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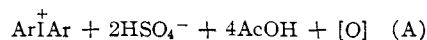
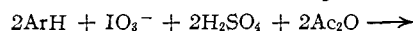
Diaryliodonium Salts. VII. 2,2'-Dithienyl- and Phenyl-2-thienyliodonium Salts¹

BY F. MARSHALL BERINGER, H. ELIZABETH BACHOFNER, ROBERT A. FALK AND MILTON LEFF

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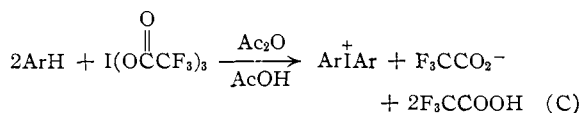
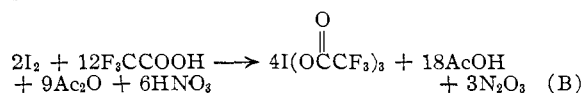
2,2'-Dithienyl- and phenyl-2-thienyliodonium salts have been prepared, and their structures have been proved. The replacement of phenyl groups in the diphenyliodonium cation by 2-thienyl groups increases the ease of electroreduction and the susceptibility to nucleophilic attack.

Synthesis.—Previous papers have reported the synthesis² of diphenyliodonium salts, their reactions³⁻⁵ and their electro-reduction.⁶ In the present work it has been shown that thiophene⁷ can be converted to 2,2'-dithienyliodonium salts in two ways. The first was treatment with an iodate in acetic acid-acetic anhydride-sulfuric acid.^{2,3}



The yield here was 28%, to be compared with a yield of 63% for diphenyliodonium chloride in a similar reaction.⁵

The second method, which is new, is the reaction of thiophene⁷ with iodine(III) trifluoroacetate,⁸ prepared by the general method of Fichter and Stern.

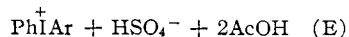
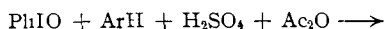


One convenience of this sequence is that at the end of the reaction solvent may be removed, leaving the iodonium trifluoroacetate, soluble in organic solvents and easily convertible to other, less soluble salts. The iodide was obtained in 67% yield.

That the thiophene rings were indeed attached through the 2-positions was shown by the decomposition of the dithienyliodonium iodide to the known 2-iodothiophene, characterized by infrared spectrum and conversion to 2-thienoic acid.



The phenyl-2-thienyliodonium salts were first prepared by the condensation of iodosobenzene with thiophene⁷ in acetic acid-acetic anhydride-sulfuric acid.



(1) This paper is taken from the doctoral dissertations of Miss Hilde Elizabeth Bachofner and Robert A. Falk and from the master's thesis of Milton Leff.

(2) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, *THIS JOURNAL*, **75**, 2705 (1953).

(3) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953).

(4) F. M. Beringer and E. M. Gindler, *ibid.*, **77**, 3203 (1955).

(5) F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **69**, 141 (1956).

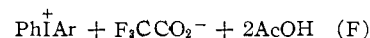
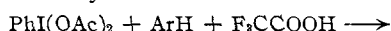
(6) H. E. Bachofner, F. M. Beringer and L. Meites, *THIS JOURNAL*, **80**, 4269, 4274 (1958).

(7) In this paper Ar represents the 2-thienyl group and Ph the phenyl group.

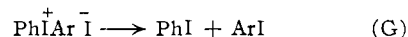
(8) F. Fichter and S. Stern, *Helv. Chim. Acta*, **11**, 1256 (1928).

This procedure gave the chloride and bromide salts in a combined yield of 49%.

More recently the condensation of iodosobenzene diacetate with thiophene⁴ in acetic acid-acetic anhydride-trifluoroacetic acid gave phenyl-2-thienyliodonium trifluoroacetate in 92% yield.



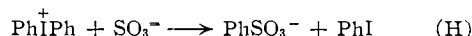
Pyrolysis of the corresponding iodide gave a 1:1 mixture of iodobenzene and 2-iodothiophene, shown by the identity of the infrared spectrum of



this mixture with a synthetic mixture of authentic materials.

Thus in accord with other substitution reactions of thiophene, electrophilic attack occurred on the 2-position of thiophene in the cases here reported and more readily than on benzene.²

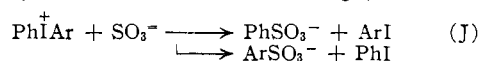
Nucleophilic Displacement.—The reaction of the diphenyliodonium cation with sulfite ion to give the benzenesulfonate ion already has been re-



ported.³ Now by a direct competitive reaction of diphenyliodonium and dithienyliodonium ions with an insufficiency of sulfite ion it has been shown (by

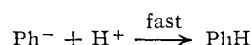
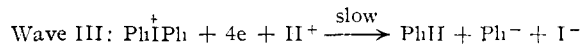
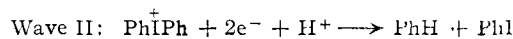
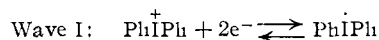


analysis of the iodobenzene-iodothiophene mixture) that the dithienyliodonium ion is more reactive by a ratio of 2:1. Also, when the unsymmetrical phenyliodonium cation was cleaved by sulfite ion in water,⁹ the ratio of attack on the thiophene ring to that on the benzene ring (determined



as the ratio PhI/ArI) was 2:1. The free energy of activation is thus slightly lower for the former reaction (about 700 cal. mole⁻¹ deg.⁻¹).

Polarographic Reduction.—It has been previously reported⁶ that the three waves in the polarographic reduction of the diphenyliodonium cation correspond to the steps



(9) Cleavage of unsymmetrically substituted diphenyliodonium salts are reported in ref. 3 and by R. B. Sandin, M. Kulka and R. McCready, *THIS JOURNAL*, **59**, 2014 (1937).

It was naturally of interest to determine the effect on the half-wave potentials of changing the aryl groups of the iodonium cation from phenyl to thienyl. Thiophene itself is not reduced polarographically. Published reports on the polarography of substituted thiophenes¹⁰ treat the thienyl group as a non-reducible substituent in a compound containing other reducible groups and mention only its influence on the half-wave potential of the reducible group.

Values for the half-wave potentials of the diphenyliodonium, phenyl-2-thienyliodonium and 2,2'-dithienyliodonium cations, for 2-iodothiophene and for 2-thienylmercuric chloride are given in Table I.

TABLE I
HALF-WAVE POTENTIALS OF THE PHENYL-2-THIENYL- AND 2,2'-DIETHIENYLIODONIUM CATIONS AND RELATED COMPOUNDS*

Substance	Half-wave potentials, v.		
	Wave I	Wave II	Wave III
Diphenyliodonium cation	-0.193	-1.142	-1.645
Phenyl-2-thienyliodonium cation	-0.138	-0.92	-1.14 -1.65
2,2'-Dithienyliodonium cation	-0.11	-0.86	-1.13
2-Iodothiophene			-1.14
2-Thienylmercuric chloride	-0.07	-0.81	

* In 1:1 ethanol-water with 0.4 *mM* iodonium salt and 0.1 *M* tetraethylammonium phosphate supporting electrolyte of apparent *pH* 8.6.

Wave III for the dithienyliodonium cation is identical to that for 2-iodothiophene, while wave III for the phenyl-2-thienyliodonium cation is divided into waves for iodobenzene and 2-iodothiophene in the ratio 55:45. This indicates almost random rupture of the iodonium ion.

Based on half-wave potentials for 2-thienylmercuric chloride, it is probable that the reduction of the iodonium cation does not go by way of the mercury derivatives.¹¹

Still unexplained is the observation that the half-wave potentials for both waves I and II decrease in the order: $\text{Ph}_2\text{I}^+ > \text{PhI}^+\text{Ar} > \text{Ar}_2\text{I}^+$. One would be tempted to attribute the effect to resonance interaction between the iodine and the aromatic ring (in the starting material, the product or both) were it not for the fact that waves I and II are not significantly affected by the introduction of electron-attracting or withdrawing groups in the diphenyliodonium cation.⁶ A remaining possibility is that the phenyl and 2-thienyl groups have different electronegativities, affecting the strength of the carbon-iodine bond and its charge distribution.

Acknowledgments.—It is a pleasure to acknowledge the early work by Emil J. Geering on

(10) R. A. Day, Jr., and W. A. Blanchard, Jr., *THIS JOURNAL*, **76**, 1166 (1951); P. J. Elving and C. M. Callahan, *ibid.*, **77**, 2077 (1955); F. Cappellina and A. Drusiani, *Gazz. chim. ital.*, **84**, 939 (1955), and *C. A.*, **49**, 10764 (1955); E. Imoto, R. Motoyama and H. Kakiuchi, *Bull. Mie Univ.*, **A3**, 203 (1955), and *C. A.*, **49**, 15537 (1955).

(11) Arguments against organomercury intermediates in the polarographic reduction of the diphenyliodonium cation are given in ref. 6. They had been proposed previously by E. L. Colichman and H. F. Maffei, *THIS JOURNAL*, **74**, 2744 (1952), and S. Wawzonek, *Anal. Chem.*, **26**, 65 (1954).

iodonium salts from thiophene,¹² and the helpful suggestion of Dr. Louis Meites on polarography.

Experimental

Analyses and Measurements.—Analytical procedures and the determination of melting points were those described in reference 2. The polarograms were run as described in reference 6.

Starting Materials.—Commercial grades of thiophene and iodobenzene were distilled before use. Iodobenzene¹³ and iodobenzene diacetate¹⁴ were prepared by standard procedures. Iodine(III) trifluoroacetate was prepared by an adaptation of the method of Fichter and Stern³ as follows. To 7 ml. of acetic anhydride at -20° there was added dropwise and with stirring 2.7 ml. of fuming nitric acid (density 1.51), 2.5 g. (10 mmoles) of iodine and 4.7 ml. (61 mmoles) of trifluoroacetic acid. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After about 30 minutes, during which nitrogen oxides were evolved, the iodine had dissolved completely. Solvent was removed by evaporation at 1–2 mm., the pot temperature never exceeding 50° . The residue of iodine(III) trifluoroacetate (20 mmoles) was used directly in syntheses.

2,2'-Dithienyliodonium Salts. Reaction A.—To a well-stirred mixture of 130 ml. of acetic acid, 40 ml. of acetic anhydride, 20 g. (93.5 mmoles) of potassium iodate and 58 g. (345 mmoles) of thiophene kept below 10° there was added over one hour a chilled mixture of 30 ml. of acetic acid and 24 ml. of sulfuric acid. After having been stirred at room temperature overnight, the reaction mixture was diluted with 200 ml. of water, extracted with benzene and then with ether until color was no longer removed and treated with activated carbon. Addition of 15 g. of potassium iodide in water gave a colorless precipitate, which was collected, washed with water and dried to yield 10.85 g. (25.8 mmoles, 28%) of 2,2'-dithienyliodonium iodide, m.p. 128–129°; see also under reaction C. From similar reaction mixtures there were also obtained 2,2'-dithienyliodonium bromide, m.p. 215–219°, and 2,2'-dithienyliodonium chloride, m.p. 229–230°. The solubilities of these salts are quite similar to those of the corresponding diphenyliodonium halides.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{BrIS}_2$: Br⁻, 21.42. Found: Br⁻, 21.15. Calcd. for $\text{C}_8\text{H}_6\text{ClIS}_2$: Cl⁻, 10.79. Found: Cl⁻, 10.84.

Reaction C.—The crude iodine(III) trifluoroacetate, prepared as described above, was treated at 20° with 15 ml. of acetic anhydride and at -10° with a solution of 6.3 ml. of thiophene (80 mmoles), 35 ml. of acetic anhydride and 5 ml. of trifluoroacetic acid. The reaction mixture was kept at 0° for 12 hours and at room temperature for two days. Removal of solvent at reduced pressure left a residue, from which 4 g. of brown-black crystals was obtained by stirring with 200 ml. of anhydrous ether and cooling to 0° . The solid was crystallized from 200 ml. of benzene (activated carbon) to give 3.2 g. (7.9 mmoles, 40%) of tan 2,2'-dithienyliodonium trifluoroacetate. Repeated crystallizations gave colorless crystals of m.p. 146–148° dec.

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{O}_2\text{F}_3\text{IS}_2$: C, 29.57; H, 1.14. Found: C, 29.41; H, 1.66.

Treatment of an aqueous solution of this salt with aqueous potassium iodide gave 2,2'-dithienyliodonium iodide, m.p. 135–136° dec. If instead of isolating the product first as the trifluoroacetate, the residue after solvent removal was dissolved in water and the solution was treated with activated carbon and then with aqueous potassium iodide, a 67% yield of 2,2'-dithienyliodonium iodide was obtained directly.

Proof of Structure.—A small sample of 2,2'-dithienyliodonium iodide was decomposed to 2-iodothiophene by heating briefly to 120° . The product was converted to the Grignard reagent and carbonated¹⁵ to give 2-thiobenzoic acid, m.p. 127–129.5° after recrystallization from water; no de-

(12) Emil J. Geering, Doctoral Dissertation, Polytechnic Institute of Brooklyn, 1954.

(13) H. P. Lucas, E. R. Kennedy and M. W. Formo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 483.

(14) K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

(15) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 282.

pression of m.p. on admixture with a sample prepared from 2-acetylthiophene.¹⁶

Another sample of 2,2'-dithienyliodonium iodide, which had liquefied on prolonged standing, was distilled to give 2-iodothiophene, whose infrared spectrum was identical to that of authentic material.

Phenyl-2-thienyliodonium Salts. Reaction E.—To a well-stirred mixture of 100 ml. of acetic acid, 25 ml. of acetic anhydride, 11 g. (50 mmoles) of iodobenzene and 7.4 g. (88 mmoles) of thiophene kept below 20° 5 ml. of sulfuric acid was added dropwise. After 15 minutes (negative starch-iodide test) 200 ml. of water was added. Two extractions with 50-ml. portions of benzene followed by two treatments with activated carbon produced an almost colorless solution, which was treated with 20 g. of ammonium chloride in 30 ml. of water and refrigerated overnight. The crystals were collected and crystallized from water to give 2.6 g. (8 mmoles, 16%) of **phenyl-2-thienyliodonium chloride**, m.p. 202–204°. A second crystallization raised the m.p. to 217–219°.

Anal. Calcd. for C₁₀H₈ClIS: Cl⁻, 10.99. Found: Cl⁻, 10.75.

To the filtrate was added a solution of 30 g. of sodium bromide in 45 ml. of water. The chilled solution gave a precipitate that was crystallized from water to give 6.6 g. (16.3 mmoles, 33%) of **phenyl-2-thienyliodonium bromide**, m.p. 160–165°. A second crystallization raised the m.p. to 170–174°.

Anal. Calcd. for C₁₀H₈BrIS: Br⁻, 21.74. Found: Br⁻, 21.46.

The combined yield of iodonium salts in this case was 49%. From another reaction mixture **phenyl-2-thienyliodonium bromide**, m.p. 165–170°, was obtained in 61% yield. Recrystallization from water raised the m.p. to 170–174°. From the filtrates there was obtained 5% of **phenyl-2-thienyliodonium iodide**, m.p. 129–132°, unchanged by recrystallization from water; see below under reaction F. These salts are somewhat more soluble than the corresponding 2,2'-dithienyliodonium halides. Thus the chloride is soluble, *inter alia*, in hot ethanol and hot chloroform, and the iodide is soluble in hot acetone, methanol and ethanol.

Anal. Calcd. for C₁₀H₈I₂S: I⁻, 30.64. Found: I⁻, 30.94.

Reaction F.—To a solution of 50 ml. of acetic anhydride, 15 ml. of trifluoroacetic acid and 16.2 g. (50.4 mmoles) of iodobenzene diacetate at -20° there was added dropwise and with stirring a solution of 8.1 ml. (103 mmoles) of thio-

phene in 60 ml. of acetic anhydride. The temperature was held below -10°. After two hours at -10°, the reaction mixture was kept at 0° for about 15 hours. Solvent removal at 1–2 mm. (pot temperature below 70°) left a residue, which was stirred well with ether and cooled in ice. The crystals of crude **phenyl-2-thienyliodonium trifluoroacetate** weighed 18.6 g. (92%). Two crystallizations from benzene gave crystals of m.p. 160.5–162°, while four crystallizations gave material of m.p. 162–163.5°. After drying *in vacuo* for two hours, the crystals still held benzene, possibly as solvent of crystallization.

Anal. Calcd. for C₁₂H₈F₃IO₂S: C, 36.01; H, 2.01. Calcd. for C₁₂H₈F₃IO₂S·½C₆H₆: C, 41.01; H, 2.52. Found: C, 41.56; H, 2.93.

Treatment of an aqueous solution of the above iodonium salt with excess aqueous potassium iodide gave a quantitative yield of **phenyl-2-thienyliodonium iodide**, m.p. 140–141°; see above under reaction E.

Thermal decomposition of this iodide at 145–160° gave an oil shown by its infrared spectrum to be 1:1 mixture of iodobenzene and 2-iodothiophene.

Cleavage with Sulfite Ion.—Boiling a solution of 1.5 g. (3.4 mmoles) of **phenyl-2-thienyliodonium trifluoroacetate** and 1.7 g. (13.6 mmoles) of sodium sulfite in 25 ml. of water gave about 0.5 ml. of a dense oil in a Dean-Stark trap. The oil was collected, dried and distilled to give 0.4 g. of product, b.p. 180–190°, containing 5.05% sulfur. On the basis that the decomposition proceeded according to equation J and that the fraction of b.p. 180–190° is a mixture of iodobenzene and 2-iodothiophene, the mixture has the composition 67% iodobenzene, 33% 2-iodothiophene. Thus, the relative reactivity of the thienyl and phenyl rings to attack by the sulfite ion is 67/33 or about 2:1.

In a similar manner, reaction of a mixture of **diphenyliodonium nitrate**¹⁷ (0.52 g., 1.5 mmoles) and **2,2'-dithienyliodonium trifluoroacetate** (0.59 g., 1.5 mmoles) with aqueous sodium sulfite (0.125 g., 1.0 mmole) gave a mixture of iodobenzene and 2-iodothiophene in the Dean-Stark trap. The oil was collected, dried and distilled to give 0.16 g. of oil of b.p. 180–190°, containing 9.90% sulfur and corresponding to 65% 2-iodothiophene and 35% iodobenzene. Calculation of the relative reactivities, *r*, of the 2,2'-dithienyl- and diphenyliodonium cations is

$$r = \frac{\log(1 - 0.65/1.5)}{\log(1 - 0.35/1.5)} = \frac{-0.247}{-0.129} \cong 2:1$$

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(16) H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 505.

(17) F. M. Beringer and E. M. Gindler, *THIS JOURNAL*, **77**, 3203 (1955).