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ALKOXY-, ALKYLTHIO-, AND (ORGANYLSELENO)DIALKYLARSINES

LAWRENCE S. SAGAN, RALPH A. ZINGARO* and KURT J. IRGOLIC
Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

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SUMMARY

Organoarsenic derivatives of the type $R_2As–X–R'$ (X = O, S, Se) have been prepared by the reaction of dialkyl(diethylamino)arsines with alcohols, thiols and selenols. The yields in these reactions are quantitative. By-products, which were formed in most of the previously reported syntheses of these compounds, were not observed. The dialkyl(diethylamino)arsines were synthesized from dichloro(diethylamino)arsine and Grignard reagents in 30–50% yields. The dichloro(diethylamino)arsine was obtained from arsenic trichloride and diethylamine in 80–90% yield. The interesting features of the NMR and IR spectra of these compounds are presented and discussed.

INTRODUCTION

Some organoarsenic compounds of the type $R_2As–X–R'$ (R = alkyl, R' = alkyl or aryl, X = O, S, Se) have been reported in the literature. Dialkyl(alkoxy)arsines have been prepared by reactions between oxybis(dialkylarsines) and alcohols[1–3]. Dialkylchloroarsines and sodium alkoxides also give alkoxyarsines[3,4].

The corresponding alkylthio compounds were obtained by the reaction of dialkylhaloarsines, R_2AsX, with sodium alkanethiolates, R'SNa[5], bis(alkylthio)mercury, $(R'S)_2Hg$[6,7], or bis(alkylthio)lead[8]. The reaction between tetramethyldiarsine and bis(trifluoromethyl) disulfide has been reported to yield dimethyl(trifluoromethylthio)arsine[7].

A literature search has brought to our attention only two dialkyl(alkylseleno)arsines, $R_2As–Se–R'$ ($R = CF_3$, $R' = CF_3$, C_3F_7) synthesized from bis(trifluoromethyl)iodoarsine and the appropriate bis(alkylseleno)mercury compound[6].

Almost all of the methods mentioned above for the synthesis of (organylchalcogeno)arsines require arsenic compounds which can be obtained only in multistep procedures. The synthetic route to the dialkylhaloarsines is described as an example. The Meyer reaction between sodium arsenite and alkyl halides yields arsonic acids, $RAsO_3H_2$, which are then reduced to alkyldichloroarsines[9]. The reactions of these arsines with alkyl halides in alkaline media give dialkylarsinic acids, R_2AsOOH, which are finally converted to dialkylhaloarsines[10].

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* Author to whom correspondence and requests for reprints should be directed.

TABLE 1. ALKOXY-, ALKYLTHIO- AND ORGANYLSELENOARSINES, R_2As-X-R′

R	*R′*	*X=O*					*X=S*					*X=Se*			
		Yield (%)[a]	*B.p. (°C/mmHg)*	*Anal.: Found (calcd.) (%)*			*Yield (%)*[a]	*B.p. (°C/mmHg)*	*Anal.: Found (calcd.) (%)*			*Yield (%)*[a]	*B.p. (°C/mmHg)*	*Anal.: Found (calcd.) (%)*	
				C	*H*	*As*			*C*	*H*	*S*			*C*	*H*
CH_3	CH_3	50	82/756	26.36 (26.47)	6.68 (6.61)		85	49/34	23.82 (23.68)	5.77 (5.92)	20.87 (21.05)				
	C_2H_5											40	96/760	20.80 (22.55)	5.25[b] (5.16)
	C_6H_5											70	100/1.0	36.54 (36.80)	4.30[c] (4.28)
	$C_6H_5CH_2$											70	108/4.0	39.10 (39.30)	4.77 (4.70)
	1-$C_{10}H_7$											83	118/0.15	46.45 (46.15)	4.20 (4.16)
	$C_2H_4SAsR_2$							91/0.1	24.05 (23.84)	5.47 (5.29)	[d]				
C_2H_5	CH_3						85	66/15	33.39 (33.33)	7.27 (7.22)	17.64 (17.81)				
	C_2H_5						85	71/12	37.22 (37.13)	7.82 (7.73)	16.74 (16.50)				
	C_6H_5											70	134/0.1	41.73 (41.52)	5.21 (5.19)
	$CH_2C_6H_5$											60	86/0.025	43.68 (43.56)	5.71 (5.61)
C_3H_7	CH_3	80	23/0.2	43.90 (43.75)	8.97 (8.85)	38.90 (39.06)	85	34/0.1	40.56 (40.38)	8.36 (8.17)	15.64 (15.38)				
	C_2H_5	80	65/10	46.42 (46.62)	9.11 (9.22)	36.54 (36.37)	85	46/4.0	43.55 (43.27)	8.58 (8.56)	14.65 (14.44)				
	C_3H_7	85	30/0.1	49.22 (49.09)	9.60 (9.54)	34.18 (34.04)	85	56/0.15	45.49 (45.76)	8.92 (8.89)	[e]				
	C_4H_9	80	40/1.35	51.57 (51.30)	10.06 (9.84)	31.79 (32.04)									
	$C(CH_3)_3$	85	31/0.15	51.07 (51.30)	9.84 (9.84)	32.05 (32.04)									
	C_6H_5											60	138/1.5	45.66 (45.42)	6.05 (5.99)

[a] Yields based on $R_2AsN(C_2H_5)_2$. [b] Not isolated in analytically pure form. [c] Found: As, 29.17; calcd.: 28.70. [d] Found: As, 49.55; calcd.: 49.66. [e] Found: As, 31.56; calcd.: 31.78

In order to reduce the number of steps required for the synthesis of dialkyl(organylchalcogeno)arsines and to avoid the troublesome side-reactions encountered with most of the earlier methods, we have investigated the reactions of dialkyl(diethylamino)arsines with alcohols, thiols and selenols.

RESULTS AND DISCUSSION

Alkoxy-, alkylthio-, and (organylseleno)dialkylarsines of the general formula R_2AsXR' (R=alkyl; R'=alkyl or aryl; X=O, S, Se) (Table 1) can be prepared with a minimum of interference from side-reactions and having a high level of purity according to eqns. (1–3).

$$AsCl_3+2\,(C_2H_5)_2NH \rightarrow Cl_2AsN(C_2H_5)_2+(C_2H_5)_2NH_2^+Cl^- \quad (1)$$

$$Cl_2AsN(C_2H_5)_2+2\,RMgX \rightarrow R_2AsN(C_2H_5)_2+2\,MgXCl \quad (2)$$

$$R_2AsN(C_2H_5)_2+R'XH \rightarrow R_2AsXR'+(C_2H_5)_2NH \quad (3)$$

The compounds containing an As–N bond are exceedingly sensitive to air and moisture. All operations, therefore, must be performed under a rigorously dry and oxygen-free atmosphere. The volatile diethylamine formed (eqn. 3) is readily removed from the reaction mixture as a gas and thus shifts the equilibrium towards the formation of the desired products. While reactions (1) and (3) are essentially quantitative, the dialkyl(diethylamino)arsines (eqn. 2) were obtained in 30–50% yields.

Dichloro(diethylamino)arsine

Dichloro(diethylamino)arsine was obtained from arsenic trichloride and diethylamine (eqn. 1) and purified by vacuum distillation. The NMR spectrum of the pure sample showed a methyl triplet (δ 1.19) and a methylene quartet (δ 3.35). Crude dichloro(diethylamino)arsine, obtained by evaporation of the ether solution, in which arsenic trichloride and diethylamine had been permitted to react, displayed an additional triplet and quartet at δ 1.10 and δ 3.20, respectively. The impurity was identified as chlorobis(diethylamino)arsine (Table 2), and was undoubtedly formed as a by-product along with the desired compound.

When pure $(C_2H_5)_2NAsCl_2$ was heated for several hours at 90°, $[(C_2H_5)_2N]_2$-AsCl was again detected in the NMR spectrum. This is an example of a redistribution reaction of the type described by Moedritzer[17] and is illustrated by eqn. (4).

$$2\,Cl_2AsN(C_2H_5)_2 \xrightarrow{\Delta} ClAs[N(C_2H_5)_2]_2+AsCl_3 \quad (4)$$

This redistribution reaction is almost certainly not responsible for the production of $[(C_2H_5)_2N]_2AsCl$ in the original reaction mixtures, since $[(C_2H_5)_2N]_2AsCl$ could be detected only after prolonged heating of pure $(C_2H_5)_2NAsCl_2$ at 90°.

Dialkyl(diethylamino)arsines

During the preparation of dialkyl(diethylamino)arsines (eqn. 2) the use of an excess of Grignard reagent must be avoided in order to minimize the cleavage of the As–N bond (eqn. 5), as first observed by Tszchach and Lange[14].

$$R_2AsN(C_2H_5)_2+RMgBr \rightarrow R_3As+(C_2H_5)_2NMgBr$$

TABLE 2

^{1}H NMR DATA[a]

Compound	*Chemical shift, δ (internal TMS)*					
	NCH_2	*—CH_3*	*RAs*	*RO*	*RS*	*RSe*
$Cl_2AsN(CH_2CH_3)_2$	3.35 (q)	1.19 (t)				
$ClAs[N(CH_2CH_3)_2]_2$	3.20 (q)	1.10 (t)				
$(CH_3)_2AsN(CH_2CH_3)_2$	2.85 (q)	0.99 (t)	0.93 (s)			
$(C_2H_5)_2AsN(CH_2CH_3)_2$	2.90 (q)	0.99 (t)	1.1 (m)			
$(C_3H_7)_2AsN(CH_2CH_3)_2$	2.91 (q)	1.00 (t)	1.4 (m)			
$(CH_3)_2AsOCH_3$			1.19 (s)	3.38 (s)		
$(C_2H_5)_2AsOCH_3$			1.4 (m)	3.45 (s)		
$(C_3H_7)_2AsOC(CH_3)_3$			1.1 (m), 1.3 (m)	1.19 (s)		
$(CH_3)_2AsSCH_3$			1.25 (s)		2.10 (s)	
$(C_2H_5)_2AsSCH_3$			1.2 (m), 1.6 (m)		2.15 (s)	
$(C_2H_5)_2AsSCH_2CH_3$			1.3 (m), 1.7 (m)		1.60 (t), 2.55 (q)	
$(C_3H_7)_2AsSCH_2CH_3$			1.5 (m), 2.1 (m)		1.70 (t), 3.05 (q)	
$(C_3H_7)_2AsSCH_2C_2H_5$			1.0 (m), 1.7 (m)[b]		2.55 (t)	
$[(CH_3)_2AsSCH_2]_2$			1.30 (s)		2.80 (s)	
$(CH_3)_2AsSeC_6H_5$			1.25 (s)			7.1 (m), 7.5 (m)
$(CH_3)_2AsSeCH_2C_6H_5$			1.19 (s)			3.81 (s), 7.1 (m)
$(CH_3)_2AsSe(1\text{-}C_{10}H_7)$			1.10 (s)			7.5 (m)
$(C_2H_5)_2AsSeC_6H_5$			1.2 (m), 1.6 (m)			7.1 (m), 7.5 (m)
$(C_2H_5)_2AsSeCH_2C_6H_5$			1.1 (m), 1.5 (m)			3.80 (s), 7.1 (m)
$(C_3H_7)_2AsSeC_6H_5$			0.9 (m), 1.6 (m)			7.1 (m), 7.5 (m)

[a] s, m, q, t designate singlet, multiplet, quartet and triplet resonances, respectively. [b] This multiplet contains a contribution from the C_3H_7S group.

For this reason, the alkylmagnesium halides were added to the aminochloroarsines. The cooling of the reaction mixture to Dry-Ice temperature was found to improve the yields in reactions employing methyl- and ethylmagnesium halides. In spite of these precautions dimethyl- and diethyl(diethylamino)arsines were obtained in yields of only 30%, while the longer chain compounds were formed in yields of about 50%. An analytically pure sample of dipentyl(diethylamino)arsine was not obtained. Careful fractionation in a spinning band distillation apparatus gave one low boiling fraction containing nitrogen and another nitrogen-free, high boiling fraction (b.p. 90°/0.05 mmHg), which did not display a methylene quartet in the NMR spectrum. It probably was tripentylarsine (lit., b.p. 149/0.7 mmHg[18], 103°/0.4 mmHg[19]). The low-boiling fraction was redistilled. Its NMR spectrum still displayed an additional quartet indicating the presence of pentylbis(diethylamino)arsine, which was probably formed by a redistribution reaction (eqn. 6). While the purest

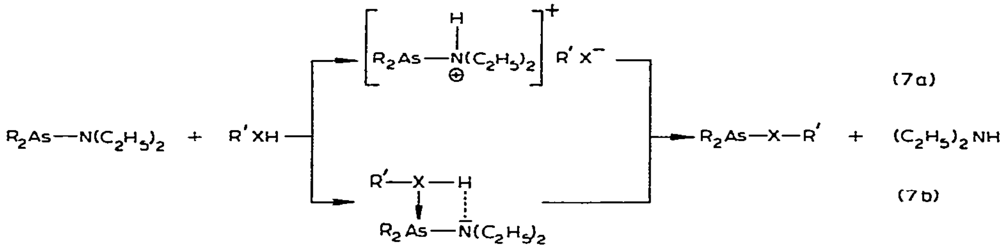
$$2\,R_2AsN(C_2H_5)_2 \rightleftharpoons R_3As + RAs[N(C_2H_5)_2]_2 \qquad (6)$$

dipentyl compound obtained still gave a carbon analysis 1% lower than calculated, the purification of the C_1 to C_4 derivatives did not present any difficulties.

Pure dialkyl(diethylamino)arsines, if well protected from moisture and oxygen, can be stored up to a year with no apparent decomposition. On contact with moist air, they rapidly undergo oxidative hydrolysis to the arsinic acids.

Dialkyl(organylchalcogeno)arsines

Dialkyl(diethylamino)arsines were found to react easily with alcohols, thiols or selenols according to eqn. (3) with the release of diethylamine. By monitoring the evolution of the amine, the progress of the reaction could be followed. Qualitative observations of this type showed that the reactivity decreases in the order selenol, thiol, alcohol suggesting that the reaction rate is proportional to the acidity of RXH (X=Se, S, O). The formation of an ammonium ion as an intermediate (eqn. 7a) is likely. The possibility of a four-center mechanism, however, must also be considered



(eqn. 7b). It is not unlikely, that the selenium atom in the selenols would form the strongest p_π–d_π bond facilitating hydrogen ion transfer to the nitrogen atom with subsequent cleavage of the As–N bond. The sulfur and oxygen atoms in the thiols and alcohols would not be as effective as the selenium atom in the formation of the four-centered intermediate due to the size disparity of the orbitals involved.

The reaction mixtures were refluxed until all the amine was expelled. The excess alcohol or thiol was then removed by distillation. All the remaining liquid distilled at constant temperature. The less than quantitative yields reported in Table 1 resulted from mechanical losses during distillation. Since the reactions with thiols and selenols were quite exothermic, ice-water cooling was employed during the addition of these reagents. When an equimolar amount of the selenol had been added to the aminoarsine, a white precipitate of diethylammonium alkaneselenolate formed from the selenol and the by-product amine. The formation of this precipitate was taken as a sign that stoichiometric amounts of the reagents had undergone reaction.

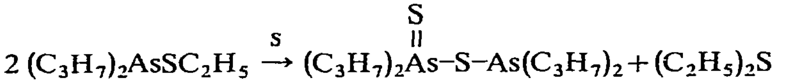
The stability of the dialkyl(organylchalcogeno)arsines towards hydrolysis and oxidation increased markedly in going from the oxygen to the selenium derivatives. The alkoxy compounds in the presence of moist air undergo very rapid hydrolysis to the dialkylarsinic acids. Attempts to isolate the intermediate dialkylhydroxyarsines were unsuccessful. The (organylseleno)dialkylarsines could be handled in the atmosphere without apparent decomposition, but exposure to water and the atmosphere for extended periods of time was found to yield the dialkylarsinic acids. The reactivity of the alkylthio compounds was intermediate. All of the compounds listed in Table 1 were stored under nitrogen for months without any change in composition.

Attempts were made to oxidize some of the dialkyl(diethylamino)arsines and dialkyl(organylchalcogeno)arsines to dialkylarsinic acid amides and esters, respectively. The reactions were carried out in sealed ampoules at 120°. Dipropyl(diethylamino)arsine and mercuric oxide were observed to react but the products were not successfully identified. Dipropyl(butylthio)arsine and HgO gave a precipitate and a brown liquid. The liquid decomposed upon distillation. The precipitate, following extraction with water yielded dipropylarsinic acid and a solid, the analysis of which corresponded closely to that of bis(butylthio)mercury. Dipropyl(phenylseleno)arsine treated similarly yielded bis(phenylseleno)mercury (eqn. 8).

$$R_2As{-}X{-}R' + HgO \rightarrow R'X{-}Hg{-}XR' + (R_2As)_2O \xrightarrow[O_2]{H_2O} 2\,R_2AsOOH \qquad (8)$$

$$R, X, R': C_3H_7, S, C_4H_9; C_3H_7, Se, C_6H_5$$

Esters of the type $R_2As(O)XR'$ were not obtained. Dipropyl(ethylthio)arsine, when heated with elemental sulfur yielded (dipropylarsinothio)dipropylarsine sulfide (eqn. 9).



$$2\,(C_3H_7)_2AsSC_2H_5 \xrightarrow{S} (C_3H_7)_2\overset{\overset{S}{\|}}{As}{-}S{-}As(C_3H_7)_2 + (C_2H_5)_2S \qquad (9)$$

It is likely that the disulfide contains pentavalent and trivalent arsenic atoms as has been observed in the corresponding methyl derivative[20].

^1H NMR spectra

The NMR spectra of all these compounds have been recorded*. The results of these investigations are summarized in Table 2.

The methylene (CH_2N) resonances in the diethylaminoarsines fall into the range δ 2.85–3.35 shifted slightly downfield from the corresponding resonances in diethylamine [$(C_2H_5)_2NH$, δ 2.58]. The signals arising from the methyl protons of the diethylamino group are located at δ 1.00 and are virtually unchanged when compared to the corresponding resonances in the free amine (δ 1.03). All the compounds with methyl groups bonded to the arsenic atom are characterized by a singlet in the range δ 0.93–1.30, the region in which other methylarsenic compounds have been observed to resonate[21]. Ethyl and propyl groups linked to the arsenic atom produced second order spectra. The approximate centers of the multiplets found for these compounds are listed in Table 2. The methoxy protons in dialkyl(methoxy)arsines gave rise to singlets near δ 3.4. In dipropyl(tert-butoxy)arsine, the methyl protons of the butoxy group resonated at δ 1.19.

The NMR chemical shifts of the protons of the methyl and methylene groups bonded to the sulfur atoms in the alkylthioarsines (Table 2) are almost identical with those observed in similar, arsenic-free sulfur compounds. As in the case of the As–O and As–S bonded compounds, bonding to the As^{III} atom causes no meaningful changes in the NMR spectra of the protons of organic groups attached to the selenium atom. Arsenic(III) thus appears to have a minimal effect on the protons of the R–X–As group (X = O, S, Se).

IR spectra

IR spectral data pertinent to the fundamental stretching modes involving the arsenic atom are summarized in Table 3.

The IR spectra of $[(C_2H_5)_2N]_nAsCl_{3-n}$ ($n = 1, 2$) were measured in order to locate the fundamental As–N single bond stretching vibration in these compounds,

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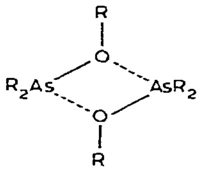
* Copies of both the NMR and IR spectra of all the compounds described in this paper have been filed with the Thermodynamics Research Center, Texas A & M University, College Station, Texas 77843.

TABLE 3

INFRARED FREQUENCIES (cm^{-1}) OF SUBSTITUTED DIALKYLARSINES

Arsine	*As–C*	*As–N*	*As–O*	*As–S*
Dichloro(diethylamino)		610 s		
Chlorobis(diethylamino)		605 m		
Dimethyl(diethylamino)	579 s	559 w		
Diethyl(diethylamino)	567 s	545 w		
Dipropyl(diethylamino)	585 w	560 w		
Dimethyl(methoxy)	585 s		[a]	
Diethyl(methoxy)	585 s		[a]	
Dipropyl(methoxy)	580 s		640 m	
Dipropyl(ethoxy)	582 m		645 s	
Dipropyl(propoxy)	575 w		650 s	
Dipropyl(n-butoxy)	582 w		653 s	
Dipropyl(tert-butoxy)	560 m		630 s	
Dimethyl(methylthio)	578 s			382 m
Diethyl(ethylthio)	565 s			390 m
Dipropyl(ethylthio)	557 w			384 w
Dipropyl(propylthio)	563 m			380 w
Dipropyl(n-butylthio)	558 m			380 w
Dimethyl(phenylseleno)	580 m			
Dimethyl(phenylmethylseleno)	575 s			
Dimethyl(naphthylseleno)	580 s			
Diethyl(phenylseleno)	562 s			
Diethyl(phenylmethylseleno)	565 s			
Dipropyl(phenylseleno)	552 m			

[a] The failure to observe ν(As–O) in these compounds may possibly arise from association of the type:



which would lower this frequency. Such association is sterically favored by the small size of the methoxy group. Thus, in the case of Et_2AsOMe, the 585 cm^{-1} is very strong and broad, and may arise from a superposition of ν(As–O) on ν(As–C).

which should be found at 612 cm^{-1} according to Gordy's rule as applied in the manner described by Chremos and Zingaro[22]. Very little information concerning this vibration is available in the literature. Singh and Burg[23] investigated the compounds $(CF_3)_2As{-}NR{-}P(CF_3)_2$ and tentatively assigned absorptions at 704 and 618 cm^{-1} (R = H), 601 cm^{-1} ($R = CH_3$) and 592 cm^{-1} [$R = P(CF_3)_2$] to ν(As–N). A strong band at 625 cm^{-1} was found in the spectrum of 1,3-diethyl-2-chloro-1,3-diaza-2-arsacyclopentane[24]. A strong absorption at 950 cm^{-1} was assigned to ν(As–N) in $[(C_6H_5)_2AsN]_4$[25].

(Diethylamino)dichloroarsine and bis(diethylamino)chloroarsine absorbed strongly at 610 and 605 cm^{-1}, respectively. Because of the difference between the outer orbital energies of arsenic and nitrogen, which would tend to minimize multiple bonding between these atoms, the assignment of ν(As–N) to these bands is reasonable.

In order to be more certain about the assignment of this band, the IR spectra of both dichloro(diethylamino)- and chlorobis(diethylamino)phosphines were measured. The aminophosphines prepared as described by Kallenbach *et al.*[26] had strong bands at 960 and 930/910 cm^{-1} (doublet), respectively. These bands are in the general region assigned to the P–N stretching vibration [927–984 cm^{-1}, $(CF_3)_2P-NR-As(CF_3)_2$[23]; 950–980 cm^{-1}, $RP[N(CH_3)_2]_2$[27]]. The phosphines are completely transparent in the region of ν(As–N). The remaining portions of the spectra are very similar.

All of the compounds listed in Table 1, which contain arsenic carbon bonds, have a band in the region 552–585 cm^{-1} (Table 3), which according to previous work[28–30] can be assigned to the arsenic–carbon vibration. Although symmetric and antisymmetric stretching vibrations are to be expected with ν_{as} occurring about 10 cm^{-1} higher than ν_{sym}[30], most of the bands were observed as single peaks. In a few instances the main band exhibited a shoulder.

In the dialkyl(diethylamino)arsines two bands were observed in the region 545–585 cm^{-1}. No absorption was observed at 610 cm^{-1}, the location of ν(As–N) in dichloro(diethylamino)arsine. The two absorptions found in the 545–585 cm^{-1} range could arise from ν_{as}(As–C), ν_{sym}(As–C) or ν(As–N). Since ν_{as} and ν_{sym} have not been observed as separate bands in the other compounds, the peak at higher wave number in the spectrum of each of these compounds has been tentatively assigned to ν(As–C). The substitution of the electronegative chlorine atoms in dichloro(diethylamino)arsine by alkyl groups might have caused ν(As–N) to shift from 610 cm^{-1} to approximately 560 cm^{-1} by increasing the electron density in the arsenic atom with a concomitant weakening of the As–N bond by lone-electron-pair repulsion.

With the exception of dimethyl- and diethylmethoxyarsine, all the dialkylalkoxyarsines absorbed at or close to 650 cm^{-1}. In accordance with published data[31–33] these vibrations very probably arise from the As–O stretch. The C–O stretch is assigned to strong absorptions observed[31–33] in the region from 1000–1050 cm^{-1}.

Zingaro *et al.*[18] calculated an upper limit of 555 cm^{-1} for the absorption due to an isolated arsenic–sulfur double bond and a lower limit of 372 cm^{-1} for an arsenic–sulfur single bond. All of the dialkyl(alkylthio)arsines showed a strong absorption in the region 380–390 cm^{-1}. This absorption was absent in the analogous As–N, As–O and As–Se derivatives. It is assigned with confidence to ν(As–S).

According to Gordy's rule[34], ν(As=Se) and ν(As–Se) should be found at 388 and 277 cm^{-1}, respectively. The values reported earlier[35] are in error. A search for this vibration was made using CsBr cells. In most of the dialkyl(organylseleno)arsines a band at 280 cm^{-1}, virtually identical with the value calculated for an isolated As–Se single bond, was detected. No statement concerning the intensity of these bands can be made, since they occurred in the cut-off region of CsBr.

The remaining portions of the spectra are associated with the well-established observations made for organic molecules and are not further discussed.

EXPERIMENTAL

Dichloro(diethylamino)arsine

The preparation of this compound was carried out as described by Kamai and

Khisatova[11] and Irgolic *et al.*[12]. It is essential that air and moisture be rigorously excluded from the reaction apparatus. The product, b.p. 64° at 2 mmHg, was obtained in 80–90% yield.

Dialkyl(diethylamino)arsines

The reactions were carried out under an atmosphere of carefully dried nitrogen in a round bottom, three-necked 1 l flask which was equipped with a mechanical stirrer, reflux condenser and dropping funnel. The flask was charged with dichloro-(diethylamino)arsine (0.83 moles) dissolved in diethyl ether (300 ml). The ether was carefully dried and transferred in the manner described by McBrearty *et al.*[13]. The alkyl magnesium halide (1.6 moles) in diethyl ether was added very slowly, with stirring, over a period of 8 h to the reaction flask cooled in an ice-water bath. After all of the Grignard reagent had been added, the mixture was refluxed for 2 h and then filtered under dry nitrogen. The ether was removed under reduced pressure and the dialkyl(diethylamino)arsine was purified by vacuum distillation. The following compounds, $R_2AsN(C_2H_5)_2$, were prepared [R; % yield; b.p./mmHg; analytical data, found (calcd.)]:

CH_3; 30; 61/35; C 40.45 (40.67), H 8.95 (9.03), N 7.77 (7.90);
C_2H_5*; 40; 81/35; C 47.04 (46.82), H 9.77 (9.74);
C_3H_7*; 45; 66/1; C 51.76 (51.50), H 10.38 (10.30), N 5.73 (6.00);
C_4H_9*; 50; 66/0.0025; C 55.26 (55.17), H 10.74 (10.72), As 29.16 (28.73);
C_5H_{11}; 50; 67/0.03; C 57.27 (58.12), H 11.02 (11.00), N 4.85 (4.84).

(Alkoxy)dialkylarsines

The dialkyl(diethylamino)arsines (5 g, 0.019–0.028 moles) were placed in a 25 ml, two-necked flask filled with dry nitrogen and equipped with a reflux condenser. A three-fold molar excess of the alcohol was added dropwise to the magnetically stirred arsine by means of a syringe through the second neck, which was sealed by a rubber septum. After all the alcohol had been added, the mixture was refluxed for 2 h. The excess alcohol was removed at reduced pressure. The dialkyl(alkoxy)arsine was purified by vacuum distillation. In the synthesis of dimethyl(methoxy)arsine only the stoichiometrically required amount of methanol was employed to facilitate purification of the product by distillation at atmospheric pressure. The compounds prepared are listed in Table 1.

(Alkylthio)- and (organylseleno)dialkylarsines

The (alkylthio)- and (organylseleno)dialkylarsines were prepared in a manner essentially identical to that described for the alkoxy compounds. The thiols were purchased from commercial sources. The selenols were prepared according to the procedure of Foster[15] and redistilled just prior to use. While a three-fold molar excess of the thiols was used, only the stoichiometric amount of the selenols was employed. During the reactions of the aminoarsines with selenols, the formation of some insoluble products, presumably salts of the type $(C_2H_5)_2NH_2^+SeR^-$ was observed towards the end of the reaction. The mixture was kept at 50° for 3 h, the precipitate removed by filtration under a nitrogen atmosphere and the filtrate was fractionated. The compounds prepared are listed in Table 1 together with pertinent data.

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* Previously reported by Tzschach[14]. The propyl derivative was not characterized.

(Dipropylarsinothio)dipropylarsine sulfide

Dipropyl(propylthio)arsine (5 g, 0.021 mole) was heated with sulfur (0.67 g, 0.021 mole) in a sealed ampoule for 6 h at 120°. The ampoule, which contained a light-yellow liquid, was cooled in a Dry-Ice/acetone bath. White crystals formed on cooling, which melted at 46–47° after recrystallization from diethyl ether. (Found: C, 37.54; H, 7.32; As, 39.17; S, 16.79. $C_6H_{14}As_2S_2$ calcd.: C, 37.79; H, 7.47; As, 38.90; S, 16.58%.)

Reaction of dipropyl(phenylseleno)arsine with mercuric oxide

Dipropyl(phenylseleno)arsine (5 g, 0.015 mole) and HgO (3.2 g, 0.015 mole) were heated in a sealed tube for 3 h at 120°. Elemental mercury and yellow crystals formed. The crystals were collected and thoroughly washed with water. Evaporation of the water caused dipropylarsinic acid to separate. The yellow, water-insoluble product following recrystallization from diethyl ether, melted[16] at 152°. (Found: C, 28.25; H, 2.00. $C_{12}H_{10}HgSe_2$ calcd.: C, 28.12; H, 1.95%.)

Spectra

The IR spectra were measured on a Beckman Model IR–12 Spectrophotometer. The NMR spectra were recorded on a Varian A–60 Spectrometer with TMS as the internal standard.

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