likely polymorphic forms of IVb. (The presence of polymorphism among diphenyl sulfides has been reported previously.[3]) The analytical sample (ethanol) was a white crystalline solid, m.p. 137–138°.

Anal. Calcd. for $C_{14}H_{11}BrClNO_2S$: C, 45.11; H, 2.95; N, 3.76. Found: C, 44.97; H, 3.28; N, 3.77.

2-Bromo-4-chloro-2′-formamidodiphenyl Sulfide (IVa).—2-Amino-2′-bromo-4′-chlorodiphenyl sulfide (2.0 g., 0.0064 mole) was heated under reflux for 4 hr. with ten times its weight of 90% formic acid. The mixture was poured into 100 ml. of ice–water and the resulting white emulsion was extracted with ether. The ether was dried ($MgSO_4$) and concentrated under reduced pressure leaving an off-white solid. Several crystallizations from ethanol afforded 1.3 g. (60%) of IVa as a white solid, m.p. 139.5–140.5°.

Anal. Calcd. for $C_{13}H_9BrClNOS$: C, 45.31; H, 2.63; N, 4.06. Found: C, 45.51; H, 2.58; N, 4.46.

Cyclization of 2-Bromo-4-chloro-2′-formamido-5′-methoxydiphenyl Sulfide (IVb)—A mixture of 5 g. (0.013 mole) of IVb, 2.1 g. of anhydrous potassium carbonate, 0.05 g. of copper–bronze catalyst,[18] and 125 ml. of DMF was heated under reflux for 2 hr. and allowed to stand at room temperature overnight. An additional trace of catalyst was added and reflux was continued until carbon dioxide evolution stopped (4 hr.). The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was extracted with 1.5 l. of boiling ligroin (60–90°) and the extracts were concentrated to give 2.5 g. of blue-gray solid. Repeated crystallization from benzene (Darco G-60) provided 3-chloro-7-methoxyphenothiazine (Vb) as very pale green plates, m.p. 202–203°.

Anal. Calcd. for $C_{13}H_{10}ClNOS$: C, 59.20; H, 3.80; Cl, 13.47; N, 5.31. Found: C, 59.17; H, 3.88; Cl, 13.08; N, 5.30.

Cyclization of 2-Bromo-4-chloro-2′-formamidodiphenyl Sulfide (IVa).—A mixture of 2 g. (0.0058 mole) of IVa, 0.83 g. (0.006 mole) of anhydrous potassium carbonate, 0.1 g. of copper–bronze catalyst,[18] and 20 ml. of DMF was heated under reflux for 11 hr. The mixture was filtered and the filtrate was poured into 300 ml. of cold water yielding 0.96 g. of pale green solid. Crystallization from benzene–petroleum ether (b.p. 20–40°) (Darco G-60) followed by crystallization from pure benzene gave 3-chlorophenothiazine (Va), m.p. 205–206°. The identity of Va was verified by mixture melting point and infrared comparison with authentic samples of 2-chlorophenothiazine[6] and 3-chlorophenothiazine.[6]

2-Amino-4-chloro-4′-methoxy-2′-nitrodiphenyl Sulfide (IX).—To a solution of 13 g. (0.33 mole) of sodium hydroxide in 195 ml. of ethanol was added 50 g. (0.13 mole) of the zinc salt of 2-amino-4-chlorobenzenethiol[19] and a solution of 52 g. (0.28 mole) of 4-chloro-3-nitroanisole[20] in 325 ml. of ethanol. The mixture was heated under reflux for 5 hr. and poured into 2 l. of cold water. The solid was extracted with ether and the extracts were dried over magnesium sulfate, decolorized, and concentrated to give 44.4 g. (55%) of yellow solid, m.p. 129–138°. This material was used directly in subsequent acylations. An aliquot was crystallized from ethanol to provide the analytical sample, m.p. 141–142°.

Anal. Calcd. for $C_{13}H_{11}ClN_2O_3S$: C, 50.22; H, 3.57; N, 9.02. Found: C, 50.20; H, 3.57; N, 9.06.

2-Acetamido-4-chloro-4′-methoxy-2′-nitrodiphenyl Sulfide (XI).—A mixture of 2.5 g. (0.008 mole) of IX, 0.9 ml. of pyridine, and 11 ml. of acetic anhydride was warmed to effect solution. The deep amber solution was allowed to cool, and a trace of undissolved solid was filtered. The filtrate was diluted with a mixture of 10 ml. of methanol and 150 ml. of water. An oil separated which solidified on standing. Crystallization from methanol (Darco G-60) afforded 1.4 g. (49%) of bright yellow crystals, m.p. 150–151°.

Anal. Calcd. for $C_{15}H_{13}ClN_2O_4S$: C, 51.07; H, 3.69; N, 7.94. Found: C, 51.43; H, 3.81; N, 7.40.

4-Chloro-2-formamido-4′-methoxy-2′-nitrodiphenyl Sulfide (X).—The amino derivative (IX) was formylated on a 0.63 mole scale, as described above for the preparation of IVa, to give a 70% yield of X, m.p. 146–147° (ethanol).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_4S$: C, 49.61; H, 3.27; N, 8.27. Found: C, 49.49; H, 3.15; N, 8.50.

2-Chloro-7-methoxyphenothiazine (VIb).—To a boiling solution of X (2.4 g., 0.0071 mole) in 200 ml. of acetone was added, in portions, 1.41 g. (0.021 mole) of powdered 85% potassium hydroxide. After reflux for an additional hour, the mixture was concentrated to 15 ml. and diluted with cold water. Two crystallizations from benzene (Darco G-60) gave 0.79 g. (44%) of VIb, m.p. 174–175°. This sample did not depress the melting point of the compound obtained by thionation of 3-chloro-4′-methoxydiphenylamine.[11,12] The infrared spectra of the two samples were identical.

4-Chloro-4′-methoxydiphenylamine (XII).—A mixture of 93.5 g. (0.50 mole) of *p*-bromoanisole, 101.7 g. (0.60 mole) of *p*-chloroacetanilide, 48.0 g. (0.35 mole) of anhydrous potassium carbonate, and 1.7 g. of copper–bronze catalyst was heated in an oil bath at 210° for 28 hr. The mixture was allowed to cool and extracted with four 300-ml. portions of boiling acetone. The acetone was removed under reduced pressure and the residue was heated under reflux for 4 hr. with a solution of 145 ml. of concentrated hydrochloric acid in 400 ml. of ethanol. The hydrolysis mixture was poured into 2 l. of cold water, basified with 20% sodium hydroxide solution, and extracted with four 300-ml. portions of ether. The extracts were combined, dried ($MgSO_4$), and concentrated. The black residual oil was distilled with a short column to give 70 g. (60%) of XII, b.p. 150–163° (0.1 mm.), m.p. 50–51°.

Anal. Calcd. for $C_{13}H_{12}ClNO$: C, 66.71; H, 5.13; N, 5.95. Found: C, 67.19; H, 5.69; N, 5.88.

3-Chloro-7-methoxyphenothiazine (Vb).—A mixture of 2.3 g. (0.01 mole) of XII, 0.64 g. (0.02 mole) of sulfur, and 0.06 g. of iodine was heated in an oil bath at 140–145° for 45 min. The brown viscous reaction mixture was extracted with ether and the combined extracts were evaporated under reduced pressure to a dark oil. A good recovery of starting material was effected by trituration of the oil with four 25-ml. portions of petroleum ether (b.p. 20–40°). The petroleum ether-insoluble, green, gummy residue was crystallized repeatedly from benzene (Darco) to give 50 mg. of Vb as very pale green glistening plates, m.p. 195–197°. The infrared spectra of this compound and the compound obtained by cyclization of IVb were identical.

Anal. Calcd. for $C_{13}H_{10}ClNOS$: C, 59.20; H, 3.80. Found: C, 59.08; H, 4.06.

Acknowledgment.—The authors gratefully acknowledge the assistance of Mr. Klaus Herrle in carrying out some of these preparations.

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The Synthesis of Thiophene Analogs of Fluorene[1]

HANS WYNBERG AND A. KRAAK[2]

Department of Organic Chemistry, The University,
Groningen, Holland

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Sometime ago we measured the dipole moments of the three isomeric dithienyls.[3] The values for 2,2′-dithienyl (0.77 D.), 2,3′-dithienyl (1.07 D.), and 3,3′-dithienyl (0.75 D.) indicated that in solution only the 2,3′-isomer could have a coplanar conformation.

It appeared interesting to measure the equilibrium constants of the dithienyl charge-transfer complexes with some electron acceptors in order to gain additional information about the conformation of these dithienyls.[4]

Truly flat (rigid) analogs of the dithienyls, such as I, II, and III, would also be valuable models in this study.

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[1] Part II in the series, "Steric Effects in Heterocyclic Systems." For part I, see H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).

[2] Fellow of the Netherlands Organization for Pure Research (Z. W. O.).

[3] H. Wynberg and H. M. J. C. Creemers, *Angew. Chem.*, **75**, 453 (1963).

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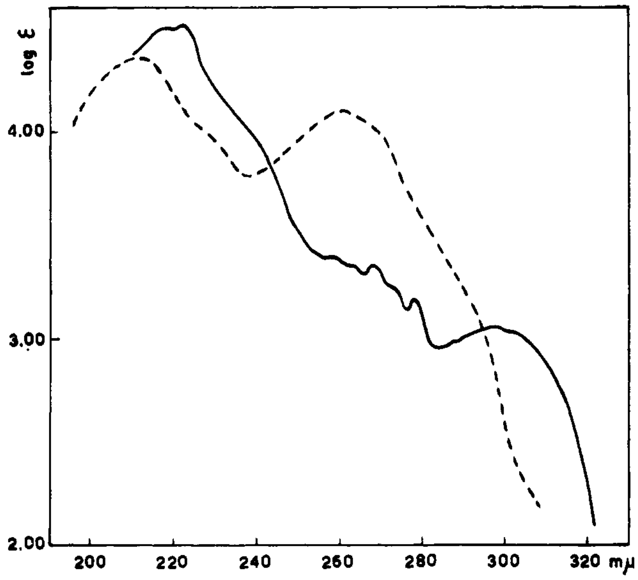
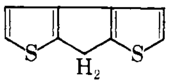
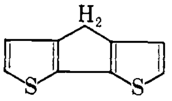


Fig. 1.—Ultraviolet spectra of ———, cyclopenta[1,2-*b*:4,3-*b*′]dithiophene; and - - - -, 3,3′-dithienyl. The solvent was cyclohexane.

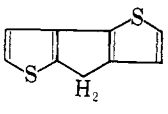
This paper reports the synthesis of the first thiophene analog (I)[5] of fluorene related to 3,3′-dithienyl.



I

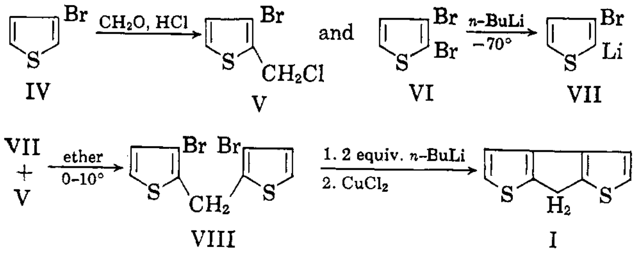


II



III

After several routes[6] had been tried in vain, the following synthetic scheme proved successful.



Chloromethylation[7] of 3-bromothiophene (IV)[8] gave 3-bromo-2-thenylchloride (V), a lachrymatory liquid, in good yield (72%). The assignment of structure V to the chloromethylated product is based on its conversion by permanganate oxidation to the known[9] 3-bromo-2-thiophene carboxylic acid.

According to the method of Löfgren and Tegnér[10] the 3-bromo-2-thenylchloride was allowed to react with 3-bromo-2-thienyllithium (VII), which was obtained by interconversion of 2,3-dibromothiophene (VI) and *n*-butyllithium at −70°.[11] 3,3′-Dibromo-2,2′-dithienylmethane (VIII) was obtained as a colorless crystalline material in low yield (16%), m.p. 37°.

Ring closure by oxidation of the dilithio derivative[12] in dilute ethereal solution with cupric chloride under ice cooling gave the desired cyclopenta[1,2-*b*:4,3-*b*′]-dithiophene (I) in a reasonable yield (38%).

The cyclopentadithiophene (I) is a colorless solid, m.p. 66–67°. The elementary analysis as well as the ultraviolet and n.m.r. spectra of I is in accord with the structure assigned. Noticeable is the fact that the absorption of the methylene protons (at τ 6.36) is identical with that found for fluorene. The ultraviolet absorption spectrum shows some similarities to that of fluorene with strong maxima at 218 and 223 mμ and characteristic fine structure in the 255–280-mμ region (Fig. 1). This fine structure has been associated with a strained nearly planar structure.[13–15] The 3,3′-dithienyl chromophore (λ_{max} 260 mμ, log ϵ 4.1)[16] no longer dominates the spectrum.

It is worthwhile noting that I, containing a five-membered ring fused to a five-membered heteroaromatic, may well show a Mills–Nixon[1] effect.

Experimental[17]

3-Bromo-2-thenyl Chloride (V).—A rapid stream of hydrogen chloride was passed into a stirred mixture of 57 g. (0.35 mole) of 3-bromothiophene[8] and 15 ml. of concentrated hydrochloric acid during 20 min. while the temperature was maintained at 0–5°. After 38 ml. of 40% aqueous formaldehyde was added dropwise, stirring was continued at 50° for 1 hr. The vigorously stirred mixture was cooled in an ice–salt bath and saturated with hydrogen chloride. The gas stream was stopped and the mixture heated on a water bath for 1 hr. at 80–90°. After cooling, the organic (lower) layer was separated and the aqueous layer extracted with ether. The combined organic layers were washed with 10% sodium bicarbonate solution and with water. After drying over magnesium sulfate, removal of the ether, and fractionation of the residue, there was obtained 53.6 g. (72%) of 3-bromo-2-thenyl chloride (V), b.p. 106.5–107.5° (12 mm.) $n^{20}D$ 1.6059.

Anal. Calcd. for C_5H_4BrClS: C, 28.39; H, 1.90; S, 15.16. Found: C, 28.57; H, 1.90; S, 15.19.

3,3′-Dibromo-2,2′-dithienylmethane (VIII).—*n*-Butyllithium (185 ml. of a 1.33 *N* ethereal solution, 0.25 mole) was siphoned under nitrogen into a 1-l. three-necked flask fitted with a mechanical stirrer, reflux condenser, dropping funnel, and low temperature thermometer. After cooling the flask to −70°, 57.2 g. (0.24 mole) of 2,3-dibromothiophene (VI) in 75 ml. of absolute ether was added during 15 min. The solution was stirred for 0.5 hr., whereupon 50 g. (0.24 mole) of 3-bromo-2-thenyl chloride (V) was added with stirring at −30°. After removal of the cooling bath, the mixture warmed spontaneously to reflux with the simultaneous appearance of a yellow precipitate. Refluxing was maintained by occasional warming for 2.5 hr. The mixture was cooled and carefully decomposed by adding 100 ml. of ice–water. The ether layer was washed with salt water, dried over magnesium sulfate, and fractionated. The product, b.p. 150–160° (0.45 mm.), crystallized and was pressed between filter paper. One recrystallization of the crude material from methanol with ice–salt cooling yielded 13 g. (16%) of colorless 3,3′-dibromo-2,2′-dithienylmethane (VIII), m.p. 37–38°. The n.m.r. spectrum showed two doublets at τ_4 3.16 and τ_5 2.92 (J = 5.0 c.p.s),

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(5) There are a total of six possible isomers of this kind. Very recently we have prepared a second isomer (II), m.p. 73–74.5°, in this series. A thiophene analog of a substituted fluorenone has recently been reported by M. Y. Poirier, *Bull. soc. chim. France*, 1523 (1963).

(6) One of the most direct routes, *viz.*, *via* chloromethylation of 3,3′-dithienyl furnished polymeric material only. See F. F. Blicke and J. H. Burckhalter, *J. Am. Chem. Soc.*, **64**, 477 (1942).

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(9) S. Gronowitz, *Arkiv Kemi*, **7**, 361 (1955).

(10) N. Löfgren and C. Tegnér, *Acta Chem. Scand.*, **6**, 1020 (1952).

(11) P. Moses and S. Gronowitz, *Arkiv Kemi*, **18**, 119 (1961).

(12) When the organometallic intermediate was carbonated instead of oxidized, 3,3′-dicarboxy-2,2′-dithienylmethane was obtained in good yield (54%), demonstrating the formation of the dilithio compound *in situ*.

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(17) All melting points are corrected unless otherwise stated. Ultraviolet spectra were recorded on a Zeiss PMQ II spectrophotometer. The n.m.r. spectra were obtained using a Varian Model A-60 spectrometer, in carbon tetrachloride solution with tetramethylsilane as an internal standard. The microanalyses were carried out in the analytical section of our department under the direction of W. M. Hazenberg.

and a singlet at τ_{CH_2} 5.80; ultraviolet spectrum (ethanol), λ_{max} 242 mμ (ϵ 12,900).

Anal. Calcd. for $C_9H_6Br_2S_2$: C, 31.97; H, 1.78; S, 18.97. Found: C, 32.09; H, 1.88; S, 18.88.

Cyclopenta[1,2-*b*:4,3-*b*′]dithiophene (I).—A solution of 3,3′-dilithio-2,2′-dithienylmethane was prepared at −70° as described above from 4.5 g. (0.013 mole) of 3,3′-dibromo-2,2′-dithienylmethane (VIII) in 80 ml. of absolute ether and 20 ml. of 1.33 *N* ethereal *n*-butyllithium (0.026 mole) in a 250-ml. three-necked flask. The yellow solution was poured under nitrogen in an externally cooled (−20°) dropping funnel, which was attached to a second 500-ml. three-necked flask containing 4 g. (0.03 mole) of anhydrous $CuCl_2$ (dried at 130° for 0.5 hr.) in 20 ml. of absolute ether, maintained under dry nitrogen. While stirring the ice-cooled suspension vigorously the dilithio compound was added dropwise in the course of 1 hr. After stirring at 0° overnight, 40 ml. of 2 *N* hydrochloric acid solution was added and the reaction mixture filtered with suction in order to remove the grayish precipitate of cuprous chloride.

The ether layer was separated and the aqueous phase extracted with ether. The combined ethereal extracts were washed several times with 4 *N* hydrochloric acid, sodium bicarbonate solution, and finally with water. After drying over magnesium sulfate and removal of the solvent, the residue crystallized on cooling. Steam distillation gave 1.5 g. of crude cyclopenta[1,2-*b*:4,3-*b*′]-dithiophene (I). One recrystallization from ethanol yielded 0.9 g. (38%) of pure product, m.p. 66–67°. The n.m.r. spectrum showed two doublets at τ_4 3.05 and τ_5 2.88 (J = 5.0 c.p.s.), and a singlet at τ_{CH_2} 6.36.

Anal. Calcd. for $C_9H_6S_2$: C, 60.61; H, 3.39; S, 35.96. Found: C, 60.56; H, 3.48; S, 35.57.

The n.m.r. spectrum of fluorene (Fa. Th. Schuchardt, Germany) under similar conditions gave, in addition to a multiplet between τ 2.3 and 3.0, one sharp singlet at τ 6.36 (>CH_2).

Ultraviolet spectrum (Fig. 1) of I in cyclohexane was λ_{max} mμ (log ϵ), 218 (4.50), 223 (4.51), 259 (3.38), 264 (3.34), 269 (3.34), 273 (3.24), 279 (3.18), and 298 (3.04).

3,3′-Dicarboxy-2,2′-dithienylmethane.—A solution of 4.5 g. (0.013 mole) of 3,3′-dibromo-2,2′-dithienylmethane (VIII) in 40 ml. of absolute ether was added over a period of 12 min. to 25 ml. of 1.33 *N* ethereal *n*-butyllithium (0.033 mole) cooled to −70° in an apparatus as described above. After 1.5 hr. the mixture was poured onto solid carbon dioxide covered with ether. After standing for 2 hr. the reaction mixture was hydrolyzed with 100 ml. of water and the ether phase extracted with 10% sodium bicarbonate solution. The combined aqueous layers gave on acidification with 4 *N* hydrochloric acid 3.7 g. crude product. Recrystallizations from an 85:15 acetic acid–water mixture (Norit) and finally from acetic acid yielded 1.9 g. (54%) of 3,3′-dicarboxy-2,2′-dithienylmethane, m.p. 257–258° (uncor.). The n.m.r. spectrum in dioxane showed two doublets at τ_4 2.81 and τ_5 2.57 (J = 5.0 c.p.s.), and a singlet at τ_{CH_2} 4.83.

Anal. Calcd. for $C_{11}H_8O_4S_2$: C, 49.23; H, 3.01; S, 23.90. Found: C, 48.96; H, 3.12; S, 23.58.

The Preparation and Pyrolysis of Certain Hexyl Thioacetates

L. T. WOLFORD AND R. M. ENGELBRECHT

Research Department, Hydrocarbons Division,
Monsanto Chemical Company, St. Louis, Missouri

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The addition of thioacetic acid to trisubstituted olefins and subsequent pyrolysis of the resulting esters to chiefly a different isomer has been described by Bailey, Mayer, and Antonucci.[1] This procedure has now been extended to certain mono-, di-, and trisubstituted hexenes.

The addition of thioacetic acid to 4-methyl-1-pentene (I), 3-methyl-2-pentene (III), 4-methyl-2-pentene (VI), and 2-hexene (X) proceeded smoothly to give the corresponding thio esters in 80–81% yields. The thioacetates were pyrolyzed to give mixtures of hexene isomers.

The addition of thioacetic acid to 4-methyl-1-pentene (I) and 3-methyl-2-pentene (III) gave the expected anti-Markownikoff addition product. Predominately one thioacetate was formed in each case. Upon pyrolysis the thioacetate from 4-methyl-1-pentene (II) gave 4-methyl-1-pentene (I), while the thioacetate from 3-methyl-2-pentene (IV)[2] yielded a mixture of 86.0% 3-methyl-1-pentene (V) and 12.6% 3-methyl-2-pentene (III). The observations on thioacetate pyrolysis are in agreement with the assumption that thioacetate pyrolysis parallels acetate pyrolysis with regard to mechanism and product formation.[1,3]

A possible steric effect of the isopropyl group of 4-methyl-2-pentene (VI) upon the addition of thioacetic acid to the double bond was anticipated. If such a steric effect was important, pyrolysis of the resulting thioacetate would be expected to give predominately 4-methyl-1-pentene (I). However, the isopropyl group of VI did not exert an important steric influence upon the addition of thioacetic acid since the gas chromatogram of the thioacetate showed two peaks with approximately equal areas, and the product of pyrolysis was found to consist of a mixture of 60.0% VI and 20.0% each of 2-methyl-2-pentene (IX) and I. The addition of thioacetic acid to 2-hexene (X) was also found to be unselective.

Examination of Table I shows that the efficiency of pyrolysis was affected by temperature and flow rate while the ratio of the product formed was largely independent of these two factors over the temperature range 450–540°. This is in agreement with previous studies on acetate pyrolysis.[4,5]

Experimental[6]

4-Methyl-1-pentene.—Phillips technical grade was used, with no other isomers found by g.c.

4-Methyl-2-pentene.—Phillips technical grade was found to be 56.8% *trans*-4-methyl-2-pentene and 43.2% *cis*-4-methyl-2-pentene by infrared. Phillips Pure Grade and Phillips Pure Grade High Boiling was found to be 100% *trans*-4-methyl-2-pentene by infrared. All grades reacted equally well.

3-Methyl-2-pentene was prepared by the method of Church, Whitmore, and McGrew.[7] They reported the dehydration of 3-methyl-3-pentanol to yield mostly 3-methyl-2-pentene with only a trace of 2-ethyl-1-butene. However, g.c. of the dehydration product obtained in the present work showed it to be a mixture of 16.4% 2-ethyl-1-butene, 30.2% *trans*-3-methyl-2-pentene, and 53.4% *cis*-3-methyl-2-pentene.

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[2] The 3-methyl-2-pentene was contaminated with 16.4% 2-ethyl-1-butene, $CH_3CH_2C(C_2H_5){=}CH_2$, which would be expected to give, after thioacetic acid addition, $CH_3CH_2CH(C_2H_5)CH_2SAc$. Subsequent pyrolysis would give back 2-ethyl-1-butene. The low over-all yield of olefin (14.0%) from pyrolysis and the small amount of 2-ethyl-1-butene (1.4%) found in the pyrolysate suggested that, under the pyrolysis conditions used, the thioacetate from 2-ethyl-1-butene was not significantly decomposed.

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