STEREOCHEMISTRY OF THE HOMOLYTIC HETEROCYCLIZATION OF ALKYNES WITH 1,2-ETHANEDITHOL INTO 1,4-DITHIANES

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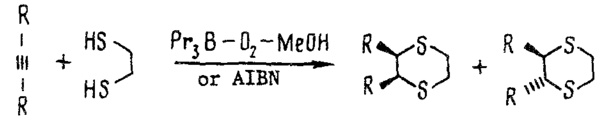
The homolytic heterocyclization of dialkyl- and diaryl-acetylenes with 1,2-ethanedithiol leads stereoselectively to cis-2,3-disubstituted 1,4-dithianes. The stereochemistry of the reactions is determined by a combination of homolytic trans addition at the triple bond and intramolecular homolytic cis addition at the double bond. The main product of the heterocyclization of dimethyl acetylenedicarboxylate is dimethyl 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate.

The progress made in the last decade in the chemistry of organic free radicals has led to the extensive introduction of homolytic methods into the arsenal of organic synthesis. Having lost completely the aureole of "exoticism," these reactions have provided effective means of synthesis in the building of new carbon–carbon and carbon–heteroatom bonds and of new heterocyclic systems [1-3].

The development of mild methods of initiating free-radical processes and the detailed study of their mechanism have enabled us to find many intermolecular [4] and intramolecular [5, 6] radical reactions which find application in the stereoselective synthesis of complex organic compounds [6].

In continuation of investigations on stereochemical aspects of homolytic reactions [7-9], in the present work we studied the stereoselectivity of the homolytic heterocylization of alkynes with dithiols: A reaction that provides a general method for the synthesis of 1,3- and 1,4-dithiacycloalkanes [10].

We found that the heterocyclization of the disubstituted acetylenes (Ia)-(Ic) containing substituents of the alkyl type at the C≡C bond with 1,2-ethanedithiol (II) initiated by tripropylborane in methanol or by azobisisobutyronitrile (AIBN) goes stereoselectively with cis-2,3-disubstituted 1,4-dithianes as the main products.*



(Ia-c) (II) (IIIa-c) (IVa-c)

R = Pr (a), CH_2OAc (b), CH_2Cl (c).

The relative amounts of stereoisomers (IIIa):(IVa), (IIIb):(IVb), and (IIIc):(IVc) are 75:25, 90:10, and 65:35, respectively; the overall yields of the mixtures of stereoisomers are 37, 40-54, and 21%, respectively. It must be emphasized that these proportions are practically independent of the method of initiating the heterocyclization.

On the other hand, the reaction between diphenylacetylene (Id) and (II) proved to be extremely sensitive to the nature of the initiator. When AIBN is used as initiator, apart from cis- and trans-2,3-diphenyl-1,4-dithianes (IIId) and (IVd), unsaturated 2,3-dihydro-

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*For previous communication, see [11].

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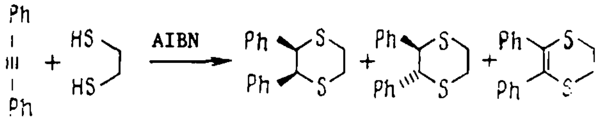
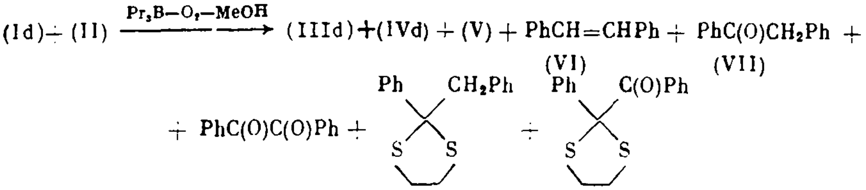
5,6-diphenyl-1,4-dithiin (V) is formed; relative amounts (IIId):(IVd):(V) = 20:2:1 [according to PMR spectral data (250 MHz)]; overall yield of (IIId), (IVd), and (V) 50%.



(Id) (II) (IIId) (IVd) (V)

When initiation of reaction is with the system Pr_3B-O_2-MeOH, a complex mixture of products is obtained: Apart from the 1,4-dithiacycloalkanes (IIId), (IVd), and (V), this contains cis-stilbene (VI), benzyl phenyl ketone (VII), benzil (VIII), and the 1,3-dithiacycloalkanes 2-benzyl-2-phenyl-1,3-dithiolane (IX) and 2-benzoyl-2-phenyl-1,3-dithiolane (X).



(VIII) (IX) (X)

Thus, also in the case of diphenylacetylene (Id) heterocyclization with (II) is a cis-stereoselective reaction, and the ratio cis-(IIId):trans-(IVd) exceeds 10:1.

The radical character of the heterocyclization reaction studied and the intermediate generation of organothio radicals were discussed by us in detail in [10]. It is known that the stereochemistry of the addition of organothio radicals at multiple bonds depends on the substituents in the unsaturated compounds and the thiols, the methods of generating the radicals, and the reaction conditions [12-14]. A number of reactions of this type go stereoselectively, but, on the whole, there are no rigorous relations determining the stereochemistry. This is determined to a large extent by the reversibility of the addition of the organothio radicals [12, 13].

In accordance with the discussion in [10], the mechanism of the reactions of (Ia)-(Id) with (II) includes the homolytic addition of 1-mercaptoethylthio radicals (XI) at the triple bond of (I) with the intermediate formation of the unsaturated thiols (XIIIa)-(XIIId).

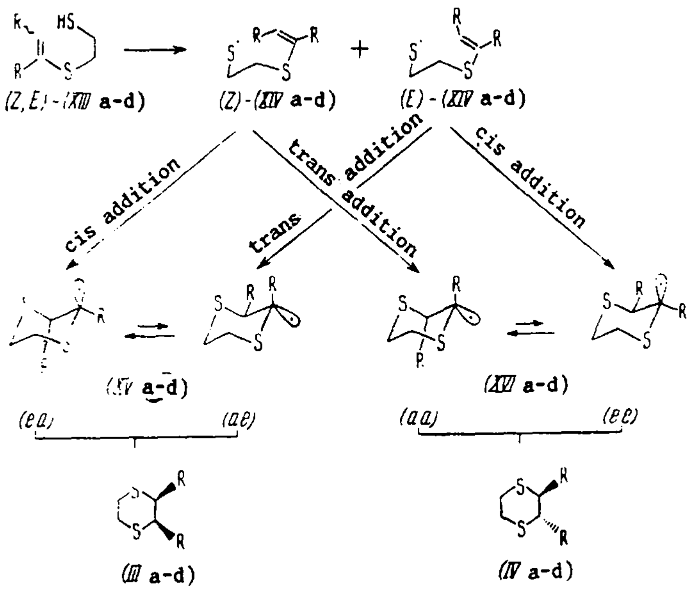
$$\underset{(II)}{HS(CH_2)_2SH} \xrightarrow{\text{initiator}} \underset{(XI)}{\dot{S}CH_2CH_2SH}$$

$$R-C\equiv C-R + \underset{(XI)}{\dot{S}CH_2CH_2SH} \rightarrow \underset{(XII)}{R\dot{C}=C(R)SCH_2CH_2SH}$$

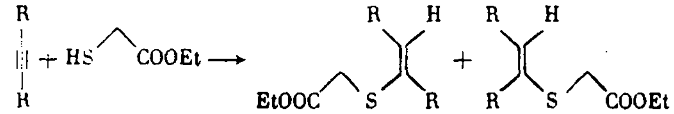
$$(XII) \xrightarrow{(II)} \underset{(XIIIa-d)}{RCH=C(R)SCH_2CH_2SH} + (XI)$$

The subsequent intramolecular homolytic cyclization of (XIIIa)-(XIIId) through the intermediate organothio radicals (XIVa)-(XIVd) leads to the stereoisomeric cyclic radicals (XVa)-(XVd) and (XVIa)-(XVId), which are precursors of the cis- and trans-1,4-dithianes (IIIa)-(IIId) and (IVa)-(IVd) (see scheme on top of following page). As can be seen from the above scheme, the following factors can have a determining influence on the stereochemistry of the process as a whole: the configuration of the double bond in the unsaturated thiols (XIIIa)-(XIIId), the steric direction of the sulfur-centered radical on the C=C bond in the intramolecular cyclization of the radicals (XIV), and the relative configurational stability (including the possibility of interconversion) of the radicals (XV) and (XVI) in the removal by them of hydrogen atoms with the formation of the cis- and trans-1,4-dithianes (III) and (IV).

In the homolytic-addition reactions of ethyl mercaptoacetate (XVII) with 4-octyne (Ia) and 1,4-diacetoxy-2-butyne (Ib), which model the first stage of the addition of 1,2-ethane-



dithiol (II) to the same alkynes, we obtained a mixture of stereoisomeric arylthio-substituted (Z)- and (E)-alkenes (XVIIIa) and (XVIIIb).



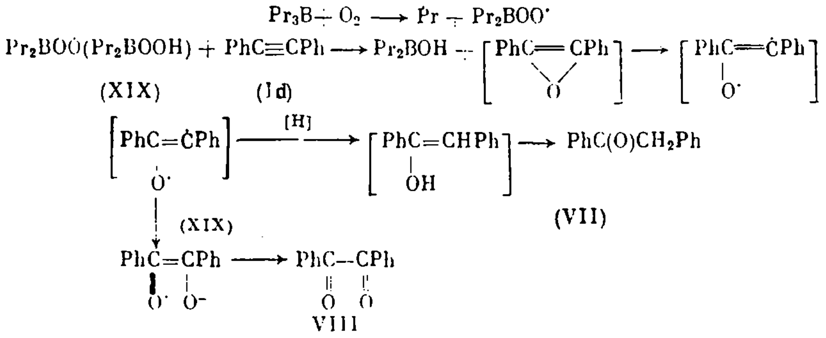
(Ia, b) (XVII) (Z)-(XVIIIa, b) (E)-(XVIIIa, b)
R = Pr (a), CH_2OAc (b).

The relative amounts of (Z) and (E) isomers are 61:39 for (XVIIIa) and 82:18 for (XVIIIb), which correlates satisfactorily with the proportions of the cis and trans isomers (IIIa):(IVa) and (IIIb):(IVb), which, as indicated above, are 75:25 and 90:10. We can justifiably suppose that in the mixtures of stereoisomers (XIIIa)-(XIIId), as also in (XVIIIa) and (XVIIIb), there is a predominance of (Z) isomers, which logically must be regarded as precursors of the cis isomers of (IIIa)-(IIId), the main reaction products. Correspondingly, the (E) isomers of (XIIIa)-(XIIId) must be converted into the trans products (IVa)-(IVd). From the scheme of the process given above it follows that this explanation can be valid if the cyclization of the radicals (XIV) proceeds completely or mainly as intramolecular radical cis addition to the double bond. Cyclization by the trans addition mechanism would lead to a reversal of the relative amounts of the products (III) and (IV). However, we can admit the possibility of trans addition if the reaction E-(XIV) → (XV) → (III) is faster than the reaction Z-(XIV) → (XVI) → (IV). Such a ratio of the rates is in full accord with the higher stability of the intermediately formed radicals ae-(XV) in comparison with aa-(XVI), in which both substituents occupy sterically unfavorable axial positions.

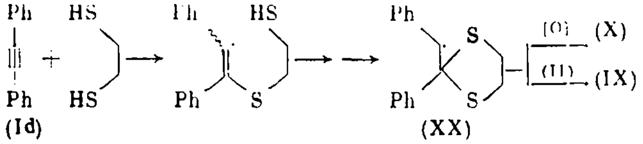
Apart from the orientation of the substituents R, substantial influence on the relative stabilities of the radicals (XV) and (XVI) is had by the orientation of the orbital occupied by the unpaired electron. The anomeric orbital interaction $n_S \rightarrow \sigma$ must stabilize the axial disposition of this orbital (similarly to compounds containing oxygen or nitrogen atoms in the ring [15]). Taking these factors into account, we must expect that the energy of the radicals rises when we pass from the radical ee-(XVI) to the radicals ea-(XV) and ae-(XV) and further to the least stable aa-(XVI). It is not known whether the conformational transitions between the radicals indicated in the scheme by two-way arrows are effected during the time taken by the reaction, or each of them is converted independently into the final product. In principle, these transitions should not influence the stereochemical result of the reaction. The picture of the transformations will be still more complex if in this process the reversibility of the addition of organothio radicals is realized [12, 13].

From the experimental results it follows that the proportions of the reaction products are influenced by the nature of the substituent R. When R = Ph or CH_2OAc, the proportion of the cis isomer (III) is appreciably higher than when R = Pr or CH_2Cl, however, a sufficiently soundly based interpretation of this fact does not appear to be possible.

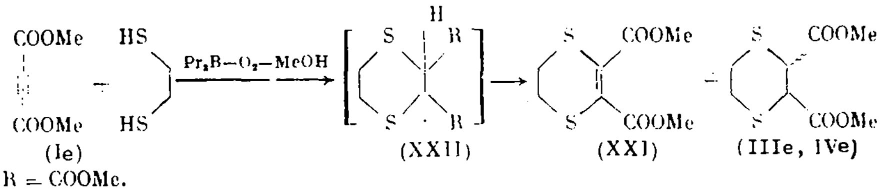
The complex composition of the mixture of the products of the reaction of (Id) with (II) when initiated by the system Pr_3B–O_2–MeOH may be explained on the view that the intermediately formed boron-containing peroxy radical (XIX) (and the corresponding peroxide) [15, 16] acts as an oxidant [oxygen carrier to the triple bond in (Id)], and the source of H atoms is the dithiol (II):



The 1,3-dithiolane (IX) is most probably formed in the radical 1,1-addition of the dithiol (II) to (Id) (cf. [10]), but the dithiolane (X) probably as a result of the oxidation of the intermediate radical (XX):



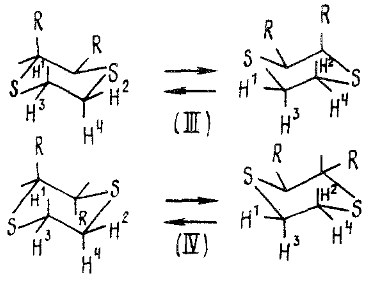
As stated above, a minor product of the heterocyclization of (Id) with (II) is 2,3-dihydro-5,6-diphenyl-1,4-dithiin (V). An analogous direction of heterocyclization becomes the main course in the case of dimethyl acetylenedicarboxylate (Ie, R = COOMe), the main product being dimethyl 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate (XXI), yield 27%. A mixture of the stereoisomers of 1,4-dithiane-2,3-dicarboxylate (IIIe) and (IVe) is formed only as a by-product. Because of the lowness of the yield of the latter, the exact proportions of the stereoisomers could not be determined.



We suppose that the intermediary in this reaction, the radical adduct (XXII, R = COOMe) containing a fairly mobile β-H atom, readily loses the latter with the formation of the conjugated ($O=CC=CC=O$) 1,4-dithiin (XXI). In an analogous way, from (XXII, R = Ph) 2,3-dihydro-5,6-diphenyl-1,4-dithiin (V) is formed. Naturally, the acidity-inducing influence of the COOMe group on β-H is substantially higher than that of Ph, which is responsible for the considerably higher yield of (XXI) in comparison with (V). By intermolecular H elimination the intermediaries (XXII, R = COOMe) and (XXII, R = Ph) are converted respectively into (IIId) + (IVd) and (IIIe) + (IVe).

In the present work we resolved the important question of the configuration of the stereoisomeric cis- and trans-2,3-disubstituted 1,4-dithianes (IIIa)-(IIId) and (IVa)-(IVd) and determined their proportions from PMR- and ^{13}C NMR-spectral data.

It is known that 1,4-dithiane and its derivatives suffer fast chair–chair conformational interconversion [18, 19]. A process of this kind is characteristic at -20°C also for the cis and trans isomers of the 2,3-disubstituted 1,4-dithianes (IIIa)-(IIId) and (IVa)-(IVd) studied. Here the protons of the fragment $S-CH_2-CH_2-S$ give a time-averaged spectrum, which is described by the spin system AA'BB'.



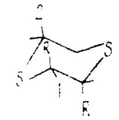
In the chair conformers of 1,4-dithiane the vicinal coupling constants have the following values: $^3J_{aa}$ = 11.5, $^3J_{ee}$ = 4.6, $^3J_{ae}$ = 4.2 Hz [18].

Because of energetic degeneracy and therefore equality of population in the cis isomers (IIIa)-(IIId), the averaged coupling constants $^3J_{1,4}$ and $^3J_{3,2}$ are equal to one another and are close to the arithmetic mean of $^3J_{aa}$ and $^3J_{ee}$ $[1/2 \cdot (11.5 + 4.6) \simeq 8$ Hz]. In the trans isomers (IVa)-(IVd), in the general case the same averaged coupling constants are not equal to one another, for the conformers are not equivalent energetically. For both isomers the coupling constants $^3J_{1,4}$ and $^3J_{3,2}$ scarcely change in the conformational transition $^3J_{ae} \rightleftarrows {}^3J_{ea}$ and are ~2.5 Hz. The proportions of the cis and trans isomers of 2,3-bis(acetoxymethyl)-1,4-dithiane (IIIb) and (IVb) and of 2,3-bis(chloromethyl)-1,4-dithiane (IIIc) and (IVc) were determined from PMR-spectral data (from the integral intensities of the nonoverlapping signals of the CH_2 groups of the substituents CH_2OAC and CH_2Cl), while the proportions of the cis and trans isomers of 2,3-diphenyl-1,4-dithiane (IIId) and (IVd) were determined from the signals of the CH protons of the fragment SCH(Ph)·CH(Ph)S.

For 2,3-dipropyl-1,4-dithiane the proportions of the stereoisomers (IIIa) and (IVa) were determined from ^{13}C NMR spectral data. The assignment of the signals of these compounds (Table 1) was based on measurements at low temperature. The signals of the cis isomer (IIIa) are broadened appreciably already at -20°C, and, when the temperature is lowered to −100°C, each of them is split into two signals of equal intensity, which corresponds to a fixed axial—equatorial arrangement of the C_3H_7 substituents. In the low-temperature spectrum of the trans isomer (IVa) each signal is also split into two, but in 1:2 proportions, which indicates some energetic preference of the axial—axial or equatorial—equatorial conformation.‡ Broadening of the signals of the dithiane ring was observed also in the ^{13}C NMR spectra of cis-(IIIb) and cis-(IIIc) at 20°C.

TABLE 1. Chemical Shifts of ^{13}C NMR Signals (ppm) of 2,3-Disubstituted 1,4-Dithianes (in acetone-d_6)

cis-(IIIa-d)



trans-(IVa-c)

Compound	R	C^1	C^2	Substituent
(IIIa)	$CH_3CH_2CH_2$	46,1	28.2	33.4(CH_2): 21.3(CH_2): 14,3(CH_3)
(IVa)	$CH_3CH_2CH_2$	45.1	26.9	36.5(CH_2): 21.0(CH_2): 14.3(CH_3)
(IIIb)	$CH_3C(O)OCH_2$	41.9	28.1	64.0(CH_2): 20.9(CH_3): 170.7(C=0)
(IVb)	$CH_3C(O)OCH_2$	36.8	24.1	64.6(CH_2): 20.9(CH_3): 170.1(C=0)
(IIIc)	$ClCH_2$	46.1	28.4	44.8(CH_2Cl)
(IVc)	$ClCH_2$	38,9	23.8	46.8(CH_2Cl)
(IIId) *	C_6H_5	48,9	28.5	140.2 (ipso), 127,7 (ortho) 126.6 (meta), 127.1 (para)
(IVd)			**	

*Solution in $CDCl_3$.

**Because of the low content of the trans isomer in the mixture, its signals in the spectrum could not be distinguished.

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‡Results of the conformational analysis of the 1,4-dithianes synthesized will be published later.

EXPERIMENTAL

The GLC analysis was conducted in a Chrom-5 chromatograph with a flame-ionization detector in a stream of N_2 on a glass column, 3 × 2450 mm, filled with 5% of Superphase on Inerton Super 0.16-0.20 mm. The PMR spectra of solutions in $CDCl_3$ were determined on a Bruker WM-250 spectrometer (250 MHz). The ^{13}C NMR spectra of solutions in $CDCl_3$ and $(CD_3)_2CO$ were determined on Bruker WM-250 (62.9 MHz) and Bruker AM-300 (75.5 MHz) spectrometers. Chemical shifts are given on the δ scale relative to TMS. Mass spectra were determined on a Varian MAT spectrometer with the direct introduction of the sample into the source of ions; energy of ionizing electrons 70 eV.

Tripropylborane was synthesized by the reaction of $BF_3 \cdot OEt_2$ with propylmagnesium bromide in accordance with [20]; yield of Pr_3B 78%, bp 53°C (10 mm). For the preparation of a 1 M solution of Pr_3B in hexane 11.2 g (15.5 ml) of Pr_3B was dissolved in 64.5 ml of hexane in an atmosphere of argon. 1,2-Ethanedithiol (II), which was supplied by Merck, 4-octyne (Ia), and diphenylacetylene (Id) were used without further purification. 1,4-Dichloro-2-butyne (Ic) was purified by vacuum distillation. By the acetylation of 1,4-butanediol by the action of AcCl—Py in CH_2Cl_2 we synthesized 1,4-diacetoxy-2-butyne (Ib); yield 79%, bp 123°C (11 mm), mp 27°C; PMR spectrum (δ, ppm): 2.0 s (6H, CH_3), 4.7 s (4H, CH_2).

Reaction of 4-Octyne (Ia) with 1,2-Ethanedithiol (II) in the Presence of AIBN. A solution of 0.33 ml (0.38 g, 4 mmoles) of the dithiol (II), 0.59 ml (0.44 g, 4 mmoles) of 4-octyne (Ia), and 0.1 g (15 mole %, 0.6 mmole) of AIBN on 40 ml of benzene was heated for 4 h at 80°C. The solution was evaporated, and by the chromatography of the residue on a column of SiO_2 (eluent hexane—ether 20:1) we isolated 0.30 g (37%) of a mixture of cis- and trans-2,3-dipropyl-1,4-dithianes (IIIa) and (IVa). Found, %: C 58.88; H 10.28; S 31.44. Calculated, %: C 58.76; H 9.86; S 31.37. PMR spectrum of the mixture of (IIIa) and (IVa) (δ, ppm): 0.92 t (6H, CH_3), 1.30-1.95 m (8H, $\underline{CH_3}C\underline{H_2}C\underline{H_2}$), 2.55-3.05 m (6H, CH_2S and CHS). The ^{13}C NMR spectral data are given in Table 1.

Reaction of 4-Octyne (Ia) with 1,2-Ethanedithiol (II) in the Presence of Pr_3B. To a solution of 0.59 ml (0.44 g, 4 mmoles) of (Ia), 0.37 ml (0.41 g, 4.4 mmoles) of 1,2-ethanedithiol (II), and 0.65 ml (0.51 g, 16 mmoles) of MeOH in 40 ml of benzene in an atmosphere of argon 4 ml of a 1 M solution of Pr_3B (4 mmoles) in hexane was added. The progress of the reaction was followed by means of GLC until the reactants (Ia) and (II) had disappeared. After 24 h the mixture was treated with 20 ml of saturated NH_4Cl solution, the organic layer was separated, the aqueous layer was extracted with three 15-ml portions of EtOAc, and the extract was dried with $MgSO_4$ and evaporated. In the residue by means of GLC we determined the overall yield (30%) of stereoisomeric cis- and trans-2,3-dipropyl-1,4-dithianes (IIIa) and (IVa). The yield of (IIIa) and (IVa) is raised to 39% by passing air into the reaction mixture for 24 h.

On the replacement of benzene as solvent by hexane (reaction time 1 h) or by THF (reaction time 4 h) without the subsequent passage of air the yields of (IIIa) + (IVa), determined by means of GLC, were 36 and 37%, respectively. For a more correct comparison of stereochemical results with different initiators (Pr_3B and AIBN) the reactions with other acetylenes were conducted in benzene.

Reaction of 1,4-Diacetoxy-2-butyne (Ib) with 1,2-Ethanedithiol (II) in the Presence of AIBN. A solution of 0.3 ml (0.83 g, 4 mmoles) of (II), 0.68 g (4 mmoles) of the alkyne (Ib), and 0.1 g (15 mole %, 0.6 mmole) of AIBN in 40 ml of benzene was heated for 2 h at 80°C. The solution was evaporated, and by the chromatography of the residue on a column of SiO_2 (eluent hexane—ether 1:1) we isolated 0.58 g (54%) of a mixture of stereoisomeric cis- and trans-2,3-bis(acetoxymethyl)-1,4-dithianes (IIIb) and (IVb). ^{13}C NMR spectral data are given in Table 1. PMR spectra (δ, ppm): (IIIb), 2.02 s (6H, CH_3CO), 2.78-2.90 m (2H) and 2.98-3.09 m (2H, SCH_2CH_2S), 3.48 t (2H, SCHCHS), 4.30 d.d (2H) and 4.43 d.d (2H, CH_2OAc); (IVb) 2.02 s (6H, CH_3CO), 2.47-2.58 m, (2H) and 2.90-3.05 m (2H, SCH_2CH_2S),3.10-3.20 m (2H, SCHCHS), 4.59 d.d (2H) and 4.68 d.d (2H, CH_2OAc).

Reaction of 1,4-Diacetoxy-2-butyne (Ib) with 1,2-Ethanedithiol (II) in the Presence of Pr_3B. This was conducted analogously to the above-described reaction of (Ia) with (II). The yield of a mixture of (IIIb) and (IVb) was 40%.

Reaction of 1,4-Dichloro-2-butyne (Ic) with 1,2-Ethanedithiol (II) in the Presence of Pr_3B. To a solution of 0.39 ml (0.49 g, 4 mmoles) of 1,4-dichloro-2-butyne (Ic), 0.37 ml (0.41 g, 4.4 mmoles) of the ethanedithiol (II), and 0.65 ml (0.51 g, 16 mmoles) of MeOH in

40 ml of benzene 4 ml of a 1 M solution of Pr_3B in hexane (4 mmoles) was added. According to GLC data scarcely any reaction had occurred after 24 h. In the reaction benzene was replaced by THF and 0.65 ml of a 10% solution of 30% H_2O_2 in MeOH was added. After 150 h the mixture was treated analogously to the mixture in the above-described reaction of (Ia) with (II), and by the chromatography of the residue on a column of SiO_2 (eluent hexane–ether 6:1) we isolated 0.18 g (21%) of a mixture of cis- and trans-2,3-bis(chloromethyl)-1,4-dithianes (IIIc) and (IVc). ^{13}C NMR data are given in Table 1. PMR spectrum (δ, ppm): (IIIc), 2.83-2.94 m (2H) and 3.00-3.10 m (2H, CH_2CH_2S), 3.56 t (2H, SCHCHS), 3.87-3.94 d.d (2H) and 3.96-4.05 d.d (2H, CH_2Cl); (IVc), 2.46-2.62 m (2H) and 3.13-3.18 m (2H, SCH_2CH_2S), 3.20-3.24 m (2H, SCHCHS), 4.10-4.18 d.d (2H) and 4.48-4.58 d.d (2H, CH_2Cl).

Reaction of 1,4-dichloro-2-butyne (Ic) with ethanedithiol (II) in the presence of AIBN, conducted like the above-described reaction of (Ia) with (II), led to the formation of a complex mixture of products with a low degree of conversion of the (Ic) taken.

Reaction of Diphenylacetylene (Id) with 1,2-Ethanedithiol (II) in the Presence of AIBN. A mixture of 0.71 g (4 mmoles) of diphenylacetylene (Id), 0.34 ml (0.38 g, 4 mmoles) of 1,2-ethanedithiol (II), 0.1 g (15 mole %, 0.6 mmole) of AIBN, and 40 ml of benzene was boiled for 7 h. On the next day we added a further 0.17 ml (0.19 g, 2 mmoles) of (II) and 0.07 g (10 mole %) of AIBN, and boiling was continued further for 5 h. The conversion of (Id) was 99%. Solvent was evaporated. The residue according to the results of GLC, PMR spectroscopy, and GLC–mass spectrometry contained cis- and trans-2,3-diphenyl-1,4-dithiane (IIId) and (IVd) (yield 66%) and 2,3-dihydro-5,6-diphenyl-1,4-dithiin (V) (M^+ 270) and 2-benzyl-2-phenyl-1,3-dithiolane (IX) (M^+ 272) (yields 6 and 8%, respectively). In the chromatography of the residue on a column of SiO_2 (eluent hexane–ether 5:1) we isolated 0.55 g (50%) of cis-2,3-diphenyl-1,4-dithiane (IIId), mp 124°C, and 109 mg of a mixture containing (V) and (IX). ^{13}C NMR spectral data for (IIId) are given in Table 1. PMR spectra (δ, ppm): (IIId), 3.05-3.20 m (2H) and 3.40-3.45 m (2H, SCH_2CH_2S), 4.60 s (2H, PhCHCHPh), 7.15-7.35 m (10H); (IVd), 4.57 s (2H, PhC$\underline{H}$C$\underline{H}$Ph).

Reaction of Diphenylacetylene (Id) with Ethanedithiol (II) in the Presence of Pr_3B. To a solution of 0.71 g (4 mmoles) of (Id) in 40 ml of benzene in an atmosphere of argon a mixture of 0.65 ml (0.51 g, 16 mmoles) of MeOH, 0.37 ml (0.41 g, 4.4 mmoles) of (II), and 4 ml of a 1 M solution of Pr_3B in hexane (4 mmoles) was added. The mixture was stirred for 72 h at ~20°C and treated as indicated above for the analogous reaction of (Ia) with (II). The residue was analyzed by means of PMR, mass spectrometry, GLC–mass spectrometry, and also GLC with the use of reference compounds. In the complex mixture of products we identified 9 compounds: unchanged (Id) (conversion 95%), trans-stilbene (VI), benzyl phenyl ketone (VII), benzil (VIII), cis- and trans-2,3-diphenyl-1,4-dithianes (IIId) and (IVd), 2,3-dihydro-5,6-diphenyl-1,4-dithiin (V), 2-benzyl-2-phenyl-1,3-dithiolane (IX), and 2-benzoyl-2-phenyl-1,3-dithiolane (X). By the chromatography of the residue on a column of SiO_2 (eluent hexane–ether 5:1) we isolated fractions containing 1) diphenylacetylene (Id); 2) the cis- and trans-dithianes (IIId) and (IVd) and the dithiin (V) [PMR spectrum of (V): singlet of SCH_2CH_2S 3.40 ppm; GLC–mass spectrum: 270 (M^+), 242: 178, 122, 121]; 3) benzil (VIII), mass spectrum (chemical ionization): 211, 0.75 (MH^+), PMR spectrum: 7.53 t (4H), 7.69 t (2H), 8.00 d (4H); 4) a mixture of trans-stilbene (δ 7.05 ppm CH═CH) and the dithiolanes (IX) and (X), which were identified by means of GLC and PMR, together with a compound of unestablished structure.

2-Benzyl-2-phenyl-1,3-dithiolane (IX) and 2-benzoyl-2-phenyl-1,3-dithiolane (X) were synthesized independently by the reactions of benzyl phenyl ketone (VII) and of benzil (VIII) with 1,2-ethanedithiol (II) in chloroform under the action of $TiCl_4$ at −10°C.

PMR spectrum of (IX) (δ, ppm): 3.25 m (4H, SCH_3CH_2S), 3.75 s (2H, CH_2Ph), 7.2-7.7 m (10H, Ph); ^{13}C spectrum: 38.80 t (SCH_2CH_2S, 51.58 t (CH_2Ph), 74.35 s (SCS).

PMR spectrum of (X): 3.40 m (4H), 7.20-7.40 m (6H), 7.70 d.d (4H); ^{13}C spectrum: 40.38 t (SCH_2CH_2S), 79.60 s (SCS), 124.10, 126.56, 128.21, 128.91, 130.96, 132.47, 134.20, 139.54 (arom. C), 191.19 s (C═O).

Reaction of Dimethyl Acetylenedicarboxylate (Ie) with 1,2-Ethanedithiol in the Presence of Pr_3B. In an atmosphere of argon, to a solution of 0.57 g (4 mmoles) of (Id), 0.37 ml (0.42 g, 4.4 mmoles) of the dithiol (II), and 0.65 ml (0.51 g, 16 mmoles) of MeOH in 40 ml of benzene, 4 ml of a 1 M solution of Pr_3B in hexane was added. After treatment analogous to that described above for the reaction of (Ia) with (II) by chromatography on a column of SiO_2 (eluent hexane–ether 4:3) we obtained 0.26 g (27%) of 5,6-dihydro-1,4-dithiin-2,3-dicarboxylate (XXI) and 0.03 g (3%) of a mixture of the 1,4-dithioane-2,3-dicarboxylates (IIIe) and (IVe). PMR spectrum of (IIIe) and (IVe) (δ, ppm): 2.80-3.40 s (4H, SCH_2CH_2S), 3.68 s and 3.86 s (6H, OCH_3). PMR spectrum of (XXI): 3.24 s (4H, SCH_2CH_2S), 3.77 s (6H, OCH_3). ^{13}C NMR spectrum of (XXI): 27.48 t (CH_2S), 52.99 q (OCH_3), 127.44 s (C=C), 164.57 s (C=O).

Reactions of 4-Octyne (Ia) and of 1,4-Diacetoxy-2-butyne (Ib) with Ethyl Mercaptoacetate (XVII) in the Presence of Pr_3B. In an atmosphere of argon, to a solution of 0.48 g (4 mmoles) of the thiol (XVII), 0.44 g (4 mmoles) of 4-octyne (Ia), and 0.65 ml (0.51 g, 16 mmoles) of MeOH in 40 ml of benzene 4 ml of a 1 M solution of Pr_3B (4 mmoles) in hexane was added, and the mixture was stirred for 65 h at -20°C. After treatment [see reaction of (Ia) with (II) above] by the chromatography of the residue on a column of SiO_2 (eluent hexane–ethyl acetate 15:1) we isolated 0.37 g (41%) of a mixture of (Z)- and (E)-ethyl (1-propyl-1-pentenylthio)acetates (XVIIIa); the proportions of the (Z) and (E) isomers, according to GLC and PMR data, were 61:39.

Analogous reaction between (Ib) and (XVII) was conducted for 72 h. By the chromatography of the residue on a column of SiO_2 (eluent hexane–ether 1:1) we isolated 0.71 g (61%) of a mixture of (Z)- and (E)-ethyl [1-(acetoxymethyl)-3-acetoxypropenylthio]acetates (XVIIIb); the proportions of the (Z) and (E) isomers, according to GLC and PMR data, were 82:18.

PMR spectrum of (XVIIIa): 9.90 m (6H, CH_3), 1.20 d.t (3H, CH_3CH_2O), 1.35 m (2H, $MeCH_2CH_2CH=$), 1.52 m (2H, $Me\underline{CH_2}CHC(SCH_2COOEt)=$), 2.05-2.25 2 m (4H, $CH_2C=$), 3.32 s [SCH_2COO, (Z) isomer] and 3.39 s [SCH_2COO, (E) isomer] (2H), 4.10 m (2H, $CH_3\underline{CH_2}O$), 5.53 t [CHC=, (E) isomer] and 5.69 t [CHC=, (Z) isomer] (1H).

PMR spectrum of (XVIIIb): 1.25 t (3H, $\underline{CH_3}CH_2O$), 2.05 and 2.10 2 s (6H, CH_3CO), 3.45 s (SCH_2COO), (Z) isomer] and 3.50 s (SCH_2COO, (E) isomer] (2H), 4.20 q (2H, $\underline{CH_2}CH_3$), 4.70-4.90 m ($\underline{CH_2}OAc$), 5.80 t ($\underline{CH}C=$, (E) isomer] and 6.15 t [CHC=, (Z) isomer] (1H).

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