A Reinvestigation of Paneth's Violet Compound. The Synthesis of Tetramethyldibismuthine

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Summary: Tetramethyldibismuthine was prepared from the reaction of trimethylbismuthine with sodium in liquid ammonia followed by treatment with 1,2-dichloroethane. Like tetramethyldistibine it shows thermochromic properties on freezing.

In 1935, Paneth reported that the reaction between methyl radicals and a heated bismuth mirror gave a trace of a violet solid which melted to a yellow liquid prior to decomposition.[1] On the basis of analogy to the thermochromic behavior (red → yellow) of tetramethyldistibine **1b**, the violet compound was assigned the structure of tetramethyldibismuthine **1a**. No other characterization of tetramethyldibismuthine has appeared in the literature, although several other dibismuthines have recently been reported.[2–5] We now wish to report on a synthesis of **1a** and on a comparison of its properties with those of **1b**[6] and other compounds of group V elements.

The reaction of trimethylbismuthine[7] with sodium in liquid ammonia afforded a red solution of $NaBi(CH_3)_2$ which on reaction with 1,2-dichloroethane gave a 70% yield of tetramethyldibismuthine as a viscous red oil ($d_{20\,°C}$ = 2.85 g/cm^3).[8] The ^1H NMR and ^{13}C NMR spectra (C_7D_8) consist of broad singlets at δ 1.62 and δ_C −18.92, respectively. The mass spectrum (70 eV) shows the expected peaks for sequential fragmentation at *m/e* (relative intensity) 478 (2.6, M$^+$), 463 (3.7), 448 (2.0), 434 (3.4), 418 (4.9), 254 (35.8), 239 (79.3), 224 (62.3), and 209 (100). The Raman spectrum of solid **1a** shows intense polarized peaks at 110 (Bi–Bi) and 445 (BiC) cm^{-1}. The corresponding bands for solid tetramethyldistibine, tetramethyldiarsine,[9] and tetramethyldiphosphine[10] occur at 179 (Sb–Sb), 271 (AsAs), 455 (PP), and 505 (SbC), 570 (AsC), and 668 (PC) cm^{-1}. This shift to lower frequency exceeds that expected for increasing mass and is consistent with a progressive weakening of the vibrational force constants.[11]

$$\mathrm{Me_3Bi} \xrightarrow[\mathrm{NH_3}]{\mathrm{Na}} \mathrm{Me_2BiNa} \xrightarrow{\mathrm{C_2H_4Cl_2}} \mathrm{Me_2BiBiMe_2}$$

$$\mathrm{Me_2BiBiMe_2} \xrightarrow[\Delta]{} \mathrm{Me_3Bi} + \mathrm{Bi}$$

Tetramethyldibismuthine is an extremely labile compound. It decomposes thermally at 25 °C with nearly quantitative formation of trimethylbismuthine and bismuth metal. In a dilute benzene solution, **1a** has a half-life of approximately 6 h. Tetramethyldistibine shows the analogous reaction at 160–200 °C.[12] Reaction of **1a** with I_2 occurs instantly at 25 °C with the formation of $(CH_3)_2BiI$, $(CH_3)BiI_2$, BiI_3, and Bi. Tetramethyldibismuthine fumes in air but is stable toward water.

As reported by Paneth, the red-yellow liquid tetramethyldibismuthine freezes reversibly at −12.5 °C to well-formed iridescent violet-blue crystals. The diffuse reflectance spectrum of solid **1a** shows a broad maximum at λ 665 nm. Pentane solutions of **1a** show only λ_{max} at 220 (ϵ 37 000) and 264 (7200) with a featureless low intensity tail to 700 nm. In comparison solid **1b** (mp 17.5 °C) shows a diffuse reflectance max at 530 nm, while cyclohexane solutions show λ_{max} <215 with a featureless tail to 360 nm. Neither tetramethyldiarsine nor tetramethyldiphosphine show thermochromic properties on melting.

This red shift between solid and liquid phase is similar to that reported for molecular iodine,[13] certain distibines,[1,14] ditellurides[15] and diselenides.[15] It appears to be a common property of many of the diatomic-like compounds of elements in the lower right-hand corner of the periodic table. Several of these compounds have been shown to display extended bonding in the solid phase.[16] Whether the solid phase colors of **1a** and **1b** are due to this effect must await the results of X-ray crystal structure determinations now in progress.

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Registry No. 1a, 82783-70-8; trimethylbismuthine, 593-91-9; 1,2-dichloroethane, 107-06-2; I_2, 7553-56-2.

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(8) Experimental procedure: The addition of 0.5 g (22 mmol) of sodium to 2.9 g (11 mmol) of trimethylbismuthine in 100 mL of liquid ammonia at −33 °C gave a red solution of sodium dimethylbismuthide. After addition of 1.1 g (11 mmol) of 1,2-dichloroethane, the ammonia was allowed to evaporate. The residue was extracted with pentane and filtered. Three recrystallizations from pentane at −20 °C gave 2.6 g (70%) of pure tetramethyldibismuthine.

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(10) Durig, J. R.; DiYorio, J. S. *Inorg. Chem.* **1969**, *8*, 2796.

(11) On the basis of a diatomic model, the force constants are BiBi, 1.88 × 10^5 dyn cm^{-1}; SbSb, 2.31 × 10^5 dyn cm^{-1}; AsAs, 2.80 × 10^5 dyn cm^{-1}; PP, 3.01 × 10^5 dyn cm^{-1}.

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Synthesis Gas Incorporation into Acylmanganese Pentacarbonyls

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Summary: Hexane solutions of $Ph(CH_2)_xC(O)Mn(CO)_5$ (x = 1 or 2) treated with 2400 psi of CO/H_2 at 70 °C gave $Ph(CH_2)_{x+1}{-}OC(O)Mn(CO)_5$. The incorporation of the syn gas probably occurs stepwise and may be represented as follows: $RC(O)Mn(CO)_5 \xrightarrow{H_2/CO} RCH_2OMn(CO)_4 \xrightarrow{2CO} RCH_2OC(O)Mn(CO)_5$. In contrast, the same reactions carried out in sulfolane yielded only the aldehydes, $Ph(CH_2)_xCHO$. Speculation on a mechanism consistent with these results is presented.

Table I. Reactions of Manganese Carbonyls at 70 °C (3 h)

R in $RMn(CO)_5$	solvent	gas mixture (psi, initial)	product	yield, %
$PhCH_2C(O)$	H[h]	H_2/CO (2400)	$Ph(CH_2)_2OC(O)Mn(CO)_5$	~100[a]
$PhCH_2C(O)$	S[h]	H_2CO (2400)	$PhCH_2C(O)H$	86[b]
$PhCH_2C(O)$	S	H_2 (1200)	$PhCH_2C(O)H$	97[b]
$PhCH_2$[7]	S	H_2/CO (2400)	$PhCH_2C(O)H$	67[b]
$PhCH_2$[7]	S	H_2 (1200)	$PhCH_2CH_2OH$	56[c]
$PhCH_2CH_2C(O)$	H	H_2/CO (2400)	$Ph(CH_2)_3OC(O)Mn(CO)_5$	~100[d]
$PhCH_2CH_2OC(O)$	H[e]	H_2/CO (2400)	$PhCH_2CH_2OC(O)H$	83[f]
$PhCH_2CH_2$[8]	H	H_2/CO (2400)	$Ph(CH_2)_3OC(O)Mn(CO)_5$	50[g]
			$PhCH_2CH_2C(O)Mn(CO)_5$	50[g]

[a] Analytically pure crystals were isolated in 24% yield after the very soluble, crude material was recrystallized twice from hexanes-ether. When this reaction was carried out at 200 °C, a 64% yield of $PhCH_2CHO$ was obtained. [b] By IR vs. standard aldehyde solution. [c] By NMR vs. internal standard; product extracted from sulfolane by hexanes. [d] Analytically pure crystals were isolated in 35% yield after the crude material was recrystallized from hexanes. [e] This reaction was carried out at 200 °C. [f] By GLC (6′, 3% S.E. 30, 180 °C vs. Ph_2CHCH_3 as standard). [g] Extent of reaction after 3 h by NMR. [h] H = hexanes; S = sulfolane.

In a recent report[1] it was shown that the reaction of $RMn(CO)_5$ (R = CH_3; $(CH_3)_3CCO_2CH_2$–) with 3.3 CO/H_2 (130 psi) in the highly polar solvent sulfolane at 75 °C gave RCHO and that similar treatment with $H_2(g)$ only gave RCH_2OH. We have repeated these reactions where R is $PhCH_2$ and obtained similar results. It was suggested[1] that acylmanganese carbonyls were intermediates in the reaction. We accordingly investigated the reaction of $PhCH_2C(O)Mn(CO)_5$ with H_2/CO in sulfolane and indeed obtained the expected $PhCH_2CHO$. However, when the reaction was repeated in hexane, the only product of the reaction proved to be $PhCH_2CH_2OC(O)Mn(CO)_5$,[2] 1 (eq 1). The *stoichiometry* of this unusual conversion corre-

$$PhCH_2C(O)Mn(CO)_5 + H_2 + CO\ (2400\ psi) \xrightarrow[3\ h]{70\ °C} PhCH_2\mathit{CH_2O}C(O)Mn(CO)_5 \quad (1)$$

1

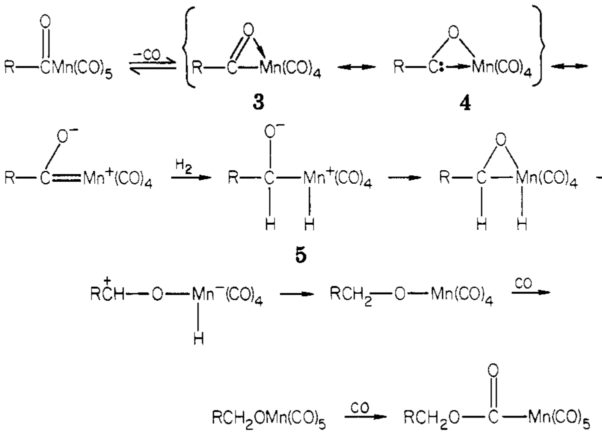
sponds to the insertion of the (italicized) combination of CO + H_2 molecules into the acylmanganese pentacarbonyl. When the homologous $PhCH_2CH_2C(O)Mn(CO)_5$[3] was treated similarly, the only compound formed was the homologue of 1, $PhCH_2CH_2CH_2OC(O)Mn(CO)_5$,[4] 2, suggesting that the reaction may be quite general.

Formates are often observed as byproducts of metal carbonyl catalyzed hydroformylation of olefins. They are assumed to arise by reduction of the aldehyde by a metal hydride followed by CO insertion and subsequent cleavage (eq 2). Treatment of aldehydes with $HCo(CO)_4$ and with

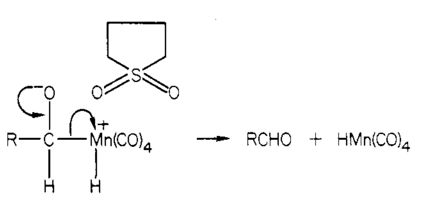
$$RCHO + HM(CO)_n \rightarrow RCH_2OM(CO)_n \xrightarrow{CO} RCH_2OC(O)M(CO)_n \xrightarrow{H_2} RCH_2OC(O)H \quad (2)$$

$HMn(CO)_5$ at high temperatures (~200 °C) and pressures in hydrocarbon solvents does in fact lead to large amounts of formates.[5] However, our treatment of $PhCH_2CHO$ with $HMn(CO)_5$ under conditions leading to 1 did not give 1; in fact no reaction occurred at all. The formate, $PhCH_2CH_2OCHO$, was formed only on treatment of 1 at 200 °C in hexanes under 2400 psi of CO/H_2 (Table I).

The difference in products obtained from the reaction of $Ph(CH_2)_xC(O)Mn(CO)_5$ in hexanes and in sulfolane may be rationalized by postulating the involvement of the sulfolane in stabilizing polar intermediates (or transition states); a speculative sequence of reactions for the hexane case is shown in eq 3. In sulfolane, polar intermediate 5 may be prevented from forming a Mn–O bond by interaction with the solvent, structure 6, collapsing instead to give the aldehyde (eq 4).



(3)



(4)

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Structure 3 represents a (η^2-acyl)manganese complex. Such structures have been postulated for higher transition-metal complexes. Indeed in the actinide series[6] facile

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(2) $PhCH_2CH_2OC(O)Mn(CO)_5$, 1: mp 76.0–76.5 °C; IR (hexanes) 2142 (w), 2044 (s), 2021 (s), 2018 (s), 1660 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.93 (t, benzyl, 2), 4.33 (t, oxy, 2), 7.28 (s, aromatic, 5). Anal. Calcd for $[Ph(CH_2)_2–OC(O)Mn(CO)_5]$: C, 48.84; H, 2.62. Found: C, 48.62; H, 2.83.

(3) $PhCH_2CH_2C(O)Mn(CO)_5$ was made by the method of: Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598. One recrystallization from hexanes gave a 45% yield of pure product: mp 73.5–74.0 °C; IR (hexane) 2138 (w), 2072 (m), 2025 (s), 2016 (s), 1665 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (m, benzyl, 2), 3.27 (m, acyl, 2), 7.23 (s, aromatic, 5). Anal. Calcd for $[PhCH_2CH_2C(O)Mn(CO)_5]$: C, 51.22; H, 2.75. Found: C, 51.13; H, 2.78.

(4) $PhCH_2CH_2CH_2OC(O)Mn(CO)_5$, 2: mp 84.2–84.7 °C; IR (hexanes) 2140 (w), 2055 (s), 2024 (s), 1663 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (m, alkyl, 2), 2.70 (m, benzyl, 2), 4.12 (t, oxy, 2), 7.27 (s, aromatic, 5). Anal. Calcd for $[Ph(CH_2)_3OC(O)Mn(CO)_5]$: C, 50.28; H, 3.07. Found: C, 50.06; H, 3.12.

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(7) The analogous reaction in hexanes (70 °C (1200 psi of H_2) yielded no recognizable organic products. A small amount of red polynuclear manganese carbonyl was isolated, but its structure has not yet been determined.

homogeneous catalytic hydrogenation of Th or U acyls leads to the corresponding alkoxide (eq 5). This is a

$$[M\eta^2\text{-}C(O)R] + H_2 \xrightarrow{\text{cat.}} [M\text{-}OCH_2R] \qquad (5)$$

precise analogue of the conversion that we have now shown to occur with a manganese acyl carbonyl in the absence of added catalyst. The addition of H_2 to the acylmanganese carbonyl, especially when the carbonyl is written in the resonance form **4**, is reminiscent of the proposed mechanism for the hydrogenation of Cr and W carbene complexes.[9] The hydrogenation of a carbonyl group of a transition-metal acyl to a transition-metal oxymethylene may be quite general and may have implications for catalytic synthesis gas chemistry including the Fischer–Tropsch process. Since R-$M(CO)_n$ readily undergoes CO insertion, it was expected that we could convert $Ph(CH_2)_2Mn(CO)_5$ into **2** on treatment with CO/H_2 in hexane solution, and indeed this proved to be the case (Table I).

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Registry No. 1, 82849-27-2; 2, 82849-28-3; $RMn(CO)_5$ (R = $PhCH_2CO$), 15022-57-8; $RMn(CO)_5$ (R = CH_2Ph), 14049-86-6; $RMn(CO)_5$ (R = $PhCH_2CH_2CO$), 82849-25-0; $RMn(CO)_5$ (R = $PhCH_2CH_2$), 82849-26-1; $PhCH_2CHO$, 122-78-1; $PhCH_2CH_2OH$, 60-12-8; $PhCH_2CH_2CHO$, 104-53-0; CO, 630-08-0; H_2, 1333-74-0; sulfolane, 126-33-0.

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[8] $PhCH_2CH_2Mn(CO)_5$ was made by refluxing a solution of $PhCH_2CH_2C(O)Mn(CO)_5$ in hexanes under N_2 for 0.5 h. Recrystallization from hot hexanes gave a 61% yield of pure crystals: mp 84.6–85.0 °C; IR (hexanes) 2120 (m), 2022 (s), 2000 (s), 1958 (w); ^1H NMR ($CDCl_3$) δ 1.27 (t, alkyl, 2), 2.98 (t, benzyl, 2), 7.20 (s, aromatic, 5). Anal. Calcd for $[PhCH_2CH_2Mn(CO)_5]$: C, 52.00; H, 3.00. Found: C, 51.97, H, 3.17.

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Octakis(trimethylsilyl)cyclotetrasilane. A Stable Cyclotetrasilane from a Silylene Precursor[†]

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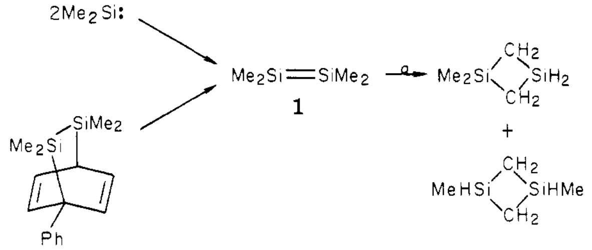
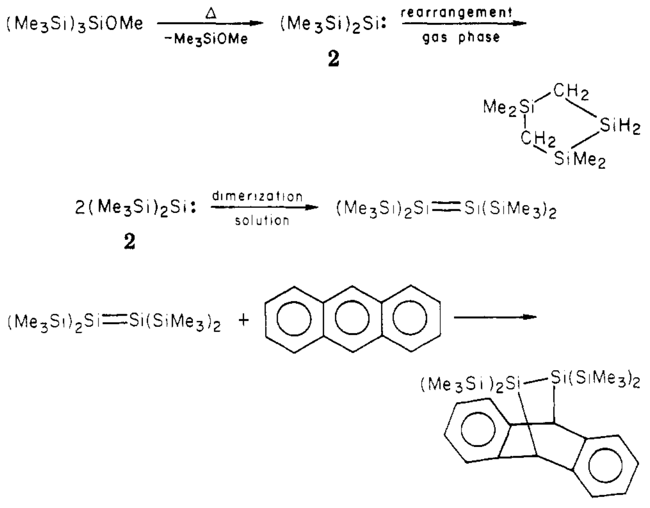
Summary: Liquid-phase pyrolysis of neat methoxytris(trimethylsilyl)silane leads to the formation of octakis(trimethylsilyl)cyclotetrasilane. This stable molecule has been characterized, and the preliminary results of the X-ray structure determination indicate that the four-membered ring is planar. The intermediacy of tetrakis(trimethylsilyl)disilene is strongly indicated, but several alternatives are considered for its conversion to the cyclotetrasilane and for its formation. It is suggested that insertion of a silylene into its own precursor, followed by direct β elimination to the disilene or by α elimination to a new silylene followed by rearrangement to the disilene, should both be considered in addition to silylene dimerization as the mechanism for disilene formation under these conditions.

Like carbene chemistry before it, the investigation of molecules containing a divalent silicon atom, silylenes, has produced both amusing molecules and challenging mechanistic problems.[1] The purpose of this communication is to report a silylene reaction that leads to the formation of a cyclotetrasilane and to describe its structure. While this finding strongly indicates the intermediacy of a disilene, the route by which the disilene is formed under these conditions is not yet clear. It is this mechanistic uncertainty and its implied warning, as well as the novelty of the product, that has prompted publication.

In 1976 Conlin was led to suggest that dimethylsilylene undergoes dimerization to tetramethyldisilene (**1**) by the observation that the same products were isolated following generation of the silylene in the gas phase[2] as had been obtained by Roark and Peddle from rearrangement of the disilene.[3]



Sakurai subsequently found a number of examples in solution in which generation of a silylene in the presence of anthracene led to the formation of a product that could reasonably be attributed to cycloaddition by a disilene that was believed to be formed by silylene dimerization.[4] The example of bis(trimethylsilyl)silylene (**2**) is pertinent to the work reported here and was also found in our laboratory.[5] It has been shown that in the gas phase, rearrangement of **2** is much more rapid than dimerization.[6]



That silylenes do indeed dimerize has been most vividly demonstrated by the work of West, Fink, and Michl, who have isolated a stable disilene from the thawing of a matrix

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[†] This work was carried out with financial support from the U.S. Department of Energy. This is technical report no. COO-1713-107.

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