Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Diacetylene as a Potential Feedstock of Commercially Prospective Organosulfur Compounds

A. N. Volkov[a]; K. A. Volkova[a]; B. A. Trofimov[a]
[a] Irkutsk Institute of Chemistry, Siberian Branch of the Academy of Sciences of Russia, Irkutsk, Russia

To cite this Article Volkov, A. N. , Volkova, K. A. and Trofimov, B. A.(2001) 'Diacetylene as a Potential Feedstock of Commercially Prospective Organosulfur Compounds', Journal of Sulfur Chemistry, 22: 3, 277 — 296
To link to this Article: DOI: 10.1080/01961770108047964
URL: http://dx.doi.org/10.1080/01961770108047964

Sulfur Reports, 2001, Vol. 22, pp. 277–296
Reprints available directly from the publisher
Photocopying permitted by license only

DIACETYLENE AS A POTENTIAL FEEDSTOCK OF COMMERCIALLY PROSPECTIVE ORGANOSULFUR COMPOUNDS

A. N. VOLKOV*, K. A. VOLKOVA and B. A. TROFIMOV

Irkutsk Institute of Chemistry, Siberian Branch of the Academy of Sciences of Russia, 1 Favorsky Street, Irkutsk, R-664033, Russia

(Received 13 March 2000; In final form 16 May 2000)

Data concerning synthesis of thiophene, alkylthiobutenynes and esters of dithiocarbamic acids and related compounds with utilization of diacetylene are briefly summarited.

Keywords: Diacetylene; Thiophene; Thiols; Alkylthiobutenynes; Liquid ammonia; Ketones; Carbon disulfide; Esters of dithiocarbamic acids

CONTENTS

*Corresponding author.

1. INTRODUCTION

The high and multi-facet reactivity of diacetylene offers a broad opportunity for preparing diverse unsaturated heteroatom compounds, which possess a number of specific properties and are of great interest in many technological aspects [1, 2].

Among these compounds, sulfur derivatives of diacetylene occupy a remarkable place. During the recent years, particular attention has been drawn to sulfur-containing diacetylenic monomers capable of topopolymerization to afford self-assembled mono- and multi-layers possessing non-linear optical properties [3–11]. Just as examples, there are to be mentioned diacetylene-bis(p-toluenesulfonate) [3]; dodeca-5,7-diyn-1,12-ylene-bis(p-toluenesulfonate) [4]; bis(p-toluenesulfonate) of 2,4-hexadiyne-1,6-diols [5]; asymmetrical diacetylenes with substituents like $MeC_6H_4SO_2CH_2O$ and $FC_6H_4SO_2CH_2O$ and their thermal polymers [6]. Others include, monomer diacetylene with bis(p-fluorobenzenesulfonate) moieties and their corresponding polymers [7]; new asymmetrical diacetylene sulfur derivatives such as 1-(4-fluorobenzenesulfonyloxy)-6-(4-trifluoromethylbenzenesulfonyloxy)-2,4-hexadiyne, which polymerize thermally in the solid state and have polar ("ferroelectric") individual chains [8]. The multi-stage synthesis of long-chain tetrathiafulvalenes containing a diacetylene group at different distance from tetrathiafulvalene moiety was described [9]. ω-Functionalized alkane thiols containing a conjugated diacetylene were also synthesized [10]. These molecules spontaneously self-assembled onto gold surface and are polymerized by *UV* irradiation [10]. The formation of self-assembled dialkyl disulfide-functionalized monolayers containing diacetylene was also reported [11].

The synthesis of novel, high density diacetylene monomers was achieved by the preparation of mono- and bis(pentafluorosulfur)-diacetylene. The derivatives are readily prepared by the addition of

pentafluorosulfur bromide (SF_5Br) to diacetylene and subsequent dehydrobromination [12].

At present there is a real possibility of using diacetylene, an inevitable product of industrial synthesis of acetylene [13], in the production of a series of practically important organosulfur products. Diacetylene and its derivatives provide convenient starting materials for the creation of new fungicides [14], drugs [15], polymeric materials [16, 17] and unsaturated compounds [18]. In the present review real possibilities of synthesizing organosulfur compounds based on diacetylene are discussed.

2. SYNTHESIS OF THIOPHENE

Thiophene and its derivatives find many uses in different fields of science and technology. On the basis of thiophene some methods for the synthesis of polyorganylsiloxanes possessing unique properties, [19, 20] herbicides [21], physiologically active [22] and fragrant compounds [23] have been developed and a series of drugs [24], including antibiotics [25] have been obtained. The compositions containing thiophene and its derivatives can be used for the treatment of central nervous system and as anti-inflammatory, cardiac-vascular, antihistamine agents, *etc.*, [25, 26].

Summarized data on thiophene were published in 1985 in Gronowiz's monograph [27], where some methods for the preparation of thiophene by a ring closure reaction and from other cyclic systems were described and the pharmacological activity of thiophene and its derivatives was considered [28].

The existing industrial methods for the preparation of thiophenes are considered in the review [29]. All these methods are based on the interaction of hydrocarbon feedstock C_4-C_8 with hydrogen sulfide at sufficiently high temperatures (560–700°C) in the presence of various catalysts. The yield of thiophene is 50–70% [30].

Thiophene can also be synthesized from slate semicoking gases or coal resin benzene fraction [31].

The development of catalytic methods is restricted by the absence of fairly stable catalysts, therefore thermal methods of thiophene

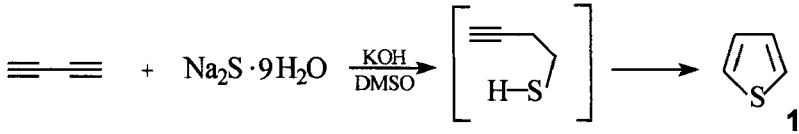
synthesis from organosulfur compounds holds much promise [32, 33]. There are some data concerning thiophene synthesis by pyrolysis of dibutyl disulfide at 500–600°C [34, 35], divinylsulfoxide (400°C, thiophene yield to 60%) [36], disulfide oil (5.5% yield) [37], dimethyl sulfide and mustard gas (400–700°C, yield to 50%) [38].

A one-pot synthesis of thiophene and thiophene derivatives from vinyl chloride, hydrogen sulfide and acetylene has been elaborated (500–700°C, with excess vinyl chloride the yield of thiophene approaches 80%) [39]. All the above methods have substantial shortcomings: comparatively high reaction temperature, use of catalysts, and the presence of impurities in the final product.

In 1962, Schulte *et al.*, [40] undertook synthesis of thiophene (yield 20%) by condensation of diacetylene with gaseous hydrogen sulfide in aliphatic alcohol or acetone in the presence of 1N NaOH (pH 9–10, 20–80°C, 4–20 h). However, the authors failed to increase the yield of thiophene in the reaction of diacetylene with saturated aqueous sodium sulfide. By this reason the process was not put into practice.

Later [41–46], a process for the preparation of thiophene by interaction of diacetylene with hydrated sodium sulfide in a superbase medium (KOH-DMSO) at 20–100°C (yield to 94%) has been worked out.

The reaction can be performed without catalyst, however the yield of thiophene does not exceed 54% in this case, whereas in the presence of equimolar amounts of KOH (relative to Na_2S) the yield is nearly quantitative (Tab. I).

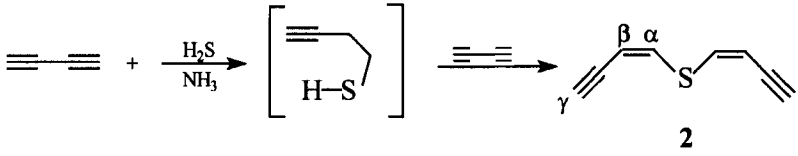


1

SCHEME 1

TABLE I Effect of the reaction conditions on the yields of thiophene in DMSO [41, 45]

Reaction conditions		*Amount of reagent, mol*			*Yield of* 1,
T,°C	*Time, h*	$Na_2S\ 9H_2O$	C_4H_2	*KOH*	%
20	1.5	0.108	0.054		44.1
55	1.25	0.083	0.038	0.08	93.9
70	1.5	0.061	0.120		54.6
100	1.25	0.140	0.072		40.0



2

SCHEME 2

The use of a highly boiling solvent allows preparation of thiophene free from impurities. The purity of thiophene isolated from the reaction mixture by evacuation without supplementary purification is about 99% (GLC).

In the aqueous medium the highest yield of thiophene (52%, purity 98.5%) is achieved when the reaction is carried out with large excess of concentrated sodium sulfide solution (9:1 relative to diacetylene) in the presence of KOH (70°C, 1.75 h) [45]. These results show good reproducibility and can serve as a basis for the thiophene production. In a column reactor of continuous performance at 70°C the yield of thiophene approaches 71%, thus supporting once more the high potential of this method [41]. A procedure for preparation of the 7.7% diacetylene solution in DMSO with the only impurity being benzene ($\sim$0.4%) from industrial hydrocarbon gas mixture was patented [47].

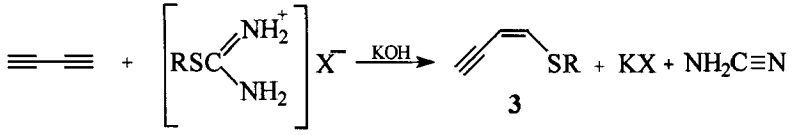
The reaction of diacetylene with hydrogen sulfide in liquid ammonia [48], which simultaneously serves as a solvent and an ionizing agent, gave not thiophene, but di(1-buten-3-ynyl)sulfide **2**, the product of sulfide-anion addition to two diacetylene molecules (Scheme 2) [46].

The sulfide **2** obtained in 89.5% yield shows a Z,Z-configuration, that points to a high *trans*-stereospecificity of the reaction. Structure **2** was proven by ^{1}H NMR spectrum (δ, ppm): 6.66 d (H_α), 5.55 dd (H_β), $^3J_{H\alpha H\beta} = 10$ Hz, $^4J_{H\alpha H\beta} = 2.5$ Hz.

3. SYNTHESIS OF ALKYLTHIOBUTENYNES

3.1. Reaction of Diacetylene with S-alkylisothiouronium Salts

The nucleophilic addition of thiols to diacetylene is readily effected by alkalis in various solvents to lead to alkylthiobutenynes [1]. However, the reaction is complicated by further addition of the thiol to the thioether and this significantly decreases (to 60%) the yield of the



R = Alk, CH_2=$CHCH_2$, HC≡CCH_2; X = Br, Cl, I

SCHEME 3

latter. A high stereospecificity of the thiylation reaction, which strictly follows the rule of *trans*-addition, has been established [49]. Solvents prone to form complexes involving hydrogen diacetylene disobey this rule [50], whereas in methanol only Z-adducts are formed.

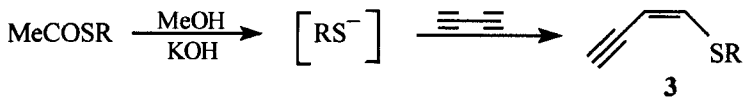
1-Alkylthio-1-buten-3-ynes **3** were obtained in 60–70% yield from the reaction of diacetylene with S-alkylisothiouronium salts in the presence of alkali in protic or aprotic solvent (alcohol, DMF, DMSO) in a temperature range from −1 to +50°C (Scheme 3) [51].

The generation of thiolate-ion from S-alkylisothiouronium salts directly in the reaction mixture in the presence of alkalis makes it possible to do without free thiols and, consequently, avoid a competing free-radical reaction, which easily occurs even under nitrogen [52].

Taking into account that the isothiouronium salts are readily prepared by thiourea alkylation and can be used without preliminary isolation, the present method provides a one-pot route to the sulfides **3** based on halogen derivatives and diacetylene. This method is especially convenient in the cases when the corresponding free thiols are volatile (methanethiol) or unstable (propargylthiol).

3.2. Reaction of Diacetylene with Thioacetates

A process for the preparation of sulfides **3** from alkylthioacetates has been developed [53]. As in an alkaline medium [54] the alkylthioacetates form thiols in high yields on hydrolysis, the reaction was carried out in the presence of KOH (1.2 mol per 1 mol of the initial thioacetate, methanol being employed as a solvent). The alkaline agent induces alcoholysis of the initial esters of thiolic acids to thiol and simultaneously catalyzes the nucleophilic addition of thiolate-ion to diacetylene. This allows the sulfides **3** to be obtained in yields of up to 80% (Scheme 4).



R = Alk

SCHEME 4

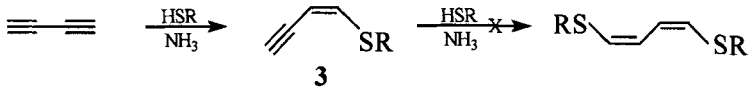
3.3. Nucleophilic Addition of Thiols to Diacetylene in Liquid Ammonia

Volkov *et al.* [55, 56] have studied in detail the interaction of diacetylene with thiols in liquid ammonia and aqueous-ammonia medium at ammonia concentration of 25–75% in the temperature range from −40 to +20°C. In the development of this method an account was taken of the high solution ability of ammonia for different classes of organic compounds, which is caused by moderate dielectric permeability and polarity, comparatively strong basicity ($K_b = 4.75$) and ability to form hydrogen bonds. The basic properties of ammonia facilitate not only the solubility of proton-donating substances, but also the formation of ammonium salts with thiols. In the ammonium solution the thiols seem to exist as both contact ion pairs with ammonium counterions and free anions. In this case, the thiolate-ion becomes more reactive because it is poorly solvated by ammonia molecules. The addition of thiols to diacetylene in liquid ammonia proceeds under exclusively mild conditions (−33°C, 2–3 h) and is over immediately after the addition of thiol. This is not affected by the diacetylene – thiol molar ratio, since in all ratios (1 : 0.5, 1 : 1.1, 1 : 1.2, 1 : 2) only enyne sulfides **3** are isolated in 84–98% yield (Tab. II). This rules out the secondary reaction leading to 1,4-dialkylthio-1,3-butadienes (Scheme 5).

The sulfides **3** prepared in liquid ammonia, represent a 6 : 1 mixture of *Z*,*E*-isomers, the spectra of which display proton signals of *Z*,*E*-ethylene fragments with typical spin-spin coupling constants (10 and 15 Hz, respectively). The portion of *E*-isomer increases with the size of the R radical and approaches a maximum (30%) when R = $(Me)_3SiCH_2$. This indicates a noticeable contribution to steric interactions in the transition state since the *E*-isomer percentage remains constant prior to and after thermal treatment of the above

TABLE II Effect of the reaction conditions on the yield of sulfides **3** [56]

	Reagents, mol		*Solvent,*		*Time,*	*Diacetylene*	
R	*Diacetylene*	*Thiol*	*ml*	*T,°C*	*h*	*Conversion, %*	*Yield, %*
Et	0.146	0.272	liq.NH_3(100)	−33	2.5	~100	89
n-Bu	0.104	0.124	liq.NH_3(75)	−33	3.0	~100	87
n-Bu	0.060	0.042	liq.NH_3(55)	−33	2.0		82
Et	0.100	0.120	70% NH_3(75)	−15	1.5	~100	83
n-Bu	0.058	0.070	50% NH_3(90)	5	1.0	86	71
n-Bu	0.048	0.058	25% NH_3(50)	20	2.4	80	72
Et	0.072	0.085	Pyridine (30)	20	1.5	98	~0
Et	0.040	0.048	Pyridine (15)	50	3.0	~100	4
n-Bu	0.043	0.050	Et_3N (15)	30	1.0	86	56
Et	0.080	0.096	Et_3N (15)	60	2.0	~100	68
Et	0.084	0.098	DMSO (15)	60	3.0	~100	~0
Et	0.080	0.096	DMF (15)	60	3.0	~100	~0
Et	0.067	0.132	20% NaOH (85)	20	2.5	19	10
n-Bu	0.031	0.040	20% NaOH (95)	60	1.0	84	52



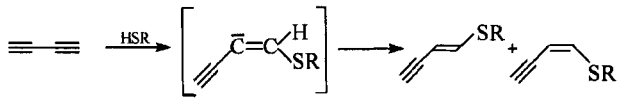
R = Alk, Ar, $(AlkO)_3(CH_2)_n$, $HOCH_2CH_2$, $HOCH_2CH(OH)CH_2$, $(Me)_3SiCH_2$

SCHEME 5

compounds. The reaction is considered to involve the formation of an intermediate carbanion followed by protonation, that allows the formation of both *Z*- and *E*-sulfides (Scheme 6).

The authors [56] could isolate individual *Z*- and *E*-sulfides **3** by preparative GLC.

The same sulfides **3** were obtained in industrial solutions of diacetylene in ammonia [55, 57].



SCHEME 6

Diacetylene thiylation can be performed in aqueous ammonia solutions to give the adducts **3** in fairly high yields, though the diacetylene conversion drops to 80% (Tab. II).

The reaction of diacetylene with thiols in a weaker basic solvent such as pyridine, for example, ($pK_b = 9.38$) proceeds very slowly since pyridine does not favor the formation of active thiolate-ion. In a stronger base, like triethylamine ($pK_b = 3.12$), the reaction occurs at a higher temperature, the yield of sulfides **3** not exceeding 68% [56]. In the diacetylene thiylation in diethylamine one could expect the formation of 1-diethylamino-1-buten-3-yne [1]. However, thiols win the competition for the triple bond, which results in the isolation of only the sulfides **3** in a yield of up to 90% [58]. In aqueous methylamine, the formation of aminovinylketones could be expected [59], but in this case again the thiolate-ion activity remains very high, and only the sulfides **3** were isolated from the reaction mixture [58]. Evidently, the thiol activation with liquid ammonia, primary, secondary and tertiary amines and aqueous solutions thereof is common in the reactions of nucleophilic addition of thiols to diacetylene.

The method of diacetylene thiylation in liquid ammonia was successfully employed for the preparation of silicon-containing sulfides [60], especially, 1-(trialkoxysilylalkylthio)-1-buten-3-ynes, which cannot be obtained in the presence of alkalis. Mild reaction conditions enable the involvement of thiols containing other functional groups. For example, with 2-mercaptoethanol and 1,2-hydroxy-3-mercaptopropanol the reaction occurs involving exclusively the thiol group, the corresponding sulfides **3** being obtained in $\sim 100\%$ yield [58].

The same method is applicable for the preparation of 1-arylthio-1-buten-3-ynes. Carrying out the reaction in liquid ammonia makes it possible to avoid the use of alkali and to increase the yield of the target product to 97%, as well as to prepare new 1-arylthio-1-buten-3- ynes **3** [58, 61]. Yields and characteristics of the sulfides **3** are presented in Table III.

The above results suggest that the sulfides **3** owing to their accessibility become promising intermediates and monomers, which can be used as bioactive compounds [62, 63] and flotation reagents [64]. They can also find application in preparative chemistry.

TABLE III Yields and characteristics of the sulfides **3** ($HC \equiv CCH{=}CH - SR$) [51, 55, 56, 58, 60, 61]

R	*Yield* %	*B.p.*, °C (*mm Hg*)	n_D^{20}	d_4^{20}	*Ratio* Z : E	*IR spectra* (*film*), *v*, cm^{-1}
Me	84	56–58(20)	1.5606	0.9763	6:1	1560, 2100, 3030, 3290
Et	89	67–68(17)	1.5420	0.9581	5:1	1560, 2100, 3045, 3290
n-Pr	98	58–60(5)	1.5341	0.9383	8:1	1560, 2090, 3035, 3290
i-Pr	87	51–53(5)	1.5290	0.9270	7:1	1560, 2103, 3035, 3290
n-Bu	87	73–75(6)	1.5250	0.9135	10:1	1565, 2100, 3040, 3300
i-Bu	84	71–72(6)	1.5231	0.9103	6:1	1560, 2105, 3040, 3290
t-Bu	89	70–73(12)	1.5230	0.9145	10:1	1560, 2095, 3040, 3288
$n\text{-}C_6H_{13}$	85	92–93(2.5)	1.5135		5:1	1560, 2100, 3035, 3290
HOC_2H_4	95	84(1)	1.5795		6:1	1560, 2100, 3030, 3290
$HOCH_2$ $CH(OH)CH_2$	93		1.5818			
$CH_2{=}CHCH_2$	60	46–48(4)	1.5545	0.9275	10:1	1565, 1635, 2100, 3040, 3085, 3290
$HC{\equiv}CCH_2$	71	65–66(1.5)	1.5730	0.9267	10:1	1540, 1570, 2100, 2140, 3050, 3295
Ph	97	118(5)	1.6303	0.9158	10:1	1552, 1580, 2100, 3060, 3085, 3300
$o\text{-}HOOCC_6H_4$	95	144–147(M.p.)			1:0	1560, 1585, 2100, 3280, 3440
$o\text{-}NH_2C_6H_4$	79		1.6510		1:0	1590–1610, 2100, 3015, 3280, 3460
$p\text{-}CH_3OC_6H_4$	89	89–93(5)	1.6143		1:0	1600, 2100, 3040, 3080, 3290
$PhCH_2$	49	140–143(4)	1.6115	0.9149	1:0	1570, 1660, 2100, 3025, 3060, 3300
$(MeO)_3SiCH_2$	94	77–80(1)	1.5053	0.9126	2:1	1570, 2100, 2955, 3320
$(MeO)_3$ $SiCH_2CH_2$	92	110–112(3)	1.5040	0.9138	5:1	1570, 2100, 2955, 3300
$(Me)_3SiCH_2$	96	63–64(5)	1.5208	0.9142	2:1	1565, 2100, 3035, 3320

TABLE III (Continued)

R	Yield %	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Ratio Z:E	IR spectra (film), ν, cm^{-1}
$(Me)_3Si(CH_2)_3$	97	84–85(3)	1.5123	0.9042	7:1	1565, 2100, 3035, 3320
$(Et)_3SiCH_2$	91	112(5)	1.5143	0.9173	2:1	1565, 2100, 3040, 3320

The nucleophilic thiylation of diacetylene in liquid ammonia or aqueous-ammonia opens a door for the practical application of diacetylene and the production of unsaturated sulfides.

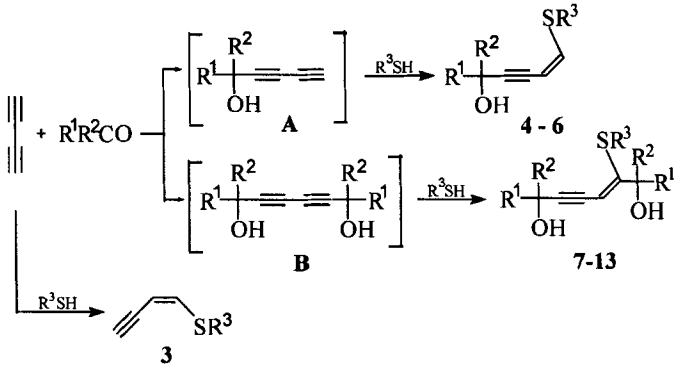
4. PREPARATION OF ALKYLTHIOENYNE ALCOHOLS AND GLYCOLS

The condensation of diacetylene with ketones in liquid ammonia is considered to be promising from the point of using diacetylene formed as a side product in the acetylene manufacturing [65]. The same is applied to the preparation of tertiary 1-alkylthioenyne alcohols **4–6** [66] and ditertiary glycols **7–13** [67, 68].

The method is based on the reaction of diacetylene with ketones in the presence of catalytic amounts of NaOH or KOH in liquid ammonia followed by treatment of the reaction mixture with the corresponding thiols, which react with diacetylene alcohols **A** or glycols **B** (Scheme 7).

To synthesize the alcohols **4–6** it is convenient to carry out the reaction with a 6–10% diacetylene solution in liquid ammonia at the ammonium boiling temperature and the diacetylene : ketone : thiol ratio = 1 : 0.5 : 1.2; 1 : 0.75 : 1.2 or 1 : 1 : 1.2 in the presence of 0.1–0.01 mole of alkali metal hydroxide. The nucleophilic addition of thiol to the terminal bond of diacetylene alcohol **A** proceeds in a regiospecific manner in accord with the *trans*-addition rule ($^3J_{HH} = 10$ Hz).

Excess of diacetylene relative to ketone is necessary to direct the reaction toward alcohols **A** only and rule out formation of glycols **B**. In this case the sulfides **3** were prepared as side products in a yield of 20–30% based on the diacetylene taken. The alkali catalyzes the condensation of diacetylene with ketones and simultaneously accelerates



$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Et$; R^1-$R^2 = (CH_2)_4$; R^1-$R^2 = (CH_2)_5$;
$R^3 = Alk$

SCHEME 7

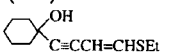
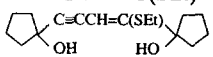
the reaction of diacetylene alcohol **A** and the residual diacetylene with thiols, which are taken in small excess and participate in the synthesis of tertiary alcohols **4–6** isolated in 83–96% yield (Tab. IV).

By varying the ratio of components the reaction can be directed toward the formation of glycols **B**. For example, glycols **7–13** were obtained in 89–95% yield at the diacetylene- ketone- thiol molar ratio equal to 1:(2.3–2.7):(1.1–1.3) in the presence of 0.19–0.27 mol of alkali metal hydroxide. Characteristics of the alcohols **4–6** and glycols **7–13** are presented in Table V.

TABLE IV Effect of the reaction conditions on yields of the alcohols **4–6** and Diols **7–13** [66–68]

		Reaction conditions (−30 *to* −33°C)					
		Reagents, mol				*Time,*	NH_3
Cpd.	*Yield, %*	*Diacetylene*	*Ketone*	*Thiol*	*NaOH*	*h*	*liq*
4	83	0.15	0.1	0.21	0.012	8	100
5	96	0.10	0.07	0.12	0.009	6	70
6	88	0.10	0.07	0.12	0.008	6	70
7	96	0.07	0.20	0.10	0.015	12	200
8	95	0.01	0.03	0.15	0.003	8	90
9	87	0.02	0.05	0.02	0.005	11	85
10	89	0.01	0.03	0.02	0.002	10	85
11	94	0.01	0.03	0.02	0.003	12	85
12	95	0.08	0.19	0.10	0.019	16	250
13	94	0.01	0.03	0.01	0.002	14	160

TABLE V Alkylthioenyne Alcohols 4–6 and Diols 7–13 [66–68]

Cpd.	*Formula*	*B.p.,°C (mm Hg) or M.p.,°C*	*IR spectra (KBr) ν, cm⁻¹*
4	$(Me)_2C(OH)C \equiv CCH{=}CHSEt$	125–128(1.5)	1562, 2220, 3035, 3400
5	$Et(Me)C(OH)C \equiv CCH{=}CHSEt$	110–113(1)	1560, 2215, 3040, 3420
6		131–134(1)	1565, 2215, 3038, 3400
7	$(Me)_2(OH)CC \equiv CCH{=}C(SEt)C(OH)(Me)_2$	67–68	1590, 2210, 3435
8	$(Me)_2(OH)CC \equiv CCH{=}C(SPr-n)C(OH)(Me)_2$	38–40	1590, 2220, 3400
9	$(Me)_2(OH)CC \equiv CCH{=}C(SPr-i)C(OH)(Me)_2$	64–65	1580, 2225, 3470
10	$(Me)_2(OH)CC \equiv CCH{=}C(SBu-n)C(OH)(Me)_2$	160(3)	1585, 2220, 3410
11	$(Me)_2(OH)CC \equiv CCH{=}C(SBu-i)C(OH)(Me)_2$	46–47	1590, 2220, 3400
12	$Et(Me)(OH)CC \equiv CCH{=}C(SEt)C(OH)(Me)Et$	152–153(4)	1580, 2220, 3410
13		184–186(4)	1580, 2210, 3400

The conjugated multiple bonds and reactive hydroxyl groups present in the molecules of alkylthioenyne alcohols **4–6** secure their high synthetic potential. Furthermore, the availability of a technologically feasible process of their production opens up a new promising trend in the industrial application of diacetylene.

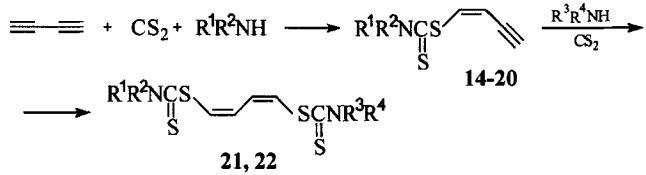
5. REACTION OF DIACETYLENE WITH CARBON DISULFIDE IN AMINES

Thio and dithiocarbamic acid derivatives, in particular, esters find many uses as flotation reagents [69], antioxidants [70], vulcanization accelerators [71]. They enhance the anti-wearing and anti-fretting properties of lubricant oils and have fungicidal and herbicidal activity [72, 73].

The process of production of dithiocarbamic acid esters normally involves the reaction of ammonium salts or the salts of alkali metal dithiocarbamate [74] with various compounds [75–86].

It has been found [87, 88] that dithiocarbamic acid esters **14–20** can readily be obtained by the reaction of diacetylene and carbon disulfide either in the presence of secondary amines or directly from diacetylene and ammonium dithiocarbamates in protic or aprotic solvents (Scheme 8).

The reaction is performed without catalyst by passing gaseous diacetylene through a mixture of secondary amine and carbon disulfide in a solvent or directly through a solution of ready dithiocarbamate at 20–30°C, and leads to esters **14–20** in a yield of up to 94% (Tab. VI).



$R^1 = R^2$ = Alk (**14,15**); R^1-R^2 = $(CH_2)_5$ (**16**); R^1- R^2 = $(CH_2)_2O(CH_2)_2$ (**17**);
$R^1 = R^2 = HOCH_2CH_2$ (**18**); $R^1 = R^2$ = H (**19**); R^1 = H, R^2 = Me (**20**);
$R^1 = R^2 = R^3 = R^4$ = Et (**21**); $R^1 = R^2$ = Et, R^3-R^4 = $(CH_2)_5$ (**22**)

SCHEME 8

TABLE VI The product yields and conditions of the reactions of ammonium dithiocarbamates with diacetylene [87, 88]

Diacetylene mol.	*Dithiocarbamate, mol.*	*Solvent, ml.*	*T, °C*	*Time, h*	*Product, %*
0.06	0.03	MeOH, 30	40	2	**14**(50), **21**(43)
0.05	0.05	MeOH, 40	40	2	**14**(16), **21**(46)
0.025	0.05	MeOH, 40	40	2	**21**(92)
0.08	0.03	Et_3N, 30	30	2	**14**(68)
0.05	0.05	THF, 15	30	3	**14**(60), **21**(24)
0.06	0.06	PhH, 15	30	2	**14**(68), **21**(15)
0.03	0.03	Ether, 20	5	3	**14**(57), **21**(13)
0.08	0.10	NH_3 liq., 70	−33	3	**14**(79)
0.10	0.05	NH_3 liq., 80	−33	5	**14**(81)
0.04	0.04	Etanol, 20	20	2	**15**(83)
0.10	0.09	NH_3 liq., 70	−33	3	**16**(94)
0.09	0.09	THF, 50	50	2	**16**(67)
0.06	0.06	DMSO, 40	40	2	**17**(25)
0.04	0.02	Acetone, 50	50	3	**17**(80)
0.09	0.09	MeOH, 20	50	3	**18**(60)
0.10	0.10	NH_3 liq., 70	−33	5	**19**(20)
0.10	0.10	NH_3 liq., 50	−33	3	**20**(90)

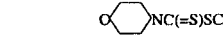
Mild reaction conditions are due to the high nucleophilicity of the dithiocarbamate ion, on the one hand, and by the high electrophilicity of the diacetylene triple bonds, on the other hand. In all the cases *Z*-isomers of the esters **14**–**20** were isolated, that indicates stereoselectivity of the process.

The reaction of diacetylene with diethylammonium diethyldithiocarbamate does not cease on the stage of addition of 1 mole of diethyldithiocarbamate, but gets involved in further formation of butadiene bis(dithiocarbamate) **21**. By varying the component ratios and reaction conditions it is possible to obtain either the ester **14** or the diester **21**.

Ammonia turned out to be the most powerful agent to suppress the second reaction stage. In this case only the ester **14** was produced. In contrast, under more harsh conditions with the diacetylene: ammonium dithiocarbamate molar ratio of 1 : 2, the diester **21** was the major reaction product (Tab. VI).

The diester **21** can also be prepared by reaction of the ester **14** with ammonium diethyldithiocarbamate in methanol. The reaction with

TABLE VII Characteristics, IR and ^1H NMR spectra of the esters of dithiocarbamic acids [87, 88]

			Spectra			
		M.p.,		^1H *NMR* (δ, *ppm*), CCl_4		
Cpd.	*Formula*	°*C*	ν, cm^{-1}	H_α*	H_β*	H_γ** *IR* (*KBr*),
14	$(Et)_2NC(=S)SCH=CHC \equiv CH$	37–38	1500, 1580, 1645, 2100, 3020, 3300	7.33d	5.75q	3.30d
15	$(n-Pr)_2NC(=S)SCH=CHC \equiv CH$	48–49	1500, 1580, 1640, 2100, 3020, 3250	7.71d	5.68q	3.20d
16	$(CH_2)_5NC(=S)SCH=CHC \equiv CH$	68–70	1480, 1590, 1650, 2100, 3010, 3320	7.71d	5.67q	3.30d
17		77–79	1420, 1585, 1650, 2100, 3025, 3270	7.67d	5.71q	3.20d
18	$(HOCH_2CH_2)_2NC(=S)SCH=CHC \equiv CH$		1500, 1540, 1590, 2100, 3030, 3290, 3400	6.61d	5.50q	3.33q
19	$NH_2C(=S)SCH=CHC \equiv CH$	27	1420, 1580, 1670, 2090, 3020, 3250	6.65d	5.51q	3.28d
20	$CH_3NHC(=S)SCH=CHC \equiv CH$		1480, 1580, 1690, 2100, 2990, 3280	6.70d	5.58q	3.38d
21	$(Et)_2NC(=S)S(CH=CH)_2SC(=S)N(Et)_2$	140	1510, 1630, 3050	7.13q	6.58q	
22	$(Et)_2NC(=S)S(CH=CH)_2SC(=S)N<(CH_2)_5$	150	1500, 1635, 3030	7.15q	6.58q	

* $JH_\alpha H_\beta \sim 10$ Hz;
** $JH_\beta H_\gamma \sim 2.4$ Hz.

other dithiocarbamates occurs in an analogous manner. With the reaction carried out in methanol, one could expect the formation of the xanthic acid derivatives, however, no esters of xanthic acid have been isolated. Basing on ^{1}H NMR spectra, the compounds **21,22** were assigned a structure with a *Z,Z*-array of substituents, which indicates the ionic character of reaction stage 2, because, when the reaction follows a free-radical mechanism, the process is non-stereospecific.

Ammonium dithiocarbamates prepared from primary amines or ammonia also react with diacetylene. However, the resultant esters **19**, **20** are rather unstable and their isolation in the individual form is difficult. The ester **19** was characterized only by spectral methods, while the major product is represented by oligomer.

The characteristics of compounds **14**–**22** are presented in Table VII.

Among the synthesized compounds **14**–**22**, some are promising for the use in diverse fields of industry [88]. These are, for example, ethers **14**–**17**, which serve as thermal stabilizers of thiuramic resins, or compound **14** which activates the fluororubber vulcanization. Compounds **15**, **17**, **21** and **22** turned out to be more effective light resin antiozonants than tributylthiourea. Thus, the vulcanizers modified with **17** and **22** show a 66 and 44% strength gain, respectively, compare with that of trimethylurea-modified samples.

6. CONCLUSION

The present review summarizes briefly the data, which clearly demonstrate that diacetylene can successfully be used for building structurally and functionally diversified organic sulfur compounds. The interest in these compounds as potent building blocks, monomers and auxiliaries is expected to grow as the problem of diacetylene utilization will soon be showed.

References

[1] Shostakovsky, M. F. and Bogdanova, A. V. (1971). *Khimiya Diatsetilena* (Nauka, Moskva,), s. 524.
[2] Takami, M., Ninagawa, Y. and Omura, Y. (1981). *Heterocycl.*, **16**, 146.
[3] Lochner, K. and Baessler, H. (1980). *Ber. Bunsen-Ges. Phys. Chem.*, **84**, 880.
[4] Wenz, G. and Wegner, G. (1983). *Mol. Cryst. Liq. Cryst.*, **96**, 99.

[5] Quan, X. D., Ando, D. J. and Bloor, D. (1983). *Mol. Cryst., Liq. Cryst.*, **93**, 201.
[6] Bertault, M., Canceill, J., Collet, A. and Toupet, L. (1988). *Mol. Cryst. Liq. Cryst.*, **161**, 145.
[7] Aime, J. P., Schott, M., Bertault, M. and Toupet, L. (1988). *Acta Crystallogr., Sect. B: Struct. Sci.*, **44**, 617.
[8] Strohriegl, P., Gmeiner, J., Mueller, I., Gruner-Bauer, P., Gormann, E. and Eukelmann, V. (1991). *Ber. Bunsen-Ges. Phys. Chem.*, **95**, 491.
[9] Khodorovsky, V. Yu., Tormos, G. V., Neilands, O. Ya., Kolotilo, N. V. and Il'chenko, A. Ya. (1992). *Tetrahedron Lett.*, **33**, 973.
[10] Taisun, K. and Richard, M. C. (1994). *Tetrahedron Lett.*, **35**, 9501.
[11] Batchelder, D. N., Evans, S. D., Freeman, T. L., Haeussling, L., Ringsdorf, H. and Wolf, H. (1994). *J. Amer. Chem. Sos.*, **116**, 1050.
[12] Kovacina, T. A., DeMarco, R. A. and Snow, A. W. (1982). *J. Fluorine Chem.*, p. 261.
[13] Maretina, I. A. (1996). *Zh. Prikl. Khim.*, **69**, 353.
[14] Bierer, D. E., Dener, J. M., Dubenko, L. G., Gerber, R. E., Litvak, J., Peterli, S., Peterli-Roth, P., Truong, T. V., Mao, G. and Bauer, B. E. (1995). *J. Med. Chem.*, **38**, 2628; (1995) *Chem. Abstr.*, **123**, 83292d.
[15] Koreeda, M. and Yang Wu. (1994). *J. Amer. Chem. Soc.*, **116**, 10793.
[16] Naarmann, H. (1994). *Ger. Offen. 4,303,080* (1995) *Chem. Abstr.*, **122**, 214847t.
[17] Bertault, M., Canceill, J., Collet, A. and Toupet, L. (1988). *J. Chem. Sos., Chem. Commun.*, p. 163.
[18] Schroth, W., Dunger, S., Billig, F., Spitzner, R., Herzschuh, R., Vogt, A., Jende, T., Isreel, G. and Barche, J. (1996). *Tetrahedron*, **52**, 12677.
[19] Khananashvili, L. M., Chernyshev, E. A., Vardosanigze, Ts. N., Markosashvili, E. G., Kantariyan, M. G., Savushkina, V. I. and Labartkava, M. O. (1983). *Zh. Obshch. Khim.*, **53**, 1575.
[20] Reinecke, M. G. and Redaja, P. (1986). *Chem. Heterocycl. Comp.*, **44** (*Thiophene Deriv.*, Pt. **2**), 159; (1987) *Chem. Abstr.*, **106**, 170661s.
[21] Mel'nikov, N. N. (1987). *Pestitsidy* (Khimiya, Moskva,), s. 711.
[22] Aberg, B. (1983). *Svedish. J. Agr. Res.*, **13**, 3.
[23] Bratus, I. N. (1979). *Khimiya Dushistykh Veshchestv* (Pishchevay Prom., Moskva,), s. 304.
[24] Navashin, S. M. and Fomina, I. P. (1984). *Antibiotiki*, **29**, 136; (1984) *Chem. Abstr.*, **100**, 99522q.
[25] Buchin, P. I., Lipkin, A. E., Rudzit, E. A., Zenin, B. A., Balmasova, I. P., Smirnov, V. A., Viderker, M. G. and Orlov, E. V. (1977). *U.S.S.R. 477,625* (1977) *Chem. Abstr.*, **87**, 128888j.
[26] Buchin, P. I., Lipkin, A. E., Rudzit, E. A., Zenin, B. A., Videker, M., Smirnov, V. A., Balmasova, I. P., Orlov, E. V. and Chichkova, L. A. (1977). *U.S.S.R. 577,207* (1978) *Chem. Abstr.*, **88**, 100346c.
[27] Gronowiz, S. (1985). In: *Thiophene and Its Derivatives* (Interscience, New York, Dronowiz, S. (Ed.)), p. 1.
[28] Press, J. B. (1985). In: *Thiophene and Its Derivatives* (Interscience, New York, Gronowiz, S. (Ed.)), p. 333.
[29] Ryashentseva, M. A. (1994). *Usp. Khim.*, **63**, 456.
[30] Zhogin, D. Yu., Myasoedov, A. M., Voropanov, G. E. and Ryashentseva, M. A. (1990). *Neftekhimiya*, **30**, 819.
[31] Ivashchenko, V. A., Sapunov, V. A., Miroshnichenko, A. A. and Korabchansky, V. I. (1971). *Koks i Khimiya*, p. 38.
[32] Voronkov, M. G. and Deryagina, E. N. (1987). *Z. Chem.*, **27**, 1.
[33] Korchevin, N. A., Sukhomazova, E. N., Levanova, E. P., Deryagina, E. N. and Voronkov, M. G. (1998). *Chemistry for Sustainable Development*, **6**, 427.
[34] Sukhomazova, E. N., Deryagina, E. N. and Voronkov, M. G. (1982). *U.S.S.R. 910,634* (1982) *Chem. Abstr.*, **97**, 38849z.

[35] Voronkov, M. G., Deryagina, E. N. and Sukhomazova, E. N. (1981). *Khim. Geter. Soed.*, p. 565.
[36] Voronkov, M. G., Deryagina, E. N., Sukhomazova, E. N., Gusarova, N. K., Efremova, G. G., Nikol'skii, N. S. and Amosova, S. V. (1982). *Izv. Akad. Nauk SSSR, Ser. Khim.*, p. 185.
[37] Deryagina, E. N., Sukhomazova, E. N., Russavskaya, N. V., Levanova, E. P. and Voronkov, M. G. (1993). *Zh. Org. Khim.*, **29**, 2315.
[38] Voronkov, M. G., Deryagina, E. N., Korchevin, N. A., Sukhomazova, E. N., Levanova, E. P., Russavskaya, N. V. and Lyamkin, V. (1993). *RU 2,063,967* (1997) *Chem. Abstr.*, **126**, 34348d.
[39] Voronkov, M. G., Deryagina, E. N., Kuznetsova, M. A. and Kalikhman, I. D. (1978). *Zh. Org. Khim.*, **14**, 185.
[40] Schulte, K. E., Reisch, J. and Horner, L. (1962). *Chem. Ber.*, **95**, 1943.
[41] Voronkov, M. G., Trofimov, B. A., Krjuchkov, V. V., Amosova, S. V., Skvortsov, Yu. M., Volkov, A. N., Mal'kina, A. G. and Mushy, R. Y. (1981). *Khim. Geter. Soed.*, p. 1694.
[42] Voronkov, M. G., Trofimov, B. A., Krjutschkov, V. V., Amosova, S. V., Skvorcov, Ju. M., Volkov, A. N., Malkina, A. G. and Muschij R. Ja. (1979). *Ger. Offen. 2,818,580* (1980) *Chem. Abstr.*, **92**, 94228e.
[43] Voronkov, M. G., Trofimov, B. A., Krjuchkov, V. V., Amosova, S. V., Skvortsov, Yu. M., Volkov, A. N., Mal'kina, A. G. and Mushy, R. Y. (1979). *U.S. 4,251,666* (1980) *Chem. Abstr.*, **92**, 94228e.
[44] Voronkov, M. G., Trofimov, B. A., Krjuchkov, V. V., Amosova, S. V., Skvortsov, Yu. M., Volkov, A. N., Mal'kina, A. G. and Mushy, R. Y. (1979). *JP 1,402,912* (1980) *Chem. Abstr.*, **92**, 94228e.
[45] Krjuchkov, V. V. (1975). *Synthesis of Divinyl Sulfide and Its Substituted by Reaction of Hydrated Sodium Sulfide with Acetylenes* (Thesis Irkutsk State University, Irkutsk,).
[46] Trofimov, B. A. (1983). *Sulfur Rep.*, **3**, 83.
[47] Omura, Y., Nagae, H., Nisida, T., Ninagawa, I. and Itoy, K. (1982). *JP 57-58324* (1984) *Ref. Zh. Khim.*, **19**, H12.
[48] Volkov, A. N., Kudyakova, R. N. and Trofimov, B. A. (1979). *Zh. Org. Khim.*, **15**, 1554.
[49] Prilezhaeva, E. N., Petrov, V. N., Vasil'ev, G. S., Nikol'skii, N. S. and Shostakovsky, M. F. (1968). In: *Khimiya Atsetilena* (Nauka, Moskva,), s. 113.
[50] Elsakov, N. V. and Petrov, A. A. (1964). *Optika i Spektr.*, **16**, 797.
[51] Volkov, A. N., Kuznetsova, A. N. and Khudyakova, A. N. (1972). *U.S.S.R. 417,418* (1974) *Chem. Abstr.*, **80**, 145402u.
[52] Gracheva, E. P., Laba, V. I., Kul'bovskaya, N. K. and Shostakovsky, M. F. (1963). *Zh. Obshch. Khim.*, **33**, 2493.
[53] Kuduakova, R. N. and Volkov, A. N. (1977). *Zh. Org. Khim.*, **13**, 934.
[54] Reid, E. E. (1962). *Organic Chemistry of Bivalent Sulfur*, **4**, 24.
[55] Volkov, A. N., Volkova, K. A., Levanova, E. P., Nikol'skaya, A. N., Babalov, G. K., Kudirov, G. I. and Stepanova, N. V. (1980). *U.S.S.R. 806,679* (1981) *Chem. Abstr.*, **95**, 24268f.
[56] Volkov, A. N., Volkova, K. A., Levanova, E. P. and Trofimov, B. A. (1981). *Izv. Akad. Nauk SSSR, Ser. Khim.*, p. 831.
[57] Stepanova, V. N., Babalov, G. K., Zuev, A. A., Kudirov, G. I., Romashkina, L. P., Petrov, A. A. and Tsil'ko, A. E. (1984). *Khim. Prom-st*, p. 145.
[58] Volkov, A. N., Volkova, K. A., Levanova, E. P. and Trofimov, B. A. (1982). *Zh. Org. Khim.*, **18**, 2049.
[59] Volkov, A. N., Sokolyanskaya, L. V. and Mushy, R. Y. (1973). *Zh. Org. Khim.*, **9**, 1599.
[60] Volkov, A. N., Kletsko, F. P., Volkova, K. A., Levanova, E. P., Vlasova, N. N. and Voronkov, M. G. (1981). *U.S.S.R. 829,632* (1981) *Chem. Abstr.*, **95**, 133144h.

[61] Volkov, A. N., Volkova, K. A. and Sigalov, M. V. (1981). *U.S.S.R. 883,023* (1982) *Chem. Abstr.*, **96**, 122412p.
[62] Nikol'skaya, A. N., Levanova, E. P., Volkova, K. A., Volkov, A. N., Shashikhina, M. N., Zhavrid, S. V., Zaporozhets, L. K., Klimovich, V. Ya. and Laguto, L. F. (1983). In: *Antivirusnue Veshestva* (Akad. Med. Nauk, Minsk,), s. 61.
[63] Bogdanova, A. V., Kugatova-Shemyakina, G. P., Volkov, A. N. and Ushakova, T. M. (1968). In: *Khimiya Atsetilene* (Nauka, Moskva,) s. 424.
[64] Novikova, N. T., Dolenko, M. N., Bystrova, I. B., Roshchakovskaya, N. Yu. and Glembotski, A. V. (1977). *U.S.S.R. 558,908* (1977) *Chem. Abstr.*, **87**, 88453e.
[65] Oleinikova, E. B., Volkov, A. N. and Skvortsov, Yu. M. (1977). *Zh. Prikl. Khim.*, **50**, 225.
[66] Volkov, A. N., Levanova, E. P., Volkova, K. A. and Nikol'skaya, A. N. (1980). *U.S.S.R. 771,090* (1981) *Chem. Abstr.*, **94**, 120842p.
[67] Volkov, A. N., Volkova, K. A., Levanova, E. P., Nikol'skaya, A. N. and Trofimov, B. A. (1980). *U.S.S.R. 791,741* (1981) *Chem. Abstr.*, **94**, 191681w.
[68] Volkova, K. A., Levanova, E. P., Volkov, A. N., Nikol'skaya, A. N. and Trofimov, B. A. (1980). *Zh. Prikl. Khim.*, **53**, 1683.
[69] Harris, G. H. and Tiler, T. D. (1971). *U.S. 3,787,471* (1974) *Chem. Abstr.*, **80**, 82142m.
[70] Wollensak, J. C. and Zaweski, E. F. (1973). *U.S. 3,778,460* (1974) *Chem. Abstr.*, **80**, 59720q.
[71] Gattuso, M. J. and Arnold, R. J. (1973). *Ger. Offen. 2,319,647* (1974) *Chem. Abstr.*, **80**, 38101y.
[72] Singhal, G. H. and Turkos, R. E. (1970). *Ger. Offen. 2,061,051* (1972) *Chem. Abstr.*, **76**, 59054t.
[73] Kimura, I., Takahashi, Y. and Ito, S. H. (1972). *Ger. Offen. 2,135,768* (1972) *Chem. Abstr.*, **76**, 136878u.
[74] Ferm, R. J. (1957). *Chem. Rev.*, **57**, 670.
[75] Mustafaev, N. P., Efendieva, Kh. K. and Gasanzade, D. R. (1977). *Zh. Org. Khim.*, **13**, 985.
[76] Kuliev, A. M., Gasanzade, D. R., Mustafaev, N. P. and Efendieva, Kh. K. (1969). *U.S.S.R. 339,545* (1972) *Chem. Abstr.*, **77**, 87900e.
[77] Dasanzade, G. R., Mustafaev, N. P. and Efendieva, Kh. K. (1970). *U.S.S.R. 371,215* (1973) *Chem. Abstr.*, **79**, 18127n.
[78] Mustafaev, N. P., Efendieva, Kh. K. and Gasanzade, D. R. (1979). *U.S.S.R. 785,310* (1981) *Chem. Abstr.*, **94**, 214383s.
[79] Mustafaev, N. P., Efendieva, Kh. K. and Novotorzhina, N. N. (1974). *U.S.S.R. 432,139* (1974) *Chem. Abstr.*, **81**, 63172a.
[80] Trofimov, B. A., Amosova, S. V., Ivanova, N. I., Vereshchagin, L. I. and Gavrilov, L. D. (1977). *U.S.S.R. 556,137* (1977) *Chem. Abstr.*, **87**, 134751a.
[81] Trofimov, B. A., Ivanova, N. I. and Amosova, S. V. (1979). *Zh. Org. Khim.*, **15**, 2337.
[82] Sauer, J. C. (1959). *J. Org. Chem.*, **24**, 1592.
[83] Nedolya, N. A., Komelkova, V. I. and Trofimov, B. A. (1985). *Zh. Org. Khim.*, **21**, 1173.
[84] Trofimov, B. A., Nedolya, N. A. and Komelkova, V. I. (1987). *Z. Chem.*, **27**, 24.
[85] Nedolya, N. A. and Trofimov, B. A. (1994). *Sulfur Rep.*, **15**, 237.
[86] Trofimov, B. A., Amosova, S. V., Ivanova, N. I., Tarasova, O. A. Al'pert, M. L. and Dmitrieva, G. V. (1986). *Zh. Org. Khim.*, **22**, 2145.
[87] Sokolyanskaya, L. V., Volkova, K. A., Volkov, A. N. and Trofimov, B. A. (1981). *Zh. Org. Khim.*, **17**, 2269.
[88] Sokolyanskaya, L. V. (1984). *Sintez Azotsoderzhashchikh Soedinenii na Osnove Diatsetilena* (Kand. Diss., Irkutsk).