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(15) Attempts to study methane elimination when hydridomethyl complexes cannot be isolated or observed (e.g., ref 7) suffer from an inherent difficulty: the methane may arise from direct electrophilic attack by acid or methylating agent upon coordinated methyl or hydride ligands, rather than by electrophilic attack upon the metal and formation of a hydridomethyl complex.

(16) The fact that CD_4 is not observed in the presence of Et_3P (vide infra) demonstrates that scrambling of labels among different molecules of **1** does not occur prior to the rate-determining step in the dinuclear elimination.

(17) Monitored by observing the disappearance of the IR band at 2063 cm^{-1}.

(18) Such facile carbonyl dissociation would have been improbable on fundamental grounds. Exchange rate data[19] on $Os_3(CO)_{12}$, extrapolated to 126 °C and corrected statistically agree within a factor of 4 with the rate observed[1] for the thermolysis of $Os(CO)_4H_2$ at that temperature. As the trans effect of hydride is thus negligible in $Os(CO)_4H_2$, there is no plausible reason carbonyl dissociation from $Os(CO)_4(H)CH_3$ should be rapid enough to be rate-determining in its comparatively rapid thermal decomposition.

(19) G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Atti Accad. Sci. Torino*, **101**, 855 (1967).

(20) In work involving impure samples of **1a**, both substitution and acceleration were suggested.[21] Substitution on **1a** is probably possible by the sort of free-radical chain mechanism recently observed by Byers and Brown[22] in rhenium systems; with the vacuum-line techniques employed in the present work, and complete exclusion of oxygen, it is reasonable that such substitution does not occur.

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(24) The reactive intermediate **4** (vide infra) shows little selectivity between Et_3P and **1**. Even in the presence of 21 equiv of Et_3P, some of the **1** still reacts according to eq 1, as demonstrated by the observation of small amounts of **2** in kinetic runs and CD_4 in crossover experiments. It is thus reasonable that, when the thermolysis of **1** is carried out under ^{13}CO as described, dissolved CO is wholly unable to compete for **4** and only reaction 1—with no label incorporation—is observed.

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(29) J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, manuscript in preparation.

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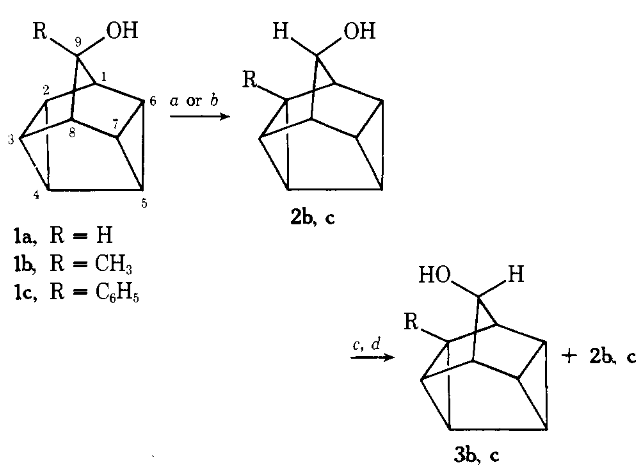
Remote and Proximate Substituent Effects on Trishomocyclopropenium Ion Formation in the Solvolysis of Methyl and Phenyl Substituted 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-Nitrobenzoates

Sir:

The significance of substituent effects upon the rate of formation of nonclassical carbonium ions in solvolysis reactions has been subject to considerable debate in spite of the large amount of kinetic data which has been obtained for this purpose.[1-5] Major uncertainties arise in many cases from the incursion of steric, conformational, and other extraneous effects which may accompany substituent changes and the troublesome possibility that the structure of the carbonium ion intermediate may be seriously altered as well. We wish to report the results of an investigation on the solvolysis of 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-nitrobenzoates (**1**-OPNB and **2**-OPNB) bearing methyl and phenyl substituents at the 2 and 9 positions. Since the formation of nonclassical trishomocyclopropenium ions from compounds of this type is well established both under solvolytic[6a] and stable ion[6b] conditions and, in the case of the unsubstituted parent (**1a**-OPNB), is attended by a kinetic enhancement of 10^{10-12} from cyclopropane participation in the solvolysis,[6a] this seemed to be a propitious structural environment in which to evaluate remote and proximate substituent effects on trishomocyclopropenium ion formation.[7,8]



1a, R = H
1b, R = CH_3
1c, R = C_6H_5

2b, c

3b, c

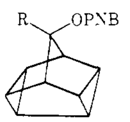
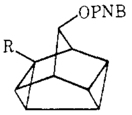
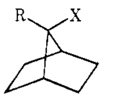
[a] **1b** → **2b**:HCO_2H, 10 °C, 13 h; OH^- (~30%). [b] **1c** → **2c**:0.1 M $HClO_4$, 80% aqueous dioxane, reflux, 8 h (73%). [c] $CrO_3 \cdot C_5H_5N$, CH_2Cl_2. [d] $LiAlH_4$, ether.

The secondary pentacyclic alcohols **2b** and **2c** were secured by means of acid-catalyzed homocyclopropylcarbinyl rearrangement of the previously reported tertiary isomers, **1b** and **1c**, respectively.[6b] The structures (**2b** and **2c**) assigned to the rearrangement products are supported by appropriate NMR spectral data, including in particular the appearance of a quartet for the carbinyl protons at C-9 (vicinal coupling to H_1 and H_8 and long range coupling to H_5)[6a] and the observation that kinetically controlled solvolyses of the corresponding *p*-nitrobenzoates regenerate the original tertiary alcohols as the major products (see below). Independent evidence which affirms the anti stereochemical relationship between the substituent and the hydroxyl group derives from the finding that lithium aluminum hydride reduction of the corresponding ketones affords epimeric alcohols as major products (**3b**:**2b** = 2:1; **3c**:**2c** = 3.4:1).

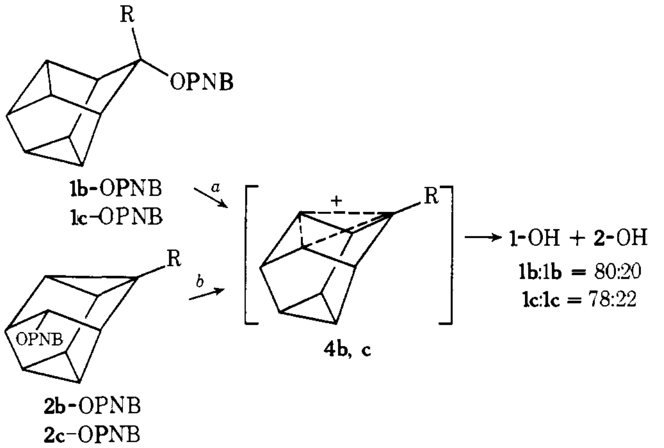
Solvolysis of either of the two methyl substituted *p*-nitrobenzoates **1b**-OPNB (mp 142–143.5 °C) and **2b**-OPNB (mp 115–116.5 °C) in 65% aqueous acetone at 100 °C furnishes the same 80:20 mixture of tertiary and secondary alcohols (70–75% isolated yield). In a similar manner, solvolysis of the tertiary phenyl substituted *p*-nitrobenzoate **1c**-OPNB at 80 °C produced a 94:6 mixture of tertiary and secondary alcohols. Since it was found that this product ratio varied with temperature, direct comparison of the product ratios for the solvolysis of the tertiary and secondary phenyl substituted *p*-nitrobenzoates, **1c**-OPNB (mp 162.5–164 °C) and **2c**-OPNB (mp 113–115 °C), was done at 125 °C. At this temperature, both isomers produced a 78:22 mixture of tertiary and secondary phenyl substituted alcohols. That these isomer ratios represent the kinetic product distributions was verified by GLC and/or LC analyses during the course of the solvolyses.[9]

The formation of the same product ratios from either tertiary or secondary *p*-nitrobenzoates in both the methyl and phenyl substituted pentacycles indicates common trishomocyclopropenium ions **4b** and **4c** as intermediates. Since these ions possess two enantiotopic secondary positions, the tertiary:secondary capture ratios for **4b** and **4c** are 8:1 at 100 °C and 7:1 at 125 °C, respectively.

Table I. First-Order Rate Constants and Relative Rates for the Solvolysis of Methyl and Phenyl Substituted 9-Pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates and Related 7-Norbornyl Compounds

	Compd	R	*t* (°C)	*k* (s^{-1})[a]	$k_{rel}^{25°}$ (R/H)	$k_{rel}^{25°}$ (1/5)
	1a-OPNB	H	25	6.62×10^{-10} [b]	(1.0)	10^{10-12} [c]
	1b-OPNB	CH_3	100	5.87×10^{-4}		
			80	7.78×10^{-5}		
			25	7.4×10^{-8} [b]	112	$10^{7.5}$
	1c-OPNB	C_6H_5	80	5.73×10^{-4}		
			60	7.35×10^{-5}		
			25	1.04×10^{-6} [b]	1600	$10^{3.6}$
	2b-OPNB	CH_3	110	7.59×10^{-5}		
			100	2.94×10^{-5}		
			90	1.05×10^{-5}		
			25	3.15×10^{-9}	4.8	
	2c-OPNB	C_6H_5	145	1.24×10^{-4}		
			125	1.82×10^{-5}		
			25	2.88×10^{-11} [b]	0.04	
	5a-OTs	H	25	2.1×10^{-14} [d]	(1.0)	
	5b-OTs	CH_3	25	2.81×10^{-6} [d]	1.3×10^{8} [d]	
	5b-OPNB	CH_3	25	2.3×10^{-15} [e]		
	5c-OTs	C_6H_5	25	0.64[f]	$3. \times 10^{13}$	
	5c-OPNB	C_6H_5	25	2.8×10^{-10} [g]		

[a] Rates of *p*-nitrobenzoates in 65% aqueous acetone. Rates of tosylates in acetic acid. Errors in rate constants ranged from 0.8 to 3.2%. [b] Extrapolated from data at higher temperatures. [c] Reference 6a. [d] Reference 3c. [e] Estimated from solvolysis rate of **5b**-Cl and relative solvolysis rate of 7-methyl-*anti*-7-norbornenyl chloride and *p*-nitrobenzoate given in ref 3d. A *Y* value of +0.45 for 65% aqueous acetone was used. [f] Estimated from solvolysis rate of **5c**-OPNB using conversion factor of 6.3×10^9: see ref 3b and 3c. [g] Estimated from rate in 70% aqueous dioxane given in ref 3b and a *Y* value of +0.45 for 65% aqueous acetone.



[a] 65% aqueous acetone at 100 °C (1b-OPNB) or 125 °C (1c-OPNB). [b] 65% aqueous acetone at 100 °C (2b-OPNB) or 125 °C (2c-OPNB).

The rates of solvolysis of the substituted *p*-nitrobenzoates in 65% aqueous acetone at various temperatures and appropriate reference data for 7-norbornyl compounds are shown in Table I. The data in the last column give the solvolysis rates of the 9-methyl and 9-phenyl pentacyclic esters (**1b**-OPNB and **1c**-OPNB) relative to those estimated for 7-methyl- and 7-phenyl-7-norbornyl *p*-nitrobenzoates (**5b**-OPNB and **5c**-OPNB), respectively. Although the rate enhancement is reduced from the 10^{10-12} level of the unsubstituted compound (**1a**-OPNB)[6a] to $10^{7.5}$ by methyl substitution and $10^{3.6}$ by phenyl substitution, it is nevertheless apparent that cyclopropane participation dominates over unassisted solvolysis by large margins in both cases.

The methyl/hydrogen and phenyl/hydrogen rate ratios for **1**-OPNB, **2**-OPNB, and 7-norbornyl tosylates (**5**-OTs) are presented in the preceding column. These data reveal a sharp reduction in the methyl/hydrogen ($1.3 \times 10^8 \rightarrow 10^2$) and phenyl/hydrogen ($3 \times 10^{13} \rightarrow 10^{3.6}$) rate ratios in **1**-OPNB as compared to **5**-OTs. The low methyl/hydrogen (4.8) and inverse phenyl/hydrogen (0.04) rate ratios for remote substitution on the participating cyclopropane ring bond in the solvolysis of **2**-OPNB are strikingly similar to those previously reported for acetolysis of 1-methyl- and 1,5-diphenyl-*cis*-3-bicyclo[3.1.0]hexyl tosylates ($CH_3/H = 5.2$, $2 \times C_6H_5/H = 0.21$).[5,10,11] Although the interpretation of the kinetic data from these bicyclic tosylates is complicated by conformational effects and various side reactions,[5,10] our results nevertheless fully support the earlier contention[10] that the small remote substituent effects are not necessarily inconsistent with predominant σ-participation. The similarity of the proximate and remote methyl/hydrogen rate ratios for cyclopropane participation to those for double bond participation in the solvolysis of 7-methyl ($CH_3/H = 44$,[3a,c] 400[3d]) and 2-methyl-7-*anti*-norbornenyl *p*-nitrobenzoates ($CH_3/H = 11$)[3a,c] bespeaks a close relationship between the trishomo- and bishomocyclopropenium ion intermediates.

The marked suppression in the methyl/hydrogen and phenyl/hydrogen rate ratios for the 9-substituted pentacyclic *p*-nitrobenzoates is attributable in part to delocalization of positive charge onto positions 2 and 3 in the incipient trishomocyclopropenium ions. Since **1**-OPNB and **2**-OPNB apparently solvolyze via common trishomocyclopropenium ions (**4**), we conclude that the kinetic substituent effects upon the formation of **4**, lie between 0.9 to 2.8 kcal/mol for methyl substitution and −1.9 to 4.4 kcal/mol for phenyl substitution. These kinetic substituent effects are substantially less than would have been expected on the basis of relative pk_{R^+} values for alkyl and phenyl substituted cyclopropenium ions.[12] Although this would seem to accord with the view that σ-delocalized ions in general exhibit lower substituent effects than π-delocalized ions,[2a,13] it is appropriate to note that trishomocyclopropenium ions such as **4** (and bishomocyclopropenium ions such as those from 7-*anti*-norbornenyl derivatives)[3] differ from other types of σ-bridged ions which have been proposed in possessing a cyclopropane ring in each of its three resonance contributors (two of three in the case of bishomocyclopropenium ions). Thus, the special delocalizing characteristics of the three-membered ring may well have a significant bearing upon the magnitude of substituent effects.[14,15]

A number of factors which might contribute to low substituent effects upon nonclassical carbonium ions in general[2a,4a,b,13] and trishomocyclopropenium ions in particular[4a,10,15] have been suggested in the literature. These include the electron-withdrawing inductive effect of the phenyl group,[2a,4a,b,10] the state of hybridization of the electron-deficient orbitals,[2a,4a,b,10] the combination of large HOMO–LUMO separations and low p coefficients for the unoccupied MO's,[13] and further delocalization of positive charge in **4a** to other positions.[15]

Acknowledgments. We wish to thank Professor H. C. Brown for exchanges of information during the course of this investigation and the A. P. Sloan Foundation and the National Institutes of Health for financial support.

References and Notes

(1) Some appropriate review and/or key leading references for substituent effects on several major types of carbonium ions are given in ref 2–5.

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(7) P. G. Gassman and A. F. Fentiman, Jr., have reported that 8-anisyl-8-*endo,anti*-tricyclo[3.2.1.$0^{2,4}$]octyl *p*-nitrobenzoate undergoes solvolysis with exclusive cyclopropane participation: *J. Am. Chem. Soc.*, **92,** 2551 (1970).

(8) A parallel study upon the solvolysis of a series of 9-aryl pentacyclic *p*-nitrobenzoates (**1**-OPNB) is reported by H. C. Brown and M. Ravindranathan, *J. Am. Chem. Soc.*, following paper in this issue.

(9) Prolonged exposure to the solvolysis medium leads to increasing proportions of the more stable secondary isomers (**1b**-OH:**2b**-OH = 43:57 after 70–74 h at 100 °C; **1c**-OH:**2c**-OH $\leq$ 3:97 after 49 h at 125 °C).

(10) (a) S. Winstein, E. C. Friederich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **8 Part II,** 621 (1966); (b) Y. Lin, Ph.D. Thesis, University of California-Los Angeles, 1967; *Diss. Abstr.*, **28,** 3651-B (1968).

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(13) C. F. Wilcox, Jr., L. M. Loew, R. G. Jesaitis, S. Belin, and J. N. C. Hsu, *J. Am. Chem. Soc.*, **96,** 4061 (1974).

(14) For example, cyclopropyl groups are considered to be relatively poor at transmitting substituent effects: C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95,** 8192 (1973).

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Solvolysis of 9-Aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates. Unambiguous Evidence for the Presence of Carbon Participation by the Application of the Tool of Increasing Electron Demand

Sir:

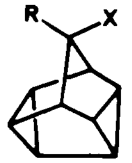
The rates of solvolysis of 9-aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoates with representative substituents in the aryl ring reveal major $\pi\sigma$-participation with increasing electron demand at the cationic center. Moreover, the very low methyl/hydrogen (127) and phenyl/methyl (14) ratios realized in this system are indicative of a transition state stabilized by carbon participation resulting in little demand by the developing carbonium ion center for further stabilization by the substitutents. Thus these results establish that the Coates' cation is formed with $\pi\sigma$-participation supporting his conclusion that the intermediate is a carbon-bridged (nonclassical) cation.

Table I. Solvolysis of 9-Aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone

Substituent in aryl[a]	10^6K_1, s^{-1} T$_1$	T$_2$	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-CH_3O[b]	97.6 (50)		5.05	22.1	−8.7
p-H	486 (100)	45.7 (75)	0.123[e]	23.8	−10.2
p-CF_3[c]	516 (125)	57.3 (100)	8.59×10^{-3}[e]	25.3	−10.3
3,5-$(CF_3)_2$[d]	399 (150)	56.5 (125)	8.57×10^{-4}[e]	25.6	−14.2
9-CH_3	834 (125)	84.2 (100)	8.62×10^{-3}[e]	26.5	−6.6
9-H	94.9 (150)	11.4 (125)	6.79×10^{-5}[e]	27.8	−11.9

[a] All new compounds gave satisfactory spectral and microanalytical data. [b] Mp 145.5–146 °C. [c] Mp 146.5–147 °C. [d] Mp 164–164.5 °C. [e] Calculated from data at higher temperatures.

The tool of increasing electron demand has unambiguously proven the presence or absence of π-, $\pi\sigma$-, and σ-participation in representative systems where such participation could be significant in solvolytic behavior.[1] The solvolysis of the parent 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoate (**1**, R = H) proceeds 10^{10}–10^{12} times faster than the related 7-norbornyl derivative (**2**).[2,3] This major rate enhancement was attributed to participation by the remote cyclopropane bond leading to the formation of a trishomocyclopropenyl cation (**3**).[2] Moreover, the solvolysis regenerates the parent alcohol in which the degenerate rearrangement has been demonstrated.[2,4] It was of major interest to test whether the tool of increasing electron demand could establish the presence of $\pi\sigma$-participation in such a system.



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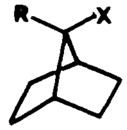

2

3

Accordingly, 9-aryl-9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl *p*-nitrobenzoates containing representative substituents in the aryl ring (**1**, R = X-C_6H_4–: X = *p*-CH_3O, *p*-H, *p*-CF_3, 3,5-$(CF_3)_2$) were synthesized by the addition of the appropriate Grignard reagents to the ketone (**4**).[5] The tertiary alcohols (**5**) were converted to the *p*-nitrobenzoates by treating their lithium salts with *p*-nitrobenzoyl chloride. The rates of solvolysis of the esters were determined in 80% aqueous acetone by the standard titrimetric procedure.[6] For comparative purposes, the rates of solvolysis of the secondary ester (**1**, R = H) and the tertiary methyl ester (**1**, R = CH_3) were also measured in this solvent. The pertinent rate data are summarized in Table I.

The aryl derivatives (**6**) reveal an excellent $\rho^+\sigma^+$ relationship.[7] The system yields a ρ^+ of −2.05 (correlation coefficient 0.999). This is comparable with the ρ^+ observed in the sol-