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STUDIES IN ORGANOMETALLIC REARRANGEMENTS

III*. REACTIONS OF UNSYMMETRICALLY SUBSTITUTED INDENYL ANIONS. ISOMERIZATION OF THE INITIAL REACTION PRODUCTS

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Summary

The unsymmetrical 1-substituted indenyl anions, 1-$RC_9H_6^-$ [I, R = CH_3; II, $Si(CH_3)_3$], react with a variety of electrophilic reagents to give products substituted at both C(1) and C(3). Anion I gives predominant or exclusive attachment of the entering group at C(3) to give 1-substituted, 3-methylindenes whereas anion II reacts at both C(1) and C(3) to give mixtures of isomers. In several cases the initial kinetic products undergo isomerization to more thermodynamically stable products, and the kinetic parameters for these reactions are reported. The results of the anion quenching reactions are discussed in terms of steric and electronic effects.

Introduction

The reaction of alkali and alkaline earth salts of π-delocalized ambident carbanions (e.g. allyl, cyclopentadienyl, indenyl) with main group and transition series metal salts is a well known method for the preparation of both σ-bonded (*monohapto*) and π-bonded (*polyhapto*) organometallic compounds [1—3]. In the case of the ambident π-delocalized carbanions, *monohapto* complexes arise from the attachment of the metal or metalloid to one of the two or more equivalent sites on the anion (two each in the case of the allyl and indenyl anions, C(1) and C(3), and five in the case of the symmetrical pentagonal cyclopentadienyl anion).

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* For part II see ref.10.

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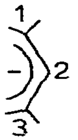
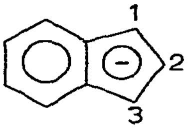
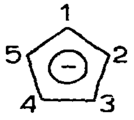
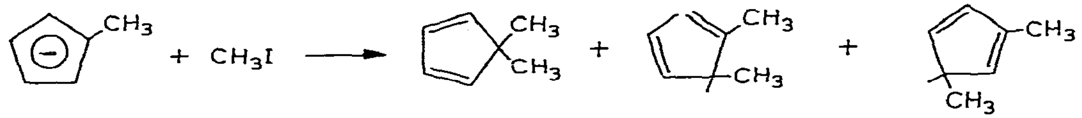






If one or more substituents are placed on the anion which serve to label one site and reduce the symmetry of the anion, then reaction can occur at structurally distinct positions, resulting in isomeric products. For example, reaction of the methylcyclopentadienyl anion with methyl iodide is reported [4] to give three isomers, differing in the position of attachment of the entering methyl group with respect to the (methyl) label. The relative amounts of the isomeric products will be determined by several factors including: the steric bulk of the label and the entering group, the nucleophilicity of the (several) attachment sites on the ambident anion, and the extent to which the label can perturb the symmetrical electronic distribution of the π-anion by inductive or resonance effects. Moreover, in some cases [4] the initial kinetic product(s) may not be the most stable isomers and isomerization may subsequently occur, leading to thermodynamically more stable product(s).



Our previous studies on the fluxional behavior [5—7] and isomerization [8—10] of organosilicon and organotin compounds have demonstrated that the *monohapto* Group IVA derivatives of unsaturated carbocyclic ligands serve as (excellent) model compounds for the study of this class of organometallic rearrangements. Accordingly, we have begun an investigation of the reactions of unsymmetrical ambident anions with several Group IVA substrates. We report here the results for the substituted indenyl anion*. In several cases the initial kinetic products were not the thermodynamically most stable isomers and the kinetics of the isomerization reactions have been studied.

Experimental

General data

All reactions and manipulations were carried out in an atmosphere of purified nitrogen. Infrared spectra were recorded on liquid films or KBr pellets using a Perkin—Elmer 257 spectrophotometer. NMR spectra were obtained using a Jeolco C60-HL spectrometer. Cyclohexane was used as an internal reference. Mass spectra were obtained at 75 eV with a Hitachi Perkin—Elmer RMU-6E spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. For those compounds which were thermally stable, gas chromatographic separations and purifications were carried out using a Varian Aerograph Model 90-P3, Model 2700, or Hewlett—Packard Model 5750

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* After the completion of this manuscript a communication appeared [11] reporting the reactions of several unsymmetrical, silicon-substituted allyl anions with various substrates. The results of these workers on the preferential site of reaction with the substrate are in substantial agreement with our results for a structurally related system.

chromatograph equipped with thermal conductivity detectors. The compounds 1-trimethylsilylindene (IX) [5], and 1-methylindene (III) [12], used to generate anions II and I respectively, were prepared as described in the literature.

Except as described below, the various products of the quenching reactions were identified by their NMR spectra and/or GLPC retention time compared with authentic samples prepared as described elsewhere: 3-methylindene (IV) [12]; 1,1-dimethylindene (V) [26]; 1,3-dimethylindene (VI) [7]; 1-trimethylstannyl-3-methylindene (VIII) [7]; 3-trimethylsilylindene (X) [8]; 1-trimethylsilyl-3-methylindene (XIII) [7]; 1,1-bis(trimethylsilyl)indene (XV) [7]; 1,3-bis-(trimethylsilyl)indene (XVI) [7].

General procedure for substituted indenyl anions

Solutions of the lithium salts of the various substituted indenyl anions were prepared in diethyl ether or THF by reaction of the appropriate indene with solutions of n-butyllithium in hexane. The methyl- and silyl-indenes were metallated at ~ 0°. Under these conditions the metallation reaction was complete within the time of mixing [13,14]. The reaction mixture was quenched both by addition of and addition to an excess of the appropriate reagent, rapidly and with efficient mixing. Identical results were obtained by both methods. The products were isolated by extraction and (for the thermally stable products) subsequent distillation or GLPC. Prior to purification, all manipulations and reactions were carried out with pre-cooled reagents and solvents.

The reaction products were identified and the composition of isomeric mixtures determined from NMR spectra. The kinetics of the isomerization reactions of the initial products were studied as previously described [8, 10].

As a typical example, the reaction of anion II with methyl iodide is given below.

Preparation of 1-trimethylsilyl-1-methylindene (XI) and 3-trimethylsilyl-1-methylindene (XII)

To a solution of 1-trimethylsilylindene (IX) (5.25 g, 0.028 mol) in diethyl ether (30 ml), cooled to $-5°$, was added dropwise with stirring over a 10 min period n-butyllithium (12.5 ml, 2.25 *M* in hexane) followed by diethyl ether (20 ml), and stirred for an additional 20 min. A two-fold excess of methyl iodide (11.4 g, 0.081 mol) in ether (15 ml) was added rapidly and with efficient stirring, and the mixture was stirred at $-5°$ for 1 h. Ice water (20 ml) was added with stirring, the organic layer was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator to remove the solvent. The proton NMR spectrum of the crude product displayed resonances assigned to compounds XI and XII as well as unreacted IX. Upon standing for 2 h at room temperature, compound XI was observed to isomerize to XIII. The mixture of 40% XII and 60% XIII and the unreacted IX were obtained by GLPC of the crude reaction mixture (12′ × 3/8″, 30% SE-30 on 45-60 Chromosorb A, 150°). We were unable to separate the mixture of isomers XII and XIII by GLPC under a variety of conditions. The combined yield of XII and XIII was 4.4 g (78% based on IX). (Anal. found: C, 77.64; H, 9.13. $C_{13}H_{18}Si$ (mixture of XII and XIII) calcd.: C, 77.15; H, 8.96%.)

The proton NMR spectrum displayed resonances at 0.25 (s, 9H), 1.15 (d, 3H), 3.35 (quart. of d, 1H), 6.72 (d, 1H) and -0.15 (s, 9H), 2.10 (t, 3H), 3.20

(quint, 1H) and 6.35 (m, 1H) in the overall ratio 40/60, and a complex multiplet at ~ 7.3 ppm.

Preparation of 2-trimethylsilyl-3-methylindene (XIV)

Thermolysis of a pure sample of 1-trimethylsilyl-3-methylindene (XIII) [7] in a sealed tube at 170° for 20 h resulted in an equilibrium mixture of 15% XIV and 85% XIII. The isomers were separated by GLPC (4' × 1/4" 20% SE-30 on 60-80 Chromosorb W, 150°, 60 ml/min at 50 psi He) with retention times of 2.0 and 3.2 min for XIII and XIV respectively. (Anal. found: (XIII) C, 77.38; H, 8.94. (XIV) C, 77.68; H, 9.04. $C_{13}H_{18}Si$ calcd.: C, 77.15; H, 8.96%.)

The proton NMR spectra (CCl_4) had the following resonances: (XIII) —0.15 (s, 9H), 2.10 (t, 3H), 3.20 (quint, 1H), 6.35 (m, 1H), 7.3 (m, 4H) ppm. (XIV) 0.20 (s, 9H), 2.15 (t, 3H), 3.20 (quart, 2H), 7.2 (m, 4H) ppm.

Preparation of trimethylsilyltrimethylstannylindene (XVII)

To a solution of IX (9.4 g, 0.05 mol) in ether (50 ml) maintained at —55° was added dropwise, with stirring n-butyllithium in hexane (22 ml, 2.25 *M*) and the mixture was stirred for 20 min. Trimethyltin chloride (10.0 g, 0.05 mol) in ether was added dropwise and the mixture was stirred for an additional hour and allowed to warm to room temperature. The reaction was recooled to —55° and quenched with dilute aqueous HCl. The organic layer was extracted with ether, dried ($MgSO_4$), and concentrated on a rotary evaporator. The product (3.9 g) was obtained by distillation (87—90°/0.1 mm) as a colorless liquid in 22% yield (based on IX). (Anal. found: C, 51.44; H, 6.93. $C_{15}H_{24}SiSn$ calcd.: C, 51.31; H, 6.89%.)

Infrared bands were observed at 3085w, 3045m, 3000w, 2982w, 2955s, 2940s, 2925s, 2910s, 1500w, 1485w, [1440, 1435, 1430s(br)]; 1263m, 1250 vs, 1220m, 1195(sh), 1190m, 1030s, 1020s, 930(sh), 925s, 855vs, 825vs, 770vs, 745vs, 725vs cm^{-1}.

The mass spectrum failed to display a signal for the molecular ion $C_{15}H_{24}$-$^{28}Si^{120}Sn$ at *m/e* 352. Prominent peaks were observed at *m/e* 277 (M—SiC_3H_9), 188 (M—SnC_3H_8), 165 (SnC_3H_9), 135 ($SnCH_3$), 115 (C_9H_7), 73 (SiC_3H_9), and 43 ($SiCH_3$).

Spectral analysis and computation

Calculations of the computer simulated spectra were carried out on a Raytheon 706 computer, using the program NMRI, a local modification (by J. Elder and C.N. Reilley) of the program LAOCN3 by A.A. Bothner-By and S. Castellano. Spectra were simulated using the computed line positions and intensities together with a Lorentzian line shape with a typical line width of 0.9 Hz. Coupling constants and chemical shifts are believed to be accurate to ± 0.2 Hz.

Results

NMR spectra of the anions

Proton NMR spectra of the indenyl, 1-methylindenyl (I), and 1-trimethylsilylindenyl (II) anions as the lithium salts in solution are displayed in Fig. 1. The observed chemical shift and coupling constant data are presented in Tables

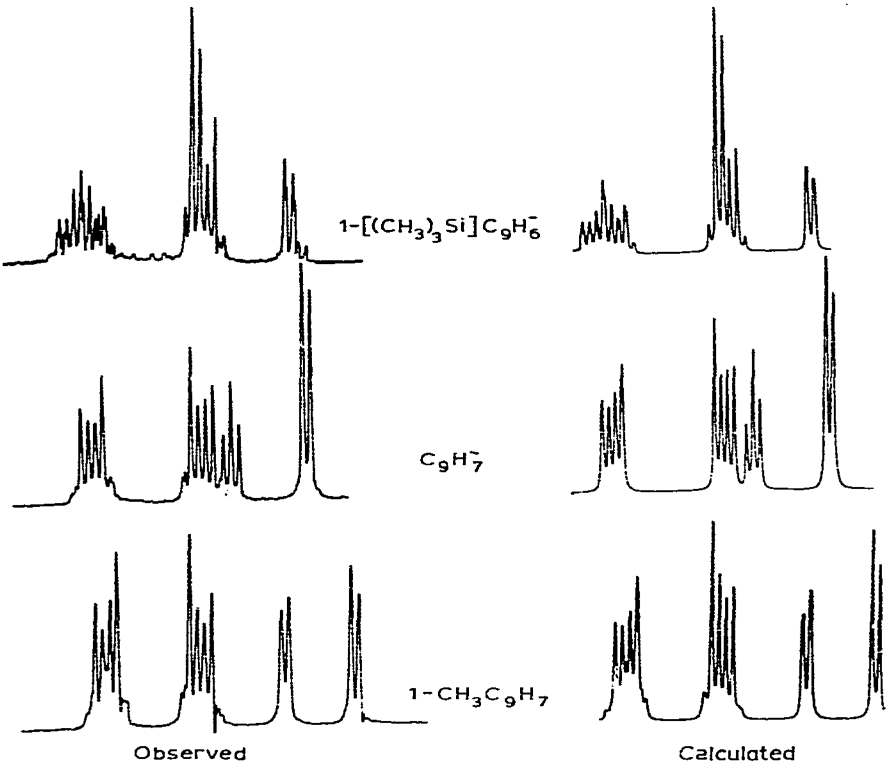


Fig. 1. Observed and computer simulated proton NMR spectra for the indenyl, 1-methylindenyl (I), and 1-(trimethylsilyl)indenyl (II) anions.

1 and 2, together with the calculated values. The most striking observation is the shift of the signal for H(2) as a function of the substituent in the 1-position. The resonance shifts from δ 6.50 for the indenyl anion to 5.69 for I and 6.73 for II.

For anion I the chemical shifts for H(4) and H(7) are, within the uncertainty of the measurements and calculations, equivalent, whereas in anion II the presence of the trimethylsilyl group at C(1) results in a 0.16 ppm chemical shift difference between H(4) and H(7). The resonance for H(7) occurs at lowest field, identified by the fine structure due to the long-range coupling J(H(3)—H(7)) 0.75 Hz. This coupling has been observed previously [15] for various substituted indenes and is diagnostic for the H(3) and H(7) resonances.

TABLE 1

^{1}H NMR CHEMICAL SHIFTS (δ) FOR THE SUBSTITUTED INDENYL ANIONS

Anion	H_1[a]	H_2	H_3	H_4	H_7	H_5	H_6	CH_3	Si—CH_3
$C_9H_7^-$	5.95	6.50	5.95	(7.51)		(6.71)		—	—
	5.93	6.60	5.93	(7.31)		(6.40)		—	—[b]
$1\text{-}CH_3C_9H_6^-$ (I)	—	5.69	6.20	7.50	7.49	6.82	6.81	2.2	—
$1\text{-}[(CH_3)_3Si]C_9H_6^-$ (II)	—	6.73	6.06	7.50	7.66	(6.69)		—	0.31

[a] Chemical shifts are in ppm downfield from TMS. [b] Ref. 18.

TABLE 2

^{1}H NMR COUPLING CONSTANTS FOR THE SUBSTITUTED INDENYL ANIONS

Anion	J_{23}	J_{13}	J_{37}	J_{45}	J_{46}	J_{56}	J_{47}
$C_9H_7^-$	3.30	0.75	0.75	8.05	1.14	6.46	0.82[a,b]
	3.23	—	—	7.97	1.13	6.17	0.80[c]
	3.20	0.75	0.75	8.05	1.10	6.46	0.75
1-$CH_3C_9H_6^-$ (I)	3.20	—	0.75	8.05	1.12	6.46	0.80
1-[$(CH_3)_3Si$]$C_9H_6^-$ (II)	3.20	—	0.75	8.05	1.13	6.45	0.80

[a] All coupling constants are in Hz. [b] Ref. 16. [c] Ref. 19.

Quenching reactions

The initial products of the quenching reactions of the methylindenyl (I) and trimethylsilylindenyl (II) anions with HCl, methyl iodide chlorotrimethylsilane and chlorotrimethylstannane are summarized in Table 3. Reaction of the 1-methylindenyl anion (I) gives largely (and in the case of quenching with trimethylchlorosilane and trimethylchlorostannane exclusively) attachment at C(3) leading to 1-substituted 3-methylindenes. In the case of the 1-trimethylsilylindenyl anion (II) the position of attachment varies from predominantly

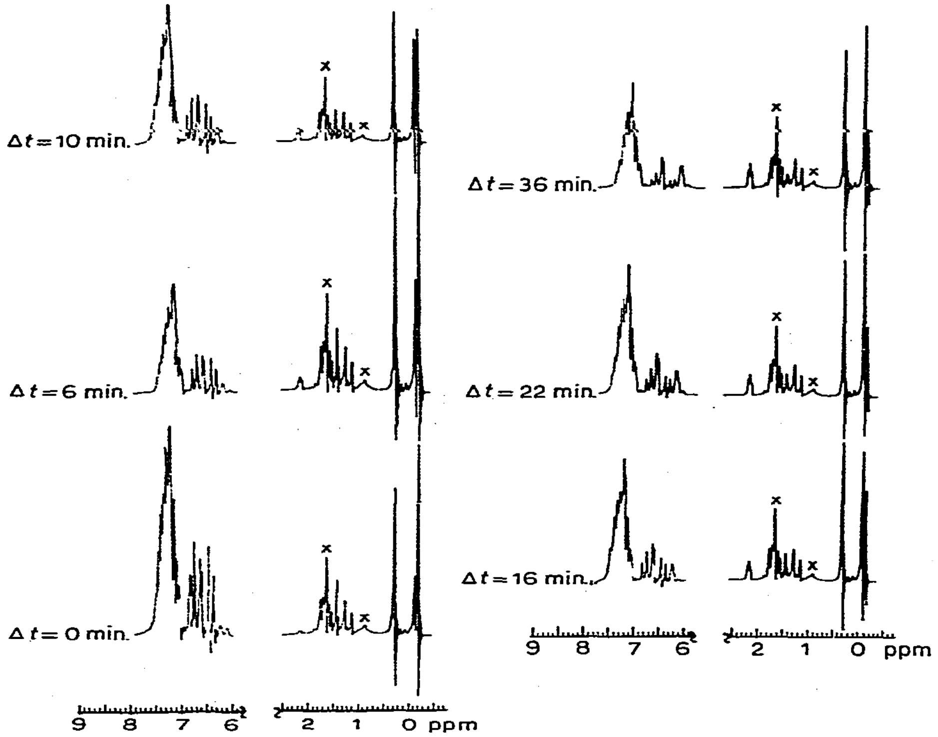


Fig. 2. Proton NMR spectra (27°) of the initial reaction product of anion II with methyl iodide. The isomerization of XI to XIII is demonstrated by the disappearance of signals at δ −0.25, 1.35, 6.60, 6.85, and the appearance of resonances at δ −0.15, 2.10, and 6.35. Compound XII is identified by signals at δ 0.25, 1.15 and 6.72. The resonances denoted by X are due to solvent (THF and hexane).

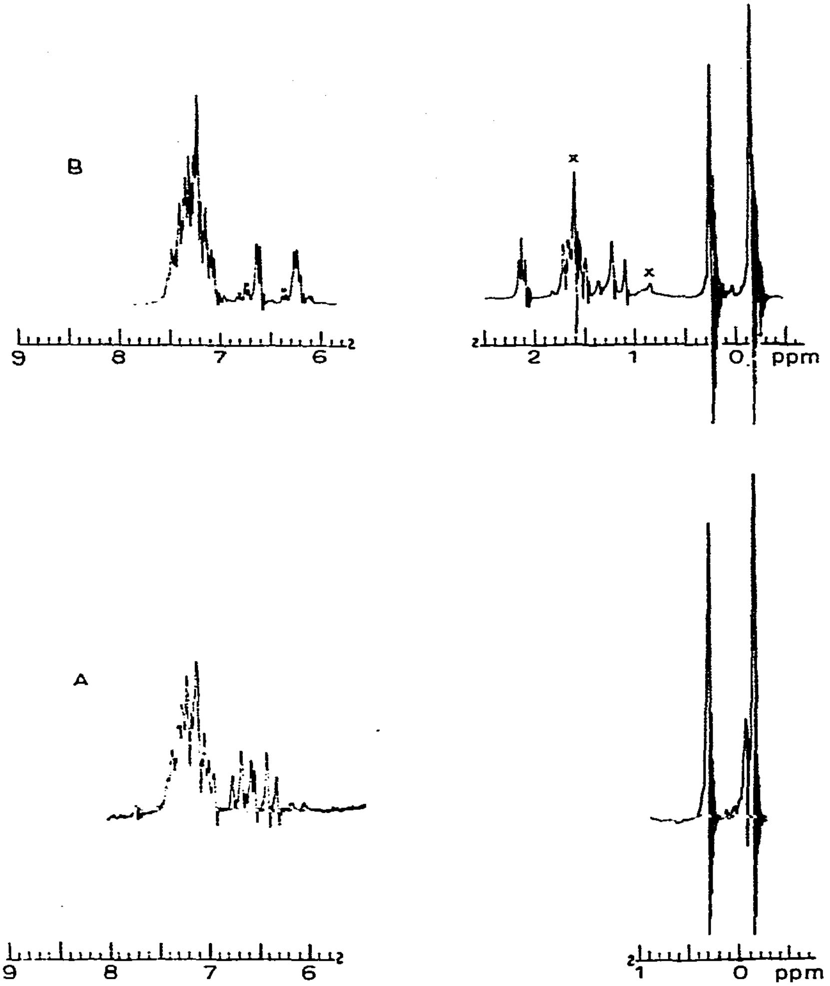


Fig. 3. Proton NMR spectra of (A) reaction product of anion II and methyl iodide before ether extraction at room temperature (60% XI and 40% XII); (B) reaction product of anion II and methyl iodide after 2 h at room temperature (60% XIII and 40% XII). The resonances denoted by X are due to solvent (THF and hexane).

C(1) in the case of HCl and methyl iodide to exclusively C(3) in the case of trimethylchlorosilane.

The initial products of the quenching reactions displayed varying degrees of stability with respect to thermal isomerization. Thus, the initial distributions of isomers obtained from the reaction of anion I with HCl, methyl iodide, and trimethylchlorostannane were essentially unchanged after heating at 170° for 24 h. By contrast, the products of quenching anion II with HCl (85% 1-isomer IX, 15% 3-isomer X) undergo a thermal isomerization to a mixture of 55% 1-isomer IX, 30% 2-isomer, and 15% 3-isomer X as reported previously [8].

The thermal rearrangements of the products of the reaction of the 1-trimethylsilylindenyl anion (II) with methyl iodide are depicted in Figs. 2, 3 and 4 (Scheme 1). The initial product consists of 40% XII and 60% XI. Compound XI undergoes a rapid isomerization even below room temperature ($\Delta G^* = 21.5 \pm 0.15$

kcal/mol; $k_{27} = 1.54 \pm 0.40 \times 10^{-4}$ sec^{-1}) to XIII as evidenced by the disappearance (Fig. 2) of resonances in the NMR spectrum assigned to XI at δ −0.25 (s, 9H, 1-Me_3Si), 1.35 (s, 3H, CH_3 (1)), 6.60 (d, 1H, H (2)), 6.85 (d, 2H, H (3)), and the simultaneous appearance of resonances for XIII at δ −0.15 (s, 9H, 1-Me_3Si), 2.10 (t, 3H, CH_3 (3)), 3.2 (quint, 1H, H (1)) and 6.35 (m, 1H, H (2)). After 2 h at room temperature the sample consists of 40% XII and 60% XIII. Subsequent heating at > 140° results (Fig. 4) in the slow disappearance of signals for XII at δ 0.25 (s, 9H, 3-Me_3Si), 1.15 (d, 3H, CH_3 (1)), 3.35 (quart of d, 1H, H (1)) and 6.72 (d, 1H, H (2)), a simultaneous increase in the resonances of XIII, and the appearance of resonances at δ 0.20 (s, 9H, 2-Me_3Si), 2.15 (t, 3H, CH_3 (3)), 3.20

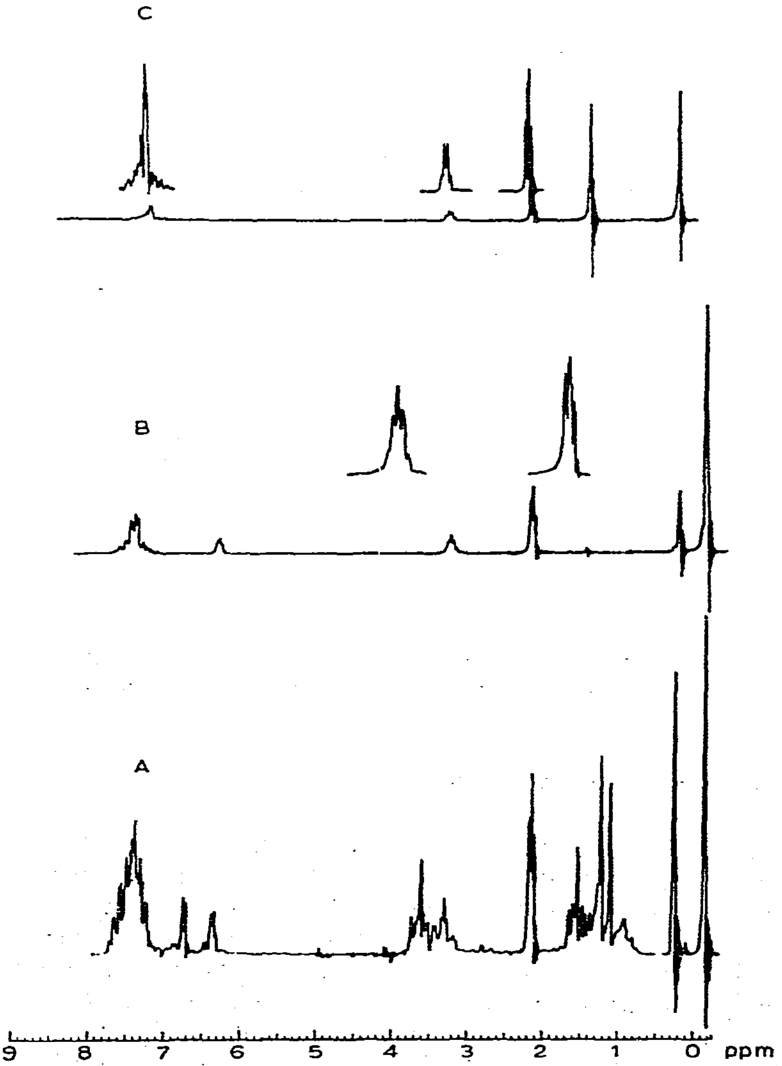
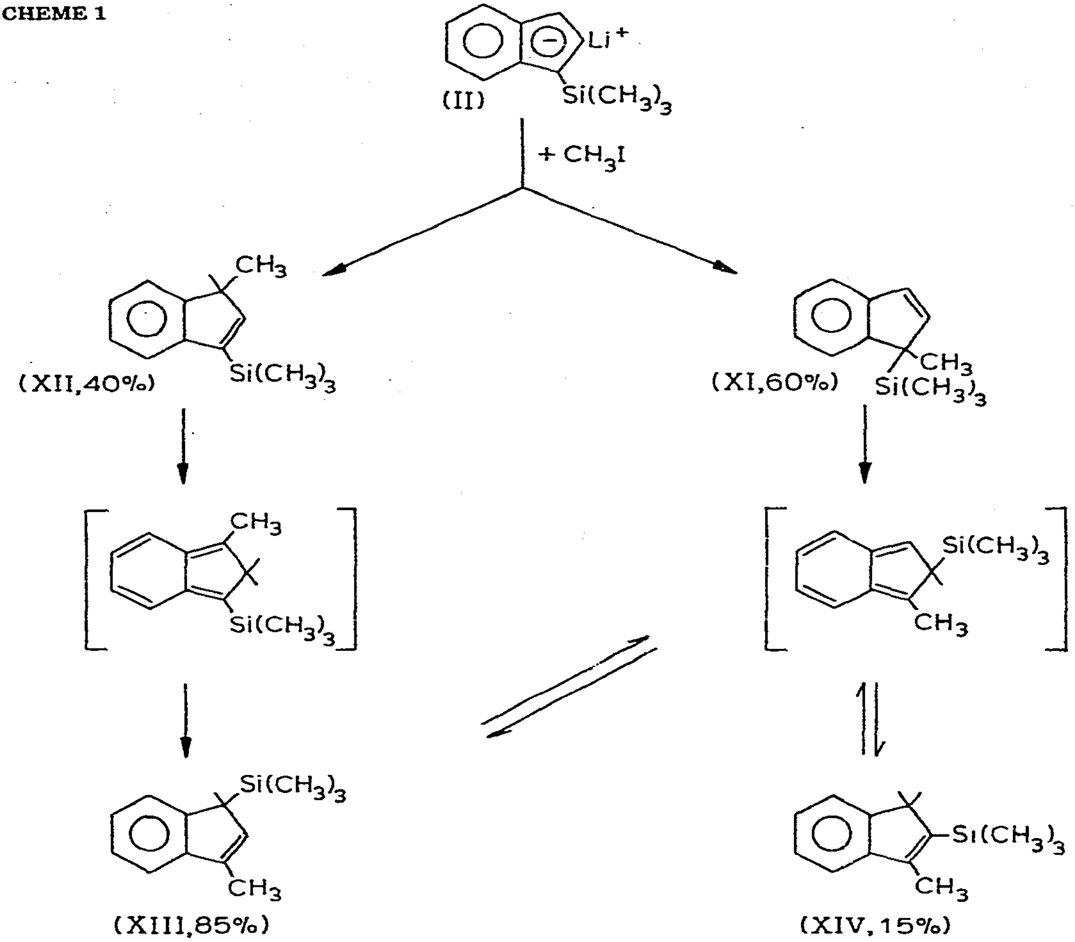


Fig. 4. Proton NMR spectra of (A) reaction product of anion II and methyl iodide after 2 h at room temperature (60% XIII and 40% XII). Signals due to residual THF appear at δ 1.55 and 3.60; (B) mixture A after several hours at 170° (85% XIII and 15% XIV); and (C) compound XIV (singlet at δ 1.42 is cyclohexane).

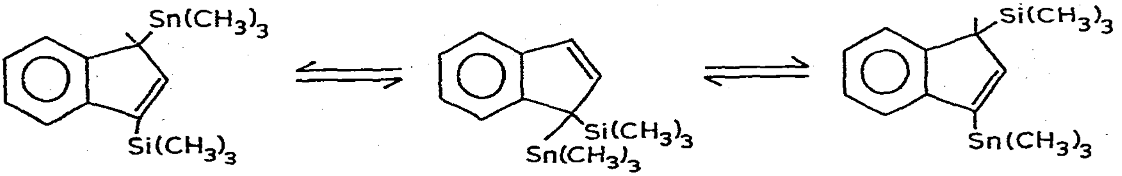
SCHEME 1



(quart, 1H, H (1)) assigned to XIV. At thermal equilibrium the mixture consists of 85% XIII and 15% XIV. An identical [9] distribution of final products is obtained when a sample of XIII obtained from the reaction of anion I with trimethylchlorosilane is heated at 170° for 24 h.

The reaction of anion II with trimethylchlorosilane results in the initial formation of exclusively the 1,3-bis(silyl) isomer XVI (Fig. 5). This compound undergoes a reversible isomerization via a series of silicon shifts, slowly at 25° and rapidly at > 50° to a mixture of 1,1-XV and 1,3-XVI isomers. The temperature dependence of the equilibrium XV $\rightleftharpoons$ XVI has been reported elsewhere [7]. The free energy of activation for the rearrangement XVI → XV has been determined to be 25.4 ± 0.05 kcal/mole; $k(57^\circ C) = 1.0 \pm 0.1 \times 10^{-4}\ sec^{-1}$.

The reaction of anion II with chlorotrimethylstanniane at −33° gives the compound (trimethylsilyl)(trimethylstannyl)indene (XVII). Variable temperature NMR spectra recorded over the temperature range −50.0 to 180.0° indicate that the molecule undergoes a rapid intramolecular rearrangement via trimethylstannyl and possibly also trimethylsilyl migrations:



(XVII b) (XVII a) (XVII c)

It was not possible, even at the lowest temperature studied, to obtain a limiting slow-exchange spectrum for the compound. Moreover, it was apparent from the spectra that the relative amounts of the isomers were temperature dependent (cf. compounds XV and XVI) [7]. Because of the rapid rate of isomerization of XVII, it was not possible to determine the site of addition of the $(CH_3)_3Sn$ group. Surprisingly, unlike the other indenyltin compounds reported in the literature [3,5,7], XVII is unaffected by moisture, at least for short periods of time. The compound can be isolated by an ether extraction following an aqueous workup of the crude reaction mixture.

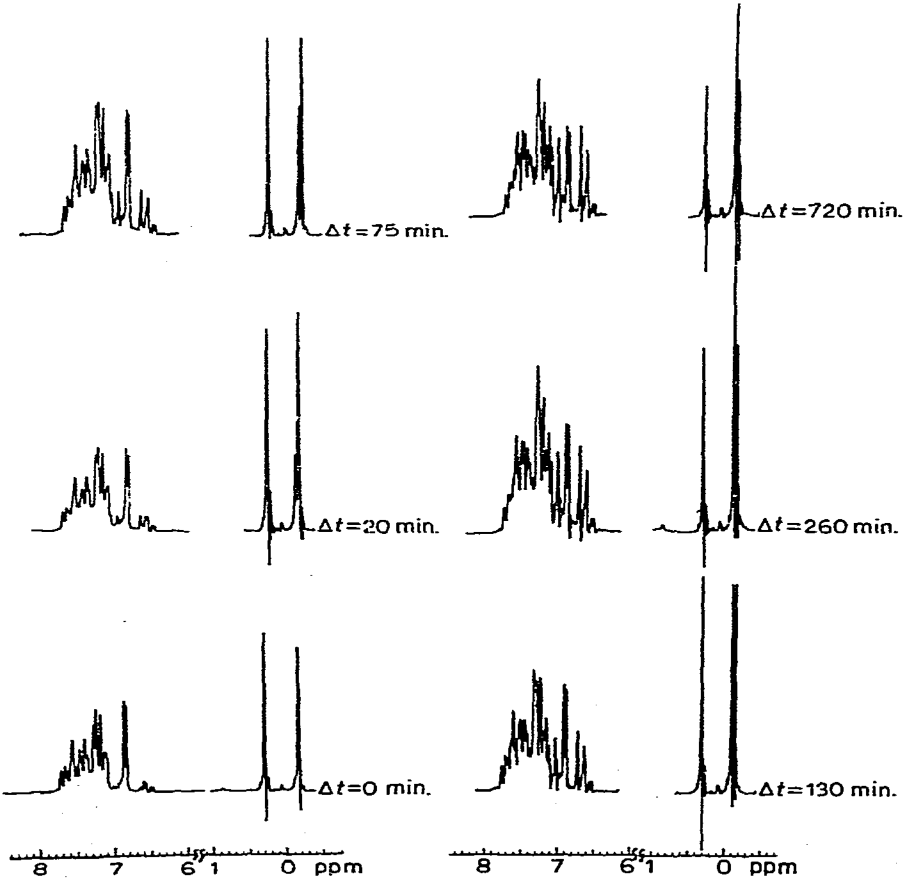


Fig. 5. Proton NMR spectra (27°) of the isomerization of XVI to a mixture (1/1) of XV and XVI.

Discussion

Nature of the anions in solution

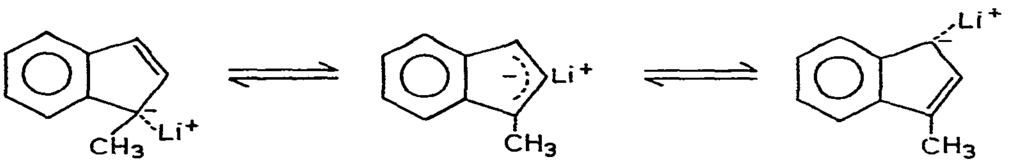
The NMR spectrum of the indenyl anion with several cations in various solvents has been reported previously [16—20]. Our results (Tables 1 and 2) are in close agreement with the earlier work. Data for the 1-methyl anion (I) and the 1-trimethylsilylindenyl anion (II) are included. Jackman [16] and coworkers have clearly demonstrated that an equilibrium exists between contact and solvent-separated ion pairs for indenyllithium in solution, and that the position of equilibrium is sensitive to the nature of the cation, the concentration, the temperature, and the solvent. From their data for indenyllithium at room temperature we calculate an equilibrium constant for contact ⇋ solvent-separated ion pairs of 2.5×10^{-1} in 1,2-dimethoxyethane and 5×10^{-4} in THF. It is clear that the predominant species in solution is the contact ion pair.

The effect of a methyl or trimethylsilyl substituent on the anion is difficult to assess quantitatively. Clearly, the substituent can alter the thermodynamic parameters which determine the equilibrium in solution by both steric and electronic effects. Moreover, the NMR parameters used to measure the equilibrium (viz. the chemical shifts and coupling constants of the resonances) are themselves altered by the substituent*.

The effect of changing the substituent R (CH_3, H, $Si(CH_3)_3$) in the 1-position on the anion is most clearly observed in the chemical shift of the resonance of H(2). The signal shifts in the order Si(lowest field) < H < CH_3 over a range of 1.0 ppm. This trend is parallel to that observed in the neutral molecules [7] although the range is greater in the case of the anions. We wish to defer a detailed discussion of the NMR parameters until completion of ^{13}C NMR studies in progress.

Initial products of quenching reactions

The results described here clearly show that the substitution of a Group IVA element on C(1) of the indenyl anion drastically alters the site(s) of attack of an electrophile. The distribution of isomers in the initial products of quenching reactions displays some regularity based on the ring substituent (R) and the group being added (M). For the methylanion I reaction occurs predominantly or exclusively at C(3), a result consistent with both steric and electronic considerations. If anion I exists in ether solution predominantly as a contact ion-pair, one can postulate the limiting structures Ia and Ib and a delocalized structure I. The observed preference for formation of products formally derived from Ib



(Ia) (I) (Ib)

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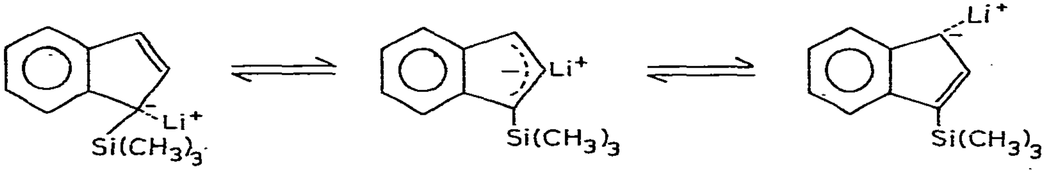
* Studies are currently in progress on the effects of substituents on the NMR spectra of Group IVA substituted carbanions.

may be due to either (1) an equilibrium in solution favoring structure Ib or an analogous covalent form, or (2) a higher kinetic reactivity for a structure like Ib coupled with a rapid equilibrium in solution between the various forms of the anion. Structure Ib represents, as in similar cases, the more stable (least highly substituted) anion and places the negative charge at the least hindered site for reaction.

The results of the quenching experiments for the trimethylsilyl anion II may reflect a balance of opposing steric and electronic effects. Upon protonation or methylation of the anion the predominant product can be envisioned as derived from IIa either due to an equilibrium favoring structure IIa or a high kinetic reactivity for that form of the anion. For the reaction of anion II with trimethylchlorosilane, the exclusive initial incorporation of the $Si(CH_3)_3$ group at C(3) can be ascribed to steric factors, inhibiting reaction at the substituted site C(1)[*,**]. That the attachment of the $Si(CH_3)_3$ group is controlled by steric effects and not by unfavorable thermodynamic or electronic considerations for the 1,1-bis(trimethylsilyl) product is demonstrated by the subsequent (rapid) isomerization of the initial (kinetic) 1,3-product (XVI) to a mixture of 1,1-XV and 1,3-XVI.



(IIa) (II) (IIb)

Recently, Bushby and Ferber [22] reported on the protonation reactions of unsymmetrically substituted 1,3-diphenylallylanions. They found that the product ratio $p\text{-}XC_6H_4CH_2CH{=}CH_2C_6H_5/p\text{-}XC_6H_4CH{=}CH{-}CH_2C_6H_5$ could be correlated with the chemical shift difference τ (H(1)) to τ (H(3)) in the NMR spectrum of the anion, and that the site of protonation was related to the electron-withdrawing or -donating ability of the group X. Bates and co-workers [23] have also noted a correlation between ^{13}C NMR parameters and reaction sites in several delocalized carbanions.

It should be noted that the initial product distribution is not controlled by the conditions of the quenching reaction. For example, reactions of anion II with water, aqueous HCl, and solid NH_4Cl followed by saturated NH_4Cl solution gave (within experimental error) identical distributions of IX and X. Moreover, the direction of addition did not influence the product distribution. Addition of or addition to the quenching agent gave identical results. Except for the thermal rearrangements discussed below, the products of the quenching reactions are stable under the conditions of the quench.

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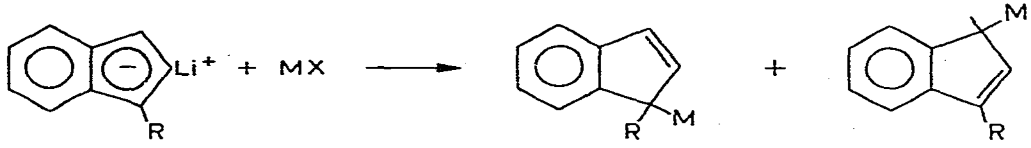
[*] The reaction of neopentylallyllithium with trimethylchlorosilane gives exclusively primary isomers (*cis* and *trans*) [21].

[**] We have been unable to effect reaction of trimethylchlorosilane with ambident anions containing only substituted reaction sites (viz. pentamethylcyclopentadienyl and 1,3-dimethylindenyl anions). cf. ref. 7.

TABLE 3

INITIAL PRODUCTS OF THE QUENCHING REACTIONS OF SUBSTITUTED INDENYL ANIONS



R	MX	Mole (%)	
CH_3 (I)	H_3O^{+b}	10 (III)	90 (IV)
	CH_3I	17 (V)	83 (VI)
	$(CH_3)_3SiCl$	0 (XI)	100 (XIII)
	$(CH_3)_3SnCl$	0 (VII)[c]	100 (VIII)[c]
$Si(CH_3)_3$ (II)	H_3O^{+b}	85 (IX)	15 (X)
	NH_4Cl^d	82 (IX)	18 (X)
	CH_3I	60 (XI)[e]	40 (XII)
	$(CH_3)_3SiCl$	0 (XV)	100 (XVI)
	$(CH_3)_3SnCl$	(XVII)[f]	[f]

[a] ± 2 mole %. [b] Dilute aqueous HCl, sufficient acid to leave the final solution slightly acidic. [c] Data from ref.8. [d] Solid NH_4Cl followed after 30 min by satd. aq. NH_4Cl. [e] Rapidly isomerizes to XIII. [f] Rapidly fluxional molecule (see text).

Isomerization of initial products

The reaction of anion II with a proton source, CH_3I, and $(CH_3)_3SiCl$ in each case results in product(s) which undergo subsequent thermal isomerization to a more stable mixture of isomers. The isomerization of trimethylsilylindene has been reported previously [8]. As illustrated in Scheme 1, neither of the initial kinetic products of the reaction of II with CH_3I is present at thermal equilibrium. Two different isomers (XIII and XIV), resulting from silicon and hydrogen shifts, appear upon thermolysis. The exclusive preference of the methyl substituent for a vinylic position in the final products is paralleled in the low temperature isomer distribution for methylcyclopentadienyltrimethylsilane [24] and in the isomerization of 1-methylallyltrimethylsilane [25] which can be converted in nearly quantitative yield to 3-methylallyltrimethylsilane.

The reaction of anion II with trimethylchlorosilane at room temperature followed by 8 h reflux was reported to give a mixture of the bis(silyl) isomers XV and XVI. When the reaction is carried out at −10°C and the mixture analyzed immediately by NMR, the product is shown to be exclusively the 1,3-isomer XVI, which rapidly rearranges even below room temperature to the observed mixture of isomers.

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