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

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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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[1] W. J. Bailey, R. A. Mayer, and J. Antonucci, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 5-O. W. J. Bailey, U. S. Patent 3,071,364 (Jan. 1, 1963).

[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.

[3] E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 247.

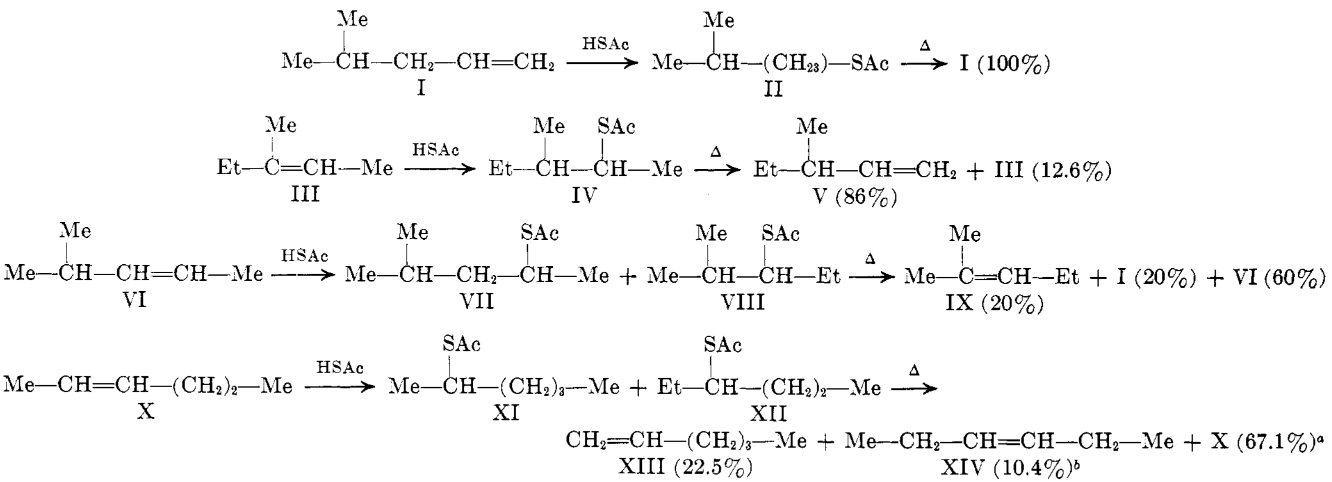
[4] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

[5] W. J. Bailey and W. F. Hale, *ibid.*, **81**, 647 (1959).

[6] Elemental analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

[7] J. M. Church, F. C. Whitmore, and R. V. McGrew, *J. Am. Chem. Soc.*, **56**, 176 (1934).

CHART I



$$\underset{\text{I}}{\mathrm{Me{-}\overset{Me}{C}H{-}CH_2{-}CH{=}CH_2}} \xrightarrow{\text{HSAc}} \underset{\text{II}}{\mathrm{Me{-}\overset{Me}{C}H{-}(CH_{23}){-}SAc}} \xrightarrow{\Delta} \text{I (100\%)}$$

$$\underset{\text{III}}{\mathrm{Et{-}\overset{Me}{C}{=}CH{-}Me}} \xrightarrow{\text{HSAc}} \underset{\text{IV}}{\mathrm{Et{-}\overset{Me}{C}H{-}\overset{SAc}{C}H{-}Me}} \xrightarrow{\Delta} \underset{\text{V (86\%)}}{\mathrm{Et{-}\overset{Me}{C}H{-}CH{=}CH_2}} + \text{III (12.6\%)}$$

$$\underset{\text{VI}}{\mathrm{Me{-}\overset{Me}{C}H{-}CH{=}CH{-}Me}} \xrightarrow{\text{HSAc}} \underset{\text{VII}}{\mathrm{Me{-}\overset{Me}{C}H{-}CH_2{-}\overset{SAc}{C}H{-}Me}} + \underset{\text{VIII}}{\mathrm{Me{-}\overset{Me}{C}H{-}\overset{SAc}{C}H{-}Et}} \xrightarrow{\Delta} \underset{\text{IX (20\%)}}{\mathrm{Me{-}\overset{Me}{C}{=}CH{-}Et}} + \text{I (20\%)} + \text{VI (60\%)}$$

$$\underset{\text{X}}{\mathrm{Me{-}CH{=}CH{-}(CH_2)_2{-}Me}} \xrightarrow{\text{HSAc}} \underset{\text{XI}}{\mathrm{Me{-}\overset{SAc}{C}H{-}(CH_2)_3{-}Me}} + \underset{\text{XII}}{\mathrm{Et{-}\overset{SAc}{C}H{-}(CH_2)_2{-}Me}} \xrightarrow{\Delta}$$

$$\underset{\text{XIII (22.5\%)}}{\mathrm{CH_2{=}CH{-}(CH_2)_3{-}Me}} + \underset{\text{XIV (10.4\%)}^{b}}{\mathrm{Me{-}CH_2{-}CH{=}CH{-}CH_2{-}Me}} + \text{X (67.1\%)}^{a}$$

[a] Maximum value; includes *cis*-3-hexene content. [b] Minimum value; amount of *cis*-3-hexene is not known.

TABLE I

PYROLYSIS OF THIOLACETATES

Thioiacetate from	Temp. of pyrolysis, °C.	Flow rate ml./min.	Yield, %				
			Olefin[a]	4-Methyl-1-pentene	4-Methyl-2-pentene	2-Methyl-2-pentene	
4-Methyl-1-pentene	530	1.3	16.3	100			
4-Methyl-1-pentene	450	1.3	0				
4-Methyl-2-pentene	450	1.4	13.2	19.4	64.0	16.6	
4-Methyl-2-pentene	490	3.5	12.9	17.5	65.5	17.0	
4-Methyl-2-pentene	490	2.5	21.0	21.6	63.0	15.4	
4-Methyl-2-pentene	490	1.3	43.0	20.0	60.0	20.0	
4-Methyl-2-pentene	520	1.3	35.0	20.8	59.5	19.7	
4-Methyl-2-pentene	530	1.3	31.0	21.3	60.3	18.4	
4-Methyl-2-pentene	540	4.0	41.5	21.4	59.0	19.6	
				3-Methyl-1-pentene	2-Ethyl-1-butene	*trans*-3-Methyl-2 pentene	*cis*-3-Methyl-2-pentene
3-Methyl-2-pentene	500	3.2	14.0	86.0	1.4	7.1	5.5
				1-Hexene	*trans*-2-Hexene, *cis*-3-Hexene	*cis*-2-Hexene	*trans*-3-Hexene
2-Hexene	500	2.0	52.0	22.5	49.7	17.4	10.4

[a] Based upon charged thioacetate.

3-Methyl-3-pentanol was prepared by the reaction of ethyl magnesium bromide and ethyl acetate in 52% yield, b.p. 120–122°.[7]

2-Hexene.—Phillips technical grade was found to be 28.2% *trans*-2-hexene and 71.8% *cis*-2-hexene by g.c.

Thioacetic Acid.—Matheson Coleman and Bell practical grade was used.

Preparation of the Thioacetates.—An equimolar mixture of the olefin and thioacetic acid was irradiated in a 250-ml. erlenmeyer flask with an incandescent bulb. A brief induction period was followed by a vigorous exothermic reaction. After a forerun of unreacted olefin and thioacetic acid, the thioacetate was collected by distillation through an 18-in. protruded metal column.

The reaction product from thioacetic acid and 4-methyl-1-pentene was obtained in 81% yield, b.p. 90° (21 mm.).

The thioacetate from 4-methyl-2-pentene was obtained in 80% yield, b.p. 78° (23 mm.)

Anal. Calcd. for $C_8H_{16}OS$: C, 59.94; H, 10.08; S, 20.00. Found: C, 60.08; H, 10.16; S, 20.41.

The thioacetate from 3-methyl-2-pentene was obtained in 80% yield, b.p. 81° (20 mm.)

Anal. Calcd. for $C_8H_{16}OS$: C, 59.94; H, 10.08; S, 20.00. Found: C, 59.98; H, 9.55; S, 20.33.

The thioacetate from 2-hexene was obtained in 80% yield, b.p. 84° (20 mm.)

Anal. Calcd. for $C_8H_{16}OS$: C, 59.94; H, 10.08; S, 20.00. Found: C, 59.43; H, 9.90; S, 19.99.

Pyrolysis of the Thioacetates.—The procedure was essentially that of Bailey and Hewitt.[8] In order to achieve uniform flow rates, the thioacetates were pumped from a 100-ml. buret by means of a microbellows pump into the Pyrex pyrolysis tube. The thioacetates were pyrolyzed at the temperatures and flow rates shown in Table I. The pyrolysate obtained was washed with water, dried over anhydrous sodium carbonate, and distilled through an 18-in. protruded metal column. The yields of olefin are shown in Table I.

Analysis.—The hexene samples were analyzed by a Fisher-Gulf partitioner (40-ft. dimethylsulfolane-on-firebrick column, helium flow 60 ml./min., inlet pressure 30 p.s.i.g.). Isomer per cent were calculated by retention time times peak height. No carbon skeleton rearrangement was observed.[3] In the products from 3-methylpentenes all isomers were resolved. In the products from 4-methylpentenes all isomers except *cis*- and trans-4-methyl-2-pentene were resolved. In the products from 2-hexene the following pairs were not separated: 1-hexene and *trans*-3-hexene, *trans*-2-hexene and *cis*-3-hexene. The per cent of 1-hexene was determined by infrared.

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(8) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).