thorough investigation of reactant-state solvation is undertaken, however, no dogmatic position on this point can be taken.

Experimental Section

Materials. Lithium perchlorate (anhydrous reagent, G. Frederick Smith) was used as obtained. All organosilicon compounds were supplied by Peninsular Chem Research. Triphenylsilane was recrystallized twice from 95% ethanol (mp 44.5–45.5°, lit.[9] 44–45°). Methanol (anhydrous, A.C.S. Analyzed Reagent from Matheson Coleman and Bell) was purified by the method of Lund and Bjerrum.[10] Methanol-d (Diaprep, Inc.) was purified by distilling it slowly through a 48-cm Vigreux column packed with glass beads, using a Drierite tube to guard against moisture. Triphenylsilane-d was prepared by the procedure of Gilman and Dunn.[11]

Gas Ratio Measurements. The molar ratio of gases HH and HD evolved in the reaction of R_3SiH with methanol of varying isotopic composition was determined by gas chromatography[6] followed by combustion of the hydrogen sample to water and thermal-conductivity measurement of the ratio of HHO to HDO. A calibration curve was constructed by analysis of known mixtures of HH and HD, produced by complete methanolysis of known mixtures of $(C_6H_5)_3SiH$ and $(C_6H_5)_3SiD$. These mixtures were prepared volumetrically from stock solutions or gravimetrically. Measurements were made on a F&M Laboratory Chromatograph Model 700.

The system consisted of a stripper column, separation column, combustion furnace, and detector. The stripper column functioned to remove air and methanol vapor from the sample so that only H_2 and HD enter the separation column. For this purpose, 10 ft of 0.25 in. o.d. copper tubing was packed with Johns Manville Chromosorb P (60–80 mesh) and maintained at −40° in an acetone–Dry Ice bath. For use in the separation column, ferric oxide–coated alumina packing was prepared according to the procedure of Shipman.[12] Ferric chloride solution (1.8 M) was added in increments with stirring to 200 ml of alumina (Varian, 60–80 mesh) until the alumina was dampened. Distilled water (250 ml) was added and the mixture was treated with 6 M ammonium hydroxide to pH 7. After settling, the excess solution was decanted, and the precipitate was filtered and washed with water until the pH of the washings was 6. The product was dried in an oven at 120° for 36 hr. Copper tubing (6 ft of 0.25 in. o.d.) was coiled in 4-in. diameter coils so that it would fit comfortably in a 4-l. dewar flask. It was packed with the ferric oxide–coated alumina and deactivated with a slow stream of carbon dioxide (about 2 cc/min) until barium hydroxide showed the passage of carbon dioxide. The column was then conditioned under flowing helium for 6 hr, and operated at −196°. The combustion furnace consisted of an 8-in. length of 0.25 in. o.d. quartz tubing packed with copper oxide, wrapped in asbestos, and placed in an 8-in. Hevi Duty combustion furnace at 700°. Connections were made by means of small stainless steel tubes and high-temperature rubber plugs. The tubing outlet to the detector was heated by means of heating tapes to prevent condensation of water.

(9) H. Gilman and H. W. Melvin, Jr., *J. Amer. Chem. Soc.*, **71**, 4050 (1949).

(10) H. Lund and I. Bjerrum, *Ber.*, **64**, 210 (1931).

(11) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **73**, 3404 (1951).

(12) G. F. Shipman, *Anal. Chem.*, **34**, 877 (1962).

σ-Sulfurane Chemistry.   Effect of Substituents on the Coupling Reactions

Barry M. Trost[*1] and Henry C. Arndt

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received January 22, 1973

Abstract: The reaction of S-aryldibenzothiophenium fluoroborates with aryllithiums reveals the ratio of formation of biaryl and dibenzothiophene (path A) compared with 2-arylthio-o-terphenyl (path B) which depends upon substituents. Electron-withdrawing substituents favor the former, whereas electron-donating substituents favor the latter. Similarly, styrene and dibenzothiophene formation predominates over 2-vinyl-2′-arylthiobiphenyl and/ or 2-arylthio-o-terphenyl formation in the reaction of the above salts with vinyllithium when electron-withdrawing groups are present in the S-aryl group. Treatment of S-phenyldibenzothiophenium fluoroborate with aryllithiums and of S-aryldibenzothiophenium fluoroborates with phenyllithium produces the same product mixture and one in which aryl–aryl coupling has occurred preferentially between the two rings which bear the most electron-withdrawing group. Interpretation of these results in terms of the tetraarylsulfuranes as intermediates is presented.

The valence shell expansion of sulfur continues to be invoked as an explanation of the many reactions occurring at sulfur. Most of these reactions involve oxidation at sulfur, and in some cases, the σ sulfurane achieves enough stability to be isolated.[2–4] The importance of these intermediates grows as their applications in problems of organic synthesis expand. Whereas it is perhaps not too surprising that such intermediates possessing strongly electronegative groups on

(1) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

(2) For example, see C. R. Johnson and J. J. Rigaw, *J. Amer. Chem. Soc.*, **91**, 5398 (1969); V. Calo, G. Scorrano, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969); G. E. Wilson, Jr., and M. M. Yang Chang, *Tetrahedron Lett.*, 875 (1971).

(3) (a) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **94**, 2339, 2341, 4327 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997, 5003 (1972); (c) E. F. Perozzi and J. C. Martin, *ibid.*, **94**, 5519 (1972); (d) I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971).

(4) For other related work, see (a) C. R. Johnson, C. C. Bacon, and W. D. Kingsbury, *Tetrahedron Lett.*, 501 (1972); (b) N. C. Baenziger,
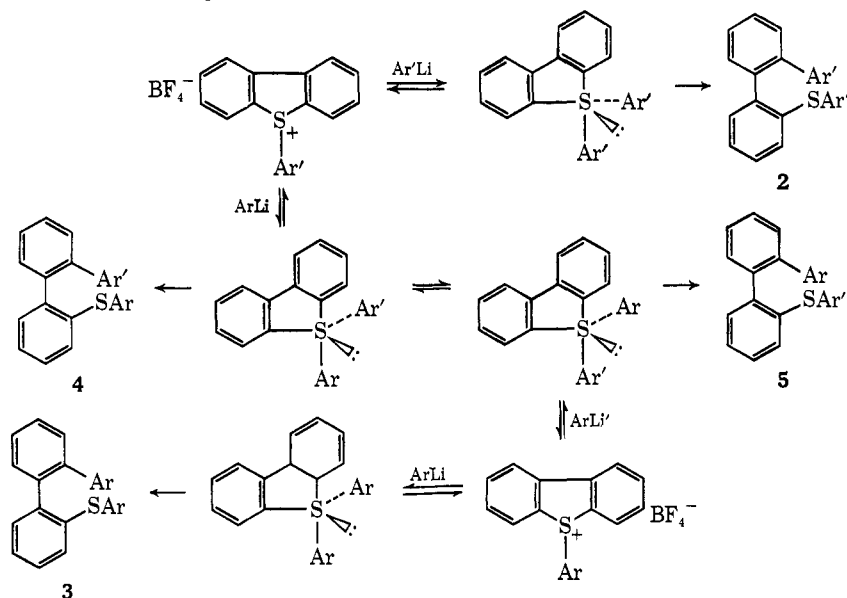
R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969); (c) J. W. Knapczyk and W. E. McEwen, *ibid.*, **91**, 145 (1969); (d) G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968); (e) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970); (f) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schultz. D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970); (g) M. G. Burdeen and J. G. Moffatt, *ibid.*, **89**, 4725 (1967); (h) E. J. Corey and T. Drust, *ibid.*, **90**, 5553 (1968); (i) E. Ciuffarin and G. Guaraldi, *ibid.*, **91**, 1745 (1969); (j) T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970); (k) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); (l) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Lett.*, 2691 (1964); (m) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

sulfur are isolable, the series possessing only carbon ligands remains elusive.[5] We have reported strong evidence favoring such intermediates in the desulfurization of episulfides,[6] thietanonium salts,[7] and 2,5-dihydrothiophenium salts[8] as well as in the coupling reaction of sulfonium salts with organolithiums possessing a π system.[9] This interpretation has been strongly reinforced by the isotopic labeling in the reaction of triphenylsulfonium fluoroborate wth phenyllithium in which the label appears statistically in the diphenyl sulfide and biphenyl products[10] and by the detection by ^{19}F nmr spectroscopy of tetrakispentafluorophenylsulfurane which thermally collapses to decafluorodiphenyl sulfide and decafluorobiphenyl.[11]

The nature of this coupling reaction of σ sulfuranes remains an intriguing mystery. From the characteristics of the reaction, a transition state represented by 1
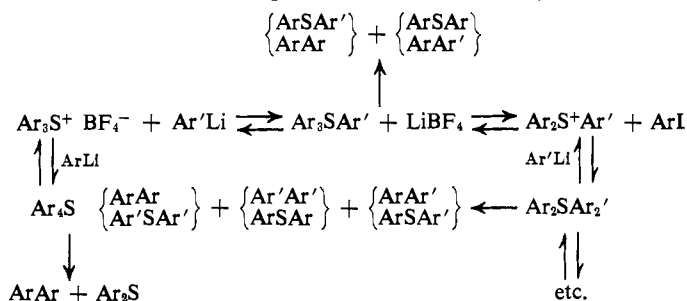

1
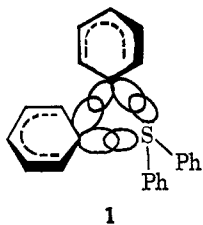
Scheme I. Coupling Scheme for Dibenzothiophenium Salts

similar characteristics led us to attempt to probe the electronic distribution by measuring substituent effects.

The use of simple substituted arylsulfonium salts with aryllithiums did not appear suitable since the formation of σ sulfurane is potentially complicated by the reversibility of its formation.[13] Thus, starting with Ar_3S^+ BF_4^- and an Ar'Li could lead via ligand exchange to a mixture possessing Ar_2S^+Ar' BF_4^- and ArLi as well as the initial reactants. This combination can lead to three different σ sulfuranes all of which can decompose to similar products. Use of S-aryldibenzothiophenium salts provides a solution to this problem as illustrated in Scheme I. Thus, if ligand exchange occurs, the "symmetrical" coupling products 2 and 3 are obtained. Such products can be readily dissected

from the "unsymmetrical" coupling products 4 and 5 whose ratio represents the migratory preferences of the substituted rings. The interpretation of the results must be tempered by the fact that the two "unsymmetrical" σ sulfuranes do not necessarily lead to the same ratio of coupling products unless they interconvert faster than coupling occurs. Even if the latter was the case, a qualitative description of the effect of substituents on the reaction would still emerge.
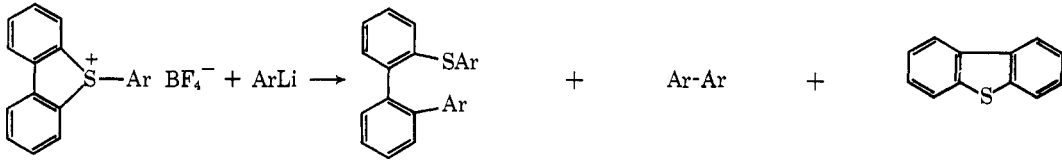
Results

The synthesis of the requisite sulfonium salts involved the treatment of S-methoxydibenzothiophenium fluoroborate with arylmagnesium halides.[9,14] Con-

was postulated.[9] The vagueness of such a picture as well as the fact that many other reactions (such as thermal decomposition of organocuprates[12]) have

(5) G. Wittig and H. Fritz, Justus Liebigs Ann. Chem., 577, 39 (1952); W. A. Sheppard, J. Amer. Chem. Soc., 84, 3058 (1962).

(6) B. M. Trost and S. D. Ziman, J. Org. Chem., in press; B. M. Trost and S. D. Ziman, Chem. Commun., 181 (1969); F. G. Bordwell, H. M. Andersen, and B. M. Pitts, J. Amer. Chem. Soc., 76, 1082 (1954); N. P. Neureiter and F. G. Bordwell, ibid., 81, 578 (1959).

(7) B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, ibid., 93, 676 (1971); B. M. Trost, W. L. Schinski, and I. B. Mantz, ibid., 91, 4320 (1969).

(8) B. M. Trost and S. D. Ziman, ibid., 93, 3825 (1971).

(9) B. M. Trost, R. LaRochelle, and R. C. Atkins, ibid., 91, 2175 (1969); R. W. LaRochelle and B. M. Trost, ibid., 93, 6077 (1971).

(10) D. Harrington, J. Weston, J. Jacobus, and K. Mislow, J. Chem. Soc., Chem. Commun., 1079 (1972).

(11) W. A. Sheppard, J. Amer. Chem. Soc., 93, 5597 (1971).

(12) See, for example, A. Cairncross, H. Omura, and W. F. Sheppard, ibid., 93, 248 (1971), and references therein; R. J. DePasquale and C. Tamborski, J. Org. Chem., 34, 1736 (1969); H. Hashimoto and T. Nakano, ibid., 31, 891 (1966).
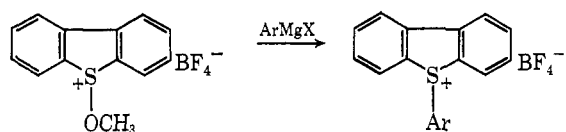
(13) V. Franzen and C. Mertz, Justus Liebigs Ann. Chem., 643, 24 (1961).

(14) For an alternative preparation of methoxydibenzothiophenium salt, see R. M. Acheson and J. K. Stubbs, J. Chem. Soc., Perkin Trans. 1, 899 (1972).

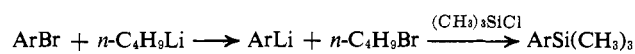**Table I.** Relative Yields in Symmetrical Coupling Reactions

Ar		%̶ yield̶	
p-CH$_3$C$_6$H$_4$	100		
C$_6$H$_5$	100		
p-CF$_3$C$_6$H$_4$	46.4	25.1	28.5
m-CF$_3$C$_6$H$_4$	53.4	26.6	20.0

6a, Ar = C$_6$H$_5$
  b, Ar = p-CH$_3$C$_6$H$_4$; 31%
  c, Ar = p-CH$_3$OC$_6$H$_4$; 26%
  d, Ar = p-CF$_3$C$_6$H$_4$; 56%
  e, Ar = m-CF$_3$C$_6$H$_4$; 35%

firmation of the structure mainly rests on the nmr spectral properties (see Experimental Section) and elemental analysis. The aryllithiums employed were generated by metal–halogen exchange between the aryl bromide and n-butyllithium. Analysis of the re-

$$\text{ArBr} + n\text{-C}_4\text{H}_9\text{Li} \longrightarrow \text{ArLi} + n\text{-C}_4\text{H}_9\text{Br} \xrightarrow{\text{(CH}_3)_3\text{SiCl}} \text{ArSi(CH}_3)_3$$

action mixture by quenching with trimethylchlorosilane indicated the completion of the reaction by the absence of n-butyltrimethylsilane and provided characterization of the organolithium as the aryltrimethylsilane.

Initial studies on the effect of substituents focused on the competition between two modes of collapse of the sulfurane 2 aryl–biphenylyl coupling (path A) and aryl–
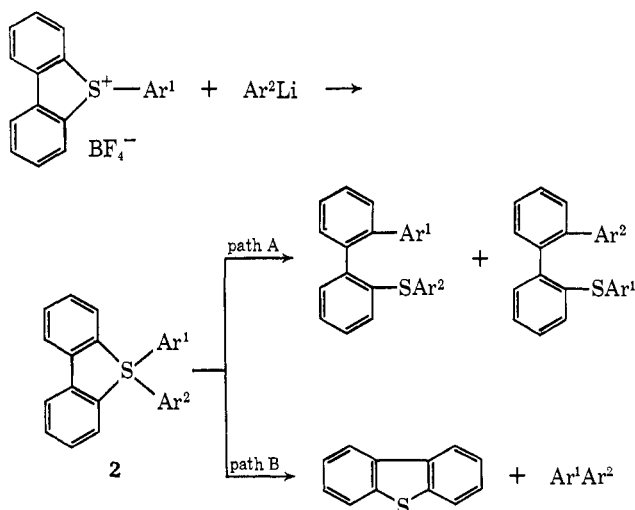
aryl coupling (path B). The ratio of these two paths is a function of the nature of the aryl groups. Table I summarizes the ratio of path A to path B for the cases of Ar^1 = Ar^2.

The products were easily separable by either vapor phase or thick layer chromatography. In the cases of Ar = p-CH$_3$C$_6$H$_4$ and C$_6$H$_5$, the absence of the biaryls was confirmed by vpc coinjections with authentic samples. The relative yields were derived either from

the vapor phase chromatograms utilizing internal standards or from the weights of isolated compounds (see Experimental Section). The structures of the arylthioterphenyl 3 rest on spectroscopic data and/or

Ar
a, p-CH$_3$C$_6$H$_4$
b, p-CF$_3$C$_6$H$_4$
c, m-CF$_3$C$_6$H$_4$
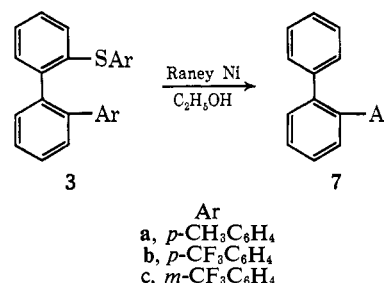
Raney nickel desulfurization to the simply substituted terphenyl.[7] In two cases, the terphenyls were independently synthesized as outlined in Scheme II to con-

Scheme II. Independent Synthesis of Terphenyls

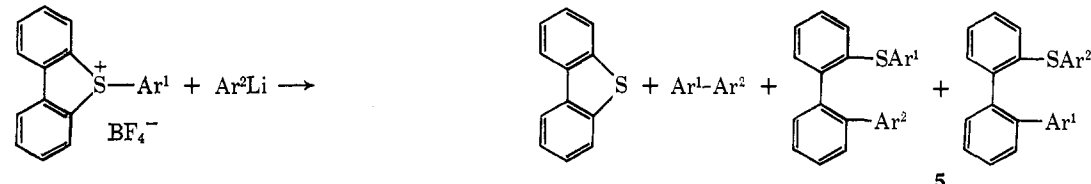Ar
a, p-CH$_3$C$_6$H$_4$
d, p-CH$_3$OC$_6$H$_4$
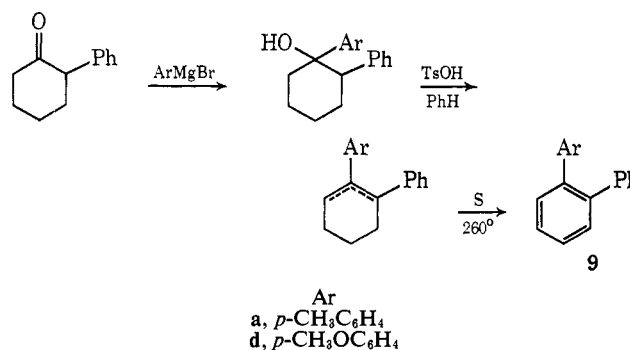
firm the positional identity of the substituents.[15] Whereas aryl groups, unsubstituted or substituted with electron-donating groups, react by aryl–biphenylyl coupling exclusively, equal amounts of aryl–aryl and aryl–biphenylyl coupling occur with aryl groups substituted with electron-withdrawing groups. Clearly, electron-withdrawing groups facilitate the aryl coupling reaction.
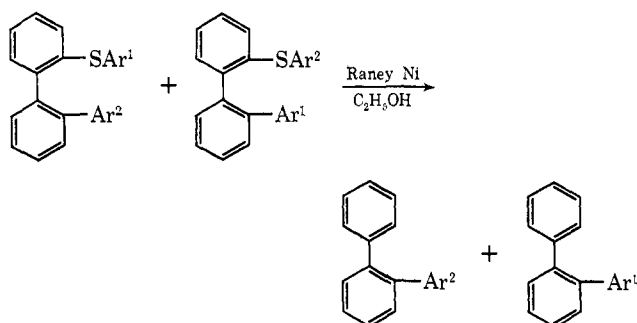
This conclusion is heavily reinforced by consideration of the reaction when Ar $\neq$ Ar' (see Table II). Analysis of these reactions was accomplished by either vapor phase chromatography utilizing internal standards or isolating each compound. Further confirmation of the ratio of arylthioterphenyls 4 and 5, as well as of their structure, arose from Raney nickel desulfurization and analysis of the terphenyl mixture in terms of their comparison to authentic samples. The structural identity of the mixed biaryls was established

(15) G. F. Woods and F. Scotti, *J. Org. Chem.,* **26,** 312 (1961).

**Table II.** Relative Yields (%) in Unsymmetrical Coupling Reactions

Ar¹	Ar²	Temp, °C	% yield			
p-CH₃C₆H₄	C₆H₅	−78			94.5	5.5
C₆H₅	p-CH₃C₆H₄	−78			6.6	93.4
p-CH₃OC₆H₄	C₆H₅	−100			100	
		−78			100	
		−20			100	
C₆H₅	p-CH₃OC₆H₄	−100				100
		−78				100
		−20				100
p-CF₃C₆H₄	C₆H₅	−78	1.6	1.6	2.5	94.3
C₆H₅	p-CF₃C₆H₄	−78	2.4	2.4	92.1	3.2
m-CF₃C₆H₄	C₆H₅	−100	18.2	18.2		63.6
		−78	29.4	27.1		43.4
		−20	30.5	24.6		44.9
C₆H₄	m-CF₃C₆H₄	−100	9.2	8.7	82.1	
		−78	3.3	2.9	93.8	
		−20	3.9	5.0	91.1	

by spectroscopic means and independent synthesis according to Scheme III. In the p-tolyl and p-anisyl

Scheme III. Independent Synthesis of Mixed Biaryls


Ar = p-CH₃OC₆H₄, p-CF₃C₆H₄, m-CF₃C₆H₄
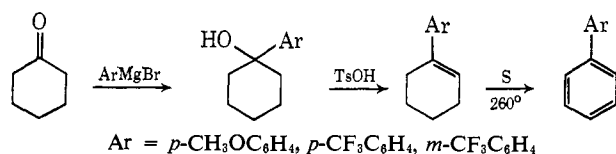
cases, absence of the biaryls was confirmed by vpc coinjection with authentic samples. Lack of p-anisyl migration in the p-anisyl case and of phenyl migration in the m-trifluoromethylphenyl case was confirmed by the absence of 3-methoxyterphenyl and terphenyl, respectively, in the desulfurization of the coupling products.

In these reactions not only is a similar trend seen in terms of the ratio of path A to path B, but also the internal competition in terms of the ratio of the two terphenyls demonstrates the facilitation of coupling by electron-withdrawing substituents. Changing from the most electron donating substituent, p-methoxy, to the most electron-withdrawing substituent, m-trifluoromethyl, a gradation from no migration to total migration of the substituted ring occurs. It may be noted that a biphenylyl group may be considered as an aryl group substituted in the ortho position by a phenyl substituent, an electron-withdrawing substituent. Thus, coupling

strongly prefers both aryl groups to bear electron-withdrawing substituents.

In the above coupling reactions, the intermediate sulfurane can exist in two geometries as illustrated below. The results, however, do not reflect that fact. To probe whether geometry can determine coupling ratios, the rate of coupling was increased relative to
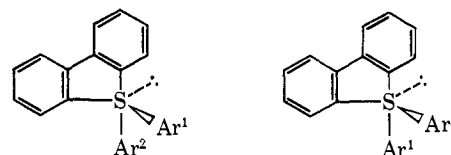
sulfurane formation. A vinylsulfurane has been demonstrated to undergo very efficient coupling. Thus, triphenylvinyl sulfurane generates styrene and no biphenyl. S-Arylvinyl-2,2′-biphenylylsulfurane (8, R
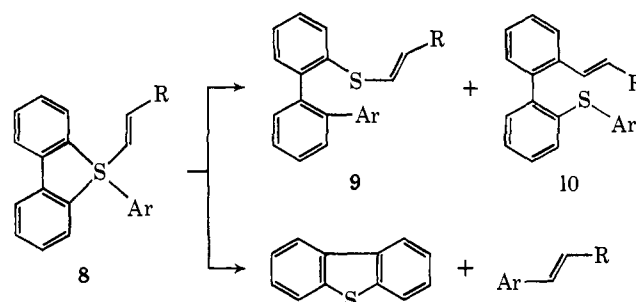
= H) may collapse to the terphenyl 9, the vinylbiphenyl 10, and/or dibenzothiophene and styrenes, the ratio being determined by substituents (see Table III). Treatment of S-aryldibenzothiophenium fluoroborate with vinyllithium generates predominantly 2-arylthio-2′-vinylbiphenyls if the aryl group possesses electron-donating substituents, but styrenes and dibenzothiophene if the aryl group is unsubstituted or substituted with an electron-withdrawing substituent. The structures and the ratios of the vinylthioterphenyls and 2-arylthio-2′-vinylbiphenyls were confirmed by desul-

Table III. Relative Yields of Vinyl Coupling

Ar	R	%yield			
p-CH₃OC₆H₄	H	3.5	3.8	80.5	12.2
p-CH₃OC₆H₄	CH₃			100.0	
p-CH₃C₆H₄	H	7.6	7.6	70.0	14.8
C₆H₅	H	41.0	41.0	11.0	7.0
p-CF₃C₆H₄	H	48.8	48.3		2.9
m-CF₃C₆H₄	H	50.3	48.1		1.6
m-CF₃C₆H₄	CH₃	41.2	36.5		22.3

Ar = p-CH₃OC₆H₄, p-CH₃C₆H₄, p-CF₃C₆H₄, m-CF₃C₆H₄
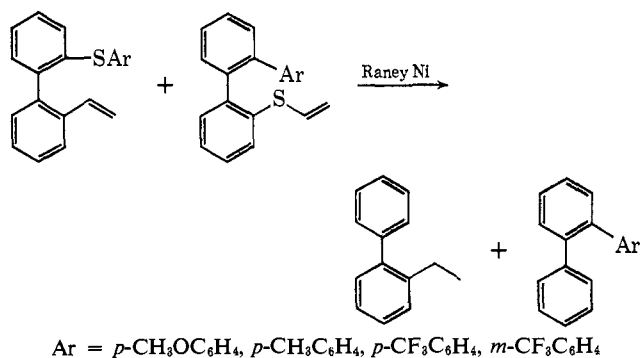
furization to terphenyls and 2-ethylbenzenes, respectively. Coinjections of authentic samples of 3-methoxyterphenyl and 2-ethylbiphenyl confirmed the absence of anisyl migration in the anisyl case and vinyl migration in the p- and m-trifluoromethylphenyl cases.

That electron-donating groups inhibit coupling in this case as well was demonstrated by the use of propenyllithium with salts **6c** and **e**. Thus, with the methoxy-substituted salt, no dibenzothiophene and substituted propenylbenzene were obtained; whereas, with the m-trifluoromethyl salt, these types of products decreased in importance.

Discussion

The present results reinforce the previous conclusions regarding the mechanism of the aryl–aryl coupling reaction.[9] In particular, the data refute the addition–elimination pathway. For example, the reaction of S-(p-trifluoromethylphenyl)dibenzothiophenium fluoroborate (**6d**) with p-trifluorophenyllithium leads to almost equal amounts of coupling via path A (leading to terphenyls) and path B (leading to biaryls and dibenzothiophene), whereas phenyllithium reacts to give products arising from path A almost exclusively with coupling between the trifluorophenyl and biphenylyl groups. That the latter does not arise from initial ligand exchange and subsequent attack of the aryllithium on the biphenylyl group is demonstrated by the lack of any symmetrical coupling products and the homogeneity of sulfonium salt recovered from the
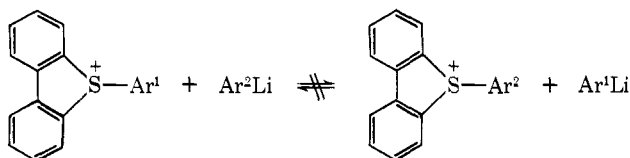
reactions. Thus, in this case the group originally bonded to sulfur ends up finally being bonded to carbon in the product, a result which cannot be reconciled by the addition–elimination route with the lack of ligand exchange. Furthermore, there is a dramatic decrease in the ratio of path A to path B merely by changing the para substituent on the aryllithium. In the addition–elimination mechanism in which the organolithium merely behaves as a nucleophile, such a structural change is inconsistent with the magnitude of the change in coupling pathways. The remaining cases reinforce these conclusions.

The pentacoordinate sulfur appears to induce electron distribution away from itself to reduce the electron density at sulfur. The ability to isolate such compounds with strongly electronegative groups supports that contention.[2–4] In the case of substituents bearing π systems, this effect causes a polarization of the π cloud away from sulfur. The presence of an electron-withdrawing group facilitates and of an electron-donating group inhibits such an electronic drift. In the former case, such a process weakens the carbon–sulfur bond of that ligand and initiates the coupling process. Unfortunately, because of the competition between several processes occurring simultaneously and because of some reflection of the thermodynamic stability of the two sulfuranes in the ratio of coupled products, attempts to obtain linear free energy relationships failed.

The significance of the migratory preferences must be tempered by consideration of the geometry of the sulfurane **2**.[16] By analogy to phosphorus chemistry,[17] the following structural assumptions are made: (1) pentacoordinated sulfur exists as a trigonal bipyramid, (2) the electron pair prefers a basal orientation, (3) the five-membered ring prefers the apical–basal orientation, and (4) groups enter and leave preferentially from an apical position. Examination of molecular models reveals that aryl groups in the apical position cannot couple with the biphenylyl group in the basal position

(16) The trigonal-bipyramid geometry appears to be supported in sulfuranes bearing electronegative substituents. See ref 3d and 4b. Also see (a) E. L. Muetterties and W. D. Phillips, J. Amer. Chem. Soc., **81**, 1084 (1959); (b) F. A. Cotton, J. W. George, and J. S. Waugh, J. Chem. Phys., **28**, 994 (1958); (c) R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc., **52**, 1052 (1956); (d) G. C. Demitras and A. G. MacDiarmid, Inorg. Chem., **6**, 1902 (1967); (e) D. T. Sauer and J. M. Shreeve, Chem. Commun., 1679 (1970); (f) I. C. Paul, J. C. Martin, and E. F. Perozzi, J. Amer. Chem. Soc., **94**, 5010 (1972).

(17) D. Gorenstein and F. H. Westheimer, ibid., **92**, 634 (1970); D. Gorenstein, ibid., **92**, 644 (1970); F. H. Westheimer, Accounts Chem. Res., **1**, 70 (1968).

without an inordinate amount of strain. In essence, the p orbitals of the two groups in such an orientation are orthogonal and thereby preclude overlap leading to coupling. Thus, sulfurane **2a**, which is the kinetic

5a   **2a**

2b   **5b**
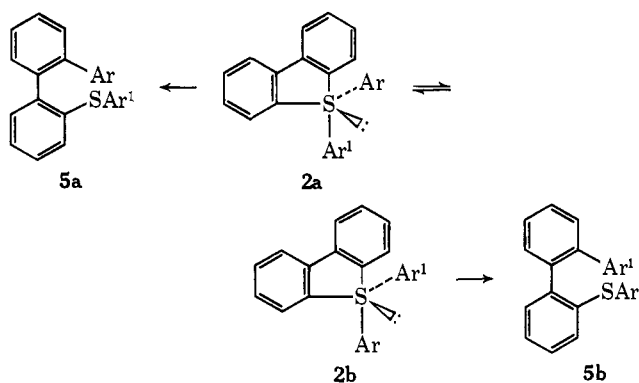
product of addition of Ar¹Li to S-Ar-dibenzothiophenium fluoroborate, gives rise to terphenyl **5a**, and sulfurane **2b**, which is the kinetic product of addition of ArLi to S-Ar¹-dibenzothiophenium fluoroborate, gives rise to terphenyl **5b**. That **2a** and **2b** interconvert faster than coupling and therefore the ratio of **5a** to **5b** reflects to a reasonable extent the relative migratory aptitude of Ar and Ar¹ is indicated by two observations. First, the ratio of **2a** to **2b** is temperature independent over the range −100 to −20°. Second, the ratio does not depend on the order of addition of the aryl groups to form the sulfurane.

On the other hand, the reaction of vinyllithium with S-aryldibenzothiophenium salts, in which the rate of coupling has been enhanced, appears to show a stereochemical effect. The ratio of the two types of products is easily rationalized if the rate of coupling is competitive or somewhat faster than sulfurane interconversion. Thus, sulfurane **8a** (R = H) is the kinetic product (see Scheme III). It can only undergo vinyl–aryl or aryl–

Scheme III. Reactions of Vinyllithium with
S-Aryldibenzothiophenium Fluoroborate

8a   I

8b   II
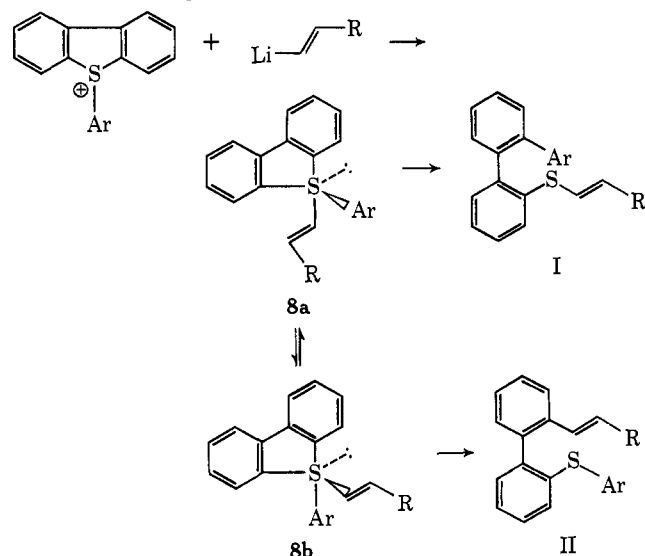
biphenylyl coupling. The alternate geometrical isomer **8b** (R = H) can undergo vinyl–aryl or vinyl–biphenylyl coupling. The previous results indicate that the vinyl and biphenylyl groups participate in the coupling most efficiently. However, when the aryl group possesses

electron-withdrawing substituents or no substituents, the rapid rate of coupling precludes isomerization of **8a** (R = H) to **8b** (R = H). The major products are thus dibenzothiophene and the substituted styrene. When the aryl group possesses electron-donating substituents, vinyl–aryl coupling is slowed. Interconversion of **8a** (R = H) and **8b** (R = H) now competes more effectively with coupling and the expected vinyl–biphenylyl coupling predominates.

Further support for this interpretation arises by consideration of the reaction of propenyllithium with S-(m-trifluoromethylphenyl)dibenzothiophenium fluoroborate. Just as in the aryl cases, alkyl substituents on the vinyl group hinder the coupling. Whereas, with sulfurane **8** (R = H and Ar = m-trifluoromethylphenyl) coupling occurred much faster than sulfurane interconversion giving dibenzothiophene and m-trifluoromethylstyrene in 98.4% yield, collapse of sulfurane **8** (R = CH₃ and Ar = m-trifluoromethylphenyl) to dibenzothiophene and m-trifluoromethylpropenylbenzene diminishes to 77.7%. The terphenyl, present in only 1.6% yield from **8** (R = H), now is present in 22.3% yield.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in ppm relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with methylene chloride, and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on an Aerograph Model 90P instrument. Internal standards for vpc analysis included diphenyl sulfide (for dibenzothiophene and biaryl yields), di-n-butyl phthalate (for 2-aryl-2'-arylthiobiphenyl yields), fluorene and p-cumene (for styrene yields), diphenyl sulfoxide, and cumene. Tlc analyses and separations were effected utilizing Merck (Darmstadt) silica gel PF-254.

Preparation of S-Aryldibenzothiophenium Fluoroborates. The various salts were prepared by virtually identical procedures, and the details of each experiment are summarized in Table IV. A typical procedure follows.

A 0.56 M solution of p-trifluoromethylphenylmagnesium bromide was prepared using 4.5 g (0.02 mol) of p-trifluoromethylbromobenzene, 0.486 g (0.02 g-atom) of magnesium turnings, and 20 ml of dry ether. To a slurry of 3 g (0.01 mol) of S-methoxydibenzothiophenium fluoroborate in 150 ml of dry (distilled from lithium aluminum hydride) tetrahydrofuran cooled in a Dry Ice–carbon tetrachloride bath, 17.6 ml (0.01 mol) of 0.56 M p-trifluoromethylphenylmagnesium bromide was added over a 10-min period. The mixture was allowed to stir 5 min and then slowly warmed to room temperature. A 25% aqueous tetrafluoroboric acid solution (70 ml) was added to the reaction mixture and then the combined mixture poured into 250 ml of 12.5% tetrafluoroboric acid. The white suspension was extracted with methylene chloride (1 l.) and the solvent partially removed in vacuo. Ether was added to the concentrated liquors and the salt allowed to crystallize. The salt was isolated by vacuum filtration and recrystallized from methylene chloride–ether to yield 1.5 g (56%) of S-(p-trifluoromethylphenyl)dibenzothiophenium fluoroborate (**6d**): mp 182–184°; ir (KBr) ν 3106 (ArH), 1605 (aromatic), 1325 (sym CF₃Ar), 1176 (asym CF₃Ar), 1163–909 (BF₄⁻), 839 (para-disubst aromatic), 755 (aromatic), 704 (aromatic); uv λ_{max}^{EtOH} 315 nm (ϵ 3200), 270 (10,800), 243 (33,200), 235 (34,000); nmr (DMSO-d_6) δ 7.49 (4 H, m) and 6.90 (8 H, m). Anal. Calcd for C₁₉H₁₂SBF₄: C, 54.82; H, 2.90; S, 7.68; F, 32.09. Found: C, 54.79; H, 2.99; S, 7.75; F, 31.81.

Table IV. Preparation of S-Aryldibenzothiophenium Fluoroborates

Salt	Methoxy-sulfonium fluoroborate, wt, g (mmol)	Grignard reagent ml, M (mmol)	THF, ml	Product wt, mg (%)	Mp, °C	Anal. Calcd Found			
						C	H	S	F
6b[a]	1.0 (3.3)	5.14, 0.64 (3.3)	62.5	358 (30.5)	194–199	62.98	4.41	8.84	
						63.00	4.18	8.76	
6c[b]	2.5 (8.0)	6.79, 1.21 (8.0)	150	820 (26)	196–199	60.33	4.00	8.46	
						60.16	3.97	8.48	
6e[c]	2.5 (8.0)	12.0, 0.67 (8.0)	150	1200 (35)	196–197	54.82	2.90	7.68	32.09
						54.61	3.14	7.74	31.97

[a] Spectral properties: ir (KBr) ν 3096 (ArH), 1577 (aromatic), 1443 (aromatic), 1175–909 (BF_4^-), 818 (para-disubst aromatic), 755 (aromatic), 703 (aromatic); uv λ_{max}^{EtOH} 320 nm (ϵ 2500), 273 sh (11,250), 243 (35,850); nmr (DMSO-d_6) 2.31 (3 H, s), 7.46 (4 H, s), 7.87 (4 H, p of m, J = 6.9 Hz), 8.34 (2 H, d of m, J = 6.9 Hz), 8.54 (2 H, d of m, J = 6.9 Hz); mass spectrum m/e (70 eV) (rel intensity) 275 (mw-BF_4^-) (5), 184 (100). [b] Spectral properties: ir (KBr) ν 3106 (ArH), 1600 (aromatic), 1497 (aromatic), 1452 (aromatic), 1312 (CO), 1269 (CH_3OC), 8.75–10.2 (BF_4^-), 11.95 (para-disubst aromatic), 762 (aromatic); uv λ_{max}^{EtOH} 315 nm (ϵ 1800), 285 sh (6950), 260 (14,500), 236 (16,900), 227 (17,800); nmr (DMSO-d_6) δ 3.82 (3 H, s), 7.14 (2 H, d, J = 9 Hz), 7.57 (2 H, d, J = 9 Hz), 7.85 (4 H, p of m, J = 6.8 Hz), 8.28 (2 H, d of m, J = 6.8 Hz), 8.49 (2 H, d of m, J = 6.8 Hz). [c] Spectral properties: ir (KBr) ν 3106 (ArH), 1449 (aromatic), 1325 (sym, CF_3Ar), 1163–980 (BF_4^-), 892 (1,3-disubst aromatic), 806 (1,3-disubst aromatic), 766 (1,2-disubst aromatic); uv λ_{max}^{EtOH} 318 (ϵ 3300), 275 (9100), 270 (31,300), 235 (31,700); nmr (DMSO-d_6) δ 8.64 (4 H, m), 8.02 (8 H, m).

Preparation of Aryllithium. Method A. A typical procedure follows. n-Butyllithium (4.74 ml, 1.5 M, 0.72 mmol) in hexane was added to 2.5 ml of dry (freshly distilled from lithium aluminum hydride) ether. The solution was cooled to $-78°$ and 1.62 g (0.72 mmol) of m-trifluoromethylbromobenzene was added over a 10-min period. The reaction was followed by quenching aliquots with trimethylchlorosilane and analyzing by vpc for trimethyl-n-butyl-silane. The organolithium was titrated for active organometallic with 0.1 N standard hydrochloric acid and found to be 0.8 M in active m-trifluoromethylphenyllithium. The organolithium was further characterized as its trimethylsilyl derivative by quenching an aliquot with excess trimethylchlorosilane: ir (CCl₄) ν 1325 (sym CF₃Ar), 1170 (asym CF₃Ar), 1130 (asym CF₃Ar); uv λ_{max}^{EtOH} 272 nm (ϵ 380), 264 (380), 258 (190), 212 (6100); nmr (CCl₄) (CH₂Cl₂ standard) δ 0.21 (9 H, s, (CH₃)₃Si), 7.38–7.81 (4 H, m, ArH); mass spectrum (m/e (70 eV) (rel intensity) 218.03722 (calcd for C₁₀H₁₃SiF₃, 218.03783) (6), 204 (24), 203 (100), 76 (10). The results for the remaining organolithiums are summarized in Table V.

Table V. Preparation of Organolithiums

ArLi	ArBr wt, g (mmol)	n-C₄H₉Li ml, M (mmol)	Normality of resultant solution
p-CH₃OC₆H₄[a]	1.30 (0.65)	4.4, 1.4 (0.65)	0.5
p-CF₃C₆H₄[b]	1.62 (0.72)	4.5, 1.5 (0.72)	0.1

[a] Spectral properties of p-anisyltrimethylsilane: ir (CCl₄) ν 3012 (ArH), 2950 (CH₃), 2849 (CH₃O), 1597 (aromatic), 1504 (aromatic), 1464 (aromatic), 1277 (CH₃OC=), 1263 (CH₃Si), 1245 (CH₃OC=), 1168 (CO), 1111 (PhSi); uv λ_{max}^{EtOH} 282 nm (ϵ 1400), 273 (1400), 228 (14,300); nmr (CCl₄) (CH₂Cl₂ standard) δ 0.15 (9 H, s, (CH₃)₃Si), 3.77 (3 H, s, CH₃OAr), 7.19 (4 H, AA'BB' pattern, J = 9, 0.5 Hz, ArH); mass spectrum m/e (70 eV) (rel intensity) 180.09983 (calcd for C₁₀H₁₆SiO, 180.09704) (19), 166 (15), 165 (100), 135 (6). [b] Spectral properties of p-trifluoromethyl-phenyltrimethylsilane: ir (CCl₄) ν 2976 (ArH), 1330 (sym CF₃Ar), 1252 ((CH₃)₃Si), 1170 (asym CF₃Ar), 1133 (asym CF₃Ar), 844 (para-disubst aromatic), 697 (aromatic); uv λ_{max}^{EtOH} 272 nm sh (ϵ 1300), 264 sh (1800), 257 sh (2300), 252 (2400), 235 (2300); nmr (CCl₄) (CH₂Cl₂ standard) δ 0.22 (9 H, s, (CH₃)₃Si), 7.38 (4 H, bs, ArH); mass spectrum m/e (70 eV) (rel intensity) 218.07669 (calcd for C₁₀H₁₃SiF₃, 218.07386) (2), 204 (7), 203 (100).

Method B. Finely cut lithium wire containing 1% sodium (0.172 g, 0.025 g-atom) was stirred with 25 ml of dry ether under an argon atmosphere. p-Bromotoluene (4.26 g, 0.025 mol) was added and the mixture allowed to react until refluxing ceased. The solution was refluxed for 3 hr and then standardized with 0.1 N hydrochloric acid. The solution was found to be 0.8 M in active organolithium. p-Tolyllithium was characterized as its trimethylsilyl derivative: ir (CCl₄) 3096 (ArH), 3040 (ArH), 2976 (CH₃), 1610 (aromatic), 1250 (CH₃Si), 1109 (CH₃Si), 839 ((CH₃)₃Si), 690

(aromatic); uv λ_{max}^{EtOH} 260 nm (ϵ 165), 226 sh (7800), 222 (9400), 217 (8450); nmr (CCl₄) δ 0.1 (9 H, s, (CH₃)₃Si), 2.22 (3 H, s, CH₃Ar), 7.25 (4 H, AA'BB', J = 8, 1 Hz, ArH); mass spectrum m/e (70 eV) (rel intensity) 164.10224 (calcd for C₁₀H₁₆Si, 164.10212) (100), 149 (89), 148 (86).

Method C. Diphenylmercury (3.54 g, 0.01 mol) was refluxed in 10 ml of dry ether under an argon atmosphere with 0.100 g (0.014 g-atom) of lithium wire for 6 hr. The solution was cooled, allowed to stand, and then standardized with 0.1 N hydrochloric acid. The solution was found to be 0.96 M in active organolithium.

Reaction of S-Aryldibenzothiophenium Fluoroborates with Organolithiums. A typical procedure follows with the results for the remaining cases tabulated in Tables VI and VII. S-Tolyldibenzothiophenium fluoroborate (50 mg, 0.14 mmol) was slurried in 25 ml of dry (freshly distilled from sodium benzophenone ketyl) tetrahydrofuran and cooled in a Dry Ice–isopropyl alcohol bath. An aliquot (0.104 ml, 0.140 mmol) of 1.33 M phenyllithium in ether was added dropwise over a 5-min period. The reaction mixture was allowed to stir at $-78°$ for 1 hr, warmed slowly to room temperature, and hydrolyzed with 25 ml of water. The products were extracted with ether using a total volume of 90 ml. The aqueous layer was further extracted with chloroform to recover sulfonium salt. The combined ether extracts were dried over anhydrous potassium carbonate, filtered, and evaporated *in vacuo* leaving 66 mg of crude product. Vpc analysis (20 ft × 1/8 in. 1% SE-30 on 60–80 mesh Chromosorb W column) of the crude reaction mixture indicated 38.5 mg (80.9% yield) of 2-p-tolylthio-o-terphenyl and 2.5 mg (5.1%) of 4''-methyl-2-phenylthio-o-terphenyl. No 4-methylbiphenyl or dibenzothiophene could be detected by vpc on a 5 ft × 0.25 in. 10% SE-30 60–80 mesh Chromosorb W column. Evaporation of the chloroform extracts yielded approximately 1 mg (2% recovery) of sulfonium salt. A duplicate experiment using 54 mg (0.15 mmol) of S-(p-tolyl)dibenzothiophenium fluoroborate and 0.112 ml (0.15 mmol) of 1.33 M phenyllithium produced 43.1 mg (88.8%) of 2-p-tolylthio-o-terphenyl and 2.5 mg (5.2%) of 4''-methyl-2-phenylthio-o-terphenyl with recovery of approximately 0.8 mg (1.5%) of starting sulfonium salt. In most cases, examination of recovered sulfonium salt revealed only the starting salt. Spectral data were obtained on the mixture of the two products collected from vpc: ir (CCl₄) ν 3067 (ArH), 2967 (CH₃), 692 (aromatic); uv λ_{max}^{EtOH} 320 nm (ϵ 1520), 280 (10,600), 255 (17,900); nmr (CCl₄) δ 2.36 (3 H, s, CH₃Ar), 6.65–7.50 (17 H, m, ArH); nmr (C₆O₆) δ 2.00 (3 H, s with small shoulder at slightly lower field; CH₃Ar), 6.65–7.60 (17 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 352.13266 (calcd for C₂₅H₂₀S, 352.12856) (14), 243 (6), 229 (19), 228 (18), 223 (18), 184 (100).

Spectral and Analytical Data. 4''-Methyl-2-p-tolylthio-o-terphenyl: ir (CCl₄) ν 3067 (ArH), 3030 (ArH), 2933 (CH₃), 2847 (CH₃), 1488 (aromatic), 1460 (aromatic), 1034 (para-disubst aromatic); uv λ_{max}^{EtOH} 285 nm sh (ϵ 9250), 252 (16,400); nmr (C₆F₇) δ 2.33 (3 H, s, CH₃Ar), 6.6–7.5 (16 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 366 (M⁺, 100), 243 (42), 228 (65), 184 (67), 119 (100), 117 (100), 82 (52).

2-p-Anisylthio-o-terphenyl: ir (CCl₄) ν 3077 (ArH), 2941 (CH₃), 2825 (ArOCH₃), 1493 (aromatic), 1460 (aromatic), 1290 (=COCH₃),

Table VI. Reaction Details for S-Aryldibenzothiophenium Fluoroborates and Aryllithiums[a]

Ar	Wt, mg	mmol	Ar¹	ml	M	mmol	Dibenzothiophene Wt, mg	%	Ar-Ar¹ Wt, mg	%	5b Wt, mg	%	5a Wt, mg	%	Recovered sulfonium salt Wt, mg	%	Vpc conditions
C_6H_5	50	0.15	$p\text{-}CH_3C_6H_4$	0.108	1.35	0.15					1.7	3.4	24.6	48.0	5	10	h, i
	150	0.44		0.324	1.35	0.44					4.5	3.2	101.0	69.0	14	9	
$p\text{-}CH_3C_6H_4$	90	0.26	$p\text{-}CH_3C_6H_4$	0.45	0.57	0.26					16	18.1[a]	b	b			
C_6H_5	50	0.15	$p\text{-}CH_3OC_6H_4$	0.197	0.74	0.15							14	26	31	62	h, i
	50	0.15		0.21	0.80	0.15							10	19	39	78	
	50[c]	0.15		0.21	0.80	0.15							18	40	23	46	
	50[d]	0.15		0.21	0.78	0.15							2	4	31	62	
$p\text{-}CH_3OC_6H_4$	50	0.13	C_6H_4	0.98	1.33	0.13					23	47			12	24	h, i
	50	0.13		0.98	1.33	0.13					21	43			12	24	
	50[c]	0.13		0.98	1.33	0.13					32	66			10	20	
	50[d]	0.13		0.98	1.33	0.13					0.9	2			42	84	
	50[e]	0.13		0.17	0.78	0.13					20.7	39			30	60	
C_6H_5	50	0.15	$m\text{-}CF_3C_6H_4$	0.19	0.79	0.15					12.9	22			25	50	h, j
	50	0.15		0.19	0.79	0.15					11.8	46			23	46	
	50[e]	0.15		0.35	0.4	0.15	0.8	2.8	1.2	3.6	10.2	20.8			34	68	
	50[d]	0.15		0.35	0.4	0.15	0.3	1	0.3	1	5.5	9.3			34	68	
$m\text{-}CF_3C_6H_4$	50	0.12	C_6H_5	0.09	1.33	0.12	2.7	12.2	3.5	13[f,g]			10.2	20.4	6.4	13	h, j
	50	0.12		0.09	1.33	0.12	3.2	14.2	3.5	13			12.2	24.5	4	8	
	50[c]	0.12		0.09	1.33	0.12	3.9	17.7	3.8	14.3			12.8	26.2			
	50[d]	0.12		0.09	1.33	0.12	0.2	1					1.6	3.4	24	49	
	50[e]	0.14		0.143	0.96	0.14	0.8	2.8	0.7	2.7			38.7	71	5	8	
$m\text{-}CF_3C_6H_4$	50	0.12	$m\text{-}CF_3C_6H_4$	0.16	0.75	0.12	2.0	8.7	3.2	8.8[g]	14	24	b	b			j
C_6H_5	50	0.15	$p\text{-}CF_3C_6H_4$	0.24	0.6	0.15	1.05	2.5			25.5	51			21	42	
	28	0.08		0.14	0.6	0.08	0.2	1.6	0.3	1.6[f,g]	37.2	62.6			17	34	
$p\text{-}CF_3C_6H_4$	50	0.12	C_6H_5	0.09	1.33	0.12	0.3	1.5					42.5	86.8	1	2	h, j
	50	0.12		0.09	1.33	0.12	0.5	2					41	83.5	2	4	
$p\text{-}CF_3C_6H_4$	150	0.36	$p\text{-}CF_3C_6H_4$	0.7	0.5	0.35	15.8	24	20	21	44	39	b	b			h

[a] All reactions at $-78°$ unless otherwise noted. [b] Does not apply. [c] Reaction run at $-20°$ utilizing a calcium chloride–water–Dry Ice bath. [d] Reaction performed at $-100°$ utilizing liquid nitrogen–ether slush. [e] Reaction performed utilizing phenyllithium generated from diphenylmercury. [f] Compound compared with independently synthesized material. [g] See J. Lichtenberger, *Bull. Soc. Chim. Fr.*, 915 (1962); D. H. Hey, F. C. Saunders, and G. H. Williams, *J. Chem. Soc.*, 554 (1961). [h] A 5 ft × 0.25 in. 10% SE-30 on 60–80 mesh Chromosorb W column was employed. [i] A 20 ft × $^1/_8$ in. 1% SE-30 on 60–80 mesh Chromosorb W column was employed. [j] A 10 ft × 0.25 in. 1% SE-30 on 60–80 mesh Chromosorb W column was employed.

Table VII. Details for Reaction of S-Aryldibenzothiophenium Fluoroborates and Vinyllithiums

Ar	Wt, mg	mmol	R	ml	M	mmol	Dibenzothiophene Wt, mg	%	Ar//R Wt, mg	%	9 Wt, mg	%	10 Wt, mg	%	Recovered sulfonium salt Wt, mg	%	Vpc conditions
$p\text{-}CH_3C_6H_4$	150	0.41	H	0.33	1.25	0.41	12.2	6.3	9.5	5.9[b]	6.8	7.4[a]	27.2	29.6[a]	46.5	31	e, f
$p\text{-}CH_3OC_6H_4$	150	0.40	H	0.32	1.25	0.40	2.7	3.6	2.6	4.9[b,c]	11.5	9.1	70.1	56.4			g
	50	0.13	CH_3	0.43	0.30	0.13							23	28			g, h
$m\text{-}CF_3C_6H_4$	100	0.24	H	0.19	1.25	0.24	28	62	22	53[d]	2.5	2.9					g
	50	0.12	CH_3	0.40	0.30	0.12	5.2	23.6	4.7	20.9	5.7	12.8					g-i
$p\text{-}CF_3C_6H_4$	150	0.36	H	0.29	1.25	0.36	64.5	98	61.7	99	7.7	2.9					j

[a] Yields obtained from isolated material of a mixture of the two isomers. Ratio determined by vpc. [b] Structure confirmed by comparison to an authentic sample. [c] W. H. Saunders, Jr., and R. A. Williams, *J. Amer. Chem. Soc.*, 79, 3712 (1957). [d] L. E. Coleman, Jr., and W. S. Durrell, *J. Org. Chem.*, 23, 1211 (1958); P. Tarrant and R. E. Taylor, *ibid.*, 24, 238 (1959). [e] A 20 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W column was employed. [f] A 10 ft × 0.25 in. 1% SE-30 on 60–80 mesh Chromosorb W column was employed. [g] A 5 ft × 0.25 in. 10% SE-30 on 60–80 mesh Chromosorb W column was employed. [h] A 5 ft × 0.25 in. 5% SE-30 on 60–80 mesh Chromosorb W column was employed. [i] A 10 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W column was employed. [j] A 10 ft × 0.25 in. 10% SE-30 on 60–80 mesh Chromosorb W column was employed.

1242 (=COC-), 1031 (=COC-), 697 (aromatic); uv λ_{max}^{EtOH} 283 nm (ϵ 7300), 255 (11,400), 230 (21,572); nmr (CCl_4) δ 3.71 (3 H, s, CH_3OAr), 6.7 (1/2 of AA'BB' pattern), 7.13 (5 H, bs, C_6H_5), 6.85–7.45 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 368.12709 (calcd for $C_{25}H_{20}OS$, 368.12338) (100), 229 (26), 228 (29), 139 (26).

3''-Trifluoromethyl-2-phenylthio-*o*-terphenyl: ir (CCl_4) ν 3077 (ArH), 1333 (asym CF_3Ar), 1325 (sym CF_3AR), 1164 (asym CF_3Ar), 1130 (asym CF_3Ar), 701 (aromatic); uv λ_{max}^{EtOH} 275 (ϵ 7750), 255 (16,600), 235 (23,900); nmr (CCl_4) δ 6.8–7.5 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 406.09835 (calcd for $C_{25}H_{17}F_3S$, 406.100296) (100), 298 (12), 297 (19), 261 (8), 257 (8), 184 (8).

3''-Trifluoromethyl-2-(*m*-trifluoromethylphenylthio)-*o*-terphenyl:

ir (CCl_4) ν 3077 (ArH), 1323 (sym CF_3Ar), 1166 (asym CF_3Ar), 1129 (asym CF_3Ar), 902 (1,3-disubst aromatic), 695 (aromatic); uv λ_{max}^{EtOH} 280 nm sh (ϵ 7100), 255 sh (14,800), 235 (20,100); nmr (CCl_4) δ 7.1–7.6 (m, ArH); mass spectrum m/e (70 eV) (rel intensiy) 474.08665 (calcd for $C_{26}H_{16}F_6S$, 474.08768) (22), 290 (81), 184 (100).

4''-Trifluoromethyl-2-phenylthio-*o*-terphenyl: ir (CCl_4) ν 303 (ArH), 1322 (asym CF_3Ar), 1166 (sym CF_3AR), 1026 (sym CF_3Ar), 888 (aromatic); uv λ_{max}^{EtOH} 284 nm (ϵ 3500), 257 (8000), 248 (8400), 235 (12,400); nmr (CCl_4) δ 6.67–7.61 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 406.10030 (calcd for $C_{25}H_{17}SF_3$, 406.10029) (100), 296 (20), 228 (24).

4''-Trifluoromethyl-2-(*p*-trifluoromethylphenylthio)-*o*-terphenyl:

ir (CCl$_4$) ν 3077 (ArH), 1328 (asym CF$_3$Ar), 1170 (sym CF$_3$Ar), 1130 (sym CF$_3$Ar); uv λ_{max}^{EtOH} 285 sh (ϵ 10,189), 255 (21,795), 236 (27,332); nmr (CCl$_4$) δ 6.80 (1/2 of AA'BB' pattern) and 7.0–7.55 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 474.08895 (calcd for C$_{26}$H$_{16}$SF$_6$, 474.08759) (100), 297 (6), 296 (40), 228 (70), 184 (16).

3,3'-Ditrifluoromethylbiphenyl:[18] ir (CCl$_4$) ν 1319 (sym CF$_3$Ar), 1168 (asym CF$_3$Ar), 1134 (asym CF$_3$AR), 700 (aromatic); uv λ_{max}^{EtOH} 322 nm (ϵ 260), 284 (1570), 235 (17,500), 237 sh (15,670); nmr (CCl$_4$) δ 7.4–7.9 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 290.05503 (calcd for C$_{10}$H$_8$F$_6$, 290.05301) (100), 271 (11), 145 (8), 69 (15).

4,4'-Ditrifluoromethylbiphenyl: ir (CCl$_4$) ν 2985 (ArH), 1325 (asym CF$_3$Ar), 1170 (sym CF$_3$Ar); uv λ_{max}^{EtOH} 253 nm (ϵ 18,000); nmr (CCl$_4$) δ 7.67 (6 s, ArH); mass spectrum m/e (70 eV) (rel intensity) 290.05503 (calcd for C$_{14}$H$_8$F$_6$, 290.05301) (100), 271 (19).

2-Vinyl-2'-p-tolylthiobiphenyl: ir (CCl$_4$) ν 3077 (=CH–), 905 (C=CH$_2$); uv λ_{max}^{EtOH} 284 nm (ϵ 2300), 248 (6800), 235 sh (8700), 215 (13,200); nmr (CCl$_4$) δ 2.27 (3 H, s, CH$_3$Ar), 5.05 (1 H, dd, J = 10, 2.5 Hz, –HC=), 6.42 (1 H, dd, J = 17, 10 Hz, –HC=), 6.52 (1 H, dd, J = 17, 2.5 Hz, ArCH=), 6.8–7.32 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 302.11270 (calcd for C$_{21}$H$_{18}$S, 302.11291) (100), 301 (50), 276 (45), 211 (20), 180 (83), 179 (78), 178 (45), 177 (32), 176 (36), 164 (27), 91 (31), 57 (31).

4''-Methyl-2-vinylthio-o-terphenyl: ir (CCl$_4$) ν 2933 (CH$_3$–), 1458 (aromatic); uv λ_{max}^{EtOH} 322 nm (ϵ 250), 285 (1500), 261 (3300), 252 (4000), 235 sh (7300), 231 (7800), 212 sh (8800); nmr (CCl$_4$) (100 MHz) δ 2.37 (3 H, s, CH$_3$Ar), 5.11 (1 H, dd, J = 12, 3 Hz, –HC=), 5.66 (1 H, dd, J = 18, 3 Hz, –HC=), 6.54 (1 H, dd, J = 18, 12 Hz, ArSCH=), 6.8–7.6 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 302.11476 (calcd for C$_{21}$H$_{18}$S, 302.11291) (69), 243 (14), 229 (6), 228 (23), 181 (68), 179 (100).

2-Vinyl-2'-p-anisylthiobiphenyl and 4''-methoxy-2-vinylthio-o-terphenyl: ir (CCl$_4$) ν 3077 (–HC=), 2941 (CH$_3$), 2841 (CH$_3$O), 1587 (aromatic), 1242 (CH$_3$OC=), 1033 (CH$_3$OC); uv λ_{max}^{EtOH} 252 nm (ϵ 8040), 230 (11,900); nmr (CCl$_4$) δ 3.49 (3 H, s, CH$_3$OAr), 5.02 (1 H, dd, J = 11, 1.5 Hz, –HC=), 5.52 (1 H, dd, J = 17, 1.5 Hz, –HC=), 6.40 (1 H, dd, J = 17, 11 Hz, ArCH=), 6.7–7.6 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 318.10766 (calcd for C$_{21}$H$_{18}$SO, 318.10774) (70), 197 (23), 179 (100), 178 (81). The two isomers were further characterized by desulfurization.

2-(1''-Propenyl)-2'-p-anisylthiobiphenyl: ir (CCl$_4$) ν 1587 (aromatic), 1493 (aromatic), 1460 (aromatic), 1244 (=COC–), 1034 (=COC–); uv λ_{max}^{EtOH} 255 nm (ϵ 8900), 228 (13,200); nmr (CCl$_4$) δ 2.78 (3 H, dd, J = 7, 1.5 Hz, CH$_3$C=), 3.76 (3 H, s, CH$_3$O), 5.4 (1 H, dq, J = 13, 7 Hz, –HC=), 6.11 (1 H, dd, J = 13, 1.5 Hz, –HC=), 6.7 (1/2 of AA'BB', ArH superimposed on complex multiplet) and 6.9–7.5 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 332.12613 (calcd for C$_{22}$H$_{20}$SO, 332.12348) (100), 292 (9), 291 (9), 193 (63), 192 (40), 178 (61), 165 (19), 151 (12), and 139 (17).

3''-Trifluoromethyl-2-vinylthio-o-terphenyl: ir (CCl$_4$) ν 3077 (=CH), 1332 (sym CF$_3$Ar), 1166 (asym CF$_3$Ar), 1130 (asym CF$_3$Ar), 701 (aromatic); uv λ_{max}^{EtOH} 320 nm (ϵ 308), 283 (6500), 275 (8000), 228 (25,900); nmr (CCl$_4$) δ 5.20 (1 H, dd, J = 16, 1.5 Hz, =CH–), 5.28 (1 H, dd, J = 10, 1.5 Hz, –HC=), 7.0–7.6 (13 H, m, ArH and ArCH=); mass spectrum m/e (70 eV) (rel intensity) 356.08462 (calcd for C$_{21}$H$_{15}$SF$_3$, 356.08464) (4), 330 (34), 329 (21), 328 (18), 297 (24), 296 (32), 229 (14), 228 (33), 57 (100), 55 (95).

m-Trifluoromethylstyrene:[19] ir (CCl$_4$) ν 3067 (=CH– or ArH), 1328 (sym CF$_3$Ar), 1245 (asym CF$_3$Ar), 1168 (asym CF$_3$Ar), 1133 (asym CF$_3$Ar), 985 (–HC=CH$_2$), 697 (aromatic); uv λ_{max}^{EtOH} 294 nm (ϵ 330), 283 (496), 275 (496), 256 sh (4100), 247 (660), 240 sh (6300), 214 sh (7300); nmr (CCl$_4$) δ 5.28 (1 H, dd, J = 11, 1 Hz, –HC=), 5.75 (1 H, dd, J = 17, 1 Hz, –HC=), 6.69 (1 H, dd, J = 17, 11 Hz, ArCH=), 7.3–7.7 (4 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 172.04988 (calcd for C$_9$H$_7$F$_3$, 172.04998) (100), 145 (6), 103 (21).

3''-Trifluoromethyl-2-(1'''-propenylthio)-o-terphenyl: ir (CCl$_4$) ν 2959 (CH$_3$), 2874 (CH$_3$), 1335 (asym CF$_3$Ar), 1170 (sym, CF$_3$Ar), 1133 (sym CF$_3$Ar); uv λ_{max}^{EtOH} 235 nm (ϵ 46,200); nmr (CCl$_4$) δ 1.68 (3 H, m, –CH$_3$C=), 5.80 (2 H, m, –HC=), 6.8–7.6 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 370.09980 (calcd for C$_{22}$H$_{17}$SF$_3$, 370.10029) (12), 329 (22), 328 (13), 135 (100), 69 (36).

1-(m-Trifluoromethylphenyl)propene: ir (CCl$_4$) ν 2941 (CH$_3$), 1335 (asym CF$_3$Ar), 1166 (sym CF$_3$Ar), 1131 (sym CF$_3$AR); uv

λ_{max}^{EtOH} 250 nm (ϵ 2500), 225 (1650); nmr (CCl$_4$) δ 1.88 (3 H, d, J = 7 Hz, CH$_3$C=), 6.3 (1 H, d, J = 12 Hz, =CH–), 7.40–7.60 (5 H, m, ArH and ArCH=); mass spectrum m/e (70 eV) (rel intensity) 186.06556 (calcd for C$_{10}$H$_9$F$_3$, 186.06563) (43), 167 (18), 117 (73), 57 (100), 55 (87).

4''-Trifluoromethyl-2-vinylthio-o-terphenyl: ir (CCl$_4$) ν 1321 (asym CF$_3$Ar), 1166 (sym CF$_3$Ar), 1126 (sym CF$_3$Ar); uv λ_{max}^{EtOH} 248 nm sh (ϵ 16,800), 230 sh (23,300); nmr (CCl$_4$) δ 5.15 (1 H, d, J = 17 Hz, –HC=), 5.19 (1 H, d, J = 10 Hz, ArCM=), 6.92–7.55 (12 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 356.08465 (calcd for C$_{20}$H$_{15}$SF$_3$, 356.08467) (66), 355 (41), 331 (23), 330 (100), 329 (69), 328 (29), 229 (48), 184 (38), 139 (48), 69 (84).

2-p-Trifluoromethylstyrene: ir (CCl$_4$) ν 1323 (sym CF$_3$Ar), 1166 (asym CF$_3$Ar), 1129 (asym CF$_3$Ar), 843 (para-disubst aromatic); uv λ_{max}^{EtOH} 292 nm (ϵ 520), 285 (1040), 280 (1040), 260 sh (7800), 250 (12,500), 238 sh (10,900), 215 sh (10,900); nmr (CCl$_4$) δ 5.30 (1 H, d, J = 10 Hz, –HC=), 5.73 (1 H, d, J = 18 Hz, –HC=), 6.70 (1 H, dd, J = 18, 10 Hz, ArCH=), 7.15–7.7 (4 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 172.0478 (calcd for C$_9$H$_7$F$_3$, 172.04998) (100), 103 (17), 69 (26).

Desulfurizations. Nickel aluminum alloy powder (75 g) was added over a 45-min period to a stirred solution of 97 g of sodium hydroxide in 375 ml of water warmed to 75°. The water temperature was maintained at about 75° during the addition of the alloy. The mixture was allowed to digest for 30 min during which time the temperature approached room temperature. The supernatant liquid was decanted and the catalyst transferred to a 1-l. graduated cylinder and washed with a continuous flow of water for about 20 min. The water was decanted and the catalyst was washed three times with 95% ethanol and finally three times with absolute ethanol. The catalyst was stored under absolute ethanol.

A typical procedure follows. The results for the remaining cases are summarized in Table VIII. 2-p-Anisylthio-o-terphenyl (51 mg, 0.14 mmol) was refluxed with 600 mg of Raney nickel in 6 ml of absolute ethanol for 20 min. The mixture was cooled and filtered, and the solvent was removed *in vacuo* leaving 26 mg (80%) of o-terphenyl (compared by vpc and nmr to authentic material).[20]

Spectral Properties. 3-Trifluoromethyl-o-terphenyl: ir (CCl$_4$) ν 1321 (sym CF$_3$Ar), 1166 (asym CF$_3$Ar), 1129 (asym CF$_3$Ar); uv λ_{max}^{EtOH} 272 nm (ϵ 950), 265 (1420), 215 (16,500); nmr (acetone-d_6) δ 7.3–7.5 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 298.09951 (calcd for C$_{19}$H$_{13}$F$_3$, 298.09951) (100), 229 (21).

4-Trifluoromethyl-o-terphenyl: ir (CCl$_4$) ν 2941 (ArH), 1621 (aromatic), 1328 (asym CF$_3$Ar), 1168 (sym CF$_3$Ar), 1130 (sym CF$_3$Ar), 698 (aromatic); uv λ_{max}^{EtOH} 250 nm (ϵ 4500), 225 sh (6200), 220 (12,400); nmr (acetone-d_6) δ 7.05–7.60 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 298.09423 (calcd for C$_{19}$H$_{13}$F$_3$, 298.09686) (30), 229 (10), 228 (18), 145 (13), 117 (100), 104 (93), 71 (100).

2-Ethylbiphenyl: ir (CCl$_4$) ν 3077 (ArH), 3040 (ArH), 2976 (aliph CH), 2941 (aliph CH), 2882 (aliph CH), 1481 (aromatic), 699 (aromatic); uv λ_{max}^{EtOH} 227 nm (ϵ 8200); nmr (CCl$_4$) δ 1.08 (3 H, t, J = 7 Hz, CH$_3$CH$_2$), 2.53 (2 H, q, J = 7 Hz, CH$_2$CH$_3$), 7.0–7.45 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 182.10848 (calcd for C$_{14}$H$_{14}$, 182.10954) (70), 167 (100), 91 (14), 77 (11).

2-n-Propylbiphenyl: ir (CCl$_4$) ν 3077 (ArH), 3030 (ArH), 2976 (aliph CH), 2941 (aliph CH), 2882 (aliph CH), 1479 (aromatic), 699 (aromatic); uv λ_{max}^{EtOH} 234 nm (ϵ 9000); nmr (CCl$_4$) δ 0.75 (3 H, t, J = 7 Hz, CH$_3$CH$_2$), 1.43 (2 H, apparent sextuplet, J = 7 Hz, CH$_3$CH$_2$CH$_2$), 2.5 (2 H, t, J = 7 Hz, CH$_2$CH$_2$Ar), 7.11 (4 H, bs, ArH), 7.25 (5 H, 6 s, Ph); mass spectrum m/e (70 eV) (rel intensity) 196.12519 (calcd for C$_{15}$H$_{16}$, 196.12519) (49), 167 (100), 77 (10).
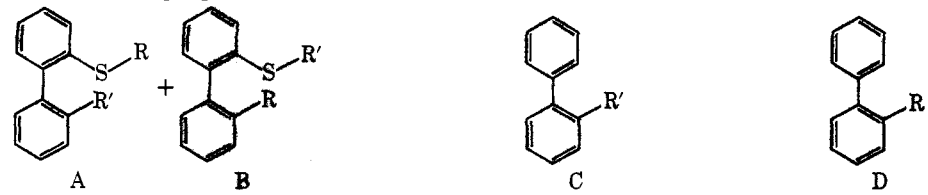
Preparation of 4-Methyl-o-terphenyl.[15] To a solution of 2-phenylcyclohexanone (544 mg, 3 mmol) in 35 ml of dry ether, 5.36 ml (3 mmol) of 0.56 M p-tolylmagnesium bromide was added at room temperature over a 5-min period. The solution was allowed to stir for 1 hr and then hydrolyzed with 200 ml of saturated aqueous ammonium chloride solution. Sodium chloride was added and the products were extracted with 200 ml of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed *in vacuo*. The crude material was separated on tlc (20 cm × 20 cm × 1.25 mm plate) using chloroform as an eluent. The bands were removed, washed with ethyl acetate and filtered, and the solvent was removed *in vacuo* leaving 724 mg (86%) of 1-p-tolyl-2-phenylcyclohexanol: ir (CCl$_4$) ν 3623 (OH), 3030 (ArH), 2941 (aliph CH), 1495 (aromatic),

(18) J. Lichtenberger, *Bull. Soc. Chim. Fr.*, 915 (1962); D. H. Hey, F. C. Saunders, and G. H. Williams, *J. Chem. Soc.*, 554 (1961).

(19) L. E. Coleman, Jr., and W. S. Durrell, *J. Org. Chem.*, **23**, 1211 (1958); P. Tarrant and R. E. Taylor, *ibid.*, **24**, 238 (1959).

(20) J. S. Edmunds and R. A. W. Johnstone, *J. Chem. Soc.*, 2898 (1965).

Table VIII. Desulfurization of Coupling Products

		A + B		C		D		Vpc
R	R'	Wt, mg	mmol	Wt, mg	%	Wt, mg	%	conditions
p-CH₃C₆H₄	C₆H₅	21	0.05	15.0	72.1e	1.0	4.9	g
	p-CH₃C₆H₄	16	0.04	8	7.5e		a	g
	-CH=CH₂	30	0.10	13.2	88.9	2.8	4.7	g
p-CH₃OC₆H₄	C₆H₅	51	0.14	26	80e			
	-CH=CH₂	80	0.25	c	86b	c	4	f
p-CF₃C₆H₄	C₆H₅	19	0.04			11.4	82	i
	p-CF₃C₆H₄	22	0.05	14	100		a	i
	-CH=CH	7.7	0.02			2.1	32	h
m-CF₃C₆H₄	C₆H₅	29	0.07			20	92	i
	m-CF₃C₆H₄	20	0.04	12.4	96		a	i
	-CH=CH₂	4.8	0.01			1.5	50	h

a Not applicable in this case. b R' = CH₃CH₂. c Absolute yields not determined. d R' = CH₃CH₂CH₂. e Compared with authentic sample. f A 20 ft × ⅛ in. 1% SE-30 on 60-80 mesh Chromosorb W column was employed. g A 5 ft × 0.25 in. 10% SE-30 on 60-80 mesh Chromosorb W column was employed. h A 5 ft × 0.25 in. 3% SE-30 on 60-80 mesh Chromosorb W column was employed. i A 10 ft × 0.25 in. 10% SE-30 on 60-80 mesh Chromosorb W column was employed.

698 (aromatic); uv λ_{max}^{EtOH} 255 nm (ε 3500), 223 (6800); nmr (CCl₄) δ 1.5-2.5 (13 H, m, HO, CH₃Ar, (CH₂)₄CHPh), 6.65-7.20 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 266.16499 (calcd for C₁₉H₂₄O, 266.16706) (43), 133 (100), 129 (44), 118 (66), 91 (37).

1-p-Tolyl-2-phenylcyclohexanol (355 mg, 1.3 mmol) was refluxed for 3 hr in 25 ml of benzene containing 30 mg of p-toluenesulfonic acid. The mixture was cooled and poured into 60 ml of sodium bicarbonate solution. The products were extracted with 60 ml of ether. The combined ether extracts were dried over anhydrous potassium carbonate and filtered, and the solvent was removed in vacuo leaving a yellow oil. The crude material was separated by tlc (20 cm × 40 cm × 1.25 mm plate) using carbon tetrachloride as an eluent. The bands were removed by washing with ethyl acetate, and the solvent was removed in vacuo leaving 210 mg (64%) of olefins. The olefinic product was a mixture of 1-phenyl-2-p-tolylcyclohexene (28) (175 mg, 83.4%) and 1-p-tolyl-6-phenylcyclohexene (29) (35 mg, 16.6%) as determined by nmr using an internal standard (methylene chloride). The olefins were not separated but characterized as the mixture: ir (CCl₄) ν 3021 (ArH), 2924 (aliph CH), 697 (aromatic); uv λ_{max}^{EtOH} 252 nm (ε 12,900); nmr (CCl₄) δ 1.18-2.5 (11 H, m, -(CH₂)₄- and CH₃ with singlet at 2.15 for CH₃Ar), 6.30 (6 t, J = 5 Hz, -HC= of 29), 6.7-7.5 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 248.1564 (calcd for C₁₉H₂₀O, 248.15649) (1), 182 (100), 91 (11), 77 (6).

The mixture of 1-phenyl-2-p-tolylcyclohexene and 1-p-tolyl-6-phenylcyclohexene (50 mg, 2 mmol) was heated with 200 mg of sulfur for 2 hr at 260° in a sealed tube. The tube was cooled and carefully opened, and the products were isolated by tlc using Skelly B as an eluent. The bands were removed by washing with ethyl acetate, and the solvent was removed in vacuo leaving 30 mg (61%) of 4-methyl-o-terphenyl: ir (CCl₄) ν 3077 (ArH), 3040 (ArH), 2941 (CH₃Ar), 1006 (p-disubst aromatic), 698 (aromatic); uv λ_{max}^{EtOH} 244 (sh) (ε 12,400), 236 (24,800); nmr (CCl₄) δ 2.30 (3 H, s, ArCH₃), 6.97 (4 H, s, ArHO), 7.18 (5 H, 6 s, Ph), 7.40 (4 H, 2, ArH); mass spectrum m/e (70 eV) (rel intensity) 244.12276 (calcd for C₁₉H₁₆, 244.12519) (100), 229 (70), 228 (45).

Preparation of p-Methoxybiphenyl.[21] Using the above procedure, 500 mg (5.1 mmol) of cyclohexanone in 25 ml of dry tetrahydrofuran was reacted with 12 ml (5.1 mmol) of 0.425 M p-anisylmagnesium bromide. Distillation of the crude material at 103-105° (0.4 mm) yielded 1.3 g (60%) of 1-p-anisylcyclohexene: ir (CCl₄) ν 3049 (ArH), 3012 (ArH), 2950 (aliph CH), 2849 (CH₃O), 1613 (C=C), 1513 (aromatic), 1250 (CH₃OC), 1042 (CH₂OC); uv λ_{max}^{EtOH} 290 nm sh (ε 880), 254 (18,800); nmr (CCl₄) δ 1.4-1.97 (4 H, m, -CH₂CH₂-), 1.97-2.5 (4 H, m, =CCH₂-), 3.72 (3 H, s,

(21) T. Inukai, K. Kobayashi, and O. Simamura, Bull. Chem. Soc. Jap., 35, 1576 (1962); J. I. G. Cadogan, J. Chem. Soc., 4257 (1962).

CH₃OAr), 5.88 (1 H, m, =CH-), 6.92 (4 H, AA'BB' pattern, J = 9, 2 Hz, ArH); mass spectrum m/e (70 eV) (rel intensity) 188.12055 (calcd for C₁₃H₁₆O, 188.12011) (64), 173 (12), 119 (96), 117 (100).

1-p-Anisylcyclohexene (140 mg, 0.74 mmol) was dehydrogenated as before with ~280 mg of sulfur. Isolation of the product from tlc using Skelly B as an eluent yielded 40 mg (34%) of p-methoxybiphenyl: ir (CCl₄) ν 3077 (ArH), 3049 (ArH), 2941 (CH₃O), 2841 (=COCH₃), 1616 (aromatic), 1517 (aromatic), 1245 (CO), 831 (para-disubst aromatic), 696 (aromatic); uv λ_{max}^{EtOH} 252 nm (ε 16,670); nmr (CCl₄) δ 3.73 (3 H, s, CH₃O), 6.79 (1/2 of AA'BB' pattern, J = 9 Hz, ArH) and 7.30 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 184.08932 (calcd for C₁₃H₁₂O, 184.08881) (100), 169 (9).

Preparation of 4-Methoxy-o-terphenyl.[20] Using the above procedure, 2-phenylcyclohexanone (400 mg, 0.23 mmol) in 50 ml of dry ether was reacted with 3.8 mg (0.23 mmol) of 0.6 M p-anisylmagnesium bromide. Isolation of the product by tlc using chloroform as the eluent yielded 308 mg (36%) of 1-(p-anisyl)-2-phenylcyclohexanol: ir (CCl₄) ν 3597 (OH), 3040 (ArH), 2950 (aliph CH), 2965 CH₃O), 1603 (aromatic), 1506 (aromatic), 1242 (CH₃-OC), 1175 (CO), 698 (aromatic); uv λ_{max}^{EtOH} 282 nm (ε 2300), 267 (3000), 225 sh (8400); nmr (CCl₄) δ 1.5-2.5 (9 H, m, (CH₂)₄CHPh), 3.72 (3 H, s, CH₃OAr), 6.63 (1/2 of AA'BB' pattern, J = 8, <1 Hz, ArH) and 6.63-7.4 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 282.16446 (calcd for C₁₉H₂₀O₂, 282.16197) (19), 264 (16), 150 (100), 135 (100), 91 (19), 77 (16).

Dehydration of 1-(p-anisyl)-2-phenylcyclohexanol (99 mg, 0.32 mmol) was achieved as described above to give, after tlc purification using carbon tetrachloride as the eluent, 60 mg (65%) of 1-(p-anisyl)-2-phenylcyclohexene: ir (CCl₄) ν 2941 (aliph CH), 2841 (CH₃O), 1605 (C=C), 1506 (aromatic), 1239 (CH₃OC), 1176 (CO), 697 (aromatic); uv λ_{max}^{EtOH} 255 nm (ε 9200); nmr (CCl₄) δ 1.6-2.0 (4 H, m, -CH₂CH₂-), 2.0-2.55 (4 H, m, -CH₂C=), 3.68 (3 H, s, CH₃O), 6.72 (1/2 of AA'BB' pattern, J = 10, <1 Hz, ArH) and 6.85-7.3 (9 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 264.15141 (calcd for C₁₉H₂₀O, 264.15140) (100), 236 (7), 235 (10), 91 (29), 77 (10).

Dehydrogenation of 1-(p-anisyl)-2-phenylcyclohexene (50 mg, 0.1 mmol) as before generated, after purification by tlc using Skelly B as the eluent, 35 mg (71%) of 4-methoxy-o-terphenyl: ir (CCl₄) ν 3077 (ArH), 3030 (ArH), 2959 (CH₃), 2841 (CH₃OAr), 1610 (aromatic), 1511 (aromatic), 1475 (aromatic), 1245 (CH₃OC), 1175 (CO), 1041 (CH₃OC), 830 (1,4-disubst aromatic), 697 (aromatic); uv λ_{max}^{EtOH} 267 nm (ε 12,800), 242 (11,800); nmr (CCl₄) δ 3.61 (3 H, s, CH₃OAr), 6.86 (1/2 of AA'BB' pattern, J = 9.5, <1 Hz, ArH) and 7.02-7.50 (13 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 260.12163 (calcd for C₁₉H₁₆O, 260.12011) (100), 259 (13), 229 (25), 228 (13), 227 (13), 77 (7).

Preparation of m-Trifluoromethylbiphenyl.[18] Using the above method, 423 mg (4.3 mmol) of cyclohexanone was reacted with 8 ml

(4.3 mmol) of 0.54 M m-trifluoromethylphenylmagnesium bromide. Distillation of the crude product at 96-97° (0.5 mm) yielded 1.05 g (84%) of 1-m-trifluoromethylphenylcyclohexanol: ir (CCl₄) ν 3625 (OH), 3050 (ArH), 2950 and 2875 (aliphatic CH), 1325 (sym CF₃Ar), 1170 (asym CF₃Ar), 1130 (asym CF₃Ar), 702 (aromatic); uv λ$_{max}^{EtOH}$ 271 nm (ε 7300), 263 (8700), 257 (7500), 252 sh (6400); nmr (CCl₄) δ 1.4-2.0 (11 H, m, -(CH₂)₄- and OH), 7.3-7.9 (4 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 244.16381 (calcd for C₁₃H₁₃OF₃, 244.16381) (19), 201 (100), 189 (28), 173 (27), 145 (17), 91 (8), 81 (9), 69 (10), 57 (14), 55 (25).

1-m-Trifluoromethylphenylcyclohexanol (43) (335 mg, 1.32 mmol) was dehydrated as above into 105 mg (66%) of 1-m-trifluoromethylcyclohexene: bp 185° (0.5 mm); ir (CCl₄) ν 3049 (-HC=), 2950 (aliph CH), 2874 (aliph CH), 1330 (sym CF₃Ar), 1170 (asym CF₃Ar), 1130 (asym CF₃Ar), 897 (meta-subst aromatic), 698 (aromatic); uv λ$_{max}^{EtOH}$ 251 nm (ε 9100), 223 (8200); nmr (CCl₄) δ 1.4-1.95 (4 H, m, -(CH₂)₂-), 1.95-2.55 (4 H, m, -CH₂C=), 6.12 (1 H, m, -HC=), 7.2-7.65 (4 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 226.09721 (calcd for C₁₃H₁₃F₃, 226.09693) (100), 157 (16).

By the standard method, 1-m-trifluoromethylphenylcyclohexene (44) (26 mg, 0.12 mmol) was dehydrogenated to 18 mg (31%) of 1-m-trifluoromethylbiphenyl: bp 120° (0.5 mm); ir (CCl₄) ν 2941 (ArH), 1335 (sym CF₃Ar), 1170 (asym CF₃Ar), 1134 (asym CF₃Ar), 702 (aromatic); uv λ$_{max}^{EtOH}$ 248 nm (ε 14,700); nmr (CCl₄) δ 7.15-7.9 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 222.0661 (calcd for C₁₃H₉F₃, 222.0656) (100), 158 (8).

Preparation of p-Trifluoromethylbiphenyl. Utilizing the standard method, 423 mg (4.3 mmol) of cyclohexanone reacted with 13.9 ml (4.3 mmol) of 0.31 M p-trifluoromethylphenylmagnesium bromide to yield 630 mg (58%) of 1-p-trifluoromethylphenylcyclohexanol:

bp 95-97° (0.5 mm); ir (CCl₄) ν 3636 (OH), 3571-3333 (OH), 2941 (ArH), 2865 (aliph CH), 1325 (asym CF₃Ar), 1168 (sym CF₃Ar), 1130 (sym CF₃Ar), 971 (aromatic), 828 (para-disubst aromatic); uv λ$_{max}^{EtOH}$ 256 nm (ε 1000), 217 (6200); nmr (CCl₄) δ 1.2-2.4 (11 H, m, -(CH₂)₅- and OH), 7.57 (4 H, s, ArH); mass spectrum m/e (70 eV) (rel intensity) 244.10656 (calcd for C₁₃H₁₅F₃O, 244.10749) (12), 226 (23), 119 (94), 117 (100), 69 (8).

Dehydration of 1-p-trifluoromethylphenylcyclohexanol (630 mg, 2.6 mmol) was achieved by the standard method to yield, after purification by tlc using Skelly B as an eluent, 370 mg (63%) of 1-p-trifluoromethylphenylcyclohexene: ir (CCl₄) ν 2959 (ArH), 1328 (asym CF₃Ar), 1168 (sym CF₃AR), 1129 (sym CF₃Ar); uv λ$_{max}^{EtOH}$ 257 nm (ε 12,800), 223 (9500), 216 (11,700); nmr (CCl₄) δ 1.3-1.95 (4 H, m, -CH₂CH₂-), 1.95-2.50 (4 H, m, -CH₂C=), 6.08 (1 H, m, HC=), 7.1-7.7 (4 H, m, ArH); mass spectrum m/e (70 eV) (rel intensity) 226.09827 (calcd for C₁₃H₁₃F₃, 226.09693) (28), 219 (100), 157 (5).

Dehydrogenation of 1-p-trifluoromethylphenylcyclohexene (190 mg, 0.84 mmol) with 800 mg of sulfur as previously described, followed by tlc purification using Skelly B-hexane as the eluent, yielded 119 mg (64%) of p-trifluoromethylbiphenyl: ir (CCl₄) ν 1328 (asym CF₃Ar), 1170 (sym CF₃Ar), 1133 (sym CF₃Ar), 696 (aromatic); uv λ$_{max}^{EtOH}$ 253 nm (ε 15,300); nmr (CCl₄) δ 7.05-7.75 (m, ArH); mass spectrum m/e (70 eV) (rel intensity) 222.06790 (calcd for C₁₃H₉F₃, 222.06563) (100), 203 (6), 152 (12), 77 (5), 69 (9).

# Preparation of Cyclopropyldiphenylsulfonium and 2-Methylcyclopropyldiphenylsulfonium Fluoroborate and Their Ylides. Stereochemistry of Sulfur Ylides

Barry M. Trost* and Mitchell J. Bogdanowicz

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received February 23, 1973

Abstract: Preparation of 3-halopropyldiphenylsulfonium fluoroborate (halo, chloro, bromo, and iodo) followed by cyclization with either sodium hydride in tetrahydrofuran or potassium *tert*-butoxide in dimethyl sulfoxide-tetrahydrofuran makes cyclopropyldiphenylsulfonium fluoroborate readily available. In a similar fashion from 3-bromo- or 3-chlorobutyldiphenylsulfonium fluoroborate, 2-methylcyclopropyldiphenylsulfonium fluoroborate as either an 80:20 or 70:30 mixture of trans and cis isomers is abundantly available. Generation of the cyclopropylide under irreversible conditions revealed a half-life of approximately 2.5 min indicating no unusual stabilization compared to an acyclic sulfonium alkylide. The 2-methylcyclopropylide shows no loss of stereochemistry at carbon at 50° in methanol-water in the presence of sodium hydroxide under conditions in which complete H-D exchange readily occurs nor in condensation with ketones. Thus, cyclopentanone led to *trans*-2-methyl-1-(1'-cyclopentenyl)cyclopropanol (methyl and hydroxyl cis) upon condensation with the methylated ylide followed by ring opening of the oxaspiropentane with lithium diethylamide. Alternatively, condensation with acetone followed by ring opening with *n*-butyllithium led to a mixture of *trans*- and *cis*-2-methyl-1-(2'-methyl-2'-hexyl)cyclopropanol in a ratio reflecting the stereochemistry of the starting sulfonium salt mixture. On the other hand, the stereochemistry of the ylide appears to be lost in dimethyl sulfoxide in the presence of potassium hydroxide.

The utility of sulfur ylides in synthesis demands that substituted reactive ylides outside of the parent system be investigated.[1] The synthesis of the novel and potentially synthetically useful ylide **1** was achieved by the ligand exchange method *via* the slow addition of cyclopropyllithium to a −78° tetrahydrofuran slurry of triphenylsulfonium fluoroborate.[2] Addition
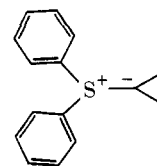
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of cyclohexanone to the solution quenched the yellow

(1) For existing reviews, see (a) C. Agami, *Bull. Soc. Chim. Fr.*, 1021 (1965); (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; (c) J. C. Block, *Ann. Chim. (Paris)*, 10, 419 (1965); (d) P. A. Lowe, *Chem. Ind. (London)*, 1070 (1970).

(2) (a) R. W. LaRochelle and B. M. Trost, *J. Amer. Chem. Soc.*, 93, 6077 (1971); (b) B. W. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Lett.*, 39, 3449 (1970).