of perylene and perylene-2-carboxylic acid were isolated (0.06 g, 8.8%, mp 265–275° and 330–333°).

Extraction of the catalyst with ethanolic potassium hydroxide was followed by acidification of the filtered solution. After filtration and drying perylene-2-carboxylic acid was isolated (0.0398 g, 5.80%, mp 341.5–342.0°). A mixture melting point with perylene-3-carboxylic acid was depressed (313–320°).

Anal. Calcd for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08. Found: C, 85.08; H, 4.42.

Attempted Dehydrogenation of 6-Acetyl-1,2,3,10,11,12-hexahydroperylene.—6-Acetyl-1,2,3,10,11,12-hexahydroperylene (2.04 g, 0.00680 mole) and 5% palladium suspended on carbon (0.91 g) were heated at 242–285° for 0.5 hr. After cooling, extraction with chloroform and crystallization from ethanol, 0.32 g of a material (mp 116.8–120.0°) having an infrared spectrum (KBr) with a strong absorption at 1232 cm^{-1}, which suggests a structure of 1-ethylperylene-β,12-cyclo oxide, 9, was isolated.

Anal. Calcd for $C_{22}H_{14}O$; C, 89.77; H, 4.79. Found: C, 90.04; H, 5.08.

1-Ethylperylene.[32]—Ethyllithium (0.053 mole, 1.78 *N*, Lithium Corp. of America) in benzene was added dropwise during 0.50 hr to a 0.033 *M* benzene solution of perylene (12.60 g, 0.050 mole) under a dry argon atmosphere with stirring. After 48 hr at 80°, the reaction mass was hydrolyzed with water (3.0 ml). Solvents were distilled and the residue was dissolved in hexane (550 ml). Chromatography of the hexane solution over alumina (Alcoa Activated Dust, Grade F-20) yielded 1-ethylperylene (3.4 g, 24%, mp 78–84°) in the early eluate fractions (eluent, hexane) together with uncrystallizable oils in some fractions.

Recrystallization of 1-ethylperylene from 95% ethanol furnished yellow needles, mp 84–85°.

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.26; H, 5.80.

The 1,3,5-trinitrobenzene derivative had mp 199–200°; ultraviolet, λ_{max} mμ (log ϵ), 251 (4.47), 257.5 (4.71), 265 infl (4.32), 383.5 (4.03), 403.5 (4.35), 427 (4.42).

A benzene solution of commercial ethyllithium (Lithium Corp.) was refluxed for 24 hr, was hydrolyzed with water, and shown to contain less than 0.07% ethylbenzene (if any) by gas chromatography. Control solutions were analyzed easily in the range 0.07–0.7% ethylbenzene.

1-*n*-Butylperylene.—Freshly prepared 0.42 *N* *n*-butyllithium[33] (58.8 ml, 0.025 mole) in diethyl ether was added to a 0.025 *M* tetrahydrofuran solution of perylene (6.30 g, 0.025 mole) under a dry nitrogen atmosphere at −30 ± 2.5° during 1.0 hr. After 1.5 hr from the start of the organolithium addition, the reaction mass was added jetwise onto Dry Ice. Ether and tetrahydrofuran were distilled and the dry residue was extracted with boiling hexane (100 ml, four times). After crystallization of small amounts of perylene, the hexane extracts (50 ml) were chilled to −30°. An oil separated and the hexane solution was decanted. The oil coagulated (0.63 g, 8.2%, mp 61–64°) furnishing 1-*n*-butylperylene. Chilling of the hexane solution at −78° afforded 1.6 g of additional crystalline 1-butylperylene (20.8%, mp 60–67°).[34] After chromatography of the hexane solution, additional purified 1-butylperylene (1.2 g, 14%, mp 70.0–70.5° (uncor) lit. mp 66.5–67.0°) was secured. The salts were not investigated.

Nmr Data.—Pmr spectra were obtained on the isomeric ethylperylenes in $CDCl_3$ at 60 Mc with internal tetramethylsilane. Integration curves were secured for 1-ethyl- and 2-ethylperylenes; 3-ethylperylene was not soluble enough to give an integration curve. The intensities found for the methyl-, methylene-, and aromatic protons are shown in Table IV.

TABLE IV

	1-Ethylperylene, 8.5% by wt	Theory, %	2-Ethylperylene, 9.1% by wt
Methyl	5.31	5.33	5.71
Methylene	8.10	8.00	8.03
Aromatic	1.45	1.45	1.43
AB type	1.29	1.38	
AB type		1.57	1.57
X type	4.50	3.67	
X type		2.75	2.45

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[32] This synthesis was run by Miss E. Ellis, National Science Foundation Undergraduate Research Participant during 1964. 1-Ethylperylene was also prepared using ethyllithium prepared from lithium and ethylchloride.

[33] R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

[34] Isolation of 1-*n*-butylperylene by fractional crystallization from hexane indicates that purification by chromatography over alumina is not essential to securing 1-butylperylene.

Oxidation Reactions of Hexaphenylditin

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The tin–tin bond of hexaphenylditin is cleaved by a variety of common oxidants to give the corresponding triphenyltin compounds. The oxidation mechanism in the reaction of hexaphenylditin with sodium methoxide and air in tetrahydrofuran was investigated. In the presence of ethyl bromide, the oxidation yielded ethyltriphenyltin along with the usual products. The results are accounted for by assuming the existence of free triphenyltin radicals.

The results of a previous investigation[1] of the oxidation addition reactions of diphenyltin were found to be in accord with a reaction mechanism which involves the formation of a reactive triphenyltin radical intermediate.

It has been shown[2,3] that hexaphenyldisilane does not dissociate into triphenylsilyl radicals. However, the bond energy of the Sn–Sn bond is much lower than that of either the C–C or the Si–Si bond.[4] Those compounds which contain a Sn–Sn bond are quite reactive and are readily cleaved to form monotin compounds. In view of this lower bond energy hexaphenylditin (I) might be expected to react by dissociation into triphenyltin radicals and if this does occur it should be possible to trap these radicals and add further credence as to their existence.

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[1] W. L. Lehn and Tsu Tzu Tsai, unpublished results.

[2] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

[3] H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[4] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text," Interscience Publishers, Inc., New York, N. Y., 1962, p 348.

TABLE I

REACTIONS OF HEXAPHENYLDITIN AND METALLIC TIN

	Hexaphenylditin	Metallic tin
+ air	$\longrightarrow$ no reaction	$\longrightarrow$ little effect[a]
+ $NaOCH_3$ + air (THF)	$\longrightarrow (C_6H_5)_3SnOH$ (92.3%)	$\xrightarrow{NaOH} SnO_2$
+ NaOH + H_2O (acetone)	$\longrightarrow (C_6H_5)_3SnOH$ (77.1%)	$\xrightarrow{soln} SnO_2$
+ H_2O (acetone)	$\longrightarrow$ no reaction	$\longrightarrow$ no reaction[a]
+ NaOH (THF)	$\longrightarrow$ no reaction	$\xrightarrow{hot} H_2 + H_2SnO_4$
+ H_2SO_4 (THF)	$\longrightarrow$ no reaction	$\xrightarrow{slow} H_2 + SnSO_4$
+ $AgNO_3$ (acetone)	$\longrightarrow Ag + (C_6H_5)_3SnNO_3$ (90.0%)	$\longrightarrow Ag + Sn(NO_3)_2$
+ $CuCl_2$ (acetone)	$\longrightarrow CuCl + (C_6H_5)_3SnCl$ (98.9%)	$\longrightarrow CuCl + SnCl_2$
+ $HgCl_2$ (acetone)	$\longrightarrow Hg + (C_6H_5)_3SnCl$ (15.0%)	$\longrightarrow Hg + SnCl_2$
[$(C_6H_5)_3SnCl + HgCl_2$	$\longrightarrow (C_6H_5)_2Hg + (C_6H_5)_2SnCl_2$]	
+ $SnCl_2$ (acetone)	$\longrightarrow$ no reaction	$\longrightarrow$ no reaction
+ $ZnCl_2$ (acetone)	$\longrightarrow$ no reaction	$\longrightarrow$ no reaction
+ HCl (THF)	$\longrightarrow H_2 + (C_6H_5)_3SnCl$ (60%)	$\longrightarrow H_2 + SnCl_2$
[$(C_6H_5)_3SnCl$ + HCl	$\longrightarrow (C_6H_5)_2SnCl_2 + C_6H_6$]	
+ $SnCl_4$ (benzene)	$\longrightarrow SnCl_2 + (C_6H_5)_3SnCl$	$\longrightarrow SnCl_2$
[$(C_6H_5)_3SnCl + SnCl_4$	$\longrightarrow (C_6H_5)_2SnCl_2$]	
+ X_2	$\longrightarrow (C_6H_5)_3SnX$	$\longrightarrow SnX_4$
[Concd $HNO_3(H_2O) + (C_6H_5)_3SnX$	$\longrightarrow (C_6H_5)_3SnOH + (C_6H_5)_3SnNO_3$]	$\longrightarrow SnO_2$
[$HNO_3 + (C_6H_5)_3SnX$	$\longrightarrow C_6H_5NO_2 + SnO_2$]	
+ active metals	$\longrightarrow (C_6H_5)_3SnM$[b]	
+ alkyl halides	$\xrightarrow{conditional} R_3SnR' + R_3SnX$[c]	$\xrightarrow{conditional} R_2SnX_2(R_3SnX)$[d]
+ $LiAlH_4$	$\longrightarrow (C_6H_5)_3SnH$ (not identified)[e]	

[a] See ref 16. [b] See ref 7 and 8. [c] See ref 8. [d] K. Sisido, Y. Takeda, and H. Nozaki, *J. Org. Chem.*, **27**, 2411 (1962). [e] See ref 9.

Therefore, a study of the reactions of hexaphenylditin was initiated.

It has been shown that hexaphenylditin undergoes cleavage reactions with potassium permanganate,[5] iodine,[6] active metals,[7,8] lithium aluminum hydride,[9] and perfluoroalkyl iodide[10] but does not oxidize in air at ordinary temperatures. It has been found that this compound, like hexaethylditin[11,12] can undergo two types of reactions: oxidation reactions in which only tetravalent organotin compounds are formed and disproportionation reactions which involve the formation of lower valent tin compounds, such as the reaction of I and aluminum chloride in which we found that divalent tin compounds were formed. A study of the latter type of reaction would be expected to be quite complex involving a number of steps and various intermediates and it would be difficult to learn much about the simple dissociation of I into triphenyltin radicals; therefore, the work presented in this report deals only with the oxidation reactions of I.

Hexaphenylditin in either the solid state or in solution is not appreciably oxidized upon exposure to air. However, when a tetrahydrofuran (THF) solution of I and sodium methoxide were stirred in the presence of air the Sn–Sn bond was cleaved and triphenyltin hydroxide was isolated as the product. The nature of the reaction is as follows. (1) No hydrogen was evolved during the course of the reaction. (2) Air is involved in the reaction, the volume of air above the reaction mixture gradually decreasing as the reaction proceeded. (3) The yield of triphenyltin hydroxide was greatly reduced when the reaction was carried out under an atmosphere of nitrogen. (4) A mixture of sodium methoxide and THF will gradually react with air. No attempt was made to identify the products. (5) The yield of triphenyltin hydroxide was low when the sodium methoxide was replaced by a concentrated aqueous solution of sodium hydroxide. The latter solution was not appreciably miscible with THF. Based on these observations the cleavage reaction appeared to be simply the oxidation of I by sodium peroxide. Similar results were obtained when I was treated with a mixture of 5% sodium hydroxide, 30% hydroxygen peroxide, and acetone in the proportions of 1:2:1, respectively. A mixture of 30% hydrogen peroxide and acetone had no effect on I.

The Sn–Sn bond in I can be cleaved smoothly at room temperature by a variety of common oxidants, Table I, to give the corresponding triphenyltin compounds. Except for the reaction with stannic chloride

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(5) Von G. Bahr, *Z. Anorg. Allgem. Chem.*, **256**, 107 (1948).

(6) J. Boseken and J. J. Rutgers, *Rec. Trav. Chem.*, **42**, 1017 (1925).

(7) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60** (5), 457 (1960).

(8) C. Tamborski and E. J. Soloski, *J. Am. Chem. Soc.*, **83**, 3734 (1961).

(9) G. A. Baun and W. J. Considine, *J. Org. Chem.*, **29**, 1267 (1964).

(10) H. D. Koesz, J. R. Phillips, and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6228 (1960).

(11) G. A. Raznvaev, N. S. Vyazankin, and O. A. Shchepetkiva, *J. Gen. Chem. USSR*, **31**, 3516 (1961).

(12) G. A. Razuvaev, N. S. Vyazankin, and Yu. I. Dergnnou, *ibid.*, **31**, 1598 (1961).

in which stannous chloride was the expected product the reactions were simple. In no case were they complicated by competing disproportionation reactions which would be expected to give stannous chloride or metallic tin as products. However, side reactions did occur. In the reactions of I with hydrochloric acid, mercuric chloride, and stannic chloride, distribution reactions between the product, triphenyltin chloride, and the oxidants did occur to give products such as diphenylmercury, diphenyltin dichloride, and others. These distribution reactions were not unexpected as they have been reported in the literature.[13] No effort was made to optimize the yields of the triphenyltin products.

The reactions of I which have been studied show a close parallel to similar reactions of metallic tin even though the conditions of the reactions are quite different. These parallel reactions are listed in Table I. Except where indicated, the reactions for metallic tin are derived from their oxidation–reduction potentials. Hague and Prince[14] have studied the ultraviolet spectra of organometallic compounds containing metal–metal bond and reported that there are intense interactions between phenyl groups on different M atoms across the metal–metal bond. In view of the similarities in reactivity of I and metallic tin the effect of this interaction on the M–M bond is small. The generally higher reactivity of hexaalkylditins over that of I would indicate that this interaction does have some effect however.

Polymeric diphenyltin reacts readily with hydrogen peroxide to form diphenyltin oxide[15] in contrast to the fact that no reaction is observed between hydrogen peroxide and either I or metallic tin.[16] The enhanced reactivity of polymeric diphenyltin may be due to an unfavorable arrangement of the tin–tin bonds resulting in a certain amount of bond strain. A similar argument has been advanced to explain the enhanced reactivity of decaphenylcyclopentasilane over that of hexaphenyldisilane.[17–19]

It is possible to trap the triphenyltin radicals formed when a solution of I and sodium methoxide in THF is oxidized with air by adding ethyl bromide to the reaction mixture. The reaction mixture, after stirring overnight at room temperature, gave ethyltriphenyltin in addition to the usual products. In the absence of sodium methoxide no reaction occurred and a quantitative recovery of hexaphenylditin and ethylbromide was realized. The function of the sodium methoxide in the air oxidation of hexaphenylditin it appears is to provide an active peroxide. The formation of ethyltriphenyltin when ethylbromide is present in the reaction mixture can be explained by the series of free-radical chain reactions in Scheme I. Although interpreted by a different reaction mechanism a similar reaction was reported for hexaethylditin.[20,21] When hexaethylditin is oxidized in carbon tetrachloride by either benzoyl peroxide or oxygen triethyltin chloride is isolated in addition to other products. It was found that hexaphenylditin could not be oxidized by either of these reagents.

SCHEME I

A. Initiation $2OOH^- \longrightarrow 2O\cdot + 2OH^-$

$Ph_3Sn\text{–}SnPh_3 + 2O\cdot \longrightarrow 2Ph_3SnO\cdot$

$Ph_3SnO\cdot + Ph_3Sn\text{–}SnPh_3 \longrightarrow Ph_3Sn\text{–}O\text{–}SnPh_3 + Ph_3Sn\cdot$

B. Propagation $Ph_3Sn\cdot + C_2H_5Br \longrightarrow Ph_3SnBr + C_2H_5\cdot$

$C_2H_5\cdot + Ph_3Sn\text{–}SnPh_3 \longrightarrow Ph_3SnC_2H_5 + Ph_3Sn\cdot$

C. Termination $Ph_3Sn\cdot + Ph_3SnO\cdot \longrightarrow Ph_3Sn\text{–}O\text{–}SnPh_3$

$2Ph_3Sn\cdot \longrightarrow Ph_3Sn\text{–}SnPh_3$

Attempts to trap the triphenyltin radical with reagents other than ethylbromide such as benzylchloride, butyl bromide, or 2-bromopropane were successful only in the case of butyl bromide where a very small quantity of the expected butyltriphenyltin was isolated. Failure of the other two reagents to react can be explained on the basis of steric hindrance. Essentially the same quantity of the normal product, triphenyltin hydroxide, was isolated in each case.

Although benzyl chloride is reported to react with hexaethylditin it did not react with hexaphenylditin even after heating for 11 hr in refluxing benzene.

Trityl chloride is reported to react with hexaethylditin to form radical intermediates as evidenced by the formation of a red reaction mixture. A similar red color formation was observed when a mixture of I and trityl chloride were heated together in refluxing benzene under an atmosphere of nitrogen. The yellowish red color which formed could be discharged to give a pale yellow solution by admitting air to the reaction mixture. The red color could be repeatedly developed and then discharged by alternately heating the reaction mixture first under an atmosphere of nitrogen and then allowing air to contact the mixture. Small amounts of impure triphenyltin chloride and benzophenone were identified as products of this reaction. Trityl peroxide was not identified among the products of the reaction.

Experimental Section

Unless otherwise indicated all melting points are uncorrected and the reactions reported were carried out under an atmosphere of dry lamp-grade nitrogen. Infrared spectra were taken with a Model 137, Perkin-Elmer Infracord.

Materials.—Hexaphenylditin was obtained from Peninsular ChemResearch, Inc., and M and T Chemicals Co. and was recrystallized from benzene, washed with methyl alcohol to re-

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(13) I. G. A. Luijten and G. J. M. Van Der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, England, 1955, p 20.

(14) (a) D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 309 (1962). (b) D. N. Hague and R. H. Prince, *J. Chem. Soc.*, 4690 (1965).

(15) H. G. Kuivila and E. R. Jaknsik, *J. Org. Chem.*, **26**, 1430 (1961).

(16) J. W. Mellon, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1947, p 326.

(17) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 1921 (1961).

(18) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *ibid.*, **83**, 4088 (1961).

(19) A referee in questioning the term bond strain has cited the work of D. H. Olson and R. E. Rundle [*Inorg. Chem.*, **2**, 1310 (1963)] who showed that diphenyltin exists in a cyclohexane type of chair conformation which shows no bond-angle deviations of significant magnitude from tetrahedral angles. However, W. P. Neumann [*Angew. Chem. Intern. Ed. Engl.*, **2**, 165 (1963)] has reported that the structure of polymeric diphenyltin varies with the method of preparation. Therefore, the enhanced reactivity cited does not necessarily involve the reaction of material of the type studied by Rundle and the existence of a certain degree of bond strain is not ruled out.

(20) G. A. Raznvaev, N. S. Vyazankin, and O. A. Shchepetkova, *Tetrahedron*, **18**, 667 (1962).

(21) G. A. Raznvaev, N. S. Vyazankin, and O. A. Shchepetkova, *J. Gen. Chem. USSR*, **30**, 8, 2483 (1960).

move triphenyltin oxide, and dried before use. Sodium methoxide was Fisher Scientific, purified grade, and was stored in a 115° oven. Ethyl bromide, colorless, was obtained from Fisher Scientific Co. and was used without further purification. Tetrahydrofuran (THF) was dried over lithium aluminum hydride and then distilled from this reagent just before use. All other chemicals and solvents used were reagent grade and were used as received.

Separation of triphenyltin hydroxide, hexaphenylditin, and ethyltriphenyltin were effected by employing the differences in solubility shown in Table II.

TABLE II

	Methanol	Petroleum ether (bp 30–60°)	Bz, $CHCl_3$
$Ph_3Sn{-}SnPh_3$	Insol	Insol	Sol
Ph_3SnOH or $Ph_3SnOSnPh_3$	Sol	Insol	Sol
$EtPh_3Sn$	Sol	Sol	Sol

Experiments 1–11 follow.

Oxidation of I by Air in the Presence of Sodium Methoxide and THF.—A mixture of 10.0 g of I and 5.0 g of sodium methoxide in 200 ml of reagent grade THF was stirred at room temperature under an atmosphere of air for 24 hr. The mixture was filtered to remove sodium methoxide and the filtrate was evaporated to dryness. The solid white concentrate was taken up in 200 ml of methanol, boiled for a few minutes to ensure complete solution of triphenyltin hydroxide, cooled, and filtered. There was recovered 4.87 g of I. The methanolic filtrate was concentrated and mixed with water. The white solid which separated was removed by filtration and recrystallized once from benzene to give 4.83 g, 92.3% based on recovered I, of bis(triphenyltin)oxide, mp 119–122° (lit.[13] mp 124°).

Control Experiments.—A. Reaction 1 was repeated under an atmosphere of nitrogen. The quantity of unreacted I recovered was 8.63 g. A small amount, 0.92 g, of bis(triphenyltin)oxide was obtained.

B. Reaction 1 was repeated with the reaction flask connected to measure gas evolution by collection over water. No gas was evolved over the 24 hr.

C. Reaction 1 was repeated under an atmosphere of air with the reaction flask connected to measure air consumption by noting the loss in volume of air contained in a water displacement air reservoir. After 24 hr, the water level in the reservoir has risen indicating air consumption.

D. Control reaction C was repeated using only I and THF, no sodium methoxide. No air uptake was noted.

E. Reaction 1 was repeated except that the sodium methoxide was replaced by sodium hydroxide. After work-up in the usual manner, 2.6 g of triphenyltin hydroxide was obtained.

Oxidation of I by Alkaline Hydrogen Peroxide.—A mixture of 10 g of I, 100 ml of 57% sodium hydroxide solution, and 100 ml of reagent grade acetone was placed in a three-necked flask fitted with a stirrer, condenser, and addition funnel. Hydrogen peroxide, 200 ml, 30%, was added dropwise with stirring from the addition funnel. Heat was evolved and the flask was cooled with ice–water. The reaction mixture was stirred for 1 hr after the addition of the peroxide was complete, 200 ml of water was then added to precipitate the triphenyltin hydroxide, and the resulting mixture was allowed to stand overnight. The precipitate was removed by filtration and recrystallized from methyl alcohol. There was obtained 6.17 g, 77.1% based on recovered I, of triphenyltin hydroxide, mp 120–124°.

Reaction of I with Cupric Chloride, Ferric Chloride, Stannous Chloride, and Zinc Chloride.—The same general procedure was used for all these reactions. A mixture of 5.0 g (0.007 mole) of I, a slight excess of the halide and 200 ml of reagent grade acetone was placed in a one-necked flask under an atmosphere of air and stirred overnight. The tin compounds were precipitated by adding 300 ml of water to the reaction mixture. The precipitate was removed by filtration and extracted with methanol to separate the insoluble I and soluble triphenyltin chloride.

In the cupric chloride experiment the yield of triphenyltin chloride was 98.9%.

The ferric chloride experiment gave 4.0 g of unreacted I and 0.27 g, 24.5% of triphenyltin chloride.

Stannous chloride and zinc chloride did not react with I under the reaction conditions employed.

Reaction of I with Mercuric Chloride.—A mixture of 5.0 g of I, a slight excess of mercuric chloride and 200 ml of reagent grade acetone in a one-necked flask was stirred at room temperature overnight. The insoluble material was removed by filtration and gave a negative test for tin when treated with 6 *N* hydrochloric acid and tested with phosphomolybdate paper. The filtrate was evaporated to dryness on a rotary evaporator. The concentrate was transferred to a separatory funnel with the aid of 200 ml of benzene and washed with 5% hydrochloric acid. The acid wash solution was discarded. The benzene filtrate was evaporated to dryness and the residue was extracted with methanol. Evaporation of the methanol extracts gave 1.11 g of a white solid. Fractional crystallization from methanol gave 0.30 g of diphenylmercury, identified by its melting point of 121° (lit.[16] 121.8) and infrared spectrum. The remaining material was identified by infrared spectrum as impure triphenyltin hydroxide. This corresponds to a 15% yield, calculated as triphenyltin chloride.

Reaction of I with Hydrochloric Acid.—Compound I (10 g) was added to a cold mixture of 20 ml of 37% hydrochloric acid and 100 ml of THF. An immediate slow but steady gas evolution occurred. After 2 hr the mixture was transferred with the aid of 500 ml of water and 200 ml of benzene to a separatory funnel, shaken, and separated. The benzene layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The residue was treated with about 100 ml of petroleum ether (bp 30–60°) and the mixture was cooled and filtered. The precipitate after recrystallization from methanol gave 6.32 g (60%) of triphenyltin chloride, mp 100–103°. The petroleum ether filtrate was found to contain 4.1 g of low-melting aromatic tin compounds as shown by the infrared spectrum of this material.

Reaction of I with Sulfuric Acid.—Compound I (10 g) was added to a cold solution of 20 ml of 50% sulfuric acid and 100 ml of THF contained in a flask fitted to measure gas evolution. In 2 days, no gas was evolved.

Reaction of I with Stannic Chloride.—An excess of stannic chloride was added to a stirred mixture of 7.0 g of I and 100 ml of benzene. An immediate reaction occurred. After 1.5 hr water was added to the reaction mixture and the presence of stannous chloride in the water layer was indicated by a positive phosphomolybdate paper test. The layers were separated and the benzene layer was washed with 10% sodium hydroxide solution to remove any diphenyltin dichloride or phenyltin trichloride. The benzene solution after work-up gave 2.34 g, 31.8%, of triphenyltin hydroxide, mp 119–121°.

Reaction of I and Nitric Acid.—A mixture of 5.0 g of I in 27% nitric acid was stirred overnight. The solution turned dark brown and smelled of nitrobenzene. The reaction mixture was treated as above and there was obtained 1.4 g of a black solid. Infrared examination of this material indicated the presence of triphenyltin hydroxide and nitrate. Further purification was not attempted.

Reaction of I with Ethyl Bromide in the Presence of Sodium Methoxide.—A mixture of 10.0 g of I, 10.0 g of sodium methoxide, 50 ml of ethyl bromide, and 100 ml of THF was stirred for 24 hr. The mixture was diluted with 200 ml of benzene, filtered, and the filtrate was evaporated to dryness. The white solid obtained was boiled with 200 ml of methanol, allowed to cool, and filtered to remove unreacted I. Concentration of the filtrate gave 4.15 g of a mixture of ethyltriphenyltin and bis(triphenyltin)oxide. The mixture was treated with petroleum ether and filtered. Recrystallization of the precipitate from benzene gave 2.1 g of bis(triphenyltin)oxide, mp 122–124°.

Concentration of the petroleum ether filtrate gave 1.19 g of a white solid identified by comparison of its infrared spectrum with that of an authentic sample as ethyltriphenyltin. Purification by chromatography over alumina in benzene gave 1.0 g of pure ethyltriphenyltin, mp 57–58° (lit.[7] mp 56–58°).

In a control experiment, carried out as above but in the absence of sodium methoxide, no ethyltriphenyltin was found, essentially all of the starting I was recovered and only a small amount, 0.12 g, of impure triphenyltin hydroxide was obtained.

Reaction of I with Benzyl Chloride, 1-Bromobutane, and 2-Bromopropane.—Experiment 9 was repeated except that the ethyl bromide was replaced in turn by benzyl chloride, 1-bromobutane, and 2-bromopropane. Only in the reaction with 1-bromobutane was any alkyltriphenyltin isolated. The trace of butyltriphenyltin isolated had an infrared spectrum similar to that of ethyltriphenyltin and had a melting point of 56–63° (lit.[7] mp 61–62°).

In each case a considerable quantity of alcohol-soluble material, triphenyltin hydroxide, as shown by its infrared spectrum, was isolated: benzyl chloride, calcd 6.24 g; 1-bromobutane, calcd 6.50 g; and 2-bromopropane, calcd 5.10 g. No effect was made to determine whether there was any triphenyltin halide formed in these reactions.

Reaction of I with Trityl Chloride in Benzene.—A solution of 4.0 g of trityl chloride in 100 ml of benzene was added from a dropping funnel to a stirred solution of 10.0 g of I and 100 ml of benzene was maintained under an atmosphere of dry nitrogen. The reaction mixture was colorless and no changes were noted after stirring at room temperature for 1 hr. The mixture was slowly heated and gradually turned first yellow and then red. After being heated at reflux for 5 hr the mixture was transferred to a one-necked flask. No insoluble trityl peroxide was observed. The solution was evaporated to dryness and the solid residue was treated with methyl alcohol and filtered. The infrared spectrum of the precipitate, 8.90 g, indicated only the presence of phenyltin compounds. The methanolic filtrate was evaporated to dryness. The infrared spectrum of the residue did not indicate the presence of either peroxide or triphenyl carbinol. The presence of triphenyltin chloride in the residue was indicated by the infrared spectrum.

The experiment was repeated except that after the red color had developed in the solution the heat was removed and air was admitted to the flask. The red color was discharged to a pale yellow. Upon further heating under nitrogen the red color would again appear and in turn could be discharged by admitting further quantities of air. This procedure was repeated several times. After heating for a total of 12 hr the solvent was removed by evaporation. The precipitate was treated with 200 ml of methanol, filtered, and the filtrate evaporated to dryness. The solid was treated with petroleum ether, filtered, and the petroleum ether filtrate was concentrated to an oily liquid. The infrared spectrum of this material was identical with that of commercial benzophenone although further attempts at purification failed to give a sample with the correct melting point.

Stereoselective Synthesis of Optically Active Aspartic Acid from Derivatives of Fumaric Acid and Maleic Acid[1]

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Optically active aspartic acid (4.5–15.4%) was synthesized by the amination of the derivatives of fumaric acid and maleic acid with (*S*)- and (*R*)-α-methylbenzylamine. Three kinds of reactions were carried out: (a) reaction of (*S*)- and (*R*)-α-methylbenzylamine [(*S*)- and (*R*)-amine] with N,N′-di-(*S*)- and -(*R*)-α-methylbenzyl fumaramide; (b) reaction of (*S*)- and (*R*)-amine with diethyl maleate; (c) reaction of (*S*)- and (*R*)-amine with diethyl fumarate. In each case, the reaction intermediates were isolated. To avoid the fractionation of the resulting optically active aspartic acid during the isolation and recrystallization procedures, a column chromatographic method for DNP-aspartic acid was employed. Possible steric courses of the reactions a, b, and c are discussed.

The nonenzymatic asymmetric synthesis of α-amino acids and of other organic compounds has long been an attractive subject in investigations of stereochemistry. Several studies of the asymmetric synthesis of α-amino acids have already been reported.[2-15] However, most of the syntheses have been carried out by the use of a catalytic hydrogenation procedure.

In previous studies from this laboratory,[13-14] optically active alanine was synthesized in solution by the Strecker method in which optically active (−)- and (+)-α-methylbenzylamine[16] functioned as asymmetric centers in the syntheses. The absolute configuration of (−)- and (+)-amine had been determined as *S* and *R*, respectively, by Leithe.[17]

In this study, the syntheses of optically active aspartic acid by the use of both *S*(−)- and *R*(+)-α-methylbenzylamine [(*S*)-amine, (*R*)-amine] and derivatives of fumaric acid and maleic acid in solution are described. Three kinds of amination reactions were carried out to synthesize optically active aspartic acid: (a) reaction of (*S*)- and (*R*)-amine with N,N′-di-(*S*)- and -(*R*)-α-methylbenzyl fumaramide [(*S*)- and (*R*)-fumaramide]; (b) reaction of (*S*)- and (*R*)-amine with diethyl maleate; (c) reaction of (*S*)- and (*R*)-amine with diethyl fumarate.

In reaction a, (*S*)-fumaramide was heated with (*S*)-amine ($[\alpha]^{25}\text{D}$ −42.3°) in butanol at 115–120° for 3 days. The α-methylbenzyl residue of the resulting N-(α-methylbenzyl)aspartic acid was removed by hydrogenolysis, using the palladium hydroxide–charcoal system of Hiskey.[12] The isolated aspartic acid (yield 64%) showed optical activity of $[\alpha]^{25}\text{D}$ −2.6° in 5 *N* HCl [10.2% optically active (*R*)-aspartic acid]. To avoid the fractionation[15,18] of the resulting aspartic acid during the isolation and recrystallization procedure, a part of the hydrogenolyzed product was converted to DNP-aspartic acid by the use of 1-fluoro-2,4-dinitrobenzene. The resulting DNP-aspartic acid was separated chromatographically by the use of a

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