H, *p*-CF_3, 3,5-$(CF_3)_2$) were determined and compared with the rates for the 2-aryl-3-methyl-2-butyl *p*-nitrobenzoates. Substituted cyclopropyl derivatives (2′,2′-dimethylcyclopropyl and 2′,2′-dichlorocyclopropyl) were also synthesized and the rates determined. The ρ^+ value for the cyclopropyl derivatives, −2.78, is considerably less negative than the value for the isopropyl derivatives, ρ^+ −4.76. The introduction of methyl groups into the cyclopropyl ring increases the electron supply, ρ^+ −2.06, whereas the chlorine substituents have the opposite effect, ρ^+ −4.99, decreasing electron supply below that of the isopropyl group. Thus, under the increasing electron demand by the cationic center the cyclopropyl group is capable of providing σ-electron supply to a much greater extent than the isopropyl group. Moreover, this σ-electron supply can be increased considerably by methyl substituents and decreased by chlorine substituents. The difference between σ conjugation and σ participation is analyzed. It is concluded that the large σ-electron supply from the cyclopropyl moiety must be classified as σ conjugation, not σ participation.

The tool of increasing electron demand has established its ability to detect the presence or absence of π participation in various homoallylic systems.[4-7] Recently we established that this tool could also be used to detect π conjugation in allylic systems.[8]

The value of this approach as a test for π participation in homoallylic systems[4-7] and for π conjugation in allylic systems[8] encouraged us to explore the possibility that it could be extended to test for σ participation and σ conjugation in appropriate systems. The cyclopropyl moiety appeared to be an appropriate one for such an exploration. Unfortunately, the available data appeared to be in conflict.

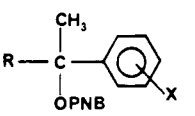
Thus an examination of the 3-aryl-3-nortricyclyl derivatives had indicated that electron supply from the system increases with increasing electron demand at the cationic center.[9] This stabilization had been attributed to major increases in σ-electron supply from the cyclopropyl moiety.

On the other hand, Shono and co-workers had examined the solvolysis of the α-arylcyclopropylcarbinyl *p*-nitrobenzoates (**1**) and had compared them with the related α-arylisopropylcarbinyl *p*-nitrobenzoates (**2**), where the powerful cyclopropyl conjugation should be absent.[10] Surprisingly, least-squares treatment of the correlation provided by their rate constants at 79.9 °C against the σ^+ constants provided values of ρ^+ −3.47 ± 0.26 (correlation coefficient 0.994) for **1** and −3.44 ± 0.80 (correlation coefficient 0.950) for **2**, suggesting the absence of such σ-electron supply in **1** (Figure 1). Careful inspection of their data indicated that the difficulty may arise from the use of the secondary derivatives with a change in mechanism occurring in **2** as more electron-withdrawing substituents are introduced.



1 **2**

Accordingly we decided to examine the corresponding tertiary *p*-nitrobenzoates (**3**). The substituent X was varied over



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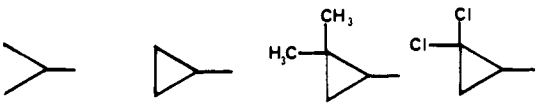
the usual range (X = *p*-CH_3O, *p*-H, *p*-CF_3, 3,5-$(CF_3)_2$) to provide a wide variation in electron demand. The group R was varied from isopropyl (**4**), cyclopropyl (**5**), 2,2-dimethylcyclopropyl (**6**), and 2,2-dichlorocyclopropyl (**7**). The four series of compounds (**3–7**) were synthesized and the rates of solvolysis in 80% aqueous acetone determined.



4 **5** **6** **7**

Results

Synthesis. The syntheses of **3–4** and **3–5** were accomplished by the addition of the appropriate aryl Grigard reagents to 3-methyl-2-butanone and to methyl cyclopropyl ketone to give the corresponding alcohols, converted into the *p*-nitrobenzoates via the lithium alkoxide method.[9]

The synthesis of 1-aryl-1-(2′,2′-dimethylcyclopropyl)-1-ethyl *p*-nitrobenzoates (**3–6**) were carried out according to the flow diagram shown in Scheme I.

The ditosylate of 2,2-dimethylpropane-1,3-diol (**9**) was treated with potassium cyanide in ethylene glycol to furnish 2,2-dimethylcyclopropanenitrile (**10**).[11] The nitrile was hydrolyzed to the acid (**11**) by refluxing with 30% potassium hydroxide solution for 48 h. Treatment of **11** with methyllithium gave the methyl ketone **12**. The addition of appropriate Grignard reagents gave the tertiary alcohols (**13**); the alcohols

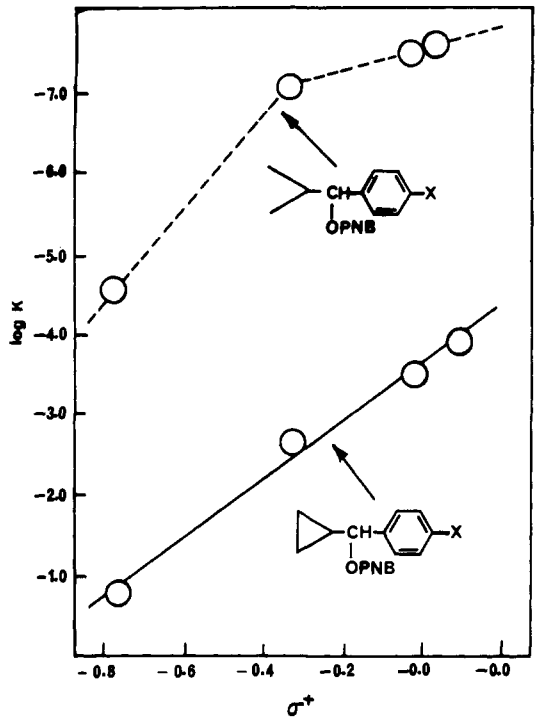
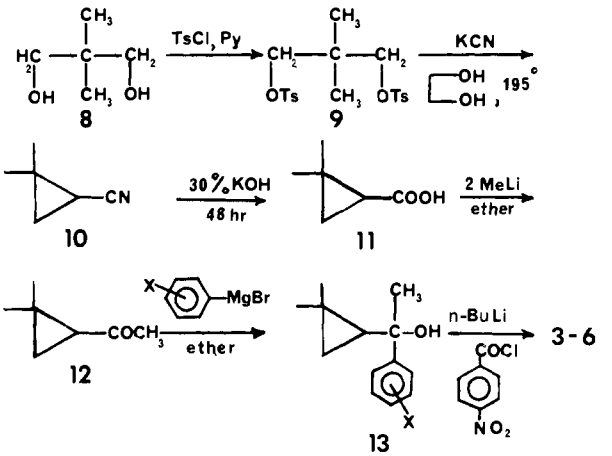


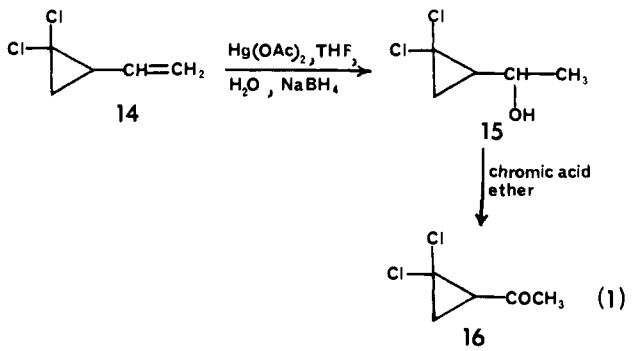
Figure 1. Log k-σ^+ plot of Shono's data for solvolysis in 65% aqueous dioxane at 79.9 °C (data from ref 10).

Scheme I. Synthesis of 1-Aryl-1-(2′,2′-dimethylcyclopropyl)-1-ethyl *p*-Nitrobenzoates



were converted to the *p*-nitrobenzoates (**3–6**) by treating their lithium salts with *p*-nitrobenzoyl chloride.[9]

The oxymercuration-demercuration[12] of 2,2-dichloro-1-vinylcyclopropane (**14**)[13] afforded the secondary alcohol (**15**). The alcohol (**15**) was oxidized to the ketone (**16**) utilizing the convenient two-phase oxidation procedure[14] (eq 1). The conversion of the ketone (**16**) into the *p*-nitrobenzoates (**3–7**) followed the procedure previously described for **3–6.**



Kinetic Studies. The rates of solvolysis of various *p*-nitrobenzoates were determined in 80% aqueous acetone. The rate constants and activation parameters are summarized in Table I.

1-*p*-Anisyl-1-cyclopropyl-1-ethyl and 1-*p*-anisyl-1-(2′,2′-dimethylcyclopropyl) *p*-nitrobenzoates or benzoates could not be isolated owing to their exceedingly high reactivity and instability. Hence their rate constants were obtained by extrapolation of the log k-σ^+ plot for the other derivatives.[15] The rate constant for 1-phenyl-1-(2′,2′-dimethylcyclopropyl) *p*-nitrobenzoate was obtained by multiplying the rate constant for the benzoate by the factor of 20.8.[16]

Discussion

Effect of Increasing Electron Demand. A perusal of Table I reveals that the rate of solvolysis of the cyclopropyl derivatives (**3–5**) increases enormously relative to the isopropyl derivative (**3–4**) with increasing electron demand (Table II).

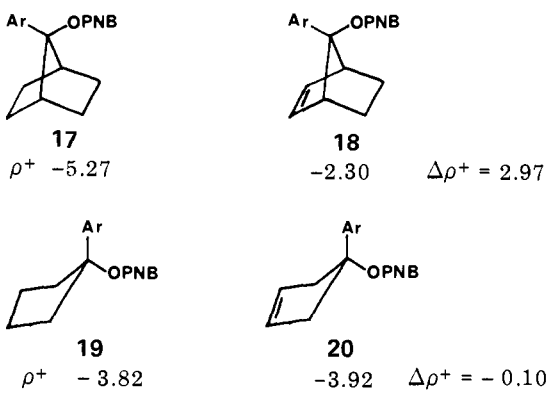
The difference in rate is even greater in the case of the dimethylcyclopropyl derivatives (**3–6**) because of the more effective charge delocalization provided by the methyl substituents. The rates of solvolysis of the dichlorocyclopropyl compounds (**3–7**) are comparable to those of **3–4,** showing that the two chlorine atoms in the cyclopropane ring are quite effective in reducing charge delocalization into the ring.

The four systems examined reveal excellent log k-σ^+ relationships.[15] Thus, **3–4** yields a ρ^+ value of −4.76 (correlation coefficient 0.999). The ρ^+ for other systems are −2.78 for **3–5** (correlation coefficient 0.999), −2.06 for **3–6** (correlation coefficient 0.999), and −4.99 for **3–7** (correlation coefficient 0.999). Thus the stabilizing effect of the cyclopropyl group is a linear function of the electron demand of the incipient carbonium ion over the range of reactivity studied. By changing the substituent in **3–5,** the ability of the cyclopropyl group to stabilize the carbonium ion center is varied from a factor of 505 in **2**-OMe to 10^6 in **2**-$(3,5\text{-}CF_3)_2$.

It is also noteworthy that ρ^+ for **3–5** is lower than the ρ^+ value of −3.7 for the benzhydryl system and is close to the ρ^+ value of −2.5 for the triarylmethyl system.[17] Thus it appears that the cyclopropyl group in **2** stabilizes the cation more than an additional phenyl group would. Similar observations that a cyclopropyl group stabilizes an adjacent cation more than a phenyl group have been reported in the literature.[18]

Participation vs. Conjugation, π and σ. The tool of increasing electron demand appears to provide a consistent probe for π electronic contributions.

Thus, it is concluded that there are π electronic contributions from the double bond in the *anti*-7-norbornenyl system[4] (**18**), but not in the 3-cyclopentenyl system[7] (**20**). The 2-norbornenyl



system appears to be borderline, revealing π electronic contributions only with major electronic demand.[5]

Table I. Rate Constants and Activation Parameters for the Solvolysis of the *p*-Nitrobenzoates in 80% Aqueous Acetone

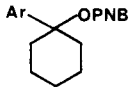
System	Aryl substituent	$k_1 \times 10^6$ s^{-1} T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3-4	*p*-CH_3O			65.3		
	p-H	100 (100)	7.11 (75)	9.51×10^{-3} [a]	26.7	−5.7
	p-CF_3	117 (150)	10.7 (125)	1.36×10^{-5} [a]	31.4	−2.8
	3,5-$(CF_3)_2$	122 (175)	10.9 (150)	1.43×10^{-7} [a]	35.8	2.8
3-5	*p*-CH_3O			33 000[b]		
	p-H	8.91 (0)		241	20.8	−5.5
	p-CF_3	83.8 (50)		3.88	22.9	−6.4
	3,5-$(CF_3)_2$	111 (75)	7.42 (50)	0.315[a]	23.6	−9.1
3-6	*p*-CH_3O			112 000[b]		
	p-H			2870[c]		
	p-CF_3			148		
	3,5-$(CF_3)_2$	344 (50)		21.6	20.6	−10.8
3-7	*p*-CH_3O	4070 (50)		233.5	21.3	−3.7
	p-H	234.4 (100)	15.7 (75)	0.018[a]	27.3	−2.3
	p-CF_3	280 (150)	25.0 (125)	2.76×10^{-5} [a]	31.8	−0.3

[a] Calculated from rates at higher temperatures. [b] The rate constant was calculated by extrapolation of the log k-σ^+ plot of the other derivatives. [c] Calculated by multiplying the rate constant for the benzoate by the factor 20.8.[16]

Table II. Comparison of Solvolysis Rates of *p*-Nitrobenzoates at 25 °C

Aryl substituent	System 3-4	3-5	3-6	3-7
p-CH_3O	1.0	505	1 700	3.6
p-H	1.0	25 300	314 000	1.9
p-CF_3	1.0	285 000	10 900 000	2.0
3,5-$(CF_3)_2$	1.0	1 210 000	83 000 000	

π contributions are also evident in the 2-cyclohexenyl system[8] (**22**).



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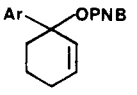

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ρ^+ −4.60 −2.52 $\Delta\rho^+$ = 2.08

It is clear that in the *anti*-7 system (**18**) we are dealing with π participation (**23**). In the 2-cyclohexenyl system (**22**) we are dealing with π conjugation (**24**). It should be noted that the

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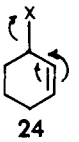

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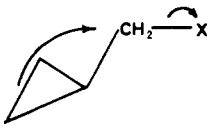
first involves π interaction with a homoallylic bond; the second, with an allylic bond.

For consistency, these distinctions should be carried over to electronic contributions from carbon-carbon single bonds to developing cationic centers.

Thus, the original proposal was that the 2,3-bonding pair of the cyclopropyl ring (C-C in the "homoallylic" position) provided σ participation (**25**). In this interpretation, one of the



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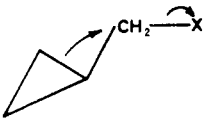

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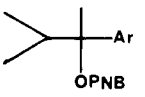
lobes of the p orbital of the developing cationic center is directed toward the center of the 2,3-bond, perpendicular to that bond,[19] in the same manner as the p orbital in **23** is directed to the π electrons of the double bond.

This picture was later modified to permit participation of the 1,2-bond with the p orbital (**26**).

Applying the tool of increasing electron demand reveals unambiguous major σ electronic contributions from the cyclopropane ring (**28**).



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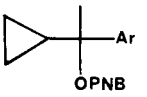

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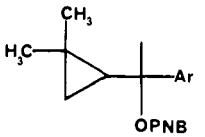
ρ^+ −4.76 −2.78 $\Delta\rho^+$ = 1.98

The introduction of methyl substituents increases these electronic contributions (**29**); the introduction of chlorine substituents greatly decreases them (**30**), even to a point less



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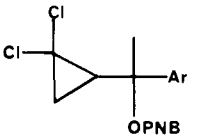

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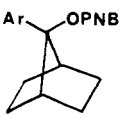
ρ^+ −2.06 −4.99

than isopropyl itself (**27**).

The question to be answered now is whether these σ electronic contributions from the cyclopropane ring are to be classified as σ participation or σ conjugation (hyperconjugation).[20] Fortunately, a comparison of the results with those realized earlier for the 3-nortricyclyl system[9] provides a reasonable answer.

The 3-nortricyclyl cation is geometrically incapable of engaging in σ participation.[21] Any electronic stabilization of the developing cationic center (**32**) must be σ conjugation.



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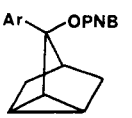

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ρ^+ −5.27 −3.27 $\Delta\rho^+$ = 2.0

The similarity in the $\Delta\rho^+$ values in the two systems argues for similar origins for the effects.[22] It is therefore concluded that cyclopropylcarbinyl is stabilized by σ conjugation.

This conclusion is consistent with all of the evidence that the

Table III. Preparation of Tertiary Alcohols

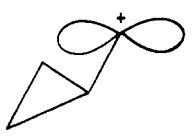
System	Aryl substituent	Yield, %	Mp or bp, °C	Molecular formula	Analyses
3-4	*p*-CH_3O[a]	89	94 (0.05 mm)	$C_{12}H_{18}O_2$	
	p-H[b]	92	62-63 (0.7 mm)	$C_{11}H_{16}O$	
	p-CF_3	88	62 (0.5 mm)	$C_{12}H_{15}F_3O$	C,H,F
	3,5-$(CF_3)_2$	83	58.3-59.2	$C_{13}H_{14}F_6O$	C,H,F
3-5	*p*-CH_3O[c]	87	103-103.8 (0.5 mm)	$C_{12}H_{16}O_2$	
	p-H[d]	91	68.6-69 (0.6 mm)	$C_{11}H_{14}O$	
	p-CF_3	90	73.9-74 (0.6 mm)	$C_{12}H_{13}F_3O$	C,H,F
	3,5-$(CF_3)_2$	88	66.0 (0.6 mm)	$C_{13}H_{12}F_6O$	C,H,F
3-6	*p*-H	75	68 (0.2 mm)	$C_{13}H_{18}O$	C,H
	p-CF_3	90	72-73 (0.3 mm)	$C_{14}H_{17}F_30$	C,H,F
	3,5-$(CF_3)_2$	60	68 (0.3 mm)	$C_{15}H_{16}F_6O$	C,H,F
3-7	*p*-CH_3O	87	142-143 (0.5 mm)	$C_{12}H_{14}Cl_2O_2$	C,H,Cl
	p-H	90	162-164 (38 mm)	$C_{11}H_{12}Cl_2O$	C,H,Cl
	p-CF_3	90	106 (0.5 mm)	$C_{12}H_{11}Cl_2F_3O$	C,H,Cl,F

[a] Lit. bp 107 °C (0.02 mm); G. S. Dutton, et al., *Can. J. Chem.*, **42**, 480 (1964). [b] Lit. bp 106-108 °C (20 mm); H. Christol, et al., *Bull. Soc. Chim. Fr.*, 2319 (1961). [c] Lit. bp 122-124 °C (0.7 mm); S. Sarel, E. Brever, Sh. Ertag, and R. Salamon, *Isr. J. Chem.*, **1**, 451 (1963). [d] Lit. bp 78-81 °C (0.3 mm); A. Maercker and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 742 (1966).

Table IV. Preparation of *p*-Nitrobenzoates

System	Aryl substituent	Yield, %	Mp, °C	Molecular formula	Analyses
3-4	*p*-CH_3O	87	90.4-91.0	$C_{19}H_{21}NO_5$	C,H,N
	p-H	91	76.5 dec	$C_{18}H_{17}NO_4$	C,H,N
	p-CF_3	88	115.8-116.1	$C_{19}H_{16}NF_3O_4$	C,H,N,F
	3,5-$(CF_3)_2$	85	71.3-72.4	$C_{20}H_{15}NF_6O$	C,H,N,F
3-5	*p*-H	89	75-76.2	$C_{18}H_{19}NO_4$	C,H,N
	p-CF_3	90	122.7-123.6	$C_{19}H_{18}NF_3O_4$	C,H,N,F
	3,5-$(CF_3)_2$	86	95.6-96.3	$C_{20}H_{17}NF_6O$	C,H,N,F
3-6	*p*-CF_3	58	108-109	$C_{21}H_{20}NF_3O_4$	C,H,N,F
	3,5-$(CF_3)_2$	45	94.5-95.5	$C_{22}H_{21}NF_6O$	C,H,N,F
3-7	*p*-CH_3O	65	130 dec	$C_{19}H_{17}NCl_2O_5$	C,H,N,Cl
	p-H	52	129	$C_{18}H_{15}NCl_2O_4$	C,H,N,Cl
	p-CF_3	70	91-92	$C_{19}H_{14}NCl_2F_3O_4$	C,H,N,Cl,F

cyclopropylcarbinyl cation is stabilized in the bisected conformation suitable for σ conjugation (**34**) and not in the parallel arrangement (**33**) required for σ participation.[23]



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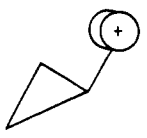

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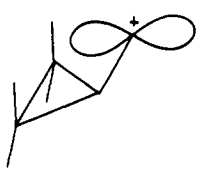
A question might be raised as to whether this conclusion holds for primary cyclopropylcarbinyl cations. After all, Olah has interpreted NMR spectra under stable ion conditions for the secondary cyclopropylmethylcarbinyl cation and the tertiary cyclopropyldimethylcarbinyl cation as involving the bisected structure, but the primary cyclopropylcarbinyl cation as involving a σ-bridged structure.[24]

However, a study of $J_{^{13}CH}$ has yielded results which do not appear to be consistent with the σ-bridged structure.[25] Moreover, the effect of methyl substituents on the rates of solvolysis of primary cyclopropylcarbinyl derivatives fails to support the unsymmetrical σ-bridged structure.[26] A reasonably good additivity was observed accompanying the introduction of one, two, three, or four methyl groups to the ring at C2 and C3. The authors concluded that electron supply from the cyclopropane ring must involve a symmetrical contribution, not compatible with a bicyclobutonium ion. Indeed in the tetramethylcyclopropylcarbinyl cation (**35**) σ participation appears to be blocked sterically, since the formation of a σ bridge would require a carbon atom to be bonded to five different carbon atoms. On the other hand, σ conjugation (**36**) offers no



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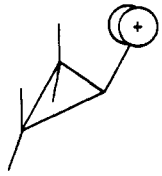

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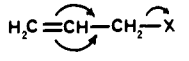
problem. We are presently investigating the tertiary tetramethylcyclopropylcarbinyl system by the application of the tool of increasing electron demand.[27]

It may be helpful to clarify the proposed difference between σ participation and σ conjugation. The enhanced rates of solvolysis of allylic derivatives are attributed to developing π conjugation, not to π participation (**37**). The enhancement in



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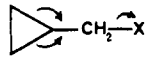

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rate in **38** is quite similar. Here the bent σ bonds supply electron density to the developing cationic center to facilitate the ionization. Clearly this is σ conjugation, not the σ participation represented by **25**.

It would appear that part of the difficulty in resolving the nonclassical ion problem may have its origin in the frequent failure to distinguish between σ participation and σ conjugation

(hyperconjugation). The latter effect was introduced in 1939 and was a generally accepted phenomenon[28] at the time σ participation was first proposed seriously to account for fast rates and rapid rearrangements.[29,30] It is hoped that clarification of this issue will contribute to a resolution of the nonclassical ion problem.[31]

We are applying the tool of increasing electron demand to the 2-norbornyl and other systems in an attempt to find unambiguous evidence for such σ participation postulated for so many years.[29,32,33]

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 137 or 700 spectrometer. NMR spectra were taken on a Varian T-60 spectrometer.

Cyclopropyl Methyl Ketone. Cyclopropyl methyl ketone (Columbia Organic Chemicals Co.) was dried over anhydrous calcium chloride and then distilled: bp 112 °C [lit.[34] bp 113 °C], n^{20}D 1.4245 [lit.[35] n^{20}D 1.4280].

3-Methyl-2-butanone. 3-Methyl-2-butanone (Eastman Organic Chemicals) was dried over anhydrous calcium chloride and then distilled: bp 94–95 °C [lit.[36] bp 92–95 °C], n^{20}D 1.3881 [lit.[36] n^{20}D 1.3878].

2,2-Dimethylpropane-1,3-ditosylate. This compound was prepared from the diol and *p*-toluenesulfonyl chloride in pyridine (94% yield), mp 120–122 °C [lit.[11] mp 121–122 °C].

2,2-Dimethylcyclopropanenitrile. The procedure described by Nelson et al. was followed. Thus from the ditosylate (206 g, 0.5 mol), potassium cyanide (97.6 g, 1.5 mol), and ethylene glycol (1 l.) was obtained the nitrile (**10**) (30.5 g, 67% yield), bp 154–156 °C [lit.[11] bp 154.5–155.5 °C], n^{20}D 1.4274 [lit.[11] n^{23}D 1.4261].

2,2-Dimethylcyclopropane-1-carboxylic Acid. The nitrile (6 g, 63 mmol) was hydrolyzed by refluxing with 30% potassium hydroxide solution (50 ml) for 48 h. The reaction mixture was acidified with hydrochloric acid and then saturated with sodium chloride. The acid was extracted with ether, the ether layer dried over anhydrous magnesium sulfate, and solvent evaporated. Distillation gave pure acid (**11**) (5.2 g, 82% yield), bp 199–200 °C (753 mm) [lit.[11] bp 198–201 °C (1 atm)], n^{20}D 1.4404 [lit.[11] n^{20}D 1.4405].

2,2-Dimethylcyclopropyl Methyl Ketone. The conversion of the acid (**11**) into the methyl ketone (**12**) was effected by treating with 2 mol of methyllithium in ether following the procedure of De Puy et al.[37] Thus starting from the acid (4.7 g, 41 mmol) and methyllithium (2.14 M, 38.3 ml, 41 mmol) was obtained the methyl ketone (**12**) (4.05 g, 88% yield), bp 132–134 °C (754 mm): ^{1}H NMR (CCl_4) δ 0.6–0.8 (q, 1 H, cyclopropyl), 1.0–1.26 (7 H, 2-methyl and cyclopropyl), 1.67–1.83 (q, 1 H, cyclopropyl), and 2.16 (3 H, s, methyl).

2,2-Dichloro-1-vinylcyclopropane (14) was prepared by following the method of Woodworth and Skell.[13] Thus from butadiene (35 g, 0.648 mol), potassium *tert*-butoxide (26.5 g, 0.242 mol) and chloroform (24.6 g, 0.206 mol) was obtained **14** (14 g, 50% yield).

1-(2′,2′-Dichlorocyclopropyl)-1-ethanol. Oxymercuration–demercuration of the olefin[12] gave the alcohol (**15**) in 85% yield, bp 96–97 °C (44 mm): ^{1}H NMR (CCl_4) δ 1.0–2.0 (m, 6 H, methyl and cyclopropyl), and 3.5 (br s, 2 H, OH and C*H*(OH)CH_3).

2,2-Dichlorocyclopropyl Methyl Ketone. The secondary alcohol (**15**) was oxidized using the convenient two-phase oxidation developed by Brown et al.[14] Thus from the alcohol (15.5 g, 0.1 mol), chromic acid solution (100 ml, 100% excess) and ether (40 ml) was obtained the ketone (**16**) (13.8 g, 90% yield), bp 78 °C (48 mm): ^{1}H NMR (CCl_4) δ 1.8–2.2 (m, 2 H, cyclopropyl), 2.35 (s, 3 H, methyl), and 2.6–2.9 (q, 1 H, cyclopropyl).

General Procedure for the Preparation of Tertiary Alcohols. The Grignard reagents of *p*-bromoanisole, bromobenzene, *p*-bromobenzotrifluoride, and 3,5-bis(trifluoromethyl)bromobenzene were prepared by the reaction of the respective bromides with magnesium in anhydrous ether. A solution of the ketone in ether was added to a stirred solution of the Grignard reagent under nitrogen at 0–5 °C. After hydrolysis of the reaction mixture with saturated ammonium chloride solution, the organic layer was separated and the aqueous layer extracted twice with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the solvent evaporated. The alcohols were purified by distillation or crystallization. Properties of the alcohols are listed in Table III.

Preparation of *p*-Nitrobenzoates. The *p*-nitrobenzoates of tertiary alcohols were prepared from the lithium alkoxide and *p*-nitrobenzoyl chloride as described by Brown and Peters.[9] Properties of these derivatives are tabulated in Table IV.

Kinetic Procedure. The procedure employed for determining the rate constants is described in the literature.[9,38]

References and Notes

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