If isolated from Ie reaction mixtures was observed. The infrared absorption spectra of both were identical.[25]

*1-Chloro-2-carbamoxy-3-(o-methoxyphenoxy)propane* (VIII). (*a*) *From Ie.* To a mixture of 120.6 g. (0.50 mole) of Ie, 47.5 g. (0.50 mole) of dry pyridine, and 500 ml. of dry benzene was added with stirring at 0–10° in 1 hr. 65.4 g. (0.55 mole) of thionyl chloride. The mixture was then slowly heated to reflux until the evolution of sulfur dioxide stopped (constant internal temperature) and for 30 min. more. Water (200 ml.) was added to the cooled (25°) reaction mixture. Two liquid phases which crystallized rapidly formed. After filtration and washing with water and benzene, 111.4 g. (87.6%) of VIII, m.p. 105–106° was obtained.

(*b*) *From If.* To an ice cooled solution of 2.41 g. (0.01 mole) of If in 1.10 g. (0.014 mole) of dry pyridine was added 1.5 g. (0.0125 mole) of thionyl chloride. After 1 hr. at room temperature and several minutes on the steam bath, water was added to the cooled reaction mixture. The crude product was filtered and recrystallized from 2-propanol to give 1.67 g. (64.5%) of VIII, m.p. 104–104.5°; m.p. 105.5–106.5° after recrystallization (2-propanol).

(*c*) *From IV.* To a stirring solution 20 g. (0.0923 mole) of IV in 135 ml. of dry toluene at 20° was added 9.9 g. (0.10 mole) of phosgene in 100 ml. of dry toluene. After 1 hr. at room temperature, 12.1 g. (0.10 mole) of dimethylaniline in 75 ml. of toluene was added below 20°. The toluene solution was washed with ice water, ice cold 5% hydrochloric acid, ice water, and added, at 0–5°, to 170 ml. of concentrated aqueous ammonia. After 4 hr. at 0–5°, the product, 4 g. (16.6%), was filtered and recrystallized twice from 2-propanol; m.p. 105–106.5°.

All three preparations showed no depressions in mixed melting points.

All gave the same infrared absorption spectra.

*Anal.* Calcd. for $C_{11}H_{15}O_4ClN$: Cl, 13.65; N, 5.39. Found: Cl, 13.58; N, 5.54.

*Reaction of VIII with nitrous acid.* To a solution of 6.8 g. (0.026 mole) of VIII in 50 ml. of acetic acid was added with stirring at 80°C in 30 min. 5 g. of sodium nitrite in 10 ml. of water. The mixture was poured into 250 ml. of water, and extracted with benzene. The benzene was removed, and the residue recrystallized from fresh benzene to give 2.2 g. (32.4%) of unchanged VIII, m.p. 104–106° C. The mother liquor was distilled (Hickman still) to give 1.7 g. (30.7%) of IV, b.p./1 μ 90–100° (bath temperature), $n_D^{25}$ 1.5430. A phenyl urethane m.p. 118.5–119.5° was obtained with phenyl isocyanate; no mixed melting point depression with the urethane from IV obtained by Marle's[10] method, m.p. 119.5–120.5°.

*Reaction of VIII with silver hydroxide.* A mixture of 5.6 g. (0.02 mole) of VIII and freshly precipitated silver hydroxide (from 3.4 g., 0.02 mole, of silver nitrate) in 60 ml. of 50% 2-propanol was refluxed for 4 hr. After filtration, removal of solvent, and benzene recrystallization, 1.0 g. of crystals m.p. 78–88° was obtained. Upon recrystallization from 2-propanol, 0.5 g. of Ie m.p. 94–96°C was obtained. No depression in mixed melting point with Ie previously prepared was observed.

NEWARK, N. J.

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(25) A Perkin-Elmer Model 21 was used.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

# Cycloalkyl- and Secondary Alkyltin Compounds and Their Cleavage by Iodine in Benzene Solution

DIETMAR SEYFERTH[1]

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The preparation of $(\text{cyclo-C}_5\text{H}_9)_2\text{SnR}_2$ and $(\text{cyclo-C}_6\text{H}_{11})_2\text{SnR}_2$ (R = Me, *n*-Bu, $C_6H_5$), $(\text{sec.-Bu})_2\text{SnMe}_2$, $(\text{iso-Pr})_2\text{SnR}_2$ (R = Me, *n*-Bu), and *n*-$\text{Bu}_2\text{SnMe}_2$ is described. These compounds were cleaved by the action of one equivalent of iodine in refluxing benzene solution to give mixtures of both possible cleavage products, except in the case of those compounds which contained phenyl groups. In the latter compounds only phenyl cleavage was observed. Twelve new organotin iodides of formula $R_2R'SnI$ are described.

Only two publications have thus far been concerned with cycloalkyltin compounds.[2,3] Similarly, organotin compounds containing secondary alkyl groups have been the subject of only a small number of studies.[4–6]

Little is known of the position of cycloalkyl and secondary alkyl groups in the cleavage series for organotin compounds. It has been established that the phenyl group is cleaved in preference to the cyclohexyl group by the action of concentrated hydrochloric acid on $(\text{cyclo-C}_6\text{H}_{11})_2\text{Sn}(\text{C}_6\text{H}_5)_2$,[3] thus showing that the latter group behaves like an aliphatic group. However, no experiments have been reported which determine the place of a cycloalkyl group in the aliphatic organotin cleavage series. It was stated by Luitjen and van der Kerk (ref. 6, p. 80) that secondary alkyl groups are cleaved from a tin atom prior to *n*-alkyl groups, but a quantitative product study of only one reaction[4]

$$(n\text{-C}_4\text{H}_9)_3\text{SnC}_4\text{H}_9\text{-}sec. + \text{I}_2 \longrightarrow (n\text{-C}_4\text{H}_9)_3\text{SnI} + sec.\text{-C}_4\text{H}_9\text{I}$$

appears to provide experimental proof for this generalization.

We now wish to report the preparation of a number of cyclopentyl-, cyclohexyl-, and secondary alkyltin compounds and the results of the cleavage of

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(1) Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.

(2) E. Krause and R. Pohland, *Ber.*, **57**, 542 (1924).

(3) T. S. Bobashinskaya and K. A. Kocheshkov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1850 (1938).

(4) Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 1047 (1944).

(5) F. Caujolle, M. Lesbre, D. Meynier, and A. Blaizot, *Compt. rend.*, **240**, 1732 (1955).

(6) J. G. A. Luitjen and G. J. M. van der Kerk, *Investigations in the Field of Organotin Chemistry*, Tin Research Institute, Greenford, England, 1955, p. 105.

TABLE I

TETRAORGANOTIN COMPOUNDS PREPARED BY THE GRIGNARD METHOD

| Compound | B.P. |  | $n_D^{25}$ | $d_4^{25}$ | Carbon, % |  | Hydrogen, % |  |
|---|---|---|---|---|---|---|---|---|
|  | °C. | Mm. Hg |  |  | Calcd. | Found | Calcd. | Found |
| (Cyclo-$C_5H_9$)$_2$SnMe$_2$ | 76–77 | 0.3 | 1.5109 | 1.231 | 50.21 | 50.20 | 8.43 | 8.48 |
| (Cyclo-$C_5H_9$)$_2$SnBu-$n_2$ | 128 | 0.3 | 1.5067 | 1.127 | 58.24 | 58.53 | 9.78 | 9.08 |
| (Cyclo-$C_5H_9$)$_2$Sn($C_6H_5$)$_2$ | M.p. | 49–50.2° |  |  | 64.26 | 64.41 | 6.86 | 6.82 |
| (Cyclo-$C_6H_{11}$)$_2$SnMe$_2$ | 101–102 | 0.6–0.7 | 1.5184 | 1.208 | 53.37 | 53.16 | 8.96 | 8.72 |
|  | 98 | 0.4 |  |  |  |  |  |  |
| (Cyclo-$C_6H_{11}$)$_2$SnBu-$n_2$ | 143 | 0.45 | 1.5126 | 1.119 | 60.17 | 60.08 | 10.10 | 10.08 |
| *n*-Bu$_2$SnMe$_2$ | 70 | 4.4 | 1.4640 | 1.124 | 45.67 | 45.92 | 9.20 | 9.38 |
| *sec.*-Bu$_2$SnMe$_2$ | 68 | 5.5 | 1.4738 | 1.143 | 45.67 | 45.92 | 9.20 | 9.24 |
| *iso*-Pr$_2$SnMe$_2$ | 68 | 29.0 | 1.4621 | 1.161 | 40.90 | 41.16 | 8.58 | 8.52 |
| *iso*-Pr$_2$SnBu-$n_2$ | 102 | 2.9 | 1.4756 | 1.074 | 52.69 | 52.42 | 10.11 | 10.07 |

these compounds by the action of iodine in refluxing benzene solution.

The compounds (cyclo-$C_5H_9$)$_2$SnR$_2$ and (cyclo-$C_6H_{11}$)$_2$SnR$_2$ (R = Me, n-Bu, $C_6H_5$), (sec.-$C_4H_9$)$_2$SnMe$_2$, (iso-$C_3H_7$)$_2$SnR$_2$ (R = Me, n-Bu), and (n-$C_4H_9$)$_2$SnMe$_2$ were prepared by the reaction of the appropriate Grignard reagent with the various R$_2$SnCl$_2$ compounds (R = Me, n-Bu, $C_6H_5$) in refluxing tetrahydrofuran (THF), which is now the solvent of choice in this laboratory for the preparation of tetraorganotin compounds.[7] The compounds prepared in this manner are listed in Table I, together with their physical constants and analytical data.

In several publications of Manulkin,[4,8] as well as in the work of Luitjen and van der Kerk (ref. 6, p. 120), it was reported that in the cleavage of mixed tetraorganotin compounds of types R$_2$SnR$'_2$ or R$_3$SnR$'$ with one equivalent of iodine in refluxing diethyl ether solution a preference is shown for only one of the two different groups present in the molecule. Thus of the two possible reactions, (a) and (b),

$$R_2SnR_2' + I_2 \longrightarrow \begin{cases} R_2R'SnI + R'I & \text{(a)} \\ RR'_2SnI + RI & \text{(b)} \end{cases}$$

*only one* was observed, and no mixtures of products were reported. However, Luitjen and van der Kerk pointed out (ref. 6, p. 80) that under more vigorous reaction conditions a mixture of the two possible products may well be obtained.

The results of our cleavage study, summarized in Table II, show that this is indeed the case. When the iodine cleavage reaction is carried out at the temperature of the refluxing benzene solution, a mixture of the two possible products results.[9] Exceptions to this generalization are provided when one of the groups is phenyl, in which case only phenyl cleavage occurs, or when one of the groups is trimethylsilylmethyl,[7b] where the other R group is cleaved and no attack on the Me$_3$SiCH$_2$-Sn link occurs even at 175° in the compounds (Me$_3$SiCH$_2$)$_2$SnMe$_2$ and (Me$_3$SiCH$_2$)$_2$SnBu-n$_2$.

TABLE II

CLEAVAGE OF SOME TETRAORGANOTIN COMPOUNDS BY IODINE IN BENZENE

| Compound | Cleavage Products, Yield, % |
|---|---|
| (Cyclo-$C_5H_9$)$_2$SnMe$_2$ | Cyclo-$C_5H_9$I (36.0), cyclo-$C_5H_9$-Me$_2$SnI (33.8), (Cyclo-$C_5H_9$)$_2$-MeSnI (45.6) |
| (Cyclo-$C_5H_9$)$_2$SnBu-$n_2$ | Cyclo-$C_5H_9$(*n*-Bu)$_2$SnI (39.3) + inseparable mixture of both tin cleavage products |
| (Cyclo-$C_5H_9$)$_2$Sn($C_6H_5$)$_2$ | $C_6H_5$I (91.6)[a] |
| (Cyclo-$C_6H_{11}$)$_2$SnMe$_2$ | Cyclo-$C_6H_{11}$I (45.4), cyclo-$C_6H_{11}$-Me$_2$SnI (44.2), (cyclo-$C_6H_{11}$)$_2$-MeSnI (45.1) |
| (Cyclo-$C_6H_{11}$)$_2$SnBu-$n_2$ | Cyclo-$C_6H_{11}$(*n*-Bu)$_2$SnI (54.2), (Cyclo-$C_6H_{11}$)$_2$(*n*-Bu)SnI (36.8) |
| (Cyclo-$C_6H_{11}$)$_2$Sn($C_6H_5$)$_2$ | $C_6H_5$I (88.0) |
| *iso*-Pr$_2$SnMe$_2$ | *iso*-PrMe$_2$SnI (50.6), *iso*-Pr$_2$Me-SnI (23.4)[b] |
| *sec.*-Bu$_2$SnMe$_2$ | *sec.*-BuMe$_2$SnI (25.0), *sec.*-Bu$_2$-MeSnI (56.1)[b] |
| *n*-Bu$_2$SnMe$_2$ | *n*-BuI (21.5), *n*-BuMe$_2$SnI (27.6), *n*-Bu$_2$MeSnI (65.5) |

[a] Reaction with two equivalents of iodine. [b] Low total yield due to appreciable intermediate fraction in the distillation.

A study of Table II shows that no general pattern emerges from the data obtained. In the case of the mixed alkyl(cycloalkyl)tin compounds, the differences in the yields obtained of the two possible products is too small to permit any firm conclusions to be drawn. We can at this time offer no explanation for the apparent great difference in the rate of cleavage of the structurally similar isopropyl and secondary butyl groups.

These cleavage reactions were carried out in refluxing benzene solution because a preliminary experiment showed that no appreciable reaction occurred between iodine and dicyclohexyldimethyltin in diethyl ether solution during a 17-hour reflux period. The cleavage of di-*n*-butyldimethyl served

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[7] (a) D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957); (b) D. Seyferth, *J. Am. Chem. Soc.*, in press. (c) See alsoS . D. Rosenberg, A. J. Gibbons, and H. E. Ramsden, *J. Am. Chem. Soc.*, **79**, 2137 (1957).

[8] Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **13**, 42, 46 (1943).

[9] This observation would seem to cast some doubt on the results claimed for the cleavage of *n*-Bu$_3$(*sec.*-Bu)Sn,[4] which was carried out in refluxing xylene solution.

TABLE III

ORGANOTIN IODIDES PREPARED BY CLEAVAGE WITH IODINE

| Compound | B.P. °C. | B.P. Mm. Hg | $n_D^{25}$ | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|
| Cyclo-$C_5H_9Me_2SnI$ | 77 | 0.5 | 1.5758 | 24.38 | 24.50 | 4.38 | 4.27 |
| (Cyclo-$C_5H_9)_2MeSnI$ | 115 | 0.7 | 1.5836 | 33.12 | 32.96 | 5.31 | 5.43 |
| Cyclo-$C_5H_9$($n$-Bu)$_2$SnI | 125 | 0.4 | 1.5497 | 36.40 | 36.52 | 6.35 | 6.16[a] |
| Cyclo-$C_6H_{11}Me_2SnI$ | 86 | 0.65 | 1.5717 | 26.77 | 27.04 | 4.78 | 4.85 |
| (Cyclo-$C_6H_{11})_2MeSnI$ | 134 | 0.4 | 1.5786 | 36.57 | 36.67 | 5.90 | 5.61[b] |
| Cyclo-$C_6H_{11}$($n$-Bu)$_2$SnI | 136 | 0.6 | 1.5494 | 37.96 | 37.95 | 6.60 | 6.42 |
| (Cyclo-$C_6H_{11})_2$($n$-Bu)SnI | 160 | 0.7 | 1.5630 | 40.97 | 41.22 | 6.66 | 6.65 |
| $n$-BuMe$_2$SnI | 88-89 | 5.4 | 1.5467[c] | 21.65 | 21.98 | 4.54 | 4.73 |
| $n$-Bu$_2$MeSnI | 82 | 0.35 | 1.5375 | 28.83 | 28.91 | 5.65 | 5.79 |
| *sec.*-BuMe$_2$SnI | 84 | 5.5 | 1.5510 | 21.65 | 22.39 | 4.54 | 4.74 |
| *sec.*-Bu$_2$MeSnI | 71 | 0.25 | 1.5498 | 28.83 | 28.64 | 5.65 | 5.54 |
| *iso*-PrMe$_2$SnI | 77-78 | 9.2 | 1.5553 | 18.84 | 19.02 | 4.11 | 4.11 |
| *iso*-Pr$_2$MeSnI | 96 | 7.6 | 1.5518 | 24.24 | 24.01 | 4.94 | 4.78 |

[a] % I: calcd., 29.59; found, 29.48. [b] % I: calcd., 29.73; found, 29.70. [c] Manulkin[8] reports b.p. 118-120° at 25 mm., $n_D^{20}$ 1.5478.

to show that the more vigorous conditions and not the structure of the organotin reactants, which in all other cases contained bonds between tin and a secondary carbon atom, were responsible for the formation of a mixture of both possible cleavage products.

It seems clear that further experiments are needed in order to place cycloalkyl and secondary alkyl groups in the organotin cleavage series. It would be advisable to use milder reaction conditions, and it is hoped that cleavage with hydrogen bromide at low temperature may provide more conclusive results.

The organotin iodides which resulted from these cleavage reactions are listed in Table III.

## EXPERIMENTAL[10]

*Starting materials.* Dimethyltin dichloride was prepared by the method of Smith and Rochow[11] and diphenyltin dichloride by the disproportionation of tetraphenyltin with tin(IV) chloride at 190°. Di-$n$-butyltin dichloride was obtained from Metal and Thermit Corp., Rahway, N. J. Tetrahydrofuran was distilled from potassium hydroxide pellets and subsequently from lithium aluminum hydride prior to use.

*Preparation of tetraorganotin compounds.* The preparation of dicyclohexyldimethyltin is given as an example of the procedure used.

Cyclohexylmagnesium chloride was prepared from 50 g. (0.42 mole) of cyclohexyl chloride and 9.7 g. (0.4 g.-atom) of magnesium turnings in 200 ml. of THF. Addition of a few drops of ethyl bromide served to initiate attack on the magnesium. To the Grignard solution was added 35 g. (0.16 mole) of dimethyltin dichloride in 70 ml. of THF at such a rate that a gentle reflux was maintained. After the addition was completed, the reaction mixture was stirred and heated at reflux for 22 hr. The mixture was then cooled to room temperature and hydrolyzed with 60 ml. of saturated ammonium chloride solution. The organic layer was decanted and the salts were washed with three portions of diethyl ether, the washings being added to the organic layer. Distillation of the organic layer, after removal of the solvents at atmospheric pressure, gave 41.3 g. (82%) of dicyclohexyldimethyltin, b.p. 98° at 0.45 mm. to 101° at 0.6 mm.

Experimental details of the other preparations are given in Table IV.

TABLE IV

TETRAORGANOTIN COMPOUNDS BY THE GRIGNARD METHOD. EXPERIMENTAL

| Tin Halide | Moles | Alkyl Halide | Moles | Yield of $R_2SnR_2'$, % |
|---|---|---|---|---|
| $Me_2SnCl_2$ | 0.16 | Cyclo-$C_5H_9Br$ | 0.4 | 51.2 |
| $n$-$Bu_2SnCl_2$ | 0.148 | Cyclo-$C_5H_9Br$ | 0.4 | 83.5 |
| $(C_6H_5)_2SnCl_2$ | 0.145 | Cyclo-$C_5H_9Br$ | 0.4 | 81.7 |
| $Me_2SnCl_2$ | 0.16 | Cyclo-$C_6H_{11}Cl$ | 0.4 | 82.0 |
| $Me_2SnCl_2$ | 0.16 | Cyclo-$C_6H_{11}Br$ | 0.4 | 69.0 |
| $n$-$Bu_2SnCl_2$ | 0.148 | Cyclo-$C_6H_{11}Br$ | 0.4 | 71.5 |
| $(C_6H_5)_2SnCl_2$ | 0.145 | Cyclo-$C_6H_{11}Br$ | 0.4 | 82.0 |
| $n$-$Bu_2SnCl_2$ | 0.312 | $CH_3Br$ | 1.0 | 90.0 |
| $Me_2SnCl_2$ | 0.34 | *sec.*-$C_4H_9Br$ | 1.0 | 86.5 |
| $Me_2SnCl_2$ | 0.34 | *iso*-$C_3H_7Br$ | 1.0 | 76.6 |
| $n$-$Bu_2SnCl_2$ | 0.312 | *iso*-$C_3H_7Br$ | 1.0 | 88.1 |

Crude dicyclopentyldiphenyltin was obtained as an orange oil after removal of the solvent. It was crystallized from a methanol-ethanol mixture at −78°. Dicyclohexyldiphenyltin similarly was obtained as an oil. Addition of ethanol caused crystallization to give a white solid, m.p. 109-113°. Recrystallization from ethanol gave pure material, m.p. 118-120° (lit.[8] m.p. 119-120°).

*Iodine cleavage reactions.* The cleavage of dicyclohexyldimethyltin is described to illustrate the procedure used. To a solution of 34.0 g. (0.108 mole) of dicyclohexyldimethyltin in 300 ml. of benzene was added 27.45 g. (0.108 mole) of iodine. The iodine was completely consumed at the end of a reflux period of 1 hr. The benzene was then distilled at atmospheric pressure. Fractional distillation at reduced pressure gave: (1) cyclohexyl iodide, b.p. 42° at 1 mm., $n_D^{25}$ 1.5462 (lit.[12] $n_D^{20}$ 1.5470), 10.3 g.; (2) a small intermediate cut; (3) cyclohexyldimethyltin iodide, b.p. 86° at 0.65 mm., 17.1 g.; (4) a small intermediate cut; (5)

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(10) Analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y. Melting points were determined using a Hershberg melting point apparatus.

(11) A. C. Smith, Jr., and E. G. Rochow, *J. Am. Chem. Soc.*, **75**, 4103 (1953).

(12) P. G. Stevens, *J. Am. Chem. Soc.*, **56**, 450 (1934).

dicyclohexylmethyltin iodide, b.p. 136–140° at 0.65 mm., 20.8 g.

In the cleavage of dicyclopentyldimethyltin the cyclopentyl iodide isolated was characterized: b.p. 41–43° at 6.8 mm., $n^{25}_{D}$ 1.5465 (lit.[13] $n^{25}_{D}$ 1.5457).

Dicyclopentyldiphenyltin was treated with two equivalents of iodine and dicyclohexyldiphenyltin with one equivalent. The iodobenzene resulting from the cleavage was recovered by distillation. The organotin cleavage products were not isolated.

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(13) M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, 68, 843 (1946).

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[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL AND THERMIT CORP.]

# Preparation of Vinylmagnesium Chloride and Some Homologs[1]

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Vinylmagnesium chloride and several of its homologs were prepared. Among the homologs were 1-propenyl, 2-propenyl, 1-but-1-enyl, 2-but-2-enyl, 4-methyl-2-pent-1-enyl, and 1-cyclohexenyl magnesium chlorides. Several characterizing reactions of vinylmagnesium chloride were carried out.

Both vinyl chloride and vinyl bromide have long been considered to be unreactive toward magnesium to form vinylmagnesium halides. Krestinsky[2] reported a lack of success in preparing vinylmagnesium bromide in ether. Austerweil,[3] however, reported a successful Wurtz reaction of vinyl bromide with 2-chloropropene to form isoprene. A patent[4] issued to the General Electric Co. showed a more recent use of vinylmagnesium bromide in ether to form vinylsilanes. Quite recently, Normant[5] has shown in excellent researches the attaining of good results using tetrahydrofuran as solvent for the preparation of vinylic magnesium bromides in high yield. In many subsequent papers Normant and co-workers have shown the use of several vinylic magnesium bromides to prepare olefinic derivatives.[6–16] However, Braude in attempts to repeat Normant's preparation of 1-isobutenylmagnesium bromide reported complete lack of success.[17]

This article is in part confirmation of Normant's preparation of vinylic magnesium bromides. Since Normant has not shown the generality of this preparation by extending it to vinylic chlorides,[18] we would like to do so here in reporting work done independently.[19,20]

Vinylmagnesium chloride was prepared by passing vinyl chloride into tetrahydrofuran and active magnesium. The Gilman titration[21] showed a 98.5% yield of Grignard reagent and recovery of magnesium showed a 94.5% consumption. Carbonation yielded acrylic acid. These results appear to be the first preparation of vinylmagnesium chloride.

Vinyl chloride is remarkably soluble in tetrahydrofuran and this property may be used to advantage in preparing vinylmagnesium chloride in techniques similar to those used for arylmagnesium

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(1) Parts of this paper were presented at the 130th National Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, September, 1956.

(2) W. Krestinsky, *Ber.*, **55B**, 2770–2774 (1922).

(3) G. Austerweil, German Patent **245,180** (1912); [*Chem. Abstr.* 6, 2334 (1912)].

(4) J. Pyle, U. S. Patent **2,448,391** (1948); [**43,** 1223 (1949)].

(5) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(6) H. Normant, *Compt. rend.*, **239**, 1811 (1954).

(7) H. Normant, *Compt. rend.* **240**, 314 (1955).

(8) H. Normant, *Compt. rend.*, **240**, 440 (1955).

(9) H. Normant, *Compt. rend.*, **240**, 631 (1955).

(10) H. Normant, *Compt. rend.*, **240**, 1111 (1955).

(11) H. Normant, *Compt. rend.*, **240**, 1435 (1955).

(12) J. Ficini, *Bull. soc. chim. France*, 119 (1956).

(13) H. Normant and C. Crisan, *Compt. rend.* **240,** 1946 (1955).

(14) H. Normant and P. Maitte, *Bull. soc. chim. France*, 951, 1439 (1956).

(15) H. Normant and J. Ficini, *Bull. soc. chim. France*, 1441 (1956).

(16) a. V. Levy and H. Normant, *Compt. rend.*, **242**, 202 (1957); b. H. Normant and G. Martin, *Bull. soc. chim. France*, 429, 728 (1957).

(17) E. A. Braude, *J. Chem. Soc.*, 3324 (1955).

(18) *Chem. Abstr.*, **50**, 228 (1956) the abstract of ref. 5 states vinylmagnesium chlorides can be made, which is true, although Normant did not so state in ref. 5.

(19) In extensive private communications with Normant during 1955 it was determined that his work and ours were initiated at about the same time, very much prior to 1954.

(20) a. This work is covered by patent applications. b. H. E. Ramsden and A. E. Balint, Brit. Pat. **777,158** (June 19, 1957).

(21) H. Gilman, H. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.* **51,** 1576 (1929).