doxyl (X. R = C_6H_5). Partial air oxidation of the latter to 2-phenylindoleninone (III) and immediate addition of the anion of X to indoleninone III in basic solution, as indicated above, can be postulated to explain the formation of 2,2′-diphenyl-2,2′-diindoxyl (VII). A similar path would explain the conversion of indoxyl (X. R=H) to indigo, via leucoindigo V.[7] While leucoindigo (V) is known[8] to air oxidize very readily to indigo, such a process is impossible for the substituted indoxyls VI and VII.

Experimental

All melting points are uncorrected. Analyses were performed by A. Bernhard, Muelheim, Germany. Infrared spectra were run in potassium bromide on a Beckman IR-5 instrument. Ultraviolet spectra were obtained in methanolic solutions. N.m.r. spectra were determined at 60 Mc. in deuteriochloroform, with tetramethylsilane as an internal standard, on a Varian A-60 spectrometer. Molecular weight determinations were obtained in benzene solution on a Mechrolab vapor pressure osmometer Model 301A.

2,2′-Dimethyl-2,2′-diindoxyl (VI).—Ethyl α-(2-carbethoxyanilino)propionate, b.p. 158–164°/3 mm. (lit.,[3] b.p. 196–202°/12 mm.) was prepared by anhydrous esterification of N-(2-carboxyphenyl)alanine (m.p. 209–211° dec.; ν_{max} 3350, 3300–2500, 1725, 1680, 1570 and 1520 cm.$^{-1}$; lit.,[3] m.p. 208–210°) or by esterification of ethyl α-(2-carboxyanilino)propionate, m.p. 95–102°, obtained in 85% yield from anthranilic acid and ethyl α-bromopropionate in neutral solution at 70°.

A solution of ethyl α-(2-carbethoxyanilino)propionate and sodium ethoxide in anhydrous ethanol was heated for 30 min. and poured into water. Aqueous hydrogen peroxide was added and VI was obtained as a yellow precipitate in 88% yield. It was crystallized from methanol–water and melted at 174–176°; reported[3] as II, m.p. 174°. If the reaction solution was poured into dilute hydrochloric acid or into water that was kept in an oxygen-free nitrogen atmosphere the same product (VI) slowly precipitated.

ν_{max} 3280 (NH, sharp and strong), 1675 and 1610 cm.$^{-1}$; $\nu_{max}^{CHCl_3}$ 3400 (NH), 1680, 1610, and 1580 cm.$^{-1}$. λ_{max} 395, 255 (shoulder), and 235 mμ (ε 6080, 17000 and 45300 respectively). Mol. wt.: 289 ± 30 (calcd. 292). N.m.r. singlet at 8.52 τ (CH_3) and weak singlet at 6.74 τ (NH) which shifts on addition of two drops of acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.50; H, 5.63; N, 9.41.

2-Methyl-3-hydroxyindoline (VIII).—To a solution of 1.0 g. of diindoxyl (VI) in 200 ml. of methanol there was added 3 g. of sodium borohydride. The yellow color of the solution disappeared within 3 hr. The solution was evaporated under reduced pressure and the colorless residue was diluted with water and extracted thoroughly with ether. The dried ether extract upon evaporation yielded an oil that solidified on standing (0.92 g.).

Crystallization of the product from ether in the cold or from ether–petroleum ether (b.p. 30–60°) furnished fine white needles of 2-methyl-3-hydroxyindoline (VIII), m.p. 92–94°. The product gave a red coloration with ferric chloride in methanol within 30 min. at room temperature. Mol. wt.: 156 ± 4 (calcd. 147). The n.m.r. spectrum showed two doublets in the methyl region at 8.75 and 8.82 τ (J = 6.5 and 4 c.p.s., respectively) with approximate relative intensities of 1:4. The proton at C-3 was found at 5.35 and 5.46 τ (J = 6.5 and 4 c.p.s. respectively) and in approximate relative intensities of 1:4. This is in accord with a 1:4 ratio of *cis-trans* isomers in VIII.[9] The N—H and O—H absorption appeared as a single concentration-dependent peak in the 7–7.5 τ region. ν_{max} 3200–3000 (NH, OH, broad) and 1610 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{11}ON$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.23; H, 7.45; N, 9.30.

Conversion of 2-Methyl-3-hydroxyindoline (VIII) to 2-Methylindole.—Five drops of 1 *N* hydrochloric acid were added to a solution of 35 mg. of 2-methyl-3-hydroxyindoline (VIII) in 2 ml. of methanol. After 5 min. the solution was made basic with 5% sodium hydroxide and the turbid solution was extracted with ether. The dried ether solution was evaporated on a steambath to leave an oil that solidified on cooling (29 mg.). Crystallization from methanol–water gave needles of 2-methylindole, m.p. 59–59.5°. Admixture with authentic 2-methylindole showed no depression in melting point. The infrared spectrum of the product was superimposable with that of authentic 2-methylindole.

Ethyl α-Bromo-α-phenylacetate.—This ester, b.p. 115° at 3 mm. (lit.,[10] b.p. 150–151° at 10–15 mm.), was prepared by addition of bromine (30 g.) to a solution of 1 g. of phosphorus pentachloride in 20 g. of phenacetyl chloride on the steambath and pouring the reaction mixture after 48 hr. into absolute ethanol.

Ethyl α-(2-Carboxyanilino)-α-phenylacetate.—Anthranilic acid (15.4 g.) was dissolved in a solution containing 1 equivalent of sodium hydroxide and 27 g. of ethyl α-bromo-α-phenylacetate was added. The mixture was stirred and warmed to 45° for 5 min. and the precipitated white solid was collected by filtration (38 g., m.p. 174–176°). The product was soluble in 5% sodium hydroxide and in concd. hydrochloric acid. On recrystallization from methanol–water ethyl α-(2-carboxyanilino)-α-phenylacetate was obtained in shiny white needles that melted at 180–181°. The compounds exhibits blue fluorescence in methanol. ν_{max} 3400 (NH), 2700–2500 (carboxy OH), 1725 (ester C=O) and 1670 cm.$^{-1}$ (carboxy C=O).

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.29; H, 5.71; N, 4.58.

Ethyl α-(2-Carbethoxyanilino)-α-phenylacetate (IX).—Esterification of ethyl α-(2-carbethoxyanilino)-α-phenylacetate with ethanol in the presence of hydrogen chloride led to diester IX as white needles, m.p. 80–81° (lit.,[3] m.p. 72°). ν_{max} 3410, 1725, 1670 and 1600 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{21}O_4N$: C, 69.70; H, 6.47; N, 4.28. Found: C, 69.08; H, 6.40; N, 4.45.

2,2′-Diphenyl-2,2′-diindoxyl (VII).—To a solution of 1.5 g. of sodium in 30 ml. of absolute ethanol there was added 6 g. of ethyl α-(2-carbethoxyanilino)-α-phenylacetate (IX). The solution was heated under reflux for 40 min. At the beginning the solution developed a deep red color which later turned yellow. The cooled solution was poured into ice–water into which a stream of air was bubbled, and an immediate yellow precipitate appear. After 15 min. of stirring the yellow solid was collected by filtration, washed, and dried to give 2 g. (80%) of crude product m.p. 140–150°. After crystallization from methanol–water and then from benzene 2,2′-diphenyl-2,2′-diindoxyl (VII) melted at 180–182°, with reddening at 175° (lit.,[5] for VII or XI, m.p. 178–180°, with reddening at 178°). ν_{max} 3500 (NH), 1675 (conj. C=O) and 1620 cm.$^{-1}$. Mol. wt. 400 ± 12 (calcd. 406). λ_{max} 400, 260, and 233 mμ (ε 5600, 15000, and 61000, respectively).

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(7) In this connection the isolation by E. Giovannini and Th. Lorenz, *Helv. Chim. Acta*, **40**, 1553 (1957), of indigo, presumably *via* leucoindigo, as a minor product in the reduction of isatin with lithium aluminum hydride should be mentioned.

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(9) A. Hassner and M. J. Michelson, *J. Org. Chem.*, **27**, 3974 (1962), have shown that, in five-membered ring *N*-containing heterocycles, $J_{cis} > J_{trans}$ and the protons absorb at higher field in the *trans* isomer than in the *cis* isomer.

(10) N. Zelinsky and L. Buchstab, *Ber.*, **24**, 1877 (1891).

The Synthesis of Organolead–Sulfur Compounds

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Although compounds of the type $(Alk)_3PbSR$ have been described,[2] the corresponding $(C_6H_5)_3PbSR$ deriv-

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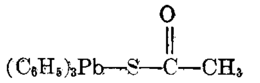
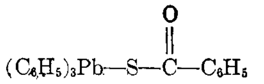
[1] Research Fellow sponsored by The Lead Industries Association, 292 Madison Ave., New York, N. Y.

(2) (a) H. McCombie and B. C. Saunders, *Nature*, **159**, 491 (1947); (b) B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 919 (1949); (c) R. Heap and B. C. Saunders, *ibid.*, 2983 (1949); (d) R. Heap, B. C. Saunders, and G. J. Stacey, *ibid.*, 658 (1951).

TABLE I

SYNTHESIS OF $(C_6H_5)_3PbSR$ COMPOUNDS[a]

	M.p., °C.	Mol. wt. $\left(\frac{\text{calcd.}}{\text{found}}\right)$	Yield, %	Analyses $\left(\frac{\text{calcd.}}{\text{found}}\right)$			
				C	H	S	Pb
$(C_6H_5)_3Pb—S—CH_3$	108–109°	486	100	46.99	3.74	6.60	42.67
		510		47.13	3.96	6.22	42.75
$(C_6H_5)_3Pb—S—C_2H_5$	67–68°	500	96	48.08	4.04	6.41	41.47
		518		48.22	4.08	6.20	41.50
$(C_6H_5)_3Pb—S—C_3H_7$	57–58°	514	95	49.10	4.32	6.24	40.34
		551		49.22	4.38	5.94	40.20
$(C_6H_5)_3Pb—S—C_4H_9$	Liquid n^{20}D 1.6500	528	78	50.07	4.59	6.08	39.27
		534		50.35	4.52	5.68	38.86
$(C_6H_5)_3Pb—S—CH_2C_6H_5$	82–83°	562	95	53.45	3.95	5.71	36.89
		577		53.72	4.12	5.54	36.77
$(C_6H_5)_3Pb—S—C_6H_5$	106–107°	548	94	52.64	3.68	5.86	37.84
		556		52.67	3.78	5.89	37.42
 $(C_6H_5)_3Pb—S—\overset{\overset{O}{\Vert}}{C}—CH_3$	92–93°	514	79	46.76	3.53	6.24	40.34
		511		46.85	3.63	6.11	40.17
 $(C_6H_5)_3Pb—S—\overset{\overset{O}{\Vert}}{C}—C_6H_5$	93–94°	576	86	52.16	3.50	5.57	35.99
		578		52.31	3.62	5.51	36.37

[a] Melting points were determined using a Thomas-Hoover melting point apparatus and are corrected. Molecular weights were determined using a Mechrolab vapor pressure osmometer Model 301A (benzene solvent).

atives, with the exception of $[(C_6H_5)_3Pb]_2S$,[3] are not known. We have investigated synthetic methods for these compounds and have obtained alkylthio, arylthio, acetylthio, and aroylthio derivatives by interaction of triphenyllead chloride with lead(II) mercaptides or lead(II) salts of thio acids. Reactions of these compounds with acids and alkyl iodides were also investigated. Of four possible routes attempted,

(1) $2(C_6H_5)_3PbCl + Pb(SR)_2 \longrightarrow 2(C_6H_5)_3PbSR + PbCl_2$

(2) $(C_6H_5)_3PbSNa\ (I) + RX \longrightarrow (C_6H_5)_3PbSR + NaX$

(3) $(C_6H_5)_3PbOH + RSH \longrightarrow (C_6H_5)_3PbSR + H_2O$

(4) $(C_6H_5)_4Pb + RSH \longrightarrow (C_6H_5)_3PbSR + C_6H_6$

the reaction of triphenyllead chloride with lead mercaptides (route 1) gave the best results. Route 2, successful in the preparation of the corresponding germanium compounds,[4] was found not to be satisfactory for the case of lead. Sodium triphenyllead sulfide (I), prepared by the reaction of triphenyllead chloride and sodium sulfide, was not stable above 30° even when anhydrous conditions were maintained. In the presence of moisture, decomposition took place at even lower temperatures yielding bistriphenyllead sulfide and sodium sulfide[5]:

$$2(C_6H_5)_3PbSNa\ (I) \longrightarrow [(C_6H_5)_3Pb]_2S + Na_2S$$

The formation of I was proved by the reaction with methyl iodide at low temperatures to yield thiomethyl triphenyllead, $(C_6H_5)_3PbSCH_3$. This reaction was accompanied by the formation of bistriphenyllead sulfide resulting from the simultaneous decomposition of the sodium salt (I).

Route 3, previously used in the synthesis of trialkyl-substituted lead compounds,[2c] when applied to triphenyllead hydroxide and 1-butanethiol yielded thiobutyl triphenyllead, $(C_6H_5)_3PbSC_4H_9$, in 65% yield.

Route 4 has previously been attempted by Koton[6] in treating tetraphenyllead and thiophenol, but under the employed conditions only diphenyl disulfide, the lead salt of thiophenol and benzene, were obtained. Working at lower temperatures (refluxing chloroform) thiophenyl triphenyllead, $(C_6H_5)_3PbSC_6H_5$ was obtained in yields of 2%, the main product isolated being unchanged tetraphenyllead. Apparently the acidity of thiophenol is too weak to cleave the lead–carbon bond at temperatures below the decomposition point of the desired product.

The more acidic thiolacetic acid in excess, cleaved two phenyl groups from tetraphenyllead yielding diphenyllead bisthiolacetate in 60% yield.[2d] The same reaction, using molar equivalents of reactants yielded a mixture of triphenyllead thiolacetate and diphenyllead bisthiolacetate.

Route 1, which had been used in the synthesis of the corresponding silicon compounds,[7,8] was experimentally preferable to route 3 or 4 and, in addition, it could be applied more satisfactorily to the synthesis of diphenyllead bisthio substituted compounds as follows:

$$(C_6H_5)_2PbCl_2 + Pb(SR)_2 \longrightarrow (C_6H_5)_2Pb(SR)_2 + PbCl_2$$

Thus, prior synthesis of the lead salt of the mercaptan followed by reaction with triphenyllead chloride (method 1) resulted in a series of organolead–sulfur compounds as described in Table I.

They are white crystalline compounds, with the exception of the liquid butyl compound, and decompose above the melting point to a dark brown material. They are readily soluble in benzene, *n*-hexane, alcohol, chloroform, and most of the other common organic solvents. The infrared absorption spectra of all

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(3) G. Grüttner, *Ber.*, **51**, 1303 (1918).

(4) M. C. Henry and W. E. Davidson, *J. Org. Chem.*, **27**, 2252 (1962).

(5) This reaction is analogous to the readily occurring dehydration of organolead hydroxides to the corresponding oxide as follows: $2(C_6H_5)_3PbOH \rightarrow (R_3Pb)_2O + H_2O$.

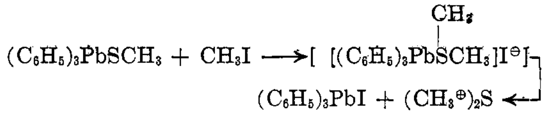
(6) M. M. Koton, E. P. Moskvina, and F. S. Florinskii, *Zh. Obshch. Khim.* (*J. Gen. Chem.*), **20**, 2096 (1950); *Chem. Abstr.*, **45**, 5644 (1951).

(7) M. Schmeisser and H. Müller, *Angew. Chem.*, **69**, 781 (1957).

(8) E. W. Abel, *J. Chem. Soc.*, 4406 (1960).

compounds show, besides the usual absorptions associated with aromatic compounds and the respective group attached to the sulfur, the band at 1052 cm.$^{-1}$, typical for organolead compounds.[9]

Methyl iodide reacted quantitatively at room temperature with thiomethyl triphenyllead to yield triphenyllead iodide and dimethyl sulfide, probably through an unstable sulfonium salt intermediate:



$$(C_6H_5)_3PbSCH_3 + CH_3I \longrightarrow [\,[(C_6H_5)_3Pb\overset{CH_3}{\overset{|}{S}}CH_3]I^{\ominus}] \longrightarrow (C_6H_5)_3PbI + (CH_3^{\oplus})_2S$$

This reaction did not take place with triphenyllead thiolacetate; apparently the acetyl group decreases the electron density at the sulfur atom so that formation of a sulfonium intermediate becomes impossible.

Mineral acids cleaved the lead–sulfur bond preferentially; however, cleavage of lead–phenyl bonds was always detected. For example, mixtures of triphenyllead chloride, diphenyllead dichloride, and lead chloride were obtained from the reaction of thioalkyl triphenyllead compounds and hydrochloric acid.

Throughout the course of this work, thin-layer chromatography was found to be valuable for separation of the organolead compounds. Dithizone spray reagent reacted to form yellow spots with the monosubstituted lead compounds, red spots from the disubstituted products, and gave no reaction with tetraphenyllead.[10]

Experimental

A typical example for the preparation of the triphenyllead sulfur compounds described by route 1 is given.

The lead mercaptides[11] were prepared from the thiol and lead acetate in aqueous alcohol and after washing with water were dried in a vacuum desiccator.

Triphenyllead chloride, 4.86 g. (10 mmoles), and lead (II) *n*-propyl mercaptide, 1.79 g. (5 mmoles), in 100 ml. benzene were refluxed with stirring for 3 hr. During this time the yellow mercaptide was converted into white lead chloride which was filtered off at the end of the reaction period. The filtrate was evaporated and the residue recrystallized from ethanol, yield 4.84 g. (95%), m.p. 57–58°.

Preparation of Thiobutyl Triphenyllead from Triphenyllead Hydroxide and 1-Butanethiol (Route 2).—Triphenyllead hydroxide,[12] 0.91 g. (2 mmoles), and 1-butanethiol, 0.18 g. (12 mmoles), were mixed in 50 ml. of ethyl ether and shaken for 24 hr. Filtration and evaporation yielded a colorless oil. The oil was purified by chromatography on neutral alumina, eluting with benzene; yield: 0.68 g. (65%).

Synthesis of Thiomethyl Triphenyllead by Route 1.—Triphenyllead chloride, 4.86 g. (10 mmoles), was added to a stirred suspension of sodium sulfide pentahydrate, 8.40 g. (50 mmoles), in 100 ml. of ethyl alcohol during a period of 1 hr. while the reaction temperature was kept below 30°. The excess sodium sulfide and sodium chloride were filtered off and the alcohol removed from the filtrate under vacuum. The white residue was extracted with benzene and the benzene evaporated. To the remaining solid was added methyl iodide, 1.41 g. (10 mmoles), in 50 ml. of benzene. After filtering and evaporation of the benzene, recrystallization from ethanol and *n*-hexane gave bistriphenyllead sulfide, 1.14 g. (25%), m.p. 139–141° (identified by mixed melting point with an authentic sample[3]).

The combined mother liquor was concentrated and yielded thiomethyl triphenyllead, 3.47 g. (68%), m.p. 103–106°, recrystallized from *n*-hexane).

Reaction of Thiomethyl Triphenyllead with Methyl Iodide.—Thiomethyl triphenyllead, 1.12 g. (2.3 mmoles), was dissolved in excess methyl iodide (30 ml.). After a few minutes the solution became cloudy and a precipitation occurred slowly over a period of 6 hr. The excess methyl iodide was removed under vacuum and the residue shown to be 1.30 g. of pure triphenyllead iodide,[13] m.p. 140–141°. Mixed melting point with an authentic sample gave no depression.

Reactions of Tetraphenyllead with Thiolacetic Acid (Route 3). Diphenyllead Bisthiolacetate.—Tetraphenyllead, 2.58 g. (5 mmoles), dissolved in 20 ml. of thiolacetic acid was refluxed for 5 min. The excess of thiolacetic acid was removed under vacuum and the residue recrystallized from ethanol. The yield was 1.55 g. (60%) and the m.p. was 94–95°.

Anal. Calcd. for $C_{16}H_{16}O_2S_2Pb$: C, 37.56; H, 3.15; Pb, 40.50; S, 12.54. Found: C, 37.73; H, 3.36; Pb, 40.50; S, 12.46.

Diphenyllead bisthiolacetate was also prepared by the reaction of diphenyllead dichloride with lead thiolacetate—analogous to route 4—in boiling toluene; yield 81%.

The reaction of tetraphenyllead with 1 mole of thiolacetic acid in boiling benzene (2 hr.) yielded 70% tetraphenyllead, 12% triphenyllead thiolacetate, and 6% diphenyllead bisthiolacetate.

Thin-layer Chromatography.—Thin-layer chromatography of the organolead compounds was carried out on silica gel G (25 μ), using benzene as a solvent in most cases. Potassium permanganate solution or a solution of dithizone in chloroform[10] was used as a spray.

Acknowledgment.—The authors are grateful to C. DiPietro of these laboratories for the microanalyses.

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The Stereochemistry of an Ivalin Degradation Product[1]

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The hydroxyketolactone II obtained by ozonolysis of dihydroivalin (I)[2] exhibited a positive Cotton effect (molecular amplitude about 1750°) which seemed surprising in view of the relatively strong negative Cotton effect displayed by 4-keto steroids (molecular amplitude −9400°) and *trans*-10-methyl-1-decalone.

The hydroxyl group, being equatorial and in the upper left quadrant, should, according to the octant rule,[3] make a positive contribution to the total dispersion picture. However, no reference compounds of incontrovertible stereochemistry had been scrutinized for the purpose of assessing the effect of hydroxyl groups in a situation of this type, and the observed inversion of the Cotton effect seemed, *a priori*, greater than might have been expected. It should also be noted that inspection of models failed to reveal any reasons for distortions due to steric or electrostatic interactions which might result in conformational changes.

To explain the observed rotatory dispersion curve, we considered the possibility that epimerization at C-5 might have taken place during the work-up. This

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