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Insertion Reactions of Diorganotin Oxides with As–O and As–Cl Bonded Compounds

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Abstract

Functionally substituted tetrabutyldistannoxanes, $GO_2As(OSnBu_2)_2X$ [X = $OAsO_2G$, Cl; G = $-CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-CH_2CH_2CH_2-$, $-CH(CH_3)(CH_3)CH-$, $-CH(CH_3)CH_2CH_2-$, $-(CH_3)_2(CH_3)_2C-$ and $-C(CH_3)_2CH_2(CH_3)CH-$] have been obtained by the reactions of dibutyltin oxide with oxybis(1,3,2-diox-arsolanes and -arsenanes) and 2-chloro-1,3,2-diox-arsolanes and -arsenanes in 2:1 molar ratios. Insertion of dibutyltin oxide into the As–Cl bond is much more facile than into the As–O–(As) bond. Study of these reactions in various molar ratios indicate the insertion of $(Bu_2SnO)_2$ as a single unit. Ph_2SnO and Me_2SnO do not react under similar conditions.

The new distannoxanes are white crystalline solids or colourless viscous liquids, soluble in common organic solvents and dimeric in freezing benzene. Based on IR and NMR (^{13}C and ^{119} Sn) data, a dimeric ladder type structure has been suggested for these compounds.

Introduction

In contrast to the well established chemistry of Sn–O–P bonded compounds [1–6], the Sn–O–As bonded compounds are still rare [7–10]. Synthesis and reactions of tris(triorganostannyl) arsenites and 2-triorganostannyl-1,3,2-diox-arsolanes and -arsenanes have been reported only recently [10]. The present study is concerned with new organostanno–arsenoxanes derived from diorganotin and 1,3,2-diox-arsolane and -arsenane moieties. In view of the already known facile insertion reactions of diorganotin oxides into Sn–O [11], Sn–Cl [12], Si–Cl [13] linkages, similar reactions with As–O and As–Cl bonded compounds were chosen as a suitable route for attaching diorganostannoxy moieties to arsenic.

Results and Discussion

1,3-Bis(arsenoxy)-tetrabutyldistannoxanes have been obtained in quantitative yields by the insertion of two moles of dibutyltin oxide into the exocyclic As–O bond of 2,2′-oxybis-1,3,2-diox-arsolanes and -arsenanes:

$$(GO_2As)_2O + 2Bu_2SnO \longrightarrow (GO_2AsOSnBu_2)_2O$$

G = $-CH_2CH_2-$ (1)
$-CH(CH_3)CH_2-$ (2)
$-CH_2CH_2CH_2-$ (3)
$-CH(CH_3)(CH_3)CH-$ (4)
$-CH(CH_3)CH_2CH_2-$ (5)
$-C(CH_3)_2(CH_3)_2C-$ (6)
$-C(CH_3)_2CH_2(CH_3)CH-$ (7)

These reactions are carried out in refluxing benzene. Dibutyltin oxide, which is initially insoluble, dissolves slowly and finally a clear solution is obtained indicating the completion of the reaction. Removal of the solvent yields the product as a colourless viscous liquid or a crystalline solid. The same product is obtained (as indicated by actual isolation or by the ^{119}Sn NMR of the product mixture) even when the reactants are taken in equimolar ratio, leaving behind half of the arsenic compound unreacted. The reluctance of the initially formed distannoxane to undergo further reaction is similar to earlier results on reactions of dibutyltin oxide with 2,2′-oxybis(1,3,2-dioxa-borolones and -borinenes) [14].

The above reactions with Me_2SnO and Ph_2SnO do not proceed to any appreciable extent even under forcing conditions (refluxing toluene ~20 h).

Reactions of dibutyltin oxide with 2-chloro-1,3,2-diox-arsolanes and -arsenanes in refluxing benzene in 2:1 molar ratio yield 1-chloro-3-arsenoxytetrabutyldistannoxanes.

$$GO_2AsCl + 2Bu_2SnO \longrightarrow GO_2As(OSnBu_2)_2Cl$$

G = $-CH_2CH_2-$ (8)
$-CH(CH_3)CH_2-$ (9)
$-CH_2CH_2CH_2-$ (10)
$-CH(CH_3)(CH_3)CH-$ (11)
$-CH(CH_3)CH_2CH_2-$ (12)
$-C(CH_3)_2(CH_3)_2C-$ (13)

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These reactions appear to be more facile than the corresponding reactions of oxybis(1,3,2-dioxarsolanes and -arsenanes). The higher reactivity of 2-chloro-1,3,2-diox-arsolanes and -arsenanes towards Bu_2SnO is further indicated by the quantitative formation of Bu_2SnCl_2 when the reactants are taken in 2:1 molar ratio.

$$2GO_2AsCl + Bu_2SnO \longrightarrow Bu_2SnCl_2 + (GO_2As)_2O$$

$G = -CH_2CH_2-$ and $-CH(CH_3)CH_2CH_2-$

^{119}Sn NMR spectra of the product mixtures show a single peak at +122.7 ppm (an equimolar mixture of Bu_2SnCl_2 and oxybis-1,3,2-dioxarsolane also give a signal at the same position).

Interestingly, the reaction between 2-chloro-1,3,2-diox-arsolanes (or arsenanes) and dibutyltin oxide in equimolar ratio does not yield the corresponding 2-(dibutylchlorostannoxy) derivative $GO_2AsOSnBu_2Cl$, instead a mixture of 1,3-dichlorotetrabutyldistannoxane and oxybis(1,3,2-diox-arsolane or -arsenane) is obtained as indicated by the ^{119}Sn NMR spectra of the product mixtures:

$$2GO_2AsCl + 2Bu_2SnO \longrightarrow ClBu_2SnOSnBu_2Cl + GO_2AsOAsO_2G$$

G = same as in compounds **8**–**13**

These results indicate that unsymmetrical distannoxanes (compounds **8**–**13**) are formed initially, which then react with excess of chloro-arsolanes (and -arsenanes) with cleavage of the Sn–O–As linkage:

$$ClBu_2SnOSnBu_2OAsO_2G + ClAsO_2G \longrightarrow (ClBu_2Sn)_2O + (GO_2As)_2O$$

The products of the above reactions do not undergo codisproportionation even under forcing condition (e.g. heating a neat mixture for 10 h at 120–130 °C).

From the results described above, it seems that all these reactions proceed with the insertion of the $(OSnBu_2)_2$ moiety as a single unit to give the stable distannoxane derivatives which do not react further with pyroarsenites but in the presence of excess of chloroarsolanes, the terminal SnOAs linkage and then the SnOSn linkage are successively cleaved. It may be pointed out that cleavage of the Sn–O–As linkage in organostannoarsenoxanes by chloroboranes and phosphanes has been demonstrated earlier [10].

Inspite of the enhanced reactivity of 2-chloro-1,3,2-diox-arsolanes and -arsenanes with Bu_2SnO, these do not appear to react with Me_2SnO and Ph_2SnO.

Arsenoxy substituted tetrabutyldistannoxanes (compounds **1**–**13**) are colourless viscous liquids or crystalline solids (Table I), soluble in common organic solvents like benzene, toluene, chloroform and carbon tetrachloride but sparingly soluble in n-hexane. The solid compounds could be recrystallised from benzene–hexane mixture. These compounds disproportionate on attempted distillation under reduced pressure at 120–170 °C/0.01–1.0 mm. Cryoscopic molecular weight determinations of representative examples show that these compounds are dimeric in freezing benzene. Symmetrical distannoxanes are susceptible towards atmospheric moisture whereas the unsymmetrical distannoxanes surprisingly are stable even in excess of water.

In the IR spectra of symmetrical and unsymmetrical distannoxanes, the ν((As)–O–C), ν(As–O–Sn) and ν(As–O(C)) modes give absorptions in the range 1165–1005, 800–740 and 680–650 cm^{-1}, respectively [10, 15] and show no appreciable shift from their positions in the corresponding triorganostannoxy derivatives [10]. These derivatives show 3 characteristic bands at 605 ± 15 (strong and broad), 550 ± 10 (strong and medium) and 515 ± 5 cm^{-1} (weak); the former two can be attributed to the presence of a four membered Sn_2O_4 ring in the dimeric structure [16, 17], whereas the last may be assigned to ν_s(Sn–C) vibrations [17, 18]. The peak due to ν_{as}(Sn–C) may be overlapping with the first band at 605 cm^{-1} [18]. A band of medium intensity at 340 ± 5 cm^{-1} present in compounds **8**–**13** but absent in compounds **1**–**7** may be assigned to ν(Sn–Cl) vibrations [17].

^1H NMR spectra give little information due to extensive overlapping of signals of glycoxy protons with those of the butyl groups attached to tin in the region δ0.50–2.50 ppm. The peak patterns, however, are consistent with the proposed structure.

The ^{13}C NMR spectra of a few representative compounds have been obtained in carbon tetrachloride (Table II) and assignment of various signals for carbons has been made on the basis of published data [19, 20] on butyltin compounds. The satellite peaks (due to coupling with ^{119}Sn) could not be fully resolved except in compounds **2** and **6** and in these, the values of $^1J(^{13}C–^{119}Sn)$ are 614.24 and 649.42 Hz respectively corresponding to pentacoordinated tin atoms [19].

^{119}Sn NMR spectra (Table III) of compounds **1**–**13** show two signals for each compound (at −152 ± 5 and −166 ± 4 ppm for compound **1**–**7** and at −129 ± 2 and −163 ± 2 ppm for compound **8**–**13**) indicating the presence of two types of pentacoordinated tin atoms in these compounds [21, 22].

Based on the molecular weight and spectroscopic data discussed above, the following ladder like dimeric structure may be proposed for 1,3-bis(arsenoxy)tetrabutyldistannoxanes (**1**–**7**).

TABLE I. Synthetic and Analytical Data

Reactants (g)		Product (g)	Compound no.[a]	Melting point (°C)	Analysis (%) Found (calc.)			Molecular weight Found (calc.)
					As	Sn	Cl	
Bu_2SnO 3.68	$(\overline{OCH_2CH_2OAs})_2O$ 2.12	$[\overline{OCH_2CH_2OAs}OSnBu_2]_2O$ 5.62	**1**		19.03 (19.14)	30.45 (30.30)		1460 (783)
Bu_2SnO 3.64	$(\overline{OCH(CH_3)CHOAs})_2O$ 2.30	$[\overline{OCH(CH_3)CH_2OAs}OSnBu_2]_2O$ 5.71	**2**		18.42 (18.48)	29.37 (29.25)		
Bu_2SnO 3.60	$(\overline{OCH_2CH_2CH_2OAs})_2O$ 2.27	$[\overline{OCH_2CH_2CH_2OAs}OSnBu_2]_2O$ 5.74	**3**	82	18.38 (18.48)	29.29 (29.25)		
Bu_2SnO 3.09	$(\overline{OCH(CH_3)(CH_3)CHOAs})_2O$ 2.13	$[\overline{OCH(CH_3)(CH_3)CHOAs}OSnBu_2]_2O$ 4.94	**4**		17.93 (17.87)	28.48 (28.28)		
Bu_2SnO 3.60	$(\overline{OCH(CH_3)CH_2CH_2OAs})_2O$ 2.48	$[\overline{OCH(CH_3)CH_2CH_2OAs}OSnBu_2]_2O$ 5.77	**5**		17.90 (17.87)	28.44 (28.28)		1534 (839)
Bu_2SnO 1.15	$(\overline{OC(CH_3)_2(CH_3)_2COAs})_2O$ 0.93	$[\overline{OC(CH_3)_2(CH_3)_2COAs}OSnBu_2]_2O$ 2.05	**6**	69	16.68 (16.75)	26.69 (26.51)		1573 (895)
Bu_2SnO 0.77	$(\overline{OC(CH_3)_2CH_2(CH_3)CHOAs})_2O$ 0.62	$[\overline{OC(CH_3)_2CH_2(CH_3)CHOAs}OSnBu_2]_2O$ 1.34	**7**		16.73 (16.75)	26.74 (26.51)		
Bu_2SnO 2.18	$\overline{OCH_2CH_2OAs}Cl$ 0.75	$\overline{OCH_2CH_2OAs}[OSnBu_2]_2Cl$ 2.78	**8**	88	11.21 (11.23)	35.69 (35.54)	5.31 (5.30)	1357 (668)
Bu_2SnO 3.40	$\overline{OCH(CH_3)CH_2OAs}Cl$ 1.26	$\overline{OCH(CH_3)CH_2OAs}[OSnBu_2]_2Cl$ 4.42	**9**		10.94 (11.00)	34.98 (34.81)	5.18 (5.20)	
Bu_2SnO 4.27	$\overline{OCH_2CH_2CH_2OAs}Cl$ 1.58	$\overline{OCH_2CH_2CH_2OAs}[OSnBu_2]_2Cl$ 5.72	**10**	92	10.84 (11.00)	34.93 (34.81)	5.22 (5.20)	1343 (682)
Bu_2SnO 5.13	$\overline{OCH(CH_3)(CH_3)CHOAs}Cl$ 2.05	$\overline{OCH(CH_3)(CH_3)CHOAs}[OSnBu_2]_2Cl$ 7.01	**11**		10.74 (10.77)	34.38 (34.11)	5.03 (5.09)	
Bu_2SnO 3.42	$\overline{OCH(CH_3)CH_2CH_2OAs}Cl$ 1.36	$\overline{OCH(CH_3)CH_2CH_2OAs}[OSnBu_2]_2Cl$ 4.56	**12**		10.65 (10.77)	34.26 (34.11)	4.97 (5.09)	
Bu_2SnO 1.82	$\overline{OC(CH_3)_2(CH_3)_2COAs}Cl$ 0.83	$\overline{OC(CH_3)_2(CH_3)_2COAs}[OSnBu_2]_2Cl$ 2.60	**13**	84	10.46 (10.34)	33.06 (32.79)	4.81 (4.89)	1391 (724)

[a] All the compounds are colourless viscous liquids except compounds **3**, **6**, **8**, **10** and **13** which are white crystalline solids. These were recrystallised in ~80% yield from benzene–hexane mixtures.

TABLE II. ^{13}C NMR Spectral Data in CCl_4

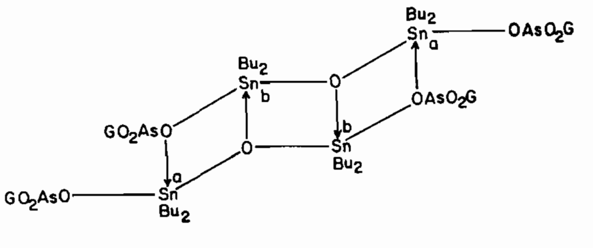
Compound number	Chemical shift δ (ppm)	
	Tin-butyl carbons $-\overset{|}{\underset{|}{Sn}}-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}\overset{4}{CH_3}$	Glycoxy carbons
1	26.49(C_1), 27.14(C_2), 26.92(C_3), 13.70(C_4)	66.57($-OCH_2$)
2	26.49(C_1)[a], 27.14(C_2), 26.92(C_3), 13.65(C_4)	19.06($-CH_3$); 74.91, 73.23, 72.84, 71.66($-OCH$, $-OCH_2$)
3	27.03(C_1, C_2, C_3, broad), 13.65(C_4)	30.98($-CH_2-$); 61.05($-OCH_2$)
6	26.49(C_1)[b], 27.04(C_2), 27.03(C_3), 13.65(C_4)	25.95($-CH_3$); 83.04($-OC$)
8	26.59(C_1), 27.14(C_2), 26.92(C_3), 13.70(C_4)	66.90($-OCH_2$)
9	26.65(C_1), 27.19(C_2), 26.97(C_3), 13.65(C_4)	18.96($-CH_3$); 74.93, 73.89, 73.13, 71.72($-OCH$, $-OCH_2$)
10	26.65(C_1), 27.04(C_2), 26.97(C_3), 13.65(C_4)	30.98($-CH_2-$); 62.62($-OCH_2$)
11	26.65(C_1), 27.19(C_2), 26.97(C_3), 13.70(C_4)	17.84($-CH_3$); 81.09, 78.44($-OCH$)

[a] $^1J(^{13}C-^{119}Sn) = 614.24$; [b] $= 649.42$ Hz.

TABLE III. ^{119}Sn NMR Spectral Data in CCl_4

Compound number	Chemical shift δ (ppm)	
	Sn^a	Sn^b
1	−156.66	−168.27
2	−157.31	−168.49
3	−150.93	−167.58
4	−153.12	−164.95
5	−150.05	−162.77
6	−147.80	−175.30
7	−153.91	−169.70
8	−129.42	−164.84
9	−129.12	−163.57
10	−127.25	−162.03
11	−130.08	−164.88
12	−129.46	−164.28
13	−131.08	−165.07

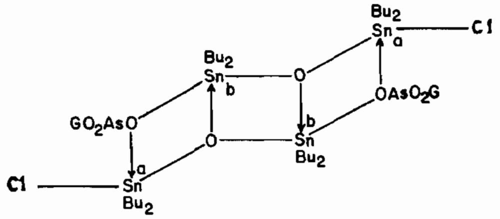
Sn^a and Sn^b correspond to the structures given below.



In the above structure the two types of tin atoms 'a' and 'b' are in different environments, and based on the data for other distannoxanes [22] the peaks at −152 ± 5 and −166 ± 4 ppm in the ^{119}Sn NMR spectra may be assigned to the tin atom 'a' and 'b' respectively.

A similar ladder like structure has also been suggested earlier for a number of symmetrical 1,3-disubstituted tetraorganodistannoxanes on the basis of ^{119}Sn NMR [22] and Mössbauer spectroscopy [23] and also confirmed by X-ray diffraction [23–26].

The presence of all the tin atoms in a pentacoordinated environment in 1-chloro-3-arsenoxytetrabutyldistannoxanes leads to the conclusion that like the symmetrical distannoxanes, these are also present in a dimeric ladder like structure. However, being unsymmetrical in nature, the dimerisation may occur head to head or head to tail. Further, the structure may involve bridging from chlorine (as in 1,3-dichlorotetrabutyldistannoxane [27]) or from arsenoxy oxygen (as in compounds 1–7). The possible structures, however, can be differentiated on the basis of ^{119}Sn NMR data and the values obtained are consistent with the following structure:



The ^{119}Sn signals at −129 and −163 ppm may be assigned to tin 'a' and tin 'b' respectively in the above structure.

It may be pointed out that a few unsymmetrical 1,3-disubstituted tetraalkyldistannoxanes, $XSnR_2OSnR_2Y$, where X and Y are oxy and halo substituents (e.g. $X = OH$, $Y = Cl$, $R = Pr^i$; $X = OH$, $Y = Cl$, $R = CH_2SiMe_2$) have recently been subjected to X-ray crystallographic studies [28] and in all these cases the bridging is from oxygen.

The ladder like dimerisation appears to impart special stability to the tetraalkyldistannoxane molecule. Thus unlike hexaalkyldistannoxanes [10], these do not undergo codisproportionation reactions with oxybis(1,3,2-diox-arsolanes and -arsenanes) even under forcing conditions. The hydrolytic stability of Sn–O–As linkages in unsymmetrical distannoxanes (compounds **8–13**) may be related to the strong bridging from arsenoxy oxygens.

Experimental

2,2′-Oxybis(1,3,2-diox-arsolanes and -arsenanes) and 2-chloro-1,3,2-diox-arsolanes and -arsenanes were synthesised by the methods described previously [29, 30].

Arsenic was determined [31] iodimetrically after decomposing the sample in boiling sodium hydroxide solution. Tin was estimated as tin oxide. Chlorine was estimated volumetrically by Volhard's method.

Infrared spectra were recorded as Nujol mulls or neat liquids using CsI pellets on a Perkin-Elmer spectrophotometer model 577 in the range 4000–200 cm^{-1}. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in CCl_4 solution using TMS and tetramethyltin as external references with downfield shift being positive on a Jeol FX 90 Q spectrometer at 89.55, 22.49 and 33.35 MHz respectively.

Reaction of Dibutyltin Oxide with 2,2′-Oxybis(1,3,2-diox-arsolane) in 2:1 Molar Ratio

A mixture of dibutyltin oxide (3.68 g) and 2,2′-oxybis(1,3,2-dioxarsolane) (2.12 g) in benzene (~40 ml) was refluxed for ~4 h. Dibutyltin oxide went into the solution and a clear solution was obtained. Benzene was removed *in vacuo* to give a colourless viscous liquid (5.62 g). Attempted distillation of the above product (4.18 g) yielded 2,2′-oxybis-1,3,2-dioxarsolane as a colourless viscous liquid (1.40 g) at 130–65 °C and 0.05 mm pressure. *Anal.* Found: As, 52.06. Calc. for $C_4H_8As_2O_5$: As, 52.44%.

Pertinent experimental data for compounds prepared from various 2,2′-oxybis(1,3,2-diox-arsolanes and -arsenanes) by the above route are summarised in Table I.

Reactions of Dibutyltin Oxide with 2,2′-Oxybis(4,4,5,5-tetramethyl-1,3,2-dioxarsolane) in 1:1 Molar Ratio

The reaction between dibutyltin oxide (0.90 g) and 2,2′-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxarsolane) (1.45 g) carried out as above yielded a white semi-solid (2.34 g) which on treatment with acetonitrile gave 1,3-bis(arsenoxy)tetramethyldistannoxane as the insoluble portion (1.63 g; melting point (m.p. 70 °C; authentic IR and ^{119}Sn NMR spectrum). Evaporation of the filtrate gave 2,2′-oxybis-4,4,5,5-tetramethyl-1,3,2-dioxarsolane) as a white solid (0.71 g; m.p. 46 °C; authentic IR spectrum).

Reaction of Dibutyltin Oxide with 2-Chloro-1,3,2-dioxarsolane in 2:1 Molar Ratio

A mixture of dibutyltin oxide (2.18 g) and 2-chloro-1,3,2-dioxarsolane (0.75 g) was refluxed in benzene (~30 ml) for ~2 h. Dibutyltin oxide dissolved slowly and a clear solution was obtained after completion of the reaction. On the removal of solvent under reduced pressure, a white solid compound (2.78 g) was obtained, which was recrystallised from benzene–n-hexane mixture in 76% yield. Similar reactions are summarised in Table I.

Reaction of Dibutyltin Oxide with 2-Chloro-4-methyl-1,3,2-dioxarsolane in 1:2 Molar Ratio

A clear solution was obtained on refluxing a mixture of dibutyltin oxide (1.65 g) and 2-chloro-4-methyl-1,3,2-dioxarsolane (2.63 g) in benzene (~30 ml) for ~1 h. Desolvation yielded a colourless viscous liquid (4.13 g), the ^{119}Sn NMR spectrum of which showed a peak at 122.7 ppm.

Reaction of Dibutyltin Oxide with 2-Chloro-4-methyl-1,3,2-dioxarsolane in 1:1 Molar Ratio

On refluxing a mixture of dibutyltin oxide (3.05 g) and 2-chloro-4-methyl-1,3,2-dioxarsolane (2.27 g) in benzene (~40 ml) for ~3 h, dibutyltin oxide went into solution and a clear solution was obtained. Benzene was removed *in vacuo* to give a white semi-solid (5.29 g). This was then treated with acetonitrile to give 1,3-dichlorotetrabutyldistannoxane (2.06 g; m.p. 112 °C; authentic IR and ^{119}Sn NMR spectra) as the insoluble portion. Evaporation of the washing gave 2,2′-oxybis(4-methyl-1,3,2-dioxarsolane) (1.83 g; authentic IR spectrum).

Reaction of 1,3-Dichloro-1,1,3,3-tetrabutyl-distannoxane with 2,2′-Oxybis(4-methyl-1,3,2-dioxarsolane) in 1:1 Molar Ratio

A mixture of 1,3-dichlorotetrabutyldistannoxane (3.15 g) and 2,2′-oxybis(4-methyl-1,3,2-dioxarsolane) (1.79 g) was heated for ~10 h at a bath temperature of 120–130 °C. On cooling a white semi-solid (4.91 g) (which was completely soluble in benzene) was obtained. This (4.0 g) when treated with acetonitrile, gave unreacted 1,3-dichlorotetrabutyldistannoxane (2.50 g; m.p. 111 °C) as the insoluble portion. Evaporation of the washing gave 2,2′-oxybis(4-methyl-1,3,2-dioxarsolane) as a colourless viscous liquid (1.63 g; authentic IR spectrum).

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