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On the Base-catalyzed Reaction of Some Methyl Nitrothiophenes with Aldehydes. An Unexpected Cyclobutane Formation

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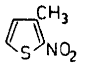
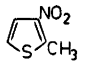
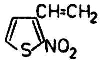
The methyl group in the *o*-methylnitrothiophenes shows varying reactivity towards aldehydes under base catalysis. 3-Methyl-2-nitrothiophene reacts to give vinyl compounds,[5,6] while 3-methyl-4-nitrothiophene does not react at all. 2-Methyl-3-nitrothiophene, with formaldehyde in methanol/water, gives, in addition to 3-nitro-2-vinylthiophene (V), a bis(3-nitro-2-thienyl)cyclobutane (IV), probably *trans*-1,2-bis(3-nitro-2-thienyl)- or *cis*-1,3-bis(3-nitro-2-thienyl)cyclobutane. 3-Nitro-2-vinylthiophene was also prepared from 1-(3-nitro-2-thienyl)-ethanol (XVI). 2-Isopropenyl-3-nitrothiophene (XXII), prepared *via* bis(2-isopropenyl-3-thienyl)iodonium chloride (XXI), gave with triethyl phosphite 6-methylthieno[3,2-*b*]pyrrole (XXIV), indicated by NMR and mass spectroscopy. 3-Nitro-2-vinylthiophene and 2-nitro-3-vinylthiophene gave no thienopyrrole upon treatment with triethyl phosphite.



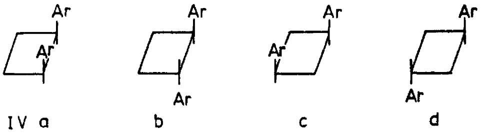
I



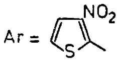
II



III



IV a



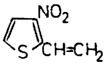
In connection with our work on heteroaromatic boron compounds (*cf.* Ref. 1), *ortho*-nitrovinylthiophenes were desired as starting materials for the synthesis of thieno-fused borazarenes. For this reason we became interested in studying the condensation of *ortho*-methylnitrothiophenes with different aldehydes. Wesslén [2] and Bakke [3,4] have shown that *o*-nitrotoluene can be condensed with formaldehyde as paraformaldehyde, using potassium *t*-butoxide in dimethyl sulfoxide as catalyst. With equimolar amounts of *o*-nitrotoluene and formaldehyde, 2-(2-hydroxyethyl)nitrobenzene was obtained as the main product. However, all of our attempts to condense 3-methyl-2-nitrothiophene (I), 2-methyl-3-nitrothiophene (II), and 5-methoxycarbonyl-2-methyl-3-nitrothiophene under the above-mentioned conditions, or under Knoevenagel reaction conditions, were unsuccessful. While this work was in progress, a short communication appeared [5] in which a facile condensation was observed when I was heated under reflux with 40 % formalin in methanol containing catalytic amounts of pyrrolidine and acetic acid, yielding 2-nitro-3-vinylthiophene (III) in 73 % yield. Similar reactions were observed with benzaldehyde and *p*-anisaldehyde. The yields of styryl derivatives were between 32 and 35 %.[6] We could confirm the formation of III, and we also found that *o*-nitrotoluene did not react under these conditions.

When II was reacted with formalin under the same conditions as I, a product (IV), m.p. 141.0 – 142.5 °C, was obtained with a molecular weight of 310 (mass spectrum). Its NMR spectrum showed, in addition to a thiophenic AB quartet (δ 7.13 and 7.54, J 5.6 Hz), complex signals at δ 4.5 and 2.5 with relative intensities 1:2. These data indicate that the product is one of the four possible bis(3-nitro-2-thienyl)-cyclobutanes (IVa – d). We supposed that decoupling of the signals centered at δ 4.5 should convert the methylene signals to an AA'BB' spectrum (for IVa – c) or an A_4 spectrum (for IVd), since cyclobutanes are known to invert rapidly.[7a] In the case of an AA'BB' spectrum it should be possible to determine the NMR parameters and consequently to determine whether the cyclobutane is 1,2- or 1,3-disubstituted. Upon attempted decoupling, however, the appearance of the methylene signals did change but not to a symmetrical pattern. The spectrum was too complex for further interpretation. Attempts to brominate IV in the benzylic positions with *N*-bromosuccinimide in carbon tetrachloride or ethylene dibromide, or with elemental bromine under basic conditions, failed. A benzylic dibrominated derivative of IV should give an AA'BB' NMR spectrum without decoupling.

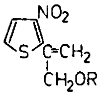
It has been demonstrated by Dodson and Zielske [8] that *trans*-1,2-diphenylcyclobutane is the thermodynamically more stable isomer, since *cis*-1,2-diphenylcyclobutane obtained by hydrogenation of 1,2-diphenylcyclobutane was isomerized to the *trans* isomer by treatment with potassium *t*-butoxide. Less than 1 % of the *cis* isomer remained. In order to establish whether IV was thermodynamically controlled we attempted deuterium exchange in monodeuteriomethanol-deuterium oxide with pyrrolidine as base. Reflux for 63 h followed by work-up gave a sample which was analyzed on the mass spectrometer *via* GLC inlet. The spectrum of monomerized IV (see below) showed that 38 % of the molecules had been deuteriated. Thus, an eventual thermodynamical control cannot be carried out by proton exchange in IV. On the other hand deuterium exchange in the benzylic positions occurred within 50 min at 60 °C in hexadeuteriodimethyl sulfoxide-deuterium oxide containing catalytic amounts of pyrrolidine as could be followed by NMR spectroscopy. Treatment of IV in dimethyl sulfoxide-water with pyrrolidine at 67 °C for 1.5 h gave after work-up a 64 % recovery of material, which according to IR spectrum was starting material.

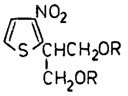
It has been found that in 1,3-disubstituted cyclobutanes the *cis* isomers generally are thermodynamically favored over the *trans* isomers.[8b] Furthermore, Lambert and Roberts found that for a substituent on a cyclobutane ring the equatorial position is favored over the axial position.[8c] These facts together with the finding by Dodson and Zielske make us believe that IV is either *trans*-1,2-bis(3-nitro-2-thienyl)cyclobutane (IVb) or *cis*-1,3-bis(3-nitro-2-thienyl)-cyclobutane (IVc). An X-ray diffraction investigation of compound IV is under progress.

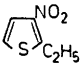
Mass spectral analysis has been used for structure determination of cyclobutanes.[7b] Gross and Wilkins reported that the two isomeric 1,2-diphenylcyclobutanes show loss of ethylene from their molecular ions.[9] Schauble *et al.* took such a loss as evidence for the structure of their photodimer of 4-nitrostyrene to be a 1,2-disubstituted cyclobutane.[10] However, the mass spectrum of *trans*-1,3-diphenylcyclobutane also shows an ion at *m/e* 180 (relative abundance 0.1 %), corresponding to loss of fragment *m/e* 28 from the molecular ion (2.6 %).[11] The fragment ion is a member of a cluster centered at *m/e* 178 as is the case of the two 1,2-diphenylcyclobutanes.[9] The abundance of 0.2 % of the fragment ion at *m/e* 282 in the mass spectrum of IV therefore seems too low to allow conclusions to be drawn about the structure of IV. On the other hand, one can argue that in the case of IV there is a competing fragmentation due to interaction between the nitro group and its *ortho* alkyl group, giving rise to a loss of OH. This *ortho* effect has been found for *ortho* alkylnitrobenzenes [12] and, in the thiophene series, for 3-nitro-4,5-dihydro-5-methyl-6H-cyclopenta[*b*]thiophene-6-one [13] and 3-methyl-4-nitrothiophene.[14] The same effect is observed for compounds II, III, V, VIII, and XXII in this paper.



V







VIII

VIa. R = H
b. R = $Si(CH_3)_3$

VIIa. R = H
b. R = $Si(CH_3)_3$

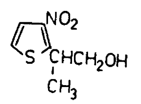
In order to ascertain that the formation of IV was not photochemically induced, the reaction was carried out in the dark. Also in this case the dimer was formed. NMR spectral analysis of the product, however, showed, along with signals from II and IV, vinylic protons, which were assigned to 3-nitro-2-vinylthiophene (V) by comparison with an authentic sample (*cf.* below). The dimer and the monomer had been formed in a ratio of 1.1:1. Also the spectrum of a reaction mixture performed in the light showed, before separation of components, the presence of compounds II, IV, and V. The reaction was not reversible: after heating of pure IV for 96 h in methanolic solution no V could be found by NMR analysis. Monomerization occurred, however, on heating to 180 °C for 30 min in dimethyl sulfoxide. Complete monomerization of IV occurred in the gas chromatograph. This is in accordance with the finding by Overberger *et al.* that the two 1,2-diphenylcyclobutanes undergo partial decomposition to styrene upon passage through the gas chromatograph.[15]

According to the Woodward-Hoffman rules, a concerted thermal $(2\pi+2\pi)$-cycloaddition is allowed only if it is suprafacial-antarafacial (*cf.* Ref. 16). Such an addition is less probable due to steric factors, as it necessitates a rotation of the carbon-carbon double bonds. Such a cycloaddition between olefins has hitherto not been observed with certainty. (For some other cases of ${}_{\pi}2_{\mathrm{s}}+{}_{\pi}2_{\mathrm{a}}$ cycloadditions, *cf.* Refs. 17–18 and refs. therein). It therefore appears reasonable to us that, if IV is formed by dimerization of V, the dimerization is not concerted, but involves ionic or radical intermediates. A way of deciding this matter would be a study of the eventual dimerization of *cis*-1-deuterio-2-(3-nitro-2-thienyl)ethene.

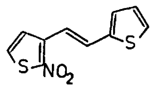
In the literature, many dimerizations of styrene derivatives are described.[19–22] In most cases in which styrene has been thermally or photochemically dimerized, cyclobutane derivatives have been obtained only in low yields, along with polymeric products. These reactions were carried out under non-polar conditions. In the thiophene field, the thermal polymerization of 2-vinylthiophene has been studied. It was found[23] that a dimer, 4-(2-thienyl)-4,5,6,7-tetrahydrobenzo[*b*]thiophene, was involved in the initiation of the polymerization (analogous to the polymerization of styrene). The photochemically induced dimerization of *β*-nitrostyrene to cyclobutane derivatives has been studied.[24]

The different reaction paths of 3-methyl-2-nitrothiophene and 2-methyl-3-nitrothiophene are interesting, but not without precedence. Thus, while 3-(3-thienyl)propyl-trimethylammonium iodide gave 3-(3-thienyl)-1-propene upon treatment with sodium amide, the corresponding 2-isomer gave 2-(cyclopropyl)thiophene.[25]

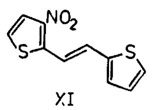
When II was condensed with formaldehyde in *N*,*N*-dimethylformamide, the reaction product was more complex. GLC-mass spectral analyses indicate that besides V or its dimer IV, appreciable amounts of a compound with a highest *m*/*e* of 185 were also formed. Silylation with *N*,*O*-bis(trimethylsilyl)acetamide prior to GLC-mass spectral analysis gave two peaks with molecular weights of 257 and 347, respectively. From the molecular weights and fragmentation patterns, it follows that these two compounds are 2-(3-nitro-2-thienyl)-3-(trimethylsilyloxy)-propene (VIb) and 1,3-bis-(trimethylsilyloxy)-2-(3-nitro-2-thienyl)propane (VIIb), respectively. The compound with a molecular weight of 185 formed in the condensation is thus 3-hydroxy-2-(3-nitro-2-thienyl)propene (VIa). If silylation is assumed to be complete, it follows that 1,3-dihydroxy-2-(3-nitro-2-thienyl)propane (VIIa) must have also been formed and that this compound either does not pass through the GLC column or is dehydrated to VIa. We have made no attempts to obtain the different reaction products in pure form. 3-Nitro-2-ethylthiophene (VIII) did not react with formaldehyde in refluxing methanol. Slowly in refluxing butanol, but faster in *N*,*N*-dimethylformamide at 110–115 °C, 2-(3-nitro-2-thienyl)propanol (IX) was formed. The structure followed from its mass and NMR spectra.



IX

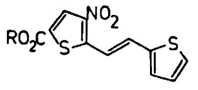


X



XI

If the condensation of I and 2-thiophene aldehyde was carried out according to Srinivasan *et al.*,[6] only a low yield of *trans*-1-(2-nitro-3-thienyl)-2-(2-thienyl)ethene (X) was obtained, together with a great deal of tars. Compound II and 2-thiophene aldehyde reacted very slowly under these conditions to yield 1-(3-nitro-2-thienyl)-2-(2-thienyl)ethene (XI). However, by reacting 1 mol of I of II with 2 mol of the aldehyde with piperidine as catalyst and without

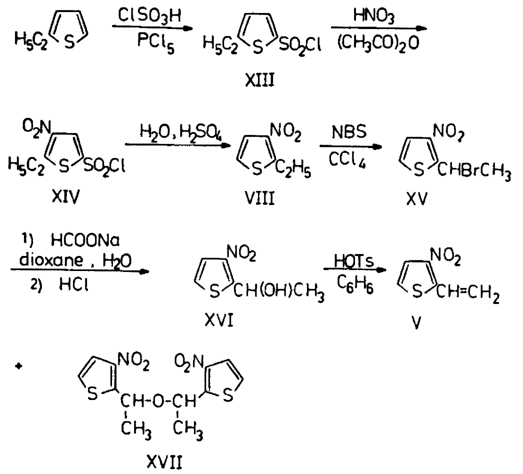


XII a R=CH$_3$
b R=H

solvent at about 100 °C, good yields of X or XI were obtained. 5-Methoxycarbonyl-2-methyl-3-nitrothiophene also reacted under these conditions to give *trans*-1-(5-methoxycarbonyl-3-nitro-2-thienyl)-2-(2-thienyl)ethene (XIIa). This compound has previously been prepared by Campaigne *et al.*[26] from the same reactants but under other conditions. XI was also obtained from XII by ester hydrolysis and subsequent decarboxylation. The facile condensation of 5-methoxycarbonyl-2-methyl-3-nitrothiophene and 3,5-dinitro-2-methylthiophene with benzaldehyde has been observed by Rinkes.[27]

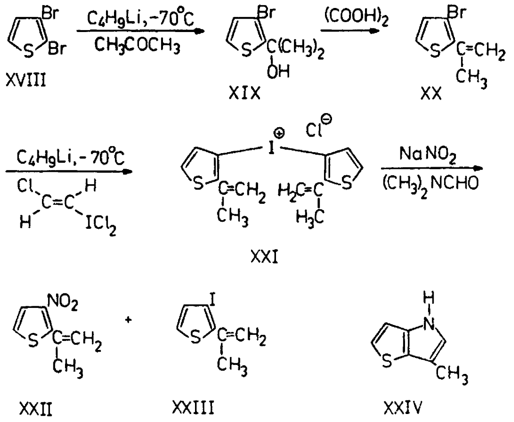
We also attempted condensation of 3-methyl-4-nitrothiophene [28] with formaldehyde, and with 2-thiophene aldehyde. However, no reaction was observed. This is perhaps expected from the well-known fact that the 4-position in 3-substituted thiophenes is not a normal *ortho* position.[29] Resonance stabilization of the benzylic carbanion by the nitro group is not possible, without including a resonance structure with ten electrons around the sulfur, or with additional charge separation.

2-Methyl-3-nitrothiophene (II) was prepared by metalation of 2-methylthiophene with butyllithium and subsequent carbonation, followed by nitration of the 2-methyl-5-thiophenecarboxylic acid according to Campaigne *et al.*[30] Decarboxylation with copper bronze and quinoline gave a better yield of II than the method used previously.[31] 2-Ethyl-3-nitrothiophene (VIII) was prepared by the same route. Alternatively, 2-ethylthiophene was chlorosulfonated to 2-ethyl-5-thiophenesulfonyl chloride (XIII) with phosphorus pentachloride and chlorosulfonic acid,[32] nitrated with a mixture of fuming nitric acid and acetic anhydride, and the resulting 2-ethyl-3-nitro-5-thiophenesulfonyl chloride (XIV) hydrolyzed and desulfonated to VIII. The latter method is preferable, as yields (based on 2-ethylthiophene) of 43 % were obtained, compared to only 14 % with the first-mentioned method. Benzoyl peroxide-catalyzed side-chain bromination of VIII with *N*-bromosuccinimide (NBS) in carbon tetrachloride gave 2-(α-bromoethyl)-3-nitrothiophene (XV) in high yield. The bromo derivative was transformed to 1-(3-nitro-2-thienyl)ethanol (XVI) by reaction with sodium formate in water-dioxane (*cf.* Scheme 1). Reaction in aqueous ethanol gave the ethyl ether in addition to the desired alcohol. Dehydration of XVI caused some difficulties. Dehydration with oxalic acid [33] or by boiling in dimethyl sulfoxide [34] failed. In benzene solution using *p*-toluenesulfonic acid, dehydration occurred easily. However, besides V (58 %), a mixture of racemic and meso 1,1′-bis(3-nitro-2-thienyl)diethyl ether (XVII) (42 %) was obtained, according to NMR analysis. The NMR spectrum showed two methyl doublets. This disturbing facile ether formation from thenyl alcohols has been observed previously.[35] By means of column chromatography V could be obtained pure.



Scheme 1.

In this connection we wish to report another approach to vinylnitrothiophene in which the nitro group is introduced after the vinyl group. Gronowitz and Holm [28] have shown that dithienyliodonium salts, prepared from thienyllithium derivatives and *trans*-chlorovinyliodoso dichloride, react with sodium nitrite to give nitrothiophenes. This approach was used for the synthesis of 2-isopropenyl-3-nitrothiophene (*cf.* Scheme 2). Reaction of 2,3-dibromothiophene (XVIII) with butyllithium followed by acetone gave 2-(3-bromo-2-thienyl)-2-propanol (XIX), which was dehydrated to 3-bromo-2-isopropenylthiophene (XX) by refluxing with oxalic acid at



Scheme 2.

reduced pressure. Halogen-metal exchange at −70 °C with butyllithium followed by reaction with *trans*-chlorovinyliodoso dichloride gave bis(2-isopropenyl-3-thienyl)iodonium chloride (XXI), which upon reaction with sodium nitrite gave 2-isopropenyl-3-nitrothiophene (XXII) and 2-isopropenyl-3-iodothiophene (XXIII), which were separated by recrystallization and chromatography on an aluminium oxide column.

On treatment with triethyl phosphite, XXII gave, along with other products, 6-methylthieno[3,2-*b*]pyrrole (XXIV), a thiophene analogue of skatole, in a way similar to that by which Srinivasan *et al.* obtained thienopyrroles from 1-(nitrothienyl)-2-aryl ethenes.[6] Although XXIV was not obtained in pure form, its NMR and mass spectra were recorded and confirmed the structure. The mass spectrum of the second abundant peak on the GLC showed a molecular ion at *m/e* 273, which underwent two successive losses of *m/e* 28 (ethylene) and a subsequent loss of water. Such a fragmentation has been reported for diethyl *N*-phenylphosphoramidate.[36] Therefore, the present substance seems to be one of the four possible diethyl thieno[3,2-*b*]pyrrolylphosphonates. A similar compound from the reaction between *o*-nitrostilbene and triethyl phosphite has been reported.[37] Unsuccessful attempts to obtain XXIV from 6-methylthieno-[3,2-*b*]pyrrole-5-carboxylic acid have been reported.[38] Thieno[3,2-*b*]pyrrole is unstable in air,[31] and so is the product obtained in the present work. The use of the same approach to prepare the parent thienopyrroles from III and V failed. Thieno[3,2-*b*]pyrrole was prepared by Snyder *et al.* from thieno[3,2-*b*]pyrrole-5-carboxylic acid.[31] Thieno[2,3-*b*]pyrrole was recently prepared by Farnier *et al.* from thieno[2,3-*b*]pyrrole-5-carboxylic acid.[39]

EXPERIMENTAL

All melting points are uncorrected. The NMR spectra were recorded on a Varian A-60. A JEOL MH 100 NMR spectrometer was used for the double resonance experiment. The mass spectra were recorded on a LKB A 9000 mass spectrometer. GLC analyses were carried out on a Perkin-Elmer 900 gas chromatograph and the chromatograms were integrated with a Varian Aerograph Model 480.

2-Methyl-3-nitrothiophene (II) was prepared according to Hörnfeldt,[40] who modified the synthesis by Snyder.[31] 225 g of dry quinoline, 38 g of copper bronze and 56.0 g of 2-methyl-3-nitro-5-thiophenecarboxylic acid[30] were introduced into a round-bottomed flask. The mixture was heated slowly on an oil-bath, and when it was liquid vacuum distillation at 11 mmHg was started. The temperature of the oil was then raised to 150 °C during a period of 4 h 45 min. The distillate containing quinoline and the title compound was mixed with ice and water, whereupon conc. hydrochloric acid was added in portions until pH 1. The remaining organic layer was taken up in ether and the acid water phase was extracted with ether. The combined ether phases were washed with sodium carbonate solution and water and yielded after evaporation 29.9 g (70 %) of the title compound. Recrystallization from low boiling petroleum ether gave 27.3 g (64 %), m.p. 43.8 – 45.0 °C, lit.[41] m.p. 44 – 45 °C. MS (direct inlet): Found $m/e = 142$ (89 %, M^+), 126 (98 %, loss of OH), the 100 % peak was at $m/e = 45$. Calc. for $C_5H_5NO_2S$: $m/e = 143$.

5-Ethyl-2-thiophenecarboxylic acid. 85.0 g (0.76 mol) of 2-ethylthiophene was dissolved in 200 ml of dry ether. With stirring and under a stream of nitrogen, 1000 ml of 0.84 M butyllithium was added at such a rate that the solution refluxed gently. After all butyllithium had been added, the reaction mixture was refluxed for an additional 2 h. The solution was then poured onto dry ice and was left over night. 5 M sodium hydroxide was added until no solid remained, and the phases were separated. The ether phase was washed with sodium hydroxide solution. The combined sodium hydroxide solutions were acidified with concentrated hydrochloric acid. The solid was collected, washed with water and dried. The yield was 109.2 g (92 %) of the title compound, m.p. 70 °C. lit.[42] m.p. 71 °C. The product was used in the next step without further purification.

2-Ethyl-3-nitro-5-thiophenecarboxylic acid was prepared as described by Gol'dfarb *et al.*[43] by nitration with nitric acid in sulfuric acid. The yield of crude product was 46 %.

5-Ethyl-2-thiophenesulfonyl chloride (XIII). This compound was prepared according to a patent by Siedel and Sturm.[32] 50 ml of chlorosulfonic acid was added dropwise with stirring and cooling with ice-water to 62 g of phosphorus pentachloride. To the resulting solution, 33.6 g (0.30 mol) of 2-ethylthiophene was added dropwise over a period of 30 min. The temperature was kept at 15 – 20 °C utilizing the ice-water bath. Immediately after the addition was finished, the reaction mixture was added from a dropping funnel to a beaker containing ice-water. After extraction with ether, the ether phase was washed with sodium hydrogen carbonate solution, dried and evaporated. The residue was distilled *in vacuo*, yielding 32.9 g (52 %) of the title compound, b.p. 95 – 100 °C/0.6 – 0.7 mmHg, lit.[32] 70 – 72 °C/0.1 mmHg. The product is pure according to GLC (SE 30 1.5 %, 2 m).

2-Ethyl-3-nitro-5-thiophenesulfonyl chloride (XIV). This nitration was carried out under the conditions used by Leandri *et al.*[44] for nitration of 5-bromo-2-thiophenesulfonyl chloride. 450 ml of nitric acid ($d = 1.52$) at a temperature of 0 – 10 °C was added dropwise with stirring to 490 ml of acetic anhydride. A solution of 182.5 g (0.870 mol) of 5-ethyl-2-thiophenesulfonyl chloride in 490 ml of acetic anhydride was added dropwise at 3 – 5 °C during a period of 50 min. The temperature was then raised and kept at 13 – 15 °C for 3 h. The mixture was poured onto crushed ice. The solution was extracted with ether, and the ether phase washed with sodium carbonate solution until neutral. After drying and evaporation, 215.9 g (98 %) was obtained. GLC (SE 30 1.5 %, 2 m) showed only one peak. The product was used directly in the next step.

2-Ethyl-3-nitrothiophene (*VIII*). A. From 2-ethyl-3-nitro-5-thiophenecarboxylic acid. The reaction was carried out in the same manner as described above for 2-methyl-3-nitrothiophene. The yield of the crude product was 33 %. and after recrystallization from petroleum ether 25 %, m.p. 38.1 – 41.0 °C.

B. From 2-ethyl-3-nitro-5-thiophenesulfonyl chloride (XIV). The method by Leandri *et al.* for the preparation of 2-bromo-3-nitrothiophene was used.[44] 215.9 g of XIV was boiled with 1500 ml of water for 3.5 h. A solution of 1000 ml of conc. sulfuric acid in 1200 ml of water was introduced into a 5 l three-necked round-bottomed flask equipped for steam distillation. Steam distillation was started using a heating mantle and superheated steam. The sulfonic acid solution was slowly introduced into the distillation flask *via* a dropping funnel. 9 l was distilled. The distillate was left over night and was then extracted with ether. The ether layer was washed with sodium hydrogen carbonate solution until neutral reaction, dried and evaporated. The crude product weighed 108.7 g (82 %). GLC (NPGS 5 %, 2 m) showed the product to be almost pure. The analytical sample of 2-ethyl-3-nitrothiophene was obtained by two recrystallizations from light petroleum ether, m.p. 41.2 – 42.0 °C. [Found: C 46.1; H 4.73; N 8.96; S 20.3. Calc. for $C_6H_7NO_2S$ (157.2): C 45.9; H 4.49; N 8.91; S 20.4.] NMR ($CDCl_3$): δ 7.53 (4), 7.05 (5), 3.26 (CH_2, q, 2 H), 1.35 (CH_3, t, 3 H), J_{45} 5.5 Hz, $J_{CH_2CH_3}$ 7 Hz. Mass spectrum (direct inlet): Found m/e 157 (78 %, M^{+}), 140 (100 %, loss of OH).

2-Nitro-3-vinylthiophene (III). 18.5 g (0.129 mol) of 3-methyl-2-nitrothiophene[45] was dissolved in 325 ml of methanol, 65 g of 34 % formaldehyde solution in water, 1.3 ml of acetic acid and 2.2 ml of pyrrolidine were added and the solution was refluxed for 46 h. After cooling, methanol was evaporated until about 100 ml of solution remained. Crystals were obtained (12.1 g; 60 %). Recrystallization from methanol gave 10.2 g (51 %) of the title compound, m.p. 47 – 48 °C, lit.[5] m.p. 49 – 50 °C. A second crop could be obtained from the combined filtrate and mother liquor. NMR ($CDCl_3$): δ 7.40 (5), 7.25 (4), 7.56 (α), 5.63 (β), 5.86 (β'). J_{45} 5.7 Hz, $J_{\alpha\beta}$ 10.1 Hz, $J_{\alpha\beta'}$ 17.9 Hz, $J_{\beta\beta'}$ 1.0 Hz. The β and β' quartets overlapped with each other, resulting in 6 signals. H_α and H_β are *cis* to each other. Mass spectrum (*via* GLC): Found $m/e = 155$; calc. for $C_6H_5NO_2S$: $m/e = 155$. The first fragment occurs at $m/e = 138$, indicating loss of OH.

Bis(3-nitro-2-thienyl)cyclobutane (IV). 10.0 g (0.070 mol) of 2-methyl-3-nitrothiophene, 40.0 g of 34 % formaldehyde solution in water, 0.35 ml of acetic acid and 0.60 ml of pyrrolidine were dissolved in 200 ml of methanol, and the solution was boiled. After 21 h. an additional 0.35 ml of acetic acid and 0.60 ml of pyrrolidine were added. The reaction was followed by GLC (NPGS 5 %, 2 m). After 72 h the heating was interrupted. On immediate scratching precipitation occurred. When cooled to room temperature the solid was filtered off and washed carefully with 50 % methanol. The weight after drying was 5.9 g, m.p. 141.0 – 142.5 °C. From the solution, an additional 0.6 g was obtained, to make a total yield of 60 %. Two recrystallizations from methanol gave the analytical sample, m.p. 142.0 – 142.5 °C. [Found: C 46.4; H 3.21; N 9.00; S 20.7. Calc. for $C_{12}H_{10}N_2O_4S_2$ (310.4): C 46.4; H 3.25; N 9.03; S 20.7.] NMR ($CDCl_3$): δ 7.54 (4), 7.13 (5), 4.5 (CH, m, 2 H), 2.5 (CH_2, m, 4 H). J_{45} 5.6 Hz. A spectrum of a solution in pentadeuteriopyridine was run at 100 MHz. In this spectrum the multiplet at δ 2.5 was divided into two. Upon saturation of the signals at δ 4.5 these two multiplets changed but no AA'BB' pattern could be obtained.

The mass spectrum *via* GLC is very like the spectrum of 3-nitro-2-vinylthiophene (see below) with the highest m/e at 155, corresponding to $C_6H_5NO_2S$. Mass spectrum *via* direct inlet: Found $m/e = 310$ (2.2 %); 293 (0.5 %, loss of OH); 282 (0.2 %, loss of C_2H_4); 280 (0.2 %, loss of NO); 278 (0.5 %); 266 (1.9 %); 265 (2.6 %); 264 (16 %); 155 (100 %).

The reaction was repeated in the dark starting from 0.5 g of 2-methyl-3-nitrothiophene. Boiling was interrupted after 62 h. The methanol was evaporated and benzene was added to dissolve the organic residue. Acetic acid and pyrrolidine were removed, and after drying the benzene was evaporated. NMR ($CDCl_3$) showed the mol ratio [V]:[IV] = 1.1, *i.e.* 65 % of the vinyl compound appeared as cyclobutane.

Deuterium exchange in bis(3-nitro-2-thienyl)-cyclobutane (IV). A. In a mixture of 5 ml of CH_3OD and 1 ml of deuterium oxide 0.2 g of IV, 2 drops of pyrrolidine and 1 drop of acetic acid were dissolved. The solution was refluxed for 63 h. After evaporation of the methanol, the residue was dissolved in chloroform, washed with 1.2 M hydrochloric acid and sodium hydrogen carbonate solution. The solution was analyzed by GLC-MS, which showed the following values (*m/e*, peak intensity): 155, 9.5; 156, 6.6; 157, 1.2. This gives 38 % of monodeuterated compound.

B. A small amount of IV was dissolved in a mixture of $CDCl_3$ and DMSO-d_6. A few drops of D_2O were added, and the 60 MHz NMR spectrum was run at 60 °C. (At lower temperature solid IV precipitated.) After adding a drop of pyrrolidine to the NMR tube, the solution was maintained at 60 °C for 50 min. The signals at δ 4.5 had now disappeared.

Equilibration of bis(3-nitro-2-thienyl)cyclobutane (IV) in dimethyl sulfoxide-water. Bis(3-nitro-2-thienyl)cyclobutane, 290 mg, was dissolved in a mixture of 1 ml of water and 9 ml of dimethyl sulfoxide. The solution was heated to 67 °C under nitrogen and 3 drops of pyrrolidine were added. After 1.5 h at 67 °C the heating was interrupted and the solution poured into ice-water. The mixture was extracted with ether, and the ether phase was washed with 1.2 M hydrochloric acid, sodium hydrogen carbonate solution, water and was dried. Evaporation gave 187 mg of material. Its IR spectrum was identical with that of IV with some minor additional absorptions. Recrystallization from methanol gave 111 mg of material, m.p. 141.0 – 143.1 °C. Its IR spectrum was identical to that of IV.

Attempt to monomerize bis(3-nitro-2-thienyl)-cyclobutane (IV) in methanolic solution. 0.18 ml of acetic acid and 0.30 ml of pyrrolidine were dissolved in 100 ml of methanol. 0.5 g of IV was dissolved in 21 ml of this solution and 10 drops of formaldehyde solution were added. After boiling for 96 h and removal of solvent and catalysts, the NMR spectrum showed signals only from IV.

Monomerization of bis(3-nitro-2-thienyl)-cyclobutane (IV) in DMSO. 0.5 g of IV was dissolved in 5 ml of dimethyl sulfoxide, dried over calcium hydride. The solution was heated on an oil bath to 180 °C for 30 min under a stream of nitrogen. The solution was poured into water and extracted with ether. After evaporation 0.2 g remained. Integration of the NMR spectrum showed the mol ratio [V]:[IV] = 3.4.

Reaction between 2-methyl-3-nitrothiophene and formaldehyde in dimethylformamide. 1.0 g (7.0 mmol) of 2-methyl-3-nitrothiophene, 35 mg of acetic acid and 51 mg of pyrrolidine were dissolved in 20 ml of freshly distilled DMF. 4.0 g of formalin was added and the solution was heated to 110 – 115 °C for 138 h. The red-brown solution was poured into water and was extracted with ether. The extract was washed twice with 1.2 M hydrochloric acid, twice with 1 M sodium carbonate, and twice with water. GLC analysis (OV 17 3 %, 2.5 m) showed two peaks, one of which corresponded to IV or V. The other component showed a mass spectrum with highest $m/e = 185$, corresponding to $C_7H_7NO_3S$ (VIa). The ether solution was treated with *N,O*-bis(trimethylsilyl)acetamide, and the GLC now showed two peaks in addition to the one from IV or V. Mass spectra gave molecular weights of 257 and 347, corresponding to $C_{10}H_{15}NO_3SSi$ (VIb) and $C_{13}H_{25}NO_4SSi_2$ (VIIb), respectively.

trans-*1-(Methoxycarbonyl-3-nitro-2-thienyl)-2-(2-thienyl)ethene (XIIa).* This synthesis is analogous to Rinkes' synthesis of 1-(5-methoxycarbonyl-3-nitro-2-thienyl)-2-phenylethene.[27] 20.1 g (0.100 mol) of 5-methoxycarbonyl-2-methyl-3-nitrothiophene, obtained by esterification of 2-methyl-3-nitro-5-thiophenecarboxylic acid[30] with methanol and hydrogen chloride,[27] was dissolved with slight heating in 22.4 g of freshly distilled 2-thiophene aldehyde. The solution was heated with stirring on an oil-bath to 120 °C, 30 drops of piperidine were added and the solution became blue. After 15 min an additional 20 drops of piperidine were added, and after another 15 min period the heating was interrupted. The mixture was immediately poured into a mortar and left to solidify. After cooling to room temperature, the solidified reaction mixture was transferred to a suction funnel, and the excess aldehyde and the catalyst were removed by suction. The crystals were washed thoroughly with ethanol. The yield of the title compound was 85 %, m.p. 134 – 138 °C. A sample recrystallized twice from methanol melted at 135.8 – 138.0 °C, lit.[26] 139 – 140 °C. The crude product was used in the next step.

trans-*1-(5-Carboxy-3-nitro-2-thienyl)-2-(2-thienyl)ethene (XIIb).* 20.0 g (0.068 mol) of 1-(5-methoxycarbonyl-3-nitro-2-thienyl)-2-(2-thienyl)ethene was dissolved with heating in 275 ml of acetic acid. 50 ml of concentrated sulfuric acid dissolved in 67 ml of water was added. The solution was boiled for 2 h. After standing over night, the resulting brown crystallized compound was filtered with suction and washed with a little acetic acid. The yield of the title compound was 16.1 g (84 %). The acid could be recrystallized from ethanol. Sublimation gave a sample melting at 230 – 235 °C. IR (KBr disc): Broad absorption at 2560 – 3100 cm^{-1} (carboxylic acid), 1670 cm^{-1} (aromatic carboxylic acid).

trans-*1-(3-Nitro-2-thienyl)-2-(2-thienyl)-ethene (XI).* A. Decarboxylation of 1-(5-carboxy-3-nitro-2-thienyl)-2-(2-thienyl)ethene. 95 g of dry quinoline was heated to 75 °C on an oil-bath. 15 g of copper bronze and 33.0 g (0.117 mol) of the acid XIIb were added with stirring. The reaction was followed by IR of the solution, observing the carbonyl absorption. The temperature was raised to 180 °C during a period of 70 min, after which the carbonyl band had disappeared. After cooling, ether was added and the copper was removed by filtration. The filtrate, water and crushed ice were introduced into a separatory funnel, concentrated hydrochloric acid was added in small portions with shaking between the additions. When the water phase had reached pH 1, the layers were separated. The water layer was extracted once with ether. The combined ether phases were washed with sodium hydrogen carbonate solution until neutral. Drying and evaporation gave 24.4 g (88 %) of the title compound. Treatment with charcoal combined with recrystallization from ethanol yielded 15.2 g (55 %), m.p. 67 °C. The analytical sample, obtained by one further recrystallization from ethanol, was of red color and melted at 65.8 – 67.2 °C. [Found: C 50.8; H 3.11; N 5.78; S 27.1. Calc. for $C_{10}H_7NO_2S_2$ (237.3): C 50.6; H 2.97; N 5.90; S 27.0.] NMR ($CDCl_3$): Signals in the region δ 6.90 – 8.00 were recorded. One half of the AB spectrum of the olefinic protons occurs at largest δ and shows a coupling constant of 16.0 Hz, indicative of two *trans* hydrogens. Further, one half of a thiophene AB quartet was distinguished with a coupling constant of 5.7 Hz.

B. From 2-methyl-3-nitrothiophene and 2-thiophene aldehyde. This method gives a purer product than A. 1.14 g (8.0 mmol) of 2-methyl-3-nitrothiophene was dissolved in 2.2 g of freshly distilled 2-thiophene aldehyde and 8 drops of piperidine were added. The mixture was kept at 120 °C for 2 h. GLC (OV 17 3 %, 2.5 m) showed that II had disappeared and a new compound had been formed. After cooling, the solution was dissolved in ethanol and added with stirring to a saturated solution of sodium hydrogen sulfite. After stirring for 30 min, the hydrogen sulfite adduct was filtered off by suction. The filtrate was extracted with ether. The hydrogen sulfite adduct was thoroughly washed with ether until all orange substance included had dissolved. After drying and evaporation, the residue was recrystallized from ethanol, yielding 0.8 g (43 %) of the title compound as glittering crystals, m.p. 68.1 – 68.8 °C. The compound is according to GLC and IR identical with that obtained above. The mother liquor was evaporated, and the residue was recrystallized from ethanol, yielding 0.2 g, m.p. 66.6 – 67.8 °C.

trans-*1-(2-Nitro-3-thienyl)-2-(2-thienyl)-ethene (X).* 14.3 g (0.100 mol) of 3-methyl-2-nitrothiophene was dissolved in 22.0 g of freshly distilled 2-thiophene aldehyde. 2.5 ml of piperidine was added and the solution was heated on an oil-bath to 90 – 100 °C. After 2 h the reaction was complete according to GLC (OV 1 3 %, 3 m). After cooling, the mixture crystallized on scratching. The substance was filtered off and thoroughly washed with ethanol until no smell of 2-thiophene aldehyde remained. After drying, the crystals weighed 14.1 g (60 %), m.p. 101 – 103 °C. Two recrystallizations from ethanol gave the analytical sample, m.p. 103.0 – 104.1 °C. [Found: C 50.6; H 3.00; S 27.2. Calc. for $C_{10}H_7NO_2S_2$ (237.3): C 50.6; H 2.97; S 27.0.] NMR ($CDCl_3$): The spectrum is complex, showing signals at δ 6.9 – 8.0. The two signals at lowest field are separated by 16.0 Hz, indicating that the olefinic hydrogens are *trans* to each other.

3-Methyl-4-nitrothiophene was a gift from B. Holm.[28]

Attempted reaction between 3-methyl-4-nitrothiophene and formaldehyde. 0.4 ml of acetic acid and 0.7 ml of pyrrolidine were dissolved in 50 ml of methanol. To 5 ml of this solution, 1.1 g of formalin was added. In 0.5 ml of this mixture, 6.9 mg of 3-methyl-4-nitrothiophene was dissolved. 0.03 ml portions were enclosed in capillary tubes which were then heated in an oil-bath to 80 °C. Samples were analyzed on GLC (NPGS 5 %, 2 m, 180 °C). Even after 40 h no new compound was detected.

Attempted reaction between 3-methyl-4-nitrothiophene and 2-thiophene aldehyde. In 0.15 ml of freshly distilled 2-thiophene aldehyde, some crystals of 3-methyl-4-nitrothiophene were dissolved. The solution was heated on an oil-bath to 100 – 110 °C for 1 h and then the temperature was raised slowly to 140 °C during a period of 70 min. GLC (OV 1 3 %, 3 m) showed that the main compound was still starting material. Four minor components were analyzed by mass spectroscopy; none of them was the expected ethylene.

2-(α-Bromoethyl)-3-nitrothiophene (XV). 7.4 g (0.047 mol) of 2-ethyl-3-nitrothiophene was dissolved in 75 ml of dry carbon tetrachloride. 8.4 g (0.047 mol) of *N*-bromosuccinimide (recrystallized from water and dried over sulfuric acid) and a small amount of dibenzoyl peroxide (dried over phosphorus pentoxide) were added. The mixture was boiled with stirring for several hours. Since nothing had happened after this time, a drop of water was added and after 75 min all of the heavy NBS had been replaced by floating succinimide. The solid was filtered off and the solvent was removed. The residue weighed 11.1 g. The product decomposed on the GLC column. Its NMR showed, however, that only monobromination had occurred. Recrystallization from light petroleum gave 8.7 g (82 %). One further recrystallization, including treatment with aluminium oxide, gave the analytical sample, m.p. 59.0 – 59.6 °C. [Found: C 30.5; H 2.48; Br 33.9; N 5.88; S 13.7. Calc. for $C_6H_6BrNO_2S$ (236.1): C 30.5; H 2.56; Br 33.9; N 5.93; S 13.6.] NMR ($CDCl_3$): δ 7.57 (4), 7.28 (5), 6.25 (CH, q, 1 H), 2.14 (CH_3, d, 2 H), J_{45} 5.7 Hz, $J_{\mathrm{CHCH_3}}$ 7.0 Hz, $J_{\mathrm{CH-5}}$ 0.5 Hz. The assignments of the thiophene proton chemical shifts were confirmed by their ^{13}C couplings ($J_{\mathrm{CH-5}}$ 189 Hz, $J_{\mathrm{CH-4}}$ 175 Hz, *cf.* Ref. 46).

1-(3-Nitro-2-thienyl)ethanol (XVI). 11.8 g (0.050 mol) of 2-(α-bromoethyl)-3-nitrothiophene was dissolved in 160 ml of peroxide-free dioxane. 10 g of sodium formate dissolved in 110 ml of water was added. The mixture was boiled for 5.5 h, whereupon 14 ml of conc. hydrochloric acid was added and boiling was continued for 4 h. After cooling, the solution was neutralized with sodium hydrogen carbonate. As much as possible of the dioxane was evaporated and the residue (two liquid phases) was extracted twice with ether. The ether phase was washed with sodium bisulfite to remove possibly formed peroxides. Integrated GLC (NPGS 5 %, 2 m) showed the product to be 98 % pure. The crude product weighed 7.6 g. Two recrystallizations from carbon tetrachloride gave 4.7 g (54 %) of the title compound, m.p. 55.5 – 56.7 °C. The solvent dioxane-water was superior to ethanol-water, in which 2-(α-ethoxyethyl)-3-nitrothiophene was formed as by-product. [Found: C 41.8; H 4.24; N 8.12; S 18.7. Calc. for $C_6H_7NO_3S$ (173.2): C 41.6; H 4.07; N 8.09; S 18.5.] NMR ($CDCl_3$): δ 7.56 (4), 7.22 (5), 5.74 (CH, q, 1 H), 1.61 (CH_3, d, 3 H), 3.75 (OH, s, 1 H), J_{45} 5.7 Hz, $J_{\mathrm{CHCH_3}}$ 6.5 Hz.

3-Nitro-2-vinylthiophene (V). 2.5 g (0.0145 mol) of 1-(3-nitro-2-thienyl)ethanol was dissolved in 400 ml of dry benzene. 30 ml of a warm saturated benzene solution of *p*-toluenesulfonic acid was added and the mixture was poured into a round-bottomed flask, which was then equipped with a Soxhlet extractor, the thimble containing molecular sieves. The solution was refluxed, the condensed liquid dropping into the thimble and thereby being dried. After refluxing over night, GLC (OV 17 3 %, 2.5 m) showed that the alcohol had disappeared. The benzene solution was shaken with water, sodium hydrogen carbonate solution, and water; it was then dried and evaporated. The residue weighed 2.2 g. NMR of the crude product showed it to consist of 3-nitro-2-vinylthiophene (V), bis(3-nitro-2-thienyl)cyclobutane (IV), and 1,1′-bis(3-nitro-2-thienyl)diethyl ether (XVII) in the mol ratio 7.0:1.7:1. The components were separated on a silica gel column using dry benzene as eluent. They occur in the eluate in the order V, IV, and XVII. From 2.0 g of the crude product 1.1 g of V, 0.2 g of IV, and 0.2 g of XVII were obtained.

The fraction containing V was dissolved in a few ml of benzene; the solution was filtered through glass wool, a few ml of methanol was added and the solution was evaporated at room temperature almost to dryness. The crystals were filtered off, washed with methanol and dried. The main part melted at 41 – 43 °C, but the remaining part did not melt below 60 °C and probably consisted of IV. [Found: C 46.5; H 3.18; N 9.05; S 20.6; Calc. for $C_5H_5NO_2S$ (155.2): C 46.4; H 3.25; N 9.03; S 20.7]. NMR ($CDCl_3$): δ 7.52 (4), 7.10 (5), 7.57 (α), 5.82 (β), 5.50 (β′), J_{45} 5.6 Hz, $J_{5\alpha}$ 0.7 Hz, $J_{\alpha\beta}$ 17.3 Hz, $J_{\alpha\beta'}$ 10.8 Hz, $J_{\beta\beta'}$ 0 Hz. MS (*via* GLC): Found $m/e = 155$ (molecular ion, 100 %), 139, 138 (loss of OH), 126. NMR ($CDCl_3$) of XVII: The material consists of diastereomers in the ratio 2:1. Major component: δ 7.55 (4), 7.23 (5), 5.46 (CH, q), 1.60 (CH_3, d), J_{45} 5.6 Hz, $J_{\mathrm{CHCH_3}}$ 6.2 Hz. Minor component: δ 7.51 (4), 7.14 (5), 3.9 (CH, q), 8.64 (CH_3, d), J_{45} 5.5 Hz, $J_{\mathrm{CHCH_3}}$ 6.1 Hz. Mass spectrum of XVII: Found: $m/e = 172$. Calc. for $C_{12}H_{12}N_2O_5S_2$ $m/e = 328$. The observed value corresponds to cleavage of the C – O bond. A similar fragmentation is known in, *e.g.* dibenzyl ether.[47]

2-(3-Bromo-2-thienyl)-2-propanol (XIX). 242.0 g (1.00 mol) of 2,3-dibromothiophene was dissolved in 400 ml of dry ether. The solution was placed in a three-necked flask swept with nitrogen. Under a stream of nitrogen, the solution was cooled to – 70 °C with dry ice-ethanol. 650 ml of 1.70 M butyllithium in hexane was added dropwise with stirring. After stirring for an additional 15 min, 90 g of dry acetone in 200 ml of dry ether was introduced at such a rate that the temperature did not increase. After an additional 30 min the cooling bath was removed, and when the temperature was + 10 °C, water was added dropwise to the solution, cautiously at first. The phases were separated and the water phase was extracted twice with ether. The combined ether layers were washed with water and dried. Evaporation gave 230.9 g of solid substance, which was used directly in the next step. Two recrystallizations from petroleum ether gave 2-(3-bromo-2-thienyl)-2-propanol, which according to GLC (NPGS 5 %, 2 m) was pure, m.p. 59.6 – 62.8 °C. [Found: C 38.0; H 4.10; Br 36.1; S 14.2. Calc. for C_7H_9BrOS (221.1): C 38.0; H 4.10; Br 36.1; S 14.5.] NMR ($CDCl_3$): δ 7.03 (5), 6.88 (4), 2.97 (OH), 1.70 (CH_3), $J_{45} = 5.3$ Hz.

3-Bromo-2-isopropenylthiophene (XX). The crude 2-(3-bromo-2-thienyl)-2-propanol prepared above was melted and 25 g of anhydrous oxalic acid was added. The melt was then refluxed at 17 mmHg using an oil-bath as heat source. The temperature of the oil was raised from 77 to 107 °C over a period of 2 h. Heating was interrupted, and after cooling the reaction mixture was dissolved in ether, shaken twice with water, then with sodium hydrogen carbonate solution until neutral reaction. After drying and evaporation, the residue was distilled, yielding 152.7 g of 3-bromo-2-isopropenylthiophene (75 % from 2,3-dibromothiophene), b.p. 96 – 98 °C/16 mmHg. [Found: C 41.0; H 3.48; Br 38.9; S 15.5. Calc. for C_7H_7BrS (203.1): C 41.4; H 3.47; Br 39.3; S 15.8.] NMR ($CDCl_3$): δ 7.00 (5), 6.84 (4), 5.48 (β, m, 1 H), 5.19 (β', quint, 1 H), 2.13 (CH_3, q, 3 H), J_{45} 5.3 Hz, $J_{\beta\beta'} = J_{\beta'-CH_3}$ 1.6 Hz, $J_{\beta-CH_3}$ 0.8 Hz. The coupling constants suggest that H_β is *trans* to the methyl group.[48]

Bis-(2-isopropenyl-3-thienyl)iodonium chlroride (XXI). This synthesis was carried out in dry flasks, swept with nitrogen. 55.0 g (0.271 mol) of 3-bromo-2-isopropenylthiophene in 250 ml of dry ether was cooled to – 70 °C and 0.30 mol of butyllithium in ether or hexane was added dropwise with stirring. The stirring was continued for 30 min, and the solution was then poured through a PVC tube into a stirred solution of 39.0 g (0.15 mol) of *trans*-chlorovinyliodoso dichloride [49] dissolved in 180 ml of toluene cooled to – 70 °C. After stirring at this temperature for 3 h, the cooling bath was removed, and when the temperature had increased to about 10 °C water was added, at first cautiously. The precipitate was filtered off on a Büchner funnel, which was troublesome because of the two liquid phases. The precipitate was washed with ether, and after drying in vacuum it was washed with water and then with a small amount of acetone, yielding after drying 28.2 g (51 %) of the title compound.

2-Isopropenyl-3-nitrothiophene (XXII) and 3-iodo-2-isopropenylthiophene (XXIII). 72.4 g (0.177 mol) of bis-(2-isopropenyl-3-thienyl)-iodonium chloride and 65.2 g (0.48 mol) of sodium nitrite were stirred in 720 ml of *N*,*N*-dimethylformamide for 3.5 h at 120 – 130 °C. The solution was poured into water and extracted with ether. The ether phase gave on drying and evaporation 58.1 g of crude product mixture, which was dissolved in 1300 ml of boiling hexane, treated with neutral aluminum oxide and the hot solution filtered and then cooled to – 70 °C. The mother liquor was decanted from the crystals, which were then washed three times with 65 ml portions of hexane at – 70 °C. The solid melted on warming to room temperature. GLC (NPGS 5 %, 2 m) showed that the material contained XXII and XXIII in the ratio 11:1. The recrystallization procedure was repeated, using 380 ml of hexane, and the solid was washed once at – 70 °C. GLC showed a ratio of 142, that is more than 99 % of XXII. Yield of 2-isopropenyl-3-nitrothiophene: 14.2 g (48 %). Two recrystallizations from hexane at – 18 °C gave m.p. 34.0 – 34.8 °C. [Found: C 49.9; H 4.20; N 8.21; S 18.9. Calc. for $C_7H_7NO_2S$ (169.2): C 49.7; H 4.17; N 8.28; S 19.0.] NMR ($CDCl_3$): δ 7.18 (5), 7.57 (4), 5.22 (β, m), 5.33 (β', quint), 2.13 (CH_3), J_{45} 5.6 Hz, $J_{\beta\beta'} = J_{\beta'-CH_3}$ 1.5 Hz, $J_{\beta-CH_3} = 0.9$ Hz. MS (*via* GLC): Found $m/e = 169$ (M^+), 152 (loss of OH), 126, 124. The combined hexane solutions were evaporated and the residue was chromatographed on neutral aluminium oxide, the column diameter being 6.7 cm and its height 19 cm. Elution with petroleum ether gave 24.5 g (55 %) of 3-iodo-2-isopropenylthiophene. Elution with ether: petroleum 30:70 gave 6.5 g of material, the GLC of which showed [XXII]:[XXIII] = 3.5. XXIII had a b.p. 69 °C/0.5 mmHg. [Found: C 34.0; H 2.91. Calc. for C_7H_7IS (250.1): C 33.6; H 2.82.] NMR ($CDCl_3$): δ 7.03 (5), 6.94 (4), 5.40 (β, m), 5.21 (β', quint) 2.11 (CH_3, q), J_{45} 5.2 Hz, $J_{\beta\beta'} = J_{\beta'-CH_3}$ 1.4 Hz, $J_{\beta-CH_3}$ 0.8 Hz. Mass spectrum (*via* GLC): Found: 250. Calc. for C_7H_7IS: 250.

6-Methylthieno[*3,2-*b]*pyrrole (XXIV).* 4.0 g of 2-isopropenyl-3-nitrothiophene was dissolved in 50 ml of triethyl phosphite, and under a stream of nitrogen the solution was warmed to 130 °C. GLC (OV 17 3 %, 2.5 m) showed that the starting material disappeared and other compounds were formed. The main product (52 %) was, according to its mass spectrum, 6-methylthieno[3,2-b]pyrrole (XXIV). The second abundant peak (38 %) on the GLC had the highest *m*/*e* 273 and showed consecutive losses of fragments 28, 28, and 18. After 2 h the starting material had disappeared. Excess triethyl phosphite was removed at 12 mmHg, followed by distillation of the residue under nitrogen. 4.5 g of almost pure triethyl phosphate was obtained as a first fraction. At 90 – 130 °C/0.35 mmHg 0.7 g of material distilled, which according to NMR consisted of 55 % 6-methylthieno[3,2-*b*]pyrrole and 45 % triethyl phosphate. The distillation residue weighed 4.2 g. NMR ($CDCl_3$): δ 6.98 (2, q), 6.81 (3, d), 6.64 (5, m), 8.2 (4, broad), 2.22 (CH_3, d), J_{23} 5.2 Hz, J_{25} 1.3 Hz, J_{5-CH_3} 1.1 Hz. Spectrum of triethyl phosphate: δ 4.09 (CH_2, quint), 1.29 (CH_3, t). MS (*via* GLC): Found $m/e = 137$ (80 %, M^+), 136 (100 %), 110, 109. The compound has an unpleasant odour, and becomes dark on standing. The red-brown picrate of XXIV was obtained from ethanol solution, m.p. *ca.* 115 °C (dec.).

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REFERENCES

1. Gronowitz, S. and Maltesson, A. *Acta Chem. Scand. 25* (1971) 2435.
2. Wesslén, B. *Acta Chem. Scand. 21* (1967) 718.
3. Bakke, J. *Acta Chem. Scand. 21* (1967) 1967.
4. Bakke, J. *Acta Chem. Scand. 23* (1969) 3055.
5. Srinivasan, K., Balasubramanian, K. K. and Swaminathan, S. *Chem. Ind. (London)* (1971) 398.

6. Srinivasan, K., Srinivasan, K. G., Balasubramanian, K. K. and Swaminathan, S. *Synthesis* (1973) 313.
7. a. Seebach, D. In Müller, E. *Methoden der organischen Chemie*, Band IV/4, Georg Thieme Verlag, Stuttgart 1971, p. 9 ff.; b. *Ibid.* p. 26 ff.
8. a. Dodson, R. M. and Zielske, A. G. *J. Org. Chem. 32* (1967) 28; b. Allinger, N. L. and Tushaus, L. A. *J. Org. Chem. 30* (1965) 1945; Wiberg, K. B. and Lampman, G. M. *J. Amer. Chem. Soc. 88* (1966) 4429; Lillien, I. and Doughty, R. A. *Tetrahedron 23* (1967) 3321; c. Lambert, J. B. and Roberts, J. D. *J. Amer. Chem. Soc. 87* (1965) 3884.
9. Gross, M. L. and Wilkins, C. L. *Tetrahedron Lett.* (1969) 3875.
10. Schauble, J. H., Freed, E. H. and Swerdloff, M. D. *J. Org. Chem. 36* (1971) 1302.
11. Farnum, D. G. *Private communication.*
12. Meyerson, S., Puskas, I. and Fields, E. K. *J. Amer. Chem. Soc. 88* (1966) 4974.
13. Skramstad, J. *Acta Chem. Scand. 22* (1968) 2445.
14. Holm, B. *Private communication.*
15. Overberger, C. G., Valentine, M. and Anselme, J.-P. *J. Amer. Chem. Soc. 91* (1969) 687.
16. Gilchrist, T. L. and Storr, R. C. *Organic Reactions and Orbital Symmetry*, Cambridge University Press, London 1972, p. 141 ff.
17. Baldwin, J. E. and Kapecki, J. A. *J. Amer. Chem. Soc. 92* (1970) 4874.
18. Huisgen, R., Feiler, L. A. and Binsch, G. *Chem. Ber. 102* (1969) 3460.
19. Bengelsdorf, I. S. *J. Org. Chem. 25* (1960) 1468.
20. Zwierzak, A. and Pines, H. *J. Org. Chem. 28* (1963) 3392.
21. Mayo, F. R. *J. Amer. Chem. Soc. 90* (1968) 1289.
22. Brown, W. G. *J. Amer. Chem. Soc. 90* (1968) 1916.
23. Kunitake, C. A. T., Shinsenji, M. and Miyazaki, H. *J. Polym. Sci. Part A-1, 7* (1969) 1497.
24. Miller, D. B., Flanagan, P. W. and Shechter, H. *J. Amer. Chem. Soc. 94* (1972) 3912.
25. Kellogg, R. M. and Buter, J. *J. Org. Chem. 36* (1971) 2236.
26. Campaigne, E., Fleming, W. L. and Dinner, A. *J. Heterocycl. Chem. 5* (1968) 191.
27. Rinkes, I. J. *Rec. Trav. Chim. Pays-Bas 52* (1933) 538.
28. Gronowitz, S. and Holm, B. *Chem. Scr. 2* (1972) 245.
29. Gronowitz, S. *Ark. Kemi 13* (1958) 295.
30. Campaigne, E. and Grose, H. G. *J. Amer.* Chem. Soc. *73* (1951) 3812.
31. Snyder, H. R., Carpino, L. A., Zack, J. F. and Mills, J. F. *J. Amer. Chem. Soc. 79* (1957) 2556.
32. Siedel, W. and Sturm, K. Farbwerke Hoechst, *German Pat.* 1,088,509 (1958) [*Chem. Abstr. 56* (1962) P 456e].
33. Zelinski, N. and Zelikov, J. *Ber. Deut. Chem. Ges. 34* (1901) 3249; Carlin, R. B. and Constantine, D. A. *J. Amer. Chem. Soc. 69* (1947) 50.
34. Traynelis, V. J., Hergenrother, W. L., Hanson, H. T. and Valicenti, J. A. *J. Org. Chem. 29* (1964) 123.
35. Gjøs, N., *Diss.*, University of Lund, Lund 1971, p. 24. This author found that acid work-up of 3-(1-hydroxyethyl)-2-phenylthiophene gave a small amount of the corresponding ether.
36. McMurray, W. J., Lipsky, S. R., Zioudrou, C. and Schmir, G. L. *Org. Mass Spectrom. 3* (1970) 1031.
37. Sundberg, R. J. *J. Org. Chem. 30* (1965) 3604.
38. Keener, R. L., *Diss.*, Urbana, Illinois 1967, p. 27.
39. Farnier, M., Soth, S. and Fournari, P. *C. R. Acad. Sci. C 277* (1973) 1149.
40. Hörnfeldt, A.-B. *Private communication.*
41. Rinkes, I. J. *Rec. Trav. Chim. Pays-Bas 51* (1932) 1134.
42. Schleicher, E. *Ber. Deut. Chem. Ges. 18* (1885) 3015.
43. Gol'dfarb, Ya. L., Fabrichnyi, B. P. and Shalavina, I. F. *J. Gen. Chem. USSR 29* (1959) 3596.
44. Carpanelli, C. and Leandri, G. *Ann. Chim. (Rome) 51* (1961) 181.
45. Rinkes, I. J. *Rec. Trav. Chim. Pays-Bas 52* (1933) 1052.
46. Gronowitz, S., Johnson, I. and Hörnfeldt, A.-B. *Chem. Scr. In press.*
47. Beynon, J. H., Saunders, R. A. and Williams, A. E. *The Mass Spectra of Organic Molecules*, Elsevier, Amsterdam 1968, p. 169 ff.
48. Jackman, L. M. and Sternhell, S. *Applications of Nuclear Magnetic Resonance in Organic Chemistry*, Pergamon, Oxford 1969, p. 316 ff.
49. Beringer, F. M. and Nathan, R. A. *J. Org. Chem. 34* (1969) 685.

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