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Organoarsenic Compounds of the Acetylene Series

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The review gives a systematic account of the literature on the methods of preparation and certain physical and chemical properties of acetylene derivatives of arsenic.
The bibliography includes 46 references.

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I. INTRODUCTION

Although the syntheses of acetylene derivatives of arsenic were first mentioned in 1921 [1] and 1923, [2] the main studies in this field were made in the last 10–15 years. Fairly complete reviews have now been published [3,4], but these are concerned only with α-ethynyl derivatives of arsenic and cover the literature up to 1967.

The methods of synthesis of acetylene derivatives of Group III–V elements are discussed by Davidson and Henry [3], who also examine the chemical properties of organoarsenic acetylene derivatives and compare them with other organic derivatives of the elements.

Apart from a brief discussion of the chemical properties, Cadiot and Chodkiewicz [4] quote infrared, NMR, and ultraviolet frequencies for certain organoarsenic acetylene derivatives.

In the present review, the first published in the USSR on this subject, an attempt is made to give a systematic account of the methods of synthesis of ethynyl organoarsenic compounds and of the types of their chemical reactions. Data published up to November 1973 and embracing organoarsenic acetylene derivatives in which the ethynyl groups are in the α- and other positions [5-10] relative to the arsenic atom were used.

Continuing the traditional review format [3,4], the authors have presented data on the methods of synthesis and certain physical properties of these compounds (including infrared, ultraviolet and NMR spectroscopic data), in the form of compilations in Tables.

II. METHODS OF SYNTHESIS

Direct and Indirect Ethynylation of Organosilicon Compounds

The commonest method of synthesising organoarsenic acetylene derivatives (OAAD) involves the interaction of organoarsenic halides with ethynyl derivatives of Group I, II, and IV metals.

In contrast to the syntheses in the series of carbochain and organophosphorus acetylenes, sodium and lithium acetylides have not found an extensive application in the OAAD synthesis. It was discovered that the reactions carried out in liquid ammonia (method 1a, Table 1) are much less effective than in oxygen-containing solvate-forming solvents (method 1b)—tetrahydrofuran (THF), [10,11] ether [12], and a 2:1 THF–benzene mixture [13] for sodium acetylides, ether [14,15] and THF [16] for lithium acetylides, and a 2:1 benzene–THF mixture for the reaction of silver acetylides with $AsCl_3$. [17] As a rule, the synthesis of OAAD by method 1b proceeds smoothly in the cold, although in certain cases heating is required to complete the reaction [12].

Carty et al. [15] obtained from ethynyldiphenylphosphine a disubstituted acetylene containing phosphorus and arsenic atoms:

$$Ph_2PC{\equiv}CH \xrightarrow[N_2;\ -78°]{n\text{-BuLi; } Ph_2AsCl} Ph_2PC{\equiv}CAsPh_2\ (50\%)\ .$$

The main bulk of OAAD have been synthesised using the Iotsich reagent (method 2). This procedure proved to be the most convenient on a preparative scale.

Compounds with the general formula $R_2AsC{\equiv}CR'$ [10,11,18,19] have been obtained in THF solution by adding a disubstituted halogenoarsine to an Iotsich reagent at room temperature. For R ranging from C_2H_5 to n-C_6H_{13} and R' = H, subsequent heating is required [18]. For R = C_6H_5 or α-$C_{10}H_7$ and R' = H, [10,11] the reaction reaches completion in several minutes. Dialkynyl compounds [10] $PhAs(C{\equiv}CR)_2$, where R = Me or Ph, and trisethynylarsines $As(C{\equiv}CR)_3$, where R = H, [20] Me, [10] or Ph, [13] are formed in high yields under similar conditions.

Polyacetylene derivatives of the type $R_2As(C{\equiv}C)_mR'$ have been synthesised [10]:

$$R_2AsX + R'(C{\equiv}C)_mMgX \xrightarrow[48-83\%]{THF} R_2As(C{\equiv}C)_mR'\ .$$

For compounds with $m = 2$, the reactions were carried out at −5°C but for $m = 3$ the reaction temperature had to be reduced to −20°C.

Diacetylene diarsenic compounds $R_2AsC{\equiv}C-C{\equiv}C-AsR_2$ (R = Et, Pr, i-Pr, n-Bu, or i-Bu) have been obtained by the reaction of dialkyliodoarsines with a diacetylene Iotsich reagent in ether [21]. OAAD with the general formula $R_2AsC{\equiv}CAsR_2$, where R = Pr, n-Bu, i-Bu, n-C_5H_{11}, or n-C_6H_{13}, were synthesised similarly [8] using $BrMgC{\equiv}CMgBr$ as the acetylenic component [17,22]. It has been shown for R=Et, C_6H_{11}, and α-$C_{10}H_7$ that the replacement of ether by chloroform promotes a greater degree of completion of the reaction [23].

Fluorine-containing OAAD $CF_3C{\equiv}CAsMe_2$ and $(CF_3C{\equiv}C)_2AsMe$ have been obtained [24] in low yields via the mechanism (n = 1, 2)

$$n\,CF_3C{\equiv}CMgI + Me_{3-n}AsI_n \xrightarrow{ether} (CF_3C{\equiv}C)_nAsMe_{3-n}\ .$$

Ethynylarsenic acids $C_6H_{11}C{\equiv}CAs(O)(OH)_2$ and $(C_6H_{13}C{\equiv}C)_2As(O)(OH)$ have been synthesised by a general method [25] using the corresponding aminohalogenoarsines:

$$n\,RC{\equiv}CMgBr \xrightarrow[3.ether,\ 30\%\ H_2O_2]{\substack{1.Cl_nAs(NEt_2)_{3-n},\ ether\\ 2.hydrolysis\ with\ dil.HCl}} (RC{\equiv}C)_nAs(O)(OH)_{3-n}\ .$$

Table 1. Acetylenic organoarsenic compounds.

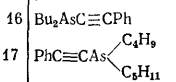
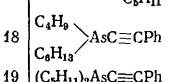
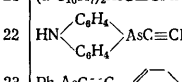
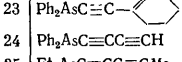
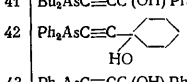
No.	Compound	Yield, %	M.p., degC	B.p., °C/mmHg	n_D^{20}	d_4^{20}	$[AR_D]_{As}$	ν, cm^{-1} C≡C	ν, cm^{-1} C≡CH	Method of preparation	Refs.
	$R_2As(C{\equiv}C)_nR'$										
1	$Et_2AsC{\equiv}CH$	32.7	—	133—133.5	1.4940	1.1430	11.19	2026 w[a]	3280, 3300 s.	2	18,34
2	$(n\text{-}Pr)_2AsC{\equiv}CH$	40.8	—	66.5—67.5 (17)	1.4884	1.0850	11.15	2024 w.	3275, 3290 s.	—	
								2030 w.[b]	3302[b]	2	18,34
3	$(n\text{-}Bu)_2AsC{\equiv}CH$	41.1	—	87—88 (11)	1.4865	1.0470	11.34	2030	3300	2	18
4	$(n\text{-}C_5H_{11})_2AsC{\equiv}CH$	12.7	—	125—127 (16)	1.4826	1.0180	11.45	2029	3282 3300 s.	2	18,34
5	$(n\text{-}C_6H_{13})_2AsC{\equiv}CH$	26.7	—	107—108 (2)	1.4827	0.9949	11.54	2026 w.	3280	2	18,34
6	$Ph_2AsC{\equiv}CH$	85	23	140 (1.5)	—	—	—	2030	3270	2	10
7	$(\alpha\text{-}C_{10}H_7)_2AsC{\equiv}CH$	—	123	—	—	—	—	—	—	1b, 2	11
8	$Ph_2AsC{\equiv}CMe$	86	—	128 (1)	—	—	—	2180	—	2	10
9	$Ph_2AsC{\equiv}CEt$	92	—	110 (0.01)	—	—	—	2180	—	2	10
10	$Bu_2AsC{\equiv}CBu$	—	—	—	—	—	—	2170 m.	—	—	34
11	$Et_2AsC{\equiv}CC_6H_{11}$	—	—	—	—	—	—	2170 m.	—	—	34
12	$Bu_2AsC{\equiv}CC_6H_{11}$	—	—	—	—	—	—	2168 s.	—	—	34
13	$Et_2AsC{\equiv}CPh$	31.2	—	104—105 (0.8)	1.5906	1.1676	13.27	2150	—	4	19
14	$Pr_2AsC{\equiv}CPh$	36.0	—	120 (0.8)	1.5710	1.1206	13.19	2150	—	4	19
15		25.9	—	141—143 (1)	1.5648	1.1043	13.09	2150	—	4	19
16	$Bu_2AsC{\equiv}CPh$	40.6	—	145—147 (1)	1.5611	1.0904	13.24	2150	—	4a, 4b, 2	19,29
17		34.2	—	164—165 (1)	1.5541	1.0730	13.34	2150	—	4a	19
18		31.5	—	151—152 (0.8)	1.5480	1.0601	13.15	2150	—	4a	19
19	$(C_5H_{11})_2AsC{\equiv}CPh$	25.2	—	164—167 (1)	1.5480	1.0598	13.18	2135	—	4b	29
20	$Ph_2AsC{\equiv}CPh$	—	43	168 (3)	—	—	—	—	—	1b, 2	8,11
21	$(\alpha\text{-}C_{10}H_7)_2AsC{\equiv}CPh$	—	142	—	—	—	—	—	—	1b, 2	11
22		—	172	—	—	—	—	—	—	1b	12
23		70	42	—	—	—	—	2120	—	2	10
24	$Ph_2AsC{\equiv}CC{\equiv}CH$	48	55	—	—	—	—	2030	3300	1a, 2	10
25	$Et_2AsC{\equiv}CC{\equiv}CMe$	83	—	70 (0.5)	—	—	—	2040, 2100	—	2	10
26	$Ph_2AsC{\equiv}CC{\equiv}CMe$	76	60	—	—	—	—	2080, 2190	—	2	10
27	$Ph_2AsC{\equiv}CC{\equiv}CPr$	75	40	—	—	—	—	2090, 2200	—	2	10
28	$Ph_2AsC{\equiv}CC{\equiv}CPh$	55	63	—	—	—	—	2100, 2200	—	2	10
29	$Ph_2AsC{\equiv}CC{\equiv}CC{\equiv}CMe$	60	125	—	—	—	—	2040, 2195	—	2	10
30	$Bu_2AsC{\equiv}CCH(OH)Me$	65.3	—	104—105 (1.5)	1.5024	1.0818	12.25	2135, 2140	—	A	31
31	$Bu_2AsC{\equiv}CCH(OH)Et$	51.5	—	115—117 (2.5)	1.5006	1.0681	12.11	2135 w	—	A	31,34
32	$Bu_2AsC{\equiv}CCH(OH)Pr$	57.5	—	119.5—120.5 (2)	1.4980	1.0450	12.71	2135, 2140	—	A	31
33	$Bu_2AsC{\equiv}CCH(OH)(i\text{-}Pr)$	48.0	—	117—118 (2)	1.4982	1.0450	12.75	2135 w.	—	A	31,34
34	$Bu_2AsC{\equiv}CCH(OH)Bu$	55.0	—	129.5—130 (2.5)	1.4942	1.0340	12.30	2135, 2140	—	A	31
35	$Bu_2AsC{\equiv}CCH(OH)Ph$	46.5	—	158—160 (2)	1.5489	1.1276	13.62	2135—2140	—	A	31
36	$Bu_2AsC{\equiv}CC(OH)Me_2$	44.9	—	98.5—100 (1.5)	1.4952	1.0550	12.32	—	—	A	18
37	$Bu_2AsC{\equiv}CC(OH)MeEt$	48.6	—	107—108 (1.5)	1.4951	1.0430	12.34	2165 w.	—	A	31,34
38	$Bu_2AsC{\equiv}CC(OH)Et_2$	48.5	—	112.5—113 (1.5)	1.4949	1.0360	12.34	2160—2170	—	A	31
39	$Bu_2AsC{\equiv}CC(OH)MeBu$	41.4	—	120—121 (1.5)	1.4909	1.0120	12.59	2160—2170	—	A	31
40	$Bu_2AsC{\equiv}CC(OH)Me(i\text{-}Bu)$	42.6	—	116.5—117.5 (2)	1.4901	1.0170	12.54	2165 w.	—	A	31,34
41	$Bu_2AsC{\equiv}CC(OH)Pr_2$	36.7	—	129—131 (2)	1.4865	1.0080	12.36	2160—2170	—	A	31
42		87	57	—	—	—	—	—	—	A	10
43	$Ph_2AsC{\equiv}CC(OH)Ph_2$	87	136	—	—	—	—	—	—	A	10
44	$Et_2AsC{\equiv}CC(O)Me$	45.2	—	72.5—73 (3)	1.5210	1.1870	13.05	2138	—	A	32,34
45	$Et_2AsC{\equiv}CC(O)Et$	53.6	—	84—84.5 (2,5)	1.5162	1.1543	13.20	2135 s.	—	A	32,34
46	$Pr_2AsC{\equiv}CC(O)Me$	24.5	—	82—83 (2,5)	1.5080	1.1190	13.24	2136 v.s.	—	A	32,34
47	$Pr_2AsC{\equiv}CC(O)Et$	46.0	—	108—109 (2,5)	1.5065	1.1001	13.32	2135 v.s.	—	A	32,34
48	$Bu_2AsC{\equiv}CC(O)Me$	42.6	—	107—108 (2,5)	1.5058	1.0864	13.18	2137 v.s.	—	A	32,34
49	$Et_2AsC{\equiv}CC(O)OH$	45.5	—	—	1.5389	1.3105	13.12	2165 s.	—	A	34,35
50	$Pr_2AsC{\equiv}CC(O)OH$	62.5	—	—	1.5270	1.2232	13.38	2165 s.	—	A	34,35

Table 1 (continued).

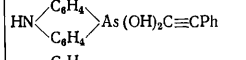
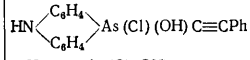
No.	Compound	Yield, %	M.p., degC	B.p., °C/mmHg	n_D^{20}	d_4^{20}	$[AR_D]_{As}$	ν, cm⁻¹ C≡C	ν, cm⁻¹ C≡CH	Method of preparation	Refs.
51	$Bu_2AsC{\equiv}CC(O)OH$	60.5	—	—	1.5192	1.1674	13.45	2165 s.	—	A	34,35
52	$Ph_2AsC{\equiv}CC(O)OH$	58	130	—	—	—	—	—	—	A	10
53	$Et_2AsC{\equiv}CC(O)OEt$	24.0	—	89—90 (2)	1.5080	1.1989	12.68	2165 s.	—	A	34,35
54	$Pr_2AsC{\equiv}CC(O)OEt$	21.6	—	103—103.5 (2)	1.5010	1.3990	12.96	2165 s.	—	A	34,35
55	$Bu_2AsC{\equiv}CC(O)OEt$	19.4	—	128—131 (3)	1.5000	1.0988	13.37	2165 s.	—	A	34,35
56	$Et_2AsC{\equiv}CCH_2NEt_2$	—	—	—	—	—	—	2150 w.	—	A	34
57	$Pr_2AsC{\equiv}CCH_2NEt_2$	—	—	—	—	—	—	2160 w.	—	A	34
58	$n\text{-}Bu_2AsC{\equiv}CCH_2NEt_2$	18	—	142.5—144 (11)	1.4889	0.9908	12.73	2157 w.	—	A	18,34
59	$Me_2AsC{\equiv}CCF_3$	35	98[c]	—	—	—	—	2210	—	2	24
60	$Ph_2AsC{\equiv}CCF_3$	65	—	79—80 (0,1)	—	—	—	—	—	1b	15
61	$Ph_2AsC{\equiv}CCl$	82	—	130 (0.03)	—	—	—	2128	—	6	30
62	$Ph_2AsC{\equiv}CPPh_2$	50	86—87	—	—	—	—	2092[d]	—	1b	15
	$R_2As(X_2)C{\equiv}CR'$										
63	$Ph_2As(O)C{\equiv}CMe$	95	105	—	—	—	—	2190	—	A	10
64	$Ph_2As(OH)_2C{\equiv}CMe$	95	68	—	—	—	—	2190	—	A	10
65	$Ph_2As(O)C{\equiv}CEt$	95	130	—	—	—	—	2190	—	A	10
66	$Ph_2As(OH)_2C{\equiv}CEt$	95	80	—	—	—	—	2190	—	A	10
67	$Ph_2As(O)C{\equiv}CC(OH)(CH_2)_4CH_2$	90	205	—	—	—	—	2180	—	A	10
68	$Ph_2As(O)C{\equiv}CC(OH)Ph_2$	90	260 (decomp.)	—	—	—	—	2200	—	A	10
69		—	150 (decomp.)	—	—	—	—	—	—	A	12
70		—	148	—	—	—	—	—	—	A	12
71	$C_6H_{11}C{\equiv}CAs(O)(OH)_2$	21	unpurified	—	—	—	—	2195	—	2	25
	$[R''R_2As(C{\equiv}C)_nR']^+X^-$										
72	$[Ph_2(Me)AsC{\equiv}CH]^+OTs^-$	10	159	—	—	—	—	2050	3280[e] 3095[f]	A	10
73	$[Ph_2(Me)AsC{\equiv}CMe]^+OTs^-$	30	170	—	—	—	—	—	—	A	10
74	$[Ph_2(Me)AsC{\equiv}CPhOH]^+I^-$	10	260	—	—	—	—	—	—	A	10
75	$[Et_2(Me)AsC{\equiv}CC{\equiv}CMe)^+I^-$	92	137 (decomp.)	—	—	—	—	—	—	A	10
76	$[Et_3AsC{\equiv}CC{\equiv}CMe]^+Br^-$	98	160	—	—	—	—	—	—	5	10
77	$[Et_3AsC{\equiv}CC{\equiv}CPh]^+Br^-$	95	170—180 (decomp.)	—	—	—	—	—	—	5	10
	$RAs(C{\equiv}CR')_2$										
78	$PhAs(C{\equiv}CMe)_2$	85	—	75 (0,01)	—	—	—	2180	—	2	10
79	$PhAs(C{\equiv}CPh)_2$	63	63	—	—	—	—	2150	—	2	10
80	$MeAs(C{\equiv}CCF_3)_2$	15	—	122—124/760	—	—	—	2210	—	2	24
81	$(C_6H_{13}C{\equiv}C)_2As(O)(OH)$	34	unpurified	—	—	—	—	2195	—	2	25
	$As(C{\equiv}CR')_3$										
82	$As(C{\equiv}CH)_3$	62,6	49—50	—	—	—	—	2054	3291	2	20
83	$As(C{\equiv}CMe)_3$	92	131	—	—	—	—	2160	—	2	10
84	$As(C{\equiv}CPh)_3$	75	127	—	—	—	—	2160	—	1b, 2	13,17
85	$As(C{\equiv}CCMe_3)_3$	99	62—63	—	—	—	—	2155,2189	—	1b	16
86	$As(O)[C{\equiv}CCMe_3]_3$	95	141—2	—	—	—	—	—	—	A	16
87	$As(S)[C{\equiv}CCMe_3]_3$	88	112—3	—	—	—	—	—	—	A	16
	Diarsenic ethynyl derivatives of various types										
88	$Me_2AsC{\equiv}CAsMe_2$	50	—	84.5	—	—	—	—	—	2	2,38
89	$Et_2AsC{\equiv}CAsEt_2$	72	—	139 (8)	—	—	—	—	—	2	23
90	$Pr_2AsC{\equiv}CAsPr_2$	42.5	—	118.5—119.5 (2)	1.5268	1.1570	12.42	—	—	2	22
91	$Bu_2AsC{\equiv}CAsBu_2$	43	—	159—160 (1.5)	1.5168	1.1154	12.46	—	—	2	22
92	$(i\text{-}Bu)_2AsC{\equiv}CAs(Bu\text{-}i)_2$	30.1	—	134—136 (2)	1.5122	1.0986	12.24	—	—	2	22
93	$(C_5H_{11})_2AsC{\equiv}CAs(C_5H_{11})_2$	17	—	196—198 (3)	1.5103	1.0600	12.77	—	—	2	22
94	$(C_6H_{13})_2AsC{\equiv}CAs(C_6H_{13})_2$	16	—	199—201 (1.5)	1.4963[g]	1.0222[h]	12.26	1960 v.w.	—	2	22
95	$(C_6H_{11})_2AsC{\equiv}CAs(C_6H_{11})_2$	70	72	—	—	—	—	—	—	2	23
96	$Ph_2AsC{\equiv}CAsPh_2$	74	105	—	—	—	—	—	—	1a, 2, 3	23, 26, 37
97	$(\alpha\text{-}C_{10}H_7)_2AsC{\equiv}CAs(C_{10}H_7\text{-}\alpha)_2$	61	232	—	—	—	—	—	—	1a, 2	23
98	$(\alpha\text{-}C_{10}H_7)_2As(O)C{\equiv}C(O)As(C_{10}H_7\text{-}\alpha)_2$	—	—	—	—	—	—	—	—	A	23
99	$Et_2AsC{\equiv}CC{\equiv}CAsEt_2$	49.3	—	125.5—126 (0.7)	1.6039	1.2736	13.86	2060	—	2	21
100	$Pr_2AsC{\equiv}CC{\equiv}CAsPr_2$	40.9	—	141.5 (0.3)	1.5740	1.1766	14.78	2060	—	2	21
101	$(i\text{-}Pr)_2AsC{\equiv}CC{\equiv}CAs(Pr\text{-}i)_2$	37.6	—	133.5—134 (0.3)	1.5740	1.1717	14.32	2060	—	2	21

Table 1 (continued).

No.	Compound	Yield, %	M.p., degC	B.p., °C/mmHg	n_D^{20}	d_4^{20}	$[AR_D]_{As}$	ν, cm⁻¹ C≡C	ν, cm⁻¹ C≡CH	Method of preparation	Refs.
102	$Bu_2AsC{\equiv}CC{\equiv}CAsBu_2$	13.15	—	182—185 (0.6)	1.5440	1.1092	13.71	2060	—	2	21
103	$(i\text{-}Bu)_2As(C{\equiv}C)_2As(Bu\text{-}i)_2$	27.7	—	172—174 (0.6)	1.5407	1.1082	13.45	2060	—	2	21
104	$Ph_2AsC{\equiv}CC{\equiv}CAsPh_2$	40	115 (decomp.)	—	—	—	—	2060	—	1a, 3	10, 27, 28
105	$(\alpha\text{-}C_{10}H_7)_2As(C{\equiv}C)_2As(C_{10}H_7\text{-}\alpha)_2$	50	218 (decomp.)	—	—	—	—	2070	—	3	27, 28
106	$[Et_2(Me)AsC{\equiv}CAsEt_2]^+I^-$	—	68	—	—	—	—	—	—	A	23
107	$[(C_6H_{11})_2AsC{\equiv}CAs(C_6H_{11})_2]^+I^-$ (Me)	—	133	—	—	—	—	—	—	A	23
	Various organoarsenic compounds containing the acetylene group										
108	$Et_2AsCH_2C{\equiv}CH$	46.7	—	56 (14)	—	—	—	—	—	2	8
109	$Et_2AsCH(Me)C{\equiv}CH$	12	—	64 (14)	—	—	—	—	—	2	8
110	$Ph_2AsCH_2C{\equiv}CH$	67.5	—	110 (0.01)	—	—	—	—	—	2	8
111	$Ph_2AsCH(Me)C{\equiv}CH$	65	—	120 (0.01)	—	—	—	—	—	2	8
112	$Et_2AsCH_2C{\equiv}CMe$	15	—	62 (14)	—	—	—	—	—	2	8
113	$Et_2AsCH(Me)C{\equiv}CMe$	48	—	72 (14)	—	—	—	—	—	2	8
114	$Ph_2AsCH_2C{\equiv}CMe$	57.7	—	120 (0.01)	—	—	—	—	—	2	8
115	$Ph_2AsCH(Me)C{\equiv}CMe$	70	—	125 (0.01)	—	—	—	—	—	2	8
116	$(p\text{—}PhC{\equiv}C)C_6H_4As(O)(OH)_2$	92	>300	—	—	—	—	—	—	6	9
117	$[Ph_2(Et)AsCH_2C{\equiv}CH]^+Br^-$	—	—	—	—	—	—	—	—	A	8
118	$[Ph(Et)AsCH_2C{\equiv}CMe]^+Br^-$	—	—	—	—	—	—	—	—	A	8
119	$[Ph_2(Et)AsCH_2C{\equiv}CPh]^+Br^-$	—	—	—	—	—	—	—	—	A	8
120	$[Ph_2(Et)AsCH_2C{\equiv}CH]^+Br^-$	99	194 (decomp.)	—	—	—	—	—	3305 3180	5	10
121	$[Ph_2(Et)AsCH_2C{\equiv}CH]^+I^-$	98	178	—	—	—	—	—	3305 3195	5	10
122	$[Ph_2(Et)AsCH_2C{\equiv}CH]^+OTs^-$	78	129 144	—	—	—	—	—	3305 3205 3200	5	10
123	$[Ph_3AsCH_2C{\equiv}CH]^+Br^-$	97	246 (decomp.)	—	—	—	—	—	3300 3150	5	10
124	$[Ph_3AsCH_2C{\equiv}CH]^+I^-$	98	196 (decomp.)	—	—	—	—	—	3300 3165	5	10
125	$[Ph_3AsCH_2C{\equiv}CH]^+OTs^-$	92	215 (decomp.)	—	—	—	—	—	3300 3190	5	10
126	$Bu_2AsC{\equiv}CCu$	—	—	—	—	—	—	—	—	A	39
127	$Ph_2AsC{\equiv}CCu$	60	—	—	—	—	—	1950 w.	—	A	36
128	$H[-(C{\equiv}CC_6H_4C{\equiv}CAs)_m(Ph)\text{—}C{\equiv}CC_6H_4C{\equiv}C]_nH$		—	—	—	—	—	—	—	1b	14

Note. a) v.s. = very strong, s. = strong, m. = medium, w. = weak, and v.w. = very weak; b) in n-hexane; c) middle fraction in distillation; d) intense band in the Raman spectrum; e) in chloroform solutions; f) in the solid state; g) n_D^{40}; h) d_4^{40}.

Compounds in which the arsenic atom is in the α-position relative to the triple bond have been examined so far. Benaim [8] synthesised a large series of propargyl derivatives of arsenic with the general formula $R_2AsCH(R')C{\equiv}CR''$ via the mechanism

$$R_2AsX + R'CH(MgBr)C{\equiv}CR'' \xrightarrow[12-70\%]{20^\circ;\ \text{ether}} R_2AsCH(R')C{\equiv}CR'' + MgBrX \quad .$$

It was established the the yield of the required product increases when the disubstituted halogenoarsine is taken in excess. The synthesis of propargyl arsines by the reaction of sodium derivatives of disubstituted arsines with propargyl bromides is not useful, since the yield is low [8]. Thus, for R = Ph, R′ = Me, and R″ = H, one obtains a 65% yield of the product via the first scheme and only 18% via the second.

$$Ph_2AsNa + Me\text{—}\underset{Br}{CH}\text{—}C{\equiv}CH \xrightarrow[18\%]{\text{liq. } NH_3;\ -40^\circ} Ph_2AsCH(Me)\text{—}C{\equiv}CH \quad .$$

The exchange reaction between diarylchloroarsines and acetylene and diacetylene dizinc and ditin derivatives, leading to the formation of diarsenic acetylene derivatives (method 3), is of theoretical interest:

$$Ar_2AsCl + Y(C{\equiv}C)_nY \xrightarrow{t^\circ} Ar_2As(C{\equiv}C)_nAsAr_2 \quad .$$

For Ar = Ph, Y = $SnMe_3$, and $n = 1$, Borisov et al. [26] used an alcoholic medium. For Ar = Ph or naphthyl, $n = 2$, and Y = ZnMe [27] or $ZnMe_3$, [28] the reaction was carried out in absolute toluene and benzene.

In 1968 Kuz'min and Panfilovich [19] proposed a novel method for the synthesis of OAAD having the general formula $R_1R_1'AsC{\equiv}CPh$, based on the use of the nucleophilic properties of phenylacetylene:

$$R_1R_2As(O)OH + HC{\equiv}CPh \rightarrow R_1R_2As(O)C{\equiv}CPh \xrightarrow{\text{thermal isomerisation}} R_1R_2AsOC{\equiv}CPh \xrightarrow{PhC{\equiv}CH} R_1R_2AsC{\equiv}CPh \quad .$$

By heating dialkylarsinic acids and phenylacetylene in molar proportions of 1 : 2 in benzene or toluene with azeotropic distillation of water, OAAD with different R were obtained: $R_1 = R_2 = C_2H_5$; $R_1 = R_2 = C_3H_7$; $R_1 = C_3H_7$, $R_2 = C_4H_9$; $R_1 = R_2 = C_4H_9$; $R_1 = C_4H_9$, $R_2 = C_5H_{11}$; $R_1 = C_4H_9$, $R_2 = C_6H_{13}$.

Subsequently this method was extended to arsenic(III) derivatives (method 4b) [29]:

$$PhC{\equiv}CH + \begin{cases} R_2AsI \\ R_2AsOC(O)Me \\ R_2AsOR \ (\text{где } R = Alk) \end{cases} \rightarrow R_2AsC{\equiv}CPh \quad .$$

Quaternary arsonium salts with the general formula $[Ph_2As(R)CH_2C{\equiv}CH]^+X^-$, where R = Ph or Et and X = Br, I, or OTs, are formed in high yields [10] when tertiary arsines are refluxed in acetonitrile with the corresponding propargyl derivatives (method 5). Diacetylene compounds $[Et_3AsC{\equiv}C-C{\equiv}CR]^+Br^-$, where R = Me or Ph, were obtained similarly in ether.

The method of indirect ethynylation of organoarsenic compounds is not of particular importance in the synthesis of OAAD (method 6). Here, mention should be made of the synthesis in high yield of the acid (p-$PhC{\equiv}C)C_6H_4As(O).(OH)_2$ from its styryl analogue (bromination of the olefin and dehydrobromination by KOH in butanol) [9] and also of chlorodiphenylarsinoacetylene via the mechanism [30]

$$Ph_2AsBr + ClCH{=}CHCl + 2Na \xrightarrow[82\%]{\text{liq. } NH_3,\ -60^\circ} Ph_2AsC{\equiv}CCl \quad .$$

2. Synthesis Based on Organoarsenic Acetylene Derivatives

Many OAAD have been obtained using ethynylarsenic(III) derivatives, described in the preceding section, with a terminal $-C{\equiv}CH$ group (method A).

Thus, secondary and tertiary ethynyl alcohols with the general formula $R_2AsC{\equiv}C-C(OH)R'R''$ have been synthesised by the carbonylation of OAAD via the Favorskii reaction [10] and by the reaction of organomagnesium derivatives of the type $R_2AsC{\equiv}CMgBr$ with compounds containing carbonyl groups [18,31]. The condensation of diphenylethynylarsine with benzophenone and cyclohexanone proceeds smoothly in the presence of KOH in THF solution [10].

Iotsich reagents obtained from dialkylarsinoacetylenes react with aldehydes and acetone with evolution of heat, while the reactions involving other aliphatic ketones (ethyl methyl, diethyl, butyl methyl, and dipropyl ketones) require heating.

The ketones $R_2AsC{\equiv}C-\underset{\underset{O}{\|}}{C}-R'$ were obtained by the reaction [32]

$$2\,R_2AsC{\equiv}CMgBr + 2\,(R'CO)_2O \rightarrow 2R_2AsC{\equiv}\underset{\underset{O}{\|}}{C}C-R' + MgBr_2 + (R'COO)_2Mg \quad .$$

When an excess of the anhydride is taken and the synthesis is carried out at a temperature not exceeding $-60^\circ C$, adding the organomagnesium derivative of the dialkylethynylarsine to an ethereal solution of the anhydride, the reaction stops at the ketone formation stage.

Dialkyl arsino-α-ethynyl ketones are slightly coloured liquids, which distil without decomposition but are unstable in air.

Diphenylarsinoacetylenecarboxylic acid $Ph_2AsC{\equiv}CCOOH$ is formed when ethynyldiphenyl arsine reacts with carbon dioxide in THF solution (using magnesium as the condensing agent) [10]. The corresponding dialkyl derivatives have been synthesised via the magnesium derivatives of the dialkylethynylarsine by adding solid carbon dioxide to its ethereal solution [33]:

$$R_2AsC{\equiv}CMgBr + CO_2 \rightarrow R_2AsC{\equiv}CCOOH \quad .$$

Ethyl esters of dialkylarsinoacetylenecarboxylic acids $R_2AsC{\equiv}CCOOEt$ were obtained [33] in low yields by the reaction of the organomagnesium derivative of dialkylethynylarsine and ethyl chlorocarbonate:

$$R_2AsC{\equiv}CMgBr + ClCOOEt \xrightarrow[-15^\circ]{\text{ether}} R_2AsC{\equiv}CCOOEt \quad .$$

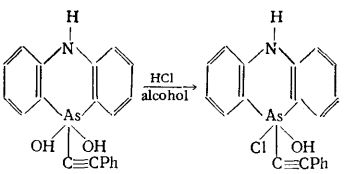
In contrast to dialkylethynylphosphines [33,34] dialkylethynylarsines enter into the Mannich reaction. The compound $Bu_2AsC{\equiv}C-CH_2-NEt_2$ is formed in low yield on heating for 24 h a reaction mixture consisting of paraformaldehyde, diethylamine, and dibutylethynylarsine in the presence of copper acetate as the catalyst [18,34,35].

The reaction of terminal OAAD with copper(I) salts in aqueous ammonia does not lead to the formation of acetylides. Copper diphenylarsinoacetylide was obtained [36] only by the decomposition with a dilute ammonia solution of the ternary complex of CuCl, the ethynyl compound, and dimethyl sulphoxide (DMSO), which had been prepared beforehand.

Oxidative addition and arsenic(III) quaternisation reactions have been used to synthesise a series of ethynyl derivatives of tetracoordinate and quinquevalent arsenic.

Owing to the reduced (compared with tervalent phosphorus) nucleophilicity of arsenic(III), the quaternisation of ethynylarsines proceeds with greater difficulty than that of the corresponding phosphines. It was established that dialkylethynylarsines are more reactive in this process than their aromatic analogues [16,19]. The quaternisation of polyacetylenic arsines with the general formula $R_{3-n}As.[(C{\equiv}C)_mR']_n$ is hardly observed in ether, but is markedly facilitated in acetonitrile [10]. Diarsenic compounds $R_2AsC{\equiv}CAsR_2$ react with methyl iodide in ether in the cold only for R = Et and C_6H_{11}. For R = Ph or α-$C_{10}H_7$, the formation of salts was not observed even after prolonged heating [23].

Ethynylarsine oxides and hydroxides have been obtained by the oxidation of OAAD with hydrogen peroxide in acetone or acetic acid. The OAAD employed were ethynyldiphenylarsines $Ph_2AsC{\equiv}C-R$, [10] tris-(t-butylethynyl)arsine [16], bis(di-α-naphthylarsino)acetylene [23], and 10-phenylethynyl-9,10-dihydrophenarsazine [12]. In the last case it was shown that one hydroxy-group in the oxidised product is readily substituted by chlorine via the reaction



Tris-(t-butylethynyl)arsine forms the sulphide [24] $(Me_3C-C{\equiv}C)_3As{=}S$ on refluxing with sulphur in CS_2.

III. CHEMICAL PROPERTIES

OAAD contain in their structure several reactive centres (As^{III}, $\equiv C-H$, $C{\equiv}C$, $As-C{\equiv}C-$), which is the reason for the wide variety of the chemical properties of compounds of this class. These properties have already been partly considered in the second part of the previous

section. Below we shall consider problems of the thermal and hydrolytic stability and light resistance of OAAD, the effect of the tetracoordination of arsenic on the properties of OAAD, and certain spectroscopic data.

1. Thermal Stability and Light Resistance of OAAD

In Davidson and Henry's review [3] OAAD are classified as potentially explosive substances. However, judging from the latest data, in the vast majority of cases no special precautions are necessary in handling OAAD.

Trisalkylethynyl derivatives of Group VB elements are known [3,4] to be unstable under the usual conditions and compounds of the type $(HC{\equiv}C)_3E$ (E = element) explode in air. As for polyethynyl derivatives of the elements in other Groups, the arsenic(III) compound with t-butylethynyl substituents $(Me_3C-C{\equiv}C)_3As$ proved to be thermally stable and insensitive to light [16].

The monoethynylarsine $Me_2AsC{\equiv}CCF_3$ is hardly coloured by ultraviolet light, but darkens on heating to 160–180°C. However, according to infrared and NMR spectroscopic data, these visual changes are not accompanied by the decomposition of the initial OAAD. [24] The diethynylarsine $MeAs(C{\equiv}CCF_3)_2$ is less stable: thus marked charring was observed after heating the specimen at 140°C; the specimen, which was colourless at the end of ultraviolet irradiation, soon became black [24].

It has been reported [16] that the compound $Ph_2AsC{\equiv}CCF_3$ may be stored for a long time at room temperature without decomposition. Dialkylethynylarsines remain unchanged after oxidative condensation [40] in the absence of a catalyst. The triethynylarsine $(MeC{\equiv}C)_3As$ is resistant to the action of oxygen and atmospheric moisture at −20°C in the course of many months [20]. Bis(dialkylarsino)acetylenes $R_2AsC{\equiv}CAsR_2$ (R = Pr, n-Bu, i-Bu, or C_5H_{11}) are stable in air indefinitely [22].

In contrast to the corresponding arsines, the acids $(C_6H_{13}C{\equiv}C)_nAs(O)(OH)_{3-n}$ (n = 1, 2) proved to be fairly unstable [9].

2. The Cleavage of OAAD at the ≡C–As Bond

As a rule ethynylarsines are fairly inert with respect to water. Thus the compound $Me_2AsC{\equiv}CCF_3$ withstands contact with water without decomposition over a period of four months at 20°C and for five days at 110°C. [24] The resistance to hydrolysis persists in diethynylarsines [for example $MeAs(C{\equiv}CCF_3)_2$] [24] and triethynylarsines [$(HC{\equiv}C)_3As$], [20] while the diarsenic alkyl derivatives $R_2AsC{\equiv}CAsR_2$ are slowly cleaved by water even in the cold [23].

Among all the OAAD whose behaviour in relation to alkalis was investigated, only 10-phenylethynyl-9,10-dihydrophenarsazine is not decomposed by aqueous solutions of alkali, but hydrochloric acid cleaves its ≡C–As bond [12].

Strong alkalis decompose the ethynylarsines $Ph_2AsC{\equiv}CPh$, $(\alpha\text{-}C_{10}H_7)_2AsC{\equiv}CPh$, and $(\alpha\text{-}C_{10}H_7)_2AsC{\equiv}CH$ with evolution of $PhC{\equiv}CH$ and acetylene respectively [11]. The cleavage of the bisarsines $R_2AsC{\equiv}CAsR_2$ by alkalis takes place readily and more so for R = C_6H_{11} than for R = Ph. [23]

The arsenic(III) derivatives of trifluoromethylacetylene $Me_nAs(C{\equiv}CCF_3)_{3-n}$ (n = 1, 2) evolve the initial acetylene in low yield (36% for n = 1 and 29% for n = 2) on treatment with 10% aqueous sodium hydroxide [24]. Triethynylarsine $As(C{\equiv}CH)_3$ is decomposed by alkalis with evolution of acetylene [20].

Bis(di-α-naphthylarsino)acetylene oxide remains unchanged when treated with alkalis, decomposing partly on refluxing with aqueous silver nitrate [23].

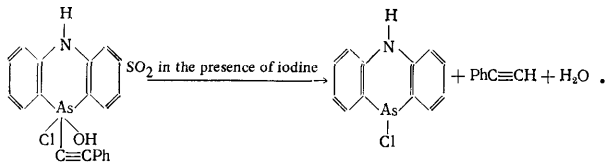
Acetylene and diacetylene derivatives of arsenic [40] are unstable on treatment with dry hydrogen chloride. Apart from hydrochlorination, the As–C≡ bond is broken.

Shpanskii [12] showed that, on treatment with iodine in the cold, 10-phenylethynyl-9,10-dihydrophenarsazine is cleaved with formation of 9-iodo-9,10-dihydrophenarsazine and iodophenylacetylene.

3. Tetracoordination of Arsenic

Although the resistance to oxidation of the acetylene derivatives of Group VB elements decreases from phosphorus to bismuth [4], OAAD do not obey this rule. In the general case the formation of ethynylarsine oxides and hydroxides under the influence of atmospheric oxygen or other oxidants (for example H_2O_2) proceeds with greater difficulty than for the corresponding ethynylphosphines [10,23]. For compounds of the type $R_2AsC{\equiv}CAsR_2$, the oxide was obtained only with R = $\alpha\text{-}C_{10}H_7$; for R = Ph or C_6H_{13}, only the cleavage of the As–C≡ bond was observed under the same conditions [23].

On passing from tervalent to quinquevalent arsenic, the properties of OAAD change significantly, in particular the resistance of the As–C≡ bond to the action of electrophilic agents increases. Thus 10-phenylethynyl-9,10-dihydrophenarsazine hydroxide no longer reacts with iodine, hydrochloric acid does not split off phenylacetylene, and on treatment with alcoholic hydrogen chloride the product of the substitution of one hydroxy-group by chlorine is formed. Its reduction proceeds via the mechanism



It has been noted [23] that bis-(di-α-naphthylarsino)-acetylene oxide is not hydrolysed by alkali, in contrast to the initial compound.

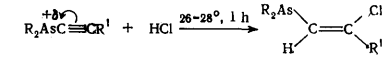
The arsenic(III) OAAD are converted into sulphides, like phosphines, on refluxing with sulphur in carbon disulphide [41–43], but they lose sulphur on isolation.

The quaternisation of ethynylarsines is difficult [10,23].

4. Addition to the Triple Bond

All attempts at the catalytic hydrogenation of ethynylphosphines were unsuccessful [44,45], while similar experiments involving arsines were not performed.

To investigate the properties of the triple bond in OAAD, Kuz'min et al. [40] hydrochlorinated certain acetylene and diacetylene derivatives of arsenic by passing hydrogen chloride through a chloroform solution of the compound:



The polarisation of the triple bond is responsible for the addition of a proton to the α-carbon atom. The chloride ion is directed to the *trans*-position, which is characteristic of disubstituted acetylene derivatives. Hydrogen chloride adds to one of the triple bonds of the diyne group of bis(diethylarsino)diacetylene.

The hydrochlorination of OAAD is accompanied by the dissociation of the As–C≡ bond with formation of the corresponding chloroarsines and monosubstituted acetylenes and diacetylenes. The increase of the polarity of the As–C≡ bond probably facilitates the nucleophilic attack on the arsenic atom and the electrophilic attack on the carbon atom. It has been shown [40] that the rate of formation of products of nucleophilic substitution at the arsenic atom is much higher than the rate of addition of hydrogen chloride to the triple bond.

The behaviour of OAAD in relation to halogens has been hardly investigated. It has been suggested that chlorine and bromine add to the triple bond in 10-phenylethynyl-9,10-dihydrophenarsazine and not to the arsenic atom [12].

Benain [4] reported the addition of diazomethane to acetylenic arsenic-containing compounds.

Cullen and Leeder [24] obtained a cyclopropane derivative, stable at 20°C and even on heating, by the reaction of an organotin trifluoromethyl derivative with a fluorine-containing ethynylarsine:

$$Me_2AsC{\equiv}CCF_3 + Me_3SnCF_3 \rightarrow Me_2As{-}\underset{\diagdown\,\diagup\ CF_2}{C{=}C}{-}CF_3 + Me_3SnF$$

Table 2. NMR and ultraviolet spectroscopic data for certain acetylenic organoarsenic derivatives

No.	Compound	Chemical shift[a] δ, p.p.m.	λ_{max} in u.v. absorption, nm ($10^{-3}\epsilon$)	Refs.
1	$(\underline{H}C{\equiv}C)_3As$	2.62	—	20
2	$Ph_2AsC{\equiv}\underline{C}H$	2.82	225 (13.5), 235 (11), 270 (9)	10
3	$[Ph_2As(\underline{Me})C{\equiv}CH]^+OTs^-$	4.50	—	10
4	$Ph_2AsC{\equiv}C{-}C{\equiv}\underline{C}H$	2.12	225 (24), 257 (5.8), 270 (3.6)	10
5	$(\underline{C}H_3)_2AsC{\equiv}C\underline{C}F_3$	(H) 1.08 (F) 27.9	—	24
6	$(\underline{C}H_3)As(C{\equiv}C\underline{C}F_3)_2$	(H) 1.44 (F) 26.4	—	24
7	$Ph_2AsC{\equiv}C\underline{C}H_3$	2.05	—	10
8	$Ph_2As(O)C{\equiv}C\underline{C}H_3$	2.10	—	10
9	$[Ph_2As(Me)C{\equiv}C\underline{C}H_3]^+OTs^-$	2.28	—	10
10	$Ph_2AsC{\equiv}CC{\equiv}C\underline{C}H_3$	1.97	258 (4.3), 271 (2.6)	10
11	$[Et_2As(Me)C{\equiv}C\underline{C}{\equiv}C\underline{C}H_3]J^-$	2.08	—	10
12	$Ph_2AsC{\equiv}CC{\equiv}CC{\equiv}C\underline{C}H_3$	1.97	226 (80), 240 (48)	10
13	$(CH_3C{\equiv}C)_3As$	1.96	228 (4.2)	10
14	$[(\underline{C}H_3)_3C{-}C{\equiv}C]_3As$	1.26	—	16

[a] For the isolated atom.

5. Reactions of the Acetylenic Hydrogen

Ethynyl derivatives of Group VB elements can be metallated by Grignard reagents [10,18] or by lithium alkyls [33].

The condensations of Iotsich reagents obtained from OAAD with a terminal ≡C–H group [18,31–33,35],

$$R_2AsC{\equiv}CMgBr + \begin{cases} \begin{matrix} R' \\ R'' \end{matrix}\!\!\diagdown C{=}O \rightarrow R_2AsC{\equiv}C\underset{\diagup\,\diagdown}{C}\begin{matrix} OH \\ | \\ R' \\ R'' \end{matrix} \\ (R'(CO_2)O \rightarrow R_2AsC{\equiv}CC(=O){-}R' \\ CO_2 \rightarrow R_2AsC{\equiv}CCOOH \\ ClCOOEt \rightarrow R_2AsC{\equiv}CCOOEt \end{cases}$$

and also the involvement of such acetylene derivatives in the Favorskii [10] and Mannich [33] reactions were examined previously (see Section II, 2). In these reactions the introduction of an arsenic atom in the α-position relative to the triple bond does not alter the type of reactivity of the ethynyl hydrogen atom. However, when an attempt was made to carry out oxidative condensation [40] to obtain organoarsenic derivatives of diacetylene,

$$2R_2AsC{\equiv}CH \xrightarrow[CuCl]{O_2} R_2AsC{\equiv}C{-}C{\equiv}CAsR_2 + 2H$$

bis(dialkylarsino)acetylenes were obtained in all the experiments instead of the expected diacetylene derivatives. Under oxidative condensation conditions, a more complex reaction probably takes place and its overall course can be represented by the equation

$$2\,R_2AsC{\equiv}CH \underset{70\%}{\rightarrow} R_2AsC{\equiv}CAsR_2 + HC{\equiv}CH$$

6. Certain Spectroscopic Data

By comparing the infrared spectra of dialkylarsinoacetylenes, dialkylarsinoacetylenic alcohols, and also dialkylarsinoacetylenic acids and their esters, Kuz'min and Pavlova [35] showed that the vibration frequency of the acetylenic bond changes only slightly as a function of the nature of the group substituting the ethynyl hydrogen atom while the intensity of the band due to the acetylenic linkage depends significantly on the substituent.

Continuing the study of the spectra of dialkylethynylarsines, dialkylarsinoalkynes, bisdialkylarsinoacetylenes, and bisdialkylarsinodiacetylenes, Shagidullin et al. [34] established that the introduction of an arsenic atom in the α-position relative to the acetylene and diacetylene groups greatly reduces the C≡C vibration frequency, which may be due both to a specific interaction of the p_π–d_π type and to the effect of the mass of the arsenic atom.

Table 3.

Compound	*m/e* for parent ion	*m/e* for fragment			
		$-CH_3$	$-(CH_3)_2$	$-(CH_3)_3$	$-(CH_3)_3C$
$^{75}As(C{\equiv}CCMe_3)_3$	318	303	288	273	261

Monosubstituted dialkylethynylarsines are capable of self-association with formation of hydrogen-bonded complexes.

The absorption and photoconduction spectra of copper acetylides having the general formula $R_2AsC{\equiv}CCu$, where R = Ph or Bu, have been investigated in detail [39]. The stretching vibration frequencies of the C≡C and ≡C–H groups are presented in Table 1. Certain NMR and ultraviolet spectroscopic data are in Table 2.

Reiff and Pant[16] reported mass-spectrometric data for tris-(t-butylethynyl)arsine (Table 3).

Organosilicon compounds containing one or several ethynyl groups in the molecule are nowadays attracting increasing attention. Such compounds are of definite theoretical and practical interest as models for the study of the transmission of conjugation via the arsenic atom and also, for example, as potential physiologically active substances.

A more vigorous investigation of the properties of organosilicon compounds of the acetylene series has been made in recent years. Thus it has been established that copper acetylides exhibit photosemiconducting properties[36].

Hay and coworkers[14] reported the synthesis of an interesting group of highly stable arsenic-containing phenylethynyl polymers.

A search is being made for new ligands among organoarsenic compounds[15]. Ethynylarsinic acid synthesised recently may find application in the extraction of heavy lanthanide ions[25].

An important practical factor is the availability of an industrial source of arsenic raw materials (the waste from non-ferrous metallurgy), which leads to the expectation of a further expansion of studies on this interesting class of compounds.

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