Organic and Biological Chemistry

Reactions of Organolithiums with Arylsulfonium Salts[1]

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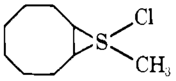
Abstract: The reaction of triarylsulfonium salts with organolithiums has been found to yield ligand coupling products. Thus, treatment of triphenylsulfonium salt with phenyl-, vinyl-, allyl-, and *tert*-butyllithium afforded biphenyl (diphenyl sulfide), styrene (diphenyl sulfide), allylbenzene (diphenyl sulfide), and biphenyl (*tert*-butylphenyl sulfide), respectively. The reactions of other arylsulfonium salts and other organolithiums proceed similarly. The coupling reaction requires both units to possess a π system and proceeds with retention of configuration at carbon. The evidence presented supports the intermediacy of sulfuranes in these reactions. This technique serves as a method to introduce aryl groups into organic compounds.

The isolation of several hydrocarbons and sulfides as side products from the generation of diphenylsulfonium allylide stimulated interest into the nature of the reaction of organolithiums with sulfonium salts.[4] Since sulfonium ylides are often synthesized by the action of an organolithium on a sulfonium salt,[5] the side reactions which occur during that process relate closely to the synthetic chemist's choice of reactants and reaction conditions. Thus, detailed knowledge of the reactions of organolithium compounds with sulfonium salts promised to suggest more efficient methods of ylide generation. Such a study also held promise to lead to new reactions of potential synthetic interest. From a mechanistic standpoint, it was of particular interest to determine the role played by pentacoordinated[6] sulfur compounds (sulfuranes) in the formation of these side products.

There is ample documentation of the chemistry of stable pentacoordinate compounds of elements in the same and adjacent columns as sulfur in the periodic chart. Wittig[7] and Hellwinkel[8] have prepared a series of seluranes and telluranes. Also, the chemistry of pentacoordinate antimony[9] and arsenic[10] compounds has been explored. The pentacoordinate compounds of phosphorus, in particular, have received detailed attention.[11]

The question of such pentacoordinate species in sulfur chemistry remains speculative despite extensive investigations. Several stable pentacoordinate sulfur compounds are known: $PhSF_3$, SF_4, SCl_4, SF_2Cl_2, and several others. All of these known compounds have highly electronegative groups as the ligands bound to sulfur. Aside from these few inorganic examples, pentacoordinate sulfur remains mainly a formalism employed in mechanistic rationalizations. This is especially the case in nucleophilic displacement reactions on electron-deficient sulfur. For example, in the reactions of Grignard reagents with sulfinate esters[12] and alkoxysulfonium salts[13] it is unclear whether these reactions are simply SN2 displacements as in the analogous transformations with substituted hydrocarbons, or involve discreet pentacoordinate intermediates. However, various workers have presented evidence to support the existence of such species in organosulfur chemistry in which at least one of the ligands is a highly electronegative group. Helmkamp[14] claims that he can observe the nmr spectrum of **1** when chloride ion is added to the corresponding episulfonium salt at −5°. Johnson[15] argues that alkoxyhalo sulfuranes such as **2**



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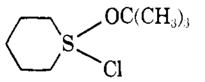

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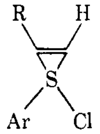

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are intermediates in the oxidation of sulfides to sulfoxides with *tert*-butyl hypochlorite. Also, Calo, *et al.*,[16] suggest that such species as **3** are formed as intermediates in the addition of sulfenyl chlorides to acetylenes.

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[1] For a preliminary communication of a portion of this work, see B. M. Trost, R. W. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969).

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[3] Author to whom all correspondence should be addressed.

[4] B. M. Trost and R. W. LaRochelle, *Tetrahedron Lett.*, 3327 (1968).

[5] For example, see J. Adams, L. Hoffman, Jr., and B. M. Trost, *J. Org. Chem.*, **35**, 1600 (1970), and E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).

[6] The term "pentacoordinate," we believe, is a more accurate description of this bonding situation than the common term "tetravalent." The use of "pentacoordinate" allows one to differentiate between a situation where four ligands and a nonbonding pair of electrons occupy the five coordination sites, and a situation such as in the sulfate anion where there are four ligands on sulfur, but where the valence at sulfur has not been increased above its usual level.

[7] G. Wittig and H. Fritz, *Justus Liebigs Ann. Chem.*, **577**, 39 (1952).

[8] (a) D. Hellwinkel and G. Fahrbach, *ibid.*, **72**, 1 (1968); (b) D. Hellwinkel and G. Fahrbach, *Chem. Ber.*, **101**, 574 (1968); (c) D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, **715**, 68 (1968).

[9] J. Wheatley, *J. Chem. Soc.*, 3718 (1964).

[10] (a) D. Hellwinkel and G. Kilthau, *Chem. Ber.*, **101**, 121 (1968); (b) D. Hellwinkel and G. Kilthau, *Justus Liebigs Ann. Chem.*, **705**, 66 (1967).

[11] (a) D. Hellwinkel, *Chem. Ber.*, **99**, 3642 (1966); (b) D. Hellwinkel, *Chimia*, **22**, 488 (1968); (c) D. Hellwinkel, *Chem. Ber.*, **99**, 3660 (1966); (d) D. Hellwinkel, *ibid.*, **99**, 3628 (1966); (e) D. Hellwinkel, *ibid.*, **99**, 3668 (1966); (f) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1966).

[12] M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968), and references therein.

[13] K. K. Andersen and N. E. Papanikolaou, *Tetrahedron Lett.*, 5445 (1966); K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

[14] D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969).

[15] C. R. Johnson and J. J. Rigau, *ibid.*, **91**, 5398 (1969).

[16] V. Calo, G. Scorrano, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969).

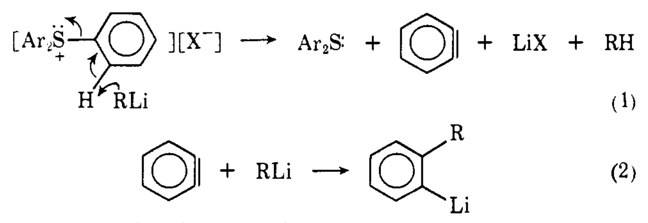
Several groups have investigated the reactions of organolithiums with sulfonium salts as an approach to pentacoordinate sulfur bearing only carbon ligands. Such an approach had been successful in many related systems. However, addition of phenyllithium to an ethereal slurry of triphenylsulfonium bromide did not yield tetraphenylsulfurane. Instead, the reaction afforded diphenyl sulfide and biphenyl. Franzen[17] has shown that ligand exchange competes with the above coupling process. Thus, ^{14}C-labeled phenyllithium experiences dilution of the label after partial reaction with triphenylsulfonium salt. He further demonstrated that the phenyl groups could be replaced by alkyl groups by utilizing alkyllithiums.[18]

McEwen[19] has examined the reaction of sulfonium salts with heteroatom nucleophiles. The reaction of lithium alkoxides appears to involve radical intermediates which could arise from homolytic scission of a C–O bond in an alkoxysulfurane. The pyrolytic decomposition of triarylsulfonium chlorides to diaryl sulfides and aryl chlorides may also involve the collapse of a halosulfurane.[20] Sheppard attempted the preparation of tetraphenylsulfurane by reaction of phenyltrifluorosulfurane with phenyllithium, but obtained only diphenyl sulfide and biphenyl.[21] The reactions of episulfides[22] and thietanonium salts[23] with organolithiums have also been claimed to involve sulfurane intermediates.

Aside from the invocation of pentacoordinate sulfur, other explanations can be advanced to explain the products from the reactions of organolithiums with triarylsulfonium salts (see Scheme I). One mechanistic route, path A, involves the generation of an aryne and subsequent addition of an organolithium to the aryne to yield the various hydrocarbons formed. The second mechanistic scheme, path B, involves the intermediacy of radicals generated either from electron-transfer processes between the organolithium and the salt or from homolysis of the C–S bond in the formed sulfurane. The former mode of radical generation would be analogous to the process of radical formation in metal–halogen exchange reactions between organohalides and alkyllithium reagents.[23] The third alternative route, path C, is a simple nucleophilic aromatic substitution by the organolithium on the salt.

Scheme I. Alternate Mechanistic Pathways for Reactions of Organolithium Reagents with Triarylsulfonium Salts

Path A. Benzyne Mechanism



Path B. Radicaloid Mechanism

$$[\mathrm{Ar_3\overset{+}{S}:}][\mathrm{X^-}] + \mathrm{RLi} \longrightarrow \mathrm{Ar_3\dot{S}:} + \mathrm{R\cdot} + \mathrm{LiX} \quad (3)$$

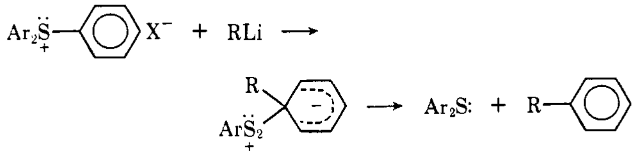
$$\mathrm{Ar_2\dot{S}:}\text{ and }\mathrm{R\cdot} \longrightarrow \text{radical coupling products} \quad (4)$$

or

$$[\mathrm{Ar_3\overset{+}{S}:}][\mathrm{X^-}] + \mathrm{RLi} \longrightarrow \mathrm{Ar_3\ddot{S}{-}R} + \mathrm{LiX} \quad (5)$$

$$\mathrm{Ar_3\ddot{S}{-}R} \longrightarrow \mathrm{Ar_3\dot{S}:} + \mathrm{R\cdot} \longrightarrow \text{radical coupling products} \quad (6)$$

Path C. Nucleophilic Aromatic Substitution Mechanism



Results and Discussion

Because of the inability of previous workers to demonstrate conclusively the intermediacy of sulfuranes in the reactions under consideration, and because of the confusion arising from the alternate mechanistic routes described in Scheme I, we undertook a systematic study of the reactions of various organolithium compounds with triarylsulfonium salts.

To simplify the analyses, we concentrated on two salts, triphenyl- (**4**) and tri-*p*-tolylsulfonium fluoroborate (**5**). Both compounds were prepared in moderate yield by reaction of the aryl Grignard reagent with the corresponding diaryl sulfoxide. The fluoroborate anion was introduced either by working up the reaction with aqueous fluoroboric acid or by the reaction of the sulfonium bromide with silver fluoroborate. We employed the fluoroborate salts since we found that their solubility in cold THF was higher than that of the corresponding bromide salts.

Benzyne Mechanism. We first chose to examine the question of aryne intermediacy in the reactions of organolithium compounds with sulfonium salts. When 1 equiv of vinyllithium was added to 1 equiv of **4** (expt 1) a quantitative yield of styrene and diphenyl sulfide was produced.

Similarly, the reaction of vinyllithium with **5** (expt 2) produced only two materials, di-*p*-tolyl sulfide (92%) and *p*-methylstyrene (80%). Infrared analysis of the isolated methylstyrene revealed the absence of any of the meta isomer.

When **5** was allowed to react with phenyllithium (expt 3) five products were generated: biphenyl (24%), *p,p'*-ditolyl (6%), *p*-tolylbenzene (40%), *p*-tolyl phenyl sulfide (3%), and di-*p*-tolyl sulfide (40%). Among the substituted biaryls no meta-substituted materials could be noted by vpc and infrared analysis.

In like manner the reaction of **5** with *p*-tolyllithium afforded quantitative yields of *p,p'*-ditolyl and di-*p*-tolyl sulfide (expt 4). Careful examination of the ir spectrum of the ditolyl formed showed no evidence whatsoever of contamination by the meta isomer.

The results of these four experiments are all inconsistent with a process involving arynes. Firstly, the stoichiometry of the reactions is in disagreement with aryne intermediacy. As depicted in Scheme I (path A), 2 equiv of organolithium per equivalent of sulfonium salt are required in the aryne process, the first organolithium to abstract the ortho proton from the salt, and the second to add to the formed benzyne. However, the reaction of **4** with vinyllithium and **5** with *p*-tolyl-

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[17] V. Franzen and C. Mertz, *Justus Liebigs Ann. Chem.*, **643**, 24 (1961).

[18] V. Franzen and C. Mertz, *Angew. Chem.*, 72, 416 (1960).

[19] J. W. Knapczyk and W. E. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969).

[20] G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, 33, 2671 (1968).

[21] W. Sheppard, *J. Amer. Chem. Soc.*, 84, 3058 (1962).

[22] B. M. Trost and S. Ziman, *Chem. Commun.*, 181 (1969).

[23] H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, 91, 746 (1969).

lithium proceeded quantitatively from equimolar amounts of the reactants.

Secondly, the formation of only para-substituted toluenes from the reactions with **5** is not in accordance with the intermediacy of 4-methyldehydrobenzene. It has been shown that in the reactions of this aryne with organolithiums meta-substituted products are formed predominantly.[24]

The result of expt 4 contrasts with the recent report of Khim and Oae[25] which claims that the reaction of phenyllithium with a refluxing ethereal slurry of **5** results in the formation of a 2:1 mixture of *m,p*- and *p,p'*-ditolyl. The authors claim that the relative percentage of the two isomers was determined by evaluation of the ir data. It is possible that a duality of mechanisms occurs in these reactions, and that at a temperature approximately 110° higher than ours and in a different solvent an alternate mechanistic pathway is followed. Nevertheless, Andersen[26,27] obtained results similar to ours under conditions comparable to those of Oae.

In addition to their implications regarding the benzyne mechanism, the results of expt 3 indicate that some ligand equilibration occurred in the reaction of phenyllithium with **5**. The formation of 24% biphenyl in the reaction implies that phenyllithium reacted with a ditolylphenylsulfonium salt, generated by exchange of one tolyl ligand on sulfur with phenyllithium. This result is then in agreement with the labeling study of Franzen in which he finds equilibration of phenyllithium with the phenyl ligands on triphenylsulfonium bromide (*vide supra*). The degree of ligand equilibration noted indicates that, whatever the mechanism of phenyl–phenyl coupling, the activation energy for that process is nearly equal to or slightly greater than the activation energy for mixing of the ligands.

Radical Mechanism. We next considered a radical mechanism (Scheme I, path B), in which radicals are postulated as precursors to the hydrocarbons formed in the reactions of organolithiums with triarylsulfonium salts. To probe for such radicaloid species, the stereochemistry of coupling of β-substituted vinyllithium reagents with sulfonium salts was investigated. *trans*-β-Styryllithium was prepared by the method of Seyferth.[28] Quenching of an aliquot of the organolithium with chlorotrimethylsilane showed that the transmetallation had yielded solely the trans organolithium. The addition of *trans*-β-styryllithium to **4** (expt 5) resulted in the formation of 3% *cis*- and 39% *trans*-stilbene besides diphenyl sulfide (59%) as the reaction products.

To identify the cause of the small amount of isomerization of the styryl moiety, we attempted to investigate the stereochemical stability of *trans*-styryllithium under the reaction conditions. Excess chlorotrimethylsilane was added to a reaction mixture of the sulfonium salt and *trans*-β-styryllithium at −78°. However, no styrylsilyl ethers could be detected by vpc analysis of the reaction products. In another control reaction, a sample of the ethereal organolithium was added to THF and stirred to duplicate the temperatures and duration of the sulfonium salt reaction. A chlorotrimethylsilane quench of the mixture revealed no silyl ethers. Our inability to quench any styryllithium species with the chlorosilane indicated that the organolithium was unstable to the reaction conditions.

Since substituted vinyllithium reagents had been shown to lose isomeric purity in THF,[29] *trans*-β-styryllithium was added to a slurry of **4** at −78° in diethyl ether. The reaction went in low yield, most likely due to the low solubility of **4** in ether. However, isomerization was noted; *cis*- and *trans*-stilbene were formed in a ratio of 1:4.

Additional control reactions showed that a known sample of *trans*-stilbene was stereochemically stable under the reaction conditions in THF.

Because of the demonstrated instability of styryllithium in THF and because of the lack of a source of *cis*-β-styryllithium,[26] which was needed for comparative purposes, we next turned to a system which provided easy access to both cis- and trans-substituted vinyllithiums. Seyferth has described the generation of both *cis*- and *trans*-propenyllithium from the corresponding *cis*- and *trans*-propenyl bromide and lithium metal.[30] A solution of 100% *trans*-propenyllithium was thus prepared by Seyferth's procedure; quenching of an aliquot of the mixture with chlorotrimethylsilane demonstrated that none of the cis isomer had been generated. The *trans*-propenyllithium was added to **4** and afforded a mixture of 98.3% *trans*- and 1.7% *cis*-propenylbenzene. In addition to the propenylbenzenes (formed in 68% yield), the reaction yielded biphenyl (6%), *trans*-propenyl phenyl sulfide (19%), and diphenyl sulfide (80%). In the vpc analysis no peak attributable to *cis*-propenyl phenyl sulfide could be noted.

Addition of a solution of 98.5% *cis*-propenyllithium to **4** (expt 7) produced 64% propenylbenzene consisting of a mixture of 97.2% *cis*- and 2.8% *trans*-propenylbenzene. Again, in this case no peak attributable to *cis*-propenyl phenyl sulfide could be noted by vpc. Instead, a 30% yield of *trans*-propenyl phenyl sulfide was detected.

To determine if we could in fact distinguish between *cis*- and *trans*-propenyl phenyl sulfide, the preparation of known samples of each sulfide was undertaken. The isomerization of allyl phenyl sulfide[31] using sodium ethoxide in refluxing ethanol gave only one product, identical in all respects with that isolated from the sulfonium salt reactions. Photolysis of the trans sulfide for 2 hr with a 450-W Hanovia mercury-vapor lamp did not result in net photoisomerization to the cis sulfide. Since the Wittig reaction has been shown to give olefinic mixtures in which the cis isomer often predominates,[32] acetaldehyde was reacted with thiophenoxymethylenetriphenylphosphorane.[33] Again, only *trans*-propenyl phenyl sulfide was detected by vpc analysis of the reaction mixture. The failure to isolate the cis sulfide

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(24) L. Friedman and J. F. Chlebowski, *J. Amer. Chem. Soc.*, **91**, 4864 (1969); F. Scardiglia and J. D. Roberts, *Tetrahedron*, 3, 197 (1968); G. B. RideGraff, J. J. denHertog, and W. C. Melger, *Tetrahedron Lett.*, 963 (1965).

(25) Y. H. Khim and S. Oae, *Bull. Chem. Soc., Jap.*, 42, 1968 (1969).

(26) K. K. Andersen, S. A. Yeager, and N. B. Peynircioglu, *Tetrahedron Lett.*, 2485 (1970).

(27) For a related investigation, see K. K. Andersen and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

(28) D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, 1, 437 (1964).

(29) D. Y. Curtin and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **84**, 1967 (1962).

(30) D. Seyferth and L. G. Vaughan, *ibid.*, 86, 883 (1964).

(31) D. S. Tarbell and M. A. McCall, *ibid.*, 74, 48 (1952).

(32) S. Trippett, *Quart. Rev., Chem. Soc.*, 17, 406 (1963).

(33) T. Mukaryama, S. Furkuyama, and T. Kumamoto, *Tetrahedron Lett.*, 3787 (1968).

Table I. Reaction Products of Triarylsulfonium Salts with Organolithium Reagents

Expt	$[\mathrm{Ar_3S^+}][\mathrm{B^-F_4}]$	Organolithium (RLi), R	Hydrocarbon products (% yield)	Sulfide products (% yield)	% $[\mathrm{Ar_3S^+}][\mathrm{B^-F_4}]$ consumed
1	4	$\mathrm{CH_2{=}CH}$	$\mathrm{PhCH{=}CH_2}$ (98)	$\mathrm{Ph_2S}$ (99)	100
2	5	$\mathrm{CH_2{=}CH}$	*p*-$\mathrm{TolCH{=}CH_2}$ (80)	(*p*-$\mathrm{Tol)_2S}$ (92)	100
3	5	Ph	PhPh (24) *p*-Tol-Ph (40) *p*-Tol-*p*-Tol (6)	*p*-Tol-SPh (3) (*p*-$\mathrm{Tol)_2S}$ (40)	53
4	5	*p*-Tol	*p*-Tol-*p*-Tol (100)	(*p*-$\mathrm{Tol)_2S}$ (100)	100
5	4	PhCH=CH (100% trans)	PhCH=CHPh (3% cis, 39% trans)	$\mathrm{Ph_2S}$ (59)	39
6	4	$\mathrm{CH_3CH{=}CH}$ (100% trans)	$\mathrm{PhCH{=}CHCH_3}$ (67% trans, 1% cis) PhPh (6)	$\mathrm{Ph_2S}$ (80) $\mathrm{CH_3CH{=}CHSPh}$ (19) (100% trans)	19
7	4	$\mathrm{CH_3CH{=}CH}$ (98.5% cis, 1.5% trans)	$\mathrm{PhCH{=}CHCH_3}$ (63% cis, 1% trans) PhPh (38)	$\mathrm{Ph_2S}$ (65%) $\mathrm{CH_3CH{=}CHSPh}$ (30) (100% trans)	20
8	4	*tert*-Bu	PhPh (51)	PhS-*tert*-Bu (51)	80
9	4	*n*-Bu	PhPh (44)	(*n*-$\mathrm{Bu)_2S}$ (19) *n*-BuSPh (53) $\mathrm{Ph_2S}$ (34)	86
10	4	$\mathrm{CH_2{=}CHCH_2}$	$\mathrm{PhCH_2CH{=}CH_2}$ (90)	$\mathrm{Ph_2S}$ (99)	100

from these syntheses, even with reactions known to give predominantly cis-substituted products, suggested that the cis isomer was unstable toward isomerization in basic media. If some *cis*-propenyl phenyl sulfide had been formed in the reactions of the propenyllithiums with **4**, it might well have isomerized to the trans product under the strongly basic conditions.

In spite of the ambiguity introduced by the isolation of only *trans*-propenyl phenyl sulfide, the stereospecificity in the propenylbenzene formation on the reactions of the propenyllithiums with **4** offers strong arguments against a radicaloid process in these reactions. The high degree of stereochemical retention noted in the propenylbenzenes generated from *cis*- and *trans*-propenyllithium indicates that vinylic radicals are not involved. It has been clearly demonstrated that substituted vinyl radicals rapidly lose stereochemical integrity.[34] The low partial loss of stereochemistry in the styryllithium reactions may indicate a duality or, more precisely, a continuum of mechanisms operative in some of these reactions. Also the demonstrated instability of the styryllithium reagent under the reaction conditions cannot be ignored in evaluating the results of the styryllithium experiments.

To further probe for radical intermediates in the reactions of organolithiums with sulfonium salts, a solution of *tert*-butyllithium (expt 8) and *n*-butyllithium (expt 9) was added to **4** with the results summarized in Table I. The products formed in the reactions of the two butyllithiums with **4** are also in disagreement with a radical mechanism. If *tert*-butyl radical had been generated in the reaction *via* an electron transfer process, a much higher yield of isobutylene would have been produced. Furthermore, it has been shown that the ratio of disproportionation to recombination for *tert*-butyl radicals in the gas phase is 4.6:1.[35] The organolithium reactions failed to produce any detectable amount of *tert*-butyl- or *n*-butylbenzene. The absence of such coupling products is also inconsistent with the intermediacy of butyl radicals.

Moreover, the formation of large amounts of biphenyl and *tert*-butyl phenyl sulfide in the *tert*-butyllithium reaction is not commensurate with radical formation *via* homolysis of the sulfurane. In such a mechanistic route, the source of the biphenyl would be phenyl radicals. However, generation of phenyl radical in preference to *tert*-butyl radical would be an energetically unfavorable process.[36]

Nucleophilic Aromatic Substitution Mechanism. A process of nucleophilic aromatic substitution can also be invoked to explain the formation of many of the products from the reactions of organolithiums with sulfonium salts (Scheme I, path C). Thus, formation of biaryls and vinyl-substituted aryls can be ascribed to the simple addition of the appropriate organolithium to one aromatic ring of the salt generating an intermediate complex. Aromatization by loss of a mole of sulfide would yield the products observed.

The alkylllithium reactions, however, at first appear inconsistent with such an interpretation. Thus, alkyllithiums would be expected to add in nucleophilic fashion at least as facilely as aryllithium with formation of alkylbenzenes. None are formed. However, such a result may arise from ligand exchange being much faster than nucleophilic addition. As previously indicated, ligand equilibration would result in generation of aryllithium and alkyldiarylsulfonium salt. Thus, alkyllithium might not be available for the nucleophilic addition.

Other evidence mitigating against the nucleophilic aromatic substitution arises from consideration of the reactions of organolithiums and *S*-phenyldibenzothiophenium fluoroborate (**6**). Reaction of this salt with phenyllithium generates the terphenyl derivative **7** exclusively, whereas reaction with vinyllithium generates a mixture of four products—dibenzothiophene (60%), styrene (60%), 2-phenylthio-2′-vinylbiphenyl (**8**, 8%), and 2-vinylthio-2′-phenylbiphenyl (**9**, 5%).

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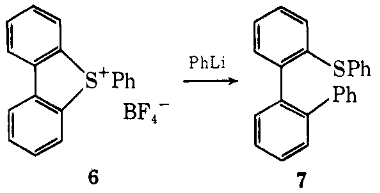
(34) J. A. Kampmeier and R. M. Fantazier, *J. Amer. Chem. Soc.*, **88**, 1959 (1966).

(35) A. V. Blackham and N. L. Eatough, *ibid.*, **84**, 2922 (1962).

(36) A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, **89**, 4578 (1967).



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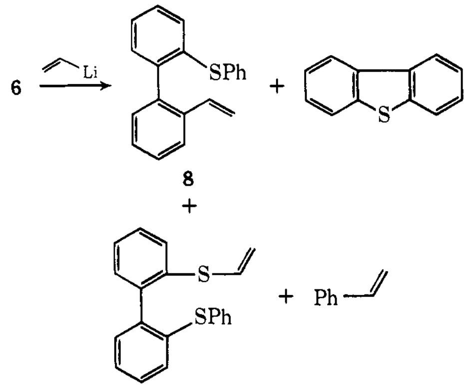

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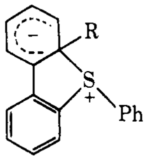

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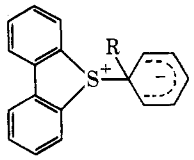

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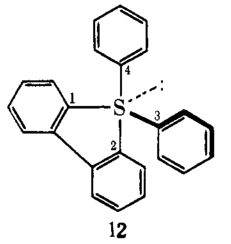
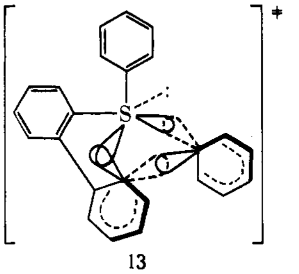
Of the two addition σ complexes, **10** and **11**, clearly **10** which has extended conjugation with the adjacent phenyl ring is the more stable. However, the above results present a dichotomy in terms of the addition–elimination mechanism in that the phenyllithium reaction requires complex **10** to be the more stable and the vinyllithium reaction requires complex **11** to be the more stable. Alternatively, the sulfurane intermediate offers a viable explanation. By analogy to phosphorane chemistry, a sulfurane is assumed to (1) possess a trigonal bipyramidal geometry, (2) require the five-membered ring in the basal–apical orientation, (3) prefer incoming and departing groups to involve apical positions, and (4) prefer the electron pair to occupy the most electronegative orbital (basal).[37]



12

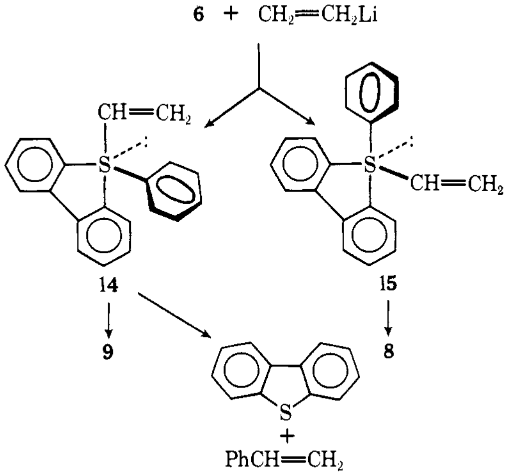


13

Examination of a molecular model of **12** illustrates that there are only two coupling modes that do not entail an inordinate amount of distortion to achieve a bonding interaction between the π systems of two ligands (see **13**). Overlap of the orbitals at C$_1$ and C$_2$ or C$_1$ and C$_4$ to generate coupling products is thus prohibited by the tremendous steric distortions required in such bonding. However, minimum motion is needed to achieve bonding between the orbitals at C$_2$ and C$_3$, C$_3$ and C$_4$, or C$_1$ and C$_3$. Since benzene rings have an inductive effect of electron withdrawal, the biphenylyl group is activated toward coupling with a suitably disposed π system.[38] Thus for sulfurane **12**, the activation energy for phenyl–biphenylyl coupling should be lower than that for phenyl–phenyl coupling. Only phenyl–biphenylyl coupling is observed.

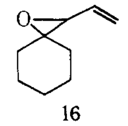
The addition of vinyllithium to **6** can lead to two stereoisomeric sulfuranes, **14** and **15** (see Scheme II).

Scheme II. Modes of Collapse of Biphenylylphenylvinylsulfurane



As discussed above for the collapse of **12**, there are two likely modes of coupling from **14**: the basal phenyl ligand can overlap with the vinyl π system to yield styrene and dibenzothiophene, or the phenyl ligand can overlap with the biphenylyl group to produce compound **9**. Vinyl–biphenylyl coupling is geometrically prohibited (*vide supra*). The coupling between a vinyl group and a phenyl group was shown to be efficient in the collapse of triphenylvinylsulfurane, completely dominating the competitive phenyl–phenyl coupling. However, coupling of a phenyl ligand to the biphenylyl group has also been shown to take precedence over phenyl–phenyl coupling. Thus, a small competition exists between phenyl–vinyl and phenyl–biphenylyl coupling in which the former predominates. Again, two modes of coupling are possible from **15**. However, the process of vinyl–biphenylyl coupling would be expected to be favored over vinyl–phenyl coupling, if the lowerings in the activation energies noted for biphenylyl coupling and vinyl coupling are cumulative. To the extent **15** is formed, it generates **8**. The formation of **15** in addition to **14** may have its origin either in basal attack being competitive to a small extent with apical attack or in pseudorotation. The available data do not allow a distinction.

Other Coupling Reactions. Addition of a solution of allyllithium (generated from tetraallylstannane) to triphenylsulfonium salt **4** at −78° afforded quantitative yields of allylbenzene and diphenyl sulfide. Addition of cyclohexanone to the solution at −78° yielded no vinyloxirane **16**. Thus, allyldiphenylsulfonium



16

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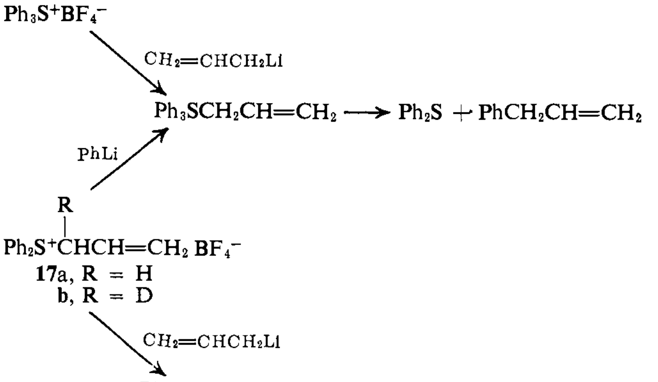
[37] For a discussion of phosphoranes see D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970); F. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970).

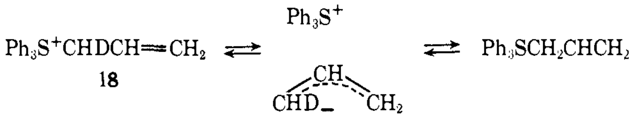
[38] H. Arndt, unpublished observations in these laboratories.

salt was not generated in the reaction. Alternatively, addition of phenyllithium to allyldiphenylsulfonium fluoroborate (**17a**) produced allylbenzene and diphenyl sulfide as the only coupling products accompanied by ylide formation. Reaction of allyllithium with allyldiphenylsulfonium salt produces only biallyl and diphenyl sulfide (see Scheme III).

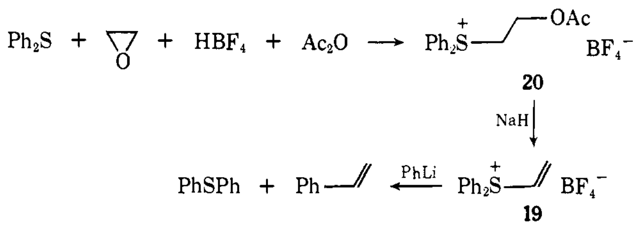
Scheme III. Chemistry of Allylsulfuranes



Rationalization of the formation of allylbenzene from the concerted collapse of allyltriphenylsulfurane requires that the concept for coupling be broadened to allow an allylic rearrangement to effect overlap of the reacting π systems. To test this hypothesis, 1-deuterioallylsulfonium fluoroborate **17b** was treated with phenyllithium. The reaction was worked up by addition of cyclohexanone to trap formed ylide. Deuterioallylbenzene isolated from the reaction contained deuterium equally distributed at the 1 and 3 positions as determined by nmr analysis. The scrambling can best be accommodated by the assumption that, in this case (as in the aryl examples), ligand exchange is faster than coupling. Expulsion of the allyl group from **18** is highly preferred. The allyl species thus generated loses the identity of the label. Attempts to circumvent the above difficulties failed.



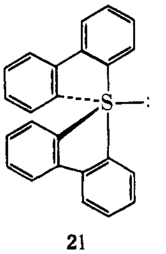
To further document the chemistry of sulfuranes, we investigated generation of triphenylvinylsulfurane *via* the alternative approach of addition of phenyllithium to diphenylvinylsulfonium fluoroborate (**19**). Preparation of the precursor of the vinyl sulfonium salt, β-acetoxyethyldiphenylsulfonium fluoroborate (**20**), was achieved by the slow addition of ethylene oxide to a cold methylene chloride solution of excess diphenyl sulfide, anhydrous fluoroboric acid, and acetic anhydride. Although attempts to purify **20** failed,[39] the crude material readily lost the elements of acetic acid upon treatment with sodium hydride in DMF solution. As expected on the basis of sulfurane intermediates, treatment of the vinyl salt with phenyllithium produced only styrene and diphenyl sulfide as the coupling products.



Discussion

The reactions of arylsulfonium salts with organolithium serve as a potential synthetic method to introduce an aryl group into an organic molecule. The available evidence provides support for the intermediacy of sulfuranes in these reactions. As such, the utilization of conversion of decet sulfur, an unstable valence state, into octet sulfur as a driving force for an organic reaction appears useful. Exploration of this concept to develop new reactions is currently under way in our laboratories.

Attempts to generate a stable sulfurane failed. By analogy to organophosphorus chemistry,[11] the spiro sulfurane **21** appears as the most promising candidate.



21

However, all approaches to such a species failed to yield a material characterizable as **21**.

The reactions reported above bear a striking resemblance to similar reactions in organophosphorus chemistry.[40] In some of the latter instances, the organophosphorane can be isolated. Such close similarities provide further support for the contention of sulfuranes as intermediates.

Experimental Section[41]

Preparation of Triphenylsulfonium Fluoroborate (5). Triphenylsulfonium bromide was prepared in 39% yield by the method of Wildi, *et al.*,[42] from 125.4 g (0.80 mole) of freshly distilled bromobenzene, 18.0 g (0.74 g-atom) of magnesium turnings, and 30.0 g (0.15 mole) of diphenyl sulfoxide. The material, mp 275–280° (lit.[42] 285–286°), was converted to the fluoroborate salt by dissolving 6.67 g (19.6 mmoles) of bromide salt in 30 ml of methylene chloride and adding the resultant solution to 5.66 g (29.2 mmoles) of silver fluoroborate in 20 ml of methylene chloride. After stirring at 25° for 5 min, filtration removed the precipitated silver bromide. Concentration *in vacuo* afforded 6.60 g (97% yield) of white solid, mp 190–192° (lit.[42] 190–191°).

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(39) The major impurities appeared to be polymeric sulfonium salts of the general structure $Ph_2S^+(CH_2CH_2O)_nAcBF_4^-$ ($n > 1$).

(40) D. Seyferth, J. Fogel, and J. K. Heeren, *J. Amer. Chem. Soc.*, **88**, 2207 (1966).

(41) 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 Microtech Laboratories, Inc. Vpc analyses were performed on an Aerograph Model 90P or Hewlett-Packard Model 5750 instrument.

(42) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, 73, 1965 (1951).

Preparation of Tri-*p*-tolylsulfonium Fluoroborate (6). To a flask under nitrogen was added 7.8 g (0.32 g-atom) of magnesium turnings. The apparatus was flame-dried.

A solution of 56 g (0.32 mole) of *p*-bromotoluene in 450 ml of dry ether was prepared; 10 ml of this solution was added to the magnesium. The reaction was initiated by stirring until cloudiness developed. The remainder of the bromide solution was added to the reaction mixture at such a rate as to maintain vigorous reflux. After refluxing had subsided, 350 ml of dry benzene was added to the solution. The condenser was fitted with a distilling head. The solvent was distilled until the distillate temperature reached 70°. A solution of 15.0 g (65.2 mmoles) of di-*p*-tolyl sulfoxide in 150 ml of dry benzene was added to the reaction. The mixture was refluxed for 23 hr, cooled to 0°, and carefully hydrolyzed with a solution of 25 ml of 50% fluoroboric acid in 25 ml of water. The layers were separated and the benzene layer was extracted with four 100-ml portions of 2.5% fluoroboric acid. The benzene layer was then extracted with four 150-ml portions of hot water. The combined aqueous layers were extracted with six 150-ml portions of chloroform. The chloroform layers were reduced *in vacuo* to an orange oil. The oil was shaken vigorously with ether to induce solidification. Recrystallization from chloroform–ether afforded a white solid, 6.00 g (24%), mp 163–164° (lit.[42] 160–161°).

Reaction of Triphenylsulfonium Fluoroborate with Vinyllithium. Over a 2-min period, 0.60 ml (1.2 mmoles) of a 2.0 *N* solution of vinyllithium in THF solution (Alfa Inorganics, Inc.) was added to a −78° slurry of the salt (1.14 mmoles), yielding a yellow slurry. After 7 min the reaction mixture became a clear yellow solution. The solution was stirred for 2.5 hr and then was warmed to room temperature. After 1.5 hr the solution was hydrolyzed with 5 ml of water, ether extracted, and dried (K_2CO_3). The dried extracts were filtered and distilled (pot temperature to 75°).

The residue was analyzed by vpc[43] between 100 and 200°. There were two peaks on the chromatogram: 15 min (styrene, 98%) and 45 min (diphenyl sulfide, 99%). Both products were identified by comparison of their vpc retention times and infrared spectra with those of authentic samples. Acenaphthene was used as internal standard.

The aqueous phase from the hydrolysis of the reaction was chloroform extracted. Evaporation of the chloroform layers revealed no recovered sulfonium salt.

Reaction of Vinyllithium with Tri-*p*-tolylsulfonium Fluoroborate. The above reaction was repeated utilizing 0.26 ml (0.54 mmole) of a 2.0 *N* solution of vinyllithium in THF solution and 246.3 mg (0.51 mmole) of tri-*p*-tolylsulfonium fluoroborate. The residue was analyzed by vpc[43] between 140 and 230°. There were two peaks on the chromatogram: 10 min (*p* methylstyrene, 80%) and 47 min (di-*p*-tolyl sulfide, 92%). Acenaphthene was used as internal standard. The styrene was identified by comparison of its infrared spectrum with that of a known sample.

The sample of methylstyrene isolated from the reaction was compared with a known sample of *m*-methylstyrene. We were not able to find vpc conditions to separate the two isomers. Their nmr spectra showed only slight chemical shift differences. However, the ir spectrum of *m*-methylstyrene contained a strong absorption at 650 cm^{-1}, which was completely absent in the reaction product.

Reaction of Phenyllithium with Tri-*p*-tolylsulfonium Fluoroborate. Over a 1-min period, 0.12 ml (0.25 mmole) of a 2.14 *N* solution of phenyllithium in 70:30 benzene–ether (Alfa Inorganics, Inc.) was added to a −78° slurry of the salt (0.25 mmole), yielding a golden slurry. After completion of the reaction as above, the residue was analyzed by vpc[43] at 205°. There were five significant peaks on the chromatogram: 15 min (biphenyl, 24%), 24 min (*p*-tolylbenzene, 40%), 34 min (*p*,*p*'-tolyl, 6%), 42 min (*p* tolyl phenyl sulfide, 3%), and 54 min (di-*p*-tolyl sulfide, 40%). The products were identified by comparison of their retention times and infrared spectra with those of known samples. Dibenzothiophene was used as internal standard.

Using a 17 ft × 0.25 in. column of 25% SE30 on Chromosorb P at 180°, *m*- and *p*-tolylbenzene could be separated (84 and 88 min, respectively). Analysis of the reaction residue under these conditions revealed none of the meta isomer.

We were unable to establish vpc conditions to separate known samples of *p*,*p*'-ditolyl and *m*,*p*-ditolyl. There were only slight differences in their nmr spectra. However, the ir spectrum of the meta isomer had strong absorptions at 1610 and 696 cm^{-1}, which were completely absent in the ir spectrum of the reaction product.

The usual analysis of the aqueous phase afforded 47 mg (47%) of recovered sulfonium salt.

Reaction of *p*-Tolyllithium with Tri-*p*-tolylsulfonium Fluoroborate. Over a 2-min period, 1.12 ml (1.28 mmoles) of a 1.14 *N* ether solution of *p*-tolyllithium was added to a −78° slurry of the salt (1.28 mmoles), yielding ultimately a bright yellow solution. After completion of the reaction similar to the above and work-up, vpc analysis[44] at 200° revealed two components: 31 min (*p*,*p*'-ditolyl, 100%) and 63 min (di-*p*-tolyl sulfide, 100%). Dibenzothiophene was used as internal standard. The ir spectrum of the ditolyl showed no absorptions at 1610 or 696 cm^{-1} which are indicative of *m*,*p*-ditolyl.

Preparation of *trans*-β-Styryllithium. An 0.11 *N* ethereal solution of *trans*-β-styryllithium was prepared by the method of Seyferth[28] from 3.50 g (7.52 mmoles) of *trans*-β-stytryltriphenyltin[45] and 6.43 ml (7.52 mmoles) of a 1.17 *N* ethereal phenyllithium in 64 ml of ether. Quenching of an aliquot in chlorotrimethylsilane showed the absence of any *cis*-β-styryltrimethylsilane. An authentic sample of the latter compound was obtained by irradiation of *trans*-β-styryltrimethylsilane.[28]

Reaction of *trans*-β-Styryllithium with Triphenylsulfonium Fluoroborate in THF. Over a 5-min period, 27 ml (2.92 mmoles) of a 0.11 *N* *trans*-β-styryllithium solution in ether were added to a −78° THF slurry of triphenylsulfonium fluoroborate (2.86 mmoles), yielding a yellow slurry. The mixture was stirred for 1.5 hr, warmed to room temperature, and stirred for 1 hr. The reaction was hydrolyzed and worked up as usual.

Chloroform extraction of the aqueous phase afforded 0.61 g (61%) of recovered sulfonium salt. The ethereal residue was examined by vpc[43] at 210°. There were four peaks on the chromatogram: 8 min (biphenyl, 43 mg), 15 min (*cis*-stilbene, 3.4%), 20 min (diphenyl sulfide, 58.6%), 30 min (*trans*-stilbene, 38.6%). Phenanthrene (retention time 38 min) was used as internal standard. Independent analysis of the phenyllithium solution used to generate the styryllithium showed that 20 mg/ml of biphenyl were present in the phenyllithium solution. An equivalent of 2.25 ml of phenyllithium (44 mg of biphenyl) was used to generate the 27 ml of styryllithium used in this experiment. Each compound was identified by comparison of its retention time and ir spectrum with those of known samples.

Reaction of *trans*-β-Styryllithium with Triphenylsulfonium Fluoroborate in Ether. The organolithium was generated as previously described. Vpc analysis of an aliquot quenched with chlorotrimethylsilane revealed that only the trans silyl ether was present. Over a 1-min period, 10.0 ml (0.72 mmole) of a 0.072 *N* styryllithium solution in ether was added to a −78° ether slurry of the salt (0.71 mmole). The white slurry was stirred for 1.5 hr, warmed to room temperature, and stirred for 1 hr. Then 0.25 ml of chlorotrimethylsilane was added to the mixture. After 2 hr, the reaction was worked up as usual.

Vpc analysis[43] of the residue indicated that the reaction had gone in poor yield. However, the ratio of *cis*- to *trans*-stilbene was determined to be 1.0:3.9. Neither the *cis*- nor *trans*-styryltrimethylsilane was observable by vpc.

Reaction of *cis*-Propenyllithium with Triphenylsulfonium Fluoroborate. Over a 1-min period 0.50 ml (3.0×10^{-4} mole) of a 0.60 *N* ether solution of *cis*-propenyllithium[30] was added to a −78° THF slurry of triphenylsulfonium fluoroborate (2.85×10^{-4} mole). The pale yellow slurry was stirred at −78° for 30 min whereupon 2 ml of water was added to quench the reaction. The mixture was warmed to room temperature and worked up as usual. Chloroform extraction of the aqueous phase afforded 80 mg (80%) of recovered triphenylsulfonium salt. Vpc analysis[44] of the organic layer at 130–200° revealed five components: 15 min (*cis*-propenylbenzene, 63%), 18 min (*trans*-propenylbenzene, 1%), 54 min (*trans*-propenyl phenyl sulfide (30%), 70 min (biphenyl, 38%), 94 min (diphenyl sulfide, 65%). Acenaphthene was used as internal standard. Each component was identified by comparison of its ir spectrum and vpc retention time with that of an authentic sample.

Reaction of *trans*-Propenyllithium with Triphenylsulfonium Fluoroborate. Over a 1-min period 0.85 ml (2.9×10^{-4} mole) of a 0.35 *N* ether solution of *trans*-propenyllithium[30] was added

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[43] An 8 ft × 0.25 in. column of 20% SE 30 on Chromosorb W was employed.

[44] An 11 ft × 0.25 in. column of 20% SE 30 on Chromosorb W was employed.

[45] G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.*, **9**, 106 (1959).

to a −78° THF slurry of 0.100 g (2.85×10^{-4} mole) of triphenylsulfonium fluoroborate. The yellow slurry was stirred at −78° for 30 min whereupon it was quenched with 5 ml of water. The mixture was warmed to room temperature and worked up as usual. Chloroform extraction of the aqueous phase afforded 81 mg (81%) of recovered triphenylsulfonium salt. Vpc analysis[44] of the organic phase revealed the presence of five components: *trans*-propenylbenzene (67%), *cis*-propenylbenzene (1.2%), *trans*-propenyl phenyl sulfide (19%), biphenyl (6%), and diphenyl sulfide (80%). Acenaphthene was used as internal standard. All compounds were identified by comparison of their ir spectra and vpc retention times with those of known samples. The propenylbenzenes were in a ratio of 98.3% *trans*- and 1.7% *cis*-propenylbenzene.

Preparation of *trans*-Propenyl Phenyl Sulfide by the Isomerization of Allyl Phenyl Sulfide with Sodium Ethoxide in Ethanol.[31] To 5 ml of absolute ethanol in a flask under nitrogen was added 0.24 g (1.04×10^{-2} g-atom) of sodium metal. The mixture was stirred until the metal dissolved. Then 0.265 g (1.89 mmoles) of allyl phenyl sulfide was added to the solution. The mixture was refluxed under nitrogen for 8 hr and was then cooled to room temperature and poured carefully onto 25 ml of ice-water. The mixture was extracted with four 5-ml portions of ether. The combined extracts were washed with water, dried (K_2CO_3), and filtered. The volume was reduced at room temperature with aspirator pressure. Vpc analysis of the residue showed only one product, identical in all respects with the *trans*-propenyl sulfide isolated from the sulfonium salt reaction.

Photolysis of *trans*-Propenyl Phenyl Sulfide. A 120 × 20 mm quartz tube was fitted with a water condenser and gas inlet. To the vessel was added a solution of 0.250 g (1.78 mmoles) of *trans*-propenyl phenyl sulfide in 25 ml of hexane. The photolysis tube was strapped to a quartz insert. The mixture was photolyzed unfiltered for 80 min with a 450-W Hanovia Hg-vapor lamp. Vpc analysis of the photolysate revealed only one discreet product, identical with the starting material.

Preparation of Propenyl Phenyl Sulfide. Reaction of Acetaldehyde with Thiophenoxymethylenetriphenylphosphorane. To 10 ml of dry THF in a flask under nitrogen was added 1.0 g (4.6 mmoles) of phenyl disulfide. The solution was chilled to −25°. Then over an 80-min period, 0.72 g (4.5 mmoles) of bromine in 6 ml of dry THF was added to the disulfide solution. The red-orange solution was stirred for 1 hr at −15°. Over a 5-min period, 9.1 mmoles of triphenylmethylenephosphorane [generated from 3.25 g (9.1 mmoles) of triphenylmethylphosphonium bromide and 9.1 mmoles of *n*-butyllithium in 15 ml of THF] was added to the sulfenyl bromide solution, yielding a light yellow solution and a heavy white precipitate. The mixture was stirred at room temperature for 1 hr; 4.7 ml (9.1 mmoles) of a 1.94 *N* hexane solution of *n*-butyllithium was added to the mixture yielding a deep red solution with a small amount of unreacted white solid remaining. The ylide was stirred at room temperature for 2 hr whereupon 0.2 g (4.5 mmoles) of acetaldehyde was added to the mixture. The resultant cloudy orange mixture was stirred at room temperature for 1 hr and was then refluxed for 8 hr. The mixture was cooled to room temperature and hydrolyzed with 10 ml of water. The mixture was ether extracted, and the extracts were dried ($MgSO_4$), filtered, and reduced in volume *in vacuo*. The residue was washed several times with pentane to eliminate triphenylphosphine oxide. Vpc analysis[44] of the pentane residue at 166° revealed two components: 17 min (*trans*-propenyl phenyl sulfide), 25 min (*n*-butyl phenyl sulfide). The propenyl sulfide was identical in all respects with authentic samples of the trans material.

Reaction of *n*-Butyllithium with Triphenylsulfonium Fluoroborate. Over a 12-min period, 0.28 ml (0.44 mmole) of a 1.5 *N* solution of *n*-butyllithium in hexane (Foote Mineral Co.) was added to −78° slurry of triphenylsulfonium fluoroborate (0.29 mmole), yielding a clear lemon-yellow solution. The solution was stirred at −78° for 15 min, whereupon 0.10 g of dry cyclohexanone was added. Most of the color faded. After 15 min the reaction was warmed to room temperature, yielding a cloudy white solution. The solution was stirred for 30 min, hydrolyzed, and worked up as usual.

Chloroform extraction of the aqueous phase afforded 14 mg (14%) of recovered sulfonium salt.

The ethereal residue was analyzed by vpc[43] between 135 and 200°. There were seven significant peaks on the chromatogram: 9 min (cyclohexanone), 23 min (di-*n*-butyl sulfide, 16%), 37 min (2-*n*-propyl-1-oxaspiro[5.2]octane, 39%), 44 min (1-*n*-butylcyclohexanol, 10%), 55 min (*n*-butyl phenyl sulfide, 50%), 57 min (biphenyl, 43%), and 68 min (diphenyl sulfide, 36%). Each product was identified by comparison of its vpc retention time and ir spectrum with those of known samples. Cycloheptanone was used as internal standard. No *n*-butylbenzene could be detected.

Reaction of *tert*-Butyllithium with Triphenylsulfonium Fluoroborate. Over a 2-min period, 0.30 ml (0.60 mmole) of a 2.0 *N* solution of *tert*-butyllithium in pentane (Alfa Inorganics, Inc.) was added to a −78° slurry of the salt (0.58 mmole), yielding a yellow slurry. The effluent gases were bubbled through a trap containing 3 g of bromine in 40 ml of carbon tetrachloride. After 30 min, the reaction mixture was warmed to room temperature and stirred for 1 hr, yielding a white slurry. A stream of nitrogen was bubbled through the reaction mixture; the effluent gases were passed through the bromine trap. After 15 min, the degassing was discontinued since the bromine trap had become cloudy (probably from reaction with carried-over THF). The reaction was hydrolyzed and worked up.

The bromine trap was reduced with aqueous sodium bisulfite solution. The organic phase was dried (Na_2SO_4) and distilled (pot temperature 90°). The carbon tetrachloride solution was analyzed by vpc[44] at 118°. There was one low-boiling product: 11 min (isobutylene dibromide, 17%). The compound was identified by comparison of its retention time and ir spectrum with that of a known sample. *m*-Methylanisole was used as internal standard.

The reaction residue was examined by vpc[44] at 118°. There were three products noted on the chromatogram: 7 min (*tert*-butyl phenyl sulfide, 51%), 13 min (biphenyl, 51%), 29 min (diphenyl sulfide, 24%). The *tert*-butyl phenyl sulfide was identified by its spectral properties: ir spectrum, 1368, 694 cm^{-1}; nmr, 1.26 (9 H, s), 7.10–7.65 (5 H, m); mass spectrum, *m/e* (% of base peak), 166 (2), 119 (93), 118 (100), 91 (35), 51 ppm (43); uv, λ_{max} (ϵ) 262 nm (1480); (lit.[46] $\lambda_{max}^{100\%\ EtOH}$ 266 (1550).

The yields reported are based on the amount of sulfonium salt consumed; 40 mg (20%) of the sulfonium salt was recovered. No *tert*-butylbenzene could be detected. Acenaphthene was employed as internal standard.

Reaction of Vinyllithium with *S*-Phenyldibenzothiophenium Fluoroborate. The reaction was carried out as usual employing 100 mg (2.93×10^{-4} mole) of the sulfonium salt and analysis[44] revealed the formation of styrene (60%) and dibenzothiophene (60%). Vpc analysis at 190° on a 5 ft × 0.25 in. 3% SE30 column on Chromosorb W revealed the formation of two additional products, **9** (5%) and **8** (8%). Acenaphthene was used as internal standard. The response factors for **9** and **8** were assumed to be 1.0.

Compound **9** showed the following characteristics: ir spectrum, 1720, 955, 697 cm^{-1}; nmr, 5.18 and 5.20 (2 H, two overlapping d, J = 17.0 and 9.0 Hz, respectively), 6.21 (1 H, d of d, J = 17.0 and 9.0 Hz), 7.0–7.5 ppm (13 H, m including s at 7.07); uv, λ_{max} (ϵ) 220 (sh) (11,200), 248 (sh) (8500), 257 (sh) (7100), 285 nm (sh) (1970); mass spectrum, *m/e* (% of base peak), 288 (6), 184 (100), 92 (17). *Anal.* Calcd for $C_{20}H_{16}S$: 288.097. Found: 288.09727 ± 0.001.

Compound **8** showed the following characteristics: ir spectrum, 1680, 1580, 908, 688 cm^{-1}; nmr, 5.06 (1 H, d of d, J = 11.0 and 1.5 Hz), 5.52 (1 H, d of d, J = 18.0 and 1.5 Hz), 6.42 (1 H, d of d, J = 18.0 and 11.0 Hz), 6.7–7.6 ppm (13 H, m); uv, λ_{max} (ϵ) 250 (sh) (6700), 285 nm (sh) (3700); mass spectrum, *m/e* (% of base peak), 288 (28), 184 (100), 92 (12). *Anal.* Calcd for $C_{20}H_{16}S$: 288.097. Found: 288.09727 ± 0.001.

Reaction of Allyllithium with Triphenylsulfonium Fluoroborate. Over a 5-min period, 5.7 ml (1.46 mmoles) of a 0.26 *N* solution of allyllithium (prepared by the method of Seyferth and Weiner[47]) in ether was added to a −78° slurry of the salt (1.43 mmoles), yielding a blood-red solution. The solution was stirred at −78° for 10 min, whereupon 0.30 g of dry cyclohexanone was added. After stirring for 2 min, the solution was warmed to room temperature. At approximately −10° the mixture became a colorless solution, with some sulfonium salt visible. After 30 min at room temperature, the mixture was hydrolyzed and worked up as usual. Chloroform extraction of the aqueous phase yielded 7 mg (1.4%) of recovered salt.

The ethereal residue was analyzed by vpc[44] at 140–210°. There were four peaks on the chromatogram: 6 min (cyclohexanone), 8 min (allylbenzene, 90%), 36 min (biphenyl, 8.5%), 46 min (di-

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(46) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 71, 84 (1949).

(47) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, 36, 4797 (1961), and references therein.

phenyl sulfide, 100%). Each product was identified by comparison of its vpc retention time and ir spectrum with those of known samples. Cycloheptanone was used as internal standard. The analysis revealed that no 2-vinyl-1-oxaspiro[5.2]octane was formed. It was calculated that all the biphenyl noted had been present in the phenyllithium solution used to generate the allyllithium.

Reaction of Allyldiphenylsulfonium Fluoroborate with Phenyllithium. Over a 3-min period, 2.65 ml (3.18 mmoles) of a 1.2 *N* ether solution of phenyllithium was added to a −78° slurry of the salt (3.18 mmoles), yielding a bright red solution. After 25 min, 0.40 g of cyclohexanone was added. After 2 min, the mixture was warmed to room temperature; the color slowly faded to give a colorless solution. The mixture was hydrolyzed and worked up as usual.

The reaction residue was analyzed by vpc at 140–200°. There were six significant peaks on the chromatogram: 6 min (cyclohexanone), 8 min (allylbenzene, 12.6%), 16 min (2-vinyl-1-oxaspiro[5.2]octane, 55%), 36 min (biphenyl, 8.6%), 46 min (diphenyl sulfide, 99%). Cycloheptanone was used as internal standard. Calculation showed that all of the biphenyl noted was present in the phenyllithium solution.

Deuteration of Allylide. To a −78° THF solution of the ylide (generated from 3.18 mmoles of allyldiphenylsulfonium fluoroborate and 3.3 mmoles of *n*-butyllithium) was added 0.25 ml of deuterioacetic acid. The red color of the solution was quenched in 15 sec yielding a white slurry. The mixture was warmed to room temperature, and 0.25 ml of water was added. The slurry was poured into a 500-ml flask; methylene chloride was added to dissolve the slurry. Ether was added to induce solidification. The precipitate was chilled in the refrigerator for 3 hr, filtered, and dried to yield 0.9 g (90%) of the sulfonium salt: nmr ($CDCl_3$) 4.83 (0.8 H, br d, J = 8.0 Hz), 5.30–5.95 (3 H, m), 7.60–8.15 ppm (10 H, m). The nmr integration showed that 1.2 deuterium atoms had been incorporated into the position α to sulfur.

Reaction of Phenyllithium with 1-Deuterioallyldiphenylsulfonium Fluoroborate. Over a 3-min period, 2.5 ml (3.0 mmoles) of a 1.2 *N* ether solution of phenyllithium was added to a −78° THF slurry of the salt (2.8 mmoles), yielding a deep red solution. After 30 min, 0.29 g of dry cyclohexanone was added. The mixture was warmed to room temperature, as it slowly became a colorless solution. The reaction was worked up as usual.

The allylbenzene was isolated by preparative vpc[44] at 140° (retention time, 8 min): nmr, 3.35 (1.4 H, br d, J = 6.5 Hz), 4.90 (0.6 H, m), 5.14 (0.8 H, m), 5.15–5.62 (1 H, m), 7.15 ppm (5 H, br s); mass spectrum (9.0 eV, 10 mA), allylbenzene-d_0 (19.4%),-d_1 (49.0%),-d_2 (31.6%). The nmr integrations showed that 0.6 deuterium atom had been incorporated into the α position (3.35 ppm) and that 0.6 deuterium atom had been incorporated into the γ position (4.90 and 5.14 ppm).

Preparation of 2-Acetoxyethyldiphenylsulfonium Fluoroborate. Acetic anhydride (7.5 g, 7.3 × 10^{-2} mole) was added to a flask. The material was chilled to 0° as 2.5 ml of 48% HBF_4 was added dropwise to the acetic anhydride. When the addition was complete, 5.5 g (3.0 × 10^{-2} mole) of diphenyl sulfide and 10 ml of methylene chloride were added. The reaction mixture was cooled in a −20° bath. In the cold room, 1.0 g (2.3 × 10^{-2} mole) of ethylene oxide was added to 10 ml of methylene chloride in a jacketed dropping funnel. The jacket was chilled to −20° with a CH_3OH–ice bath. The funnel was attached to the reaction vessel, and the ethylene oxide solution was added to the reaction mixture over a 30-min period. The mixture was then stirred at −20° for an additional 30 min and at room temperature for 1 hr. The volatile components were removed *in vacuo* to yield a nearly colorless oil. Chloroform was added to dissolve the mass, and ether was added to induce cloudiness. The mixture was chilled overnight in the refrigerator. The supernatant liquid was then decanted from the oil deposit. The remainder of the solvent was removed by pumping on the oil with a vacuum pump for several hours at 50°. An nmr spectrum ($CDCl_3$) of the oil showed singlets at 1.95 and 2.05 ppm, a broad multiplet at 3.5–4.7 ppm including a singlet at 4.58, multiplets at 7.7–7.9 and 8.0–8.3 ppm. The 1.95-ppm singlet was assigned to the acetoxy methyl group in the monomer; the 2.05-ppm singlet was assigned to the acetoxy methyl in the polymeric salt. The 4.58-ppm singlet was assigned to the two methylene groups in the monomeric salt. An nmr spectrum of the material in acetone resolved this singlet into a crude multiplet. The low-field multiplets were assigned to the phenyl protons in the various salts.

The oil was dissolved in ethanol and triturated with ether at −78°. The oil (approx 80% pure by nmr) was further purified by dissolving the material in a minimum of ethanol at room temperature and chilling the solution overnight at −20° to induce oiling out of the salt mixture. A final yield of 1.63 g (20%) of a salt mixture (approx 85% pure) was realized by this procedure.

Preparation of Diphenylvinylsulfonium Fluoroborate. To a flask was added 0.250 g of a 50% mineral oil dispersion of sodium hydride (5.0 mmoles). The dispersion was washed with three 5-ml portions of dry pentane. Then 10 ml of dry DMF was added to the sodium hydride. A solution of 0.49 g (1.33 mmoles) of the sulfonium salt mixture in 10 ml of DMF was added to the sodium hydride suspension. The mixture was stirred at room temperature for 45 min, until the evolution of hydrogen ceased. The mixture was then filtered through sintered glass. The DMF solvent was removed on the Rotovap at 60° at 2 mm of Hg; 10 ml of chloroform was added; the insoluble polymeric impurity was filtered from the reaction mixture. The filtrate was reduced *in vacuo* to an oil which was dissolved in a minimum of ethanol. Over a period of 24 hr, a small amount of diethyl ether was slowly added to the oil to induce a faint cloudiness. The mixture slowly deposited a crude white solid after 24 hr at −20°. Recrystallization afforded 0.20 g (50%) of the desired salt, as long white needles: mp 70–71°; ir spectrum ($CHCl_3$), 1730, 1050 cm^{-1}; nmr (CD_3COCD_3), 6.83 (1 H, d of d, J = 8.5 and 2.0 Hz), 6.53 (1 H, d of d, J = 16.0 and 2.0 Hz), 7.58 (1 H, d of d, J = 8.5 and 16.0 Hz), 7.70–8.25 ppm (10 H, m); uv, λ_{max} (ϵ) 259 (1640), 267 (1890), 273 nm (1360). *Anal.* Calcd for $C_{14}H_{13}SBF_4$: C, 56.02; H, 4.36; S, 10.68. Found: C, 56.25; H, 4.47; S, 10.74.

Reaction of Phenyllithium with Diphenylvinylsulfonium Fluoroborate. Over a 1-min period, 142 μl (1.7 × 10^{-4} mole) of a 1.2 *N* ether solution of phenyllithium was added to 50 mg (1.66 × 10^{-4} mole) of the salt in 5 ml of dry THF at −78°. The bright yellow slurry was stirred at −78° for 2.5 hr and then warmed slowly to room temperature. The colorless slurry was then hydrolyzed with 5 ml of H_2O and worked up as usual. Vpc analysis[44] of the mixture revealed two products: styrene (8.6%) and diphenyl sulfide (68%). Chloroform extraction of the aqueous phase revealed no recovered salt. Acenaphthene was used as the internal standard. The appropriate response factors were employed to determine the yields.

Preparation of Dibenzothiophene *S*-Oxide.[48] To a flask under nitrogen were added 19.7 g (0.107 mole) of dibenzothiophene, 62 ml of 30% hydrogen peroxide, and 76 ml of glacial acetic acid. The stirred slurry was heated to reflux (bath temperature, 135°) and was refluxed for about 10 min, until the cloudy solution suddenly turned clear. The heating bath was quickly removed, and the solution was cooled for a few minutes. The solution was then poured into 300 ml of water in an erlenmeyer flask; the material was cooled under tap water and filtered. The filtered solid was recrystallized from hot benzene to yield 15.9 g (74%) of a white solid: mp 186–188° (lit.[48] 186–187°); ir spectrum ($CHCl_3$), 1022, 1067 cm^{-1}; nmr ($CDCl_3$), 7.40–8.10 ppm (8 H, m).

Preparation of *S*,*S*-2,2′-Biphenyl-*S*-methoxysulfonium Fluoroborate. To 400 ml of dry methylene chloride in the flask under nitrogen were added 15.9 g (79 mmoles) of dibenzothiophene *S*-oxide and 11.8 g (79 mmoles) of trimethyloxonium fluoroborate. The yellow slurry was stirred for 1.5 hr at room temperature, during which time the slurry became a clear yellow solution. The solution was filtered through a glass wool plug and reduced in volume *in vacuo* yielding a heavy yellow slurry in a small amount of solvent. Ether was added, and the mixture was shaken vigorously. The solid was stored under ether at 0° overnight. The salt was then filtered, yielding 21 g (89%) of a "sulfur" yellow salt: mp 167–168°; ir spectrum (CH_2Cl_2), 1590, 1055, 9.43, 8.75 cm^{-1}; nmr (acetone-d_6), 3.70 (3 H, s), 7.78–8.66 ppm (8 H, m); uv, λ_{max} (ϵ) 222 (29,000), 248 (26,200), 278 (4650), 285 (4880), 312 (1260), 324 nm (1370), plus trailing into the visible region. *Anal.* Calcd for $C_{13}H_{11}OSBF_4$: C, 51.80; H, 3.67; S, 10.60. Found: C, 51.75; H, 3.72; S, 10.52.

Preparation of *S*-Phenyldibenzothiophenium Fluoroborate. To 13 ml of dry THF in the flask at −20° was added 0.173 g (0.57 mmole) of the methoxysulfonium salt. Over a 10-min period, 0.72 ml (0.57 mmole) of a 0.8 *N* phenylmagnesium bromide solution in ether was added to the yellow slurry. During the reaction the bright yellow slurry slowly formed a heavy white slurry. The mixture was stirred for 5 min and warmed to room temperature. The mixture was then hydrolyzed with 5 ml of 25% fluoroboric

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(48) H. Gilman and D. L. Esmay, *J. Amer. Chem. Soc.*, 74, 2021 (1952).

acid, and the resultant solution was poured into 30 ml of 12.5% fluoroboric acid. The white suspension was ether extracted. The aqueous phase was extracted with four 60-ml portions of methylene chloride. *In vacuo* evaporation of the solvent gave a white solid. Recrystallization from methylene chloride–ether afforded a white solid: 0.133 g (69%); mp 240–242°; nmr spectrum (DMSO-d_6), 7.60–8.80 ppm (13 H, including s at 7.64); uv (CH_3CN), λ_{max} (ϵ) 235 (32,700), 268 (9200), 317 nm (2100). *Anal.* Calcd for $C_{18}H_{13}SBF_4$: C, 62.10; H, 3.77; S, 9.21. Found: C, 61.87; H, 3.76; S, 9.08

Reaction of *S*-Phenyldibenzothiophenium Fluoroborate with Phenyllithium. To a slurry of 0.312 g (0.89 mmole) of *S*-phenyldibenzothiophenium fluoroborate in 32.5 ml of dry THF at −78° was added 0.49 ml (0.89 mmole) of 1.82 *M* phenyllithium. After completion and work-up of the reaction as above, the crude product was chromatographed on silica gel PF-254 (elution with 97:3 hexane–ether) to yield, after recrystallization from 95% ethanol, 125 mg (42% yield) of 2-phenyl-2'-thiophenoxybiphenyl (R_f 0.52): mp 89–90°; infrared spectrum (CCl_4), 1585, 1480, 1460, 696, 690 cm^{-1}; nmr ($COCl_3$), 6.8–7.5 ppm; mass spectrum, *m/e* (% of base peak) 338 (98), 229 (100), 228 (75); uv (C_2H_5OH), λ_{max} (ϵ) 275 sh (10,500), 256 (16,850), and 223 sh (35,900). *Anal.* Calcd for $C_{24}H_{18}S$: C, 85.24; H, 5.34; S, 9.42. Found: C, 85.17; H, 5.36; S, 9.45. Vpc analysis (5 ft × 0.25 in. 3% SE30 on Aeropak 30 column) revealed the absence of dibenzothiophene. A small amount of biphenyl (approximately 4 mg) attributable to the phenyllithium solution was detected.

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Nuclear Magnetic Resonance Studies of the Conformational Behavior of Alkylcycloheptatrienes

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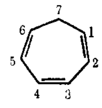
Abstract: In contrast to other simple cycloheptatrienes, 7-*tert*-butyl-1-methylcycloheptatriene undergoes slow inversion at room temperature. The conformer with the "axial" 7-*tert*-butyl group, **2a**, has been found to be more stable than **2b** where the 7-butyl group is "equatorial." There is restricted rotation of the 7-*tert*-butyl group in **2b** which allows the first nmr observation of three distinct methyl resonances for this group. The ring inversion and rotational barriers for **2** have been determined. Using some rigid cycloheptatrienes as models, a conformational analysis for 7-alkylcycloheptatrienes is advanced.

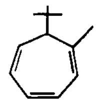
It is now well established that cycloheptatriene (**1**) exists as an interconverting pair of nonplanar conformers with an inversion barrier (**1a** ⇌ **1b**) of approximately 6 kcal/mol.[2,3] Several 7-substituted cycloheptatrienes have also been shown to exist as ring inverting conformers. Based on nuclear magnetic resonance (nmr) studies, the conformational preference of the 7-substituent has been shown to be the equatorial position in the case of deuterium,[2b] methyl[4a] (see below), isopropyl,[4a] *tert*-butyl,[4a,b] and phenyl.[4] More highly substituted derivatives of **1** have also been studied. The 7-methyl groups in 2-*tert*-butyl-3,7,7-trimethylcycloheptatriene are anisochronous at −100°, indicating a nonplanar ring.[5,6] In contrast, Roberts and coworkers[7] found that the 7-trifluoromethyl groups in 7,7-bis(trifluoromethyl)cycloheptatriene remain isochronous down to −185°. These authors argue that the observed increase in the vicinal coupling constant, $J_{2,3}$, is due to a more planar ring, which thus has a lower barrier to inversion.[8]



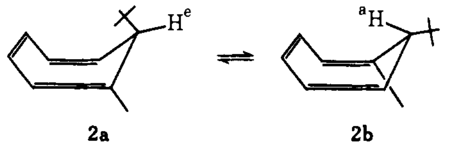
1

1a 1b

We reported[9] recently a preliminary account of our studies concerned with a simple derivative of **1**, namely, 7-*tert*-butyl-1-methylcycloheptatriene (**2**). The conformational and spectral behavior of **2**, as studied by nmr, proved to be quite interesting: (1) this tropilidene undergoes slow ring inversion at room temperature; (2) the conformer with the "axial" 7-*tert*-butyl group is more stable; (3) in the less stable conformer, there is restricted rotation of the "equatorial" 7-*tert*-butyl group—three distinct methyl resonances for this group can be observed. We present below a more complete description and analysis of the conformational be-



2



2a 2b

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[1] National Science Foundation Trainee, 1968–1969.

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[3] For an electron diffraction study of **1** and other leading references see M. Traetteberg, *ibid.*, **86**, 4265 (1964).

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[6] $\Delta F^{\ddagger}$ for ring inversion of this derivative has been estimated by Anet[2a] to be 9 kcal/mol.

[7] J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 3896 (1965).

[8] For a somewhat related example see, H. J. Reich, E. Ciganek, and J. D. Roberts, *ibid.*, **92**, 5166 (1970). $\Delta F^{\ddagger}$ for ring inversion in 7,7-dicyano-2,5-bis(difluoromethyl)cycloheptatriene is estimated to be 7 kcal/mole.

[9] W. E. Heyd and C. A. Cupas, *ibid.*, **91**, 1559 (1969).