acetone 1719 cm.$^{-1}$) may be caused either by a slight opening of the C—CO—C bond angle to 123°[5] or by an interaction of the d-electrons of the adjacent iron atom with the π-electrons of the carbonyl groups.

Experimental

1,1'-(α-Carbomethoxy-β-ketotrimethylene)ferrocene.—To a solution of dimethyl 1,1'-ferrocenediacetate (0.22 g., 0.67 mmole) dissolved in anhydrous ether (20 ml.) was added an ethereal solution of sodium triphenylmethide (0.12 *M*). The reaction was maintained under an atmosphere of nitrogen and the addition was continued until the distinctive red color of sodium triphenylmethide persisted. An orange precipitate immediately formed. The molar ratio (methide/ester) required was 2.9 for several runs. After standing at room temperature for 4 hr., the solution was shaken with water, the orange precipitate dissolving in the ether phase. The ethereal solution was washed with water, dried over anhydrous sodium sulfate, and the ether removed. The residue was chromatographed on a silicic acid–Celite column with hexane–dichloromethane as eluent. The first band of triphenylmethane was followed by the product which was crystallized from heptane yielding 0.17 g. (85%) of orange needles, m.p. 121–121.5°.

Anal. Calcd. for $C_{15}H_{14}O_3Fe$: C, 60.41; H, 4.74; Fe, 18.74. Found: C, 60.34; H, 4.93; Fe, 18.90.

Enol Acetate of 1,1'-(α-Carbomethoxy-β-ketotrimethylene)-ferrocene.—1,1'-(α-Carbomethoxy-β-ketotrimethylene)-ferrocene (0.1 g., 0.24 mmole) was added to 20 ml. of isopropenyl acetate which contained 0.2 g. of sulfosalicylic acid as catalyst. The mixture was heated to 90° and held at that temperature for 6 hr. The solution (containing a dark red precipitate) was neutralized with sodium bicarbonate solution and then extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and the ether removed. The residue was chromatographed on a column of silicic acid–Celite with hexane–chloroform eluent. The product was recrystallized from heptane yielding 0.06 g. (75%) of orange needles, m.p. 149–150°.

Anal. Calcd. for $C_{17}H_{16}O_4Fe$: C, 60.03; H, 4.74; Fe, 16.43. Found: C, 60.22; H, 4.91; Fe, 16.27.

1,1'-(β-Ketotrimethylene)ferrocene.—1,1'-(α-Carbomethoxy-β-ketotrimethylene)ferrocene (0.25 g., 0.84 mmole) was dissolved in a mixture of 20 ml. of glacial acetic acid and 3 ml. of concentrated hydrochloric acid. The mixture was heated at 100° for 30 min. After cooling, the solution was neutralized to pH 8 with sodium hydroxide followed by sodium bicarbonate, extracted with ether, and the ether dried over anhydrous sodium sulfate. After removing the ether, the residue was chromatographed over silicic acid–Celite with hexane–dichloromethane eluent, and the product recrystallized from heptane, yielding yellow-orange needles (0.17 g., 85%) m.p. 154–155°.

Anal. Calcd. for $C_{13}H_{12}OFe$: C, 65.01; H, 5.04; Fe, 23.28. Found: C, 65.12; H, 4.79; Fe, 23.46.

1,1'-Trimethyleneferrocene.—1,1'-(β-Ketotrimethylene)-ferrocene (52 mg. 0.22 mmole) was dissolved in 10 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid and 5 ml. of methyl mercaptan were added. The mixture was allowed to stand at 0° for 20 min. and was then neutralized with sodium hydroxide and extracted with ether. After removal of the ether the product was crystallized from octane, yielding 52 mg. (73%) of orange crystals, m.p. 160–162°. Without further purification, the thioketal was refluxed with W-5 Raney nickel in absolute ethanol for 3 hr. with mechanical stirring. The reaction mixture was filtered, acidified, and the product extracted with ether. The ether was evaporated and the residue chromatographed on Merck neutral alumina with hexane as eluent. A yellow solid thus was obtained which after sublimation at 2 mm. at 64° had m.p. 105–106° (lit.,[3] 105–106°). The same product was obtained by Clemmensen reduction of 1,1'-(α-ketotrimethylene)ferrocene.[6]

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Formation of an Organotin-Nitrogen Bond

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Tin-nitrogen bonding in triammonotin halides, $Sn(NH_2)_3X$ (where X stands for a halogen atom), are known,[1-3] but the same bonding in organotin compounds has apparently not been described as yet.

The reaction of ammonia or an amine with organotin compounds gives complex addition compounds containing one or two moles of ammonia or amine as coordinating components.[4-8]

It has been discovered that the reaction of diethylaminomagnesium bromide with trialkyltin chlorides gives trialkyl(diethylamino)tins having an organotin-nitrogen bonding (equation 1). The aminotin compounds could be isolated analytically pure by distillation under reduced pressure. The oily product reacted with hydrochloric acid to give trialkyltin chloride and the same amine hydrochloride (equation 2), both compounds being identified by the infrared spectra and the melting points. Upon exposure to air trialkyl(diethylamino)tin compounds were attacked very quickly by atmospheric moisture and carbon dioxide to afford diethylamine and trialkyltin carbonate (equation 3). The infrared spectra of triethyltin carbonate thus obtained coincided in every respect with those of the authentic sample prepared from carbon dioxide and bis(triethyltin) oxide.

$$R_3SnCl + (C_2H_5)_2NMgBr \longrightarrow R_3SnN(C_2H_5)_2 + MgBrCl \quad (1)$$

$$R_3SnN(C_2H_5)_2 + 2HCl \longrightarrow R_3SnCl + (C_2H_5)_2NH{\cdot}HCl \quad (2)$$

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$$2R_3SnN(C_2H_5)_2 + CO_2 + H_2O \longrightarrow (R_3Sn)_2CO_3 + 2(C_2H_5)_2NH \quad (3)$$

$$(R = C_2H_5,\ n\text{-}C_3H_7,\ \text{or}\ n\text{-}C_4H_9)$$

Infrared absorptions characteristic to the diethylaminotin grouping, Sn—N$(C_2H_5)_2$, were observed at 1290 (m), 1173 (vs), 1010 (s), 880 (s), and 780 (s) cm.$^{-1}$, all being common to the three trialkyl(diethylamino)tins herein described. These bands completely disappeared on exposure of the sample to air for several minutes on a sodium chloride plate, when characteristic bands of organotin carbonate appeared at 1560–1520 (vs), 1370 (vs), 1070 (m), and 840 (m) cm.$^{-1}$ instead.

These results show that the organotin–nitrogen bonding is rather stable to heating, as indicated by no change upon distillation, but is highly reactive toward proton-containing reagents.

Experimental

Analyses.—A microelementary analysis for carbon and hydrogen was given up because of the too high sensitivity of the sample to air (equation 3). As soon as a sealed ampoule was cut, diethylamine which was recognized by the strong odor vaporized.

Nitrogen was analyzed by titration according to equation 2: an exactly weighed sealed ampoule containing about 2.0 g. of the sample was crushed with a glass rod in 30 ml. of standardized 0.5 *N* hydrochloric acid, and the excess acid was back-titrated with 0.5 *N* sodium carbonate with methyl orange as an indicator.

Tin analyses were carried out according to Farnsworth and Pekola.[9] In this case the vaporization of diethylamine has no effect on the analytical values of tin.

Triethyl(diethylamino)tin.—A tetrahydrofuran solution of diethylaminomagnesium bromide prepared from 2.9 g. (0.12 g.-atom) of magnesium, 10.9 g. (0.1 mole) of ethyl bromide, and 7.3 g. (0.1 mole) of diethylamine in 50 ml. of tetrahydrofuran was added dropwise to a solution of 14.5 g. (0.06 mole) of triethyltin chloride[10] (b.p. 86–88°/9 mm.) dissolved in 50 ml. of tetrahydrofuran. An exothermic reaction was observed during this procedure. After refluxing for 4 hr. the solvent was distilled and the reaction product was fractionated under reduced pressure. A fraction boiling at 72–88°/11 mm. was collected; yield, 10.5 g. (63%). Redistillation gave 9.5 g. of an analytically pure fraction boiling at 114–117°/23 mm. All procedures were carried out in a nitrogen atmosphere. This sample gave a negative Beilstein test for halogen. The product was stored in sealed ampoules under nitrogen.

Anal. Calcd. for $C_{10}H_{25}NSn$: Sn, 42.69; N, 5.04. Found: Sn, 42.64, 42.98, 42.45; N, 4.92.

Tri-*n*-propyl(diethylamino)tin and tri-*n*-butyl(diethylamino)tin were also obtained in about 70% yields by an analogous way from tri-*n*-propyltin chloride[10] (b.p. 122–123°/10 mm.) and tri-*n*-butyltin chloride[10] (b.p. 130–132°/4 mm.), respectively.

Tri-*n*-propyl(diethylamino)tin had b.p. 118–120°/13 mm.

Anal. Calcd. for $C_{13}H_{31}NSn$: Sn, 36.97; N, 4.36. Found: Sn, 37.41; N, 3.95.

Tri-*n*-butyl(diethylamino)tin distilled at 124–134°/8 mm.

Anal. Calcd. for $C_{16}H_{37}NSn$: Sn, 32.77; N, 3.87. Found: Sn, 32.62; N, 3.40.

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Attempted Hydrogenolysis of Amines with Triphenyltin Hydride[1]

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It has been reported that allylamine[4] (I) and benzylamine[5] (II), *n*-butylamine and *n*-hexylamine[6] are hydrogenolyzed to the parent hydrocarbons, propylene, toluene, butane and hexane, respectively, using triphenyltin hydride (III). Ammonia was claimed as one product of the reactions and hexaphenylditin (IV) was also isolated.

In attempting to repeat these results it was found that I or II with III does give IV and a steady evolution of gas. However, no propylene (using vapor phase chromatography), toluene (using vapor phase chromatography and infrared analysis), or ammonia (Nessler's reagent) could be detected. In the reaction of II with III, a considerable amount of benzene was formed. These results are in direct contrast to the successful reports of van der Kerk and Noltes, who, however, failed to identify positively the expected propylene and ammonia.[7] These results are also in sharp contrast to those of Kupchik and Connolly. The latter reported that a superimposable infrared spectrum of toluene was obtained from the first drops of distillate of the reaction mixture, which is difficult to understand. We were unable to find any trace of toluene. Benzene invariably accompanies the reaction of benzylamine with triphenyltin hydride and therefore should have been present in the first drops of distillate. Again, no positive evidence for ammonia was provided.

In the course of our attempts to hydrogenolyze carbon–nitrogen bonds, we also examined *p*-toluidine, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine. In these experiments IV and a gas were always obtained, but no hydrocarbon nor ammonia (see Experimental). In the case of *p*-toluidine and III, which was carried out in a sealed tube, the gas was not condensable at −80°. Qualitatively, the rate of formation of IV

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[2] Taken from the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

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