Organometallics 1983, *2*, 1573–1577 1573

Synthesis and Spectra of Tetravinyldistibines

Arthur J. Ashe, III,* Edward G. Ludwig, Jr., and Hans Pommerening

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

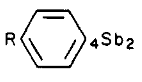
Received April 19, 1983

New tetravinyldistibines, R_4Sb_2 (where R = vinyl, **16**; isopropenyl, **17**; 1(*E*)- and 1(*Z*)-propenyl, **18** and **19**; 2-methyl-1-propenyl, **20**, and 1-methyl-1(*E*)-propenyl, **21**), have been prepared from the reaction of the corresponding tertiary stibines with active metals in liquid ammonia followed by treatment with 1,2-dichloroethane. While all the distibines show yellow liquid phases, **16** and **17** freeze to violet and orange solids. Compounds **18**–**21** freeze to yellow solids. ^1H NMR, Raman, UV, and mass spectra of **16**–**21** are discussed.

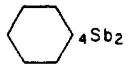
In 1934 Paneth reported the synthesis of tetramethyldistibine, **1**, from the reaction of methyl radicals with an antimony mirror.[1a] This compound shows unusual thermochromic behavior. It is a bright red solid that melts reversibly at 17 °C to a pale yellow liquid. Similarly, solutions of **1** are pale yellow. In the intervening 49 years, six other thermochromic distibines **2**,[1a] **3**,[2] **4**,[3] **5**,[4,5] **6**,[6] and **7**[7] have been reported. Solid-phase colors range from deep yellow for **2** to violet for **4**, but the liquid phases are invariably pale yellow (see Figure 1).

Crystal structures of **1**,[1b] **4**,[3] and **5**[5] show very similar crystal packing (Figure 2). Each molecule adopts a staggered trans conformation about the Sb–Sb axis. All the antimony atoms are nearly colinear with short Sb···Sb intermolecular contacts. This suggests that the solid-phase colors of the thermochromic distibines are due to electronic interactions along the Sb–Sb···Sb–Sb chain.[3,8]

However, not all distibines show thermochromic properties. Distibines **8**,[9,10] **9**,[10] **10**,[10] **11**,[11] **12**,[12] **13**,[2] **14**,[13] and **15**[14] form yellow crystalline solids. These colors are qualitatively similar to the liquid-phase colors reported for **1**–**7**. In addition, there are a number of distibines that have been reported only as yellow oils.[15]



8, R = H
9, R = CH_3
10, R = Br



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$(CF_3)_4Sb_2$

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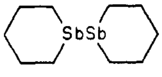

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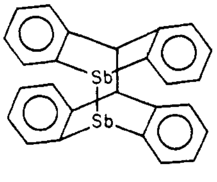

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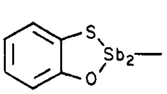

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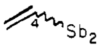
A crystal structure available for tetraphenyldistibine, **8**[16] reveals a molecular structure similar to that of **1**, **4**, and **5** but with very different crystal packing. The antimony atoms are not aligned in chains, and there are no intermolecular Sb···Sb contacts closer than 4.29 Å. The bulky phenyl groups are arranged in such a way that there is little free space on the backside of the Sb–Sb bond. One assumes that the bulky substituents of all of the nonthermochromic distibines prevent the intermolecular interaction responsible for the colors of **1**–**7**.[3]

In order to define the requirements for thermochromism, it would be useful to examine a series of closely related distibines with small variations in steric bulk. We have prepared the series of tetravinyldistibines **16**–**21** and now wish to report in detail on their spectra.



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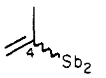

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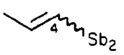

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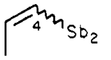

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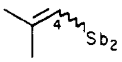

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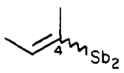

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Results and Discussion

Synthesis. The tetravinyldistibines **16**–**21** could be prepared by the standard scheme[15c] outlined in Scheme I.

Tertiary vinylstibines **22** are easily available from the reaction of corresponding lithium or Grignard reagents with antimony trichloride. Active metal cleavage of **22** afforded the corresponding metal divinylstibine **24** which gave the distibine on treatment with 1,2-dichloroethane. We have noted considerable differences in the facility of cleavage of **22**. While trivinylstibine undergoes efficient cleavage with lithium in tetrahydrofuran, the larger tertiary vinylstibines are inert under these conditions. Trivinyl-

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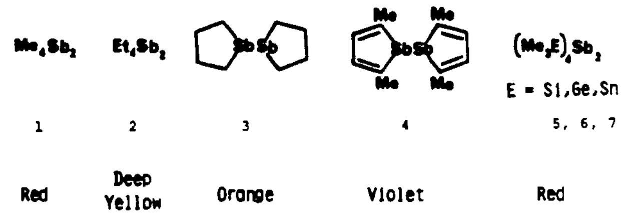


Figure 1. Thermochromic distibines (solid-phase colors are indicated).

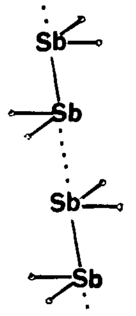
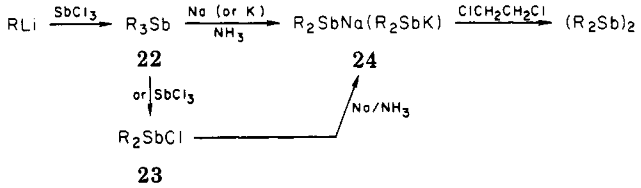


Figure 2. Schematic representation of the Sb–Sb⋯Sb–Sb chain in tetramethyldistibine (1), tetramethylbistibolyl (4), and tetrakis(trimethylsilyl)distibine (5).

Scheme I



stibine, triisopropenylstibine, and tri-1(*Z*)- and tri-1(*E*)-propenylstibines are readily cleaved on treatment with sodium in liquid ammonia. On the other hand, tris(2-methyl-1-propenyl)stibine and tris(1-methyl-1(*E*)-propenyl)stibine are cleaved only on treatment with potassium in liquid ammonia. Alternatively these trivinylstibines may be converted by treatment with antimony trichloride to the corresponding divinylchlorostibines which are highly reactive toward sodium in liquid ammonia. Noltes had previously observed that bulky tertiary alkylstibines are cleaved more slowly by sodium in ammonia.[15c]

The tetravinyldistibines **16–21** are all highly sensitive to oxygen but may be conveniently handled by using drybox or Schlenk-ware techniques. They are unreactive toward water, mild acids, or bases. We have found it convenient to purify them by low-temperature recrystallization from pentane. They show melting points ranging from −53 °C for **16** to +51 °C for **21**. The distibines show good thermal stability to ∼100 °C, but above this temperature they darken with production of antimony metal and the corresponding tertiary stibines.[15c]

UV–Visible Spectra. All the tetravinyldistibines **16–21** show yellow liquid phases. The solution UV spectra show maxima near 300 nm for **17**, **20**, and **21**, but the most characteristic feature of **16–21** is a low intensity smooth tail extending out to ∼400 nm. Presumably this tail corresponds to their pale yellow color.

Tetravinyldistibine freezes at −53 °C to violet crystals close in color to **4**. We have experienced some difficulty measuring reflectance spectra at this temperature, although the higher melting tetrakis(alkylvinyl)distibines have presented few problems. Tetraisopropenyldistibine (**17**), mp −3 °C, shows an orange solid phase. The diffuse reflectance spectrum of solid **17** has a broad absorption maximum centered at 475 nm (see Figure 3). This is nearly 200 nm red shifted from the maximum (290 nm) shown by the solution-phase UV spectrum of **20**. However, it is considerably blue shifted from the diffuse reflectance maximum of solid tetramethylbistibolyl (**4**) at 605 nm.

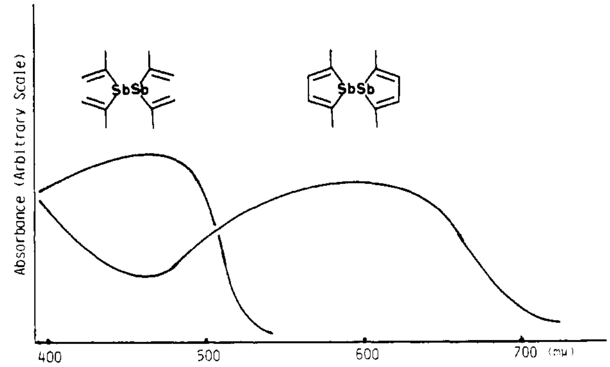


Figure 3. The diffuse reflectance spectra of tetraisopropenyldistibine (**17**) and tetramethylbistibolyl (**4**). The vertical scale is arbitrary.

The color of **4** has been associated with intermolecular interaction along its Sb–Sb⋯Sb–Sb axis.[3,8] It is plausible to assume that the color of **17** is due to a similar electronic interaction. However, the intermolecular distances along the Sb–Sb⋯Sb–Sb chain of **17** are probably greater than those of **4**. In contrast to the planar dimethylstibolyl rings of **4**, the two isopropenyl moieties attached to each Sb atom are unlikely to be coplanar.[17] A conformational structure of **17** analogous to that of **4** would place the cis-H atoms in the same volume of space. A rotation about the Sb–C bonds would eliminate this offending interaction, but only at the price of congesting the backside of the Sb–Sb bond axis. Thus, the effective larger steric bulk of the two isopropenyl stibyl groups of **17** is likely to make the intermolecular Sb⋯Sb distances greater.

In this respect the comparison of the structure of **4** with **5** is instructive. Although the crystal packing structures are similar, the intermolecular Sb⋯Sb separation increases from 3.63 Å for **4** to 3.99 Å for **5**. The color of **5** (qualitatively described only as red) corresponds to absorption of higher energy light than for **4**. This larger band gap corresponds to the weaker intermolecular interaction. Presumably the 0.5 eV greater band gap for **17** over **4** also corresponds to larger intermolecular Sb⋯Sb separation. We hope to obtain structural data for **17** to confirm the hypothesis.

We were rather surprised and disappointed that the tetravinyldistibines **18–21** did not show thermochromic properties. Presumably these compounds do not have intermolecular Sb⋯Sb association. At present we have no adequate explanation for their lack of thermochromism. It may be that the Sb⋯Sb interaction is a rather weak one and that it is overwhelmed by crystal packing forces of the larger alkyl groups. Again good structural data are needed.

Finally, since there have been no systematic spectroscopic investigations of distibines, we have cataloged the spectra that are useful in their characterization.

Mass Spectra. The mass spectra have been determined on samples volatilized from a heated solid probe using electron-impact ionization (70 eV). The spectra of **16–21** show very similar fragmentation patterns summarized in Table I. All the distibines show weak but easily observable molecular ions, followed by weak peaks for sequential loss of carbon groups: $R_4Sb_2^+$, $R_3Sb_2^+$, $R_2Sb_2^+$, RSb_2^+, and

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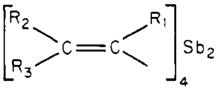
(17) This steric problem is virtually identical with that of the ortho hydrogen atoms of 8. In this case the phenyl groups are rotated by 80.5°.

Table I. Mass Spectra of the Tetravinyldistibines, R_4Sb_2[a]

ion	vinyl 16	isopropenyl 17	1(*Z*)-propenyl 18	1(*E*)-propenyl 19	2-methyl-1-propenyl 20	1-methyl-1(*E*)-propenyl 21
R_4Sb_2	350 (19.7)	406 (17.1)	406 (5.0)	406 (17.9)	462 (14.1)	462 (9.6)
R_3Sb_2	323 (2.1)	365 (11.2)	365 (0.8)	365 (4.2)	407 (3.7)	407 (4.5)
R_2Sb_2	296 (0.3)	324 (4.0)	324 (0.5)	324 (2.0)	352 (0.8)	352 (3.3)
RSb_2	269 (54.5)	283 (63.3)	283 (5.8)	283 (17.2)	297 (5.9)	297 (19.5)
Sb_2H	243 (26.4)	243 (1.2)	243 (3.8)	243 (10.5)	243 (1.2)	243 (4.8)
Sb_2	242 (42.5)	242 (25.4)	242 (7.8)	242 (12.7)	242 (9.8)	242 (7.4)
R_2Sb	175 (100)	203 (30.6)	203 (31.2)	203 (64.0)	231 (54.0)	231 (16.9)
RSbH	149 (38.0)	163 (21.5)	163 (50.1)	163 (62.1)	177 (43.9)	177 (29.6)
RSb	148 (70.5)	162 (9.0)	162 (50.9)	162 (17.0)	176 (19.4)	176 (17.1)
SbH	122 (26.7)	122 (small)	122 (9.3)	122 (6.7)	122 (1.0)	122 (0.8)
Sb	121 (92.8)	121 (38.7)	121 (55.6)	121 (52.0)	121 (10.9)	121 (6.1)
(R_2-H)	53 (34)	81 (100)	81 (100)	81 (100)	109 (96.5)	109 (47.8)
R	*b*	*b*	*b*	*b*	55 (100)	55 (100)

[a] The *m/e* values are given for ^{121}Sb only. The relative intensities are for (^{121}Sb + ^{123}Sb). [b] Peaks *m/e* <45 were not observed.

Table II. ^1H NMR Chemical Shift (δ) Values of Tetravinyldistibines



distibine	R_1	R_2	R_3
vinyl 16	6.70	6.07	5.63
isopropenyl 17	2.25	5.90	5.55
1(*Z*)-propenyl 18	6.50	6.50	1.70
1(*E*)-propenyl 19	6.23	1.78	6.23
2-methyl-1-propenyl 20	6.40	1.90	1.90
1-methyl-1(*E*)-propenyl 21	2.12	1.58	6.00

Sb_2^+. Of these, RSb_2^+ is usually strongest.

The peaks assigned to R_2Sb^+ are quite intense. These daughter ions are also prominent in mass spectra of the corresponding tertiary stibines. Since tertiary stibines are the pyrolysis products of distibines, a portion of the R_2Sb^+ intensities may be due to fragmentation from the corresponding tertiary stibines.

^1H NMR Spectra. The chemical shift values of **16**–**21** are summarized in Table II. These spectra are very similar to those shown by the corresponding tertiary stibines. The coupling constants and chemical shift values are almost identical. Typically the signals for the vinyl proton are shifted only 0.1–0.2 ppm downfield for the distibines.

Raman Spectra. We have found Raman spectroscopy to be the most useful method for characterizing distibines. Metal–metal stretching vibrations normally give rise to intense and easily identifiable Raman peaks. Thus the Raman spectra of **16**–**21** show intense polarized bands for γ_{SbSb} in the range of 140–180 cm^{-1}. These data together with the previous literature[18] data on **1**, **2**, and **5** are collected in Table III.

The Raman spectrum of liquid tetramethyldistibine **1** has been reported to show two Sb–Sb bands of comparable intensities at 175 and 143 cm^{-1}. These have been assigned to trans and gauche conformers. The Raman spectrum of the solid shows a great decrease in the intensity of the 143-cm^{-1} band, suggesting that tetramethyldistibine crystallized predominantly in the trans conformation.[19]

Table III. γ_{SbSb} (cm^{-1}) from the Raman Spectra of R_4Sb_2 in Solid and Liquid Phases

R_4Sb_2, R	γ_{SbSb} liquid	γ_{SbSb} solid
vinyl 16	163	
isopropenyl 17	158	152
1(*Z*)-propenyl 18	154	165
1(*E*)-propenyl 19	152	155
2-methyl-1-propenyl 20	144	151
1-methyl-1(*E*)-propenyl 21	148	154
CH_3 1	143, 175[a]	180[a]
C_2H_5 2	163[a]	
C_6H_5 8		141[a]
$(CH_3)_3Si$, 5	140[a]	137[a]
H		(194)[b]

[a] Reference 18. [b] Estimated, see ref 20.

We have measured the Raman spectra of **16**–**21** in both solid and liquid states. While there are small shifts between solid and liquid, no new bands appear in either phase. Exempting the possibility that different conformers may show the same γ_{SbSb}, this observation suggests that the tetravinyldistibines populate the same conformers in both liquid and solid. Since **1**, **4**, **5**, and **8** are known to crystallize in the transoid conformation, we tentatively suggest that the tetravinyldistibines populate the trans conformation in both liquid and solid phases.

The observed range of γ_{SbSb} from 137 cm^{-1} for **5** to 180 cm^{-1} for solid **1** appears to be due mostly to a mass effect. A plot of γ_{SbSb} vs. $1/(\mu_{SbR_2})^{1/2}$ yields a good linear regression of $\gamma = (36.7 + 745\ (1/\mu_{SbR_2}))\ cm^{-1}$, $r = 0.91$. The quality of this correlation suggests that the vibrational force constants are relatively invariant and that the vibrations are largely localized Sb–Sb bands. In any event, this empirical correlation should allow good prediction of the γ_{SbSb} of new distibines. For example, we expect Sb_2H_4 (trans conformation) to have a γ_{SbSb} of close to 194 cm^{-1}.[20]

Experimental Section

General Data. Proton NMR spectra were run on either a Varian Associates T60A or a Bruker WM 360 NMR spectrometer, and ^{13}C NMR spectra were recorded on a JEOL FX90Q NMR spectrometer. Tetramethylsilane was used as an internal reference. IR spectra were obtained on a Beckman IR 4240 spectrophotometer calibrated with the polystyrene 1601.4-cm^{-1} absorption band. UV–visible spectra were obtained on a Varian Associates Cary 219 spectrophotometer, and solid reflectance data were determined on the same instrument using a Varian Associates in-cell space diffuse reflectance accessory. This was accomplished by placing the sample on a microscope slide topped with a cov-

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(18) (a) Breunig, H. J.; Breunig-Lyriti, V.; Fichtner, W. *Z. Anorg. Allg. Chem.* **1982**, *487*, 111. (b) However, see: Bürger, H.; Eujen, R.; Becker, G.; Mundt, O.; Westerhaussen, M.; Witthauer, C. *J. Mol. Struct.* **1983**, *98*, 265.

(19) For previous studies of closely related arsines and phosphines see: Durig, J. R.; Casper, J. M. *J. Chem. Phys.* **1971**, *55*, 198. Thompson, J. W.; Witt, J. D.; Durig, J. R. *Inorg. Chem.* **1972**, *12*, 2124.

(20) Only the mass spectrum of Sb_2H_4 has been reported: Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 50.

erslip, and the sample was frozen by clamping a piece of dry ice against it. Mass spectral determinations were made by using a Finnigan 4023 GC/MS with an electron ionization energy of 70 eV. Raman spectra were obtained on a Spex 1401 double spectrometer using the 6328-Å excitation line of a Spectra Physics Model 125 helium–neon laser. Elemental analyses were performed by either Galbraith Laboratories or Spang Microanalytical Laboratories. All operations were performed under nitrogen.

Trivinylstibine. Trivinylstibine was prepared in 70% yield from the reaction of vinylmagnesium bromide with antimony trichloride:[21] bp 44 °C (16 torr); ^{1}H NMR (C_6D_6, 360 MHz) δ 5.63 (dd, $^{3}J_{\mathrm{H,H\text{-}trans}} = 18$ Hz, $^{2}J_{\mathrm{H,H\text{-}gem}} = 3$ Hz, H_{cis}), 6.07 (dd, $^{3}J_{\mathrm{H,H\text{-}cis}} = 12$ Hz, $^{2}J_{\mathrm{H,H\text{-}gem}} = 3$ Hz, H_{trans}), 6.70 (dd, $^{3}J_{\mathrm{H,H\text{-}cis}} = 12$ Hz, $^{3}J_{\mathrm{H,H\text{-}trans}} = 18$ Hz, H_α); ^{13}C NMR (C_6D_6, 90.56 MHz) δ 132.62 ($^{1}J_{\mathrm{CH}}$ = 156.3 Hz, $^{1}J_{\mathrm{CH'}}$ = 155.9, $^{2}J_{\mathrm{CH}}$ = 2.9 Hz, C_2), 136.40 ($^{1}J_{\mathrm{CH}}$ = 154.8 Hz, C_1).

Triisopropenylstibine. In the same manner the reaction of antimony trichloride (10.3 g, 45 mmol) in 40 mL of tetrahydrofuran with isopropenylmagnesium bromide, which had been prepared from 3.9 g (160 mmol) of magnesium turnings and 19.4 g (160 mmol) of isopropenyl bromide, gave 6.4 g (57%) of triisopropenylstibine as a colorless, air-sensitive liquid:[22] bp 45–47 °C (2 torr); ^{1}H NMR (C_6D_6) δ 2.00 (m, 9 H), 5.35 (m, 3 H), 5.85 (m, 3 H); MS, *m/e* (relative intensity) 246 (18.6, M^+), 244 (24.8), 205 (19.5), 203 (26.8), 164 (50.6), 162 (68.4), 123 (39.6), 121 (63.8), 81 (100.0), 67 (18.3), 55 (16.2). Anal. Calcd for $C_9H_{15}Sb$: C, 44.13; H, 6.17. Found: C, 43.96; H, 6.25.

Tri-1(*Z*)-propenylstibine. In the same manner the reaction of 10.3 g (45 mmol) of antimony trichloride in 40 mL of tetrahydrofuran with 1(*Z*)-propenylmagnesium bromide, generated from 19.4 g (160 mmol) of 1-bromo-1(*Z*)-propene and 3.9 g (160 mmol) of magnesium turnings in 120 mL of tetrahydrofuran, gave 8.1 g (71%) of tri-1(*Z*)-propenylstibine as a colorless, air-sensitive oil:[22] bp 72–74 °C (3 torr); ^{1}H NMR (C_6D_6, 60 MHz) δ 1.73 (apparent d, 9 H), 6.4 (m, 6 H). Anal. Calcd for $C_9H_{15}Sb$: C, 44.13; H, 6.17. Found: C,43.98; H, 6.31.

Tris(2-methyl-1-propenyl)stibine. In the same manner the reaction of 13.7 g (60 mmol) of antimony trichloride in 60 mL of tetrahydrofuran with (2-methyl-1-propenyl)magnesium bromide,[23] generated from 30.4 g (225 mmol) of 1-bromo-2-methyl-1-propene[24] and 5.5 g (225 mmol) of magnesium in 150 mL of tetrahydrofuran, gave 9.8 g (57%) of tris(2-methyl-1-propenyl)stibene as a colorless, air-sensitive oil: bp 66–68 °C (0.1 torr); ^{1}H NMR (C_6D_6) δ 1.85 (apparent d, 18 H), 6.10 (m, 3 H); IR (CCl_4) 2961 (s), 2930 (s), 2905 (s), 2850 (m), 1606 (m), 1435 (s), 1376 (m), 1366 (m), 1274 (m) cm^{-1}; MS, *m/e* (relative intensity) 288 (7.2, M^+), 286 (10.1), 233 (5.2), 231 (7.4), 178 (60.9), 176 (88.8), 123 (8.9), 121 (11.4), 95 (100.0), 55 (92.0); UV–visible (cyclohexane) λ_{max} <220 nm. Anal. Calcd for $C_{12}H_{21}Sb$: C, 50.21; H, 7.37. Found: C, 50.24; H, 7.32.

Tri-1(*E*)-propenylstibine.[22] A solution of 1(*E*)-propenyllithium was prepared from 7.65 g (100 mmol) of 1-chloro-1(*E*)-propene and excess (2.8 g) 2% sodium–lithium alloy in 75 mL of ether.[25] The excess lithium was removed. Antimony trichloride (5.3 g, 23 mmol) in 30 mL of ether was added dropwise over 30 min with stirring to 1(*E*)-propenyllithium solution at −20 °C. After being heated to reflux for 1 h, the solution was cooled to 0 °C and 50 mL of saturated aqueous ammonium chloride was added. The mixture was filtered under nitrogen. After separation of the layers, the ether layer was dried over anhydrous magnesium sulfate. The solvent was removed, and distillation of the residue gave 4.75 g (84%) of pure tri-1(*E*)-propenylstibine as a clear, colorless air-sensitive liquid: bp 59–60 °C (1 torr); ^{1}H NMR (C_6D_6) δ 1.78 (apparent d, 9 H), 6.23 (m, 6 H).

Tri-2(*E*)-but-2-enylstibine. In the same manner a solution of 2(*Z*)-but-2-enyllithium was prepared from 13.5 g (100 mmol) of 2-bromo-2(*E*)-butene and 2.5 g of 2% sodium–lithium alloy in 75 mL of ether.[26] The reaction of 6.8 g (30 mmol) of antimony trichloride with the lithium reagent gave 7.9 g (92%) of tri-2-(*E*)-but-2-enylstibine as a colorless, air-sensitive liquid: bp 67–69 °C (0.01 torr); ^{1}H NMR (C_6D_6) δ 1.63 (apparent d, 9 H), 1.95 (br s, 9 H), 5.90 (m, 3 H); IR (CCl_4) 3004 (m), 2970 (s), 2940 (s), 2918 (s), 2856 (s), 2725 (w), 1618 (m), 1437 (s), 1372 (m) cm^{-1}; MS *m/e* (relative intensity) 288 (2.4), 286 (3.3), 233 (0.5), 231 (0.8), 178 (19.3), 176 (26.2), 123 (2.0), 121 (2.4), 109 (12.6), 95 (20.7), 55 (100.0); UV–visible (cyclohexane) λ_{max} 248 nm (ϵ 5140). Anal. Calcd for $C_{12}H_{21}Sb_2$: C, 50.21; H, 7.37. Found: C, 50.21; H, 6.94.

Tetravinyldistibine 16. Method a. An excess (2 g) of freshly cut lithium wire was added to 3.0 g (5 mmol) of trivinylstibine in 75 mL of tetrahydrofuran. The reaction mixture was gently heated until the red color of the anion appeared. After being stirred at 25 °C for 2 h, the solution was decanted from the unreacted lithium. 1,2-Dibromoethane (2.8 g, 15 mmol) in 20 mL of dry tetrahydrofuran was added dropwise to the stirred solution over 30 min during which the red color slowly disappeared. Following filtration under nitrogen, the solvent was removed. Distillation of the residue gave 1.5 g (57%) of pure tetravinyldistibine as an air-sensitive, yellow liquid, bp 61–62 °C (0.005 torr), which freezes, mp −58 to −53 °C, to a purple solid: ^{1}H NMR (C_6D_6, 360 MHz) δ 5.74 (dd, $^{3}J_{\mathrm{H,H\text{-}trans}} = 19$ Hz, $^{2}J_{\mathrm{H,H\text{-}gem}} = 2$ Hz, H_{cis}), 6.11 (dd, $^{3}J_{\mathrm{H,H\text{-}cis}} = 12$ Hz, $^{2}J_{\mathrm{H\text{-}H\text{-}gem}} = 2$ Hz, H_{trans}), 6.89 (dd, $^{3}J_{\mathrm{H,H\text{-}trans}} = 19$ Hz, $^{2}J_{\mathrm{H,H\text{-}cis}} = 12$ Hz, H_α); ^{13}C NMR (C_6D_6, 90.56 MHz) δ 131.3 ($^{1}J_{\mathrm{CH}}$ = 155.7 Hz, C_1), 133.0 ($^{1}J_{\mathrm{CH}}$ = 156.6 Hz, $^{1}J_{\mathrm{CH'}}$ = 157.8, $^{2}J_{\mathrm{CH}}$ = 2.8 Hz, C_2); IR (CCl_4) 3156 (w), 3055 (m), 2985 (s), 2940 (m), 1582 (w), 1390 (s), 1234 (s) cm^{-1}; UV–visible (cyclohexane) λ_{max} <220 nm. Anal. Calcd for $C_8H_{12}Sb_2$: C, 27.32; H, 3.44. Found: C, 27.65; H, 3.65.

Method b. Sodium metal (0.62 g, 27 mmol) was added piecewise to 2.75 g (13.6 mmol) of trivinylstibine in 100 mL of liquid ammonia. The red solution was allowed to stir for 1 h, after which the 1.1 mL of 1,2-dichloroethane was added over 30 min. The solution turned yellow on addition. After the ammonia had evaporated, 50 mL of pentane was added, the solution was filtered under nitrogen, and the pentane was removed to give 2.05 g (86%) of pure tetravinyldistibine.

Tetraisopropenyldistibine (17). Method c. Antimony trichloride (1.85 g, 8.0 mmol) and triisopropenylstibine (4.0 g, 16 mmol) in 5 mL of tetrahydrofuran were allowed to stir for 30 min. Distillation gave 4.0 g (73%) of chlorodiisopropenylstibine as an air-sensitive liquid: bp 72–75 °C (6 torr); ^{1}H NMR (C_6D_6) δ 2.00 (m, 9 H), 5.43 (m, 3 H), 5.90 (m, 1 H); MS, *m/e* (relative intensity) 242 (1.6), 240 (8.5), 238 (7.7), 207 (10.1), 205 (16.0), 204 (18.3), 203 (22.7), 202 (23.5), 164 (53.2), 162 (72.7), 123 (26.1), 121 (43.9), 81 (100.0).

Since chlorodiisopropenylstibine decomposes on standing, it was used immediately to prepare the distibine. Sodium metal (0.6 g, 26 mmol) was added piecewise to a solution of 3.1 g (13 mmol) of chlorodiisopropenylstibine in 100 mL of liquid ammonia. The red color of the solution was discharged by the addition of 0.5 mL of 1,2-dichloroethane. After the ammonia had evaporated, 50 mL of pentane was added. The solution was filtered, and the solvent was evaporated and the residue recrystallized from pentane to give 2.15 g (81%) of tetraisopropenyldistibine as a yellow oil which freezes to an orange solid, mp −3 to −1 °C. Alternatively, 18 can be prepared in 86% yield by method b: ^{1}H NMR (C_6D_6) δ 2.25 (m, 12 H), 5.55 (m, 4 H), 5.90 (m, 4 H); IR (CCl_4) 3041 (w), 3019 (w), 2950 (s), 2910 (m), 2825 (w), 1597 (w), 1430 (m), 1366 (w) cm^{-1}; UV–visible (cyclohexane) 290 (ϵ 9750), 208 nm (35 000); diffuse reflectance, maximum absorbance 475 nm. Anal. Calcd for $C_{12}H_{20}Sb_2$: C, 35.34; H, 4.94. Found: C, 35.53; H, 4.94.

Tetra-1(*Z*)-propenyldistibine (19). This distibine was prepared by method b above from 1.0 g (4.1 mmol) of tri-1-(*Z*)-propenylstibine and 0.19 g (8.2 mmol) of sodium in 100 mL of liquid ammonia. An 80% yield of **19** was obtained. Pure **19** is a yellow, air-sensitive liquid which freezes, mp −7 to −5 °C, to a yellow solid: ^{1}H NMR (C_6D_6, 60 MHz) δ 1.70 (m, 12 H), 6.5 (m, 8 H); IR (CCl_4) 2990 (s), 2955 (m), 2912 (m), 2870 (w), 2850 (w), 1604 (s), 1442 (s), 1380 (m), 1320 (s) cm^{-1}; UV–visible (cyclohexane) λ_{max} <220 nm. Anal. Calcd for $C_{12}H_{20}Sb_2$: C, 35.34; H, 4.94. Found: C, 35.23; H, 4.86.

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Tetra-1(*E*)-propenyldistibine (18). Compound **18** was prepared by method b from 4.0 g (16 mmol) of tri-1(*E*)-propenylstibine and 0.74 g (32 mmol) of sodium in 100 mL of liquid ammonia. A 77% yield (2.5 g) of pure **18** was obtained as a yellow, air-sensitive liquid which freezes, mp -4 to -3 °C, to a yellow solid: ^{1}H NMR (C_6D_6) δ 1.80 (apparent d, 12 H), 6.15 (m, 8 H); IR (CCl_4) 2990 (m), 2962 (m), 2942 (m), 2915 (s), 2870 (w), 2850 (m), 1609 (s), 1443 (s), 1375 (w), 1320 (w), 1200 (w) cm^{-1}; UV-visible (cyclohexane) λ_{max} <220 nm. Anal. Calcd for $C_{12}H_{20}Sb_2$: C, 35.34; H, 4.94. Found: C, 35.43; H, 4.78.

Tetra-2(*E*)-but-2-enyldistibine (21). Method d. Potassium metal (0.63 g, 16 mmol) in pieces was added to 2.3 g (8.0 mmol) of tri-2(*E*)-but-2-enylstibine in 100 mL of liquid ammonia. After the deep red solution was allowed to stir for 1 h, 0.78 g of ammonium bromide was added. After 30 min, 0.34 mL of 1,2-dibromoethane was added dropwise. The ammonia was allowed to evaporate and 50 mL of pentane was added. The solution was filtered, and the pentane was evaporated under reduced pressure. Four recrystallizations from cold pentane gave 1.28 g (69%) of pure **21** as a yellow, air-sensitive liquid which freezes, mp 2.5-3.5 °C, to a yellow solid: ^{1}H NMR (C_6D_6) δ 1.58 (m, 12 H), 2.12 (m, 12 H), 6.00 (m, 4 H); IR (CCl_4) 3006 (m), 2936 (m), 2917 (m), 2855 (m), 1614 (w), 1436 (m), 1374 (w) cm^{-1}; UV-visible (cyclohexane) λ_{max} 280 nm (ϵ 12 400); diffuse reflectance, maximum absorbance 350 nm. Anal. Calcd for $C_{16}H_{28}Sb_2$: C, 41.43; H, 6.08. Found: C, 41.28; H, 6.06.

Tetrakis(2-methyl-1-propenyl)distibine (20). Method e. Antimony trichloride (1.19 g, 5.2 mmol) and 3.0 g (10.5 mmol) of tris(2-methyl-1-propenyl)stibine in 15 mL of tetrahydrofuran were stirred for 30 min. Distillation of the residue at reduced pressure gave 3.7 g (88%) of bis(2-methyl-1-propenyl)antimony chloride as an air-sensitive liquid which decomposed on standing: bp 69-70 °C (0.08 torr); ^{1}H NMR (C_6D_6) δ 1.65 (apparent d, 18 H), 6.50 (m, 3 H); MS, *m/e* (relative intensity) 267 (1.0, M$^+$), 265 (0.6), 233 (0.9), 231 (1.3), 178 (13.8), 176 (19.3), 123 (8.7), 121 (12.8), 110 (83.0), 95 (54.3), 55 (100).

Tetrakis(2-methyl-1-propenyl)distibine was prepared from 2.2 g (8.3 mmol) of bis(2-methyl-1-propenyl)antimony chloride and 0.38 g (16.5 mmol) of sodium in 100 mL of liquid ammonia. The yield was 1.55 g (81%). Alternatively, **20** could be prepared in 76% yield by method d. Compound **20** may be purified by recrystallization from pentane at -20 °C. It is a yellow air-sensitive solid which melts, mp 49-51 °C, to a yellow liquid: ^{1}H NMR (C_6D_6) δ 1.90 (s, 24 H), 6.40 (br s, 4 H); IR (CCl_4) 2960 (m), 2930 (m), 2904 (s), 2850 (w), 1608 (m), 1440 (s), 1380 (w), 1370 (w), 1278 (w) cm^{-1}; UV-visible (cyclohexane) 312 (ϵ 1630), 294 (1630), 207 nm (22 700); diffuse reflectance, maximum absorbance 290 nm. Anal. Calcd for $C_{16}H_{28}Sb_2$: C, 41.43; H, 6.08. Found: C, 41.50; H, 6.02.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. **16**, 87011-60-7; **17**, 86993-83-1; **18**, 86993-85-3; **19**, 86993-84-2; **20**, 86993-87-5; **21**, 86993-86-4; **22** (R = vinyl), 5613-68-3; **22** (R = isopropenyl), 87011-57-2; **22** (R = 1(*Z*)-propenyl), 86993-81-9; **22** (R = 1(*E*)-propenyl), 86993-82-0; **22** (R = 2-methyl-1-propenyl), 87011-58-3; **22** (R = 2(*E*)-but-2-enyl), 87011-59-4; **23** (R = isopropenyl), 86993-88-6; **23** (R = 2-methyl-1-propenyl), 86993-89-7.

Alkylation of the Stilbene Dianion

James G. Smith,* Edward Oliver, and Thomas J. Boettger

Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received April 15, 1983

The stilbene dianion, **2**, formed by reducing stilbene, **1**, with alkali metals, was alkylated with methyl halides, isopropyl halides, and *tert*-butyl halides. In the case of the primary and secondary alkyl halides, the alkylation products were found to vary markedly with the leaving group and, to a lesser extent, with the cation associated with **2**. This variation was rationalized on the basis of competitive mechanisms involving nucleophilic substitution and single electron transfer. The product mixtures formed with *tert*-butyl halides were especially complex. Alkylation products containing a 1,4-cyclohexadiene ring were isolated and characterized.

Anionic species derived by the reductive metalation of unsaturated substrates with alkali metals have been of synthetic[1] and mechanistic[2] interest since the early investigations of Schlenk[3] and co-workers. Insofar as the reactions of these anionic derivatives with alkyl halides are concerned, evidence has accumulated that these reactions can proceed by mechanistic routes other than nucleophilic substitution. This has been clearly substantiated[2] in mechanistic studies with the radical anion of naphthalene. Electron transfer from the radical anion to the alkyl halide leads to formation of an alkyl radical. Subsequent combination of the alkyl radical with a second radical anion leads to an alkylated monoanion and, eventually, an alkylated dihydronaphthalene.

Similar conclusions have been reached[4] in the alkylation of the benzophenone[4a] radical anion and the anthracene[4b] radical anion with chiral alkyl halides.

Numerous substrates when reduced by alkali metals form (monomeric) dianions rather than radical anions. Mechanistic studies[5,6] of their alkylations also indicate that

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