

distilled over magnesium according to the procedure of Fieser,¹² and (4) deuteriobenzene was distilled and dried over molecular sieve.

Benzophenone Hydrazone.—The extraction thimble of a Soxhlet extractor was filled with 20 g of molecular sieve; 9.1 g (0.050 mol) of benzophenone and 8.8 g (0.176 mol) of 99–100% hydrazine hydrate were refluxed overnight (16–24 hr). The hot alcoholic solution was filtered, and evaporation of solvent yielded 7.2 g (73%) of crude product, mp 90–94°. After one recrystallization from ethanol, the product melted at 98–99° (lit.¹³ mp 97–98°).

Photolysis of Benzophenone Hydrazone.—Samples consisting of 0.2 mmol of hydrazone in 10 ml of solvent were irradiated in a Rayonet chamber reactor equipped with a "merry-go-round," at 2537 and 3000 Å. Degassed samples were evacuated to 10⁻⁵–10⁻⁴ mm in four to five freeze-thaw cycles on a high-vacuum line, and helium was pumped through the samples for 5 min after the final cycle. Sample tubes were sealed with a high-vacuum stopcock. Aliquots were periodically withdrawn for vpc analysis through a side arm equipped with serum cap. Analyses were carried out on a Varian Model 1200 flame ionization gas chromatograph using a 5 ft × 1/8 in. column packed with 3% SE-30 on 100/120 Varaport 30. Samples for product identification were collected by column chromatography on Florisil and by preparative vpc on a Varian Model 700 using a 10 ft × 3/8 in. 10% SE-30 on 30–60 Chromosorb W column.

Diphenylmethane and benzophenone were identified by comparison of vpc retention times and ir and nmr spectra with those of commercial samples.

Benzophenone azine was prepared according to the procedure of Szmant and McGinnis, mp 163–164° (lit.¹³ mp 164°). A mixture melting point with a sample of photoproduct collected by column chromatography showed no depression, and the infrared spectra of the samples were identical.

Benzophenone imine was prepared from the Grignard reaction of phenyl bromide and benzonitrile,¹⁴ bp 85–86° (0.2 mm) [lit.¹⁴ bp 127° (3.5 mm)]. Infrared spectra of prepared and col-

lected samples had characteristic bands at 3.1 and 6.4 (NH) and 6.25 μ (C=N).

Benzhydryl methyl ether, prepared according to the method of Welch and Smith,¹⁵ had bp 129–130° (2 mm) [lit.¹⁵ bp 153.2–153.5 (14.5 mm)]. The infrared spectrum was identical with that of the photoproduct ether, showing strong CO absorption at 9.1 μ.

Benzophenone azine with formaldehyde was prepared by a procedure similar to that used for starting material. Refluxing 0.8 g (0.004 mol) of benzophenone hydrazone with 0.25 g (0.008 formula wt) of paraformaldehyde in 20 ml of methanol in a Soxhlet extractor (molecular sieve) for 3 hr resulted in a quantitative yield of benzophenone azine with formaldehyde, bp 97–98° (0.03 mm), ir 3.34 and 3.42 (CH₂), and 5.98 and 6.25 μ (C=N). The nmr resonance peak for the methylene group was not observed and was felt to be part of the phenyl multiplet at δ 7–8, since no other peaks were present in the spectrum.

Quantum Yield Studies.—A 0.006 M solution of potassium ferrioxalate, prepared according to the method of Calvert and Pitts,¹⁶ and a 0.002 M degassed solution of benzophenone hydrazone in methanol were simultaneously irradiated for 2 hr through a 2540 Å band-pass filter using a 450-W Hanovia high-pressure mercury lamp. During this time, <5% of the hydrazone and >95% of the ferrioxalate reacted, and it was therefore impossible to accurately determine the reaction quantum yield by this technique.

Sensitization Studies.—All sensitized reactions were carried out with a 10:1 concentration ratio of sensitizer:hydrazone. Benzene solutions of triphenylene and hydrazone were degassed to <5 × 10⁻⁵ mm and allowed to stand 24 hr prior to irradiation. Photolyses at 3500 Å were run in a Rayonet reactor. Azine-hydrazone mixtures were photolyzed using the Hanovia lamp with a 3130-Å band-pass filter.

Registry No.—Benzophenone hydrazone, 5350-57-2.

Acknowledgment.—The authors wish to thank Dr. Roger Foltz, Battelle Memorial Institute, Columbus, Ohio, for his mass spectral analyses.

(15) C. M. Welch and H. A. Smith, *J. Amer. Chem. Soc.*, **72**, 4748 (1950).

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 785.

(12) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p 289.

(13) H. H. Szmant and C. McGinnis, *J. Amer. Chem. Soc.*, **72**, 2890 (1950).

(14) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

Photochemistry of Thiophenes. IX.¹ Rearrangements of Alkylthiophenes and the Dithienyls

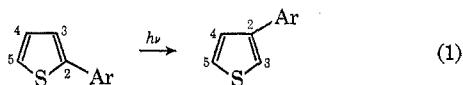
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Irradiation of 2-methyl-, benzyl-, neopentyl-, and *t*-butylthiophenes leads to their irreversible transformation to the corresponding 3-substituted derivatives. Yields vary from 8 to 27%. 2,5-Di-*t*-butylthiophene rearranges irreversibly to 2,4-di-*t*-butylthiophene which compound is remarkably stable under the reaction conditions. Irradiation of 2,2'-dithienyl leads to 2,3'-dithienyl and a small amount of benzo[*b*]thiophene. 2,3'-Dithienyl affords 3,3'-dithienyl and benzo[*b*]thiophene as major products. 5,5'-Dideuterio-2,2'-dithienyl gives 5,5'-dideuterio-2,3'-dithienyl upon irradiation while 2',5'-dideuterio-2,3'-dithienyl gives 2,5'-dideuterio-3,3'-dithienyl and 4,7'-dideuteriobenzo[*b*]thiophene. A valence bond isomerization reaction is proposed to account for the results.

We reported previously that arylthiophenes transpose ring atoms upon irradiation.² For 2-arylthiophenes these valence bond isomerizations are characterized both by an irreversible interchange of the 2- and 3-carbon atoms of the thiophene ring (eq 1) and main-



(1) Paper VIII: R. M. Kellogg and H. Wynberg, *Tetrahedron Lett.*, 5895 (1968).

(2) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **89**, 3501 (1967), for a summary.

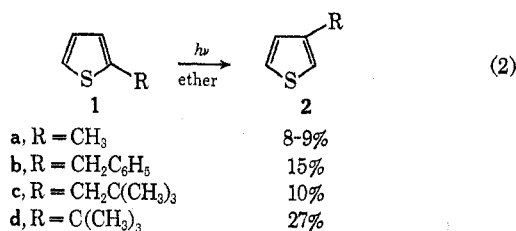
tenence of structural integrity in the migrating substituent.

Experiments with arylalkyl-disubstituted thiophenes indicated that the aryl group migrates in preference to the alkyl group.³ In this paper we show that simple alkylthiophenes may also rearrange, although usually in somewhat lower yield. Moreover, we find that heteroaromatic substituted thiophenes (*i.e.*, dithienyls) undergo photochemical interconversion.

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

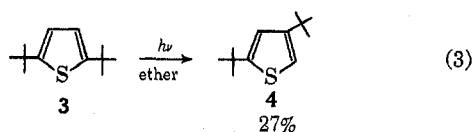
Results

Thiophenes with alkyl substituents in the 2 position rearrange upon irradiation to give the corresponding 3-substituted isomers (eq 2). The yields given are



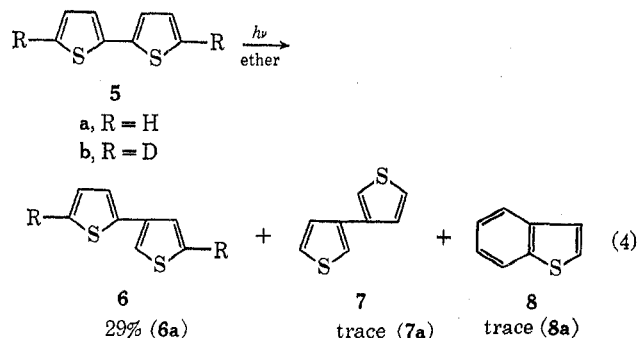
based on consumed starting material; intractable solids account for the balance of products. Irradiation of the 3-substituted isomers 2a-d led to their decomposition; no isomeric products could be detected.

Rearrangement of 2,5-di-*t*-butylthiophene (3) took place to give 2,4-di-*t*-butylthiophene (4) (eq 3). Re-



markably, 4, under a variety of conditions, failed to rearrange and, moreover, seemed to be unusually stable to irradiation (see Experimental Section).

Some significant deviations in behavior were observed with the dithienyls. Irradiation of 2,2'-dithienyl (5a) yielded 2,3'-dithienyl (6a) as the major product with trace amounts of 3,3'-dithienyl (7a) and benzo[*b*]thiophene (8a) (eq 4). Irradiation of 5b, wherein deute-



rium has been substituted for hydrogen at the 5,5'-position,⁴ led to the same products. The rearranged product 6b was identified as 5,5'-dideuterio-2,3'-dithienyl. The spectral properties of all deuterated compounds⁶ are given in detail in the Experimental Section. Owing to the low yield the products 7b and 8b could not be isolated. The recovered starting material 5b had not been observably isomerized.⁷

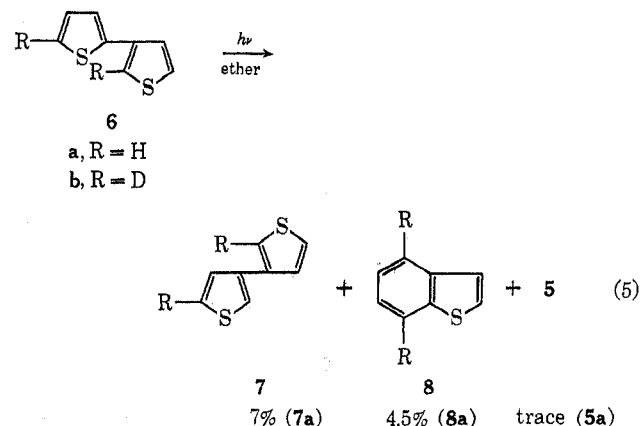
(4) The results with the dithienyls were discussed at the Second IUPAC Symposium on Photochemistry, Enschede, The Netherlands, July 1967; the use of deuterium in elucidation of rearrangement paths in arylthiophenes has been described previously.⁵ The methods used in the syntheses of the deuterated dithienyls have been published separately.⁶

(5) R. M. Kellogg and H. Wynberg, *J. Amer. Chem. Soc.*, **89**, 3495 (1967).

(6) R. M. Kellogg, A. P. Schaap, E. T. Harper, and H. Wynberg, *J. Org. Chem.*, **33**, 2902 (1968).

(7) Observable scrambling of the deuterium label in starting material does occur when 2-pentadeuteriophenyl-5-deuteriothiophene is irradiated.⁵

Irradiation of 2,3'-dithienyl (6a) leads to 3,3'-dithienyl (7a) and benzo[*b*]thiophene (8a) as the major products with a trace amount of 2,2'-dithienyl (5a) (eq



5). Yields are abnormally low owing to the excessive irradiation time used in the preparative experiment. When 2',5'-dideuterio-2,3'-dithienyl (6b) was irradiated, the major products were 2,5'-dideuterio-3,3'-dithienyl (7b) (ca. 90% this isomer) and 4,7-dideuterio-benzo[*b*]thiophene (8b) (ca. 80% this isomer) plus a trace quantity of 2,2'-dithienyl. The nmr spectrum of 8a was solved using the published complete analysis of the benzo[*b*]thiophene spectrum as a guide.⁸

Neither 3,3'-dithienyl (7a) nor any of its deuterated isomers gave any photochemical reaction other than decomposition. Considerable care must be exercised in handling deuterated isomers of 7a as well as other deuterated dithienyls since they have a propensity to lose deuterium under extremely mild acid-catalyzed conditions leading to erroneous interpretations of nmr spectra.⁹ This problem is especially pronounced with 2,2'-dideuterio-3,3'-dithienyl.

Some brief investigations of the effects of solvents on the photochemical reactions of the dithienyls were made. Low yields precluded determination of the quantum yields of products but the quantum yield for disappearance of starting material in various solvents could be measured. Qualitatively, the rate of consumption of 2,2'- and 2,3'-dithienyl increased in the following order: ethanol < ether < cyclohexane (see Table I below).

TABLE I
QUANTUM YIELDS FOR DISAPPEARANCE OF
DITHIENYLS IN VARIOUS SOLVENTS

Dithienyl	Solvent	Φ_d
2,2'	Ether	0.07
2,2'	Ethanol	≤ 0.01
2,2'	Cyclohexane	0.10
2,3'	Ether	0.07
2,3'	Ethanol	0.05
2,3'	Cyclohexane	0.09
3,3'	Ether	0.12
3,3'	Cyclohexane	0.16

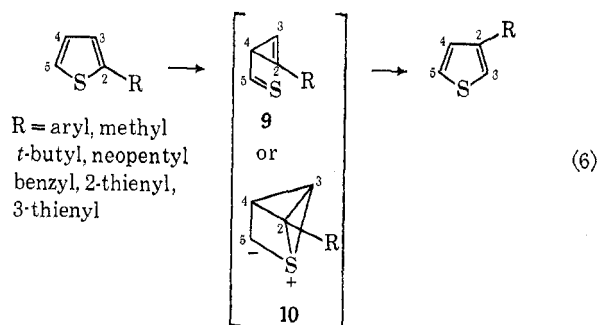
(8) K. Takahashi, I. Ito, and Y. Matsuki, *Bull. Chem. Soc. Jap.*, **39**, 2316 (1966).

(9) R. M. Kellogg, A. P. Schaap, and H. Wynberg, *J. Org. Chem.*, **34**, 343 (1969).

In ethanol solution, 2,2'-dithienyl was so stable that its rate of disappearance could scarcely be observed even using long irradiation periods.

Discussion

In an earlier publication² we suggested that the irreversible rearrangement of 2-aryl to 3-arylthiophenes involved at some stage either cyclopropenylthioaldehyde (9) or sulfur valence-shell expanded bridged structures (10) (eq 6).¹⁰ Our sentiments lay with 10 which



we felt was an excited- rather than a ground-state intermediate. We later observed that various dienes caused inhibition of the 2-phenyl to 3-phenylthiophene rearrangement, led to quenching of 2-phenylthiophene fluorescence, and added photochemically to 2-phenylthiophene.¹ All these reactions were shown to involve an excited singlet state of 2-phenylthiophene.

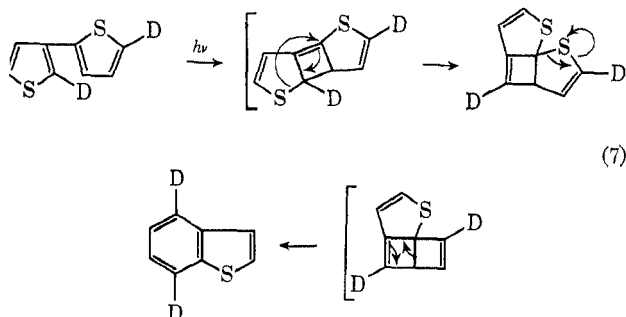
The rearrangements described in this paper complement previously accumulated data on arylthiophenes and illustrate the ubiquity of these thiophene rearrangements.¹¹ The irreversibility of rearrangement, retention of structural integrity of the migrating substituent, and failure to isolate intermediates are trademarks of thiophene photorearrangements. Unfortunately, the present results allow no choice between intermediates 9 and 10. This choice may be academic, however, since 9 and 10 could easily be two equivalent graphic representations of the same excited-state intermediate.

(10) A number of reports of photochemically induced valence bond isomerizations have appeared recently. The following list is representative—(a) pyrazine to pyrimidine: F. Lahmani and N. Ivanoff, *Tetrahedron Lett.*, 3913 (1967); (b) isothiazole to thiazole: J. P. Catteau, A. LaBlanche-Combiere, and A. Pollet, *Chem. Commun.*, 1018 (1969); (c) imidazoles: H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmidt, *Helv. Chim. Acta*, **50**, 2244 (1967); (d) imidazoles and pyrazoles: P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Lett.*, 5315 (1967); (e) 1,3,5-tri-*t*-butylbenzene in solution: I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 5868 (1968); (f) 1,3,5-benzene-*d*₃ in gas phase: K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968); (g) references, through early 1967 are given in ref. 2. Stable ring-opened intermediates have been obtained in some cases; (h) poly-*t*-butylfurans in solution: E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968); (i) azirine intermediates from 3,5-diphenylisoxazole: B. Singh and E. F. Ullman, *ibid.*, **89**, 6911 (1967), and E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966); (j) for further isoxazole reactions see M. Kojima and M. Maeda, *Tetrahedron Lett.*, 2379, 1969; (k) ring-opening has been postulated in gas phase irradiations of furans: R. Srinivasan, *J. Amer. Chem. Soc.*, **89**, 1758 (1967); (l) R. Srinivasan, *ibid.*, **89**, 4812 (1967); (m) H. Hiraoka and R. Srinivasan, *ibid.*, **90**, 2720 (1968); (n) ring-opening is also observed in dihydrofurans: P. Scribe, M. R. Monot, and J. Wieman, *Tetrahedron Lett.*, 5157 (1967); (o) D. W. Boykin, Jr., and R. E. Lutz, *J. Amer. Chem. Soc.*, **86**, 5046 (1964).

(11) To be on completely safe ground, one would have to identify the position of every carbon atom after rearrangement in each example and to establish that the migrating substituent never departs from the carbon atom to which it is bound in the starting material. The point of diminishing returns is quickly reached in such research, however, and we are inclined to accept results established with arylthiophenes as articles of faith for the present examples.

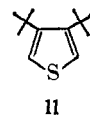
Noteworthy is the observation that thiophene, when irradiated (unsensitized) in the gas phase, yields ethylene, allene, methylacetylene, carbon disulfide, vinylacetylene, and polymeric material. Cyclopropene, a likely product from thiodecarbonylation of cyclopropenylthioaldehyde, is conspicuously absent.¹² On the other hand, cyclopropene is one of the major products formed during (sensitized) gas phase irradiation of furan.^{10k}

Two departures from the expected rearrangement pattern deserve comment.¹³ First, the rearrangement of 2,5'-dideuterio-2,3'-dithienyl (6b) to chiefly 4,7-dideuteriobenzo[*b*]thiophene (8b) (in addition to the 3,3'-dithienyl 7b) must involve an involved recombination of atoms. A possible mechanism, not involving hydrogen (deuterium) shifts, is shown in eq 7. A different route



must be followed in the formation of benzo[*b*]thiophene from 2,2'-dithienyl, but the small amount formed and absence of labeling data prevent speculation regarding its origin. This product does appear, however, simultaneously with 2,3'-dithienyl indicating it *not* to be a secondary irradiation product of the latter compound.

A second anomaly is the absence of rearrangement of 2,4-di-*t*-butylthiophene. Were rearrangement to take place, the thus far unknown 3,4-di-*t*-butylthiophene (11)



would be formed. It is tempting to suppose that a sufficiently high barrier is met in passing to this necessarily highly strained system¹⁴ that the intermediate simply drops back to starting material and does so with efficiency. The rearrangements to the respective 3,4-disubstituted thiophenes proceed with 2,4-diphenylthiophene¹⁵ and 4-methyl-2-phenylthiophene,³ here, however, much smaller groups are involved.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 instrument in the specified solvent using tetramethylsilane (TMS) as internal standard. Ir spectra were run on a Perkin-Elmer 257 instrument. Analytical gas-liquid chromatography (glpc) was carried out on a F & M Model 810 gas

(12) H. A. Weibe and J. Hecklen, *Can. J. Chem.*, **47**, 2965 (1969).

(13) An interesting deviation has been reported. Irradiation of either 2- or 3-methylthiophene in primary amines gives pyrroles in unreported yield. The mechanism is unclear: A. Couture and A. LaBlanche-Combiere, *Chem. Commun.*, 524, 1969.

(14) For a leading reference on the structure and strain of *o*-di-*t*-butyl heteroaromatics, see G. J. Visser, A. Vos, Ae. de Groot, and H. Wynberg, *J. Amer. Chem. Soc.*, **90**, 3253 (1968).

(15) H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *ibid.*, **89**, 3487 (1967).

chromatograph equipped with hydrogen flame detectors. Preparative separations were done on a Wilkens A-700 Autoprep or on a F & M 775 Prepmaster.

Irradiations were carried out with lamps previously described. Compounds cited without reference were prepared by standard, published procedures. In particular, the syntheses of the deuterated dithienyls used in this study have been described earlier.⁹

2-Benzylthiophene^{16a} was prepared by Wolff-Kishner reduction of 2-benzoylthiophene.^{16b,17,18}

3-Benzylthiophene was prepared by the di-*t*-butyl peroxide induced addition of toluene to maleic anhydride to give α -benzylsuccinic anhydride which was treated with P₄S₇ to give 3-benzylthiophene: bp 152° (44 mm), n_{20}^D 1.5929 [lit.^{20,21} bp 135–137° (17 mm); n_{20}^D 1.5928]; and nmr (C₆D₆O) δ 3.88 (s, 2, CH₂) and 7.0–7.5 (m, 8, aromatic).

2-Neopentylthiophene was prepared by allowing thiophene (6.4 g, 0.08 mol) in benzene (80 ml) to react with pivaloyl chloride (10 g, 0.08 mol) in the presence of SnCl₄ (20.8 g, 0.08 mol).²² After several hours of standing the reaction mixture was poured into H₂O; the benzene layer was separated and was washed with H₂O and thereafter was dried over MgSO₄. Removal of the benzene and distillation gave 8.75 g (62%) of *t*-butyl-2-thienyl ketone, bp 115° (13 mm), n_{20}^D 1.5303. A single *t*-butyl peak at δ 1.37 in the nmr spectrum established that only the 2-isomer had been formed. Wolff-Kishner reduction of the ketone gave 2-neopentylthiophene: bp 185–186 (atm); n_{20}^D 1.4945; nmr (C₆D₆O) δ 0.94 [s, 9, (CH₃)₃C], 2.72 (s, 2, CH₂), 7.0–7.5 (m, 3, thienyl protons); uv (96% ethanol) λ_{max} 236 (ϵ 8050).

Anal. Calcd for C₉H₁₀S: C, 70.07; H, 9.14; S, 20.78. Found: C, 70.14; H, 9.15; S, 20.54.

2-*t*-Butylthiophene, **3-*t*-butylthiophene**, and **2,5-di-*t*-butylthiophene** were obtained by either distillation with a spinning-band column or by preparative glpc on mixtures obtained from the *t*-butylation of thiophene.²⁴

2,4-Di-*t*-butylthiophene was obtained by allowing a 20-g mixture of 2,5- and 2,4-di-*t*-butylthiophene²⁴ to stand for 16 hr (with occasional shaking) in 75–100 ml 96% H₂SO₄. Work-up and distillation gave 2,4-di-*t*-butylthiophene: bp 221–223° (atm); n_{20}^D 1.4903 [lit.²⁴ bp 220° (atm); n_{20}^D 1.4916]; nmr (C₆D₆O) δ 1.37 [s, 9, (CH₃)₃C], 1.27 [s, 9, (CH₃)₃C], 6.68 (d, 1, *J* = 1.5 Hz, ring proton), 6.61 (d, 1, *J* = 1.5 Hz, ring proton).

Irradiation of 2-methylthiophene was carried out with a total of 7.2 g (0.073 mol) as a 10⁻² M solution in ether using a Rayonet reactor equipped with 2540 Å lamps. After 9 hr 25% of the starting material was consumed and the remaining material consisted of 3% 3-methylthiophene and 97% 2-methylthiophene. Preparative glpc (Carbowax 20M, 8 ft, 103°) allowed the isolation of 3-methylthiophene which was identified from its nmr spectrum.

Irradiation of 2-benzylthiophene was carried out with 2.66 g (0.0153 mol) as a 5.8 × 10⁻³ M solution in ether using a high pressure Hg lamp. After 8 hr 50% of the starting material had been consumed and the remaining material consisted of 30% 3-benzylthiophene and 70% 2-benzylthiophene. Preparative glpc (Carbowax 20M, 8 ft, 176°) was only partially successful resulting in enrichment of the 3-benzylthiophene fraction. The nmr and ir spectra of this mixture were identical with those of an authentic mixture of 2-benzyl- and 3-benzylthiophene of the same composition.

(16) (a) P. Truitt, E. H. Holst, and G. Sammons, *J. Org. Chem.*, **22**, 1107 (1957). (b) W. Minnis, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, 520.

(17) The procedure described by Steinkopf¹⁸ for the preparation of 2-benzylthiophene involving the zinc chloride catalyzed addition of benzylalcohol to thiophene gives a 2:1 mixture of 2-benzyl and 3-benzylthiophenes as shown by glpc (Carbowax 20M, 6 ft, 175°). This problem seems not to have been appreciated by several more recent workers.^{19a-c}

(18) W. Steinkopf and W. Hanske, *Justus Liebigs Ann. Chem.*, **541**, 238 (1939).

(19) (a) G. H. Jeffery, R. Parker, and A. I. Vogel, *J. Chem. Soc.*, 570 (1961); (b) J. J. G. Cadogan, D. H. Hey, and W. A. Sanderson, *ibid.*, 3205 (1960). (c) K. Takahashi, T. Sone, Y. Matsuki, and G. Hazato, *Bull. Chem. Soc. Jap.*, **36**, 108 (1963).

(20) H. Scheeter and H. C. Barker, *J. Org. Chem.*, **21**, 1473 (1956).

(21) E. C. Kooyman and J. B. H. Kroon, *Recl. Trav. Chim. Pays-Bas*, **82**, 464 (1963).

(22) An alternative synthesis of *t*-butyl-2-thienyl ketone involving the exhaustive methylation of 2-acetylthiophene with methyl iodide in the presence of KOH gave poorer yields and required more strenuous conditions than those reported for an analogous reaction on acetophenone.²³

(23) J. U. Nef, *Justus Liebigs Ann. Chem.*, **310**, 316 (1900).

(24) H. Wynberg and U. E. Wiersum, *J. Org. Chem.*, **30**, 1058 (1965).

Irradiation of 2-neopentylthiophene was carried out with a total of 1.80 g (0.0117 mol) as a 6.5 × 10⁻³ M solution in ether using a Rayonet reactor equipped with 2540 Å lamps. After 6 hr 75% of the starting material had disappeared. The remainder consisted of 32% 3-neopentylthiophene and 68% 2-neopentylthiophene. The 3-neopentylthiophene was collected by preparative glpc (Carbowax 20M, 7 ft, 90°): nmr (C₆D₆O) δ 0.90 (s, 9, (CH₃)₃C), 2.53 [s, (broad), 2, CH₂] and 7.1–7.5 (m, 3, ring protons); uv (96% C₂H₅OH) λ_{max} 235 m μ (extinction not measured because of lack of material). The mass spectrum of the isolated photoproduct showed the same cracking pattern as that of 2-neopentylthiophene but with some variations in relative abundances. These data identify the photoproduct as 3-neopentylthiophene.

A dark tar formed during irradiation that, after removal of the solvent, became solid after standing for several days. This material was soluble in ether and acetone and had mp 70–80°. It resisted further characterization.

Irradiation of 2-*t*-butylthiophene was carried out with a total of 3.10 g (0.0221 mol) as a 10⁻² M solution in ether using a Rayonet reactor equipped with 2540 Å lamps. After 7 hr 45% of the starting material had disappeared and the remainder consisted of 23% 3-*t*-butylthiophene and 77% 2-*t*-butylthiophene. The 3-*t*-butylthiophene was isolated by preparative glpc (Carbowax 20M, 8 ft, 132°) and was identified from its nmr spectrum in CCl₄.

Irradiation of 2,5-di-*t*-butylthiophene was carried out with 1.14 g (0.0058 mol) in 10⁻² M ether solution using a Rayonet reactor equipped with 2540 Å lamps. The optimum irradiation time was 18 hr after which time 66% of the starting material had disappeared and the remainder consisted of 53% 2,4-di-*t*-butylthiophene and 47% 2,5-di-*t*-butylthiophene. The 2,4-di-*t*-butylthiophene was isolated by preparative glpc (Carbowax 20M, 8 ft, 140°) and was identified from its nmr spectrum in CCl₄.

Irradiation of 2,4-di-*t*-butylthiophene was done in a variety of solvents and with several different lamps. Usually after about 12 hr the solutions became slightly yellow and after 24 hr usually ca. 50% of the starting material had been destroyed. In no case were any detectable amounts of new products seen. Irradiations at 0° and 50° failed to give significantly different results.

Irradiation of 3-methyl, benzyl, neopentyl, and *t*-butylthiophenes led only to their destruction. No new products could be observed by glpc during the course of the irradiations.

Irradiation of 2,2'-dithienyl was carried out with 0.60 g (0.0036 mol) in 500 ml of ether using a Hanau Q-700 lamp. The reaction mixture was irradiated 6 hr and the lamp was cleaned of deposit after 3 hr. Glpc analysis (DEGS, 6 ft, 190°) indicated the mixture to consist of 2,2'-dithienyl (260 mg), 2,3'-dithienyl (100 mg), 3,3'-dithienyl (ca. 10–15 mg), and benzo[*b*]thiophene (ca. 5 mg). One minor compound of short retention time was not identified. The above products were isolated by preparative glpc (Carbowax 20M, 7 ft, 180°) and were identified from their uv and ir spectra.

Irradiation of 2,3'-dithienyl was carried out with 1.0 g (0.0060 mol) in 500 ml of benzene using a Hanau Q-700 lamp. Irradiation was carried out for 90 hr with cleaning every 24 hr (reactions proceeded slower in benzene owing to competitive light absorption). Glpc (DEGS, 6 ft, 190°) showed the reaction mixture to consist of 2,3'-dithienyl (100 mg), 3,3'-dithienyl (65 mg), benzo[*b*]thiophene (ca. 40 mg), and 2,2'-dithienyl (trace). The above compounds were isolated by preparative glpc (Carbowax 20M, 7 ft, 180°) and were identified from their uv and ir spectra.

Irradiation of 3,3'-dithienyl was carried out in various solvents with different lamps and at different concentrations but in no case could any isomeric compounds be detected. The only observable reaction was slow decomposition of the 3,3'-dithienyl.

Effect of conditions on the irradiation of 2,3'- and 3,3'-dithienyl was investigated. In general, irradiations in benzene solution using a low pressure Hg lamp went slower than in ether solution but the same products were formed. Irradiation of either 2,2'- or 2,3'-dithienyl at 3500 Å in benzene solution led to neither isomerization nor disappearance of starting material. Addition of benzophenone to these solutions under the same irradiation conditions led to very slow destruction of the dithienyls but no isomerization was observed; the benzophenone was unaffected. Both 2,2'- and 2,3'-dithienyls were unchanged when irradiated in acetone using a Pyrex filter. During some irradiations in ether solution using an S-81 lamp, considerable amounts of finely divided glass wool were added to increase the surface area; this seemed to neither help nor hinder isomerization.

Irradiation of 5,5'-dideuterio-2,2'-dithienyl was carried out with 3.93 g (0.0234 mol) in 3.6 l. of ether using a Hanau Q-700 lamp. The irradiation was carried out for 4-5 hr with 600 ml batches and the lamp was cleaned of deposit after 2 hr. The combined irradiation solutions consisting of ca. 27% 2,3'-isomer and 73% 2,2'-isomer plus traces of 3,3'-isomer and benzo[b]thiophene were filtered of solid deposit, were evaporated to dryness, and the solid residue was chromatographed over a short Al₂O₃ column using benzene as eluent. Preparative glpc (Carbowax 20M, 6 ft, 155°) was carried out allowing the isolation of 2,2'-dithienyl, 2,3'-dithienyl, and traces of benzo[b]thiophene and 3,3'-dithienyl (not enough for nmr spectra). The recovered 2,2'-isomer had nmr spectra in CCl₄ and C₃D₈O essentially identical with those of 5,5'-dideuterio-2,2'-dithienyl.⁹ Within an accuracy limit of 5% neither deuterium scrambling nor deuterium loss took place. The recovered 2,3'-isomer (after subtracting peaks for 14% contamination of 2,2'-isomer) had nmr (C₃D₈O) δ 7.37 [d (deuterium broadened), 1, $J = 1.2$ Hz, 4'-H], 7.55 (d, 1, $J = 1.2$ Hz, 2'-H), 7.03 [d (deuterium broadened), 1, $J = 3.6$ Hz, 4-H], and 7.20 (d, 1, $J = 3.6$ Hz, 3-H); (CCl₄) 7.20 [m (poorly resolved), 2, 2',4'-H], 6.89 [d (deuterium broadened), $J = 3.8$ Hz, 4 H], and 7.07 (d, 1, $J = 3.8$ Hz, 3 H). These data are consistent with the spectra expected for 5,5'-dideuterio-2,3'-dithienyl. Within the accuracy limits, integration ratios indicated no loss of deuterium.

Irradiation of 2,5'-dideuterio-2,3'-dithienyl was carried out with the same amounts and under the same conditions described for 5,5'-dideuterio-2,2'-dithienyl. The crude irradiation product, as determined by glpc (DEGS, 6 ft, 160°), consisted of 7% benzo[b]thiophene, 2% 2,2'-dithienyl, 79% 2,3'-dithienyl, and 12% 3,3'-dithienyl. Preparative glpc (Carbowax, 6 ft, 175°) allowed separation into the individual components. The recovered 2,3'-isomer was greater than 99% pure as estimated by glpc. Its nmr spectrum in both C₃D₈O and CCl₄ closely resembled those of the starting material. Some minor differences were noted, particularly in the region where absorption for the 3-substituted ring would be expected; no interpretation was possible, however. The recovered 3,3'-isomer was 7% contaminated with the 2,3'-isomer and had (after subtracting impurity absorptions) nmr (CCl₄) δ 7.22 (s, all protons); (C₃D₈O) 7.59 (d, 1.00, $J = 1.4$ Hz, 2-proton) and 7.43 [s (broad), 3.25, 3,4',5'-protons]. Very weak absorptions were seen around the δ 7.59 doublet. These spectra are consistent with those expected for ca. 90% 2,5'-dideuterio-3,3'-dithienyl with ca. 10% unknown isomers.⁹

The recovered amount of 2,2'-isomer was not pure and consisted of ca. 60% 2,2'-isomer, 33% 2,3'-isomer, and 7% benzo-

[b]thiophene. After subtracting impurity peaks two sets of doublets, $J = 3.6$ Hz and $J = 5.1$ Hz, could (with imagination) be distinguished. This dubious assignment would indicate the presence of 3,5'-dideuterio-2,2'-dithienyl.

The isolated benzo[b]thiophene was >99% pure as estimated by glpc. The nmr (CCl₄) consisted of a series of peaks located between δ 7.48 and 7.12 from which two sets of doublets at δ 7.22 ($J = 5.4$ Hz) and 7.35 ($J = 5.4$ Hz) [reported⁸ for 3 and 2 protons, $J = 5.5$ Hz at δ 7.22 and 7.35 respectively] could be resolved as well as a broad singlet at ca. δ 7.22 [reported⁸ for 5 proton, 7.26 and 6-proton; 7.24]. In addition, a weak set of peaks ranging from δ 7.73 to 8.03 were present; assuming a total of 4 protons in the molecule these peaks accounted for less than one proton. This spectrum is consistent with that expected for 4,7-dideuteriobenzo[b]thiophene in which the 5,6-protons have collapsed to a singlet. Integration ratios indicate about ca. 80% this isomer plus ca. 20% unidentified isomer(s).

Irradiation of 2,2'-dideuterio-3,3'-dithienyl and 2,2',5,5'-tetradideuterio-3,3'-dithienyl in 6.10⁻² M ether solution led to considerable decomposition. The recovered compounds showed minor differences in their nmr spectra that were not readily interpretable.

Solvent effects on dithienyl irradiations were determined using a Rayonet reactor equipped with 2537 Å lamps. A quartz vessel with a screw type stirrer was used. Light intensities were determined by using *o*-nitrobenzaldehyde in alcohol solution as an actinometer;²⁵ a quantum yield of 0.5 was taken for the isomerization to *o*-nitrobenzaldehyde acid. The average light intensity absorbed by the contents of the flask was 1.7 \pm 0.1.10²¹ quanta/hr. The quantum yields for disappearance of 2,2'- and 2,3'-dithienyl in various solvents are summarized in Table I.

Registry No.—2-Methylthiophene, 554-14-3; 2-benzylthiophene, 13132-15-5; 2-neopentylthiophene, 4891-29-6; 2-*t*-butylthiophene, 1689-78-7; 2,5-di-*t*-butylthiophene, 1689-77-6; 2,2'-dithienyl, 492-97-7; 2,3'-dithienyl, 2404-89-9; 5,5'-dideuterio-2,2'-dithienyl, 18592-88-6; 2',5'-dideuterio-2,3'-dithienyl, 18592-89-7.

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