presence of lactones among the products; however, these could not be isolated in pure form owing to the easy rearrangement during the column chromatography and recrystallization. Further investigation concerning the mechanism and application of this reaction is being undertaken.

Experimental Section[10]

Commercially available iodobenzene was treated with concentrated sulfuric acid, washed with water, and then distilled. Nickel carbonyl was prepared by the procedure of Chiusoli and Mondelli.[11] Styrene and ethyl acrylate were distilled under reduced pressure before use. Tetrahydrofuran was refluxed with sodium and benzophenone until the solution turned blue and was then distilled. All solvents were saturated with argon before use.

The Reaction of Iodobenzene with Nickel Carbonyl in the Presence of Styrene. A. In Tetrahydrofuran.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.2 g (0.05 mol) of styrene in 50 ml of tetrahydrofuran was stirred at 50–60° for 100 hr under an atmosphere of argon. The reaction mixture was filtered to remove nickel iodide deposited during the reaction. The filtrate was distilled under reduced pressure to give the following fractions: fraction 1, bp 140–190° (0.5 mm), 2.5 g; fraction 2, bp 190–230° (0.5 mm), 2.3 g; and 1.0 g of polymeric residue. The ir spectrum of fraction 1 showed that this fraction consisted mainly of esters of benzoic acid, which were probably formed from the cleavage of tetrahydrofuran. Chromatography of fraction 1 on silica gel using petroleum benzine (bp 70–80°) as an eluent gave 0.4 g of white crystals and 0.5 g of pale yellow crystals. The former was recrystallized from ethanol to give white needles, mp 124°, and was found to be *trans*-stilbene by mixture melting point with an authentic sample. The latter was also recrystallized from ethanol to give pale yellow needles, mp 56°, and was identified as benzalacetophenone by mixture melting point with an authentic sample. Fraction 2 crystallized on standing and these crystals were recrystallized from ethanol to give 1.5 g of white crystals, mp 109°. This compound was shown to be 2,4-diphenyl-$\Delta^{3,4}$-crotolactone (V) (lit.[12] mp 109–110°) by the following data. The ir spectrum showed a carbonyl band at 1760 cm^{-1} and the nmr spectrum in $CDCl_3$ showed signals at τ 4.10 (one proton) and at 2.2–2.8 (ten aromatic protons and one olefinic proton).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12; mol wt, 236. Found: C, 80.98; H, 5.17; mol wt (in benzene), 240.

B. In Benzene.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.2 g (0.05 mol) of styrene in 50 ml of benzene was treated in a similar manner to that described above. From the reaction mixture 4.8 g of iodobenzene was recovered and vacuum distillation gave two fractions: fraction 1, bp 130–160° (1 mm), 2.7 g; and fraction 2, bp 190–230° (1 mm), 2.5 g. Chromatography of fraction 1 gave a small amount (<0.1 g) of benzalacetophenone and 2.5 of benzylacetophenone, mp 72–73° (lit. mp 73°), and no depression resulted on admixture with an authentic sample. Fraction 2 was triturated in petroleum ether (bp 50–60°) and 1.4 g of 2,4-diphenyl-$\Delta^{3,4}$-crotolactone (V) was obtained.

C. In the Presence of Amine.—An equimolar mixture (0.05 mol) of iodobenzene, nickel carbonyl, styrene, and dicyclohexylethylamine in 50 ml of benzene was treated as described above. Distillation at reduced pressure gave a fraction of bp 130–150° (0.7 mm), 2.4 g. Chromatography of this fraction gave 2.0 g of benzalacetophenone; no benzylacetophenone was detected.

The Reaction of Iodobenzene and Nickel Carbonyl in the Presence of Acrylonitrile.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.3 g (0.1 mol) of acrylonitrile in 50 ml of benzene was treated as described above. Distillation at reduced pressure gave two fractions: fraction 1, bp 135–170° (1 mm), 2.7 g; and fraction 2, bp 185–240° (1 mm), 2.5 g. Fraction 1, which crystallized on standing, was recrystallized from ethanol to give 2.3 g of white needles, mp 70°. This compound was identified as 3-benzoylpropionitrile as follows. The ir spectrum showed a nitrile band at 2270 and a carbonyl band at 1680 cm^{-1}. The nmr spectrum showed a triplet at τ 7.27 (two protons), a triplet at 6.67 (two protons), and a broad band at 2.0–2.8 (five protons).

Anal. Calcd for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80; mol wt, 159. Found: C, 75.71; H, 5.88; N, 8.54; mol wt (in N,N-dimethylformamide), 159.

The ir spectrum of fraction 1 showed also weak bands at 2250, 1675, and 1610 cm^{-1}, indicating the presence of small amounts of unsaturated 3-benzoylacrylonitrile. Fraction 2, which crystallized on standing, was recrystallized from benzene and petroleum benzine (bp 70–80°) to give 1.8 g of white crystals, mp 123–124°. This compound showed in its ir spectrum a nitrile band at 2270 and a carbonyl band at 1742 cm^{-1} but showed no bands characteristic for ester group. The nmr spectrum in $CDCl_3$ showed a doublet at τ 6.70 (two protons), a triplet at 4.15 (one proton), and a broad band at 2.0–3.0 (ten protons).

Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32; mol wt, 263. Found: C, 77.84; H, 5.03; N, 5.13; mol wt (in N,N-dimethylformamide), 265.

Thus this material was assigned the structure of 4,4-diphenyl-2-cyanobutylolactone (VI).

The Reaction of Iodobenzene with Nickel Carbonyl in the Presence of Ethyl Acetate.—A mixture of 10.2 g (0.05 mol) of iodobenzene, 8.5 g (0.05 mol) of nickel carbonyl, and 5.0 g (0.05 mol) of ethyl acrylate was treated as described above. The fraction, bp 100–160° (1.5 mm), 3.5 g, was hydrolyzed by KOH in diethylene glycol to give 2.5 g of white leaflets. These crystals, recrystallized from ethanol and water, mp 116°, was identified as 3-benzoylpropionic acid by mixture melting point with an authentic sample.

Registry No.—Iodobenzene, 591-50-4; nickel carbonyl, 13463-39-3; 3-benzoylpropionitrile, 5343-98-6; 4,4-diphenyl-2-cyanobutylolactone, 19598-21-1.

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[10] Nmr spectra were taken with a Model JNM-G-60 spectrometer (Japan Electron Optics Laboratory Co.). Infrared spectra were taken with a Shimazu IR-27C spectrometer. Molecular weights were determined in benzene or in N,N-dimethylformamide by using a Mechrolab vapor pressure osmometer. Melting points and boiling points are uncorrected.

[11] G. P. Chiusoli and G. Mondelli, *Chem. Ind.* (Milan), **43**, 259 (1961).

[12] A. Anshütz and W. F. Montfort, *Ann.*, **284**, 5 (1895).

Preparation and Spectral Characteristics of Some Allyltins. Nature of Allyltin Interactions

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In the course of our kinetic study of acid cleavage reaction,[1] we have observed a red shift in the uv spectrum of allyltin compounds compared with that of vinyl derivatives.

A red shift is observed in the spectrum of allylmercuric iodide, too.[2] This suggests an interaction between the allyl group and the metal atom. Spectral data for a series of $R_3M(CH_2)_nCH{=}CH_2$ compounds (in which M = C, Si, Ge, Sn; R = alkyl or halogen, and n = 1 or 2) have been reported.[3] The results show that the red shift increases with the atomic weight of M. It was proposed that these shifts result from an interaction between the σ C–M bond and the allylic double bond.

As a means of probing further into the cause of this red shift, we have prepared, and examined some spec-

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[1] H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.*, 119 (1964).

[2] M. M. Kreevoy, P. J. Steinwand, and T. S. Straub, *J. Org. Chem.*, **31**, 4291 (1966).

[3] V. A. Petukhov, V. F. Mironov, and P. P. Shorygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2203 (1964).

TABLE I

NMR SPECTRAL DATA OF ALLYLTIN COMPOUNDS[a]

Compound	Registry no.	τ			J, cps			
		SnCH$_3$	SnCH$_2$–		^{119}SnCH$_3$	^{117}SnCH$_3$	SnCH$_2$–	
(CH$_2$=CHCH$_2$)$_4$Sn	7393-43-3		8.04	8.18			63.0	63.1
(CH$_2$=CHCH$_2$)$_3$RSn								
R = CH$_3$	19713-79-2	9.90	8.08	8.21	50.9	48.6	63.9	64.5
R = C$_6$H$_5$	19713-80-5		7.87	8.03			65.8	66.1
R = n-C$_3$F$_7$			7.73	7.88			69.4	70.2
(CH$_2$=CHCH$_2$)$_2$R$_2$Sn								
R = CH$_3$	19434-15-2	9.89	8.11	8.27	52.0	49.8	65.3	65.8
R = C$_6$H$_5$	10074-32-5		7.72	7.85			68.3	68.6
R = C$_2$F$_5$			7.47	7.60			75.7	77.5
(CH$_2$=CHCH$_2$)R$_3$Sn								
R = CH$_3$	762-73-2	9.90	8.18	8.31	53.1	51.0	66.0	65.5
R = C$_6$H$_5$	76-63-1		7.53	7.67			75.6	75.6

[a] Spectra were obtained at 60 Mc by a Varian Associates A-60A spectrometer using 20% carbon tetrachloride solution.

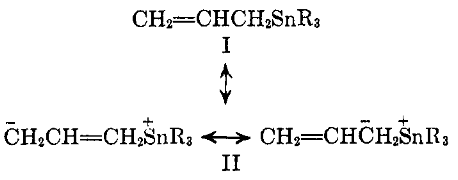
tral characteristics of, a series of allyltins in which the electronegativity of the groups on the tin atom is varied.

Results and Discussion

Absorption spectra of the compounds were measured in n-hexane and acetonitrile in order to test the effect of solvent polarity. In each case, a strong band was observed in the 190–220-mμ region. The locations of the maxima and extinction coefficients are given in Table I.

In general, the greater the number of allyl groups attached to tin, the lower is the stability. This may be the cause, in some cases, for the lower extinction coefficients than expected in some of the compounds.

The presence of a strong band in the 190–220-mμ region with an extinction coefficient around 10,000 per allyl group requires comment. Thus the values for allyltri-n-propyltin, diallyldi-n-propyltin, and triallyl-n-propyltin show values of 1.1 × 10^4, 1.80 × 10^4, and 2.88 × 10^4, respectively. Clearly, these intense absorptions are due to the combination of the allylic group and the metal atom. The red shift resulting upon change from the nonpolar solvent n-hexane to the more polar acetonitrile suggests that an electron polarization already present in the ground state is increased in the excited state. One possible interaction in the ground state is a π–π interaction between the two chromophores through space as suggested for allylmercuric iodide.[2] The other is a hyperconjugation-like interaction, I–II, between the σ C–Sn bond



$$\begin{array}{c} CH_2{=}CHCH_2SnR_3 \\ \text{I} \\ \updownarrow \\ \bar{C}H_2CH{=}CH_2\overset{+}{S}nR_3 \longleftrightarrow CH_2{=}CH\bar{C}H_2\overset{+}{S}nR_3 \\ \text{II} \end{array}$$

and the allylic double bond, as has been suggested for allyl compounds of the group IVB metals[3] and for α,β-unsaturated sulfides.[4] On the basis of our data we tend to suggest the latter possibility. If the tin atom functions as an electron π acceptor, substitution of alkyl groups by perfluoroalkyl groups should result in a red shift due to a decrease in electron density at the tin atom. As a matter of fact, the observed effect is in the opposite direction, the blue shift being about 10 mμ in the perfluoroalkyl derivatives. On the other hand, perfluoroalkyl groups should strengthen the σ allyl carbon–tin bond with the result that the hyperconjugation-like interaction would be smaller than in alkyl derivatives, and a blue shift should be observed. This is the case. Thus the red shifts observed in a series of allyltin compounds may be expressed in terms of an interaction between the σ allyl–tin bond and the allyl group (I–II) in the ground state. This also accounts for the high reactivity toward electrophilic attack.

Other spectral characteristics lend support to this type of formulation. Substitution of perfluoroalkyl for alkyl causes a 10-cm^{-1} shift to higher wavelength $\nu_{C=C}$. If the double bond were functioning as a donor into vacant d orbitals of the tin atom, the opposite effect should be observed. The increase of $\nu_{Sn-C(allyl)}$ and J_{SnCH_2-} in perfluoroalkyl derivatives seem to suggest the strengthening of the σ allyl carbon–tin bond.

Experimental Section

Materials.—Six new allyltin compounds have been prepared along with ten other known analogs. Typical procedures are described for the preparation of diallylbis(pentafluoroethyl)tin and triallylpentafluoroethyltin. All preparative work was done in an atmosphere of argon.

Diallylbis(pentafluoroethyl)tin and Triallylpentafluoroethyltin.—Anhydrous ether was obtained by refluxing commercial ether over LiAlH$_4$ under the atmosphere of argon. Pentafluoroethyl iodide (0.28 mol, 46.0 g) was placed in 400 ml of anhydrous ether in a 1-l. three-necked flask with a mechanical stirrer and two pressure-equalized dropping funnels which were immersed in a Dry Ice–acetone cooling bath. Methyllithium (0.17 mol, 108 ml of 1.6 M solution in ether) was added to pentafluoroethyl iodide over a period of 10 min. The reaction mixture was stirred for 5 min, and then allyltin bromides mixture[5] was added. The reaction mixture was again stirred for 4 hr during which time the temperature was allowed to rise up to that of the room. It was concentrated, filtered, and the filtrate was distilled under reduced pressure. The distillate was fractionally distilled over a column (height of 15 cm; packed with Heli-Pack stainless steel, 0.05 × 0.100 × 0.100 in.) to give diallylbis(pentafluoroethyl)tin [bp 48° (3.1 mm); ir (neat) 1631 ($\nu_{C=C}$), 909 (γ_{C-H}), 500 cm^{-1} ($\nu_{Sn-(allyl)}$); nmr (CCl$_4$) 7.47, 7.60 ppm (SnCH$_2$–), J = 75.7, 77.5 cps (SnCH$_2$–) (*Anal.* Calcd for C$_{10}$F$_{10}$H$_{10}$Sn: C, 27.37; F, 43.20; H, 2.30. Found: C, 27.77; F, 43.25; H, 2.64)] and triallylpentafluoroethyltin [bp 58° (2.4 mm) (*Anal.* Calcd for C$_{11}$F$_5$H$_{15}$Sn: C, 36.61; H, 4.19; Sn, 32.89. Found: C, 36.54; H, 4.10; Sn, 32.8)].

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(4) H. P. Koch, *J. Chem. Soc.*, 387 (1949).

(5) The direct synthesis of diallyltin dibromide by Shishido and Takeda [*J. Org. Chem.*, **26**, (1961)] resulted in the mixture of diallyltin dibromide and triallyltin bromide.

Triallylheptafluoro-*n*-propyltin was prepared similarly: bp 64–68° (2.7 mm); ir (neat) 1630 ($\nu_{C=C}$), 896 (γ_{C-H}), 497 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$); nmr (CCl_4) 7.73, 7.88 ppm ($SnCH_2$–), J = 69.4, 70.2 cps ($SnCH_2$–). *Anal.* Calcd for $C_{12}H_7F_{15}Sn$: C, 35.07; F, 32.36; H, 3.68; Sn, 28.88. Found: C, 36.09; F, 31.45; H, 3.85; Sn, 27.8.

Alkyl derivatives were prepared from alkyltin chlorides and allylmagnesium halides. New compounds are as follows: triallylmethyltin [bp 100–101° (23 mm); ir (neat) 1620 ($\nu_{C=C}$), 880 (γ_{C-H}), 486 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$); nmr (CCl_4) 9.90 ($SnCH_3$), 8.08, 8.21 ppm ($SnCH_2$–), J = 48.6 ($^{117}SnCH_3$), 50.9 ($^{119}SnCH_3$), 63.9, 64.5 cps ($SnCH_2$–) (*Anal.* Calcd for $C_{10}H_{18}Sn$: C, 46.72; H, 7.06; Sn, 46.21. Found: C, 46.97; H, 7.25; Sn, 46.5)]; triallylethyltin [bp 60–61 (0.6 mm); ir (neat) 1621 ($\nu_{C=C}$), 881 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$) (*Anal.* Calcd for $C_{11}H_{20}Sn$: C, 48.75; H, 7.44; Sn, 43.80. Found: C, 48.52; H, 7.37; Sn, 44.0)]; triallyl-*n*-propyltin [bp 51–52 (0.2 mm); ir (neat) 1623 ($\nu_{C=C}$), 882 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$) (*Anal.* Calcd for $C_{12}H_{22}Sn$: C, 50.57; H, 7.78; Sn, 41.65. Found: C, 50.85; H, 7.94; Sn, 42.0)].

Other spectral data are as follows: triallyl-*n*-propyltin [ir (neat) 1623 ($\nu_{C=C}$), 882 (γ_{C-H}), 487 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$)]; diallyldiethyltin [ir (neat) 1621 ($\nu_{C=C}$), 879 (γ_{C-H}), 488 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$)]; diallyldimethyltin [ir (neat) 1622 ($\nu_{C=C}$), 882 (γ_{C-H}), 488 cm^{-1} ($\nu_{Sn\text{-}C(allyl)}$); nmr (CCl_4) 9.89 ($SnCH_3$), 8.11, 8.27 ppm ($SnCH_2$–), J = 49.8 ($^{117}SnCH_3$), 52.0 ($^{119}SnCH_3$), 65.3, 65.8 cps ($SnCH_2$–)].

Measurements of Electronic Absorption Spectra.—The solvents were all spectrograde and were used, as supplied, without further purification. The solutions were made under argon, and concentrations were such as to give optical densities between 0.3 and 0.7 at the maximum. The spectra were obtained with a Cary 14 spectrophotometer, using 1-mm cells.

Registry No.—Diallylbis(pentafluoroethyltin), 19647-32-6; triallylpentafluoroethyltin, 19713-76-9; triallylheptafluoro-*n*-propyltin, 19647-33-7; triallylethyltin, 19713-77-0.

The Reaction of Dimethylmethylchromium Carbenoids with Olefins

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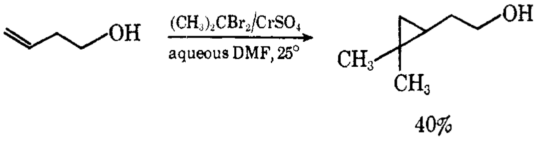
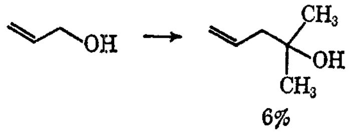
The general chemistry of the reduction of geminal halides and polyhalomethanes with chromous sulfate has been outlined.[1] An important feature of these reactions is the generation of a unique dialkylcarbenoid entity that does have the capacity to react with water and olefins in addition to being reduced and undergoing rearrangement. Adduct formation[2] was typified by eq 1 and 2.



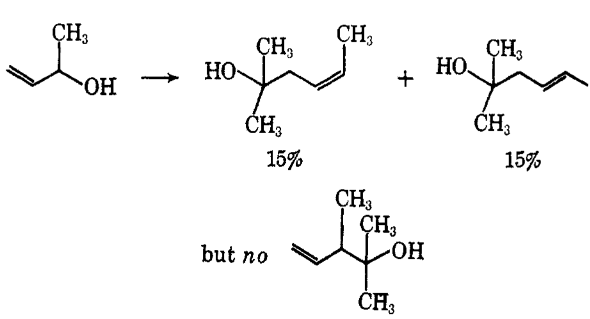
(1)



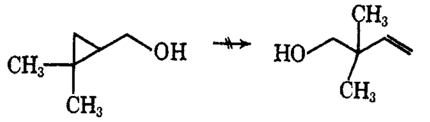
(2)

This Note corrects the suggestion that cyclopropanes are intermediates in reactions with allylic alcohols and eliminates a direct C–O insertion.[3]

We have confirmed the results of the reactions with 3-buten-1-ol (eq 1) and allyl alcohol (eq 2). However, reaction with 3-buten-2-ol (eq 3) and an examination of the possible rearrangement of the potential cyclopropane intermediates (under reaction and work-up conditions, eq 4 and 5 are revealing. Moreover, reaction 1 at −5° yields *no* olefinic trapping product[4] (eq 6). The ratio of isopropyl alcohol to propylene and propane produced is constant throughout the run. The over-all kinetics at this temperature (Figure 1) are in accord with the initial buildup of $(CH_3)_2C(Br)$-Cr^{2+}.



(3)



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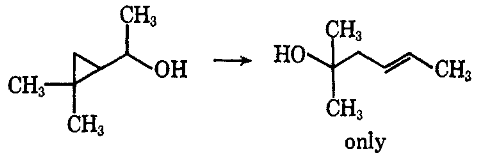
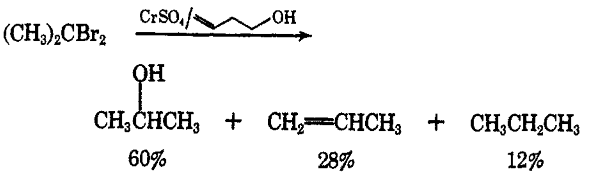
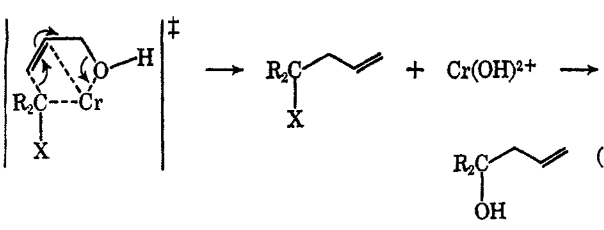


(5)



$$\underset{60\%}{CH_3\overset{OH}{C}HCH_3} + \underset{28\%}{CH_2{=}CHCH_3} + \underset{12\%}{CH_3CH_2CH_3} \quad (6)$$

Taken together the data suggest a transition state for olefin insertions that resembles that written for addition by haloalkyllithiums (eq A).[5] In the absence



(A)

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[1] C. E. Castro and W. C. Kray, *J. Amer. Chem. Soc.*, **88**, 4447 (1966).

[2] For clarity only adducts are depicted. All yields are based on Cr(II) consumption. Unreacted olefin can be recovered.

[3] C–O insertion by a Cu(II) complex of carbethoxycarbene has been reported: H. Nozaki, S. Moruta, H. Takaya, and R. Noyori, *Tetrahedron Lett.*, **48**, 5239 (1966).

[4] Comparative yields at room temperature in the absence of olefin are propane (2%), propylene (21%), and isopropyl alcohol (76%).

[5] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4274 (1965).