using three freeze–thaw cycles and sealed under a pressure of about 3×10^{-4} torr in 13 × 100 mm Pyrex culture tubes. Irradiation was done in a "quantum yield merry-go-round" using light of 3130 A. Vapor chromatographic analysis on a 12-ft fluorosilicone column was used to follow both the disappearance of the ketone and the appearance of the dimers. The relative rates of reaction were determined and, in the case of low concentrations where under 99% of the light was absorbed by the enone, the rates were corrected for incomplete absorption before calculation of quantum yields. A correlation of the relative quantum yield with the absolute quantum yield was made by irradiation of a solution 1.016 *M* in cyclohexenone to 20% conversion with cyclohexadiene actinometers. The quantum yield for the disappearance of the ketone was found to be 0.286.

Product Distribution. The cyclohexenone dimers were analyzed on the 12-ft fluorosilicone column and the relative areas under the peaks were taken as the relative amounts of the dimers formed. The column temperature was 250°.

Quenching by Piperylene. Solutions containing the same concentration of cyclohexenone (1.024 *M*) but containing different concentrations of piperylene (from none to 2 *M*) were prepared, degassed in the usual manner, and irradiated in the "quantum yield merry-go-round" with the 3660-A filter system until a conversion of 15% was obtained in the sample containing no piperylene. The tubes were opened and analyzed for the appearance of dimers by vapor chromatography using the fluorosilicone column.

Intersystem Crossing Efficiencies. One set of solutions containing 0.05, 0.10, 0.2, and 0.4 *M* cyclohexenone and 0.0526 *M* *cis*-1,2-diphenylpropene and another set containing the same concentrations of cyclohexenone along with 0.0525 *M* *trans*-1,2-diphenylpropene were prepared as usual and irradiated using the 3660-A filter system. Actinometric solutions containing 0.06 *M* benzophenone and 0.0526 *M* *cis*-1,2-diphenylpropene or 0.0528 *M* *trans*-1,2-diphenylpropene were irradiated in parallel with the test solution. The tubes were opened and analyzed using the fluorosilicone column described above. Conversions were 6% or less. The values of ϕ_{io} were calculated using the published method assuming that ϕ_{io} for benzophenone is unity and that decay of diphenylpropene triplets gives 44.5% of the *trans* isomer.

Acknowledgment. This study was supported by a grant from the National Science Foundation.

The Photochemistry of Thiophenes. IV. Observations on the Scope of Arylthiophene Rearrangements

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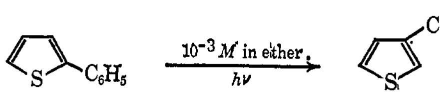
Contribution from the Department of Organic Chemistry, The University, Groningen, The Netherlands. *Received February 1, 1967*

Abstract: Upon irradiation with ultraviolet light in benzene or ether solution 2-phenylthiophene rearranges smoothly and irreversibly to 3-phenylthiophene. The phenyl group remains attached to the same carbon atom during rearrangement as shown by a ^{14}C labeling experiment. A series of previously unreported arylthiophenes have been synthesized to help establish the scope and mechanism of the reaction. Experiments with 2-*p*-tolyl- and mesitylthiophenes show that rearrangement is confined to the thiophene ring and does not occur in the phenyl ring. Photolysis of 2-(α-naphthyl)thiophene leads to 3-(α-naphthyl)thiophene and similarly 2-(β-naphthyl)-thiophene affords 3-(β-naphthyl)thiophene upon photolysis. 2,3-Diphenylthiophene undergoes a cyclohexatriene-type ring closure to form the previously unreported phenanthro[9,10-*b*]thiophene. 3,4-Diphenylthiophene rearranges to 2,3-diphenylthiophene (isolated as phenanthro[9,10-*b*]thiophene) plus a small amount of 2,4-diphenylthiophene. Photolysis of 2,4-diphenylthiophene gives 3,4-diphenylthiophene as the primary photolysis product. 2,5-Diphenylthiophene is virtually unreactive even upon extended photolysis.

The photoinduced rearrangement of 2-phenyl- to 3-phenylthiophene (eq 1) and variations of this reaction have been briefly described by us.[2-5] Attempts have been made to investigate both the scope and mechanism of this rearrangement and to correlate some of our findings with new results in the rapidly growing field of photolysis of aromatic systems. The possible connection between this photorearrangement and those reported in some benzenoid systems was pointed out earlier,[2,3] and investigations on this reaction have been designed to shed some light on this hypothesis. This paper reports studies of the reaction scope from which certain mechanistic conclusions can be drawn. Following papers[6,7] report labeling experiments carried out to elucidate the mechanism in more detail and conclusions are contained in the last paper of this series.[8]



1 2 (1)

Results

Irradiation of 2-phenylthiophene in dilute ether solution leads to 3-phenylthiophene as the exclusive rearrangement product (eq 1). No rearrangement occurs in the absence of ultraviolet irradiation. Careful gas chromatographic analysis of reaction mixtures failed to give any evidence of the presence of other products even in trace amounts. Solutions became light yellow on extended irradiation and a solid, intractable precipitate formed on the lamp. The progress of the reaction with time is shown in Figure 1. The

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(1) Royal Dutch Shell Fellow, 1963–1966.

(2) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

(3) H. Wynberg and H. van Driel, *Chem. Commun.*, **204** (1966).

(4) H. Wynberg and R. M. Kellogg, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(5) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **88**, 5047 (1966).

(6) R. M. Kellogg and H. Wynberg, *ibid.*, **89**, 3495 (1967).

(7) H. Wynberg, G. E. Beekhuis, H. van Driel, and R. M. Kellogg, *ibid.*, **89**, 3498 (1967).

(8) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967).

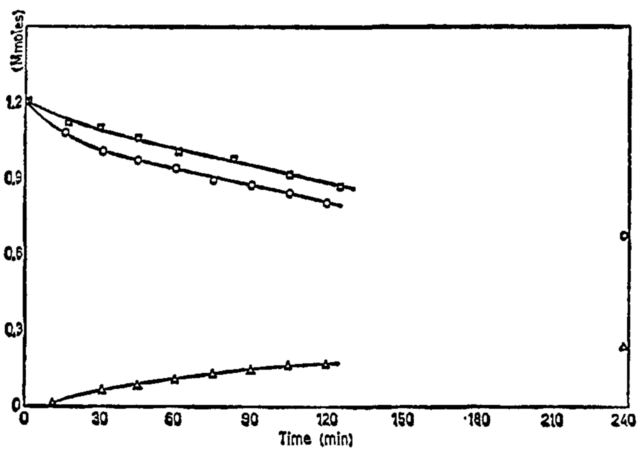
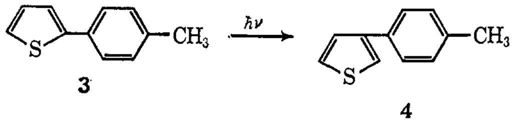


Figure 1. Rate of disappearance of 6 × 10^{-3} M ether solution of 2-phenylthiophene, ○; rate of formation of 3-phenylthiophene from 6 × 10^{-3} M 2-phenylthiophene, △; and rate of disappearance of a 6 × 10^{-3} M solution of 3-phenylthiophene in ether, □.

reaction tends toward a steady-state concentration after a few hours irradiation (roughly 6 hr). During the first 120 min it may be seen that 40–50% of the 2-phenylthiophene that has disappeared is found as 3-phenylthiophene.[9] Qualitative experiments at *ca.* −40 and 20° in ether solution indicated no appreciable rate change in the rearrangement. The rate of disappearance of 2-phenylthiophene increases in more polar solvents (see Experimental Section).

Photolysis of 3-phenylthiophene in solution leads only to decomposition; the rate of decomposition of 3-phenylthiophene is shown also in Figure 1. Gas chromatography under conditions capable of detecting 2-phenylthiophene in amounts as small as 0.25% of the remaining 3-phenylthiophene failed to detect any of this isomer or any other products.

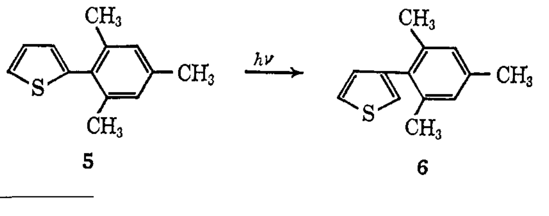
Photolysis of 2-(*p*-tolyl)thiophene (**3**) gave only 3-(*p*-tolyl)thiophene (**4**) (eq 2) identified by comparison of



3 4 (2)

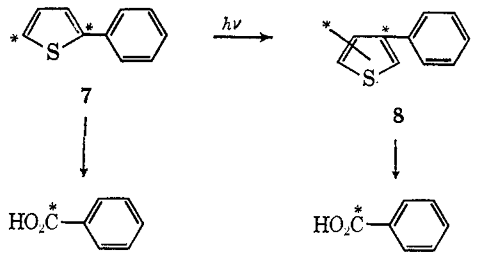
infrared, nmr, and ultraviolet spectra and gas chromatographic retention times with those of authentic material synthesized by an unambiguous route (see Experimental Section). As a further check 3-(*m*-tolyl)- and 3-(*o*-tolyl)thiophene were prepared and were shown to have characteristics different from those of **4**. Photolysis of **4** alone led only to decomposition.

2-Mesitylthiophene (**5**) was prepared and photolyzed (eq 3). The rearrangement product was shown to be 3-mesitylthiophene (**6**) identical in all respects with authentic material. Photolysis of **6** alone led to no new products.[10]



5 6 (3)

The synthesis and irradiation of 2,5-^{14}C-2-phenylthiophene (**7**) has been briefly described.[3] This compound was prepared from 1,4-^{14}C-labeled succinic acid by a modification of the method of Chrzaszczewska.[11] Photolysis of **7** was carried out in *ca.* 10^{-3} M ether solution, and the active 3-phenylthiophene (**8**), which was recovered, was oxidized[12] to benzoic acid which was counted[13] (eq 4). Within experimental error the activity of recovered benzoic acid (rigorously purified) was the same from the 2- and 3-phenylthiophenes. The particular method of degradation accounts only for the ^{14}C originally in the 2 position of starting material **7**. The results establish that the phenyl group remains attached to the same carbon atom during rearrangement.

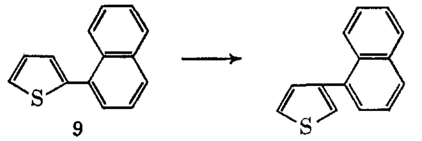


7 8 (4)

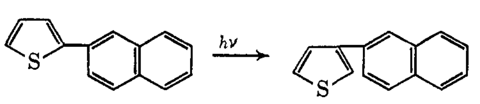
0.0310 ± 0.0003 m curies/mole

0.0318 ± 0.0007 m curies/mole

The four isomeric naphthylthiophenes were synthesized to provide systems with a different aryl substituent. 2-(α-Naphthyl)thiophene (**9**) and 2-(β-naphthyl)thiophene (**10**) were synthesized from the 3-naphthoylpropionic acids. 3-(α-Naphthyl)thiophene (**11**) and 3-(β-naphthyl)thiophene (**12**) were prepared by the general method of Wynberg, Logothetis, and VerPloeg.[14] Photolysis of **9** in dilute ether solution gave **11** as the only product (eq 5). The identification of **11** was accomplished by comparison of gas chromatographic retention times, infrared spectra, and ultraviolet spectra with those of known compounds. Photolysis of **10** in dilute ether solution gave only **12** as product (eq 6). Within limits of gas chromatographic detec-



9 11 (5)



10 12 (6)

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[9] Photolysis in benzene in the presence of $Na_2S_2O_3 \cdot 6H_2O$ appears to give considerably higher yields of 3-phenylthiophene. We cannot currently explain this observation. Some diphenyl is produced in this reaction, apparently originating from the benzene.

[10] The rate of rearrangement (and decomposition) qualitatively appears to increase with increasing alkyl substitution, *i.e.*, the order of rates is 5 > 3 > 1. The rate difference may be due to differences in ultraviolet absorption intensities caused by alkyl substitution.

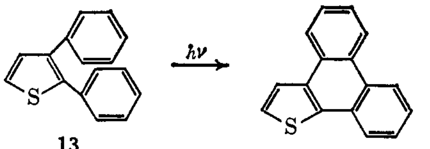
[11] A. Chrzaszczewska, *Roczniki Chem.*, **5**, 1 (1925); *Chem. Abstr.*, 20, 1078 (1926).

[12] General method of H. Wynberg and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 3308 (1963), used for the oxidation of biphenyls.

[13] We thank Professor Dr. M. Gruber, Department of Biochemistry of this university, for providing facilities and Dr. J. U. Veenland for performing the radioactivity measurements in the laboratory of Professor Dr. Th. J. de Boer of the University of Amsterdam.

[14] H. Wynberg, A. Logothetis, and D. VerPloeg, *J. Am. Chem. Soc.*, **79**, 1972 (1957).

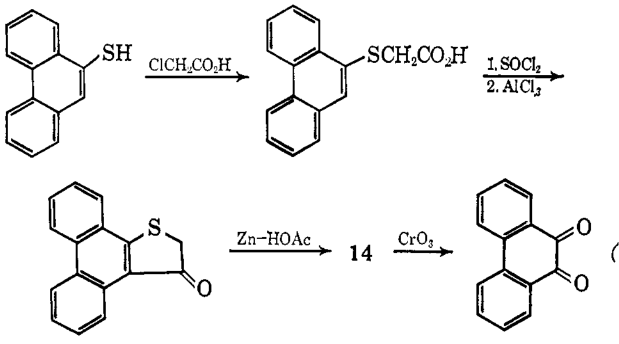
tion no α to β or β to α rearrangements occurred in the naphthalene ring. Photolysis of **11** or **12** in dilute ether solution led only to very slow decomposition. No new products were formed in detectable amounts.



(7)

13 **14**

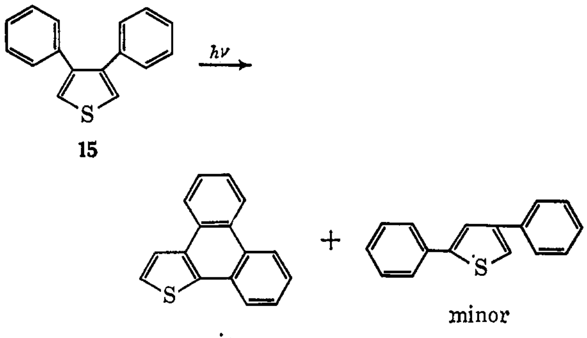
Further information on the scope and mechanism of the reaction was obtained from photolysis of the isomers of diphenylthiophene. Irradiation of 2,3-diphenylthiophene (**13**) in dilute ether solution gave a single product (eq 7) isolated in high yield which was identified as phenanthro[9,10-*b*]thiophene (**14**) from physical and chemical data (see Experimental Section). For unambiguous structure proof, previously unreported **14** was prepared by direct synthesis as shown in eq 8. The intermediate products in the synthesis were carefully characterized and analyzed because of inadequate descriptions in the literature.[15] Subsequent investigations have shown that **14** can be synthesized in one step in 17% yield by the photolysis of 2,3-diiodothiophene in benzene.[16]



(8)

The reaction of 2,3-diphenylthiophene represents another example of the extensively studied stilbene-type ring closures to yield phenanthrene derivatives.[17a–c] Dissolved oxygen in the system serves as the oxidant. A direct analogy of this reaction is the recently reported formation of phenanthro[9,10-*b*]furan from 2,3-diphenylfuran upon photolysis[17d] and the formation of triphenylene from *o*-terphenyl.[17e] Apparently in this case a ring closure is preferred to any possible rearrangement reaction (with the exception of the interchange of the 2,3-carbon atoms which cannot be detected).

Photolysis of 3,4-diphenylthiophene (eq 9) in dilute ether solution gave a major product identified as phenanthrol[9,10-*b*]thiophene (**14**). The product was shown definitely not to be phenanthro[9,10-*c*]thiophene (**17**).[18]

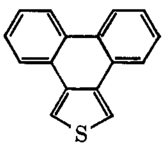


15

(9)

major
14

minor
16

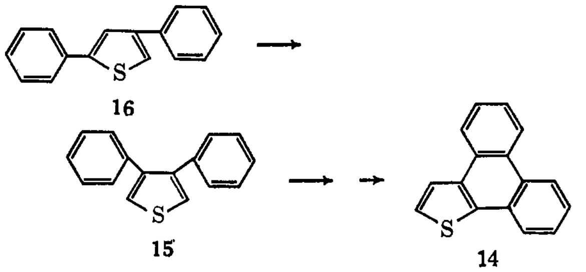


17

In addition to **14**, a second product (*ca.* 8% the amount of **14**) was formed during photolysis. This material had the same retention time as 2,4-diphenylthiophene (**16**) and a sample trapped from the gas chromatograph exit port had the same ultraviolet spectrum as authentic **16**. The structure was further confirmed by the identification of 1,3-diphenylbutane upon desulfurization of a reaction mixture with Raney nickel.

The 3,4-diphenylthiophene most likely rearranges first to 2,3-diphenylthiophene and 2,4-diphenylthiophene. The 2,3-diphenylthiophene then undergoes rapid ring closure to form the phenanthro derivative. The failure of 3,4-diphenylthiophene to form **17** by direct photochemical ring closure may be associated with the lack of sufficient "double-bond" character between the 3,4-carbons of the thiophene ring or rearrangement may represent a more favorable path in this case.[19]

Photolysis of 2,4-diphenylthiophene (**16**) in dilute ether solution led first to the formation of 3,4-diphenylthiophene (**15**) as identified by infrared spectra and gas



16
15
14
(10)

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(15) (a) R. Wilputte and R. H. Martin, *Bull. Soc. Chim. Belges*, **65**, 874 (1956); (b) P. C. Dutta, *J. Indian Chem. Soc.*, **18**, 469 (1941).

(16) These results were obtained in conjunction with an extensive investigation of the photolysis of mono- and diiodothiophenes in various aromatic solvents (benzene, mesitylene, naphthalene, thiophene). This technique has been shown to be a convenient preparative method for a number of arylthiophenes. Correlations have also been carried out on the relative rates of arylation of the 2 and 3 positions of thiophene. A brief description of the photolysis technique can be found in paper V of this series. The photolysis of 2,3-diiodothiophene and 2,3-diiodothianaphthene has also been examined with a view toward the photochemical generation of thiophynes. The use of iodoaromatics in photoarylations has been extensively described: W. Wolf and N. Kharasch, *J. Org. Chem.*, 30, 2493 (1965), and references contained therein. While this work was in progress a description of the photolysis of 2- and 3-phenylthiophene in benzene and substituted benzenes appeared confirming some of our results: L. Benati and M. Tiecco, *Boll. Sci. Fac. Chim. Ind. Bologna*, 24, 45 (1966); *Chem. Abstr.*, **65**, 8710*f* (1966). The work done in our laboratories will soon be published.

(17) (a) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964). (b) J. Cornelisse, Thesis, Leiden University, 1964. (c) Similar ring closure reactions have been observed in this laboratory with dithienylethylenes and difurylethylenes: R. M. Kellogg, M. B. Groen, and H. Wynberg, paper in preparation. (d) A. Padwa and R. Hartman, *J. Am. Chem. Soc.*, **88**, 3759 (1966). These authors further report that they failed to observe rearrangements with the other diphenylfuran isomers. (e) N. Kharasch, T. G. Alston, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 242 (1965).

(18) We thank Dr. S. van der Werf of this laboratory for providing us with authentic 17.

(19) Interestingly, on tetraphenylthiophene photolysis in dilute ether solution for over 100 hr failed to show any detectable change except for a lowering of the ultraviolet extinction. No-reaction reactions involving carbon–carbon interchange could not, of course, be detected.

chromatographic retention time. Further irradiation gave phenanthrene **14** as a secondary photolysis product (eq 10).

2,5-Diphenylthiophene (**17**) upon photolysis for extended periods gave no major photolysis products. Two very small peaks with the same retention times as **15** and **14** were seen in the gas chromatogram. Examination of the ultraviolet spectrum of irradiated material showed small, sharp peaks at 254 and 260 mμ highly characteristic of **14** (see Experimental Section).

Discussion

The photochemical rearrangement of 2-aryl-substituted thiophenes occurs with a number of different aryl substituents, thus phenyl, *p*-tolyl, mesityl, and naphthyl all are rearranged to the 3 position. These rearrangements must occur by some mechanism involving extensive rebonding in the thiophene ring; the results of ^{14}C labeling require this conclusion.

The rearrangements of the diphenylthiophenes are more involved than those of monoarylthiophenes. The most remarkable result obtained is perhaps the specificity of rearrangement leading to one primary product in all cases. This suggests a general path for the rearrangement which could be elucidated if one knew the location of all the carbon atoms in the thiophene ring after rearrangement. Experiments designed to answer this question are described in the next two papers and mechanistic conclusions are presented in the last paper of this series.

Experimental Section

All melting points are corrected; boiling points are uncorrected. Merck Grade aluminum oxide was used for column chromatography. Ultraviolet spectra were taken on a Zeiss PMQ II spectrophotometer, and reactions were followed with a Cary Model 15 scanning spectrophotometer; wavelengths are reported in millimicrons with the corresponding extinction coefficients (ε). Infrared spectra were taken on a Perkin-Elmer Model 125 infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were taken with a Varian A-60 instrument with tetramethylsilane (TMS) as internal reference. Phosphorescence and fluorescence spectra were measured with the instrument previously described[2] or with an Aminco-Bowman spectrophotofluorometer and spectra photographed from the oscilloscope trace. Spectra were taken in EPA glass at liquid nitrogen temperature. Analytical gas chromatography (glpc) was carried out with an F & M Model 810 gas chromatograph equipped with hydrogen flame detectors and occasionally with a Perkin-Elmer fractometer with hydrogen flame detectors and a 165-ft butane diolsuccinate (BDS) capillary column. Preparative separations were performed with a Wilkens A-700 Autoprep. Specially designed high-efficiency trapping tubes were attached directly to the exit port of the chromatography.

Many of the ultraviolet, infrared, and nmr spectra were taken by Miss K. S. Meijer and Miss H. de Groot. Microanalyses were carried out by the analytical section of this university under the direction of Mr. W. Hazenberg.

Large-scale photolyses were done with a Hanau Q-700 lamp enclosed in a quartz jacket and cooled with recirculated twice-distilled water. The lamp was immersed in a cylindrical reaction vessel capable of holding approximately 550 ml of solution. Stirring was provided by a large Teflon paddle magnetically coupled with a stirrer set at the bottom of the vessel. Facilities were provided for running reactions under a nitrogen atmosphere and for removing samples as desired. Smaller scale photolyses (100–125 ml) were carried out with Hanau S-81 high-pressure mercury lamps mounted in quartz jackets. A cooling system was used consisting of twice-distilled water (or filter solution if desired) which was continually repumped through the lamp. Facilities were built into the circulating line to allow ±1° temperature control from 20 to 80°. Reactions were run under constant nitrogen pressure and samples could be withdrawn as desired. The high-pressure mercury lamp could be readily exchanged for a Hanau NK 6-20 low-pressure lamp (2537 A).

2-Phenylthiophene (1) was usually obtained by heating the sodium salt of 3-benzoylpropionic acid (obtained by acylation of benzene with succinic anhydride) with P_4S_7 in the described manner[20] with yields of 10–15%,[21] mp 34.5–35° (lit.[20] mp 35.9–36.1°). The material was 99–100% pure as determined by glpc on a 4-ft diethylene glycol succinate (DEGS) column at 190°; ultraviolet spectrum in cyclohexane: λ_{max} 282 (13,400) and λ_{max} 222 (7500); in 96% ethanol: λ_{max} 283 (18,300) and λ_{sh} 225 (7800). The compound showed weak phosphorescence at 540 ± 5 mμ.

3-Phenylthiophene (2) was prepared by reaction of phenyl Grignard reagent (0.5 mole) with 3-ketotetrahydrothiophene[14] (50 g, 0.5 mole). The reaction mixture was acidified with 2 *N* HCl and extracted with ether; the ether layer was neutralized with $KHCO_3$ and dried over $MgSO_4$. Removal of the ether left 64.5 g of oily carbinol. This oil was heated slowly with $KHSO_4$ (10 g) and S (18 g) (a considerable excess of $KHSO_4$ and S are necessary for good reaction) to 225° until water and H_2S ceased to be evolved. The remaining material was steam distilled to give 3-phenylthiophene (35.2 g, 0.22 mole, 44% yield), gas chromatographically pure; mp 89–91°, after recrystallization from methanol (lit.[22] 91–92°); ultraviolet spectrum in cyclohexane: λ_{max} 227 (15,300) and λ_{max} 259 (13,700); in 96% ethanol: λ_{max} 227 (12,800) and λ_{max} 259 (12,000). The compound showed a strong phosphorescence at 490 ± 5 mμ.

2-(*p*-Tolyl)thiophene (3) was prepared from 4-(*p*-tolyl)-4-ketobutyric acid synthesized according to the general method of de Barry-Barnett and Sanders.[23] A suspension of succinic anhydride (80 g, 0.8 mole) and toluene (81 g, 0.88 mole) was refluxed in tetrachloroethane (300 ml) until homogeneous. Anhydrous aluminum chloride (240 g, 1.80 moles) was added, and the reaction mixture was refluxed for 1.5 hr and stirred overnight at room temperature. The reaction mixture was poured into 10% HCl solution and the crude precipitate was purified by repeated extractions with aqueous KOH followed by precipitation with HCl solution. Neutralization gave the sodium salt of 4-(*p*-tolyl)-4-ketobutyric acid (130 g, 0.61 mole, 76% yield). A sample of the free acid recrystallized from hot water had mp 145.5–146° (lit. 120°[24] and 127°[25]). The nmr spectrum completely supported the structure of the acid.

The dry sodium salt of the acid (31 g, 0.15 mole) and P_4S_7 (44 g, 0.13 mole) were heated in a flask equipped with a cooler and a trap for escaping gas. The flask was heated at 150° for 0.5 hr followed by a slow increase to 180° until vigorous reaction ceased followed by further heating to 250° for 0.75 hr. After cooling, water was carefully added until the reaction stopped; concentrated NaOH solution was added and the solution slowly steam distilled. The steam distillate was extracted with ether which was dried and removed. The product was decolorized twice with Norit in methanol, chromatographed over Al_2O_3 (methanol eluent), and concentrated to yield, after standing, 2-(*p*-tolyl)thiophene (3.2 g, 0.018 mole, 12.7% yield), mp 63–64° (lit.[11] 63–64°); ultraviolet spectrum in 96% ethanol: λ_{max} 285 (15,500) and λ_{sh} 224 (6400).

3-(*p*-Tolyl)thiophene (4) was prepared according to the general method of Broun and Voronkov.[26] *p*-Methylacetophenone (24 g, 0.18 mole) was allowed to react with excess ethyl Grignard reagent. The crude carbinol obtained after acidification and extraction of the reaction mixture was heated with a few crystals of iodine which effected dehydration. The I_2 was removed by shaking with aqueous $NaHSO_3$. After extraction and drying the residue was distilled to give 2-(*p*-tolyl)butene-2, bp 87–92° (11 mm) (18 g, 0.12 mole, 59% yield), $n^{20}D$ 1.5313; ultraviolet spectrum in 96% ethanol: λ_{max} 246 (10,900).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 89,7; H, 9.6.

The 2-(*p*-tolyl)butene-2 (15 g, 0.1 mole) and S (13 g, 0.4 g-atom) were heated for 7 hr at 200°. After addition of water followed by steam distillation, the product obtained was precipitated twice out of glacial acetic acid and recrystallized from 70% methanol–water

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[20] J. L. Melles and H. J. Backer, *Rec. Trav. Chim.*, 72, 314 (1953).

[21] Yields as high as 30% when prepared by method of Chrzaszczewska.[11]

[22] H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers Inc., New York, N. Y., 1952, p 477.

[23] E. de Barry-Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

[24] E. Burker, *Bull. Soc. Chim. France*, 49, 449 (1888).

[25] H. Limprickt, *Ann.*, **312**, 110 (1900).

[26] A. S. Broun and M. G. Voronkov, *J. Gen. Chem. USSR*, 17, 1162 (1947); *Chem. Abstr.*, 42, 1591*a* (1948).

to give 3-(*p*-tolyl)thiophene (1 g, 0.006 mole, 6% yield), mp 113–113.5° (lit.[11] 111–112°); ultraviolet spectrum in 96% ethanol: λ_{max} 261 (14,800) and λ_{max} 228 (14,800).

3-(*m*-Tolyl)thiophene was prepared by reaction of 3-ketotetrahydrothiophene (5 g, 0.95 mole) with the Grignard reagent from *m*-bromotoluene (0.05 mole). After acidification and extraction with ether there remained, after removal of the ether, the carbinol (7.5 g, 78.5% yield), bp 116–120° (0.25 mm), n^{20}D 1.6064. The most satisfactory method of aromatization involved heating the carbinol (3.7 g, 0.019 mole) with $KHSO_4$ (0.5 g) and S (0.8 g) very slowly to 225° until cessation of gas evolution. The reaction can be carried out stepwise with $KHSO_4$ followed by S but in poorer yields. The mass was taken up in water and steam distilled. The steam distillate was extracted with ether and was distilled, bp 92–96° (0.6 mm), n^{20}D 1.6200 (1.2 g, 0.0075 mole, 40% yield). The product was purified by treatment with $HgCl_2$ in 96% ethanol to form the mercuric chloride salt. The yellow precipitate formed after standing at room temperature was recrystallized out of dioxane and decomposed by heating with 5 ml of 2 *N* HCl solution. The organic material was extracted with benzene to give gas chromatographically pure 3-(*m*-tolyl)thiophene, bp 84–86° (0.3 mm), n^{20}D 1.6248; ultraviolet spectrum in 96% ethanol: λ_{max} 260 (11,400) and λ_{sh} 228 (12,700).

Anal. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78; S, 18.40. Found: C, 76.0; H, 5.8; S, 18.1.

3-(*o*-Tolyl)thiophene was prepared by reaction of 3-ketotetrahydrothiophene (7.2 g, 0.07 mole) with the Grignard reagent from *o*-bromotoluene (0.07 mole). The carbinol obtained was treated with $KHSO_4$ (0.73 g) and S (1.16 g) as described above to give a main product (4.0 g, 0.028 mole, 33% yield), bp 85–98° (0.3 mm), n^{20}D 1.6203. The material was not pure and further purification through the mercuric chloride salt prepared as described above was necessary. After 4 weeks of standing, a precipitate was obtained which was decomposed with 2 *N* HCl to give 3-(*o*-tolyl)thiophene, bp 94–98° (2 mm), n^{20}D 1.6140, gas chromatographically pure; ultraviolet spectrum in 96% ethanol: λ_{max} 247 (9100).

Anal. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78; S, 18.40. Found: C, 75.9; H, 5.7; S, 18.2.

2-Mesitylthiophene (5) was prepared by ring closure of 3-mesitoylpropionic acid. Succinic anhydride (20 g, 0.20 mole) and mesitylene (26.5 g, 0.22 mole) in tetrachloroethane (75 ml) were refluxed with anhydrous aluminum chloride (60 g, 0.45 mole) for *ca.* 1 hr. The reaction mixture was worked up by adding aqueous HCl; the tetrachloroethane was removed by steam distillation, and the remaining acid was allowed to crystallize. The acid was dissolved in aqueous NaOH, decolorized with Norit, and reprecipitated with aqueous HCl to give 3-mesitoylpropionic acid (40 g, 0.18 mole, 90% yield), mp 110.5–112°.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.9; H, 7.3.

The well-dried sodium salt of the acid (30 g, 0.12 mole) was carefully heated with P_4S_7 (40 g, 0.115 mole) to 180° and held at this temperature for 1 hr. Aqueous NaOH was added to the cooled mixture until all reaction stopped and the residue slowly steam distilled. The steam distillate was saturated with NH_4Cl and extracted with CCl_4. After removal of the CCl_4 and distillation, 2-mesitylthiophene was obtained, bp 101–107° (1.8 mm), n^{20}D 1.5773 (4 g, 0.02 mole, 16% yield), as a yellow-red oil. Upon standing the oil crystallized, and after several recrystallizations from 70% methanol–water at −40° light rose crystals of 2-mesitylthiophene, mp 29.5–30.5°, were obtained which were gas chromatographically pure; ultraviolet spectrum in 96% ethanol: broad absorptions, λ_{sh} 240 (9200) and λ_{sh} 220 (13,200).

Anal. Calcd for $C_{13}H_{14}S$: C, 77.18; H, 6.97; S, 15.85. Found: C, 77.2; H, 6.9; S, 15.6.

3-Mesitylthiophene (6) was prepared after several unsuccessful attempts by reaction of mesityl Grignard reagent with 3-ketotetrahydrothiophene. 2-Bromomesitylene[27] (10 g, 0.05 mole), magnesium (1.3 g, 0.05 g-atom), and ether (25 ml) were allowed to reflux under extremely dry conditions for 16 hr. 3-Ketotetrahydrothiophene (5.0 g, 0.05 mole) in 15 ml of ether was slowly added followed by 2 hr of stirring. After work-up, the unreacted 3-ketotetrahydrothiophene and mesityl bromide were distilled under water aspirator vacuum. The residue was slowly heated with $KHSO_4$ (0.25 g) and S (0.4 g) to 225° and held at this temperature for 1 hr. The reaction mixture was extracted with 1:1 ether–methanol and the extract chromatographed over Al_2O_3 to give 1 g of impure product. A pure sample (25 mg) was obtained by preparative gas chromatography (7-ft Carbowax, 170°), mp 32–34;[28] ultraviolet spectrum in 96% ethanol: broad spectrum, λ_{sh} 240 (8500) and λ_{sh} 220 (17,200).

Anal. Calcd for $C_{13}H_{14}S$: C, 77.18; H, 6.97; S, 15.85. Found: C, 76.9; H, 7.0; S, 15.7.

Preparation of 3-(α-naphthoyl)- and 3-(β-naphthoyl)propionic acids was carried out by acylation of naphthalene (80 g, 0.63 mole) with succinic anhydride (40 g, 0.40 mole) in nitrobenzene (300 ml) in the presence of anhydrous aluminum chloride (110 g, 0.83 mole). After 21 hr at room temperature, dilute HCl was added and the nitrobenzene and excess naphthalene distilled. The remaining acid was dissolved in hot Na_2CO_3 solution, filtered, and precipitated. The acid mixture was recrystallized out of glacial acetic acid. The precipitate was mostly 3-(β-naphthoyl)propionic acid, and the 3-(α-naphthoyl)propionic acid remained in solution. Successive recrystallizations[29] of the precipitate out of methanol gave 3-(β-naphthoyl)propionic acid (26 g, 0.12 mole, 28% yield), mp 169–171° (lit.[30] 173–174°). Recovery of the mother liquors and successive recrystallizations out of methanol gave 3-(α-naphthoyl)-propionic acid (29 g, 0.13 mole, 32% yield), mp 129–130° (lit.[30] 131.0–132.5°).

2-(α-Naphthyl)thiophene (9) was prepared by heating the dried sodium salt of 3-(α-naphthoyl)propionic acid (22 g, 0.088 mole) with P_4S_7 (30 g, 0.08 mole) slowly to 250° for 0.5 hr. After cooling, the mass was treated with NaOH solution and steam distilled. After extraction of the organic material followed by drying and evaporation of the solvent an oil was obtained which gave 2-(α-naphthyl)thiophene (2.5 g, 13.5%) upon distillation, bp 126–127° (0.25 mm), n^{20}D 1.6905 [lit.[31] bp 165° (1 mm)]; ultraviolet spectrum in 96% ethanol: λ_{max} 296 (9700) and λ_{max} 224 (42,300)

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.9; H, 4.9; S, 15.2.

2-(β-Naphthyl)thiophene (10) was prepared by heating the dry sodium salt of 3-(β-naphthoyl)propionic acid (22 g, 0.088 mole) with P_4S_7 (30 g, 0.086 mole) for 1.5 hr at 200°. After steam distillation 2-(β-naphthyl)thiophene (2.08 g, 11% yield) was obtained as silver gray crystals, mp 104–105° after recrystallization from methanol; ultraviolet spectrum in 96% ethanol: λ_{max} 311 (16,200), λ_{max} 273 (24,200), λ_{max} 265 (25,800), and λ_{max} 219 (41,200).

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.6; H, 4.8; S, 14.9.

3-(α-Naphthyl)thiophene (11) was prepared by the reaction of the Grignard reagent (0.05 mole) formed from α-bromonaphthalene (Fluka A. G., Switzerland) and 3-ketotetrahydrothiophene (5.0 g, 0.05 mole). Slow addition of the bromo compound and extended refluxing were necessary to form the Grignard reagent. After hydrolysis, extraction, and distillation, the carbinol (5.6 g, 49% yield), bp 165–175° (0.15 mm), was obtained. The carbinol (1.7 g, 0.0073 mole) was heated with $KHSO_4$ (0.25 g) and S (0.4 g) to 200° until H_2S and water ceased to be evolved. The product was not steam distillable so the pyrolysis mixture was purified by chromatography over Al_2O_3 (petroleum ether–methanol–ether, 94:3:3). In this manner gas chromatographically (Apiezon L, 270°) pure 3-(α-naphthyl)thiophene (1.1 g, 71% yield from the carbinol) was obtained as a viscous, colorless liquid, n^{20}D 1.6892, which failed to crystallize on prolonged standing at −30°;[32] ultraviolet spectrum in 96% ethanol: λ_{max} 292 (9500) and λ_{max} 224 (59,400).

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.8; H, 4.9; S, 14.9.

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(27) L. I. Smith, *Org. Syn.*, 11, 24 (1931).

(28) A much better preparation of this compound is the photolysis of 3-iodothiophene in mesitylene.[16]

(29) Method of R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

(30) M. S. Newman, R. B. Taylor, H. Hodgson, and A. B. Garrett, *J. Am. Chem. Soc.*, **69**, 1784 (1947).

(31) J. Szmuszkovicz and E. J. Modest, *ibid.*, **72**, 571 (1950).

(32) J. Schmitt, R. Fallard, and M. Suguet, *Bull. Soc. Chim. France*, 1147 (1956), report the isolation of 3-(α-naphthyl)thiophene from a mixture of products formed from the reaction of 2-naphthylbutene-2 with S. These authors report mp 147° for their compound in contrast to our liquid material (see above). Careful comparison of infrared spectra of our 3-(α-naphthyl)thiophene with those of the other three naphthylthiophene isomers prepared by us showed a good correlation of many characteristic peaks. The gas chromatographic retention time agreed well with that expected from the other isomers. Our structure is further confirmed by the fact that a material with spectral properties identical with those of our isomer is formed from the photolysis of 2-(α-naphthyl)-thiophene. Furthermore photolysis of 3-iodothiophene in naphthalene[16] gave a product with spectral properties identical with a mixture of our 3-(α-naphthyl)- and 3-(β-naphthyl)thiophenes.

3-(β-Naphthyl)thiophene (12) was prepared with considerable difficulty from the Grignard reagent from β-bromonaphthalene (obtained from the diazonium salt of β-naphthylamine).[33] The Grignard reagent from β-bromonaphthalene (21 g, 0.10 mole) was prepared in ether–benzene (4:1)[34] and allowed to react with 3-ketotetrahydrothiophene (10.2 g, 0.10 mole). After work-up and distillation, the carbinol (15.5 g, 0.071 mole, 71% yield), bp 175° (10 mm), obtained was immediately heated with $KHSO_4$ (1.75 g) and S (2.8 g) to 225° over 0.5 hr. Work-up and chromatography over Al_2O_3 (petroleum ether–ether–methanol, 94:3:3) gave 3-(β-naphthyl)thiophene (10 g, 0.048 mole, 68% yield) as a dark solid. After repeated chromatography and recrystallization from petroleum ether, a pure sample was obtained, mp 145.5–146.5°; ultraviolet spectrum in 96% ethanol: λ_{max} 301 (12,000), λ_{max} 290 (14,700), λ_{max} 279 (12,900), λ_{max} 254 (37,200), and λ_{max} 228 (39,600).

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79; S, 15.25. Found: C, 79.9; H, 4.7; S, 15.2.

2,5-Diphenylthiophene (17) was obtained from a student collection and had been prepared[35] from a modified procedure.[36] Recrystallization from benzene–ethanol gave colorless plates, mp 153–154° (lit.[22,35] 153–154°); ultraviolet spectrum in 96% ethanol: λ_{max} 324 (28,400) and λ_{max} 230 (11,900). A very strong fluorescence emission at 390 mμ was observed, phosphorescence could not be detected.

3,4-Diphenylthiophene (15) was obtained from a sample[35] prepared by decarboxylation of 3,4-diphenyl-2,5-dicarboxylthiophene. Recrystallization from benzene–methanol gave material, mp 113.5–114°, (lit.[22,35] 114°); ultraviolet spectrum in 96% ethanol: λ_{max} 234 (24,500) and λ_{sh} 260 (12,300). Medium intensity fluorescence at 342 mμ was detected and also very strong phosphorescence at 480 mμ.

2,4-Diphenylthiophene (16) was prepared by heating styrene with sulfur in the presence of 2-mercaptobenzothiazole.[37] Redistilled styrene (40 g, 0.38 mole), sulfur (10 g, 0.3 g-atom), and 2-mercaptobenzothiazole (100 mg) were refluxed for 7 hr. The excess styrene was steam distilled in the presence of 10% NaOH; the undistilled residue was extracted with benzene and the benzene was dried and evaporated to leave a solid mass. The material was recrystallized twice out of benzene–methanol and chromatographed over Al_2O_3 (benzene eluent). Addition of methanol to the benzene solution precipitated 2,4-diphenylthiophene (8.5 g, 0.036 mole, 19% yield), mp 121.0–121.5° (lit.[32,34] 120.7–121.7°); ultraviolet spectrum in 96% ethanol: λ_{max} 258 (33,800), λ_{sh} 305 (9400), and λ_{sh} 224 (16,000). Strong fluorescence at 362 mμ was detected and medium phosphorescence at 545 mμ.

2,3-Diphenylthiophene (13) was obtained from a supply previously synthesized by reaction of the sodium salt of 3-phenyl-3-benzoylpropionic acid with phosphorus trisulfide.[35] This material was recrystallized from methanol and had mp 82.5–83° (lit.[20] 82.5–83°); ultraviolet spectrum in 96% ethanol: λ_{max} 278 (11,400) and λ_{max} 238 (20,300). Medium fluorescence at 390 mμ was observed and weak phosphorescence at 560 mμ.

Synthesis of Phenanthro[9,10-*b*]thiophene (14).[38] The synthesis of 9-phenanthrylthioglycolic acid was carried out using a modified combination of the methods of Wilputte and Martin[15a] and that of Dutta.[15b] 9-Bromophenanthrene was prepared by bromination of phenanthrene.[39] The Grignard reagent was formed by reaction of the 9-bromophenanthrene (102 g, 0.4 mole) with magnesium (9.7 g, 0.4 g-atom) in a mixture of 150 ml of dry benzene and 100 ml of dry ether. The mixture was refluxed 1.5 hr; 100 ml of a 1:1 benzene–ether mixture was added, and the reaction mixture was allowed to reflux 40 hr. In small portions crystallized sulfur (14 g, 0.44 g-atom) was added. The reaction mixture became viscous during the addition and 300 ml of a 2:1 benzene–ether solution was added to overcome this. The reaction mixture was refluxed 5 hr, cooled, and hydrolyzed with 150 ml of 10% HCl and stored under N_2. Zinc (110 g, 1.68 g-atom) was added followed by 250 ml of 36% HCl. The reduction was allowed to run 24 hr. The upper organic layer was separated; 200 ml water was added and the solution extracted with 150-ml portions of 10% NaOH. The aqueous solution of the sodium salt of the thiol was cooled in ice and monochloroacetic acid (40 g, 0.43 mole) was added dropwise. The reaction mixture was warmed, filtered, and carefully acidified with concentrated HCl to pH 3–4. The acid was filtered off and dried over P_2O_5 in a desiccator to give 9-phenanthrylthioglycolic acid (69.7 g, 0.26 mole, 65% yield), mp 138–140° after recrystallization from water (lit.[15b] 134–135°); ultraviolet spectrum in 96% ethanol: λ_{max} 225 (19,900), λ_{max} 250 (38,400), λ_{sh} 253 (37,800), λ_{sh} 255 (37,300), and λ_{max} 304 (9900). The nmr spectrum completely supported the structure of the acid.

Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.61; H, 4.51; S, 11.95. Found: C, 71.0; H, 4.7; S, 11.8.

The 9-phenanthrylthioglycolic acid (3.6 g, 0.013 mole) was dissolved in 45 ml of dry petroleum ether (bp 40–60°) with thionyl chloride (3.2 g, 0.027 mole) and refluxed 5 hr. After several days at −20°, a yellow material crystallized which was filtered. The thionyl chloride was evaporated to leave 9-phenanthrylthioglycoloylchloride (3 g, 0.010 mole, 78% yield). The anilide, mp 153–154°, was prepared for analysis.

Anal. Calcd for $C_{22}H_{17}NOS$: C, 76.94; H, 4.99; S, 9.34. Found: C, 76.8; H, 5.0; S, 9.4.

The impure acid chloride obtained from several preparations (4.1 g, 14.3 mmoles) was refluxed with aluminum chloride (5 g, 3.7 mmoles) in 35 ml of carbon disulfide for several hours. The solvent was removed and the reddish residue dried under vacuum over P_2O_5 to give phenanthro[9,10-*b*]thiophen-3(2H)-one (2.8 g, 11.2 mmoles, 78% yield), mp 150–155°. Several recrystallizations from ethanol gave material, mp 171–172° (lit.[15b] 173–175°). Infrared spectra taken on two different samples were completely different. In one case, a broad OH band was obtained with no carbonyl (enol form), and in the other case, only carbonyl absorption was observed. The keto–enol equilibrium may depend on the method of sample preparation.

The impure material from above (2 g, 8 mmoles) was refluxed in 40 ml of acetic acid with zinc (1.6 g, 2.45 mg-atoms) and 2 ml of 36% HCl for 21 hr. The reaction mixture was made alkaline and extracted with ether. Removal of the ether left a white material which, after being chromatographed several times over Al_2O_3 (benzene eluent) and recrystallized from petroleum ether (bp 80–100°), afforded phenanthro[9,10-*b*]thiophene (200 mg, 0.87 mole, 11% yield), mp 151–153°; ultraviolet spectrum in 96% ethanol: λ_{max} 253 (57,600), λ_{max} 260 (54,900), λ_{max} 279 (13,800), λ_{max} 290 (17,500), λ 311 (9500), λ 334 (5300), λ 341 (3200), and λ 351 (1500); picrate mp 202–203°.

Anal. Calcd for $C_{16}H_{10}S$: C, 82.02; H, 4.31; S, 13.67. Found: C, 81.95; H, 4.28; S, 13.68.

The material was identical with that obtained from the photolysis of 2,3-diphenylthiophene or from the photolysis of 2,3-diiodothiophene in benzene.[16] Oxidation of **14** (100 mg, 0.43 mmole) with chromium trioxide (1 g) in 15 ml of glacial acetic acid plus 2 ml of water at 45° gave, upon work-up and recrystallization from ethanol, orange-yellow crystals of 9,10-phenanthroquinone, mp 208–210°, undepressed with authentic material.

Photolysis of 2-phenylthiophene (1) was first carried out in benzene solution at 80° in the presence of sodium thiosulfate. These conditions were chosen because the rearrangement had originally been noted during the photolysis of 2-iodothiophene in benzene to give 2-phenylthiophene.[16] 2-Phenylthiophene (98 mg) was irradiated for 38 hr in 100 ml of benzene to which $Na_2S_2O_3 \cdot 5H_2O$ (1.5 g) had been added. The lamp was cleaned once and 1.5 g more $Na_2S_2O_3 \cdot 5H_2O$ added. The reaction mixture was filtered and evaporated and the residue chromatographed over Al_2O_3 (benzene eluent) to give 40 mg of material which glpc (4-ft DEGS, 190°) indicated to be 3-phenylthiophene with a little 2-phenylthiophene. The material was purified by preparative glpc (25-ft DEGS, 170°) to give authentic 3-phenylthiophene, mp 90–91° after recrystallization from 70% methanol–water, undepressed with authentic 3-phenylthiophene. The ultraviolet and infrared spectra were identical with those of 3-phenylthiophene.

Further investigations showed that the reaction could be carried out in benzene without added sodium thiosulfate (the over-all yields appear to be higher with added sodium thiosulfate). The most convenient solvent was found to be ether at 20°. No detailed concentration studies were made but the same reaction occurs working at ultraviolet concentrations (*ca.* 10^{-5} *M*) to concentrations

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[33] M. S. Newman and P. H. Wise, *J. Am. Chem. Soc.*, **63**, 2847 (1941).

[34] L. F. Fieser and E. B. Hershberg, *ibid.*, **59**, 1032 (1937).

[35] J. L. Melles, Thesis, University of Groningen, Netherlands, 1957.

[36] S. Kapf and C. Paal, *Ber.*, **21**, 3053 (1880).

[37] T. K. Hanson and L. M. Kinnard, British Patent 696,439 (Sept 2, 1953); *Chem. Abstr.*, **51**, 15587*e* (1957).

[38] This synthesis was performed by Mr. J. de Valk of these laboratories.

[39] C. A. Dornfeld, J. E. Collin, and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 134.

as high as 10^{-2} *M*. Reactions proceeded equally well in the presence or absence of oxygen. An attempt was made to carry out the rearrangement with solid 2-phenylthiophene in a KBr pellet but apparently only decomposition occurred. Quantitative experiments (Figure 1) on the rate of 2-phenylthiophene rearrangement were carried out with a 6.0×10^{-3} *M* ether solution using the S-81 lamp at 20°. Reaction was carried out in a N_2 atmosphere and the rate was followed by glpc (4-ft DEGS, 175°) using sulfolane as an internal standard. Sulfolane was shown not to undergo any decomposition over the times used for photolysis. Both ultraviolet and glpc investigations of the reaction mixture failed to show any product besides 3-phenylthiophene. Examination of solutions immediately after photolysis failed to show any unaccounted absorptions from short-lived intermediates. Intermediates with lifetimes shorter than 5–10 min would probably not have been detected by either ultraviolet or gas chromatographic techniques. Reactions were carried out at −40° in ether, 20° in ether, and 80° in benzene using the same lamp and concentrations, and qualitatively, no difference in the rate of decomposition could be observed.

Irradiations were carried out in different solvents. The rearrangement of 2-phenyl- to 3-phenylthiophene occurred in all solvents investigated, and no new products could be detected except in benzene where diphenyl was formed apparently from the benzene (*no* diphenyl was formed in any other solvent investigated). The rate of decomposition varied greatly with solvent. The relative rates of disappearance after a 2.5-hr irradiation of a 6.4×10^{-3} *M* solution of 2-phenylthiophene (irradiated with the same S-81 lamp) at 20° are benzene–cyclohexene–ether–dichloromethane–methanol (1.0:1.7:2.2:5.1:5.9). Considerable amounts of tar were formed in the methanol photolysis but attempts to characterize addition products failed.[40]

Photolysis of 3-phenylthiophene (2) was carried out with a 6×10^{-3} *M* solution in ether at 20° under an N_2 atmosphere using an S-81 lamp. The rate of reaction was followed by glpc (4-ft DEGS, 175°) using sulfolane as an internal standard. The rate of decomposition is shown in Figure 1. No products could be detected by gas chromatography. 2-Phenylthiophene could have been detected in amounts as small as 0.25% of the remaining 3-phenylthiophene. No trace of this isomer was discovered.

Photolysis of 2-(*p*-tolyl)thiophene (3) was carried out at 20° in the Q-700 apparatus. 2-(*p*-Tolyl)thiophene (1.0 g, 5.75 mmoles) in 530 ml of ether was irradiated for 93 hr, the lamp was cleaned after 50 hr. Monitoring of the reaction by glpc (4-ft DEGS, 190°) showed one product had been formed and that the starting material had nearly disappeared. The reaction product was filtered; the solvent was removed and chromatographed over Al_2O_3 (benzene eluent). Preparative glpc (25-ft DEGS, 170°) allowed the isolation of the photoproduct. This had a retention time identical with that of 3-(*p*-tolyl)thiophene and different from the authentic *o*- or *m*-tolyl isomers. Infrared, nmr, and ultraviolet spectra of the photoproduct were identical with those of authentic 3-(*p*-tolyl)-thiophene.

Photolysis of 2-mesitylthiophene (5) (600 mg) was carried out in 500 ml of ether at 20° under N_2 with the Q-700 lamp for *ca.* 6 hr. The red-brown reaction mixture was analyzed by glpc (4-ft DEGS, 190°) from which it was estimated that about 100 mg of 2-mesitylthiophene remained and 30 mg of 3-mesitylthiophene had been formed. After filtration, chromatography over Al_2O_3 (benzene eluent) twice, and recrystallization from 96% ethanol, white crystals were obtained, mp 24–26°, which consisted of 2- and 3-mesitylthiophenes in a 4:1 ratio as determined by glpc. The nmr spectrum in CCl_4 of the product displayed absorptions completely assignable to a 4:1 mixture of 2- and 3-mesitylthiophenes by comparison with the spectra of the two authentic isomers. Expanded sweep width examination of the methyl absorptions failed to produce evidence of any new peaks assignable to isomerized methyl groups in the phenyl ring. The infrared spectrum of the product agreed in all details with that of an authentic mixture of 2- and 3-mesitylthiophene.

Photolysis of 2-(α-naphthyl)thiophene (9) (126 mg) was carried out at 20° in the S-81 apparatus for 24 hr. The progress of the reaction was followed by ultraviolet spectroscopy. The ether was evaporated, and the product was dissolved in hot ethanol to remove vacuum grease and chromatographed over Al_2O_3 (benzene eluent) to give 105 mg oil. Gas chromatography under conditions capable of separating all four of the naphthylthiophene isomers (4-ft Carbowax, 190°) showed the product to consist of approximately equal amounts of starting material and 3-(α-naphthyl)thiophene. No trace of the β-naphthyl isomers could be seen. The infrared and ultraviolet spectra corresponded precisely to those expected for a mixture of 2- and 3-(α-naphthyl)thiophenes.

Photolysis of 2-(β-naphthyl)thiophene (10) (57 mg) was carried out in 125 ml of ether at 20° in the S-81 apparatus for 40 hr. After removal of the ether and chromatography over Al_2O_3 (benzene eluent), 18.6 mg of white crystals were obtained. Glpc (4-ft Carbowax, 190°) indicated the product consisted of 63% 2-(β-naphthyl)-thiophene and 37% 3-(β-naphthyl)thiophene as determined from peak heights. No trace of the α-naphthyl isomers could be detected. The infrared and ultraviolet spectra were in complete agreement with the gas chromatographic evidence.

Photolysis of 3-(α-naphthyl)thiophene (11) (108 mg) was carried out in 125 ml of ether at 20–23° in the S-81 apparatus for 47 hr. After removal of the ether and chromatography over Al_2O_3 (benzene eluent), 78 mg of liquid was obtained. Glpc (4-ft Carbowax-190°) indicated the material to be 3-(α-naphthyl)thiophene, and this conclusion was supported by the ultraviolet and infrared spectra which were identical with those of starting material.

Photolysis of 3-(β-naphthyl)thiophene (12) (70 mg) was carried out in 125 ml of ether at 20° for *ca.* 40 hr. After removal of the ether and chromatography over Al_2O_3 (benzene eluent), 51 mg of white solid was obtained. The glpc (4-ft Carbowax, 190°), ultraviolet spectrum, and infrared spectrum were all identical with those of starting material.

Synthesis[41] of 2,5-^{14}C-2-phenylthiophene (7) was carried out starting from 1,4-^{14}C-succinic acid (Philips-Duphar, specific activity 4 mcuries/mmole). The radioactive succinic acid (3 mg) was diluted with inactive succinic acid (6 g, 5.5 mmoles) and dissolved in 15 ml of ether to allow mixing. Removal of the ether left crystalline succinic acid which was treated with acetyl chloride (10.5 ml, excess) to form the anhydride (4.7 g, 4.45 mmoles, 81% yield), mp 119°. The anhydride (2.5 g, 25 mmoles) was allowed to react with 20 g of benzene in the presence of dry aluminum chloride (7.4 g, 5.6 mmoles).[42] Work-up gave 1,4-^{14}C-4-phenyl-4-ketobutyric acid, mp 115–116°, which was converted to the dried sodium salt (2.5 g, 12.3 mmoles, 49% yield). The labeled sodium salt (2.5 g, 12.3 mmoles) and unlabeled salt (0.5 g, 2.5 mmoles) were mixed with 5 g of dry sand and P_4S_7 (4 g, 1.15 mmoles) and heated to 190°. Gas evolution began, and the apparatus was attached through a cold trap to a water pump to help withdraw the gas; the pot was slowly warmed to 250° and held for 15 min. The residue was treated with 20 ml of 20% KOH solution and steam distilled. The material obtained from the steam distillation was chromatographed over alumina (benzene eluent) and recrystallized out of 60% methanol–water to give 2,5-^{14}C-2-phenylthiophene (244 mg, 1.49 mmoles, 10% yield),[21] mp 34–35°, undepressed with authentic material. The infrared and ultraviolet spectra were identical with those of authentic 2-phenylthiophene.

Photolysis of 2,5-^{14}C-2-phenylthiophene (7) was carried out with the radioactive 2-phenylthiophene diluted *ca.* tenfold with inactive phenylthiophene (2.909 total weight) in 3.5 l. of ether at 20° in the Q-700 apparatus. Control experiments showed 6 hr to be the optimum irradiation time; approximately equal amounts of 2- and 3-phenylthiophene were formed after this time. Irradiation was carried out with batches of 500 ml, and the lamp was cleaned of solid deposit after 3 hr of irradiation. The yellowish photolysis mixture was evaporated to 100 ml; the insoluble material (0.66 g) was filtered out and the filtrate was evaporated. The residue was chromatographed twice over Al_2O_3 (benzene eluent) to yield 2.03 g of light yellow material consisting of approximately equal amounts of 2- and 3-phenylthiophene as determined by glpc (4-ft DEGS, 190°). The mixture was separated by preparative glpc (25-ft 25% DEGS on Chromosorb P, 155°). The material with the same retention time as 2-phenylthiophene melted at 34–34.5° and was not further investigated. The component with the same retention time as 3-phenylthiophene (*ca.* 500 mg) contained 1% 2-phenylthiophene as determined by glpc. The material was recrystallized several times from methanol to give a product, mp 89–91°; the melting point was undepressed with authentic 3-phenylthio-

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[40] The photochemically induced addition of methanol to benzenoid systems has been elegantly demonstrated: L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, 88, 2881 (1966).

[41] We thank Mr. H. Sinnige of these laboratories for expert technical help in the preparation and oxidation of the radioactive phenylthiophenes.

[42] L. F. Sommerville and C. F. H. Allen, *Org. Syn.*, 13, 12 (1933); E. L. Martin and L. F. Fieser, *ibid.*, **15**, 92 (1935).

phene. The infrared spectrum was identical with that of 3-phenylthiophene.

Oxidation[12] **of 2,5-^{14}C-2-phenylthiophene (7)** (200 mg, 1.23 mmoles) was carried out with CrO_3 (1.4 g, excess) in 25 ml of hot glacial acetic acid for 2 hr. The solvent was removed and the residue was dissolved in water and extracted with three 25-ml portions of ether which were in turn washed with water. The ether solution was dried over anhydrous $MgSO_4$; the ether was removed and the residue was decolorized in hot water with Norit. After filtration of the Norit, benzoic acid (50 mg, 0.41 mmole, 33% yield), mp 120–121°, undepressed with authentic material, was obtained.

Oxidation[12] **of ^{14}C-3-phenylthiophene (8)** was carried out as described for the 2-phenyl isomer. The product isolated from the gas chromatograph (400 mg, 2.48 mmoles) was oxidized with CrO_3 (2.8 g, excess) in 50 ml of hot glacial acetic acid. After workup benzoic acid (40 mg, 0.33 mmole, 14% yield), mp 120–121°, undepressed with authentic material, was obtained.

Measurement of activity of 7 and 8 was carried out with a Packard Tri-Carb liquid scintillation counter, Type 314-ES. The activity was measured by comparison with a sample of ^{14}C-benzoic acid of standard activity. The activity of the benzoic acid obtained from oxidation of the 2-phenyl isomer after correction for internal quenching was found to be 0.0310 ± 0.0003 mcurie/mole. The activity of the benzoic acid obtained from oxidation of the 3-phenyl isomer after internal quenching correction was 0.0318 ± 0.0007 mcurie mole.

Photolysis of 2,3-diphenylthiophene (13) (496 mg) dissolved in 500 ml of ether was carried out at 20° for 6 hr in the Q-700 reactor. The ether was removed, and the reddish crystalline residue was chromatographed over Al_2O_3 (benzene eluent). After removal of the benzene 350 mg (70% yield) of white crystals were recovered, mp 153–154°, after two recrystallizations from petroleum ether (bp 60–80°). The material displayed intense ultraviolet spectra leading to the suspicion that it was a phenanthrene derivative. The melting point was undepressed with the authentic phenanthro[9,10-*b*]thiophene, synthesized as described. The ultraviolet and infrared spectra of the photoproduct were identical with phenanthro[9,10-*b*]thiophene. The yield calculated from the ultraviolet spectrum (absorption at 253 mμ) was 81%.

Anal. Calcd for $C_{16}H_{10}S$: C, 82.02; H, 4.31; S, 13.67. Found: C, 81.95; H, 4.28; S, 13.68.

Photolysis of 3,4-diphenylthiophene (15) (495 mg) in 500 ml of ether was carried out at 20° for 11.5 hr in the Q-700 reactor. An ultraviolet spectrum of the reaction mixture resembled that of phenanthro[9,10-*b*]thiophene. The ether was removed and the semisolid material chromatographed over Al_2O_3 (benzene eluent) to give 278 mg of brown, crystalline material. With the aid of preparative thin layer chromatography (silica gel, petroleum ether eluent) a series of bands were eluted, the uppermost of which was removed and extracted with benzene. After filtration and removal of the benzene a white solid material was obtained which was chromatographed over Al_2O_3 (benzene eluent) to give 146 mg (29% yield) of white crystals, mp 125–135° after recrystallization from petroleum ether. Sublimation (100°, 6 mm) gave needles, mp 153–154°, mixture melting point undepressed with authentic phenanthro[9,10-*b*]thiophene. Infrared and ultraviolet spectra were identical with those of authentic phenanthro[9,10-*b*]thiophene.

3,4-Diphenylthiophene (1.0 g) in 500 ml of ether was irradiated at 25° for 45 hr in the Q-700 apparatus. After removal of the ether, the residue was chromatographed over Al_2O_3 (benzene eluent). A gas chromatogram (4-ft SE-30, 270°) of the product showed starting material, a product with retention time the same as 2,4-diphenylthiophene or 2,5-diphenylthiophene which had the same retention time under the conditions used, and phenanthro[9,10-*b*]thiophene in approximate ratio of 4:1:12, respectively. A trapping device mounted on the exit port of the gas chromatograph allowed collection of the minor component in an ultraviolet cuvette. The ultraviolet spectrum corresponded to that of 2,4-diphenylthiophene incompletely separated from 3,4-diphenylthiophene. A portion of the reaction mixture was desulfurized with Raney nickel in ethanol. Gas chromatographic analysis of the products on two columns (4-ft DEGS, 175°; 165-ft BDS, 178°) gave peaks of the same retention time as 2,3-diphenylbutane, 1,3-diphenylbutane, and possibly a trace of 1,4-diphenylbutane.

Photolysis of 2,4-diphenylthiophene (16) (1.0 g) in 500 ml ether was carried out at 20° in the Q-700 apparatus for 23 hr. The ether was removed, and the product was chromatographed over Al_2O_3 (benzene eluent) and decolorized with Norit to yield light yellow crystalline material. The infrared and ultraviolet spectra corresponded to those expected from a mixture of 2,4- and 3,4-diphenylthiophene in *ca.* 1:1 ratio. Desulfurization of a portion of the reaction mixture with Raney nickel in boiling ethanol gave, as determined by glpc (4-ft DEGS, 175°; 165-ft BDS, 175°), 1,3- and 2,3-diphenylbutane in approximately equal amounts.

2,4-Diphenylthiophene (4.2×10^{-3} *M*) in ether solution was irradiated at 20° in small quartz tubes mounted around the S-81 lamp (Vycor filter). Samples were analyzed by glpc (4-ft SE-30, 275°) at 1-, 4-, and 8-hr intervals. A new peak corresponding to 3,4-diphenylthiophene appeared after 1 hr and steadily increased in size. After 8 hr a small peak corresponding to phenanthro[9,10-*b*]thiophene was detected. This is apparently a secondary photolysis product arising from photolysis of 3,4-diphenylthiophene.

Photolysis of 2,5-diphenylthiophene (17) was carried out a number of times under similar conditions used for the other isomers. The progress of the reaction was followed both by ultraviolet spectroscopy and glpc (4-ft SE-30, 275°). Slight traces of products corresponding to either 2,3- or 3,4-diphenylthiophene and phenanthro[9,10-*b*]thiophene were detected by these techqniues but even after a 260-hr irradiation no definite products could be identified. Desulfurization of reaction mixtures with Raney nickel in boiling ethanol failed to produce any conclusive evidence of the presence of other isomers.

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