Aspects of the Preparation of Cyclohexenyl- and Menthenylthioenynes *via* Ring-Opening of Thiophenes

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Treatment of 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene (IIIa) and 2,5-dimethyl-3-(1-cyclohexenyl)-4-bromothiophene (IIIb) with butyllithium gave the thiodienynes Va and Vb, respectively, *via* ring-opening of the corresponding 3-lithio derivatives. 2,5-Dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-dioxide (IV) gave the sulfone VI under similar conditions. The uv spectra of IIIa-b, IV, Va-b and some related compounds have been recorded and compared. The rotational barrier of compound VI was determined.

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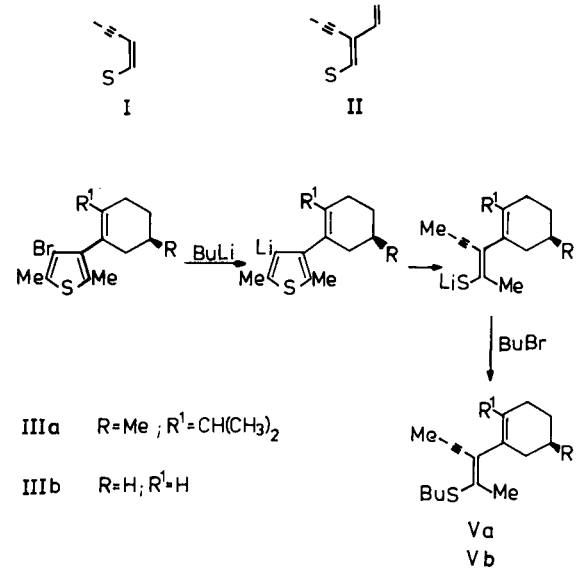
Introduction.

The organolithium-induced ring-opening of thiophenes, leading to compounds with thioenyne fragment I with *cis* geometry around the double bond, has recently been studied extensively in our laboratories (1,2). The stability of the intermediate 3-lithium derivative, which undergoes an E1cB type elimination, has been found to be quite dependent on the substitution pattern of the thiophene ring, and the effects of several different substituents have been examined (1,3-6). In order to evaluate the utility of this ring-opening reaction for the synthesis of compounds with the cross-conjugated thiodienyne fragment II, we have now carried out an investigation starting with two thiophene derivatives, each substituted with a vinyl function, a functionality whose effects on the reaction had not previously been studied. The easily available 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene (IIIa) and 2,5-dimethyl-3-(1-cyclohexenyl)-4-bromothiophene (IIIb) which were used as precursors in an ongoing study of the chiroptical properties of bicyclic systems, were chosen as starting materials.

Secondly, we wish to report results in connection with our recent finding that the reaction between different substituted 3-halothiophene 1,1-dioxides and organolithium reagents affords products resulting from two different ring-opening sequences (7). We regarded 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-dioxide (IV), with its bulky β-menthenyl substituent, as an interesting substrate.

Results and Discussion.

Treatment of IIIa and IIIb with 1 equivalent of butyllithium at room temperature in ether for one hour, and subsequent alkylation with excess butyl bromide, gave *(E)*-2-butylthio-3-(1-menthenyl)-2-hexen-4-yne (Va) and *(Z)*-2-butylthio-3-(1-cyclohexenyl)-2-hexen-4-yne (Vb) in yields of 62% and 44%, respectively. Apparently it is possible to utilize these vinylthiophenes in the ring-opening reaction for specific preparation of compounds with the structural element II, in a convenient way.



Scheme 1

The uv spectra of the products were found to be similar, with a λ max at 280 nm. In the parent system XI, without the cyclohexenyl group present, the λ max of the enyne chromophore appears at 5 nm shorter wavelength (Figure 1). These results, and observations in connection with the ring-opening of IV (*vide infra*) prompted us to record and compare the uv spectra of the starting materials IIIa and IIIb, a compound with intermediate bulkiness around the pivot bond, 2,5-dimethyl-3-(2-methyl-1-cyclohexenyl)-4-bromothiophene (IIIc) and the derivatives 3-(1-menthenyl)-thiophene (IIId) and 3-(1-cyclohexenyl)thiophene (IIIe) without 2,4- and 5-substituents present on the thiophene nucleus (Figure 2). All five compounds showed λ max in the region 240-245 nm. The monosubstituted thiophenes IIId and IIIe gave somewhat broader absorption in this region. The least substituted derivative, 3-(1-cyclohexenyl)thiophene (IIIe), where we expected no steric hindrance to coplanarity, gave a λ max at 222 nm. The corres-

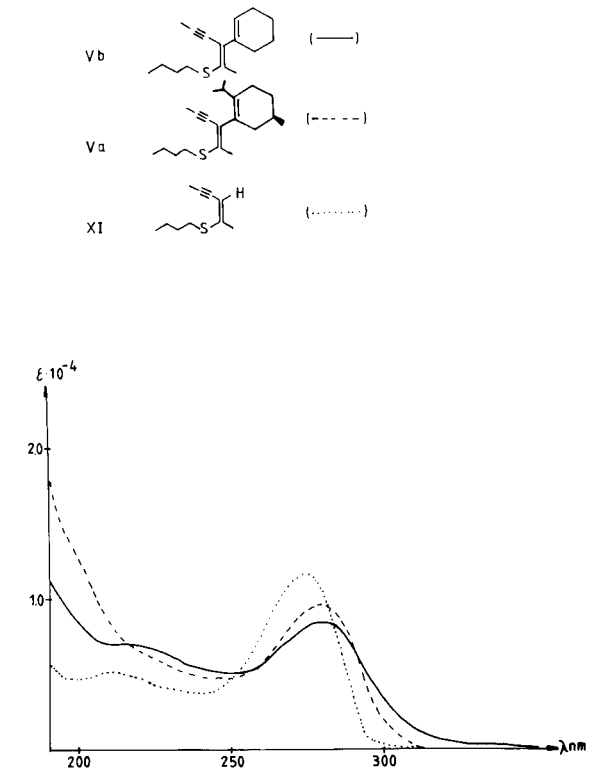
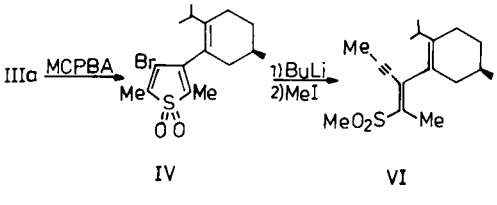
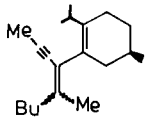


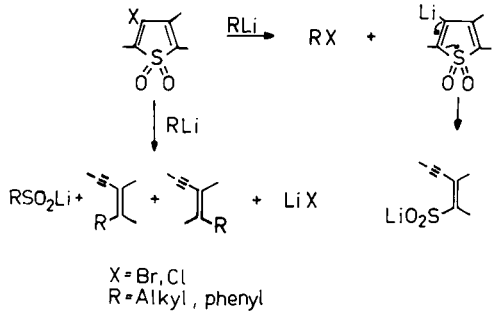
Figure 1. The uv spectra of 2-butylthio-3-(1-menthenyl)-2-hexen-4-yne (Va), 2-butylthio-3-(1-cyclohexenyl)-2-hexen-4-yne (Vb) and 2-butylthio-2-hexen-4-yne (XI) in acetonitrile.



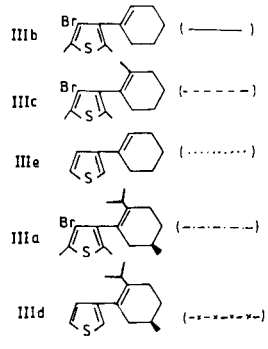
IV VI



VII



Scheme 2



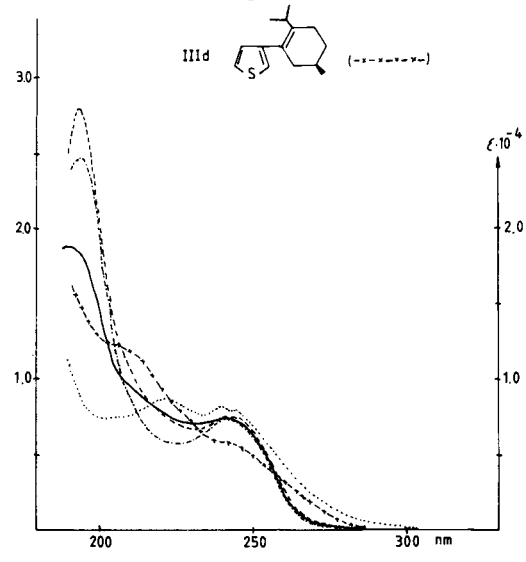


Figure 2. The uv spectra of 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene (IIIa), 2,5-dimethyl-3-(1-cyclohexenyl)-4-bromothiophene (IIIb), 2,5-dimethyl-3-(2-methyl-1-cyclohexenyl)-4-bromothiophene (IIIc), 3-(1-menthenyl)thiophene (IIId) and 3-(1-cyclohexenyl)thiophene (IIIe) in acetonitrile.

ponding absorption in the uv spectra of the other monosubstituted thiophene derivative IIId seems to appear at shorter wavelength, 210 nm. The weak shoulder in the spectrum of the tetrasubstituted thiophene, with no alkyl substituents in the cyclohexene moiety IIIb, indicates that the same band has been shifted further toward shorter wavelength. A tendency toward a shoulder around 210 nm can be seen in the spectrum of IIIc. No corresponding absorption appears in the spectrum of IIIa, where the bulkiness around the pivot bond is optimized. We assume this absorptions to be due to conjugation between the double bond and the aromatic part of the molecule, and thus more steric hindrance to coplanarity, resulting in removal of conjugation, gives rise to a hypsochromic effect. Similar observations have been reported concerning the other 3-methene-substituted thiophenes (8), phenylcyclohexenes (9) and naphthylcyclohexenes (10).

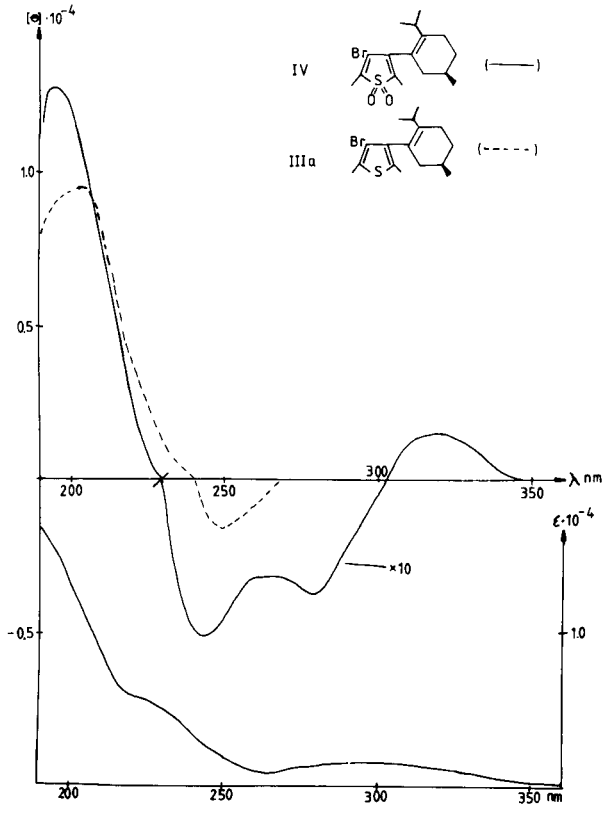


Figure 3. The cd and uv of 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-dioxide (IV) and 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene (IIIa) in acetonitrile.

The cd and uv spectra of the optically active menthene derivatives IIIa, Va, IV and VI are shown in Figures 3 and 4. All of them exhibit Cotton effects around 200 and 250 nm. The data are summarized in Table I.

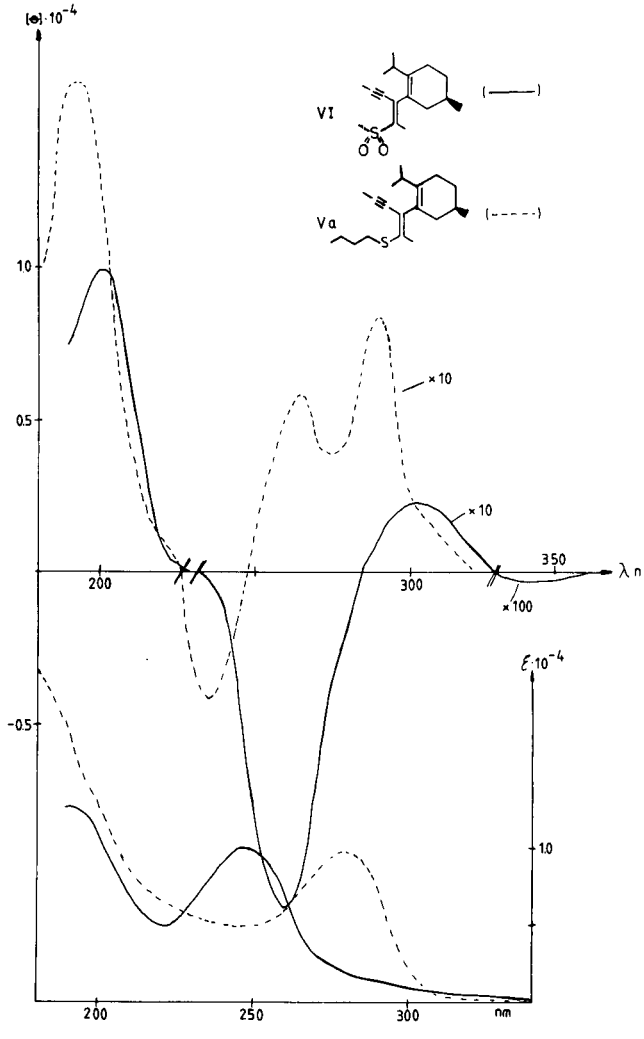


Figure 4. The cd and uv of 2-butylthio-2-(1-menthenyl)-2-hexen-4-yne (Va) and 3-(1-menthenyl)-2-methylsulfonyl-2-hexen-4-yne (VI) in acetonitrile.

Table I

CD and UV Values

Compound (a)	λ max (nm) and ε			λ max (nm) and [θ] max			
IIIa	193 (24400)	244 (7400)		205 (+ 9500)	250 (− 80)		
IV	220 (6000)	300 (1600)		195 (+12700)	244 (− 510)	280 (−380)	320 (+150)
Va		280 (9600)		203 (+15900)	245 (− 420)	275 (+580)	300 (+830)
VI	190 (12600)	247 (10000)		200 (+ 9800)	260 (−1100)	302 (+220)	340 (− 30)
IIIb	190 (18800)	241 (7400)					
IIIc	193 (28000)	241 (7400)					
IIId	207 (12400)	240 (5800)					
IIIe	221 (8800)	240 (8200)	244 (8000)				
Vb	215 (7000)	280 (8400)					
XI	210 (5000)	275 (11600)					

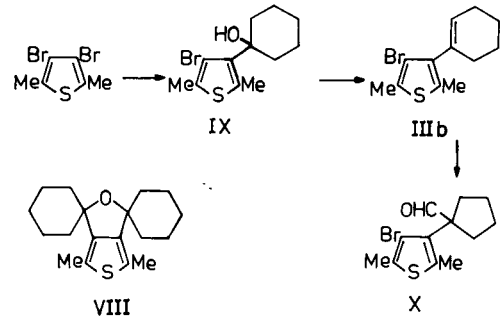
(a) Solvent: acetonitrile.

The reaction of the dioxide IV with butyllithium at -70° in ether gave, after quenching the reaction mixture with methyl iodide in dimethyl sulfoxide, 3-(1-menthenyl)-2-methylsulfonyl-2-hexen-4-yne (VI) in 34% yield, and also a 63% yield (glc) of butyl bromide. According to glc/ms analysis, the crude material after work-up consisted of several by-products, none of which corresponded to the expected VII. Furthermore, compound VII could not be traced in the reaction mixture before treatment with methyl iodide. The glc signals from compounds in lower yield than *ca.* 2% of the total amount passing the column were not analyzed. This result was of interest, considering our earlier findings concerning ring-opening of thiophene 1,1-dioxides (7). We established that 2,5-dialkyl-3-halothiophene 1,1-dioxides ring-open either *via* a) an organolithium attack on the 5-carbon or b) *via* a halogen-metal exchange reaction, as outlined in Scheme 2. The formation of the isomeric vinylacetylenes is interesting from a preparative point of view and it is possible to get a high isomer ratio by changing 5-substituents. This reaction is favoured when the halogen exhibits little tendency to undergo halogen-metal exchange. Thus, bromo derivatives afforded products from both reaction sequences, while chloro derivatives gave exclusively products as a result from an initial nucleophilic attack. The possibility that a one electron transfer reaction is involved in the mechanisms cannot be excluded, but will not be discussed here. Based on earlier indications (8) that the bromo atom of IIIa undergoes halogen-metal exchange very slowly, we argued that the corresponding dioxide IV could be expected to give products resulting from an initial organolithium attack on the 5-carbon. However, formation of VI, and the high yield of butyl bromide, show that halogen-metal exchange had occurred predominantly. Although the reason for the dominant halogen-metal exchange is not obvious, steric factors due to non-coplanarity between the rings as suggested by the uv spectrum of the corresponding thiophene IIIa and by Dreiding molecular models, might be invoked. Electronic effects of the exocyclic double bond favouring halogen-metal exchange can however not be excluded. As a comparison, 3-bromo-5-*t*-butyl-2-methylthiophene 1,1-dioxide under the same conditions gives a low yield (5.5%) of products derived from butyllithium attack on the 5-carbon (11).

The ^{1}H nmr spectra of Va and VI both exhibited a doublet and a singlet around 2 ppm. We expected the signals from the propargylic and vinylic methyl groups to appear as singlets in this region as in the spectrum of the cyclohexene derivative Vb. To establish the origin of the doublets, whether long-range coupling or hindered rotation were involved, we recorded the spectrum of VI on a 360 MHz nmr spectrometer. From this it became clear that the splitting was due to hindered rotation, since the splitting is field dependent. Furthermore a "doubling" of the entire spectrum could be seen at room temperature at the higher frequency. We found the coalescence of the doublet to occur at 59° in *o*-dichlorobenzene at 100 MHz, corresponding to a rotational barrier of 18.4 ±0.3 kcal/mol ($\Delta\nu$ = 2.4 Hz). In *o*-dichlorobenzene the singlet at 2.07 ppm (deuteriochloroform) moved upfield, whereas the doublet did not move to any great extent. This indicates the singlet to originate from the propargylic methyl group, since this should be better solvated and more shielded by the aromatic solvent than the vinyl one close to the electronegative sulfonyl moiety. Also our results clearly show the menthenyl substituent to be out of the enyne plane, which we also believe is the case for the other menthenyl derivative Va.

Applying reported methods (8,12,13) for the preparation of IIIa and IIIc-e to the synthesis of IIIb gave the [c]-annelated thiophene derivative VIII as a by-product. A smaller amount of 2,5-dimethyl-3,4-dibromothiophene also remained. The yield of VIII was lower when the halogen-metal exchange was performed in dilute solution. We preferred to prepare IIIb *via* isolation of the initially formed lithium alcoholate of the alcohol IX. Treatment of IX with *p*-toluenesulfonic acid in toluene gave IIIb in 23% yield.

After oxidation of IIIa with *m*-chloroperbenzoic acid, 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-dioxide (IV) was obtained. When the cyclohexene derivative IIIb was subjected to the same reaction conditions, a ring contraction occurred instead, probably *via* epoxidation (14), resulting in the formation of 2,5-dimethyl-3-(1-formylcyclopentenyl)-4-bromothiophene (X) as the main product.



Scheme 3

EXPERIMENTAL

All metalations were performed in dry solvents under nitrogen, using septum technique. The ^{1}H nmr spectra were recorded on a Jeol MH 100 and a Nicolet 360 WB spectrometer equipped with a ^{1}H probe. The uv spectra were recorded on a Cary 16 spectrophotometer and the ir spectra were recorded on a Perkin-Elmer 298 spectrometer. Mass spectra were obtained using a Finnigan 4021 (Data System Incos 2100) gas chromatography-mass spectrometer and were in accordance with the proposed structures. Gas chromatograms were recorded on a Varian 3700 equipped with a OV 101, 3%, 2.5 m, Varaport 30,80/100 mesh and F.I.D. The glc yields were determined by comparison of the increase of the glc peak integrals upon addition of known amounts of authentic material. Com-

pounds IIIa (8), IIIc (12), IIId (8) and IIIe (13) were available in our laboratories.

2,5-Dimethyl-3-(1-cyclohexenyl)-4-bromothiophene (IIIb).

To a solution of 11.2 g (40 mmoles) of 3,4-dibromo-2,5-dimethylthiophene in 150 ml of dry ether, 26.8 ml (40 mmoles) of 1.5 *N* butyllithium in hexane was added at −70°. After 30 minutes, 3.92 g (40 mmoles) of cyclohexanone in 5 ml of ether was added to the reaction mixture, and after another 10 minutes the cooling bath was removed and the stirring stopped. The solvent was decanted and the precipitate was carefully washed with ether and was then hydrolysed with water. The organic material was taken up in the ether, and after drying and evaporation it was dissolved in toluene and refluxed with 1.0 g of *p*-toluenesulfonic acid for 30 minutes. The organic phase was washed with water and aqueous sodium hydrogen carbonate, dried (magnesium sulfate) and evaporated to give 2.45 g (23%) of the title compound (IIIb) as an oil after chromatography (silica/hexane); nmr (deuteriochloroform): δ 5.56 (bt, 1H, vinyl), 2.32 (s, 6H, CH_3), 2.15-1.70 (m, 8H, CH_2).

Anal. Calcd. for $C_{12}H_{15}BrS$: C, 53.1; H, 5.57; S, 11.8. Found: C, 52.8; H, 5.50; S, 12.1.

In one run the total reaction mixture was subjected to the elimination procedure described. A glc/ms analysis was performed before chromatography, showing that 3% of the starting material remained and that compound VIII had been formed in 6% yield. Performing the halogen-metal exchange in a more concentrated solution resulted in 6% of the starting material and formation of dispiro[cyclohexane-1,1',4',6'-dimethylthieno-[3,4-*c*]furan-3',1''-cyclohexane] (VIII) in 19% isolated yield. It crystallized from the crude product upon standing and was recrystallized from hexane, mp 157-158°; nmr (carbon tetrachloride): δ 2.22 (s, 6H, CH_3), 1.65 (m, 20H, CH_2).

Anal. Calcd. for $C_{18}H_{26}OS$: C, 74.4; H, 9.02; S, 11.0. Found: C, 74.4; H, 9.02; S, 11.0.

(+)-2,5-Dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-Dioxide (IV).

To a solution of 326 mg (1.00 mmole) of 2,5-dimethyl-3-menthenyl-4-bromothiophene (IIIa) in 25 ml of methylene chloride at 5°, 382 mg (2.00 mmoles) of *m*-chloroperbenzoic acid was added. After 4 days the reaction mixture was filtered and the filtrate was then extracted several times with an aqueous sodium carbonate solution. After evaporation of the dried (magnesium sulfate) methylene chloride phase, the crystalline residue was recrystallized from hexane to give 240 mg, 67%, of the title compound IV; $[\alpha]_D^{25}$ = +45.6 (c = 0.50, ethanol); ir: 1300, 1180 cm^{-1} (SO_2); nmr (deuteriochloroform): δ 2.10 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.04-0.86 (m, 9H, $CH(CH_3)_2$ and $CH—CH_3$), J_{CH,CH_3} = 6.8 Hz.

Anal. Calcd. for $C_{16}H_{23}BrSO_2$: C, 53.5; H, 6.45; S, 8.92. Found: C, 53.1; H, 6.34; S, 9.01.

2,5-Dimethyl-3-(1-formylcyclopentyl)-4-bromothiophene (X).

A solution of 277 mg (1.00 mmole) of 2,5-dimethyl-3-(1-cyclohexene)-4-bromothiophene (IIIb) in 25 ml of methylene chloride was prepared and 191 mg (1.00 mmole) of *m*-chloroperbenzoic acid was added at 5°. After reaction for 4 days and the same work-up procedure as for the preparation of IV, 114 mg (40%) of 2,5-dimethyl-3-(1-formylcyclopentyl)-4-bromothiophene (X) was obtained as an oil after chromatography (silica, hexane/ethyl acetate, 90/10). The compound decomposed on standing; ir: 1720 cm^{-1} (C=O); nmr (deuteriochloroform): δ 9.36 (s, 1H, CHO), 2.47 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.75-1.50 (m, 8H, CH_2).

Ring-opening Reactions.

(E)-(+)-2-Butylthio-3-(1-menthenyl)-2-hexen-4-yne (Va) and *(Z)*-2-Butylthio-3-(1-cyclohexenyl)-2-hexen-4-yne (Vb).

To a stirred solution of 3.5 mmoles of 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene (IIIa) and of 2,5-dimethyl-3-(1-cyclohexenyl)-4-bromothiophene (IIIb), respectively, in 20 ml of ether, 2.6 ml (3.9 mmoles) of 1.5 *N* butyllithium in hexane was added dropwise at room temperature. After one hour, excess butyl bromide (14 mmoles) was added and the stirring was continued over night. The reaction mixture was poured into water and the aqueous phase was extracted several times with ether. The combined organic phases were washed with water, dried (magnesium sulfate) and evaporated to give oils. Chromatography (silica, hexane/ethyl acetate, 95/5) was used for isolation of the title compounds.

(E)-(+)-2-Butylthio-3-(1-menthenyl)-2-hexen-4-yne (Va).

This compound was obtained in a yield of 62% (0.58 g); $[\alpha]_D^{25}$ = +60.3 (c = 0.74, ethanol); ir: 2205 cm^{-1} (C≡C); nmr (deuteriochloroform): δ 2.75 (t, 2H, SCH_2), 1.1-2.5 (m, 8H, aliphatic), 2.02 (s, 3H, propargylic or vinylic CH_3), 1.90 (d, 3H, vinylic or propargylic CH_3), 0.80-1.00 (m, 12H, aliphatic CH_3), J_{SCH_2,CH_2} = 7.0 Hz, J_{CH,CH_3} = 6.8 Hz, J_{CH_2,CH_3} = 7.0 Hz.

Anal. Calcd. for $C_{20}H_{32}S$: C, 78.8; H, 10.6; S, 10.5. Found: C, 78.6; H, 10.3; S, 10.8.

(Z)-2-Butylthio-3-(1-cyclohexenyl)-2-hexen-4-yne (Vb).

This compound was obtained in a yield of 0.40 g (44%); ir: 2205 cm^{-1} (C≡C); nmr (deuteriochloroform): δ 5.68 (m, 1H, vinylic), 2.76 (m, 2H, SCH_2), 2.03-2.30 (m, 4H, allylic), 2.04 (s, 3H, propargylic or vinylic CH_3), 2.01 (s, 3H, propargylic or vinylic CH_3), 1.3-1.8 (m, 8H, aliphatic), 0.97 (t, 3H, butyl-CH_3), J_{CH_3,CH_2} = 7.0 Hz.

Anal. Calcd. for $C_{16}H_{24}S$: C, 77.4; H, 9.74; S, 12.9. Found: C, 77.2; H, 9.35; S, 13.0.

(Z)-2-Butylthio-2-hexen-4-yne (XI).

This compound was prepared in the same way as Va and Vb from 23 g (0.10 mmole) of 2,5-dimethyl-3-iodothiophene (15) in 200 ml of dry ether, 73 ml (0.11 mmole) of 1.5 *N* butyllithium and 70 g (0.40 mmole) of butyl bromide, yield, 9.2 g (55%), bp_{10} 107-115°; ir: 2230 cm^{-1} (C≡C); nmr (deuteriochloroform): δ 5.36 (m, 1H, 3-H), 2.82 (t, 2H, SCH_2), 2.04 (m, 3H, 6-CH_3), 1.99 (bs, 3H, 1-CH_3), 1.1-1.7 (m, 4H, aliphatic), 0.90 (t, 3H, CH_2CH_3), $J_{3\text{-}H,6\text{-}CH_3}$ = 1.5 Hz, J_{CH_2,CH_3} = 6.5 Hz.

Anal. Calcd. for $C_{10}H_{16}S$: C, 71.4; H, 9.58. Found: C, 71.9; H, 9.26.

(E)-(+)-3-(1-Menthenyl)-2-methylsulfonyl-2-hexen-4-yne (VI).

To a solution of 0.40 g (1.2 mmoles) of 2,5-dimethyl-3-(1-menthenyl)-4-bromothiophene 1,1-dioxide (IV) in 20 ml of ether, 1.8 ml (2.7 mmoles) of 1.5 *N* butyllithium in hexane was added at −70°. After reaction for one hour, a sample of the reaction mixture was hydrolysed and analysed on glc/ms. The main part of the reaction mixture was evaporated and 10 ml of dimethyl sulfoxide was added followed by excess of methyl iodide (10 mmoles). After stirring over night at room temperature, a sample for glc/ms analysis was again removed, and the main part of the reaction mixture was poured into ether/water. The aqueous layer was extracted and the combined organic phases were washed, dried (magnesium sulfate) and evaporated. After chromatography (silica, hexane/ethyl acetate, 80/20) 0.11 g (31%) of *(E)*-(+)-3-(1-menthenyl)-2-methylsulfonyl-2-hexen-4-yne (VI) was isolated as an oil; $[\alpha]_D^{25}$ = +12.8 (c = 0.078, ethanol); ir: 2205 cm^{-1} (C≡C); nmr (deuteriochloroform): δ 3.01 (s, 3H, CH_3SO_2), 1.0-2.8 (m, 8H, aliphatic), 2.07 (s, 3H, propargylic CH_3), 2.02 (d, 3H, vinylic CH_3), 0.85-1.03 (m, 9H, $—CH(CH_3)_2$ and $—CH—CH_3$), J_{CH,CH_3} = 6.8 Hz.

Anal. Calcd. for $C_{17}H_{26}SO_2$: C, 69.8; H, 8.90; S, 10.9. Found: C, 69.9; H, 8.52; S, 11.3.

The coalescence experiments were carried out in *o*-dichlorobenzene in a Jeol MH 100 MHz NMR Spectrometer. The coalescence of the doublet at 2.02 ppm occurred at 59°. At 100° a coupling of 0.7 Hz between the propargylic and vinylic methyl groups appeared clearly.

Acknowledgement.

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