necessary to neutralize the hydrogen chloride formed in the mixed anhydride preparation.

2,4-Dimethylpentanol-3 (XIV). 2,4-Dimethylpentanone-3 (86.6 g., b.p. 122–124°, n_D^{25} 1.3981) was added over a period of 1 hr. to a suspension of 8.36 g. of lithium aluminum hydride in 300 cc. of dry ether. The mixture was then refluxed 1 hr., water was added cautiously dropwise until gas evolution ceased, and the reaction mixture was poured into 150 cc. of ice water, to which was added 600 cc. of 10% sulfuric acid solution. The aqueous solution was extracted twice with ether, the ether was washed with water until neutral, was dried, and the solvent was removed. Distillation yielded 66.0 g. (75%) of product,[35] b.p. 133–137°, n_D^{20} 1.4235. The phenylurethan melted at 92.5–94.5°; Conant and Blatt[23] reported 95°.

2,4-Dimethylpentanol-3 chlorocarbonate (XV). In a 250 cc. three-necked flask cooled in a dry ice–acetone bath was condensed 93.0 g. (0.95 mole) of phosgene. The flask was transferred to an ice bath, fitted with a stirrer, a condenser with an outlet tube leading to a drain, and a dropping funnel. The alcohol XIV (76 g., 0.66 mole) was added over a period of 45 min. The ice bath was removed and the mixture was allowed to stand at room temperature overnight. The excess phosgene was removed by an aspirator over a period of 90 min. Distillation at 60–70 mm. yielded material, b.p. 76–90°, n_D^{20} 1.4218–1.4220, which was a mixture of chlorocarbonate and starting material, because it showed absorption at 3330 and 1773 cm.$^{-1}$ Further distillation yielded two fractions, b.p. 90–100°, n_D^{20} 1.4225, and b.p. 99° (n_D^{20} 1.4235). These two fractions weighed 40 g., which is a 34% yield of chlorocarbonate; they showed no absorption at 3330 cm.$^{-1}$; but did have the band at 1773 cm.$^{-1}$

Anal. (sample with n_D^{20} 1.4235). Calcd. for $C_8H_{15}ClO_2$: C, 53.77; H, 8.48. Found: C, 53.62; H, 8.39.

2,4-Dimethylpentanol-3 carbamate (XVI). The chlorocarbonate (1.0 g., n_D^{20} 1.4225) dissolved in 10 cc. of ether at 5° was treated with 15 cc. of concentrated aqueous ammonia; the ether layer was decanted, and the aqueous layer was extracted twice with ether. The white residue obtained from the combined ether layers gave, after two crystallizations from benzene, material of m.p. 124–124.8°. The melting point was raised to 125.2–126.2° by vacuum sublimation.

Anal. Calcd. for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.59; H, 11.00; N, 8.76.

Action of benzoic-2,4-dimethylpentanol-3 carbonic anhydride on ethanol. A solution of the benzoic-carbonic anhydride was prepared in 50 cc. of toluene from 0.05 mole of benzoic acid, triethylamine, and 2,4-dimethylpentanol-3 chlorocarbonate. After this mixture had been stirred at 0° for 20 min., 2.3 g. of absolute ethyl alcohol was added. The mixture was allowed to come to room temperature overnight. The triethylamine hydrochloride was filtered off, washed with toluene, and the combined toluene solutions were washed with saturated bicarbonate. No benzoic acid was obtained on acidification. The toluene solution was washed with water, dried, and the solvent was removed. The residue on distillation yielded 1.57 g. (20%) of material, b.p. 97–102° (21 mm.) which was mainly ethyl benzoate. The fractions (6.31 g., 57%), b.p. 145–155° (22 mm.) n_D^{26} 1.4828–1.4872, were shown to be 2,4-dimethylpentanol-3 benzoate[36] by saponification to benzoic acid and 2,4-dimethylpentanol-3, which was identified through the crystalline phenylurethan.

Rochester, N. Y.

---

[35] These agree with the reported values (G. Poletaeff, *Ber.*, 24, 1309 (1891).

[36] G. Vavon, M. Barbier, G. Thiebaut, *Bull. soc. chim. France*, [5] 1, 812 (1934), report the following properties for this ester: b.p. 141–142° (15 mm.); n_D^{19} 1.4916.

[Contribution from the Chemical Laboratories of Iowa State College]

Organotin Compounds: Cyclopentadienyl and Related Derivatives

HENRY GILMAN and LEWIS A. GIST, Jr.

Received September 13, 1956

Triphenyl-1-cyclopentadienyltin, diphenyldi-1-cyclopentadienyltin, phenyltri-1-cyclopentadienyltin, and diphenyldi-1-indenyltin were prepared. Cyclopentadienyl derivatives of tin are unstable in the presence of air and light. Triphenyl-1-cyclopentadienyltin is readily hydrolyzed by water and is cleaved by bromine and by n-butyllithium to yield bis-(triphenyltin)oxide, triphenyltin bromide, and tetraphenyltin, respectively. Triphenyl-1-indenyltin and diphenyldi-1-indenyltin were not hydrolyzed under analogous conditions. Addition products were obtained from the Diels-Alder reaction of triphenyl-1-cyclopentadienyltin with maleic anhydride, with diethyl maleate, and with diethyl acetylenedicarboxylate. Triphenyl-2-furyltin did not react with maleic anhydride under corresponding conditions.

Organometallic compounds containing the cyclopentadienyl group have been reported frequently. The recent interest in metallic derivatives of cyclopentadiene, however, has been centered primarily around the preparation and the properties of bis-(cyclopentadienyl)iron (ferrocene)[1–5] and analogous derivatives[6–11]; and the information accumulated in this area has been reviewed.[12] Very little is known about cyclopentadienyl derivatives of the Group IV-B metals. Organotin compounds of this

---

[1] Wilkinson, Rosenblum, Whiting, and Woodward, *J. Am. Chem. Soc.*, 74, 2125 (1952).

[2] Woodward, Rosenblum, and Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952).

[3] Jaffe, *J. Chem. Phys.*, 21, 156 (1953).

[4] Pauson, *J. Am. Chem. Soc.*, 76, 2187 (1954).

[5] Broadhead and Pauson, *J. Chem. Soc.*, 367 (1955).

[6] Wilkinson, *J. Am. Chem. Soc.*, 74, 6146 (1952).

[7] Fischer and Jara, *Z. Naturforschung*, **8B**, 217 (1953).

[8] Wilkinson, Pauson, Birmingham, and Cotton, *J. Am. Chem. Soc.*, 75, 1011 (1953).

[9] Wilkinson, Pauson, and Cotton, *J. Am. Chem. Soc.*, 76, 1970 (1954).

[10] Summers, *J. Am. Chem. Soc.*, 76, 2278 (1954).

[11] Wilkinson, *J. Am. Chem. Soc.*, 76, 209 (1954).

[12] Fischer, *Angew. Chem.*, 67, 475 (1955); see also Cotton, *Chem. Revs.*, 55, 551 (1955).

type, for example, were mentioned very briefly in a patent,[13] but no specific compounds were included in the reference.[14]

This report is concerned with the preparation and the properties of some organotin compounds containing the cyclopentadienyl and the indenyl groups. In addition, the Diels-Alder reaction has been investigated between triphenyl-1-cyclopentadienyltin (I), on the one hand, and maleic anhydride, diethyl maleate, and diethyl acetylenedicarboxylate, on the other, and the results obtained have been included herein.

Cyclopentadienylmagnesium bromide was prepared by a previously described procedure,[15,16] then treated with the appropriate organotin chloride to obtain triphenyl-1-cyclopentadienyltin (I), diphenyldi-1-cyclopentadienyltin (II), and phenyltri-1-cyclopentadienyltin (III). The preparation of tetra-1-cyclopentadienyltin (IV) was also attempted, but the isolation of this derivative proved to be somewhat troublesome, and the product obtained decomposed before it was completely characterized. The following equations are illustrative of the method used for the preparation of these derivatives:

$$C_2H_5MgBr + C_5H_6 \xrightarrow{\text{(benzene-ether)}} C_5H_5MgBr + C_2H_6$$

$$y(C_5H_5MgBr) + (C_6H_5)_{4-y}SnCl_y \longrightarrow (C_6H_5)_{4-y}Sn(C_5H_5)_y + y(MgBrCl)$$

(I), (II),
(III), and (IV)

Incidental to this investigation, it was observed that cyclopentadienylmagnesium bromide did not give a positive Color Test I, when this test was taken in the conventional manner.[17] This apparently anomalous behavior of cyclopentadienylmagnesium bromide (prepared by a known method) was investigated further. It was found, however, that the apparently anomalous behavior of this Grignard reagent was due to a lower degree of reactivity than normally encountered. When the reaction time was extended sufficiently, however, a positive Color Test I was obtained. The minimum time required for a specific concentration of cyclopentadienylmagnesium bromide to give a positive Color Test I is given in Table I.

Freshly prepared cyclopentadienyl derivatives of tin were from pale yellow to canary yellow in color, depending on the number of cyclopentadienyl groups in the molecule. On standing, all of these derivatives [(I), (II), (III), and (IV)] gradually darkened, finally turning rust brown. The rate at which this change occurred was dependent upon the number of cyclopentadienyl groups in the molecule and was accelerated by both light and air.

TABLE I

A POSITIVE COLOR TEST I FOR CYCLOPENTADIENYLMAGNESIUM BROMIDE

Concentration[a] of Michler's Ketone	Concentration[b] of Cyclopentadienylmagnesium Bromide	Minimum Time, in Minutes, for Positive Test at:	
		30°C.	20°C.
1	0.84	3–4	15–18
1	0.68	3–4	15–18
1	0.48	3–4	15–18
1	0.27	3–4	16–18
1	0.10	4–5	16–18
0.5	0.075	6–8	16–19
0.5	0.05	6–9	16–20
0.25	0.025	9–10	20–22
0.1	0.01	>18	>30

[a] Concentration expressed in weight per cent solution of benzene. [b] Concentration expressed in moles per liter as indicated by titration with acid.

The nature of the products obtained from the spontaneous decomposition of (II), (III), and (IV) was not investigated. These decomposition products apparently resulted from a combination of oxidation and polymerization. Several observations made in the course of this investigation were suggestive of the fact that these derivatives are rather sensitive to oxidation. For example: First, on several occasions (IV) caught fire spontaneously. Second, both (III) and (IV) reacted violently with concentrated nitric acid (incidental to analysis), and the reaction was accompanied by the evolution of both heat and light. Third, the per cent of tin found on the attempted analysis of (IV) was consistently below the theoretical value, and it became progressively lower as the sample aged.

Ketone derivatives of ferrocene have been obtained through the Friedel-Crafts reaction,[4] carboxylic acid derivatives have been obtained through metalation with *n*-butyllithium followed by carbonation,[18] and substitution products have been obtained through reactions with diazonium salts.[5] In contrast, triphenyl-1-cyclopentadienyltin (I) is readily hydrolyzed by aqueous alcohol at room temperature, giving triphenyltin hydroxide; it is cleaved by bromine giving triphenyltin bromide; and it undergoes cleavage and redistribution reactions[19,20] in the presence of *n*-butyllithium, giving tetraphenyltin as the principal product.

The relative ease with which (I) was cleaved by water, as well as the pyrophoric nature of (IV) indicated that these derivatives resemble more closely the saltlike alkali metal derivatives of cyclo-

---

(13) Mack and Parker, U. S. Patent **2,604,483** [*C. A.*, **47**, 4358 (1953)].

(14) There has just appeared a note on the preparation of dicyclopentadienyltin by reaction of tin(II) chloride with cyclopentadienyllithium in dimethylformamide: Fischer and Grubert, *Z. Naturforschung*, **11B**, 423 (1956).

(15) Grignard and Courtot, *Compt. rend.*, **158**, 1736 (1914).

(16) Courtot, *Ann. chim.*, **4**, 71 (1915).

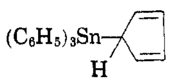
(17) Gilman and Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(18) Benkeser, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

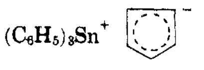
(19) Gilman, Moore, and Jones, *J. Am. Chem. Soc.*, **63**, 2482 (1941).

(20) Gilman and Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

pentadiene[21] than they resemble ferrocene and its analogs. The resonance stabilization gained in the cyclopentadienyl anion of structure (VI) over the conjugated bonds of structure (V) is probably a contributing factor in the relative ease with which triphenyl-1-cyclopentadienyltin (I) undergoes hydrolytic cleavage. In any event, the relative ease



V



VI

with which these derivatives underwent hydrolytic cleavage made it desirable to purify the organotin compounds (I), (II), (III), and (IV) without first hydrolyzing the reaction mixture. This was accomplished by first concentrating the reaction mixture to a paste, then digesting this paste with a mixture of benzene and petroleum ether. The organotin compounds were soluble in this mixture, while the magnesium salts and cyclopentadienylmagnesium bromide were insoluble and could be removed by filtration.

At the time of this investigation, the preparation of triphenyl-1-indenyltin (VII) had not been reported. Subsequently, it has been prepared through the reaction of indenyllithium with triphenyltin chloride.[22] In this investigation, indenylmagnesium bromide was prepared by a previously described procedure[16,23] and treated with the appropriate organotin chloride to obtain triphenyl-1-indenyltin (VII) and diphenyldi-1-indenyltin (VIII). Under conditions analogous to those used for the hydrolysis of (I), triphenyl-1-indenyltin (VII) and diphenyldi-1-indenyltin (VIII) were not hydrolyzed.

Trimethyl-1-cyclopentadienylsilane and dimethyldi-1-cyclopentadienylsilane have been prepared by Frisch.[24] Molecular weight measurements made by this investigator[24] indicated that these derivatives were monomeric. Furthermore, the reaction of trimethyl-1-cyclopentadienylsilane and dimethyldi-1-cyclopentadienylsilane with maleic anhydride, to give the expected Diels-Alder adduct, indicated that the cyclopentadienyl ring still possessed conjugated double bonds, capable of undergoing a Diels-Alder reaction.

In the course of an earlier investigation in this laboratory[25] concerned with the synthesis of organotin compounds as potential chemotherapeutic agents, the reaction of triphenyl-2-furyltin with maleic anhydride was attempted as a possible method for introducing water-solubilizing groups into the organotin compounds. The reaction did not proceed as expected, and its failure was attributed to a reduced reactivity associated with the triphenyltin linkage.

The properties of triphenyl-1-cyclopentadienyltin (I) discussed above, suggested that this derivative might be similar to trimethyl-1-cyclopentadienylsilane, and thus, might undergo a Diels-Alder reaction. This possibility was investigated. Unlike triphenyl-2-furyltin, triphenyl-1-cyclopentadienyltin (I) reacted readily with maleic anhydride to give a good yield of 7-(triphenylstannyl)bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride[26] (IX). Infrared analysis[27] of this derivative (IX) showed the presence of the anhydride linkage. In fact, the spectrum of this derivative was very similar to the spectra of both succinic anhydride and maleic anhydride. The spectrum of (IX) differed primarily from the spectrum of succinic anhydride in the presence of bands characteristic of a monosubstituted benzene.

An extension of this investigation, to determine the scope and the limitations of this reaction, indicated that (I) underwent Diels-Alder reactions with diethyl maleate and with diethyl acetylenedicarboxylate as well. The products isolated were 7-(triphenylstannyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (X) and 7-(triphenylstannyl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid diethyl ester (XI), respectively.

Since a Diels-Alder adduct was obtained from the reaction of triphenyl-1-cyclopentadienyltin with maleic anhydride, diethyl maleate, and diethyl acetylenedicarboxylate, the reaction of triphenyl-2-furyltin was reinvestigated. Under conditions identical with those described above for the reaction of triphenyl-1-cyclopentadienyltin with maleic anhydride, triphenyl-2-furyltin did not give an addition product. This organotin compound was recovered in 94% yield. A second attempted reaction between triphenyl-2-furyltin and maleic anhydride gave essentially the same results.

EXPERIMENTAL

All operations involving the use of Grignard reagents were run in an oxygen-free nitrogen atmosphere. All melting points are uncorrected. The tin analyses were performed according to a recent procedure.[28]

Starting materials. The tetraphenyltin was obtained from the Hooker Electrochemical Co. This was converted to triphenyltin chloride,[29] diphenyltin dichloride,[30] and phenyltin trichloride[30] by published procedures.

Cyclopentadienylmagnesium bromide. Cyclopentadienylmagnesium bromide was prepared in yields of 75–85% (as indicated by titration with hydrochloric acid), through the

---

[21] Thiele, *Ber.*, **34**, 68 (1901).

[22] Zimmer and Sparmann, *Naturwissenschaften,* **40**, 220 (1953); *Ber.*, **87**, 645 (1954).

[23] Grignard, Bellet, and Courtot, *Ann. chim.*, **4**, 56 (1915).

[24] Frisch, *J. Am. Chem. Soc.*, **75**, 6050 (1953).

[25] Gilman and Goreau, *J. Org. Chem.*, **17**, 1470 (1952).

[26] The nomenclature used was recommended by *Chemical Abstracts.*

[27] The authors are grateful to Dr. V. A. Fassel and Messrs. R. McCord and R. Kross of the Atomic Institute, for the infrared analyses.

[28] Gilman and Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

[29] Gilman and Rosenberg, *J. Am. Chem. Soc.*, **74**, 5580 (1952).

[30] Gilman and Gist, *J. Org. Chem.*, in press.

reaction of ethylmagnesium bromide with cyclopentadiene according to a published procedure.[15,16]

Cyclopentadienylmagnesium bromide with Michler's ketone. A stock solution was prepared containing 1 g. of N,N,N′,N′-tetramethyldiaminobenzophenone per 100 ml. of anhydrous benzene, and an aliquot of this solution was diluted with the required amount of benzene when lower concentrations of this ketone were desired.

A stoppered vial containing 1 ml. of an 0.84*M* benzene-ether solution[31] of cyclopentadienylmagnesium bromide and 1 ml. of a 1% solution of Michler's ketone was placed in a water bath at 30° for 1 min. The reaction mixture was then hydrolyzed, and treated dropwise with a 0.2% solution of iodine in glacial acid until the color of iodine did not fade. No trace of the expected green color was observed. Similarly, a negative test was obtained when the reaction mixture was hydrolyzed after 2 min. at 30°; a faint positive test was obtained after 3 min.; and a distinctly positive test after 4 min. When the reaction was carried out at 20° the time required for a positive test was considerably longer.

Lower concentrations of this Grignard reagent were obtained by diluting an aliquot with anhydrous ether. The minimum time required for a specific concentration of cyclopentadienylmagnesium bromide to give a positive Color Test I (characteristic green color) at both 20° and 30° was given in Table I.

Triphenyl-1-cyclopentadienyltin (I). A solution of 20 g. (0.05 mole) of triphenyltin chloride in 200 ml. of ether was added rapidly to a solution containing 0.1 mole of cyclopentadienylmagnesium bromide in 105 ml. of benzene-ether.[31] After heating the reaction mixture at the reflux temperature for a 4-hr. period, it was concentrated to a paste. This paste was digested twice with 200-ml. portions of a (1:1) mixture of benzene-petroleum ether (b.p. 57–70°) and filtered hot. After concentrating and cooling the filtrate, there was obtained 17.4 g. (84%) of triphenyl-1-cyclopentadienyltin which melted between 124 and 129°. After two recrystallizations from petroleum ether (b.p. 57–70°), 14.8 g. (71.5%) of pure product was obtained, melting at 130–131°.

Anal. Calcd. for $C_{23}H_{20}Sn$: Sn, 28.60. Found: Sn, 28.54, 28.70.

Diphenyldi-1-cyclopentadienyltin (II). To 115 ml. of an ether-benzene solution[31] containing 0.1 mole of cyclopentadienylmagnesium bromide was added 8.7 g. (0.025 mole) of diphenyltin dichloride dissolved in 100 ml. of ether. The reaction mixture was heated at the reflux temperature for a period of 48 hr., then concentrated to a paste. The paste was digested twice with 200-ml. portions of a (1:1) mixture of benzene-petroleum ether (b.p. 57–70°) and filtered hot. After the solvents had been removed at 50° under reduced pressure, the residue was dissolved in a minimum of hot petroleum ether (b.p. 57–70°) and cooled in a bath of dry ice. The crude product obtained (10.7 g. melting between 97 and 101°) was recrystallized first from petroleum ether (b.p. 57–70°), then from carbon tetrachloride, to give 7.1 g. (70%) of pure diphenyldi-1-cyclopentadienyltin, melting at 105–106°.

Anal. Calcd. for $C_{22}H_{20}Sn$: Sn, 29.45. Found: Sn, 29.50, 29.54.

Phenyltri-1-cyclopentadienyltin (III). To 285 ml. of an ether-benzene solution[31] containing 0.3 mole of cyclopentadienylmagnesium bromide was added 15.1 g. (0.05 mole) of phenyltin trichloride dissolved in 30 ml. of benzene. After 100 ml. of ether had been added, the reaction mixture was heated at the reflux temperature for 16 hr., then concentrated to a paste. This residue was digested three times with 200-ml. portions of petroleum ether (b.p. 57–70°) and the insoluble materials were removed by filtration. The filtrate was concentrated to 100 ml., and then cooled in a bath of dry ice-acetone. The product was removed by filtration, and dried in a vacuum desiccator to obtain 18.0 g. (59%) of crude phenyltri-1-cyclopentadienyltin melting over the range 43–60°. The product (III) was dissolved in a minimum of boiling petroleum ether (b.p. 57–70°), the amorphous rust brown solid was removed by filtration, and the filtrate was cooled in a bath of acetone and dry ice to obtain 12.13 g. (40%) of pure product melting at 64–65°.

Anal. Calcd. for $C_{21}H_{20}Sn$: Sn, 30.36. Found: Sn, 30.38, 30.49.

On exposure to air, a sample of (III) turned rust brown within 4 hr., and the resulting compound decomposed without melting over the range of 200–220°. This rust brown solid was not investigated.

Tetra-1-cyclopentadienyltin (IV). To 415 ml. of an ether-benzene solution[31] containing 0.4 mole of cyclopentadienylmagnesium bromide was added 13.05 g. (0.05 mole) of anhydrous tin(IV) chloride diluted with 40 ml. of benzene. The mixture was heated at the reflux temperature for a period of 24 hr., and then concentrated to a paste. The resulting paste was digested three times with 200-ml. portions of petroleum ether (b.p. 57–70°) and the resulting solutions were filtered hot. The combined filtrate was concentrated under reduced pressure to a volume of 100 ml., and then cooled in a dry ice-acetone bath to obtain 12.5 g. of crude material melting between 71 and 75°. (After drying this product in a vacuum desiccator over paraffin for 3 hr., the weight and the melting point were determined.) The crude product was dissolved in a minimum of hot petroleum ether (b.p. 57–70°), and filtered hot to remove 2.42 g. of amorphous brown solid. The filtrate was cooled in a dry ice-acetone bath to obtain 8.70 g. (41.5%) of relatively pure material melting at 71–73°.

The infrared spectrum of freshly prepared (IV), when determined in carbon disulfide, as well as in bromoform, did not differ essentially from the spectrum of either (I), (II), or (III), except for an increase in the intensity of the bands characteristic of conjugated double bonds, and a complete absence of the bands characteristic of monosubstituted benzene. When this compound was subjected to analysis for tin, however, the results were less informative. After drying the product for 24 hr. and for 72 hr. in a vacuum desiccator, this derivative gave results that were 2.67% and 3.95% below the theoretical value, respectively.

Anal. Calcd. for $C_{20}H_{20}Sn$: Sn, 31.32. Found (24 hr.): Sn, 28.60, 28.71. Found (72 hr.): Sn, 27.23, 27.52.

Indenylmagnesium bromide. Indenylmagnesium bromide was prepared by a published procedure.[16,23] The resulting product was used as a fine suspension. The heterogeneous nature of this organometallic compound made it undesirable to transfer this reagent or to determine its yield. An excess of this intermediate was, therefore, used in all subsequent reactions.

Triphenyl-1-indenyltin (VII). To a suspension of 0.2 mole of indenylmagnesium bromide in 600 ml. of ether was added 38.5 g. (0.10 mole) of triphenyltin chloride in 300 ml. of ether. The mixture was heated at the reflux temperature for a period of 48 hr., cooled to room temperature, and then poured slowly into an aqueous ammonium chloride solution. The organic layer was separated, dried over calcium sulfate for 24 hr., and then concentrated. The unreacted indene was removed under reduced pressure, and the residue was crystallized from chloroform-petroleum ether (b.p. 57–70°) to obtain 23.9 g. (54%) of crude triphenyl-1-indenyltin, melting over the range of 111–123°. After two recrystallizations from the same solvent pair 21.0 g. (45.5%) of pure product (VII) was obtained, melting at 129–130°.

Anal. Calcd. for $C_{27}H_{22}Sn$: Sn, 25.52. Found: Sn, 25.50, 25.55.

Diphenyldi-1-indenyltin (VIII). To a suspension of 0.4 mole of indenylmagnesium bromide in one liter of ether was added 34.4 g. (0.10 mole) of diphenyltin dichloride in 100

---

(31) This benzene-ether solution had a boiling point of 60°. A solution with this boiling point is obtained when cyclopentadienylmagnesium bromide is prepared according to the procedure of Courtot.[16]

ml. of ether. The mixture was heated at the reflux temperature for a period of 24 hr., concentrated to half-volume, and heated at the reflux temperature for an additional 24 hr. The reaction mixture was hydrolyzed with aqueous ammonium chloride, the organic layer was separated and dried for 24 hr. over calcium sulfate, and the solvents were removed. The indene was removed under reduced pressure. The residue was crystallized from a (1:1) mixture of chloroform-petroleum ether (b.p. 57–70°) to obtain 21.2 g. (42%) of crude (VIII), melting between 81 and 103°. After two recrystallizations from the same solvent pair 14.8 g. (29.9%) of pure diphenyldi-1-indenyltin (VIII) was obtained, melting at 108–110°. Subsequent recrystallization of this product did not improve the melting point.

Anal. Calcd. for $C_{30}H_{24}Sn$: Sn, 23.59. Found: Sn, 23.62, 23.67.

REACTIONS OF TRIPHENYL-1-CYCLOPENTADIENYLTIN (I)

With water. In one experiment, a solution of 4.15 g. (0.01 mole) of triphenyl-1-cyclopentadienyltin in 100 ml. of 95% ethanol was heated at the reflux temperature for 15 min., and then concentrated to near dryness. The resulting oil was dehydrated by azeotropic distillation using benzene, and crystallized from petroleum ether (b.p. 57–70°) to obtain 3.30 g. (92%) of bis(triphenyltin)oxide, melting at 123–124°. A mixture melting point with an authentic specimen was not depressed.

In another experiment, 4.15 g. (0.01 mole) of triphenyl-1-cyclopentadienyltin was dissolved in 100 ml. of 95% ethanol at room temperature, the flask was stoppered and allowed to stand for 24 hr., and then poured into ice water. The product obtained weighed 3.72 g. and melted over the range of 112–117°. This compound was dehydrated by azeotropic distillation using benzene, and then recrystallized from petroleum ether (b.p. 57–70°) to obtain 2.91 g. (81%) of bis(triphenyltin)oxide, melting sharply at 124°. A mixture melting point with an authentic specimen was not depressed.

With n-butyllithium. A solution of 0.03 mole of *n*-butyllithium in 35 ml. of ether was added dropwise at room temperature to a solution of 12.45 g. (0.03 mole) of triphenyl-1-cyclopentadienyltin dissolved in 200 ml. of a (1:1) mixture of benzene-ether. The mixture became turbid almost immediately, and later developed into a heavy gelatinous mass. One-half hour after the addition had been completed, the mixture was poured into a slurry of ether and dry ice, and the carbonated product was allowed to come to room temperature. The mixture was hydrolyzed with water, filtered, and the two layers were separated. The 7.1 g. of solid removed by filtration was subsequently recrystallized from benzene to obtain 5.2 g. (46.5%) of tetraphenyltin melting at 224–225°. A mixture melting point with an authentic specimen showed no depression.

An oil weighing 3.1 g. was obtained by concentrating the ether layer. This oil was not resolved into any pure products.

After acidification of the water layer, and extracting the organic material, 1.7 g. of an acidic oil was removed, which gave a negative qualitative test for tin.[25] This material was not investigated further.

The reaction of triphenyl-1-cyclopentadienyltin with *n*-butyllithium was also investigated at the temperature of a dry ice-acetone bath, using a mixture of ether and toluene as the solvent of the reaction. Under conditions otherwise identical to those described above, a 33% yield of tetraphenyltin was obtained melting at 222–224°.

With bromine. To 12.45 g. (0.03 mole) of triphenyl-1-cyclopentadienyltin in 250 ml. of carbon tetrachloride was added 4.8 g. (0.03 mole) of bromine dissolved in 100 ml. of carbon tetrachloride. The dropwise addition was carried out at room temperature. The color of the bromine was discharged almost instantaneously. After the addition had been completed, the solvent was removed by distillation, and the product was crystallized from petroleum ether (b.p. 57–70°) to obtain 7.8 g. (60.5%) of crude triphenyltin bromide melting over the range of 99–106°. After recrystallization from the same solvent, 6.7 g. (52%) of triphenyltin bromide was obtained melting at 120–121°. A mixture melting point with an authentic specimen showed no depression.

With maleic anhydride. To a solution of 12.45 g. (0.03 mole) of triphenyl-1-cyclopentadienyltin in 30 ml. of benzene was added a suspension of 2.94 g. (0.03 mole) of maleic anhydride in 20 ml. of benzene. The mixture became warm spontaneously. After the initial reaction had subsided, the mixture was heated at the reflux temperature for 1 hr., then the benzene was removed by distillation. The crude product was digested with 50 ml. of petroleum ether (b.p. 57–70°) to remove any unreacted starting material, cooled, and filtered. The residue was recrystallized from carbon tetrachloride to obtain 11.0 g. of crude 7-(triphenylstannyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride[26] (IX) melting between 138 and 150°. After two recrystallizations from carbon tetrachloride 9.1 g. (59%) of pure product was obtained, melting at 144–145°. A duplicate reaction gave essentially the same results. This product was too insoluble to determine the neutral equivalent.

Infrared analysis of this derivative showed the acid anhydride absorption bands characteristic in the spectra of maleic anhydride and succinic anhydride.

Anal. Calcd. for $C_{27}H_{22}O_3Sn$: Sn, 23.13. Found: Sn, 22.83, 23.03.

With diethyl maleate. To a solution of 12.45 g. (0.03 mole) of triphenyl-1-cyclopentadienyltin dissolved in 50 ml. of benzene was added 5.67 g. (0.033 mole) of diethyl maleate, and the mixture was heated at the reflux temperature for a 4-hr. period. The solvent was removed under reduced pressure, and the resulting oil (20 g.) was dissolved in 100 ml. of not methanol, filtered, concentrated, and cooled to obtain 10.4 g. (59%) of crude product, melting between 101–106°. Two subsequent recrystallizations from 75% ethanol gave 8.8 g. (49.9%) of relatively pure 7-(triphenylstannyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester[26] (X), melting at 107–109.5°. From this product an analytical sample was obtained by an additional recrystallization from diethyl ether using a dry ice-acetone bath. The analytical sample melted at 109.5–111°.

Anal. Calcd. for $C_{31}H_{32}O_4Sn$: Sn, 20.21. Found: Sn, 20.25, 20.29.

With diethyl acetylenedicarboxylate. A solution of 12.45 g. (0.03 mole) of triphenyl-1-cyclopentadienyltin dissolved in 300 ml. of ether was treated with 5.10 g. (0.03 mole) of the diethyl acetylenedicarboxylate. The mixture was heated at the reflux temperature for a period of six hr., concentrated to 150 ml. and cooled in a dry ice-acetone bath. The crystallized product was removed by filtration; the mother liquor was concentrated to 50 ml. and returned to the bath. The first crop of crystals weighed 4.3 g. and melted over the range of 100–104°, while the second crop weighed 5.3 g. and melted over the range of 97–102°. The combined crude product (7.6 g. or 44.5%) of 7-(triphenylstannyl)bicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid diethyl ester[26] was twice recrystallized from diethyl ether to obtain 6.9 g. of pure product melting at 107–108°.

A duplicate reaction gave essentially the same results.

Anal. Calcd. for $C_{31}H_{30}O_4Sn$: C, 63.60; H, 5.18; Sn, 20.28. Found: C, 63.22, 63.15; H, 4.92, 5.10; Sn, 20.13, 20.10.

Triphenyl-2-furyltin with maleic anhydride. To a solution of 4.17 g. (0.01 mole) of triphenyl-2-furyltin in 10 ml. of benzene was added a suspension of 0.98 g. (0.01 mole) of maleic anhydride in 10 ml. of benzene. The mixture was heated at the reflux temperature for a period of one hr., the benzene was removed by distillation, and the crude product was recrystallized from carbon tetrachloride to obtain 3.94 g. (94% recovery) of triphenyl-2-furyltin, melting at 160–

161°. A mixture melting point with an authentic specimen was not depressed.

For a duplicate reaction 3.73 g. (88%) of triphenyl-2-furyltin was recovered, melting at 159–160°.

Acknowledgment. This investigation was aided by a fellowship from The National Medical Fellowships, Inc., through funds appropriated by The National Foundation for Infantile Paralysis. One of us (L.A.G.) wishes to express his appreciation for this assistance.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN ONTARIO]

Organometallic Reactions of ω-Fluoroalkyl Halides. II.[1,2]

Reactions of ω-Fluoroalkylmagnesium Chlorides

W. C. HOWELL, W. J. COTT, AND F. L. M. PATTISON

Received September 14, 1956

The study of Grignard reagents formed from ω-fluoroalkyl halides has been extended to include a variety of typical reactions through the use of such reagents as acid chlorides, acid anhydrides, ethylene oxide, benzonitrile, and triethyl orthoformate. This has led to new methods for preparing ω-fluorocarboxylic esters, ω-fluoroalkyl ketones, ω-fluoroalcohols and ω-fluoroaldehydes, all of which are of pharmacological interest.

In the preceding paper of this series[2] a general method was outlined for the preparation of Grignard reagents from various ω-fluoroalkyl halides. From this study, the longer chain ω-fluoroalkyl chlorides (C_6–C_{10}) emerged as potentially valuable intermediates in the synthesis of new ω-fluoroalkylated derivatives. At that time, however, it was established only that these Grignard reagents reacted with carbon dioxide. To determine the general usefulness of the method, other reactions have been examined both for the diversity of reaction type, and for possible pharmacological interest of the products. The reactants selected were: (*a*) *Ethyl chloroformate:* reaction of a carbonyl halide; formation of ω-fluorocarboxylic esters.[3,4] (*b*) *Acid chlorides:* reaction of a carbonyl halide; formation of ω-fluoroalkyl ketones.[5] (*c*) *Carboxylic anhydrides:* addition to a carbonyl group; formation of ω-fluoroalkyl ketones.[5] (*d*) *Ethylene oxide:* cleavage of an epoxide; formation of ω-fluoroalcohols.[6] (*e*) *Benzonitrile:* addition to an unsaturated C—N system; formation of ω-fluoroalkyl phenyl ketones.[5] (*f*) *Triethyl orthoformate:* cleavage of an ether-acetal; formation of ω-fluoroaldehydes.[7]

First to be examined were the reactions of ω-fluoroalkylmagnesium chlorides with ethyl chloroformate[8–10] giving rise to ω-fluorocarboxylic esters. A large excess of chloroformate was used and the reaction was completed by heating for a short time under reflux; by this means, tertiary alcohol formation was minimized, but ketones were occasionally isolated, formed by reaction of excess Grignard reagent with the main product. A representative example is described in the Experimental section, and results are summarized in Table I. Similar conditions were found to be satisfactory for the use of acid chlorides[11] in the preparation of ω-fluoroalkyl ketones, although tertiary alcohol formation appeared to occur to a greater extent than in the reactions with ethyl chloroformate. The lower ω-fluorocarboxylic acid chlorides failed to react under the conditions employed; thus fluoroacetyl chloride, 3-fluoropropionyl chloride, 4-fluorobutyryl chloride and 5-fluorovaleryl chloride gave none of the desired ketones. The successful reactions are shown in Table I.

The use of carboxylic anhydrides[12–16] for the preparation of ketones was next investigated. A series of ω-fluoroalkyl methyl ketones (Table I)

---

[1] (*a*) Issued as DRB Report No. SW-29. (*b*) To avoid ambiguity, fluorine is not generally referred to as halogen in this communication.

[2] Part I, F. L. M. Pattison and W. C. Howell, *J. Org. Chem.*, **21**, 879 (1956).

[3] F. J. Buckle, F. L. M. Pattison, and B. C. Saunders, *J. Chem. Soc.*, 1471 (1949).

[4] F. L. M. Pattison, S. B. D. Hunt, and J. B. Stothers, *J. Org. Chem.*, **21**, 883 (1956).

[5] R. R. Fraser, J. E. Millington, and F. L. M. Pattison, *J. Am. Chem. Soc.*, in press.

[6] F. L. M. Pattison, W. C. Howell, A. J. McNamara, J. C. Schneider, and J. F. Walker, *J. Org. Chem.*, **21**, 739 (1956).

[7] J. F. K. Wilshire and F. L. M. Pattison, *J. Am. Chem. Soc.*, **78**, 4996 (1956).

[8] J. Houben, *Ber.*, **36**, 3087 (1903).

[9] R. Gaertner, *J. Am. Chem. Soc.*, **73**, 3934 (1951).

[10] A. I. Krutman, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 1385 (1952) (Engl. translation).

[11] W. C. Percival, R. B. Wagner, and N. C. Cook, *J. Am. Chem. Soc.*, **75**, 3731 (1953).

[12] Tissier and Grignard, *Compt. rend.*, **132**, 683 (1901).

[13] H. Fournier, *Bull. soc. chim. France*, [3], **31**, 483 (1904); [3], **35**, 19 (1906); [4], **7**, 836 (1910).

[14] M. S. Newman and W. T. Booth, *J. Am. Chem. Soc.*, **67**, 154 (1945).

[15] M. S. Newman and T. J. O'Leary, *J. Am. Chem. Soc.*, **68**, 258 (1946).

[16] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).