Anomeric Effect Involving Carboxyl and Ethynyl Group in Sulfur-Containing Heterocycles

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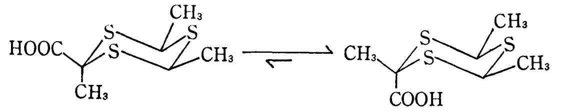
Normal anomeric effect is found in 1,3-dithiane-2-carboxylic acid, 1,3,5-trithiane-2-carboxylic acid, and their esters, in contrast to a report that oxane-2-carboxylic acid derivatives exhibit reverse anomeric effect. The results are interpreted from the difference in bond lengths between oxanes and polythianes which affects the extent of 1,3-diaxial interaction. The anomeric effect is found to be larger in 1,3-dithianes than in 1,3,5-trithianes. The differences is discussed on the ground of the energy levels of available electrons. Phenylethynyl derivatives also show small but definite anomeric effect.

During the course of other study, we needed a pair of 2,4,5-trimethyl-1,3,5-trithiane-2-carboxylic acids. Since the electrophilic reaction of 1,3,5-trithianide or 1,3-dithianide anion is known to proceed from the equatorial side,[1,2] it is no wonder to obtain 2,*c*-4,*c*-6-trimethyl-1,3,5-trithiane-*r*-2-carboxylic acid (**1e**) on treatment of 1,3,5-trithianide anion with carbon dioxide. We then tried to equilibrate **1e** with 2,*t*-4,*t*-6-trimethyl-1,3,5-trithiane-*r*-2-carboxylic acid (**1a**) with the aid of an acidic catalyst. The result was, however, almost a complete conversion to **1a**.



1e **1a**

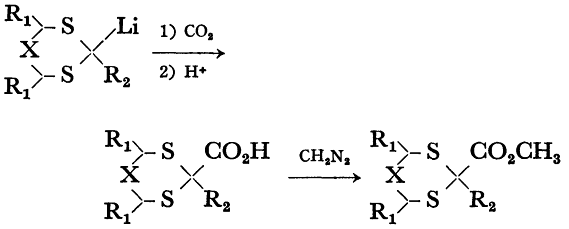
The result indicates that the carboxyl-axial form is more stable than the carboxyl-equatorial form by *ca.* 2 kcal/mol or more and aroused our interest for the following reasons. The equilibration results may be explained by the stabilization of isomers governed by the anomeric effect,[3] since the carboxyl group is electronegative and provides a low-lying lowest unoccupied molecular orbital (LUMO). The anomeric effect in trithiane is known to be strong.[4] Contrary to these considerations, however, methyl oxanecarboxylate derivatives were found to be more stable in the methoxycarbonyl-equatorial conformation[5] and the phenomenon is referred to as reverse anomeric effect.

This sharp contrast of the trithiane case to the case of oxanes stimulated the further study on the reverse and/or normal anomeric effect and a series of studies of the polythiane cases have been undertaken. This paper is to describe the results of such studies, which conclude the presence of anomeric effect in the carboxypolythianes.

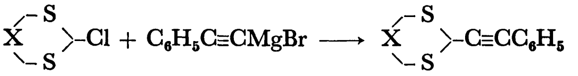
Syntheses and Structural Assignment

The monocarboxylic acids were prepared by carbonation of the corresponding lithio derivatives. Esters of the acids were prepared by the action of diazomethane on the free acids. Action of thionyl chloride to form acid chloride gave satisfactory results with the stable carboxylic acids but caused isomerization when applied to the less stable ones.

Phenylethynyl derivatives were prepared from chloropolythianes and phenylethynylmagnesium bromide.



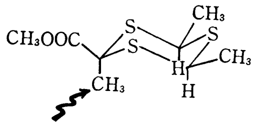
1: $R_1=R_2=CH_3$, X=S **5**: $R_1=R_2=CH_3$, X=S
2: $R_1=CH_3$, R_2=H, X=S **6**: $R_1=R_2$=H, X=S
3: $R_1=R_2$=H, X=S **7**: $R_1=R_2$=H, X=CH_2
4: $R_1=R_2$=H, X=CH_2



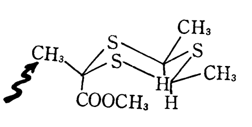
8: X=S
9: X=CH_2

When a compound in question carries an α-proton to the carboxyl or methoxycarbonyl group, the structural assignment is straightforward. The proton gives a singlet signal and the paramagnetic shift is observed for the axial proton owing to the anisotropy of the C–S bonds.[6] Therefore the carboxyl-axial form gives a singlet signal at a higher field than the counterpart. In addition, the axial isomer gives a broad signal for the equatorial proton due to the presence of W-type long range coupling.[7] The difference in chemical shifts of methylene protons is also a clue for diagnosis of the conformation of 2-substituted 1,3,5-trithianes. The substituent-axial conformation gives larger difference in chemical shifts than the counterpart because of the anisotropy effect of the substituent.[4]

Those which possess a methyl group in α-position may be assigned in a similar manner. However, ambiguity may arise because of the long averaged distance of the methyl protons from the C–S bonds. Firm evidence for the configurations of **5a** and **5e** was obtained by measurement of the nuclear Overhauser effect. On irradiation of the methyl protons in position 2 of compound **5e**, the absorption intensity of the methine protons in positions 4 and 6 increased by 16%. In contrast, the same operation for the isomer **5a** caused no measurable enhancement. The results unambiguously show that 4- and 6-H's and 2-methyl are located closely in compound **5e** and consequently compound **5e** has the structure as shown.



5e



5a

Results and Discussion

Equilibration of Polymethyltrithianecarboxylic Acids. Equilibration was carried out by using boron trifluoride etherate as a catalyst in various solvents and the results are summarized in Table 1.

Table 1. Conformational equilibrium data of polymethylpolythianecarboxylic acids and their derivatives at 23 °C

System	Solvent	ε	K	$\Delta G°$ (kcal/mol)
1a$\rightleftarrows$**1e**	CCl_4	2.2	<0.02	>2.3
	CH_3CN	37.5	<0.02	>2.3
5a$\rightleftarrows$**5e**	CCl_4	2.2	<0.005	>3.2
	$ClCH_2CH_2Cl$	10.7	<0.005	>3.2
	CH_3CN	37.5	~0.01	~2.7
2a$\rightleftarrows$**2e**	CH_3CN	37.5	0.4	0.24

The results indicate that the axial form **1a** is one-sidedly more stable than the equatorial isomer **1e** in various solvents. The solvent effect on population is hardly seen because of the strong stabilization of the axial isomer: it is only acetonitrile that enabled us to measure the population of the less stable form of the ester and to calculate the difference in free energies at 23 °C which was obtained as 2.7 kcal/mol. In a series of cyclohexane derivatives, *A* values for methyl and methoxycarbonyl groups are known to be 1.7 and 1.2 kcal/mol, respectively.[8,9] Therefore the difference in conformational energies between cyclohexane analogs of **1a** and **1e** may amount to 0.5 kcal/mol: if we assume the same steric conditions in polythianes, the methyl-equatorial form is favored over the methyl-axial form and the ratio may be 1/3—1/2 with the former predominating. Since the ratio in reality is large in favor of the methyl-equatorial form, there must be reasons which stabilize that form and/or destabilize the other form. Anomeric effect can be present in these compounds because the carboxyl group has a low-lying LUMO. If the above-cited solvent effect is taken to be significant, it also supports the presence of anomeric effect because the magnitude of stabilization by the anomeric effect is suppressed in polar solvents.[3]

The equilibration of 4,6-dimethyl-1,3,5-trithiane-2-carboxylic acid (**2**) should provide data which are only affected by the conformational energy of the carboxyl group. As is seen in Table 1, $\Delta G°$ value becomes smaller because of the erasure of the effect of the methyl group, but the axial form (**2a**) is still favored in acetonitrile. Unfortunately, equilibration in other solvents failed because of extensive deterioration of the substrate.

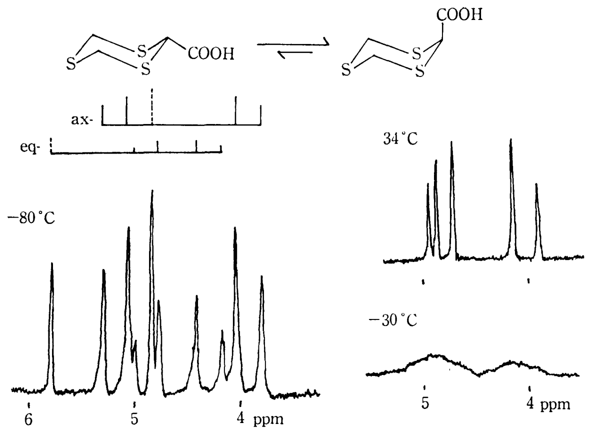
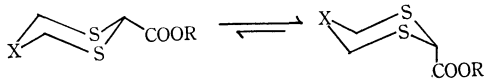


Fig. 1. ^1H NMR spectra of **3** in acetone-d_6 at three temperatures.

Low Temperature NMR Study of Polythianecarboxylic Acids. The difficulty seen in equilibration allured us to investigate the flexible polythianecarboxylic acids at low temperature. 1,3,5-Trithiane-2-carboxylic acid (**3**) and its methyl ester (**6**) showed only averaged signals at room temperature. The signal, however, broadened considerably at −40——50 °C,[10] and split into two sets of 2-H and 4,6-H's at −80 °C (Fig. 1). The results are shown in Table 2. It is interesting to note that the



3e	**3a** R=H, X=S
4e	**4a** R=H, X=CH_2
6e	**6a** R=CH_3, X=S
7e	**7a** R=CH_3, X=CH_2

Table 2. Data concerned with conformational equilibria of polythianecarboxylic acids and their derivatives at −80 °C

Compound	Solvent	Chemical shift of 2-H (δ)		a-Form/e-Form	$\Delta G°$ (kcal/mol)	*A*-Value
		e-Form	a-Form			
3	CD_3COCD_3	5.75	4.82	1.5	0.15	1.43
	CD_3COCD_3-$CDCl_3$ (3:1)	5.71	4.69	2.35	0.31	
4	CD_3COCD_3	5.42	4.48	5.5	0.66	
6	CD_3COCD_3	5.75	4.88	3.0	0.43	1.22
	CD_3COCD_3-$CDCl_3$ (3:1)	5.70	4.87	5.0	0.54	
7	CD_3COCD_3	5.44	4.53	8.5	0.83	
	CD_3COCD_3-$CDCl_3$ (3:1)	5.20	4.34	9.5	0.87	
	CS_2-$CDCl_3$ (1:1)	5.02	4.10	20	1.15	

difference in chemical shifts of the axial and equatorial protons in 2-position is almost constant at 0.9 ppm in these compounds.

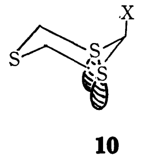
One can clearly see, from the data in Table 2, that the axial form is preferred in every case. The results are contrary to the case of 2,4,6-trimethyl-1,3,5-trithianes[11] in which the *cis* form is more stable because it has no axial methyl group. Anomeric effect is a probable cause again for the presence of the axial form. Solvent effects on the populations of the axial and the equatorial forms are in agreement with the anomeric effect: the less polar is the solvent, the more is the axial form preferred. We may now conclude that the anomeric effect is seen in polythianecarboxylic acids.

The magnitude of anomeric effect may be expressed by the following equation.[3]

$$\Delta\Delta G^\circ = (\Delta G^\circ_{\text{substituent}})_{\text{hetero ring}} - (\Delta G^\circ_{\text{substituent}})_{\text{cyclohexane}}$$

Comparison of the results reveals that the magnitude of the anomeric effect is larger in 1,3-dithiane than in 1,3,5-trithiane.

The results seem to be explained by the delocalization of electrons. The UV spectra of 1,3-dithiane and 1,3,5-trithiane[12] indicate that the lone pair electrons in the latter are more delocalized than those in the former. Sweigart and Turner reported the results of photoelectron spectroscopy which reveal that the ionization potential of lone pair electrons in 1,3,5-trithiane is higher than those in 1,3-dithiane.[13] Thus transfer of lone pair electrons on sulfur to the antibonding orbital involving the axial substituent, as discussed by Hoffmann *et al.*,[14] must be smaller in its extent in trithianes (**10**) than in dithianes (**11**). By taking advantage of the above discussion, we may understand the weaker anomeric effect and consequently less population of the substituent-axial isomer of 1,3,5-trithiane derivatives than those of the 1,3-dithianes.



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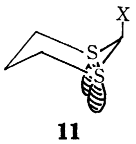

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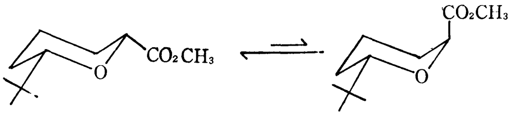
The anomeric effect is larger with the free carboxylic acids than the corresponding esters, both in trithiane series and in dithiane series. It is also known that the methoxycarbonyl group gives less preference in free energy than the carboxyl group in cyclohexane series, although the equatorial form is favored in this case.[9] The differences are almost constant at 0.2 kcal/mol. These results suggest that the difference is not of the electronic or electric origin but of the steric origin. Since the carboxyl group shows less preference of the axial form than the corresponding esters in polythianes, the latter may be taken as giving less steric effect. This is reasonable because the acid dimerizes under the conditions of the NMR measurement. Negligence of the electronic-electic effect will not give an important defect, since Hammett σ_m values of the carboxyl and methoxycarbonyl groups are 0.36 and 0.32, respectively.[15]

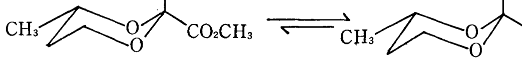
Comparison of the above results with those of oxane series is worthy of note. Methyl 5-*t*-butyloxane-2-carboxylate (**12**) was equilibrated with a base catalyst to show that the methoxycarbonyl-equatorial form (**12e**) is predominant in the equilibrium mixture. The phenomenon has been referred to as reverse anomeric effect.



12e **12a**

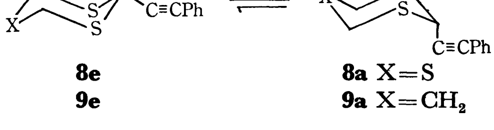
However, owing to the short distance of the C–O bond in oxanes, the 1,3-*syn*-diaxial interaction must be more severe in oxane series.[5] This disfavors the axial conformation. In trithianes and dithianes, the C–S bond is much longer than the C–O and the 1,3-diaxial interaction is surpressed to a great extent. Normal anomeric effect thus becomes detectable as conformational equilibrium constants.

Eliel *et al.* prepared ethyl 2,4-dimethyl-1,3-dioxane-2-carboxylate (**13**) under the conditions of thermodynamic control and found that the ethoxycarbonyl-axial conformation (**13a**) is disfavored in less polar solvents. The results are in line with the reverse anomeric effect,



13e **13a**

but the system may be too complicated to interprete in a straightforward manner, as suggested by the authors.[16]



8e **8a** X=S

9e **9a** X=CH$_2$

Finding the presence of anomeric effect in polythianecarboxylic acids, we were allured to investigate the case of phenylethynylpolythianes. The results are shown in Table 3.

Table 3. Data concerned with conformational equilibria of 2-phenylethynylpolythianes at −80 °C

Compd.	Solvent	Chemical Shift of 2-H (δ)		a-Form/e-Form	ΔG° (kcal/mol)
		e-Form	a-Form		
8	CD$_3$COCD$_3$	6.00	5.68	1.18	0.07
	CS$_2$–CDCl$_3$ (1:1)	5.21	4.96	3.3	0.46
9	CD$_3$COCD$_3$	5.62	5.21	1.57	0.18
	CS$_2$–CDCl$_3$ (1:1)	5.16	4.73	3.1	0.44

The data suggest the presence of small but distinct anomeric effect in the phenylethynyl compounds: the axial forms (**8a** and **9a**) are preferred over the equatorial forms (**8e** and **9e**) in the solvents examined and the preference becomes less in more polar solvents. The 2-phenylethynyl group, providing a low-lying LUMO, seems to be effective in accepting the electrons from the sulfur atoms in 1 and 3 positions.

Experimental

^{1}H NMR Measurement. The ^{1}H NMR spectra were recorded on a Hitachi R 20B spectrometer (60 MHz) equipped with a temperature variation accessory. Temperature was read by the difference in chemical shifts between protons of methanol.

Preparation of Carboxylic Acids and Their Esters. A general procedure of preparation of carboxylic acids will be described by taking the case of 1,3-dithiane-2-carboxylic acid (**4**) as an example. To a solution of 2.0 g (16.7 mmol) of 1,3-dithiane in 100 ml of tetrahydrofuran was added 18.5 mmol of butyllithium in 30 ml of ether at −20 °C and the mixture was stirred for 1 h at that temperature under a nitrogen atmosphere. Dried carbon dioxide was introduced into the solution for 3 h, during which time the temperature was allowed to rise to 0 °C, and the mixture was left to stand overnight. The solvent was evaporated and the residue was shaken with a mixture of dilute aqueous sodium hydroxide and ether. The aqueous layer was separated, acidified with hydrochloric acid, and extracted with ether. The ethereal solution was dried over magnesium sulfate and evaporated. 1,3-Dithiane-2-carboxylic acid (**4**), mp 112—113.5 °C, was obtained in 1.8 g (66%) yield. Found: C, 36.48; H, 4.69; S, 39.11%. Calcd for $C_5H_8O_2S_2$: C, 36.57; H, 4.91; S, 39.04%. IR: 1685—1690 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR: (δ, CDCl$_3$): 2.1 (m, 2H), 2.4—3.7 (m, 4H), 4.17 (s, 1H), *ca.* 9 (s, 1H).

The methyl ester (**7**) was prepared almost quantitatively by treatment of the acid with diazomethane in ether. It was purified by chromatography on silica gel with benzene, oil (mp between 20 and 30 °C). Found: C, 40.53; H, 5.59; S, 35.81%. Calcd for $C_6H_{10}O_2S_2$: C, 40.43; H, 5.65; S, 35.97%. IR: 1730 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CDCl$_3$): 3.77 (s, 3H), 2.10 (m, 2H), 2.4—2.8 (m, 2H), 3.2—3.65 (m, 2H), 4.20 (s, 1H).

It could also be prepared by treating the corresponding acid with thionyl chloride in carbon tetrachloride–chloroform (9: 1) at reflux temperature for 5 to 7 h followed by treatment with methanol.

1,3,5-Trithiane-2-carboxylic acid (3), mp 273 °C (decomp.), was prepared similarly from 1,3,5-trithiane. Found: C, 26.65; H, 3.35; S, 52.57%. Calcd for $C_4H_6O_2S_3$: C, 26.37; H, 3.32; S, 52.77%. IR: 1690 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, acetone-d_6): 4.02 and 4.77 (q, J=14.5 Hz, 4H), 4.83 (s, 1H).

The methyl ester (**6**) melted at 96—97 °C. Found: C, 30.83; H, 4.34; S, 49.22%. Calcd for $C_5H_8O_2S_3$: C, 30.59; H, 4.11; S, 49.00%. IR: 1715 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CCl$_4$): 3.78 (s, 3H), 3.46 and 5.06 (q, J=15 Hz, 4H), 4.22 (s, 1H).

Treatment of *cis*-2,4,6-trimethyl-1,3,5-trithiane with butyllithium followed by carbonation gave 2,*c*-4,*c*-5-trimethyl-1,3,5-trithiane-*r*-2-carboxylic acid (**1e**), mp 137—138.5 °C, as a sole product. Found: C, 37.72; H, 5.14; S, 42.77%. Calcd for $C_7H_{12}O_2S_3$: C, 37.48; H, 5.39; S, 42.87%. IR: 1703 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CDCl$_3$): 1.59 (d, 6H), 2.07 (s, 3H), 4.39 (q, 2H), *ca.* 9 (s, 1H).

The methyl ester (**5e**) melted at 53—54 °C. Found: C, 40.25; H, 5.72; S, 40.35%. Calcd for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92; S, 40.35%. IR: 1737 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CCl$_4$): 1.54 (d, 6H), 1.95 (s, 3H), 3.82 (s, 3H), 4.29 (q, 2H).

Treatment of *cis*-2,4-dimethyl-1,3,5-trithiane with butyllithium followed by carbonation afforded *c*-4, *c*-6-dimethyl-1,3,5-trithiane-*r*-2-carboxylic acid (**2e**), mp 165—166 °C (decomp.), as a sole product. Found: C, 34.35; H, 5.03; S, 45.51%. Calcd for $C_6H_{10}O_2S_3$: C, 34.26; H, 4.79; S, 45.73%. IR: 1695 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, acetone-d_6): 1.53 (d, 6H), 5.26 (s, 1H). The carboxyl proton was obscured because of the presence of water in the solvent.

t-*4*,t-*6-Dimethyl-1,3,5-trithiane*-r-*2-carboxylic Acid (2a).* *c*-4,*c*-6-Dimethyl-1,3,5-trithiane-*r*-2-carboxylic acid (**2e**) (0.2 g) was dissolved in 5 ml of dry acetonitrile and heated at 80 °C with 0.1 ml of boron trifluoride etherate for 3 h. The solvent was evaporated and the residue was shaken with a mixture of 20 ml of ether and 10 ml of 1 M hydrochloric acid. Evaporation of the ether layer afforded a mixture of *ca.* 3: 2 **2a** and **2e** which was extracted with carbon tetrachloride. Concentration of the carbon tetrachloride solution followed by standing afforded *ca.* 0.05 g (25%) of **2a**, mp 114—115 °C. Found: C, 33.99; H, 4.76%. Calcd for $C_6H_{10}O_2S_3$: C, 34.26; H, 4.79%. IR: 1685 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CCl$_4$): 1.50 (d, 6H), 4.76 (q, 2H), 4.58 (s, 1H), *ca.* 11.5 (s, 1H).

*2,*c-*4,*c-*6-Trimethyl-1,3,5-trithiane*-r-*2-carboxylic Acid (1a)*, mp 135.0—135.5 °C, was similarly prepared by heating 2.0 g of **1e** with 10 ml of boron trifluoride etherate at 60 °C in 75% yield. Found: C, 37.32; H, 5.12; S, 42.44%. Calcd for $C_7H_{12}O_2S_3$: C, 37.48; H, 5.39; S, 42.87%. IR: 1690 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CDCl$_3$): 1.55 (d, 6H), 1.78 (s, 3H), 4.69 (q, 2H), *ca.* 10 (s, 1H).

The methyl ester (**5a**) melted at 33.5—34.5 °C. Found: C, 40.52; H, 5.84; S, 40.41%. Calcd for $C_8H_{14}O_2S_3$: C, 40.31; H, 5.92; S, 40.35%. IR: 1728 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR (δ, CCl$_4$): 1.51 (d, 6H), 1.70 (s, 3H), 3.70 (s, 3H), 4.66 (q, 2H).

Equilibration. Either of the equatorial or the axial form of the substrate (0.2 g) was dissolved in 2 ml of an appropriate solvent, mixed with 0.031 ml (*ca.* 1/3 equivalent) of boron trifluoride etherate, and allowed to stand at 23±2 °C. The progress of equilibration was followed by ^{1}H NMR spectra. It took *ca.* 60 days for equilibration of **1** in acetonitrile which required the longest time among the solvents used.

The analyses of the products were performed with integration of the ^{1}H NMR signals and the error is estimated to be ±2%. The esters were analyzed with vapor phase chromatography and the results are believed to be accurate within the error of ±0.5%.

2-Phenylethynyl-1,3-dithiane (9). To a solution of 2.2 g (18.5 mmol) of 1,3-dithiane in 20 ml of sodium-dried benzene was added 2.7 g (20.3 mmol) of *N*-chlorosuccinimide during a 15 min period at 20 °C under a nitrogen atmosphere. The mixture was stirred for 15 min under the same conditions and filtered. To this solution was added phenylethynylmagnesium bromide in ether which was prepared from 2.55 g (25 mmol) of phenylacetylene and isopropylmagnesium bromide (from 3.25 g of isopropyl bromide, 0.7 g of magnesium and 50 ml of ether) at 35 °C. The mixture was stirred for 2 h at room temperature and treated with dilute hydrochloric acid. Extraction of the mixture with chloroform afforded 2.6 g of crude 2-phenylethynyl-1,3-dithiane, which was purified by chromatography on silica gel. Elution with benzene–hexane (8: 2) gave a pure compound, mp 54—55.5 °C in 35% yield. Found: C, 65.40; H, 5.54%. Calcd for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49%. IR: 2220 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (δ, CCl$_4$): 1.8—2.3 (m, 2H), 2.5—3.5 (m, 4H), 4.63 (s, 1H), 7.3 (m, 5H).

2-Phenylethynyl-1,3,5-trithiane (8), mp 66—67 °C, was similarly prepared from 1,3,5-trithiane. Found: C, 55.17; H, 4.03; S, 40.19%. Calcd for $C_{11}H_{10}S_3$: C, 55.42; H, 4.23; S, 40.35%. IR: 2205 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (δ, CDCl$_3$): 3.91 and 4.83 (q, J=14.5Hz, 4H), 5.04 (s, 1H), 7.39 (m, 5H).

References

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