

Nitromethylation of Aromatics with Nitromethane–Manganese(III) Acetate¹

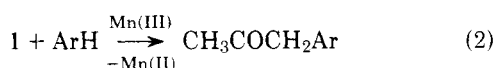
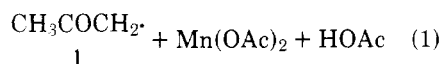
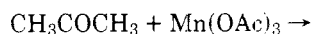
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Manganese(III) acetate was found to effect aromatic substitution by a nitromethyl group when reacted with an aromatic and nitromethane in acetic acid. Based on similarities to previously studied manganese(III) acetate systems, a mechanism involving the generation of and substitution by nitromethyl radicals is proposed. The partial rate factors, ρ value (vs. σ^+) of -1.1 , and the failure to substitute on nitrobenzene suggest that the nitromethyl radical exhibits appreciable electrophilic character. This reaction, which proceeds in a clean, reasonably high-yield manner, might well provide an alternate route to synthesizing certain aryl nitromethanes, which are currently made through multistep, side-chain substitutions involving α -halo- or α -cyanotoluenes.

Though metal salts have been used extensively to aid in aromatic substitutions by oxy radicals,²⁻⁴ there are only a few cases of metal salt promoted homolytic aromatic alkylations. For example, the interaction of manganese(III) acetate with toluene and acetic acid at reflux has been shown to produce carboxymethyl radicals which react with the aromatic by side-chain hydrogen abstraction or ring addition leading subsequently to benzyl acetate and methylphenylacetic acids, respectively.⁵ Further reaction of the latter in the system generates a xylyl radical which is converted to isomeric xylyl acetates. The reaction of toluene or benzene with acetone in refluxing acetic acid containing manganese(III) acetate was recently reported to lead to aromatic substitution by an α -oxyalkyl radical (1, eq 1 and 2).⁶



In view of our interest in homolytic substitutions promoted by metal salts,^{2,3} we set out to see if manganese(III) acetate could be utilized to generate and substitute other types of radicals onto aromatics. Specifically, we studied the interaction of nitroalkanes and aromatics with manganese(III) acetate in the hope of producing aryl nitroalkanes by way of homolytic aromatic substitution involving nitroalkyl radicals.

Results and Discussion

Manganese(III) acetate⁷ was allowed to react with toluene in refluxing glacial acetic acid according to the method described by Heiba and Dessau.⁵ After workup, product analysis indicated that benzyl acetate (15%), methylbenzyl acetate (40%), and tolylacetic acid (10%) were formed as reported earlier.⁵

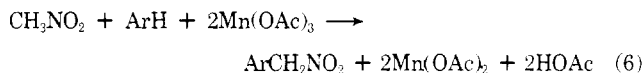
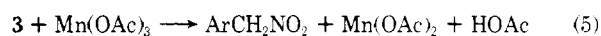
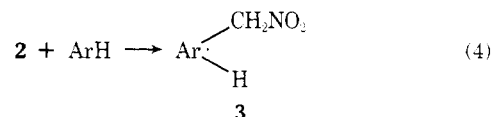
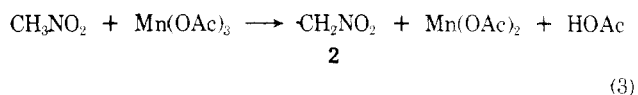
Inclusion of nitromethane in the above system led to striking results. Instead of observing products due to carboxymethyl radicals, the only aromatic products formed were nitromethylated toluenes (isomeric α -nitroxylenes). Various ratios of nitromethane, toluene, and acetic acid, all present in 7–70 molar excess to the manganese(III) limiting reagent, caused minor fluctuations (41–61%) in substitution product yield. However, equal volumes of toluene, nitromethane, and glacial acetic acid seemed to give the best substitution yields for this system, and these amounts (25 mL each of aromatic, nitromethane, and acetic acid and 10 mmol of manganese(III) acetate) were adopted as our standard procedure.

Other aromatics were reacted with the nitromethane–manganese(III) acetate system in the same manner, though

different reflux conditions pertained in each case (Table I). As with toluene, the only aromatic products observed were $-\text{CH}_2\text{NO}_2$ adducts in moderate to good yields. Better yields were obtained with the more electron-rich aromatics (e.g., anisole, or toluene); on the other hand, no substitution was noted with nitrobenzene. Removal of salt by washing and the evaporation of excess solvent and reactants yielded the pure aryl nitromethane directly (Table I, isolated yield).

Table I reveals that the higher the reflux temperature, the shorter the reaction time (e.g., the nitrobenzene case). The reaction time is the same for the anisole and chlorobenzene cases which reflux at the same temperature despite the wide variance in aromatic reactivity. This suggested that the rate-determining step does not involve the aromatic, but rather the manganese(III) salt and nitromethane common to all the reactions.

Based on analogy to previously studied manganese(III) acetate systems,^{5,6} a free radical mechanism is proposed for aromatic nitromethylation (eq 3–5). Nitromethyl radicals, **2**, are generated by the oxidation of nitromethane by manganese(III) acetate (eq 3) and substituted onto the aromatic ring to give a cyclohexadienyl radical, **3** (eq 4). This in turn is oxidized by another manganese(III) acetate to give $-\text{CH}_2\text{NO}_2$ adducts (eq 5). The overall stoichiometry is shown in eq 6.



Previously, Heiba⁵ had demonstrated that small amounts of cupric acetate inhibited the carboxymethylation process (eq 4) and attributed this to the efficient oxidation of the carbon radical by cupric⁸ preventing its attack on the aromatic. Introduction of cupric acetate to our system had no effect on the nitromethylation process. We attribute this to the higher expected ionization potential of the nitromethyl radical which makes it resistant to the usual cupric-facilitated oxidation.⁹

To get a better idea of the influence of temperature on this substitution process, the nitromethylation of anisole was studied at different temperatures (Table II). Though the reaction time varied as expected, not much difference was noted in the yields, with the exception of the slightly lower result at

Table I. Nitromethylation of Aromatics with Nitromethane^d-Manganese(III) Acetate^e at Reflux^a

Aromatic	Registry no.	Temp, °C	Time, ^b min	% ArCH ₂ NO ₂ ^c	
				By GC	Isolated
Benzene	71-43-2	87	110	46	31
Toluene	108-88-3	97	40	78	66
Anisole	100-66-3	106	30	72	62
Chlorobenzene	108-70-7	107	30	27	
Nitrobenzene	98-95-3	112	25		

^a Equal volumes (25 mL) of aromatic, nitromethane, and acetic acid and manganese(III) acetate (10 mmol) were refluxed under a nitrogen gas atmosphere. ^b Time at reflux until the brown manganese(III) color changed to light yellow with white manganese(II) acetate precipitate. ^c Yield is based on the stoichiometry of 2 mol of manganese(III) acetate/mol of product formed (eq 6). ^d Registry no.: 75-52-5. ^e Registry no.: 993-02-2.

Table II. Effect of Temperature on Anisole-Nitromethane-Manganic Acetate Reaction

Temp, °C	Time, min	Yield, %
69	1380	55
83	140	77
93	75	67
106	30	72

Table III. Nitromethylation of Aromatics at 83 °C

Aromatic	Yield	Isomer distribution		
		ortho	meta	para
Benzene	78			
Toluene	77	52	27	21
Anisole	77	71	5	24
Chlorobenzene	20	52		48 ^a

^a The meta and para isomer could not be separated.

69 °C. The optimum yield was obtained at 83 °C, the temperature which was chosen to more carefully study the nitromethylation product distribution.

Yields and isomer distributions for aromatics under these conditions are listed (Table III) and, except in the chlorobenzene case, were improved at this temperature. The reaction time was 140 min for all reactions. The isomer distributions were obtained by a combination of NMR and GC comparative analyses of the product mixtures to those of authentic isomers synthesized by alternate routes (see Experimental Section).

The isomer distribution resulting from attack of the nitromethyl species onto toluene resembles that observed from toluene methylations (*o/m/p* = 56/27/17¹⁰ or 52/32/15¹¹). However, with anisole, which is more susceptible to the polar nature of the substituting entity, the pattern of nitromethylation is actually more similar to that found from substitution of anisole by a carboxymethyl radical (*o/m/p* = 78/5/17)⁵ than by a methyl radical (*o/m/p* = 74/15/11).¹⁰

Competition reactions between pairs of aromatics, both present in large molar excess, were carried out with the nitromethane-manganese(III) acetate system (Table IV). The relative reactivities so observed were in the usual order observed for electrophilic substitutions (anisole > toluene > benzene > chlorobenzene). A good check for the apparent validity of the relative rates was the excellent agreement between $K_{C_6H_5OCH_3}/K_{C_6H_6}$ obtained directly and obtained as the product of $(K_{C_6H_5OCH_3}/K_{C_6H_5CH_3})(K_{C_6H_5CH_3}/K_{C_6H_6}) = 14.80$.

Partial rate factors (Table V) were determined using the

Table IV. Nitromethylation Competition Reactions^a

Molar Ratio C ₆ H ₅ X/C ₆ H ₅ Y	-X	-Y	Molar ratio ^b	Rel rate
			XC ₆ H ₄ CH ₂ NO ₂ / YC ₆ H ₄ CH ₂ NO ₂	K _{C₆H₅X} / K _{C₆H₅Y}
0.84	-CH ₃	-H	3.65	4.34
0.27	-OCH ₃	-H	4.00	14.84
0.88	-Cl	-H	0.33	0.37
0.98	-OCH ₃	-CH ₃	3.34	3.41

^a Total aromatics:manganic acetate:nitromethane = 20:1:40.

^b Average of at least duplicate reactions in good agreement.

Table V. Partial Rate Factors for Nitromethylation

Partial rate factor ^a	σ ⁺ ^b
$P_f^{-CH_3} = 5.47$	-0.31
$M_f^{-CH_3} = 3.52$	-0.07
$P_f^{-OCH_3} = 21.37$	-0.78
$M_f^{-OCH_3} = 2.23$	+0.12

^a P_f is for para isomer, M_f for meta isomer. ^b See ref 12.

Table VI. Comparison of ρ Values for Alkyl Radical-Arene Reactions

Radical	π	Method, reference	
		Arene substit	Hydrogen abstract. from subst toluene
C ₆ H ₁₁	1.1	14	
<i>i</i> -C ₃ H ₇	0.9		15
3- <i>n</i> -C ₇ H ₁₅	0.7		16
<i>n</i> -C ₁₁ H ₂₃	0.5		17, 18
CH ₃	0.1, -0.2	11	19
CH ₂ CO ₂ H	-0.6	5	
CH ₂ NO ₂	-1.1	this study	
CCl ₃	-1.5		20
C ₆ H ₅ CO ₂	-1.6	3	
<i>p</i> -O ₂ NC ₆ H ₄ C- O ₂	-2.5	3	

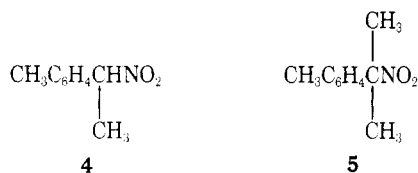
relative rates and isomer distributions for toluene and anisole. Failure to separate the *m*- and *p*-chloro- α -nitrotoluenes prevented us from calculating these partial rate factors. A plot of the log of the partial rate factor vs. σ^+ values¹² gave a good straight line from which a ρ value of -1.08 was obtained (correlation coefficient = 0.994; least-squares treatment). A better fit was observed using σ^+ substituent values rather than σ values, a situation noted previously for more electrophilic radicals.^{3,13} The negative ρ value suggested appreciable positive charge buildup in the transition state and indicates that the nitromethyl-substituting entry possesses a good deal of electrophilic character.

The ρ value for nitromethylation is compared to those obtained for other radical-aromatic processes either by way of radical substitution onto arenes or side-chain hydrogen abstraction from substituted toluenes (Table VI). Table entries are mostly limited to radicals derived from carbons of sp³ hybridization. Most unsubstituted alkyl radicals, with the exception of methyl, exhibit nucleophilic tendencies. However, those substituted with electron-withdrawing substituents take on electrophilic properties. As anticipated from common substituent effects, nitromethyl is more electrophilic than carboxymethyl, yet less so than trichloromethyl (Table VI). Most oxy radicals, for comparison, are still more electrophilic in their reactivity with arenes (Table VI).

It is interesting to note that the nitromethyl radical preferentially attacks the aromatic ring of toluene rather than abstracting an α -carbon hydrogen. No products indicative of side-chain abstraction were noted throughout this study. Such

behavior is consistent with an electrophilic radical species.²

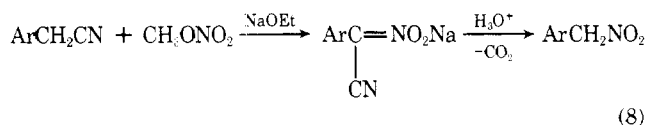
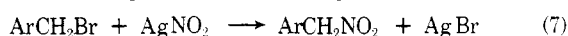
In order to determine the scope of this reaction, nitroalkylations of toluene were attempted with nitroethane and 2-nitropropane. In the former case, small amounts of the expected nitroethyl adducts 4 were obtained; however, the expected product 5 was not found in the 2-nitropropane reaction.



These findings suggest that the aci form of the nitroalkane is the species actually undergoing oxidation to produce the radical. Tautomerization is much more rapid for nitromethane than for the other two nitroalkanes.²¹

Other compounds possessing labile α -carbon hydrogens (acetonitrile, ethyl acetate, and malononitrile) were also reacted with manganese(III) acetate and toluene, but in these cases no substitution product was observed.

Previous substitutions by α -substituted radicals^{5,6} gave rather low yields due to competing side reactions. The reasonable yields, absence of side products, and ease of workup suggest possible synthetic utility for the nitromethylation reaction. Examination of the literature indicates two general synthetic methods for making aryl nitromethanes. One involves the reaction of silver nitrite with the corresponding benzyl bromide (eq 7).²² The other (eq 8) utilizes the action



of freshly prepared methyl nitrate on the appropriate aryl nitrile, followed by a rather lengthy workup procedure.²³ In both cases, the starting material is already an α -substituted arene, whereas in our case simple, commonly available aromatics are utilized. One drawback with the nitromethylation reaction is the occurrence of isomeric product mixtures with many simple aromatics (Table III). However, with benzene and certain other para-disubstituted aromatics from which only one substitution product is possible, this method looks promising.²⁴

Experimental Section

The aromatics and nitroalkanes were shown to be of greater than 99% purity by GC and were used directly. All inorganic reagents and aralkyl bromides and cyanides were analyzed commercial products and used as supplied. Many of the expected products of nitromethylation were synthesized by alternate literature methods. Thus, α -nitrotoluene (70% GC purity), α -nitro-*p*-xylene (50% GC purity), and α -nitro-*m*-xylene (60% GC purity) were prepared from the corresponding α -bromo compound by the method of Kornblum et al.²² α -Nitro-*m*-chlorotoluene, α -nitro-*p*-chlorotoluene, α -nitro-*o*-methoxytoluene, and α -nitro-*p*-methoxytoluene were synthesized from the corresponding benzyl cyanide, methyl nitrate, and sodium ethoxide.²³ Manganese(III) acetate was prepared according to a literature procedure⁷ and found to be 97% pure by iodometric titration.

Mass spectral analyses were carried out on a Finnegan Model 3000 GC peak identifier with a quadrupole mass filter. Mass spectra were obtained at 70 eV of the organic products from the ethereal extracts of reaction mixtures eluted from a 6.0 ft \times 0.125 in. stainless-steel, 10% SE-30/Chrom-W column.

Infrared spectra were recorded on Perkin-Elmer Models 700 and 710B infrared spectrophotometers, while NMR spectra were run on a Varian EM-300X NMR spectrophotometer.

GC analyses were made on a Hewlett-Packard Model 5830A gas chromatograph or a Varian Model 1400 equipped with hydrogen flame-ionization detectors. Products were determined on the following

columns: 1.67 ft \times 0.125-in. stainless-steel UCW-982/Chrom-W, 6.0 ft \times 0.125 in. stainless-steel OV-225/Chrom-W, and 6.0 ft \times 0.125 in. glass 10% SP 1000/Chrom-W.

Reaction of Nitromethane-Manganese(III) Acetate with Aromatics. General Procedure. Manganese(III) acetate (0.01 mol) was dissolved in glacial acetic acid (25 mL) at 70 $^\circ\text{C}$, and an excess amount of aromatic (25 mL) and nitromethane (25 mL) was added through an addition funnel. The mixture was then refluxed under nitrogen atmosphere with continuous magnetic stirring until the brown color changed to a light yellow (a white manganese(II) acetate precipitate formed continuously during the reaction). For quantitative GC determinations, an internal standard, *p*-nitrotoluene (2 mmol), was added to the cooled reaction mixture. Workup involved washing the reaction mixture with water (2 \times 50 mL) (the white precipitate was dissolved by water) and drying the organic portion over anhydrous sodium sulfate. After stripping off the solvent on a rotary evaporator, the residue was then analyzed by GC, GC-MS, and in some cases IR and NMR.

For reactions performed at temperatures other than reflux, the reactants were heated in a jacketed vessel containing specific refluxing solvents (dichloroethane, 83 $^\circ\text{C}$; hexane, 69 $^\circ\text{C}$; and methyl isopropyl ketone, 93 $^\circ\text{C}$), and allowing for continuous stirring. The same general procedure was followed using either nitroethane or 2-nitropropane instead of nitromethane. Workup and analysis was done as before.

For copper salt effects, the reaction was carried out under the same conditions but in the presence of a small amount (\sim 0.1 g) of cupric acetate. For the concentration-effect studies, the reactions are carried out under the same conditions, except for changes in the composition of the solutions.

A number of experimental variations were performed in an effort to regenerate manganese(III) from that salt which was reduced during the course of the reaction. In one case, oxygen was continually bubbled through the refluxing reaction mixture (with benzene as the aromatic). Upon workup only a small amount of α -nitrotoluene was detected by GC. Controls in which manganese(II) acetate in refluxing acetic acid was treated with a stream of oxygen or ozone in oxygen gave rise to salt mixtures which contained manganese(IV) dioxide (iodometry and liberation of chlorine from aqueous HCl²⁵) in small and large amounts, respectively. In another reaction, portions of KMnO₄ (1.4 molar equiv to the original manganese salt) were added to the reaction mixtures after the dark color of the manganese(III) species lightened up. This process was repeated with additional increments of KMnO₄ (six additions overall). The usual workup led to a complex product mixture with only a trace of the desired aryl nitromethanes. A similar procedure was used to try to generate manganese(III) acetate in situ from manganese(II) acetate, nitromethane, and either toluene or benzene in acetic acid. In these cases, complex product mixtures resulted. Benzoic acid was detected in the toluene run and aldehydic products were detected in the benzene reaction.

The reaction of toluene and manganese(III) acetate in acetic acid was carried out as reported in the literature.⁵ The attempted reaction of acetonitrile with toluene in the presence of manganese(III) acetate was carried out in the same manner using acetonitrile instead of nitromethane. A similar product pattern as for the reactions without acetonitrile was noted.⁵

Competition Reaction for Two Aromatics in Nitromethane-Manganese(III) Acetate. General Procedure. Manganese(III) acetate (0.01 mol) was dissolved in glacial acetic acid (20 mL) in a constant-temperature reactor with refluxing ethylene dichloride as jacket liquid. Equal volumes of two different aromatic (10 mL of each) and nitromethane (20 mL) were added through the condenser. The reaction was heated at 83 $^\circ\text{C}$ under nitrogen for 140 min and then cooled, and the reaction mixture was washed twice with water (50 mL) and dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was analyzed by GC and the peak area ratios of the respective aromatic substitution products were used to determine relative reactivities.

Qualitative Analysis of Organic Products. In all cases where authentic were available, products were identified by comparison of their GC retention times and their MS and NMR spectra with those of the authentic. In this manner, α -nitrotoluene [MS peak at *m/e* 119, base peak at *m/e* 77; NMR singlet (5 H) at 7.2 ppm, singlet (2 H), at 5.2], α -nitroxylenes [MS parent peak at *m/e* 151, base peak at *m/e* 105; NMR singlet (4 H) at 7.0 ppm, isomeric singlets (2 H) at 5.2 ppm, singlet (3 H) at 2.2 ppm], methoxy- α -nitrotoluenes [MS peak at *m/e* 135, base peak at *m/e* 121; NMR multiplet (4 H), at 7.2 ppm, isomeric singlets (2 H) at 5.5 ppm, singlet (3 H) at 4.0 ppm], and chloro- α -nitrotoluenes [MS peak at *m/e* 155, base peak at *m/e* 111; NMR weak signals at 7.3 and 5.6 ppm] were identified. No authentic were available for the 1-tolyl-1-nitroethanes and 2-tolyl-2-nitropropanes.

However, the mass spectra of the aromatic products (apparently isomers) from the nitroethane-toluene (MS parent peak at m/e 165, base peak at m/e 119, others at m/e 91, 104) were consistent with the expected product structures.

For quantitative yield determinations, an internal standard, *p*-nitrotoluene, was added in known amount to the reaction mixture before workup. After workup, the solutions were analyzed by GC and yields were obtained by comparing the relative peak areas of the products and internal standard (internal standard program of the automatic integrator). Percent yield was based on the stoichiometry of 0.5 mol of product per mol of manganese(III) as the limiting reagent. The average yield of at least duplicate reactions in good agreement are reported in the tables.

Registry No.—2, 16787-85-2; α -nitrotoluene, 622-42-4; α -nitroxylene, 64147-35-9; methoxy- α -nitrotoluene, 64147-36-0; chloro- α -nitrotoluene, 64147-37-1.

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- Some efforts were made to further enhance the preparative aspects of this reaction by trying to generate manganese(III) in situ from the more readily available manganese(II) acetate and by trying to regenerate manganese(III) directly in the reaction medium. However, in all systems studied to date, the oxidants used (oxygen, ozone, and potassium permanganate), in hopes of converting manganese(II) to manganese(III), either occasioned unwanted oxidation of the arene or produced manganese(IV) dioxide, an ineffective promoter.
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A Study of the Capacity of Group 4 Substituents for Directing the Course of Silver(I)-Catalyzed Tricyclo[4.1.0.0^{2,7}]heptane Rearrangement into the Elusive Type δ Manifold¹

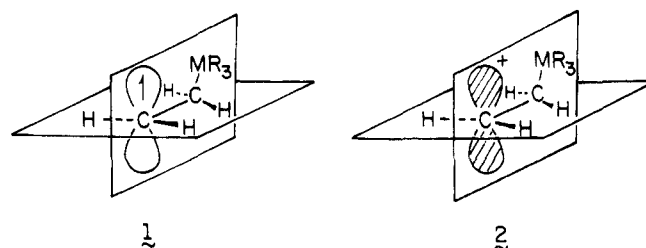
Richard T. Taylor² and Leo A. Paquette*

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The effect of 1-trimethylsilyl and 1-trimethylgermyl substitution on the course of Ag^+ - and H^+ -catalyzed rearrangement reactions of the tricyclo[4.1.0.0^{2,7}]heptane ring system has been investigated. When no other substituents are present, as in the case of **12a** and **12b**, exposure to Ag^+ causes ring opening according to the type α mechanism with formation of 2-Me₃M-1,3-cycloheptadienes. When treated with acids or anhydrous ethereal magnesium bromide, these strained molecules were efficiently converted to 2-norcarene **16** and/or its positional isomer **17**. An additional methyl substituent at C₂ resulted in 2-norcarene production irrespective of the catalyst. However, the use of Ag^+ led chiefly to **21**, whereas *p*-TosOH afforded predominantly **22**. By attaching a deuterium atom at C₇ as in **25**, it could be shown that C₂-C₇ bond cleavage proceeded with overall retention of configuration at C₇. The 7-methyl derivatives **28a** and **28b** underwent polymerization in the presence of Ag^+ but smoothly isomerized to **29a** and **29b**, respectively, under conditions of *p*-TosOH catalysis. These results can be fitted to a mechanistic profile in which electrophilic attack at a given edge bicyclobutane bond is dependent upon the locus of the alkyl substituent, the timing of the transition state, and, most importantly, the ability of certain cationic intermediates to become stabilized by virtue of exalted C-Si and C-Ge hyperconjugative and homoconjugative interaction.

The exceptional stabilization provided by group 4 β -(metallomethyl) substituents to neighboring free-radical³ and carbonium ion centers⁴ is a subject which has been accorded considerable attention. Electron spin resonance studies performed on intermediates of type **1** (M = Si, Ge, and Sn) have revealed the sizable hyperconjugative delocalization of the odd electron to the C-M σ bond to be roughly comparable in magnitude to its p-d homoconjugative delocalization onto the metal p orbitals.⁵ To permit maximum interaction in **1** (the level of which can approach 5 kcal/mol),⁶ that conformational orientation is adopted where the β C-M bond eclipses the half-filled carbon p orbital. In the structurally related carbocations **2**, there is again no doubt that the substituent effect



is likewise very sensitive to the relative orientation of the β C-M linkage and the plane of the electron-deficient p orbital. Furthermore, substantial chemical^{4,7} and spectroscopic evi-