Journal of Organometallic Chemistry, 70 (1974) 367—382
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTRON SPIN RESONANCE STUDIES OF GROUP IV ORGANOMETALLIC RADICAL ANIONS

II*. ORGANOMETAL-SUBSTITUTED ALKYLBENZENES

HERBERT J. SIPE, Jr and ROBERT WEST
Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53706 (U.S.A.)

(Received May 22nd, 1973)

Summary

Electron spin resonance (ESR) spectra are reported for anion-radicals of trimethylsilyl-substituted toluenes, xylenes, mesitylene and t-butylbenzenes and for trimethylgermyl-t-butylbenzenes. The spectra may be interpreted in terms of substituent perturbations that stabilize or destabilize the lowest unfilled benzene molecular orbital and which are accompanied by small redistributions of spin density within that molecular orbital. In all compounds studied, the organometal substituent dominates the ordering of MO energy levels by accepting electron density more effectively than the alkyl substituents release it. Hückel molecular orbital calculations agree well with experimental spin density when the organometal substituent is treated as a heteroatom in the molecular π-electron system and alkyl substituents are treated by an inductive-hyperconjugative model. The HMO eigenvectors have significant contributions to bonding π-MOs from the pseudo-π-center on silicon and, to a lesser extent, from that on germanium.

Introduction

The qualitative molecular orbital (MO) theory of monosubstituted benzenes, in which the substituent has a weakly perturbing effect on the form of the benzene MOs, has been discussed by Carrington et al. [1], and applied to multiply-substituted benzenes [2, 3]. The investigations reported here were concerned with extending the weak perturbation model to ESR studies of benzene radical anions which were multiply-substituted by both alkyl and organometal groups. These molecules offer the possibility of semiquantitative comparisons between alkyl and organometal substituents.

---

*For part I see page 353.

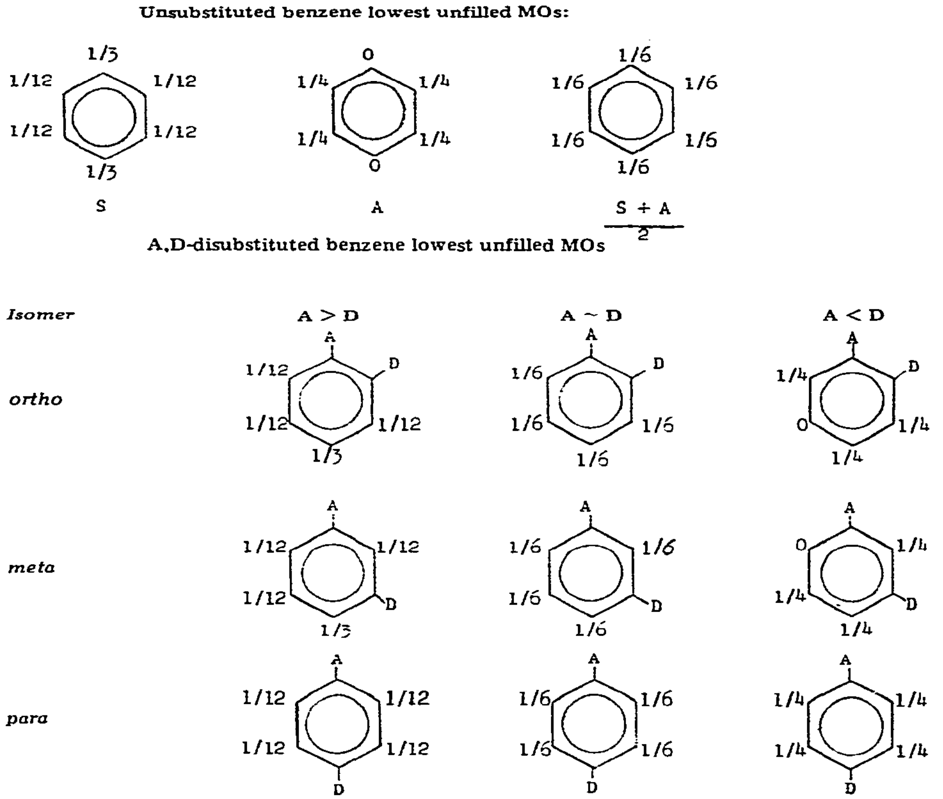


Fig. 1. Spin density distributions in benzene radical anions predicted for acceptor (A) and donor (D) substituents.

In benzene radical anion, the unpaired electron occupies a MO which is a mixture of the two lowest-energy unfilled MOs of neutral benzene: the antisymmetric (A) and symmetric (S) MOs. Substitution of the benzene nucleus by a weakly perturbing substituent will leave A unchanged in energy but S will be raised or lowered depending on the electron-releasing or -withdrawing nature of the substituent [1, 3]. If the benzene nucleus is substituted by several weakly perturbing groups, the unpaired electron again will occupy the MO (perhaps itself a mixture of benzene MOs) that is lowest in energy. Fig. 1 summarizes the spin-density distributions expected for *ortho*-, *meta*- and *para*-disubstituted benzene anions. Observation of the hyperfine coupling constants (hfcc) and the number of protons with a given hfcc indicates which relationship exists between substituent effects for a given radical anion.

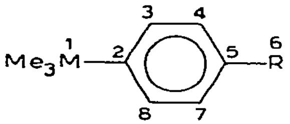
Results and discussion

Hyperfine coupling constants and *g*-values of a series of organometal-substituted alkylbenzene anions are reported in Table 1. The ESR spectra of *o*-, *m*- and *p*-trimethylsilyltoluene anions (Figs. 2a, 2b and 3) are consistent with occupation of the S-type MO by the unpaired electron. Note especially the large

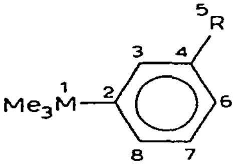
(continued on p. 371)

TABLE 1

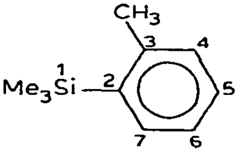
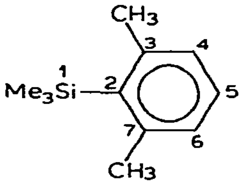
HYPERFINE COUPLING CONSTANTS AND g-VALUES FOR ORGANOMETAL-SUBSTITUTED ALKYLBENZENE RADICAL ANIONS



M	R	g	a_1	a_3	a_4	a_6
C	Me	—	0.08^a	5.17^a	5.17^a	0.91^a
C	t-Bu	—	No Radical Anion			
Si	Me	2.0028	0.20 $(0.20)^b$	3.20 $(3.25)^b$	1.50 $(1.47)^b$	8.20 $(8.43)^b$
Si	CH_2SiMe_3	2.0028	—	3.72	1.35	6.48
Si	Et	2.0028	0.24	3.21	1.38	6.02
Si	i-Pr	2.0028	0.24	3.39	1.27	4.83
Si	t-Bu	2.0029	0.24 $(0.23)^b$	3.40 $(3.40)^b$	1.23 $(1.22)^b$	—
Ge	Me	—	No Radical Anion			
Ge	t-Bu	2.0031	—	3.38	2.23	—
Sn	t-Bu	—	No Radical Anion			

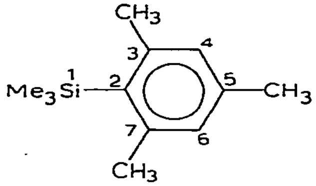
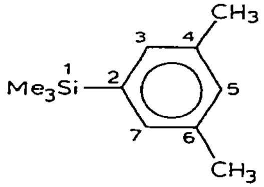


M	R	g	a_3, a_8	a_6	a_7	a other
Si	Me	2.0027	2.60	8.09	1.06	$a_5 = 1.06, a_1 = 0.$
Si	t-Bu	2.0028	2.46	8.04	1.68	$a_1 = 0.28$
Ge	t-Bu	2.0030	2.33	7.79	1.41	

	g	a_1	a_3	a_4	a_5
	2.0028	0.32 $(0.4)^d$	2.83^c $(2.8)^d$	1.06 $(0.4?)^d$	8.42 $(8.1)^d$
	2.0028	0.22	3.10^c	0.87	8.31

(continued)

TABLE 1 *(continued)*

	g	a_1	a_3	a_4	a_5
	2.0027	0.20	3.10[c]	0.87	8.30[e]
	2.0027	0.29	2.34	1.20[f]	7.67

[a] Values taken from ref. 31.
[b] Independent results of Gerson et al. [32, published while this manuscript was in preparation].
[c] *Ortho*-methyl proton hfcc.
[d] Independent results of Kazakova et al. [33, published while this manuscript was in preparation].
[e] *Para*-methyl proton hfcc.
[f] *Meta*-methyl proton hfcc.

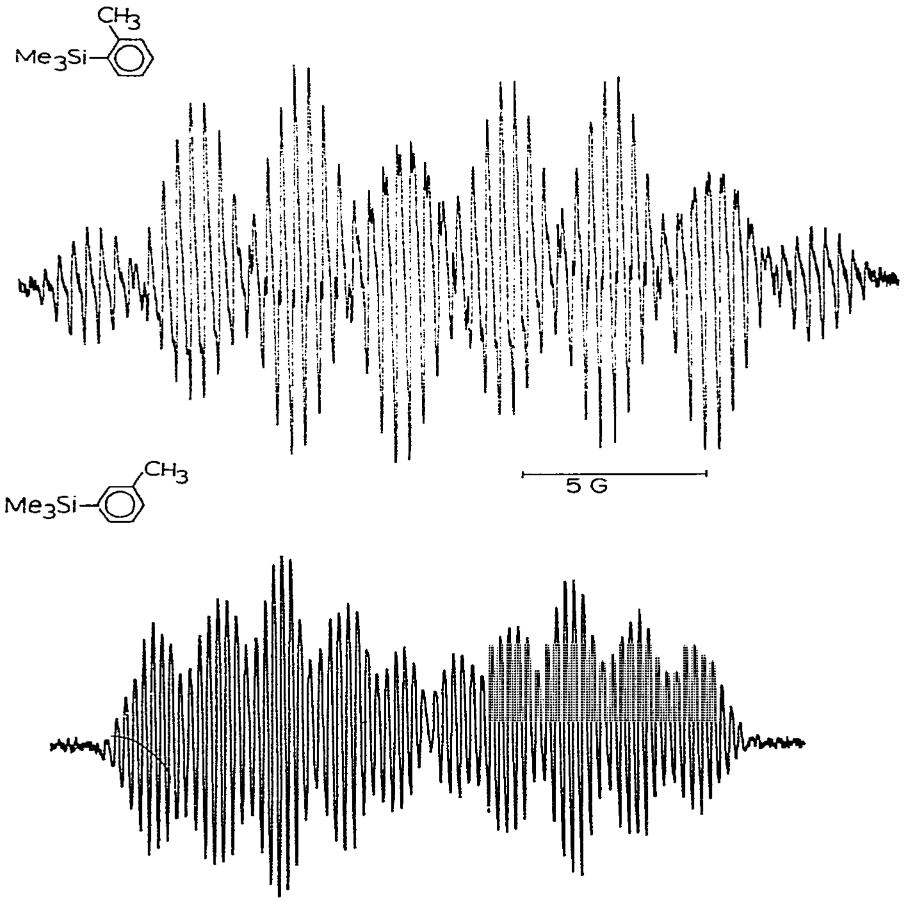


Fig. 2. (a) (top) ESR spectrum of *o*-trimethylsilyltoluene anion, −80°. (b) (bottom) ESR spectrum of *m*-trimethylsilyltoluene anion, −80°.

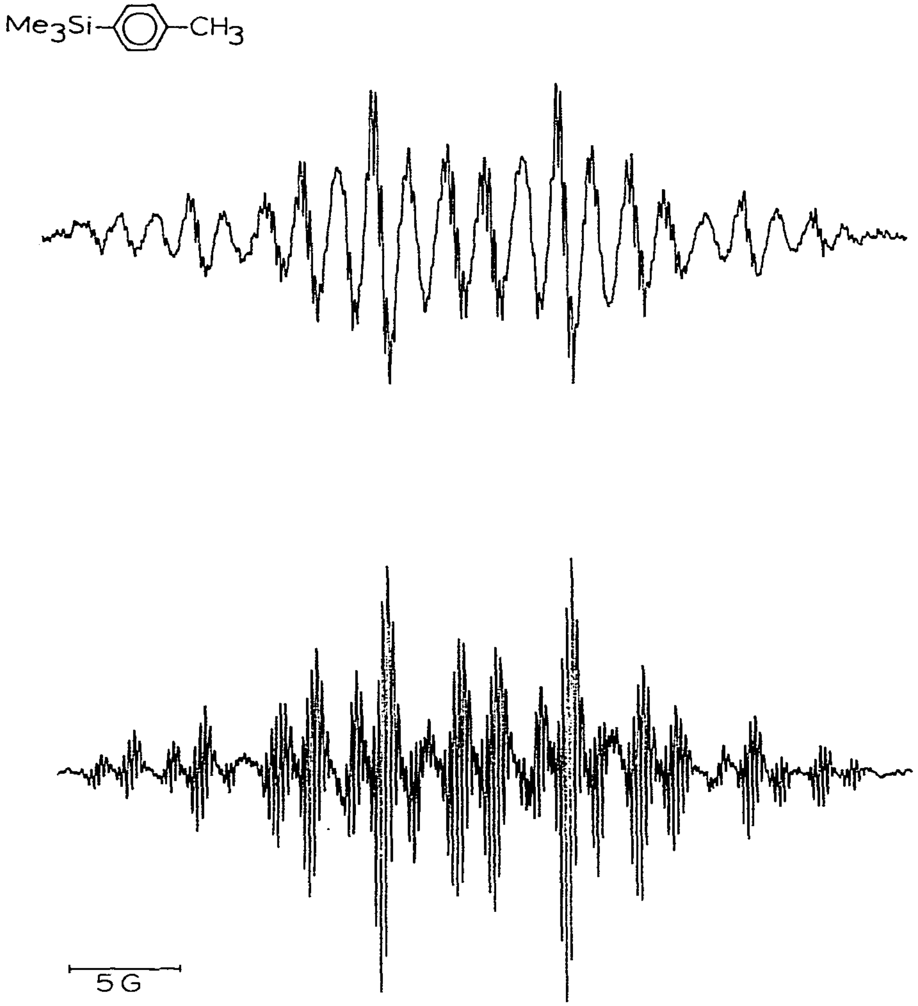


Fig. 3. (a) (top)ESR spectrum of 1-trimethylsilyltoluene anion. (b) (bottom) Same spectrum with resolution enhanced by line sharpening, −70°

methyl proton hfcc in Fig. 3 which is consistent only with the S-type spin density distribution. The total spectrum width of 1,3-dimethyl-2-trimethylsilylbenzene anion is greater than that of the 1,3-dimethyl-5-trimethylsilylbenzene anion (cf. Figs. 4a and 4b). This observation verifies the assignment of the larger of the two ring hfccs to the *ortho* position in trimethylsilylbenzene anion [1]. Again a large spin density *para* to the trimethylsilyl group is evident in the very wide spectrum observed for 2-trimethylsilylmesitylene anion (see Fig. 5). The ESR spectra of all of the *p*-alkyl-substituted trimethylsilylbenzenes (Table 1) can also be explained only if an S-type MO is occupied, and similar results are obtained for the *m*-trimethylsilyl-t-butylbenzene and *m*- and *p*-trimethylgermyl-t-butylbenzene anions. (Figs. 6 and 7) Thus all of the experimental results are consistent with occupation of the S-type MO by the unpaired electron. The organosilyl- and organogermyl-substituents are therefore electron acceptor substituents in these compounds.

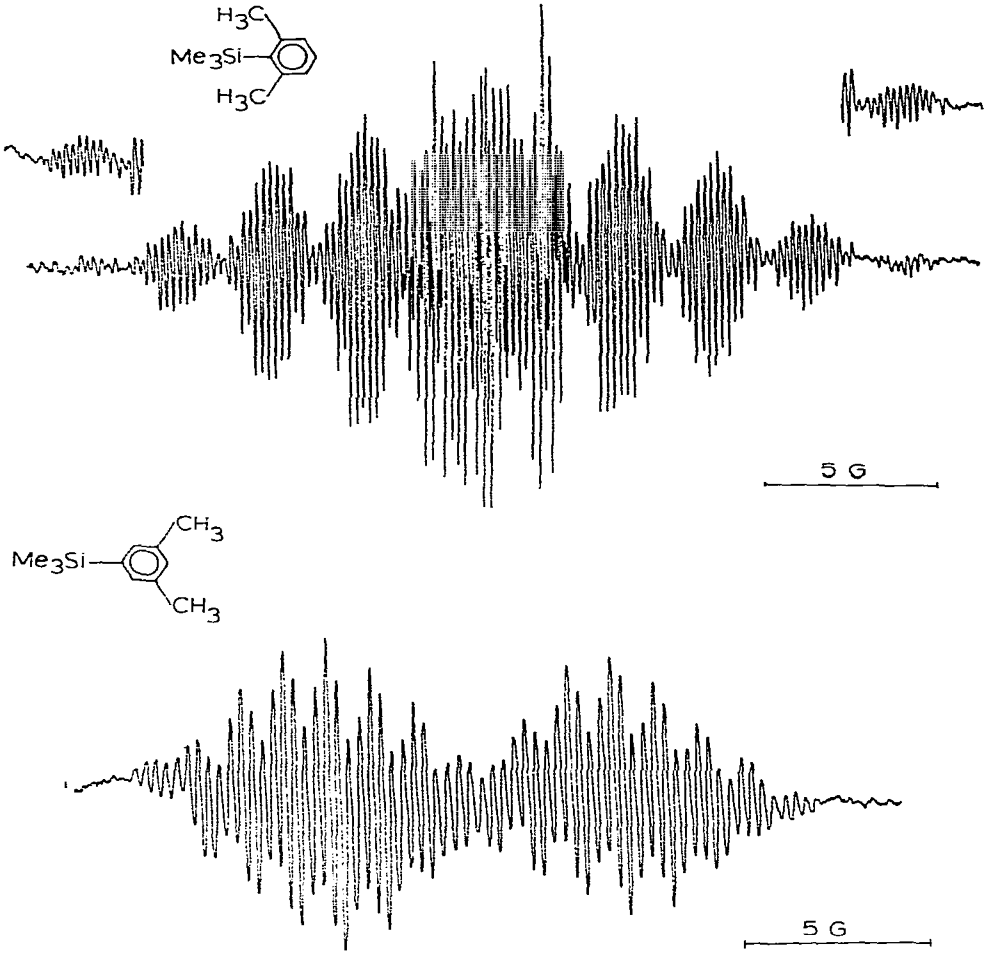


Fig. 4. (a) (top) ESR spectrum of 2-trimethylsilyl-*m*-xylene anion, −70°. (b) (bottom) ESR spectrum of 5-trimethylsilyl-*m*-xylene anion, −80°.

Furthermore, the magnitude of their stabilizing effect on the benzene S orbital is greater than the destabilizing effect of any of the alkyl groups studied.

Molecular orbital calculations. Hückel molecular orbital calculations provide estimates of unpaired electron distribution for comparison with the experimental density distribution. The latter is available from hfcc for ring protons via the well known McConnell equation: $a_{\mathrm{H}_i} = Q^{\pi}_{\mathrm{CH}}\,\rho^{\pi}_{\mathrm{C}_i}$ [4]. The value of $Q^{\pi}_{\mathrm{CH}} = -28.0$ gauss has been used throughout this work [5,6]. The organometal substituent is treated as a heteroatom participant in the molecular π-electron system via an empty orbital of π-type symmetry. Coulomb and resonance integrals for the heteroatom were scaled in terms of the corresponding integrals for an ordinary aromatic system [7]:

$$\alpha_{\mathrm{X}} = \alpha_{\mathrm{C}} + h_{\mathrm{X}}\beta_{\mathrm{CC}} \qquad \beta_{\mathrm{CX}} = k_{\mathrm{CX}}\beta_{\mathrm{CC}}$$

(continued on p. 377)

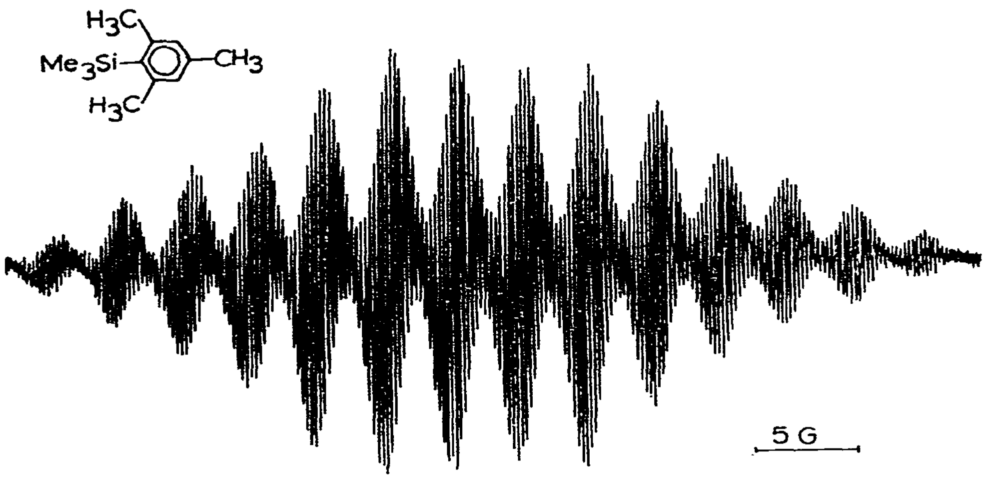


Fig. 5. ESR spectrum of trimethylsilylmesitylene anion, —70°.

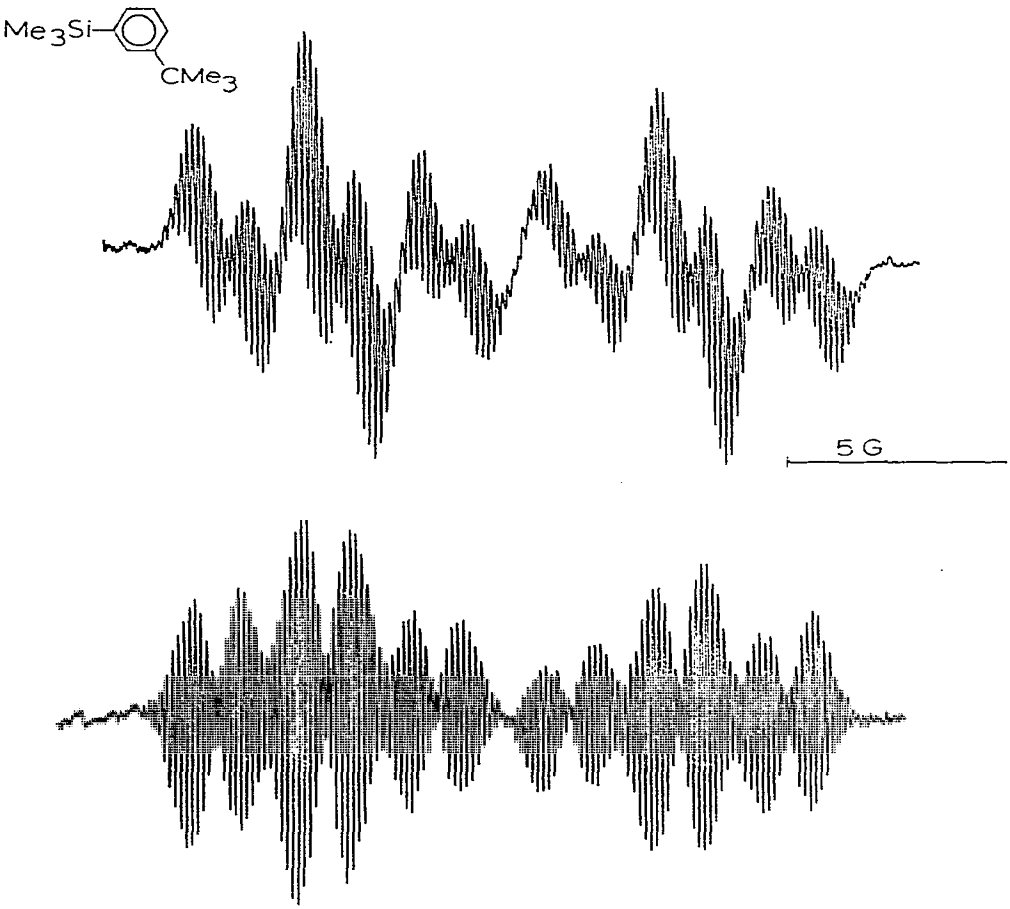
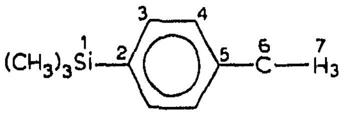
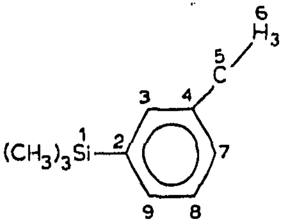
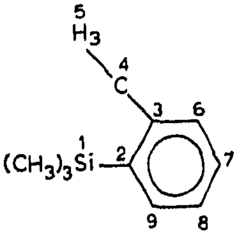
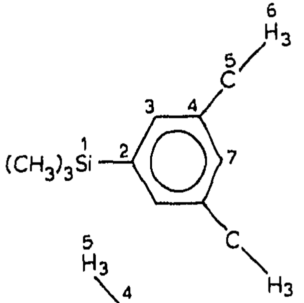
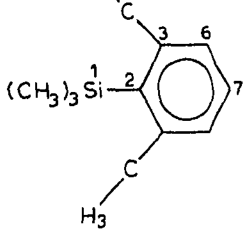
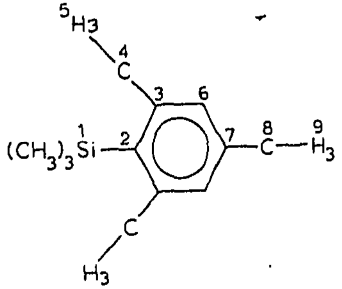
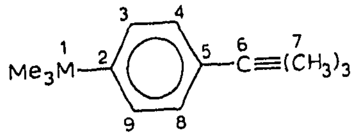


Fig. 6. (a) (top) ESR spectrum of *m*-trimethylsilyl-t-butylbenzene anion. (b) (bottom) Same spectrum with resolution enhanced by line sharpening, —70°.

TABLE 2

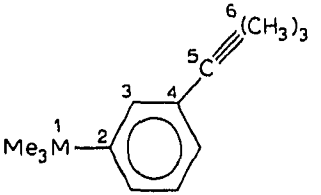
HMO RESULTS FOR ORGANOMETAL-SUBSTITUTED BENZENES[a,b,c]

Compound	M	Atom i	$\rho_{i,\mathrm{exp}}$[d]	$\rho^{\pi}_{i,\mathrm{calc}}$	ρ^{π}_{i}[e]	Atom—Atom i,j	$p^{\pi}_{i,j}$[f]
		1	—	0.113	0.047	1—2	0.213
		2	—	0.267	0.976	2—3	0.649
		3	0.114	0.093	0.998	3—4	0.674
		4	0.054	0.055	1.024	4—5	0.641
		5	—	0.273	0.952	5—6	0.260
		6	—	0.001	1.074	6—7	0.962
		7	0.048	0.049	0.908		
		1	—	0.117	0.045	1—2	0.206
		2	—	0.279	0.958	2—3	0.656
		3	0.093	0.109	1.023	2—9	0.649
		4	—	0.050	0.955	3—4	0.645
		5	—	0.000	1.074	4—5	0.259
		6	0.006	0.009	0.908	4—7	0.641
		7	0.289	0.282	1.021	5—6	0.962
		8	0.038	0.069	0.998	7—9	0.669
		9	0.093	0.083	1.016	8—9	0.667
		1	—	0.115	0.048	1—2	0.216
		2	—	0.274	0.983	2—3	0.628
		3	—	0.080	0.953	2—9	0.655
		4	—	0.000	1.074	3—4	0.261
		5	0.017	0.014	0.908	3—6	0.645
		6	0.038	0.074	1.024	4—5	0.961
		7	0.300	0.284	0.996	6—7	0.670
		8	0.038	0.048	1.061	7—8	0.662
		9	0.101	0.110	0.998	8—9	0.667

		1	—	0.119	0.045	1–2	0.206
		2	—	0.273	0.957	2–3	0.653
		3	0.084	0.096	1.040	3–4	0.643
		4	—	0.068	0.954	4–5	0.259
		5	—	0.000	1.074	4–7	0.645
		6	0.007	0.010	0.908	5–6	0.962
		7	0.274	0.276	1.046		
		1	—	0.113	0.051	1–2	0.225
		2	—	0.267	1.006	2–3	0.631
		3	—	0.093	0.952	3–4	0.261
		4	—	0.000	1.074	3–6	0.643
		5	0.018	0.017	0.907	4–5	0.961
		6	0.031	0.060	1.040	6–7	0.667
		7	0.296	0.281	0.994		
		1	—	0.109	0.053	1–2	0.230
		2	—	0.254	1.022	2–3	0.628
		3	—	0.090	0.951	3–4	0.260
		4	—	0.000	1.074	3–6	0.647
		5	0.018	0.016	0.907	4–5	0.961
		6	0.031	0.054	1.065	6–7	0.642
		7	—	0.267	0.950	7–8	0.260
		8	—	0.001	1.074	8–9	0.962
		9	0.049	0.048	0.907		
	Si	1	—	0.102	0.048	1–2	0.220
		2	—	0.257	1.018	2–3	0.646
		3	0.119	0.097	0.983	3–4	0.677
		4	0.043	0.053	1.029	4–5	0.628
		5	—	0.266	0.941	5–6	0.318
		6	—	0.002	1.071	6–7	0.944
		7	—	0.072	0.899		

(continued)

TABLE 2 (continued)

	M	Atom i	$\rho^{d}_{i,\mathrm{exp}}$	$\rho^{\pi}_{i,\mathrm{calc}}$	$\rho^{\pi\,c}_{i}$	Atom—Atom i, j	$p^{\pi\,f}_{i,j}$
(For formula see preceding page)	Ge	1	—	0.157	0.023	1—2	0.149
		2	—	0.253	0.977	2—3	0.656
		3	0.121	0.079	1.007	3—4	0.674
		4	0.080	0.057	1.026	4—5	0.634
		5	—	0.255	0.957	5—6	0.298
		6	—	0.002	1.072	6—7	0.950
		7	—	0.062	0.905		
	Si	1	—	0.115	0.045	1—2	0.206
		2	—	0.276	0.958	2—3	0.658
		3	0.088	0.090	1.023	2—9	0.648
		4	—	0.062	0.953	3—4	0.634
		5	—	0.000	1.071	4—5	0.316
		6	—	0.017	0.902	4—7	0.629
		7	0.287	0.283	1.025	5—6	0.944
		8	0.060	0.056	0.998	7—8	0.671
		9	0.088	0.098	1.019	8—9	0.666
	Ge	1	—	0.165	0.022	1—2	0.143
		2	—	0.266	0.957	2—3	0.665
		3	0.083	0.082	1.036	2—9	0.656
		4	—	0.060	0.953	3—4	0.636
		5	—	0.000	1.072	4—5	0.297
		6	—	0.015	0.004	4—7	0.634
		7	0.278	0.269	1.031	5—6	0.950
		8	0.050	0.059	0.998	7—8	0.671
		9	0.083	0.084	1.027	8—9	0.665

---

[a] Organometal substituents are treated as heteroatoms with coulomb and resonance parameters reported in ref. 4. [b] Alkyl substituents are treated by an inductive-hyperconjugative model (CH_3) or as heteroatoms (t-Bu). [c] "Experimental" spin densities are estimated from ring proton hfcc using McConnell's relation with $Q^{\pi}_{\mathrm{CH}} = -28.0$. [d] Spin densities in the methyl group pseudo-orbital were estimated by the relation

$$\left(a_{\mathrm{CH_3}}\,\frac{\text{gauss}}{\text{proton}}\right) \times \left(\frac{1\ 1s\ \text{electron}}{508\ \text{gauss}}\right)(3\ \text{protons}) = \rho_{\mathrm{CH_3}}$$

$$^{e}q^{\pi}_{i} = \sum_{s}^{\mathrm{occ}} 2\,C^{2}_{is}. \quad {}^{f}p^{\pi}_{ij} = \sum_{s}^{\mathrm{occ}} 2\,C_{is}C_{sj}.$$

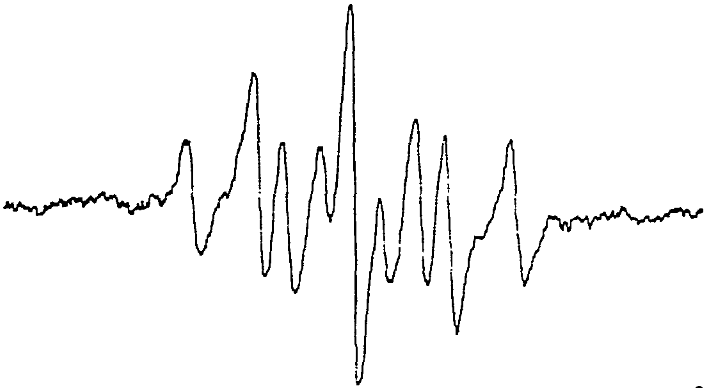


Fig. 7. ESR spectrum of *p*-trimethylgermyl-t-butylbenzene anion, —100°.

We have employed values for h_X and k_{CX} established earlier [3] : $h_{Si} = -2.00$, $h_{Ge} = -1.45$ and for k_{CX}, $k_{CSi} = 0.70$ and $k_{CGe} = 0.40$. The inductive effect of substituents was included via the usual auxiliary inductive parameter [7] :

$$\alpha_{C'} = \alpha_C + \delta h_X \beta_{CC} ; \delta = 0.10$$

Several techniques are commonly used to incorporate alkyl substituents into Hückel calculations [7, 8], but two separate studies of various models indicate that the inductive-hyperconjugative model used below gives best agreement of calculated and experimental spin densities [9, 10]. Methyl groups are considered to be modified vinyl groups, contributing two π-electrons to the system: $C'—C{\equiv}H_3$. Is is also assumed that the methyl groups will have an inductive influence on the coulomb integral of the ring carbon atom that is the site of methyl substitution. The following heteroatom parameters were used for the methyl compounds:

$$\alpha_C = \alpha + h_C \beta_{CC} ; h_C = -0.10$$

$$\alpha_{H_3} = \alpha + h_{H_3} \beta_{CC} ; h_{H_3} = -0.10$$

$$\alpha_{C'} = \alpha + h_{C'} \beta_{CC} ; h_{C'} = -0.30$$

$$\beta_{C'C} = k_{C'C} \beta_{CC} ; k_{C'C} = 1.0$$

$$\beta_{CH_3} = k_{CH_3} \beta_{CC} ; k_{CH_3} = 2.80$$

These differ from those of Sullivan and Bolton [9] only in the value for $k_{C'C}$ of 1.0 rather than 0.80; our value gave slightly better agreement between calculated and experimental spin densities (Table 2). While other, simpler models of alkyl substituents can reproduce ESR results for specific isomeric trimethylsilyltoluenes, only with the inductive-hyperconjugative model has it been possible to obtain one set of transferable heteroatom parameters which work equally well for all isomers [10].

For the t-butyl compounds, $k_{C'C}$ was taken as 1.16 for the germanium compounds and 1.24 for the silicon compounds; C—C hyperconjugation in the t-butyl groups was neglected. The results of the Hückel MO calculations using the models described above for organometal and alkyl substituents are reported in Table 2. Calculated and experimental densities agree to ±0.04 electron in the worst case and usually to ±0.01 electron (the reported charge densities and bond orders are calculated for the neutral molecules). Silicon—carbon π-electron bond orders of ca. 0.20 are comparable to the values found earlier for related compounds [3, 6], and the germanium—carbon π-bond order of 0.14 is identical with that calculated for trimethylgermylbenzene [3]. The extent of dative interaction between the metal pseudo-π-orbital and the benzene π-electron system is indicated by the magnitude of the carbon—metal π-bond order and by the extent of charge transferral to the metal (i.e., metal π-electron charge density: $q_{Si} = 0.04$ and $q_{Ge} = 0.02$ electron). Presumably this dative interaction is the result of a small amount of metal *d*-orbital character in the wave functions of the molecule [3, 6], but the admixture of higher energy, empty AOs of π-symmetry, e.g., 4*p*, cannot be ruled out [11]. (However, since the systems studied all have α-metal substituents, symmetry considerations rule out significant σ/π interactions of the kind that are observed in systems with β-metal substituents [12, 13]). Both the bond order and charge density criteria indicate greater dative interaction to silicon than to germanium. This may be rationalized in terms of better spatial overlap of Si 3*d* AOs with the benzene π-system compared with Ge 4*d* AO overlap.

Experimental

Electron spin resonance spectra. First derivative ESR spectra were determined using a Varian V-4502-13 X-band spectrometer with 100 kHz field modulation, Fieldial, V-4540 variable temperature accessory, and V-4532 dual cavity. Fremy's salt was used as the reference sample in *g*-value determinations by the dual cavity technique. The spectrometer X—Y recorder was calibrated relative to the hyperfine splittings of tetracene radical cation [14]. The appearance, and hence ease of hfcc assignment, of certain ESR spectra was improved by admixing third and fifth derivatives, in appropriate phases and relative magnitudes, with the first derivative spectrum [15]. Anion radicals were prepared from the appropriate organometallic compounds by reduction with sodium—potassium alloy in 2/1 2-methyltetrahydrofuran-1,2-dimethoxyethane solution at —95°, and the spectra were recorded at —70 to —80°. Details of the reduction procedures have been published [16—18].

Materials. *p*-t-Butyltoluene and *p*-di-t-butylbenzene were obtained from Aldrich Chemical Company and were used as received following a purity check by gas chromatography. The three isomeric (i.e., *o*-, *m*- and *p*-)trimethylsilyl toluenes [19] were prepared by Dr. Priscilla Jones of these laboratories. They were purified by preparative scale gas chromatography on a QF-1 (fluorosilicone) column before use.

Analytical data, given for all previously unreported compounds, were determined by Galbraith Laboratories, Knoxville, Tennessee.

p-Trimethylgermyltoluene. An organolithium interconversion reaction was employed in the synthesis of this compound [20]. To 90 ml of 1.6 *M* (0.15 mole) n-butyllithium in hexane (Foote Mineral Co.) under a nitrogen atmosphere, was added a solution of 17.1 g (0.10 mole) *p*-bromotoluene (Aldrich) in 50 ml petroleum ether. The petroleum ether had been freshly dried by distillation from lithium aluminum hydride. This mixture was stirred at gentle reflux for 6 h. Then

8.3 g (0.054 mole) trimethylgermanium chloride (Alfa Inorganics), dissolved in 20 ml dry hexane, was added and the reaction mixture was refluxed for 2 h. Following hydrolysis of any remaining lithium reagent, the organic layer was separated, washed, dried over anhydrous $MgSO_4$, and vacuum distilled. A center cut of 9.4 g (83%) of compound was obtained with b.p. 77 - 78°/12 mm. Gas-chromatographic analysis of the center cut showed it to be quite pure. The infrared spectrum had the characteristic phenyl structure ca. 800 cm^{-1}, methyl C—H absorbtions ca. 3000 cm^{-1}, and the characteristic alkylgermanium absorbtions at 1080 cm^{-1} and 1225 cm^{-1} [21, 22]. NMR (neat) τ 9.67 (s, 9), 7.77 (s, 3) and 2.83 (m, 4, J 8 Hz). Anal. Found: C, 57.72; H, 7.90; Ge, 34.60. $C_{10}H_{16}Ge$ calcd.: C, 57.52; H, 7.72; Ge, 34.76%.

p-t-Butyl(trimethylsilyl)benzene. This compound was synthesized by the lithiation of t-butylbenzene followed by a coupling reaction of the lithium reagent with trimethylchlorosilane. In a 500 ml flask under positive nitrogen pressure, 100 g (0.75 mole) t-butylbenzene (Aldrich) and 5 ml (0.025 mole) *N,N,N',N'*-tetramethylethylenediamine (Aldrich) were stirred overnight with 67 ml (0.10 mole) n-butyllithium (Foote Mineral Co.). To the pale yellow solution which resulted was added a 20 ml (excess of 0.10 mole) trimethylchlorosilane (Dow Corning). Workup and rough distillation of the reaction mixture produced a solution of *p*-trimethylsilyl-t-butylbenzene in t-butylbenzene. The desired compound was collected by preparative scale gas chromatography and identified by its melting point, 78°C (lit. [23] 78°C), and NMR spectrum (CCl_4): τ 9.75 (s, 9, $Si(CH_3)_3$), 8.85 (s, 9, $C(CH_3)_3$), and 2.75 (s, 4, C_6H_4).

p-t-Butyl(trimethylgermyl)benzene. This compound was prepared by a coupling reaction between *p*-t-butylphenyllithium and trimethylgermanium chloride in anhydrous ether solution under argon atmosphere. 10 ml (0.05 mole) *p*-bromo-t-butylbenzene (Columbia Chemicals) was treated with 0.52 g (0.075 mole) lithium wire and 7.7 g (0.05 mole) trimethylgermanium chloride (Alfa Inorganics). On workup and vacuum distillation, a white oily solid was collected, b.p. 75 - 80°C/0. 5 - 1.0 mm, m.p. 72 - 75°C. After purification by vacuum sublimation, the compound was identified by physical properties: IR: $Ge—CH_3$ 1070 cm^{-1}, NMR (CCl_4): τ 9.65 (s, 9, $Ge(CH_3)_3$), 8.70 (s, 9, $C(CH_3)_3$), and 2.70 (s, 4, C_6H_4). Anal. Found: C, 62.13; H, 8.79; Ge, 29.17. $C_{13}H_{22}Ge$ calcd.: C, 62.23; H, 8.84; Ge, 28.93%.

Hereafter, the "standard procedure" refers to coupling reactions involving lithium reagents generated from the reaction of an aryl bromide and metallic lithium.

p-t-Butyl(trimethylstannyl)benzene. This compound was prepared by the standard procedure: 10 ml (0.05 mole) *p*-bromo-t-butylbenzene (Columbia Chemicals) was treated with 0.52 g (0.075 mole) lithium wire and 10.0 g (0.05 mole) trimethylstannyl chloride (Alfa Inorganics). After the workup, the reaction mixture was distilled with difficulty, b.p. ca. 80°C/0.5 mm; m.p. 56 - 60°C. Physical properties confirmed that the desired compound was obtained: NMR (CCl_4): τ 10.03 (s, 9, $Sn(CH_3)_3$), 9.07 (s, 9, $C(CH_3)_3$), and 3.00 (s, 4, C_6H_4). Anal. Found: C, 52.72; H, 7.60; Sn, 39.68 (by difference). $C_{13}H_{22}Sn$ calcd.: C, 52.57; H, 7.47; Sn, 39.96%.

1-Ethyl-4-trimethylsilylbenzene. By the standard procedure, 10.0 ml (0.070 mole) 1-bromo-4-ethylbenzene (Aldrich) was treated with 1.0 g (0.14 mole) lithium wire in the presence of 10 ml (excess of 0.070 mole) trimethylchlorosilane (Dow Corning). Workup of the reaction mixture and vacuum distillation produced a center cut of 8.3 g (66%) of compound with b.p. 88 - 90°C/8 mm (lit. [24] 94 - 99°/17 mm; 207 - 208.5°/760 mm. NMR (CCl_4): τ 9.8 (s, 9, $Si(CH_3)_3$, 8.8 (t, 3, J 8 Hz, CH_2CH_3), 7.4 (q, 2, J 8 Hz, CH_2CH_3), and 2.9 (m, 4, J 8 Hz, C_6H_4).

1-Isopropyl-4-trimethylsilylbenzene. By the standard procedure, 10.0 g (0.050 mole) 1-bromo-4-isopropylbenzene (K and K laboratories) was treated with 1.0 g (0.14 mole) lithium wire in the presence of 10.0 g (0.09 mole) trimethylchlorosilane (Dow Corning). Workup of the reaction mixture followed by vacuum distillation yielded a center cut of 6.6 g (69%) of compound with b.p. 110 - 111°C/8 mm (lit. [24] 126 - 127°/40 mm, 222°/760 mm). NMR (CCl_4): τ 9.85 (s, 9, $Si(CH_3)_3$), 8.85 (d, 6, J 7 Hz, $CH(CH_3)_2$), 7.25 (m, 1, J 7 Hz, $CH(CH_3)_2$ and 2.9 (m, 4, J 8 Hz, C_6H_4).

α,p-Bis(trimethylsilyl)toluene. By the standard procedure, 11.5 g (0.046 mole) α, *p*-dibromotoluene (Aldrich) was treated with 1.3 g (0.184 mole) lithium in the presence of 10 g (excess of 0.10 mole) trimethylchlorosilane (Dow Corning). Following the workup of the reaction mixture, a vacuum distillation produced a center cut of 6.9 g (64%) of compound with b.p. 136 - 138°C/10 mm, (lit. [25] 85 - 86°/4 mm, 151.5°/45 mm). NMR (CCl_4): τ 9.9 (s, 9, $Si(CH_3)_3$), 9.65 (s, 9, $Si(CH_3)_3$); 7.85 (s, 2, $CH_2Si(CH_3)_3$) and 2.8 (m, 4, C_6H_4).

2-Trimethylsilyl-m-xylene. By the standard procedure, 10.0 g (0.054 mole) 2-bromo-*m*-xylene (Aldrich) was treated with 0.75 g (0.108 mole) lithium wire in the presence of 5.9 g (0.054 mole) trimethylchlorosilane (Dow Corning). Following the workup of the reaction mixture, a vacuum distillation produced a center cut of 5.1 g (53%) of compound with b.p. 94 - 95°C/7 mm (lit. [26] 85 - 86°/5 mm, 224 - 226°/760 mm). NMR (CCl_4): τ 9.7 (s, 9, $Si(CH_3)_3$), 7.7 (s, 6, CH_3) and (3.25 (m, 3, C_6H_3)).

5-Trimethylsilyl-m-xylene. By the standard procedure, 10.0 g (0.054 mole) 5-bromo-*m*-xylene (Aldrich) was treated with 0.75 g (0.11 mole) lithium wire in the presence of 5.9 g (0.054 mole) trimethylchlorosilane (Dow Corning). Following workup of the reaction mixture, a vacuum distillation yielded a center cut of 6.0 g (62%) of compound with b.p. 94 - 96°C/8 mm (lit. [26] 73 - 74°/4 mm, 210°/760 mm) [27]. NMR (CCl_4): τ 9.8 (s, 9, $Si(CH_3)_3$), 7.85 (s, 6, CH_3), 3.3 (s, 1, C_6H_3) and 3.2 (s, 2, C_6H_3).

2-Trimethylsilylmesitylene. By the standard procedure, 10.0 g (0.05 mole) 2-bromomesitylene (Eastman Kodak) was treated with 0.69 g (0.10 mole) lithium metal in the presence of 5.5 g (0.05 mole) trimethylchlorosilane (Dow Corning). Following the workup of the reaction mixture, a vacuum distillation produced a center cut of 5.8 g (60%) of compound with b.p. 111 - 112°C/5 mm (lit. [27] 225 - 230°/760 mm). NMR (CCl_4): τ 9.85 (s, 9, $Si(CH_3)_3$), 8.00 (s, 3, CH_3), 7.85 (s, 6, CH_3) and 3.55 (s, 2, C_6H_2).

m-Bromo-t-butylbenzene. This compound was not commercially available and was required as a starting material for the syntheses of 1-trimethylsilyl-3-t-butylbenzene and 1-trimethylgermyl-3-t-butylbenzene. The route chosen for this synthesis was as follows: t-butylbenzene was nitrated to produce *p*-t-butylnitrobenzene which was then reduced to *p*-t-butylaniline, which was finally then converted to the acetamide [28]. Bromination of the acetamide was patterned after a procedure reported by Johnson and Sandborn for the bromination of toluidine [29]. Then 2-bromo-4-t-butylamiline was recovered from the acetamide; finally, a diazotization reaction adapted from the work of Marvel et al. completed the synthesis [30]. In the manner outlined, one mole of t-butylbenzene was converted into 40 g (20% overall) of *m*-bromo-t-butylbenzene.

1-Trimethylsilyl-3-t-butylbenzene. The standard procedure was followed using 10.4 g (0.05 mole) of the custom-synthesized *m*-bromo-t-butylbenzene and 1.0 g (0.14 mole) lithium wire in the presence of 7.5 g (0.05 mole) trimethylchlorosilane (Dow Corning). Following the workup of the reaction mixture, a vacuum distillation produced a center cut of 4.9 g (48%) of compound with b.p. 105 - 108°C/9 mm (lit. [24] 82°/6 mm). NMR (neat): τ 9.75 (s, 9, $Si(CH_3)_3$), 8.70 (s, 9, $C(CH_3)_3$); 2.75 (m, 3, C_6H_4) and 2.43 (s, 1, C_6H_4).

1-Trimethylgermyl-3-t-butylbenzene. The standard procedure was followed using 10.4 g (0.05 mole) *m*-bromo-t-butylbenzene and 0.7 g (0.10 mole) lithium wire in the presence of 7.6 g (0.05 mole) trimethylgermanium chloride (Alfa Inorganics). Following workup of the reaction mixture, a vacuum distillation yielded a center cut of 4.9 g (41%) of compounds with b.p. 78°C/2 mm. NMR (neat): τ 9.77 (s, 9, $Ge(CH_3)_3$), 8.70 (s, 9, $C(CH_3)_3$), 2.78 (s, 3, C_6H_4) and 2.50 (s, 1, C_6H_4). Anal. Found: C, 62.03; H, 8.86; Ge, 28.87. $C_{13}H_{22}Ge$ calcd.: C, 62.23; H, 8.84; Ge, 28.93%.

Acknowledgement

This research was sponsored by the United States Air Force Office of Scientific Research (SRC), OAR, USAF, Grant No. AF-AFOSR 69-1772.

References

1 J.A. Bedford, J.R. Bolton, A. Carrington and A.H. Prince, Trans. Faraday Soc., 59 (1962) 53.
2 G. Vincow, in E.T. Kaiser and L. Kevan (Eds.), Radical Ions, Interscience, New York, 1968.
3 H.J. Sipe, Jr. and R. West, J. Organometal. Chem., 70 (1974) 353.
4 H.M. McConnell, J. Chem. Phys., 24 (1956) 632; 24 (1956) 764.
5 P.H. Rieger and G.K. Fraenkel, J. Chem. Phys. 37 (1962) 2795.
6 M.D. Curtis and A.L. Allred, J. Amer. Chem. Soc., 87 (1965) 2554.
7 A.J. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, Wiley., New York, 1961, p 117 ff.
8 A. Streitwieser, Jr. and P.M. Nair, Tetrahedron, 5 (1959) 149.
9 P.D. Sullivan and J.R. Bolton, J. Amer. Chem. Soc., 90 (1968) 5366.
10 H.J. Sipe, Jr., Ph.D. Dissertation, University of Wisconsin, Madison, Wisconsin, 1969.
11 C.G. Pitt, R.N. Carey and E.C. Toren, Jr., J. Amer. Chem. Soc., 94 (1972) 3806.
12 T. Kawamura, P. Meakin and J.K. Kochi, J. Amer. Chem. Soc., 94 (1972) 8065.
13 D. Griller and K.U. Ingold, J. Amer. Chem. Soc., 95 (1973) 6459.
14 M.K. Carter and G. Vincow, J. Chem. Phys., 47 (1967) 292.
15 S.H. Glarum, Rev. *Sci. Inst.*, 36 (1965) 771.
16 D.E. Paul, D. Lipkin and S.A. Weissman, J. Amer. Chem. Soc., 78 (1956) 116.
17 G.R. Husk and R. West, J. Amer. Chem. Soc., 87 (1965) 3993.
18 P.R. Jones and R. West, J. Amer. Chem. Soc., 90 (1968) 6978.
19 R. West and P.C. Jones, J. Amer. Chem. Soc., 90 (1968) 2656.
20 H. Gilman, W. Langham and F.W. Moore, J. Amer. Chem. Soc., 62 (1940) 2327.
21 E.G. Rochow, J. Amer. Chem. Soc., 73 (1951) 5486.
22 R. West, J. Amer. Chem. Soc., 75 (1953) 6080.
23 C. Eaborn, J. Chem. Soc., (1956) 4858.
24 R.A. Benkeser, R.A. Hickner and D.I. Hoke, J. Amer. Chem. Soc., 80 (1958) 2279.
25 C. Eaborn and S.H. Parker, J. Chem. Soc., (1955) 126.
26 R.A. Benkeser, D.I. Hoke and R.A. Hickner, J. Amer. Chem. Soc., 80 (1958) 5294.
27 C. Eaborn and R.C. Moore, J. Chem. Soc., (1959) 3640.
28 R. Adams, J.R. Johnson and C.F. Wilcox, Jr., Laboratory Text in Organic Chemistry, 5th ed., MacMillan, New York, N.Y., 1963.

29 R. Johnson and L.T. Sandborn, Organic Syntheses, Collective Vol. I, Wiley., New York, N.Y., 1942, p 111 ff.
30 C.S. Marvel, J. Amer. Chem. Soc., 66 (1944) 914.
31 J. Colpa and E. de Boer, J. Phys. Chem., 71 (1967) 21.
32 F. Gerson, J. Henzer, H. Bock, H. Alt and H. Seidl, Helv. Chim. Acta, 51 (1968) 707.
33 V.M. Kayakova et al., Zh. Strukt. Khim., 13 (1972) 28.