saturated aqueous NH_4Cl. The aqueous layer was extracted with ether (4 × 250 mL). The extracts were washed with 10% aqueous $Na_2S_2O_3$ and dried ($MgSO_4$). Removal of solvent left a dark brown oil (113.5 g, 65%). To the crude oil in CCl_4 at 0 °C was added *tert*-butyl hypochlorite (500 mmol, 54.35 g, 54.1 mL). The resulting yellow precipitate was recrystallized from $CHCl_3$ to give 105.5 g (260.8 mmol, 85%) of chloroiodinane **15**: mp 166–168 °C; ^1H NMR ($CDCl_3$–Et_2O) δ 7.63–7.88 (m, 3), 8.09 (d, 1, H ortho to I); ^{19}F NMR ($CDCl_3$–Et_2O) δ −76.2 (s). Into a solution of 105.5 g of **15** in 500 mL of $CHCl_3$ was bubbled H_2S for 1 h. The product, an orange oil, was distilled (75–78 °C, 0.28 torr) to give iodo alcohol **11b** as a clear oil which crystallized as the dihydrate (81.1 g, 199.8 mmol, 76.6%, overall from **3**, 42.3%): mp 30–32 °C; ^1H NMR δ 7.07 (t of d, 1, J = 7.8, 1.2 Hz, H para to fluoroalkyl), 7.40 (t of d, 1, J = 7.8, 1.8 Hz, H para to I), 7.60 (d, 1, J = 8.4 Hz, H ortho to fluoroalkyl), 8.10 (dd, 1, J = 7.8, 1.2 Hz, H ortho to I); ^{19}F NMR δ −74.05 (s); mass spectrum (70 eV), *m/e* (relative intensity) 370 (100.0, M^+), 301 (73.6, $M^+ - CF_3$), 231 (62.3, $M^+ - CF_3 - HCF_3$), 204 (12.4, $M^+ - HI - F_2$), 145 (25.7), 123 (12.6), 105 (40.97), 77 (22.2), 76 (14.5), 69 (10.1, CF_3), 50 (10.45, CF_2). Anal. ($C_9H_5F_6OI{\cdot}2H_2O$) C, H, I.

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′(3*H*,3′*H*)-spirobi[2,1-benzoxasilole] (12). A solution of lithium reagent **3** (0.745 mol, method B) was added over 45 min at −78 °C to stirred silicon tetrachloride (74.0 g, 0.436 mol) under N_2. The mixture was stirred at 25 °C for 12 h. After being quenched with water (50 mL) the mixture was dissolved in ether and extracted with 0.5 M HCl (4 × 300 mL) and water (300 mL). The ether phase was dried ($MgSO_4$) and filtered, and the solvent removed under vacuum. The residue was crystallized from hexane to give an off-white solid (119 g, 0.232 mol, 62.4%). Recrystallization of a portion of the crude product (54.6 g, 0.107 mol) from hexane followed by sublimation gave **12** (36.7 g, 0.0716 mol, 67.0%): mp 131.8–132.2 °C; ^1H NMR δ 7.9–7.55 (m); ^{19}F NMR δ −76.35 and −76.8 (A_3B_3, J_{FF} = 7.8 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 512 (55.56, M^+), 443 (100.00, $M^+ - CF_3$), 239 (78.71). Anal. ($C_{18}H_8F_{12}O_2Si$) C, H, F.

Reactions of Silane 12. (a) With Phenyllithium. To silane **12** (1.036 g, 2.02 mmol) in 5 mL of THF under N_2 was added phenyllithium (1.01 mL of a 2.0 M solution in 70:30 benzene–ether, 2.02 mmol). The mixture was stirred for 1 h, warmed to 25 °C, extracted with water, and dried ($MgSO_4$), and the solvent removed under vacuum to give off-white solid (1.1 g, 1.85 mmol, 91.3%). Recrystallization of 245 mg of product from pentane–chloroform–ether gave white needles (0.060 g, 0.101 mmol, 24.5%): ^1H NMR (acetone-d_6) shows the four aromatic peaks characteristic of **6d** with minor peaks for ether and THF; ^{19}F NMR (acetone-d_6) δ −73.4 and −74.7 (A_3B_3, $J_{FF} \simeq$ 8 Hz). Tetramethylammonium bromide (0.178 g, 1.16 mmol) was added to a solution of crude product (0.23 g, 0.386 mmol) in 15 mL of water to give a white precipitate (0.18 g, 0.302 mmol, 70.3%): ^1H NMR (acetone-d_6) shows the four aromatic peaks characteristic of **6d** and that due to tetramethylammonium cation; minor impurity peaks occur at δ 8.1 and 2.8; ^{19}F NMR (acetone-d_6) δ −73.3 and −74.6 (A_3B_3, J_{FF} = 9.3 Hz) for silicate **6d** (combined integration = 58.9% with a multiplet hidden superposed on the peak at −74.6 (41.1%)).

(b) With 4-(Dimethylamino)pyridine. To silane **12** (0.0529 g, 0.103 mmol) in 1.5 mL of $CHCl_3$ was added 4-(dimethylamino)pyridine (0.0139 g, 0.114 mmol). After 90 min of stirring a precipitate was removed by filtration, washed ($CHCl_3$), and dried to give 0.0309 g of silicate **13** (47.2%), mp 192–195 °C. A sample was purified by sublimation [140 °C (0.05 torr)]: mp 203–206 °C; ^1H NMR (THF-d_8) δ 7.98 (m, 4.0, H ortho to Si on spirobicyclic rings and on pyridine ring), 7.36 and 7.14 (m, 5.9, remaining H on spirobicyclic rings), 6.74 (d, 2.0, remaining H on pyridine ring), 3.08 (s, 5.9, $N(CH_3)_2$); ^{19}F NMR (THF-d_8) δ −72.9 and −74.3 (A_3B_3, J_{FF} = 8.5 Hz); FD mass spectrum (3.0 kV), *m/e* (relative intensity) 635 (1.97, $M^+ + 1$) 513 (100.00, $M^+ + 1 - NC_5H_4N(CH_3)_2$), 123 (99.9, $^+NC_5H_4N(CH_3)_2 + H$), 122 (96.1, $^+NC_5H_4N(CH_3)_2$). Anal. Calcd for $C_{25}H_{18}F_{12}N_2O_2Si$: C, 47.32; H, 2.86; N, 4.42. Found: C, 46.83; H, 3.05; N, 4.20.

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Registry No. 3, 70091-67-7; **5**, 718-64-9; **6a**, 70083-64-6; **6b**, 70083-66-8; **6c**, 70083-67-9; **6d**, 70083-69-1; **7a**, 76215-46-8; **7b**, 64343-89-1; **8**, 76248-61-8; **9**, 70091-68-8; **10**, 76248-62-9; **11a**, 28180-48-5; **11b**, 76215-47-9; **12**, 70091-69-9; **13**, 76233-03-9; **15**, 76215-48-0; $PhSiCl_3$, 98-13-5; $POCl_3$, 10025-87-3; $SOCl_2$, 7719-09-7; S, 7704-34-9; $BrCH_2CA_2Br$, 106-93-4; $SiCl_4$, 10026-04-7; PhLi, 591-51-5; *p*-$Me_2NC_5H_5N$, 1122-58-3; Br_2, 7726-95-6; I_2, 7553-56-2; CH_3SiCl_3, 75-79-6.

Free-Radical and Anion Intermediates in the Reactions of 5-Halo-2-norbornenes and 3-Halonortricyclenes with (Trimethyltin)sodium

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The reaction of (trimethyltin)sodium with *exo*-5-chloro- and 5-bromo-2-norbornenes, *endo*-5-bromo-2-norbornene, and 3-bromo- and 3-iodonortricyclene in tetrahydrofuran has been examined. Use of dicyclohexylphosphine as a trap for intermediate radicals by hydrogen atom transfer showed that the bromides and chloride reacted predominantly by way of free-radical intermediates and by geminate reactions. The geminate products showed complete equilibration of the intermediate radicals. 3-Iodonorbornene reacted predominantly by an anionic intermediate mechanism as shown by trapping of the anions with *tert*-butylamine.

The reactions of group 4 organometallic anionoids with organic halides are frequently useful in synthesis. They also display characteristics which suggest interesting mechanistic diversity. Yet they have received relatively little attention and are not well understood. Thus one has little basis upon which to select reaction parameters which will lead to satisfactory yields in synthetic applications. These observations, along with interesting observations on the stereochemistry as a function of solvent,[1-3] have led us into a systematic study of the mechanism of organotin alkalis with organic halides. Among the general mechanisms which have been suggested are direct processes involving S_N2 displacement on carbon[2-6] or four-center al-

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Table I. Reaction of 3-Iodonortricyclene (RX) with (Trimethyltin)sodium in THF at 0 °C

entry	[Me_3SnNa], M	[RX], M	addend (concn, M)	% NT-*Sn*	% *exo*-NB-*Sn*	% NB-H	% NT-H	% total
1	0.24	0.14		60	12	12	11	95
2	0.24	0.14	TBA (0.13)	14	1.8	8	74	98
3	0.24	0.15	TBA (0.32)	13	2.4	6	73	95
4	0.24	0.15	TBA (0.70)	9	2.0	6	76	93
5	0.24	0.15	TBA (1.4)	8	2.0	6.5	79	95
6	0.24	0.14	TBA (1.7)	7	1.6	8.8	81	98
7	0.27	0.15	DCPH (0.9)	25	2.4	16	52	95
8	0.36	0.19	TBA (1.9), DCPH (1.3)	5	<1	18	77	100

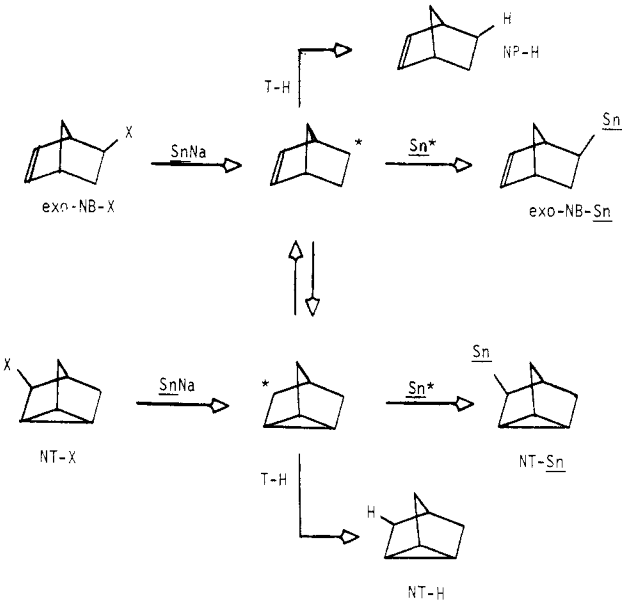
kyl-metal exchange,[3] those involving carbanion intermediates,[1,3,4,7,8] and those involving free radicals.[3,4,8,9] Two or even three of the mechanisms may occur in competition in the reaction with a given halide.[10,11] This has been established by trapping free-radical intermediates with dicyclohexylphosphine and anionic intermediates with *tert*-butyl alcohol or *tert*-butylamine.

In the work repored here we have chosen to examine norbornenyl and nortricyclyl halides. Because of steric and anglular strain in the transition state, the S_N2 mechanism would have a high activation energy, making it probable that the free-radical and/or anionic mechanisms would be the dominant processes. Both trapping studies and the facile interconversion of nortricyclyl and norbornenyl intemediates also could serve as probes for providing complementary information.

Results

Replicate reactions of the halides with (trimethyltin)sodium in tetrahydrofuran (THF) were conducted usually at 0 °C. Control experiments established the course of the overall reactions which gave high yields of isomeric substitution products (Scheme I). Trapping of carbanion intermediates was effected with *tert*-butylamine (TBA).[10,11] Dicyclohexylphosphine (DCPH) was used to trap free radicals.[10,11] It also traps anions because its p*K* of about 38 is sufficiently low to make it a good proton donor to simple carbanions. However, it proved to be less efficient than TBA in this respect in most cases. If both TBA and DCPH effected trapping, experiments were also conducted with both used together. Results will be discussed in terms of Scheme I in which *Sn* is Me_3Sn, an asterisk on carbon represents an unpaired electron or a halogen atom, and T-H represents either TBA or DCPH as a proton or hydrogen atom donor. The reactions between T-H and R* must occur after the latter have diffused from the solvent cage in which they were formed. Those between *Sn** and *R** may be geminate and, therefore, could not be distinguished in this study from direct reaction between RX and *Sn*Na.

Scheme I



When DCPH was effective in trapping R·, the appearance of hexamethylditin (*Sn*–*Sn*) was noted along with a peak in the gas chromatogram with a higher retention time than that of DCPH. This suggests that the stoichiometry of the trapping reaction in such a case is as shown in eq 1. Similarly, when TBA was effective in trapping, the

$$2RX + 2\,SnNa + 2R_2PH \rightarrow 2RH + Sn\text{–}Sn + R_2P\text{–}PR_2 + NaX \quad (1)$$

appearance of hexamethylditin was noted, but no other new peak appeared in the chromatogram, suggesting the overall reaction of eq 2. The *Sn*–*Sn* of eq 1 is formed by

$$RX + 2SnNa + 2RNH_2 \rightarrow RH + Sn\text{–}Sn + RNHNa + NaX \quad (2)$$

coupling of *Sn*·, and that of eq 2 is formed by the reaction between *Sn*X and *Sn*Na. To assure complete consumption of halide, we used an excess of (trimethyltin)sodium in all experiments. High mass balances of the C_7 units indicated that no significant side reactions were consuming the halides.

The 3-substituted nortricyclenes and 5-substituted 2-norbornenes are designated in the following text and in the tables by symbols shown in Scheme I.

3-Iodonortricyclene. Results obtained with NT-I are gathered in Table I. Entry 1 shows that good yields of the substitution products NT-*Sn* and *exo*-NB-*Sn* are obtained, with the former predominating by a factor of 5. In addition, about equal amounts of NT-H and NB-H are obtained. Entries 2–6 reveal that TBA causes an increase in the yield of the hydrocarbons at the expense of the organtins. Only about 9% of the latter is obtained at the highest TBA concentration. The presence of DCPH also increases the yield of reduction products at the expense of substitution, but the effect for a given concentration is

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Table II. Reaction of 5-Bromo-2-norbornenes (NB-Br) with (Trimethyltin)sodium in THF at 0 °C

entry	isomer	[Me$_3$SnNa], M	[RX], M	addend (concn, M)	% NT-*Sn*	% *exo*-NB-*Sn*	% NB-H	% NT-H	% total
1	exo	0.38	0.17		73	26	0	0	99
2		0.38	0.17	TBA (0.58)	69	22	3	<1	95
3		0.31	0.16	DCHP (0.51)	35	12	25	28	100
4		0.31	0.16	DCHP (0.98)	22	7	34	35	98
5		0.31	0.16	DCHP (1.5)	22	7	37	36	102
6	endo	0.36	0.14		73	26	0	0	99
7		0.36	0.14	TBA (0.49)	67	21	2.9	1.5	93
8		0.36	0.14	DCPH (0.49)	47	15	19	16	97
9		0.37	0.11	DHPH (0.66)	37	12	25	22	96
10		0.37	0.11	DCPH (0.99)	29	9	28	27	93
11		0.37	0.12	DCPH (1.3)	25	8	34	33	100

Table III. Reaction of 3-Bromonortricyclene (RX) with (Trimethyltin)sodium in THF

entry	[Me$_3$SnNa], M	[RX], M	addend (concn, M)	% NT-*Sn*	% *exo*-NB-*Sn*	% NB-H	% NT-H	% total
1	0.35	0.25		72	23	<1	<1	95
2	0.35	0.23	TBA (0.69)	72	26	3.0	<1	100
3	0.31	0.14	DCPH (0.42)	58	18	12	13	101
4	0.30	0.14	DCPH (0.84)	45	12	21	21	99
5	0.35	0.14	DCPH (1.2)	35	8.1	24	27	94
6	0.30	0.15	DCPH (1.7)	22	5.5	35	37	98
7	0.35	0.22	 (0.66)	70	21	<1	<1	92

Table IV. Reaction of *exo*-5-Chloro-2-norbornene (RX) with (Trimethyltin)sodium in THF at 23 ± 1 °C

entry	[Me$_3$SnNa], M	[RX], M	addend (concn, M)	% NT-*Sn*	% NB-*Sn*	% NB-H	% NT-H	% total
1	0.40	0.14		71	25	0	0	96
2	0.44	0.14	TBA (0.42)	71	26	0	0	97
3	0.44	0.14	DCPH (0.42)	59	23	5.2	5.4	93
4	0.44	0.14	DCPH (0.81)	55	23	9.3	9.7	98
5	0.44	0.13	DCPH (1.2)	35	23	15	17	90

smaller than that for TBA. When the two traps were used together (entry 8), the yields of substitution products were decreased to ca. 6% from the 10% formed when TBA was used alone. The ratio of NT-H to NB-H changes from unity in the absence of a trap to 3.25 in the presence of 0.9 M DCPH and to about 10 in the presence of 1.7 M TBA.

5-Bromo-2-norbornenes. Both the exo and endo isomers were examined with the results displayed in Table II. The results are strikingly similar for the two cases. In the absence of a trap virtually quantitative yields of NT-*Sn* (73%) plus NB-*Sn* (26%) were obtained with no detectable hydrocarbon products. In the presence of TBA the yields were similar although small amounts of the hydrocarbons (<4%) were observed. In the presence of increasing amounts of DCPH the yield of substitution products decreased to about 30% while that of the hydrocarbons increased to about 70%. The NT-*Sn* and NB-*Sn* formed by the geminate reaction were in the ratio of 3:1, and the same was true of that formed from trappable radicals which was taken as the difference between the amounts formed in the experiments of entries 1 and 5 and of entries 6 and 11. The results are seen to be almost identical, the exception being that trapping by DCPH appears to be more efficient at the lower concentrations with the exo isomer than with the endo.

3-Bromonortricyclene. In this case, as with the isomeric bromides, the yield of substitution products was virtually quantitative, with only traces of reduction products being observed (Table III). TBA gave only 4% of hydrocarbon, but increased amounts were formed with increased concentrations of DCPH. NB-H and NT-H were formed in essentially equal amounts. The geminate NT-*Sn*/NB-*Sn* ratio was 4 for geminate reaction and about 2.9 for product formed from diffusive combination of radicals. These results are, as expected for free-radical processes, very similar to those obtained for the bromonorbornenes.

The high efficiency of DCPH as a radical trap was emphasized by the observations that 1,4-cyclohexadiene was ineffective as a trap, as shown by the results in entry 7.

***exo*-5-Chloro-2-norbornene.** Entries 1 and 2 of Table IV show that the results with this chloride are very much like those observed with the three bromides discussed above in the absence of a trap and in the presence of TBA. Qualitatively they are also similar when DCPH is present. However, there is a significant quantitative difference. At 1.2 M DCPH a total of 32% of hydrocarbons is formed from *exo*-NB-Cl whereas at 0.98 M DCPH the hydrocarbon yield is 73% from *exo*-NB-Br. This indicates considerably more geminate reaction in the case of the chloride. It should be noted that the yield of *exo*-NB-*Sn* from *exo*-NB-Cl remains almost constant in all five experiments. This suggests the possibility of an S_N2 mechanism as its origin. But inversion should yield *endo*-NB-*Sn*. Careful examination of its proton magnetic resonance spectrum showed that the methyl protons at tin appeared at δ 0.02 vs. δ −0.13 for the endo isomer, and the vinyl protons appeared as two unsymmetrical quartets centered at δ 6.10 and 5.81 vs. a triplet centered at δ 5.90 for the endo isomer.[12]

3-Chloronortricyclene. Satisfactory results were not obtained with this substrate. The reaction was extremely slow at ambient temperature—about 50% reaction occurred in 1 day, and only a half of the halide which was

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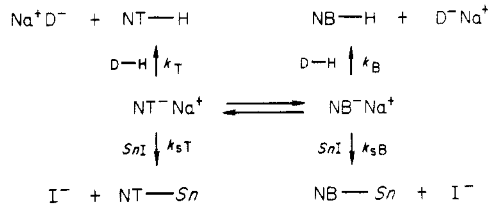
[12] Kennedy, J. D.; Kuivila, H. G.; Pelczar, F. L.; Tien, R. Y.; Considine, J. L. *J. Organomet. Chem.* 1973, *61*, 167.

Scheme II



consumed could be accounted for as substitution or reduction product. The rate or course of the reaction was not affected by the presence of 0.76 M TBA. The presence of DCPH in concentrations up to 1.4 M resulted in decreases in the rate of the reaction, the appearance of reduction products, and the absence of substitution products, suggesting that no geminate reaction occurs in this case. However, the nature of the results does not permit definitive conclusions to be drawn.

Discussion

The results of the reaction of NT-I with Me_3SnNa clearly indicate that the reaction goes entirely by a halogen–metal exchange process followed by reaction of nongeminate NT-Na and NB-Na with Me_3SnI. They also permit elimination of a two-step electron-transfer for the halogen–metal mechanism as shown in eq 3. The results

$$\text{NT-I} + Sn\text{Na} \rightarrow \text{NT}{\cdot}Sn{\cdot}\text{Na}^{+}\text{I}^{-} \rightarrow \text{NT}^{-}Sn^{+}Na^{+}\text{I}^{-} \qquad (3)$$

obtained with the bromides, which display electron transfer, lead to at least 30% of geminate product formation. The iodide leads to less than 6% of geminate product formation. The process of eq 3 thus is reasonable only if the presence of iodide in the geminate cluster leads to much faster electron transfer or slower alkyl–trimethyltin radical coupling than the presence of bromide.

The ratio % NT-H/% NB-H is nearly constant with a value of 10 ± 2 in the TBA trapping experiments. This suggests equilibration of the carbanions as depicted in Scheme II. If D-H is the solvent, k_T and k_B are slow relative to the equilibration of the anions, and the distribution of hydrocarbon products is determined by the position of the equilibrium and the magnitudes of k_T and k_B. When D-H is TBA, these rate constants are much larger, the NT^- can be trapped to a large extent before conversion to NB^-, and NT-H is the major reduction product. When D-H is DCPH, the rate constants are intermediate, and NT-H predominates over NB-H as reduction product, but to a lesser degree than in the case of TBA. Similarly, *Sn*I reacts, with rate constant k_{sT}, sufficiently fast so that only partial equilibration occurs, and NT-*Sn* is formed in greater yield than NB-*Sn*. These results for trapping of the anions with proton donors differ from those observed by Stille and Sannes.[13] They generated the nortricyclyl and the 5-norbornenyl anions by oxidation of the hydrazines in basic *tert*-butyl alcohol or water and found a 57:43 ratio of nortricyclene to norbornene. This could well be due to solvent effects on the equilibria between the carbanions. However, these results do indicate that the equilibration of the anions is fast because it is complete in the presence of much better proton donors than TBA.

In the trapping experiments with TBA or DCPH alone the yield of *exo*-NB-*Sn* remained essentially constant while that of NT-*Sn* varied with the concentration of TBA. Also the yield of NT-*Sn* was unexpectedly high when DCPH was the trap. The reasons for these observations are obscure at this time. A similar phenomenon was observed in the reaction of *exo*-NB-Cl from which the yield of NB-*Sn* remained virtually constant as the DCPH concentration was varied, although the yield of NT-*Sn* decreased with increased DCPH concentration (Table IV).

We previously observed that cyclic secondary bromides such as cyclopentyl, cyclohexyl, and 2-adamantyl reacted by a free-radical mechanism.[11] In these cases less than 7% of geminate reaction was observed with concentrations of DCPH around 1.8 M. The 5-bromo-2-norbornenes and 3-bromonortricyclene studied in this work showed 32% and 28% coupling of trimethyltin and cycloalkyl radicals, respectively. These figures are somewhat higher than have been usually observed. The reduction products NT-H and NB-H are formed in essentially equal amounts. The geminate coupling products NT-*Sn* and *exo*-NB-*Sn* are formed in a ratio of about 3:1, and the products formed from coupling of diffusively separated radicals are formed in the ratio of about 2.7:1 from all three isomeric bromides. This reveals that equilibration of the norbornenyl and nortricyclyl radicals is fast relative to their rates of diffusive separation. Because this also indicates anticipated low activation energies for coupling, the figure 2.7:1 should represent reasonably well the proportions of the isomeric radicals at equilibrium. Thus the fact that equal amounts of reduction products result from trapping of the radicals by DCPH suggests that norbornenyl radicals react about 2.7 times faster with DCPH than do nortricyclyl radicals.

The norbornenyl–nortricyclyl radical system has been the subject of a number of investigations.[14] Germane to this work are observations concerning the rate constant for the interconversion of the radicals. On the basis of limited data on the triphenyltin hydride reduction of 3-bromonortricyclene,[15] one estimate for this constant is about 10^8 s^{-1}.[16] Another study on the 7-acetoxy analogue led to a value of 4×10^7 s^{-1}.[17] Our results indicate a value of at least 10^9 s^{-1} because the equilibration of the isomers competes effectively with diffusion.

Experimental Section

General Methods. Proton nuclear magnetic resonance spectra were obtained at 60 MHz by using a Varian A-60A instrument. Samples requiring ^{13}C spectra were obtained at 90 MHz by using a Bruker WH-90 NMR spectrometer. Analytical gas chromatographic analyses were performed on an F&M Hewlett-Packard Model 5750 instrument equipped with a thermal-conductivity detector. Analysis of the products from the norbornenyl and nortricyclyl halides was performed on a 16 ft × 0.25 in stainless-steel column packed with 10% Apiezon L on Chromosorb W, AW-DMCS. The injection port and detector were maintained in the temperature range of 250–270 °C. Peak areas in the chromatogram were determined by digital integration with a Columbia Scientific Industries automatic digital integrator, Model CRS-208, equipped with an angular base-line corrector and a digital printer. Yields were determined by using internal standard techniques, with standardization plots as response factors obtained from authentic samples.

All reactions with (trimethyltin)sodium were conducted under an atmosphere of high-purity nitrogen (99.996%). Tetrahydrofuran (THF) was dried by distillation from molten potassium. 3-Bromonortricyclene was prepared by the method of Kwart and Kaplan.[18] *exo*-5-Bromo-2-norbornene was prepared by the

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method of Kwart and Kaplan.[19] The endo isomer was prepared by the method described by Roberts et al.[20] 5-Chloro-2-norbornene was obtained by the addition of hydrogen chloride to norbornadiene.[19] 3-Chloronortricyclene was prepared by the addition of chlorine to norbornene.[21]

3-Iodonortricyclene was prepared by the following modification of the procedure of Diner and Lown.[22] Silver nitrate (61.1 g, 0.36 mol) was dissolved in 300 mL of chloroform and 150 mL of pyridine. Iodine monochloride (66.8 g, 0.40 mol) in 150 mL of pyridine was added dropwise to the stirred solution. The resultant mixture was filtered and washed with 100 mL of pyridine. Norbornene (36.0 g, 0.38 mol) was added at once to the filtrate. After the mixture was stirred for 4 h, 200 mL of ether was added, the mixture was filtered, the filtrate was washed repeatedly with water, dried over magnesium sulfate, and concentrated, and the product was distilled: bp 40 °C (0.6 torr); 40% yield.

(Trimethyltin)sodium was prepared in THF solution and its concentration determined as previously described.[11]

Reaction of (Trimethyltin)sodium with Halides. In a typical trapping experiment appropriate amounts of halide and DCPH or TBA were added to THF to form solutions of the desired concentrations which were cooled in ice at least 15 min under nitrogen. A THF solution of (trimethyltin)sodium at 0 °C was added in approximately 2-fold excess over halide. Reactions with bromides and the iodide were complete almost upon mixing; 5-chloro-2-norbornene required about 1 h for completion. Yields of isomeric organotin substitution products and of hydrocarbons were determined by GLC.

(Norborn-2-en-5-yl)trimethyltin was isolated from reactions of 3-bromonortricyclene and 5-chloro-2-norbornene with (trimethyltin)sodium: NMR δ 0.06 ($^2J(^{119}\mathrm{SnC{-}H})$ = 49.5 Hz, 9 H, $(CH_3)_3Sn$), 5.9 (m, 2 H, **HC═CH**), 0.83–1.43 (m, 7 H, C_5H_7).[23] 3-Nortricyclyltrimethyltin was isolated from the reaction of 3-bromonortricyclene: NMR δ 0.048 ($^2J(^{119}\mathrm{SnC{-}H})$ = 50.7 Hz, 9 H, $(CH_2)_3Sn$), 0.83–1.43 (m, 9 H, C_7H_9).[23]

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Registry No. NI-I, 36071-35-9; NT-Br, 695-02-3; *exo*-NB-Cl, 3721-19-5; *exo*-NB-Br, 5889-54-3; *endo*-NB-Br, 5810-82-2; NT-Sn, 21942-28-9; *exo*-NB-Sn, 21957-51-7; NB-H, 498-66-8; NT-H, 279-19-6; *Sn*, 16643-09-7; iodine monochloride, 7790-99-0.

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o-Benzoylbenzoic Acids by the Reaction of Lithium 2-Lithiobenzoates with Acid Chlorides. A Contribution to the Chemistry of Alizarin and Podophyllotoxin

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Although aryllithium reagents usually react with acid chlorides to yield tertiary alcohols, the addition at −100 °C of aroyl chlorides to lithium *o*-lithiobenzoate and its congeners affords a useful route to *o*-benzoylbenzoic acids. The usefulness of this new method is illustrated by the synthesis of four *o*-benzoylbenzoic acids which experience has shown to be difficult or impossible to prepare by previously available methods. These acids include 2-benzoyl-5-methoxybenzoic acid, 2-(3-methoxybenzoyl)-5-methoxybenzoic acid, 2-(2,3-dimethoxybenzoyl)benzoic acid (a new intermediate for the preparation of alizarin dimethyl ether), and 2-(3,4,5-trimethoxybenzoyl)-4,5-(methylenedioxy)benzoic acid, a degradation product of podophyllotoxin.

With certain exceptions the reaction of an organolithium reagent with an acid chloride can be expected to lead to a tertiary alcohol.[3] Wakefield[4] states that "Halide ions are such good leaving groups that elimination from the complex...must take place almost synchronously with addition to the carbonyl group. Thus it is almost impossible to avoid a situation where the ketone and organolithium reagent are present together so that the final product is a tertiary alcohol". The few intances[5] in which satisfactory yields of ketones have been obtained by the reaction of organolithium reagents with acid chlorides appear to be those in which the ketone formed is so sterically hindered as to limit further reaction.

The purpose of the present work was to discover whether satisfactory yields of keto acids could be obtained by reaction of acid chlorides with lithium 2-lithiobenzoate and its congeners.[6] We have found that direct addition of benzoyl chloride to lithium 2-lithiobenzoate (**1**) at −100 °C affords a 62% yield of pure 2-benzoylbenzoic acid (**5a**). Similar yields were obtained with *p*-anisoyl and *m*-anisoyl chlorides (Table I), but the more sterically hindered ortho isomer gave only a 40% yield of the desired keto acid (**5d**). Analysis of the reaction mixture from the *o*-methoxybenzoyl chloride reaction showed, after hydrolysis, the presence of anisic acid and the absence of high molecular weight byproducts, even after the reaction mixture had been allowed to warm to room temperature, suggesting that the rate of anionic decay for **1** is greater than the rate of addition to the ortho-substituted carbonyl group of the acid chloride. In each experiment the acid chloride was added *directly* to the organolithium reagent (**1**); hence all but the last increment must be exposed to the action of

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