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ARSONIC ACIDS

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SUMMARY

The application of bis(diethylamino)chloroarsine (BDCA) as a useful intermediate in the preparation of arsonic acids, especially those having long chain alkyl groups, has been demonstrated. The arsonic acids, through the n-C_{20} derivative, have now been characterized. As do the fatty acids and the arsinic acids, the members of this group of compounds exhibit alternations in their melting points. The results of infrared and differential thermal analysis studies are reported.

INTRODUCTION

A number of methods have been developed for the synthesis of aliphatic arsonic acids[1-7]. However, all of the procedures possess the disadvantage that they require intermediates which are usually best prepared from the arsonic acids themselves. In 1883 Meyer[8] reported that methyl iodide reacted with sodium arsenite to form disodium methylarsonate. The original Meyer method using alkyl iodides gave large amounts of side products[9]. Various modifications of the Meyer reaction were proposed[10,11] and a number of new arsonic acids were synthesized[11,12].

The most extensive study of the application of the Meyer reaction was carried out by Banks and coworkers[13]. They reported the synthesis of n-alkylarsonic acids, $RAsO(OH)_2$, R being CH_3 through C_7H_{15}. The methyl and ethyl derivatives were obtained in 85 and 87% yields, but the n-heptyl compound only in 35% yield. The reaction time was found to increase significantly with increasing carbon chain length and varied from 70 to 200 h. Pietsch[14] was able to increase the reaction rate in the case of longer straight chain alkyl bromides. No attempts have been made to synthesize higher alkylarsonic acids using this method. It is probable that the reaction times will increase considerably with a concurrent decrease in the yields.

The utility of (diethylamino)dichloroarsine for the synthesis of long chain arsinic acids has been recently demonstrated[15]. It seemed reasonable that the arsonic acids could also be synthesized by using a reaction sequence similar to that reported for the preparation of arsinic acids. Bis(diethylamino)chloroarsine (BDCA) contains only one chlorine atom. This compound when reacted with Grignard reagents should form alkylbis(diethylamino)arsine. Hydrolysis and oxidation of this intermediate has been found to give arsonic acids through the C_{20} derivative in high purity and good yields.

EXPERIMENTAL

Reagents

Ether anhydrous (J. T. Baker and Fisher reagent grade) was used after drying over sodium wire and distillation. Magnesium metal turnings were purchased from J. T. Baker Chemical Co. Arsenic trichloride, practical grade, was purchased from Matheson, Coleman and Bell, and was used without further purification. Diethylamine, practical grade, was purchased from Matheson, Coleman and Bell and was distilled after storage over sodium hydroxide pellets before use. Reagent grade alkyl halides were purchased from Matheson, Coleman and Bell, Eastman Chemical Co. and the J. T. Baker Chemical Co. and were used without further purification. 1-Nonadecanol, reagent grade, was purchased from the K&K Chemical Company. 1,2,3,4-Tetrahydronaphthalene(tetraline), reagent grade, was purchased from Matheson, Coleman and Bell. n-Nonadecyl bromide was prepared from n-nonadecanol[16].

Hydrogen peroxide, technical grade, was purchased from Fisher Chemical Co. Bromine, reagent grade, was purchased from B&A Chemical Co.

Bis(diethylamino)chloroarsine (BDCA)

To 460 of diethylamine (6.3 moles) in 2 l of anhydrous ether contained in a 5 l three-necked flask, was added dropwise 273 g (1.5 moles) of arsenic trichloride over a period of 3 h. The reaction flask was cooled by means of an ice–water bath. Vigorous stirring was maintained throughout the course of the addition. Voluminous amounts of diethylamine hydrochloride precipitated. The reaction mixture was then filtered under an atmosphere of nitrogen into a specially constructed filtration–distillation apparatus which permitted the separation of amine hydrochloride from the ethereal BDCA solution under oxygen free and anhydrous conditions. The precipitated amine hydrochloride was washed with 700 ml of anhydrous ether.

The clear ether filtrate was then transferred under positive nitrogen pressure into a one liter distilling flask containing boiling chips and equipped with a magnetic stirring bar. The ether and any unreacted diethylamine were separated from the higher boiling aminoarsine by distillation. An orange colored liquid remained in the distilling flask. Vacuum distillation of the residue yielded BDCA which boiled at 131–132° at 25 mm. Redistillation in a vacuum jacketed fractional distillation column gave a clear, colorless liquid in overall yields of up to 65%. (Found: Cl, 13.8. $C_8H_{20}AsClN_2$ calcd.: Cl, 13.9%.)

Synthesis of n-octylarsonic acid

The synthesis of n-octylarsonic acid will be described in detail because the preparation of this compound served to establish the optimum conditions for the synthesis of the n-butyl- through n-tridecylarsonic acids.

To 300 ml of 0.23 *M* octylmagnesium bromide (0.069 moles), 17.6 g of BDCA (0.069 moles) was added dropwise by means of a 20 ml hypodermic syringe with vigorous stirring under an atmosphere of dry nitrogen. The temperature was maintained at 0° throughout the addition. A viscous, grey-white suspension formed in the solution. After the addition of BDCA was completed, the reaction mixture was allowed to warm to room temperature while the stirring was continued. The mixture

TABLE 1

ALKYLARSONIC ACIDS. $RAs(O)(OH)_2$

n-R	Analyses, found (calcd.) (%)			Recryst. solvent (s)	M.p. (°C)	Neut. equiv., found (calcd.)	Yield (%)
	C	H	As				
C_4H_9	26.70 (26.38)	6.39 (6.08)	41.50 (41.1)	Water Acetone	160–162	180.6 (181.9)	50.5
C_5H_{11}	30.56 (30.61)	6.47 (6.68)	37.78 (38.2)	Water Acetone	163–165	194.3 (195.9)	55
C_6H_{13}	34.80 (34.32)	7.30 (7.15)	35.83 (35.68)	Water Acetone	163–165	210.3 (209.9)	62
C_7H_{15}	37.66 (37.51)	7.30 (7.63)	33.20 (33.43)	Water Acetone	157–159	226.2 (224.1)	55
C_8H_{17}	40.20 (40.33)	7.80 (8.03)	31.60 (31.47)	Water Acetone	162–163	238.8 (238.0)	77
C_9H_{19}	42.96 (42.89)	8.27 (8.33)	29.56 (29.73)	Water Acetone	157–158	250.6 (251.9)	80
$C_{10}H_{21}$	45.34 (45.15)	8.60 (8.65)	28.01 (28.16)	Water Acetone	155–157	261.9 (265.9)	75
$C_{11}H_{23}$	46.97 (47.15)	9.00 (8.98)	26.35 (26.74)	Water Acetone	152–153	280.4 (280.2)	60
$C_{12}H_{25}$	48.83 (48.98)	9.23 (9.24)	25.46 (25.46)	Water/acetone Water/ethanol Acetone	151–152	295.0 (294.2)	82
$C_{13}H_{27}$	50.66 (50.65)	9.52 (9.47)	24.42 (24.30)	Acetone/water n-Butyl ether Ethanol/water	146–147	305.5 (308.3)	72
$C_{14}H_{29}$	51.93 (52.17)	9.51 (9.68)	22.99 (23.24)	Acetone/water n-Butyl ether	146–147	323.5 (322.3)	60
$C_{15}H_{31}$	52.90 (53.57)	9.56 (9.88)	22.46 (22.28)	Ethanol/water Acetone/water n-Butyl ether	143–145	336.7 (336.3)	31
$C_{16}H_{33}$	55.13 (54.85)	10.22 (10.06)	21.63 (21.38)	Ethanol/water n-Butyl ether	142–146	350.3 (350.5)	68
$C_{17}H_{35}$	56.37 (56.03)	10.20 (10.22)	21.05 (20.56)	Ethanol/water n-Butyl ether	138–140	369.0 (364.4)	52
$C_{18}H_{37}$	57.35 (57.13)	10.12 (10.38)	20.03 (19.80)	Ethanol/water Ethanol n-Butyl ether	143–144	383.0 (378.3)	74
$C_{19}H_{39}$	58.34 (58.15)	10.61 (10.52)	18.91 (19.09)	Ethanol/water n-Butyl ether	135–137	397.8 (392.4)	65
$C_{20}H_{41}$	59.44 (59.11)	10.72 (10.64)	18.29 (18.43)	Ethanol/water n-Butyl ether	137–139	411.0 (406.4)	51
3-Methylbutyl	30.50 (30.61)	6.72 (6.67)	38.25 (38.22)	Water	190–191	196.9 (196.0)	90

was then refluxed for approximately 2 h. The suspension reverted to a solid during this time.

The flask was again cooled to 0° and hydrochloric acid (3.6 *N*) was added dropwise. Initially, a white precipitate was formed in the solution accompanied by the liberation of heat. The addition of a total of 170 ml of acid caused two clear, tan colored layers to separate. After refluxing for an additional 2 h the aqueous layer was withdrawn under reduced pressure and discarded.

Twenty seven ml of 30 % H_2O_2 (0.23 moles) was added dropwise to the cooled ether solution. The oxidation reaction was exothermic so that the addition had to be carried out slowly. The reaction mixture was refluxed for 1 h and then filtered, washed with ether and dried. n-Octylarsonic acid was recrystallized from water. The yield was 12.4 g (77 %) of recrystallized product melting at 162–163°. The pertinent analytical data along with those obtained for the other arsonic acids prepared in this study are given in Table 1.

Preparation of Grignard reagents where $R > C_{13}$

For the preparation of arsonic acids with carbon chains longer than n-C_{13} additional precautions were found to be necessary in the synthesis of the Grignard reagent. A specially constructed three-necked reaction flask (Fig. 1) equipped with reflux condenser, stirrer and pressure equalizing dropping funnel, was charged with magnesium turnings and connected to a second flask (S) containing ether and sodium wire. A positive pressure of carefully dried nitrogen was maintained inside this system. Ether was distilled into the reaction flask which absorbed the residual moisture within the system. The slightly moist solvent was then trained into the sodium containing flask by closing the upper stopcock (a) before cooling flask S. Water was removed

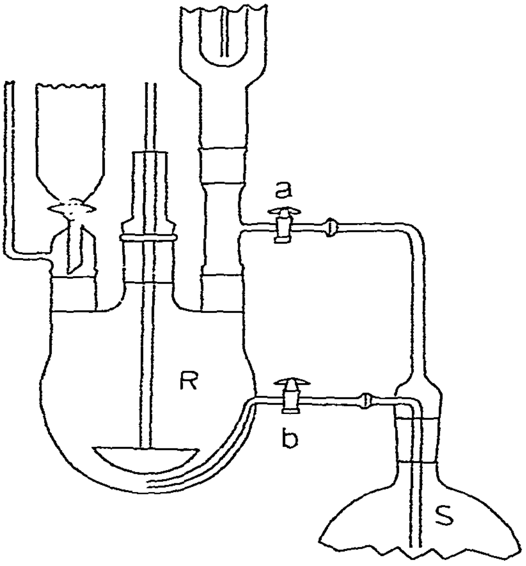


Fig. 1. Apparatus for complete drying of reaction flask and ether solvent (adapted from Suida and Gemassmer[27]).

from the ether by the sodium metal. This procedure was repeated until the system was dried sufficiently as indicated by the blue color of the ketyl radical formed from benzophenone dissolved in the ether. The volume of anhydrous ether necessary for the preparation of the Grignard reagent was then distilled into the reaction flask. Both stopcocks, (a) and (b), were closed and flask S disconnected. The halide was then added dropwise. During the preparation of Grignard reagents from long-chain alkyl halides the formation of hydrocarbons was noted. The purification of the arsonic acid was found to be difficult where these long chain alkanes were present as impurities. Therefore the major portion of the hydrocarbon was separated from the Grignard solution by filtration through glass wool placed in the stem of the funnel, by rotation of the flask, R.

The Grignard solution flowed through the pressure equalizing tube into the attached graduated funnel. In this way the volume of the Grignard solution was determined. One ml aliquots were withdrawn to determine the concentration of the Grignard reagent by acid titration. The hydrocarbon, the glass wool plug and any unreacted magnesium were removed and the system was dried by recirculating the ether. The Grignard solution was then returned to the flask. The reaction of aminoarsine with the alkylmagnesium halide, and the hydrolysis and oxidation steps were all carried out in the same vessel.

Synthesis of n-nonadecylarsonic acid

The preparation of this derivative serves to illustrate the manner of synthesis of those arsonic acids in which the alkyl group was longer than C_{13}.

To 150 ml of 0.23 *M* n-nonadecylmagnesium bromide (0.035 moles) was added 9.48 g (0.037 moles) of BDCA at 0° with vigorous stirring under an atmosphere of dry nitrogen. A yellow white precipitate was formed. After refluxing for 2 h the mixture was cooled to 0° and 240 ml of 3.2 *N* hydrochloric acid was added to the flask from a pressure equalizing dropping funnel. Following a 1.5 h reflux period an additional 100 ml of acid was added.

To the ether solution was added 12 ml of 30% hydrogen peroxide (0.11 moles) at 0°. This resulted in the formation of a white pasty product which was separated by filtration and washed several times with ether. From the reaction mixture 10.1 g of the nonadecylarsonic acid (74% of theory) was recovered. Recrystallization from 80% ethanol gave white needles with a melting point of 135–137°. The yield of purified n-nonadecylarsonic acid was 65%.

Physical measurements and instrumentation

Melting points of all of the compounds were determined following their recrystallization both with an oil bath melting point apparatus and a Fisher–Johns melting point apparatus. Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

Neutralization equivalents were determined for all of the compounds using a Corning Model 12 pH meter equipped with a glass electrode and saturated calomel reference electrode. The acids were titrated in water/ethanol solutions containing from 50 to 80% ethanol by volume. In the case of the arsonic acids with alkyl groups longer than n-C_{12} the titration had to be performed at an elevated temperature, usually 65°, in order to completely dissolve the acids.

Infrared spectra of all of the compounds were measured in the region from 200–4000 cm^{-1} on a Beckman IR 12 Infrared Spectrometer. Differential thermal analysis (DTA) curves were obtained using an R. L. Stone Differential Thermal Analyzer.

RESULTS AND DISCUSSION

Seventeen n-alkylarsonic acids, n-butyl through n-eicosyl, and the branched chain derivative, (3-methylbutyl)arsonic acid, were synthesized during the course of this study. The arsonic acids prepared, their melting points, the yields obtained and the analytical data are shown in Table 1.

All of the arsonic acids reported in this study were prepared by the reaction of the appropriate Grignard reagent with BDCA under anhydrous conditions followed by acid hydrolysis and oxidation. The reaction sequence used in these preparations can be represented by the following equations:

$$AsCl_3 + 4\,(C_2H_5)_2NH \rightarrow [(C_2H_5)_2N]_2AsCl + 2\,(C_2H_5)_2NH \cdot HCl \tag{1}$$

$$[(C_2H_5)_2N]_2AsCl + RMgX \rightarrow [(C_2H_5)_2N]_2AsR + MgXCl \tag{2}$$

$$[(C_2H_5)_2N]_2AsR + 2\,H_2O \rightarrow RAs(OH)_2 + 2\,(C_2H_5)_2NH \tag{3}$$

$$RAs(OH)_2 + H_2O_2 \rightarrow RAs(O)(OH)_2 + H_2O \tag{4}$$

The reaction intermediate, BDCA, was prepared in a single step by the reaction of one mole of arsenic trichloride with four moles of diethylamine (eqn. 1) rather than the two-step procedure described by Kamai[17]. This intermediate was stored for periods of up to six months in glass stoppered flasks. During this time the initially colorless material became pale yellow, but its reactivity was not affected. Steps (2), (3) and (4) were carried out successively in the same reaction vessel. In general, 1.5 to 2 h of reaction time was allowed for each of the last three steps.

Purification difficulties were experienced, particularly with the higher homologs of this series. For acids above dodecylarsonic acid the major impurity was the hydrocarbon formed in the reaction of the alkylmagnesium bromide with unreacted alkyl bromide. These hydrocarbons with a chain length twice that of the starting halides exhibited solubility properties similar to the arsonic acids.

Water/acetone and water/ethanol mixtures proved to be most effective as solvents for recrystallization. From crude n-heptadecylarsonic acid 0.5 g of a white solid was isolated and identified as di-n-heptadecylarsinic acid. Small amounts of insoluble solids which melted at temperatures higher than those of the expected hydrocarbons were noted during recrystallization of several other arsonic acids. This suggests the formation of some arsinic acids, probably due to the presence of some diethylaminodichloroarsine in the BDCA. Because they are insoluble in ethanol/water mixtures they were easily separated.

Attempts to prepare n-alkylarsonic acids with alkyl groups containing fewer than four carbon atoms were unsuccessful. The failure of this method to yield short chain derivatives is consistent with the observation made in the arsinic acid syntheses[15], where derivatives with alkyl groups shorter than n-pentyl could not be prepared.

In all of the present preparations the aminohaloarsines were added to the

Grignard reagent. Thus, an excess of Grignard was present. Tzschach and Lange[18] showed that excess Grignard reagent can cleave the arsenic–nitrogen bond

$$(C_2H_5)_2NAs(C_2H_5)_2+C_2H_5MgX \rightarrow As(C_2H_5)_3+(C_2H_5)_2NMgBr$$

Russian investigators[19] however, reported the synthesis of dialkylhaloarsines in good yields by the reaction of (diethylamino)dichloroarsine with Grignard reagents. The preparation of arsinic acids[15] follows a similar procedure. If bis(diethylamino)chloroarsine (BDCA) should behave similarly, then the cleavage of the arsenic–nitrogen bond cannot be responsible for the very low yields of short chain arsonic acids and for the failure to isolate propylarsonic acid. However, no reports on pertinent reactions of bis(diethylamino)chloroarsine have been found in the literature. It is very likely that the intermediates $RAs[N(C_2H_5)_2]_2$ are formed in good yields, and that these, on hydrolysis, yield $RAs(OH)_2$. These compounds might be decomposed upon addition of hydrogen peroxide. However, the failure to obtain the short chain compounds by means of this reaction remains an unanswered question at the present time.

The low yield of 31% for the n-pentadecylarsonic acid was probably a result of the failure to take special precautions to insure anhydrous conditions. Best results were obtained for the higher derivatives in those preparations where the Grignard reagent was prepared and reacted directly with BDCA without being exposed to the atmosphere. It is interesting to point out that phenylmagnesium bromide reacted with BDCA. However, phenylarsonic acid was not isolated as a product.

Behavior of arsonic acids on fusion

In Fig. 2 (Curve B) the melting points for the n-alkylarsonic acids as determined

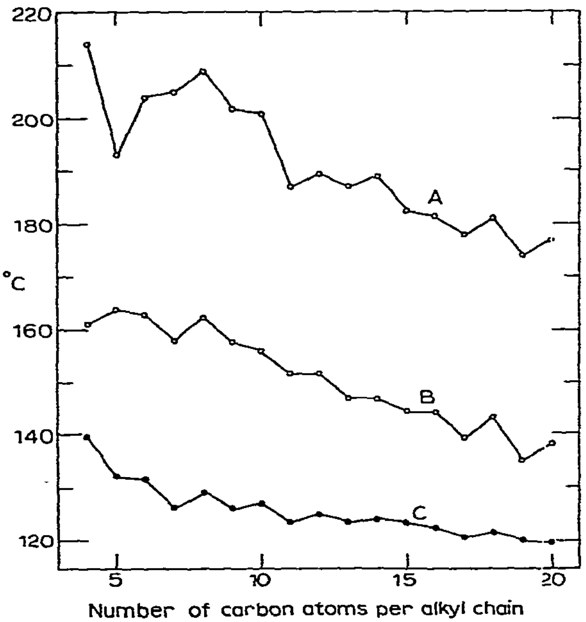


Fig. 2. Melting points of n-alkylarsonic acids (curve A.: determined on Fisher–Johns; curve B: determined in capillary tubes) and di-n-alkylarsinic acids (curve C).

in capillary tubes are plotted against the number of carbon atoms in the alkyl chain of the acid. Beginning with the pentyl derivative, an alternation in the melting points is observed. A similar alternation has been observed in the case of di-n-alkylarsinic acids[15] (Fig. 2, Curve C) and such behavior seems to be characteristic of long chain carbon compounds.

When melting points of the n-alkylarsonic acids were determined on the Fisher–Johns melting point apparatus, a change in the physical appearance of the crystal was noted when the temperature range of the melting point observed in capillary tubes was reached.

In Fig. 2 (Curve A) the melting points observed on the Fisher–Johns apparatus are plotted. Some acids, notably the n-octyl, n-decyl and n-heptadecyl derivatives showed no melting in the range of Curve B but appeared to undergo a change in crystalline form and then melted at the temperature shown on Curve A. This phenomenon was never visually observed in capillary tubes. Thermograms of all the arsonic acids showed an endothermic peak at temperatures close to the melting points observed in capillary tubes. A second endothermic peak appeared at approximately 180° in the case of the C_4, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{15} and C_{18} derivatives. Between 200 and 250° an exothermic decomposition occurred in all cases.

With the exception of C_4, C_5, C_6 and C_8 arsonic acids one or more endothermic peaks were observed below 100°. These endotherms cannot be the result of hydrocarbon impurities since good elemental analyses could not have been obtained with more than 1 % hydrocarbon in the arsonic acids. Long chain carbon compounds have been shown to undergo crystalline phase transitions and it is likely that such transitions give rise to the low temperature peaks.

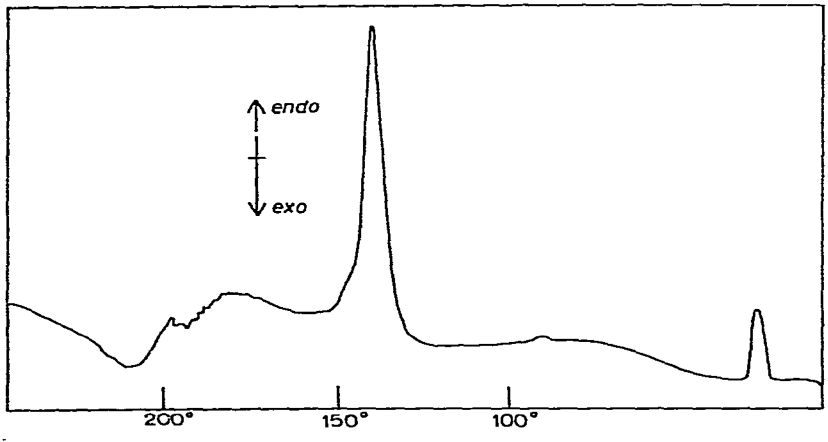


Fig. 3. Differential thermal analysis curve of n-heptylarsonic acid. (DTA, $(C_7H_{15})As(O)(OH)_2$; sample, 2.2 mg; reference, Al-foil; atmosphere, air; heating rate, ~5°C/min; gain, 96 microvolts; chart speed, 12.5″/h; D. Thermocouple, Platinel II; Instrument, R. L. Stone Co.)

Fig. 3, for n-heptylarsonic acid, represents a typical thermogram. The peak at ~140° may correspond to a chemical reaction which occurs close to the melting point as determined in a capillary tube. It is possible that two molecules of arsonic acid lose a molecule of water with the formation of an anhydride. The melting of the anhydride could cause the broad endothermic peak at 180°. Baud[20] showed that methylarsonic acid was converted to the anhydride upon heating to 130° and decomposed to As_2O_3 and CH_3OH at 180°. Preliminary studies of weight changes upon heating of heptyl- and dodecylarsonic acids using a microbalance also suggest anhydride formation. More detailed differential thermal analysis studies as well as thermogravimetric and powder X-ray studies are currently being pursued in this laboratory.

Infrared spectra

The infrared spectra of the n-alkylarsonic acids were measured as KBr pellets on a Beckman IR 12 double beam recording spectrophotometer in the range from 4000 to 200 cm^{-1}. Representative curves are shown in Fig. 4.

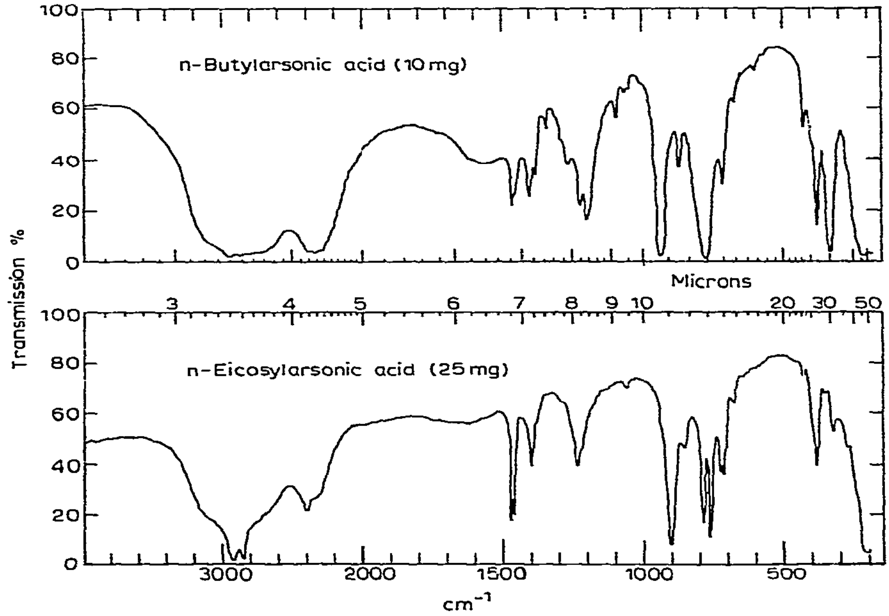
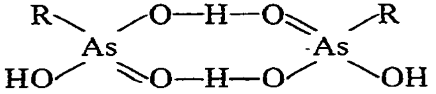


Fig. 4. Typical infrared spectra of n-alkylarsonic acids.

All of the compounds investigated show three broad bands at 1600 cm^{-1}, 2300 cm^{-1} and 2800 cm^{-1}. The 1600 cm^{-1} band was that of lowest intensity. This pattern of broad regions of absorption has been observed by Braunholtz and coworkers[21] for phosphinic and arsinic acids. Arsinic acids[22] display their highest frequency O–H absorption at 2720 cm^{-1}, 80–100 cm^{-1} below that observed in the arsonic acids. Strong hydrogen bonding is the obvious reason for the lowering of O–H frequencies. The higher frequency bands at 2800 cm^{-1} and 2300 cm^{-1} have been assigned to O–H stretching vibrations, while no agreement has been reached as to the origin of the 1600 cm^{-1} band.

The C–H stretching modes are almost obscured by the strong O–H band. The methyl and methylene group deformation modes, the methylene out-of-plane mode and carbon skeleton vibrations are found in the expected regions. Arsonic acids show a rather strong peak at 1200 cm^{-1}, which sometimes is split into a doublet and may have shoulders and side bands.

The spectra of the arsonic acids from n-C_4 through n-C_{14} including n-C_{16} are characterized in the region of 720 cm^{-1} to 1000 cm^{-1} by two very strong absorption bands at 775 cm^{-1} and 940 cm^{-1} with an additional peak of minor intensity at 870 cm^{-1}. The C_{15}, C_{17}, C_{19} and C_{20} derivatives show absorption at 905 cm^{-1} and a doublet at 765 and 790 cm^{-1}. Several workers have assigned As–O stretching frequencies to this region. Merijanian and Zingaro[23] found an average value of 890 cm^{-1} for the fundamental As–O vibration in 15 triaryl- and trialkylarsine oxides. An arsonic acid molecule contains two oxygen atoms bonded differently to the arsenic atom. The O–H vibrations occurring at relatively low frequencies suggest that these acids are at least dimeric in the solid state.



If the hydrogen bonded atoms in the dimer are equidistant from the two oxygen atoms, there would be the possibility of symmetric and asymmetric arsenic–oxygen stretching vibrations, which could be correlated with the bands at 775 and 940 cm^{-1}, respectively. The oxygen atom not involved in forming hydrogen bonds could give rise to the 870 cm^{-1}, low intensity band.

Two strong bands were observed at 330 cm^{-1} and 380 cm^{-1} in all of the spectra. Jensen and Nielsen[24] assigned a band at 595 cm^{-1} in the spectrum of the coordination compound between $PtBr_2$ and triethylarsine to the arsenic–carbon stretching vibration. Claeys and Van der Kelen[25] reported the following values for the arsenic–carbon stretching frequencies: 582 cm^{-1} (CH_3AsCl_2), 575 cm^{-1} (CH_3AsBr_2), and 580 and 573 cm^{-1} for the symmetrical arsenic–carbon stretch for $(CH_3)_2AsCl$ and $(CH_3)_2AsBr$, respectively. The same authors assign 568 cm^{-1} to the symmetrical arsenic–carbon stretch and 583 cm^{-1} to the doubly degenerate arsenic carbon vibration in $(CH_3)_3As$[26].

The spectra of the arsonic acids show that the samples are almost completely transparent in the region where the arsenic–carbon stretching vibration is normally observed. The same observation has been made in the arsinic acid series[22]. Since the bands due to arsenic–carbon interactions should not occur at frequencies higher than 700 cm^{-1}, the absorption bands between 300 and 400 cm^{-1} may arise from arsenic–carbon modes. Further investigations are being carried out so that these bands may be assigned with confidence.

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