out of the reaction vessel into another reaction vessel held in a liquid nitrogen bath. Careful technique allowed the recovery of 96–97% of the hexadeuteriobenzene. The photolysis was repeated three times, each time with the same amount of 2-iodothiophene. The combined reaction residues were taken up in benzene, filtered, decolorized with Norit, and chromatographed on alumina (benzene eluent) to yield 2.35 g (14.6 mmoles, 68% yield) of crude **1**. Glpc (diethylene glycol succinate, 6 ft, 190°) showed the product **1** to contain less than 1% of the 3-phenyl derivative. Recrystallization (70% methanol–water) of a sample prepared in a separate reaction gave **1** as white platelets, mp 36–38°; ultraviolet spectrum in cyclohexane: λ_{max} 282 (13,700) and λ_{sh} 214 (8000).

2-Pentadeuteriophenyl-5-bromothiophene (**2**) was prepared by reaction of **1** (2.35 g, 14.6 mmoles) with NBS (2.64 g, 14.8 mmoles) and benzoyl peroxide (0.057 g, 0.24 mmole) in 24 ml of CCl_4.[20] Work-up followed by chromatography on alumina (benzene eluent) gave 2.89 g (1.2 mmoles, 81% yield) of crude **2**. Recrystallization from methanol gave white leaflets, mp 78° (lit.[20] for 2-phenyl-5-bromothiophene from methanol, 84–85°).

2-Pentadeuteriophenyl-5-deuteriothiophene (**3**) was prepared by treatment of **2** (1.44 g, 6 mmoles) with 280 mg of fresh magnesium in 7 ml of ethyl ether followed by reaction with deuterium oxide (1.0 ml). Filtration of the precipitate and chromatography of the product on alumina gave 0.83 g (5.1 mmoles, 85% yield) of **3**, mp 31–34°, after recrystallization from 70% methanol–water, 33.5–35°; ultraviolet spectrum in cyclohexane: λ_{max} 282 (14,500), and λ_{sh} 217 (7200).

3-Pentadeuteriophenylthiophene (**4**) was prepared by photolysis of 3-iodothiophene (3.0 g, 14.3 mmoles) in 1.5-g batches in hexadeuteriobenzene as described for **1**. Reaction temperature was maintained at 80°, and irradiation was carried out for 48–54 hr. Work-up as for **1** and recrystallization from 80% methanol–water gave 0.415 g (2.5 mmoles, 17% yield) of **4**, mp 89–90°; ultraviolet spectrum in cyclohexane: λ_{max} 258 (13,400) and λ_{max} 227 (14,800).

2-Bromo-3-pentadeuteriophenylthiophene (**5**) was prepared by treatment of **4** (0.317 g, 1.91 mmoles) with NBS (0.37 g, 2.08 mmoles) in 15 ml of refluxing CCl_4.[8] A small amount of benzoyl peroxide was added. When all the starting material had disappeared the reaction mixture was worked up as described for **2** to yield 0.3 g (1.22 mmoles, 64% yield) of the product **5**. The nmr spectrum in acetone showed two doublets, J = 5.6 cps, consistent with 4,5 coupling in the thiophene ring.[5,8]

2-Deuterio-3-pentadeuteriophenylthiophene (**6**) was prepared by refluxing **5** (0.30 g, 1.22 mmoles) with a mixture of acetic anhydride (1.3 ml) and deuterium oxide (1.3 ml) to which Zn (0.52 g, 8 mg-atom) had been added.[9] Reaction was carried out for 3 hr. The resulting mixture was diluted with water, filtered, and extracted three times with ether, and the ether extracts were washed with aqueous $NaHCO_3$ until neutral and once with water. The ether extracts were dried over $MgSO_4$. Removal of the ether left 2-deuterio-3-pentadeuteriophenylthiophene (**6**) (0.19 g, 97% yield), nmr (acetone) singlet.

Photolysis of 3 was carried out with 600 mg of **3** in 600 ml of analytical grade diethyl ether at 25° under a nitrogen atmosphere. A Hanau Q-700 industrial medium-pressure mercury lamp was used. After 5-hr irradiation, gas chromatography indicated that approximately equal amounts of 2- and 3-pentadeuteriophenylthiophenes remained. Filtration, concentration, and chromatography on alumina yielded 0.295 g of material of which an nmr (CCl_4) was taken. The mixture was separated by preparative gas chromatography (diethylene glycol succinate, 8 ft, 155°) and yielded 117 mg of 2-substituted material **8**, mp (after recrystallization from 70% methanol–water) 33–36.5° [ultraviolet spectrum in cyclohexane: λ_{max} 282 (14,100) and λ_{sh} 216 (7540)] and 135 mg of 3-substituted isomer **9**, mp (after recrystallization from 70% methanol–water) 89.5° [ultraviolet spectrum in cyclohexane: λ_{max} 258 (13,600) and λ_{max} 227 (15,300)]. The combined nmr spectra of **8** and **9** in CCl_4 were the same as that taken before gas chromatography; rearrangement during chromatography is thus precluded.

Photolysis of 2-deuterio-3-pentadeuteriophenylthiophene (**6**) (0.124 g, 0.75 mmole) was carried out with a Hanau S-81 medium-pressure mercury lamp in 125 ml of diethyl ether for 5.5 hr. Filtration and chromatography on alumina gave 65 mg (0.39 mmole) of material which by gas chromatography was shown to be only 3-pentadeuteriophenylthiophene. The nmr spectrum in acetone was that expected for a mixture of **9**, **10**, and **11** (see Figure 6).

Dark reactions of **3** or **6** were not observed when samples were allowed to stand in ether solution. No change in the nmr spectra occurred indicating no rearrangement in the absence of ultraviolet light.

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[20] A. Kosak, R. J. F. Palchak, W. A. Steele, and C. M. Selwitz, *J. Am. Chem. Soc.*, **76**, 4450 (1954).

The Photochemistry of Thiophenes. VI. Photorearrangement of Phenylmethylthiophenes

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Contribution from the Department of Organic Chemistry, The University, Groningen, The Netherlands. *Received February 1, 1967*

Abstract: The six isomers of the phenylmethylthiophenes have been prepared and subjected to photolysis. The 2-phenyl-substituted isomers formed, as major rearrangement products, the 3-phenyl-substituted thiophene obtained by interchange of the 2,3-carbon atoms. Small amounts of the other possible isomers appear to be formed in the primary photochemical reaction. The 3-phenyl-substituted isomers formed one or two major products depending on the point of substitution of the methyl group. Small amounts of the other isomers were again formed in the primary photochemical process.

Arylthiophenes undergo deep-seated photoreorganization reactions involving changes in the order of carbon–carbon and carbon–sulfur bonding in the thiophene ring.[2,3] Interpretation of the mechanism can be furthered if the positions of all the carbon atoms in the thiophene ring after rearrangement are known. This may be accomplished by substituent labeling which involves preparation of each possible substituted isomer and determination of the rearrangement products. Analysis of the results from these types of experiments coupled with previous knowledge that the aryl group remains attached to the same carbon atom during rearrangement[2,4] and that no rearrangement occurs

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[1] Royal Dutch Shell Fellow, 1963–1966.

[2] H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *J. Am. Chem. Soc.*, **89**, 3487 (1967).

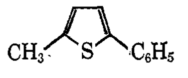
[3] R. M. Kellogg and H. Wynberg, *ibid.*, **89**, 3495 (1967).

[4] H. Wynberg and H. van Driel, *Chem. Commun.*, 204 (1966).

in the aryl group[2] would permit detailed analysis of the changes involved during photorearrangement. The experiments described in the previous paper[3] using deuterium atom labeling could not be extended to the use of other positional isomers because of synthetic difficulties. A methyl group was chosen as the labeling substituent because of the synthetic availability of the phenylmethylthiophenes.

Results

The isomeric phenylmethylthiophenes, **1–6**, were prepared according to literature methods (see Experimental Section) in yields varying from 6 to 38%. Physical properties agreed with those reported in the literature; structures were further confirmed by determination of the nmr coupling constants of the AB pattern of the thienyl ring protons. These were in agreement with those expected.[5] Gas chromatography under conditions capable of separating all six isomers (see Experimental Section) showed each isomer to be uncontaminated with any of the other possible isomers. Purities were 99% or better.[6]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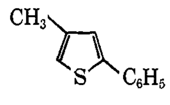
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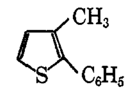
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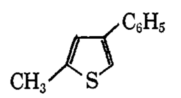
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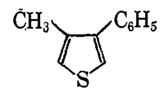
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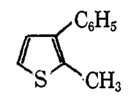
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2-Phenyl-5-methylthiophene (**1**), when irradiated in dilute ether solution for 6 hr with a mercury high-pressure lamp gave, in addition to recovered starting material, five new photoproducts as detected by gas chromatography. The retention times were identical with those of the other five phenylmethylthiophene isomers; the major new component had a retention time identical with 2-methyl-4-phenylthiophene (**4**). Preparative gas chromatography separated the reaction mixture into one group containing three photoisomers and one containing two photoisomers plus incompletely separated starting material. The infrared and ultraviolet spectra of the first group were identical with a synthetic mixture of **3**, **5**, and **6** prepared in ratios estimated from gas chromatographic peak heights. Similarly, the spectra of the second group corresponded to a mixture of **2** and **4** plus starting material **1**. This was taken as positive isomer identification and for subsequent experiments gas chromatographic retention times determined on two different columns were used for isomer identification.

The other five isomers were irradiated under conditions identical with those described for **1**, and the product distribution was determined by gas chromatographic analysis. The results are listed in Table I. In all irradiations varying amounts of decomposition occurred producing a solid, intractable deposit. No trace of unstable photointermediates was obtained.

Table I. Relative Percentages of Isomers Formed from Irradiation of the Isomeric Phenylmethylthiophenes[a]

Starting material	Products 1	2	3	4	5	6
1	80.0	0.8	0.3	17.1	1.1	0.7
2	0.5	53.1	1.5	2.9	37.7	4.3
3	0.1	0.03	75.6	0.1	2.6	21.6
4	0.1	0.6	0.4	95.5	3.0	0.4
5	0.8	0.1	12.1	0.8	69.9	16.3
6	1.1	0.3	<4.2[b]	4.9	19.1	70.4

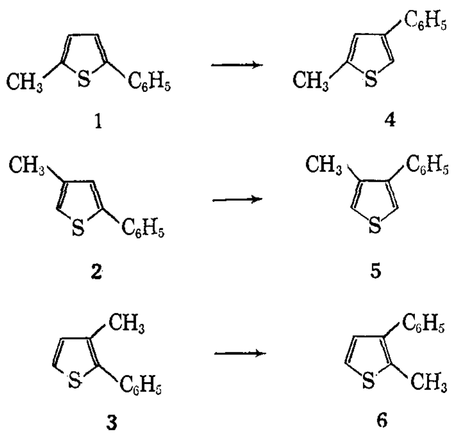
[a] Irradiations carried out for 6 hr in 1.1 × 10^{-2} *M* diethyl ether solution. Yields of recovered isomer mixtures ranged from 42 to 82%. [b] Absolute maximum value; precise value could not be accurately determined because of separation difficulties. The actual value is probably much less than this figure.

Examination of all isomers showed them to be indefinitely stable in ether solution in the absence of ultraviolet light.

In the cases of compounds **3**, **5**, and **6** isomer formation was followed as a function of photolysis time. Although the analytical difficulties were considerable, extrapolation to zero time indicated that the product ratios in Table I remained roughly constant with time. Apparently all isomers are formed in the primary photochemical act and are not products of secondary photolysis.

Discussion

Examination of Table I shows that the 2-phenyl-substituted isomers undergo a reasonably specific rearrangement. The major products are given in eq 1–3. The major rearrangement product from 2-phenyl-5-methylthiophene (**1**) has the same substitution pattern as the major rearrangement product from 2-pentadeuteriophenyl-5-deuteriothiophene.[3] This suggests that substitution of a methyl for deuterium in the thiophene ring has not changed the mechanism of rearrangement. If, as seems likely, the same mechanism of rearrangement applies for **1**, **2**, and **3**, rearrangement must involve only an interchange of the 2- and 3-carbon atoms in the starting material.


(1)

(2)

(3)

3-Phenyl-substituted thiophenes also produce specific rearrangement products upon photolysis. The major rearrangement products are shown in eq 4–6. Discussion of possible rearrangement mechanisms is deferred to the following paper.

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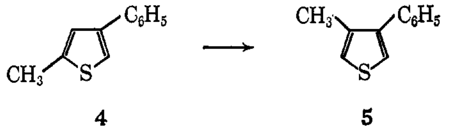
(5) S. Gronowitz, *Advan. Heterocyclic Chem.*, **1**, 8 (1963).

(6) Further structure proofs were carried out as a student exercise in these laboratories. All six phenylmethylthiophene isomers were desulfurized with Raney nickel and the hydrocarbons obtained shown to be the same as the expected phenylpentanes prepared by independent and unambiguous syntheses.



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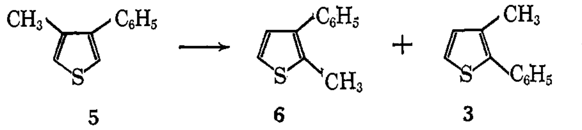

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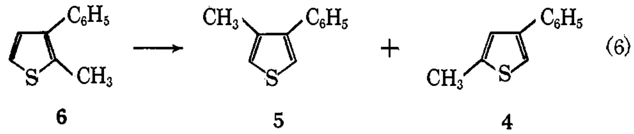

(6)

Experimental Section

Photolyses were carried out using a Hanau Q-700 high-pressure mercury lamp or a smaller Hanau S-81 lamp. The apparatus has been described earlier.[2] Analytical gas chromatography was done on an F & M Model 810 with flame-ionization detectors using an 8-ft diethylene glycol succinate column (10% on Chromosorb B) at 140° and with a Perkin-Elmer Model 116E gas chromatograph using a 165-ft capillary column with butane diolsuccinate as the substrate at 120°. All analytical identifications were confirmed on both pieces of equipment. Preparative chromatography was done on an Aerograph A-700 Autoprep with $^3/_8$ in. × 8 ft diethylene glycol succinate column (25% on Chromosorb W) at 175°. Ultraviolet spectra, measured in 96% ethanol on a Zeiss PMQ-II, are reported in millimicrons with the corresponding extinction coefficients (ϵ). Infrared spectra were taken on a Perkin-Elmer 125 infrared spectrophotometer, and nmr spectra were run on a Varian A-60 using carbon tetrachloride solutions, tetramethylsilane (TMS) as internal standard. Melting points and boiling points are uncorrected.

2-Phenyl-5-methylthiophene (1) was prepared according to the method of Demerseman, Buu-Hoi, and Royer[7] in 38% yield, mp 48-49° (lit.[7] 51°); ultraviolet spectrum: λ_{max} 291 (15,300); nmr spectrum: (thiophene protons) $J = 3.5$ cps.

2-Phenyl-4-methylthiophene (2) was prepared according to Voronkov and Gol'shtein[8] in 7% yield, bp 278-280° (1 atm) [lit.[8] bp 280° (1 atm)], $n^{20}D$ 1.6310 (lit.[8] $n^{20}D$ 1.63216); ultraviolet spectrum: λ_{max} 288 (13,300) and λ_{max} 267 (9100); nmr spectrum: (thiophene protons) $J = 1.2$ cps.

2-Phenyl-3-methylthiophene (3) was prepared according to Voronkov and Gol'shtein[8] in 6% yield,[9] $n^{17.9}D$ 1.6169 (lit.[9] $n^{20}D$ 1.61584); ultraviolet spectrum: λ_{max} 267 (9100); nmr spectrum: (thiophene protons) $J = 5.0$ cps.

2-Methyl-4-phenylthiophene (4) was prepared according to Broun and Voronkov[10] in 8.9% yield, mp 73.5-74° (lit.[10] 73.5-73.7°); ultraviolet spectrum: λ_{max} 262 (13,000) and λ_{max} 231 (18,600); nmr spectrum: (thiophene protons) $J = 1.2$ cps.

3-Phenyl-4-methylthiophene (5) was prepared according to Broun, Voronkov, and Gol'dburt[11] in 15% yield after preparative chromatography, bp 256° (1 atm) [lit.[11] bp 256.3-256.6° (1 atm)], $n^{19}D$ 1.6156 (lit.[11] $n^{20}D$ 1.6160); ultraviolet spectrum: λ_{max} 251 (11,200) and λ_{max} 224 (13,400); nmr spectrum: (thiophene protons) $J = 3.5$ cps.

3-Phenyl-2-methylthiophene (6) was prepared according to the method of Broun and Voronkov[10] in 15% yield, bp 262-265° (1 atm) [lit.[10] bp 258.8-260° (1 atm)], $n^{20}D$ 1.6141 (lit.[10] $n^{20}D$ 1.59713); ultraviolet spectrum: λ_{max} 253 (10,500) and λ_{max} 228 (16,300); nmr spectrum: (thiophene protons) J values were not measurable because thienyl ring protons have the same chemical shifts.

Irradiations of phenylmethylthiophenes were carried out with the Q-700 lamp. A solution of 1 g of isomer in 530 ml of ether (1.1×10^{-2} *M*) was irradiated for 6 hr at *ca.* 20° under an N_2 atmosphere with vigorous stirring. The yellow solution was filtered; the ether was removed and the semisolid residue chromatographed over grade 1 Al_2O_3 (benzene eluent) to remove the last traces of solid and colored materials. After removal of the benzene, the product was analyzed by gas chromatography on the two analytical columns described above. The identification of each isomer was tested on both columns by adding portions of authentic isomer to a sample of the reaction mixture and observing the increase in relative size of the suspected isomer peak. Complete resolution of each peak was impossible so relative amounts of products were determined by comparing the ratios of the products of retention time times peak height. Checks with known combinations of isomers confirmed the approximate validity of the approach. Isomer ratios were reproducible within ±5%.

Spectral identification of products from 2-phenyl-5-methylthiophene (1) was carried out on a reaction product isolated as described above. Gas chromatography showed five new peaks with retention times equal to the other five phenylmethylthiophene isomers. The major new peak had a retention time the same as 2-methyl-4-phenylthiophene (4). By preparative glpc on the column described above the photoproduct was separated into two groups of isomers. The first group consisted of materials with the same retention times as isomers **3**, **5**, and **6** and the second group of isomers **2** and **4** plus starting material **1**. The presence of isomers **3**, **5**, and **6** in the first group was confirmed by the characteristic infrared peaks at 1085, 790, and 715 cm^{-1}, respectively. The infrared and ultraviolet spectra of a mixture of **3**, **5**, and **6** mixed in the proportions estimated from the gas chromatogram of the isolated material were precisely the same as those of the isolated material. The second group of isomers was identified in a similar manner utilizing the infrared absorptions at 938 (**1**), 912, 590 (**2**), and 497 cm^{-1} (**4**).

Isomer formation as a function of time was determined for isomers **3**, **5**, and **6** by irradiating ether solutions 1.15×10^{-2} *M* of isomer in small quartz test tubes arranged concentrically about a Hanau S-81 high-pressure mercury lamp. The temperature was held at 20° by water-bath cooling. Samples were withdrawn periodically and analyzed by glpc (165-ft BDS, 120°). Within experimental error (which was considerable for the isomers formed in very small amounts) the isomer ratios remained constant upon extrapolating to zero time.

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(7) P. Demerseman, N. P. Buu-Hoi, and R. Royer, *J. Chem. Soc.*, 4193 (1954).

(8) M. G. Voronkov and B. L. Gol'shtein, *J. Gen. Chem. USSR*, 20, 1218 (1950); *Chem. Abstr.*, 45, 1577*c* (1951).

(9) Yield after preparative gas chromatographic separation from another component was reported[8] to be 3-benzylthiophene. Nmr spectra of the recovered component suggested it is actually a mixture of 3-benzylthiophene and 1,2-diphenylethane.

(10) A. S. Broun and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, **59**, 1293 (1948); *Chem. Abstr.*, 43, 2614*i* (1949).

(11) A. S. Broun, M. G. Voronkov, and F. J. Gol'dburt, *Nauchn. Byul. Leningr. Gos. Univ.*, 18, 14 (1947); *Chem. Abstr.*, **43**, 5392*d* (1949).