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Reactions of Triarylsulfonium Salts with Sodium Alkoxides

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Abstract: The reaction of a triarylsulfonium halide with a sodium alkoxide in a solution in the corresponding alcohol at an elevated temperature produces a mixture of aromatic hydrocarbon, alkyl aryl ether, diaryl sulfide, and aldol resin (or a ketone if the alkoxide is derived from a secondary alcohol). We have now uncovered evidence which clearly indicates that the aromatic hydrocarbon and carbonyl compound are the products of a free radical chain reaction, whereas the alkyl aryl ether is the product of an aromatic nucleophilic displacement reaction.

We have recently presented evidence in the form of a preliminary communication[2] that triarylsulfonium salts undergo competing radical and ionic reactions with sodium alkoxides, aromatic hydrocarbons and aldehydes (which subsequently form aldol resins) or ketones arising by radical chain reactions, and alkyl aryl ethers arising by bimolecular aromatic nucleophilic displacement reactions; diaryl sulfides are formed in both types of reaction. We have also shown that, when all possible sources of radical chain inhibitors are excluded from the reaction mixtures, the aromatic hydrocarbons are usually the major products. On the other hand, the deliberate addition of an inhibitor, such as 1,1-diphenylethylene or diphenylpicrylhydrazyl, to the reaction mixtures causes the products of the aromatic SN reactions to become the major ones. The presumed initiation and propagation steps for the radical chain reaction, as illustrated for the reaction of a triphenylsulfonium halide with sodium ethoxide, are shown in Scheme I.

Scheme I

(1) Initiation

$$(C_6H_5)_3S^+ + CH_3CH_2O^- \rightleftharpoons \underset{\mathbf{1}}{(C_6H_5)_3S{-}O{-}CH_2CH_3} \rightleftharpoons$$

$$(C_6H_5)_2\dot{S}{-}O{-}CH_2CH_3,\ C_6H_5\cdot) \rightleftharpoons$$

$$(C_6H_5)_2\dot{S}{-}O{-}CH_2CH_3 + C_6H_5\cdot{}^{*a}$$

(2) Propagation

$$(C_6H_5)_3S{-}O{-}CH_2CH_3 + C_6H_5\cdot \longrightarrow$$

$$(C_6H_5)_3S{-}O{-}\dot{C}HCH_3 + C_6H_6$$

$$(C_6H_5)_3S{-}O{-}\dot{C}HCH_3 \longrightarrow (C_6H_5)_3S\cdot + CH_3CHO$$

$$\underset{\mathbf{2}}{(C_6H_5)_3\dot{S}} \longrightarrow C_6H_5SC_6H_5 + C_6H_5\cdot$$

[a]* Alternatively, $(C_6H_5)_3S\cdot + CH_3CH_2O\cdot$ may be formed.

We have now extended the previously reported studies[2,3] to include: (1) the use of sodium alkoxides other than sodium ethoxide; (2) the use of diphenyl-*p*-tolylsulfonium and tris(*p*-tolyl)sulfonium salts; (3) an evaluation of the effects of numerous additives; and (4) an evaluation of the effects of changes in solvent polarity. The new data are summarized in Tables I-VII.

The essence of the evidence for the competing radical and ionic pathways, as applied to the reaction of diphenyl-*p*-tolylsulfonium iodide with sodium ethoxide in ethanol solution, is as follows: (1) The reaction of 0.001 mol of the sulfonium iodide with 0.003 mol of sodium ethoxide in 3.00 ml of absolute ethanol in a sealed tube at 80° for 24 hr affords benzene (41.4% yield), toluene (14.1%), phenetole (22.1%), diphenyl sulfide (19.3%), and phenyl *p*-tolyl sulfide (84.0%) as the major products when no effort is made to remove oxygen of the air from the system. (The ratio of hydrocarbons to ethers is greater when an argon atmosphere is provided.) These and additional data are shown in Tables I and II. (2) When the same reaction is carried out in the presence of 0.001 mol of 1,1-diphenylethylene, the major products and yields are benzene (8.0%), toluene (2.3%), phenetole (75.5%), *p*-methylphenetole (2.1%), diphenyl sulfide (8.2%) and phenyl *p*-tolyl sulfide (92.5%); 1,1-diphenylethylene is recovered unchanged in 87.5% yield. Thus, in relatively high concentration, 1,1-diphenylethylene is effectively inhibiting the radical chain reaction leading to the formation of aromatic hydrocarbons, presumably by capturing aryl radicals.[4a] It is also of interest that the efficiency of the hydrocarbon additives as inhibitors of the radical chain reaction follows the order 1,1-diphenylethylene > styrene > *trans*-stilbene, and this parallels the data on "methyl affinities" compiled by Szwarc and Binks,[4b] which, in turn, parallels the relative rates of addition of phenyl radicals to unsaturated systems.[4a]

The effects of such well-known radical traps as galvinoxyl and diphenylpicrylhydrazyl on the system under consideration are of interest but subject to some ambiguity in interpretation owing to the fact that these radicals can undergo reactions with strong bases. When 5×10^{-5} mole of diphenylpicrylhydrazyl is added to the reaction mixture described above, without exclusion of oxygen, the major products are benzene (54.1%), toluene (16.5%), phenetole (18.9%), diphenyl sulfide (18.8%), and phenyl *p*-tolyl sulfide (77.0%). With the same amount of diphenylpicrylhydrazyl present, but with exclusion of oxygen (argon atmo-

Table I. Reactions of Diphenyl-*p*-tolylsulfonium Iodide (0.001 mol) with Sodium Ethoxide (0.003 mol) in Ethanol (5 ml) at 80° for 24 hr in Sealed Tubes

Atmosphere	Additive	Products, % yield						
		C_6H_6	C_6H_5Me	C_6H_5OEt	*p*-MeC_6H_4-OEt	*p*-MeC_6H_5S-C_6H_5	$(C_6H_5)_2S$	C_6H_5–C_6H_5
Air	None	41.4	14.1	22.1	0.8	84.0	19.3	1.5
Argon	None	62.8	20.6	11.5	Trace	75.0	19.3	
Air	*trans*-Stilbene[a]	15.7	4.9	42.0	3	83.0	14.6	Trace
Air	*trans*-Stilbene[b]	47.1	17.3	20.9	Trace	85.0	19.0	Trace
Air	1,1-Diphenylethylene[c]	8.1	2.3	75.5	2.1	92.5	8.2	
Air	1,1-Diphenylethylene[b]	36.4	14.1	29.6	~2	85.0	16.9	Trace
Air	Styrene[d]	11.5	4.3	52.0	5.5	72.0	10.3	
Air	DPPH[e]	9.8	Trace	8.2		47.5	9.0	2
Air	DPPH[b]	54.1	16.5	18.9	0.6	77.0	18.8	Trace
Argon	DPPH[b]	39.7	14.1	28.7	1.0	78.0	17.7	
Air	Galvinoxyl[f]	22.5	6.9	18.2		77.5	23.2	1
Air	Galvinoxyl[b]	48.1	16.8	24.6	0.9	83.5	18.8	Trace
Argon	Galvinoxyl[b]	50.0	16.8	23.0	Trace	81.5	18.7	Trace

[a] 0.001 mol, of which not less than 98% was recovered unchanged. [b] 0.00005 mol. [c] 0.001 mol, of which not less than 87.5% was recovered unchanged. [d] 0.001 mol, of which not less than 91.1% was recovered unchanged. [e] 0.001 mol of diphenylpicrylhydrazyl. [f] 0.001 mol.

Table II. Reactions of Diphenyl-*p*-tolylsulfonium Iodide (0.001 mol) with Various Concentrations of Sodium Ethoxide in Ethanol (3.0 ml) at 80° for 24 hr in Sealed Tubes

Molar ratio of iodide : ethoxide	Atmosphere	Products,[a] % yield						
		C_6H_6	C_6H_5Me	C_6H_5OEt	*p*-MeC_6H_4-OEt	*p*-MeC_6H_4S-C_6H_5	$(C_6H_5)_2S$	C_6H_5–C_6H_5
1:0.1	Air	<1	Trace	7.5	Trace	16.3[b]	2.0	
1:0.5	Air	14.8	5.0	16.0	Trace	41.0	9.4	<1
1:0.5	Argon	25.6	10.9	15.4		58.0	14.8	Trace
1:1	Air	30.4	8.2	23.6		60.0	14.4	Trace
1:1	Argon	41.0	15.2	16.8		74.0	19.5	
1:3	Air	41.4	14.1	22.1	0.8	84.0	19.3	1.5
1:3	Argon	62.8	20.6	11.5	Trace	75.0	19.3	
1:5	Air	42.0	14.1	22.9	Trace	74.6	17.8	Trace
1:8	Air	32.8	10.6	22.1	0.9	82.0	20.1	1.5

[a] Resins were also obtained in each reaction. [b] About 70% of the starting sulfonium salt was recovered unchanged.

Table III. Reactions of Diphenyl-*p*-tolylsulfonium Iodide (0.001 mol) with Sodium Methoxide (0.003 mol) in Methanol (5 ml) at 80° for 24 hr in Sealed Tubes

Atmosphere	Additive	Products, % yield						
		C_6H_6	C_6H_5Me	C_6H_5OMe	*p*-MeC_6H_4-OMe	*p*-MeC_6H_4S-C_6H_5	$(C_6H_5)_2S$	C_6H_5–C_6H_5
Air	None	19.4	6.5	28.7	~2	69.5	18.6	1.2
Argon	None	23.6	7.1	25.8		67.0	18.2	
Air	1,1-Diphenylethylene[a]	4.5	Trace	62.0	~2	73.8	11.8	
Air	Galvinoxyl[b]	14.1	6.3	19.4	Trace	63.5	23.1	2
Air	Galvinoxyl[c]	30.8	9.8	29.6	Trace	77.0	18.0	2

[a] 0.001 mol, of which not less than 90% was recovered unreacted. [b] 0.001 mol. [c] 0.0001 mol.

Table IV. Reactions of Tris(*p*-tolyl)sulfonium Iodide (0.001 mol) with Sodium Methoxide (0.003 mol) in Methanol (5 ml) at 80° for 24 hr in Sealed Tubes

Atmosphere	Additive	Products, % yield			
		C_6H_5Me	*p*-MeC_6H_4OMe	(*p*-$MeC_6H_4)_2S$	(*p*-$MeC_6H_4)_2$
Air	None	24.6	10.7	56.1	2
Argon	None	24.1	11.3	56.9	1.4
Air	1,1-Diphenylethylene[a]	11.4	23.9	61.0	Trace
Air	Galvinoxyl[b]	19.5	2.8	57.7	3

[a] 0.001 mol. [b] 0.001 mol.

sphere), the products are benzene (39.7%), toluene (14.1%), phenetole (28.7%), diphenyl sulfide (17.7%), and phenyl *p*-tolyl sulfide (78.0%). Evidently, when both oxygen and diphenylpicrylhydrazyl, each of which functions as an inhibitor of the radical chain reaction in its own right, are present in small concentrations, they neutralize each other. Indeed, diphenylpicrylhydrazyl is known to form a complex with oxygen.[5]

The presence of 5 × 10^{-5} mol of galvinoxyl in the reaction mixture, with or without exclusion of oxygen, leads to the production of benzene (48–50%), toluene (16.8%), phenetole (23.0–24.6%), diphenyl sulfide (18.7%), and phenyl *p*-tolyl sulfide (81.5–83.5%). Thus, the amount of galvinoxyl surviving reaction with base[6] appears to inhibit somewhat the production of aromatic hydrocarbons but not that of phenetole. Even when a relatively large amount of galvinoxyl (0.001 mol) is added to the reaction mixture, the yield of phenetole is not decreased noticeably. Since galvinoxyl is known to be an efficient trap for alkoxyl radicals,[7] it is apparent that phenetole is not arising by a radical reac-

Table V. Reactions of $(p\text{-Y-}C_6H_4)_3S^+X^-$ with Various Sodium Alkoxides in the Corresponding Alcohols (2 ml) at 71°

X^-	Salt concn, *m*	Alkoxide (concn, *m*)	Time, hr	% yield Acetone	 C_6H_5Y	 *p*-YC_6H_4OR	 (*p*-$YC_6H_4)_2S$	Y	Additives (concn, *m*)
Br^-	7×10^{-4}	*n*-BuO^- (14×10^{-4})	14		10	31	43	CH_3	
Br^-	7×10^{-4}	*n*-BuO (14×10^{-4})	14		Trace	31	37	CH_3	DPE (7×10^{-4})
Br^-	7×10^{-4}	*n*-BuO (14×10^{-4})	14		2	31	41	CH_3	*cis*-Stilbene (7×10^{-4})
Br^-	7×10^{-4}	*n*-BuO (14×10^{-4})	14		13	31	44	CH_3	O_2 (sat)
Br^-	5×10^{-4}	*i*-Pro^- (7×10^{-4})	19	17	18	53	70	CH_3	
Br^-	5×10^{-4}	*i*-PrO^- (7×10^{-4})	19	48	48	27	68	CH_3	O_2 (sat)
Br^-	5×10^{-4}	*i*-PrO^- (7×10^{-4})	19	Trace	Trace	58	70	CH_3	DPE (5×10^{-4})
Cl^-	5×10^{-4}	*i*-PrO^- (7×10^{-4})	22	1	0.0	89	89	-H	
Cl^-	5×10^{-4}	*i*-PrO^- (7×10^{-4})	22	21	0.0	89	92	-H	O_2 (sat)
Cl^-	5×10^{-4}	*i*-PrO^- (7×10^{-4})	22	0.0	0.0	88	89	-H	DPE (5×10^{-4})
I^-	5×10^{-4} [a]	*i*-PrO^- (7×10^{-4})	22	1.5	Trace	78	86	-H	
I^-	5×10^{-4} [a]	*i*-PrO^- (7×10^{-4})	22	34	28	61	90	-H	O_2 (sat)[b]
I^-	5×10^{-4}	*i*-PrOH	19	32	Trace	0.0	0.03	-H	$(PhCO_2)_2$ (2.5×10^{-4})
I^-	5×10^{-4}	*i*-PrOH	19	9	0.0	0.0	0.01	-H	$(PhCO_2)_2$ (1.0×10^{-4})

[a] The sulfonium iodides were initially only partially soluble in the alcohol. However, complete solubility was effected after a few hours of reaction. [b] Iodine also appeared to be produced.

Table VI. Effects of Changes in Solvent Polarity on the Reactions of Triphenylsulfonium Bromide with NaOEt[a]

Solvent % EtOH	 % additive	Product, % yield PhH	 PhOEt	 Ph_2S	 Ph-Ph
100		86	11	100	0.20
90	10 (toluene)	70	20	91	0.11
80[b]	20 (toluene)	47	37	90	0.06
90	10 (*n*-hexane)	79	18	100	0.24
80[b]	20 (*n*-hexane)	64	29	97	0.22

[a] 3.50×10^{-4} mol of $Ph_3S^+Br^-$ treated with 7.00×10^{-4} mol of NaOEt in 2 ml of specified solvent at 80° for 24 hr (argon atmosphere). [b] The limit for the preparation of a homogeneous solution.

Table VII. Effects of Small Amounts of Toluene, Benzene, or *n*-Hexane on the Reactions of Triphenylsulfonium Bromide with NaOEt[a]

Additive (equiv)	Product, % yield PhH	 PhOEt	 Ph_2S	 Ph-Ph
Toluene (1)	81	10	92	0.17
Benzene (1)	80[b]	10	93	0.14
n-Hexane[c] (1.1)	85	12	97	0.24
n-Hexane[c] (1.8)	85	13	100	0.26

[a] Concentrations of reagents and conditions the same as specified in Table VI; solvent, absolute EtOH. [b] 100% recovery of additive assumed. [c] No evidence of dodecanes or phenylhexanes found by glpc.

tion involving ethoxyl radicals. Furthermore, the fact that phenetole is produced in much larger amounts than *p*-methylphenetole constitutes valid additional evidence for the aromatic nucleophilic displacement process.[8]

The data found in Tables I-V and a previous paper[3] permit several generalizations to be made. (1) For a given triarylsulfonium salt, the ratio of ether to aromatic hydrocarbon formed in reaction with an alkoxide anion decreases in the order *n*-butoxide ≥ isopropoxide > methoxide > ethoxide. (2) The reactions of tris(*p*-tolyl)sulfonium salts with sodium alkoxides are slower and give a higher ratio of hydrocarbon to ether than the corresponding reactions of triphenylsulfonium salts. (3) The reactions of triarylsulfonium iodides with sodium alkoxides are slower and give a higher ratio of hydrocarbon to ether than those of the other triarylsulfonium halides. (4) The effects of oxygen on the reactions vary markedly, depending on the nature of the sulfonium salt and the nature of the sodium alkoxide.

These effects can be rationalized in terms of the competing radical chain reaction leading to aromatic hydrocarbon plus carbonyl compound (derived from the alkoxide ion) and the aromatic SN reaction leading to alkyl aryl ether. The variation in ratio of ether to hydrocarbon with change of alkoxide ion depends mainly on two factors. With a given triarylsulfonium cation, the order of reactivity in the aromatic SN reaction should be as follows: *i*-PrO^- > *n*-BuO^- > EtO^- > MeO^-. However, in the competing radical chain reaction, the carbinyl hydrogen of the isopropoxy group has a lower bond dissociation energy than that of either of the carbinyl hydrogens of the *n*-butoxy group. In like manner, the ethoxy carbinyl hydrogens have a lower bond dissociation energy than the methoxy carbinyl hydrogens.[9] This effect clearly favors the radical chain reaction leading to aromatic hydrocarbon in the case of the isopropoxide reaction over the *n*-butoxide reaction and in the ethoxide reaction over the methoxide reaction. Thus, it is a properly weighted contribution of these effects which leads to the order *n*-BuO^- ≥ *i*-PrO^- > MeO^- > EtO^- in the determination of the decreasing ratio of ether to hydrocarbon formed.

The relatively slow reactions of the tris(*p*-tolyl)sulfonium salts as against the triphenylsulfonium salts is attributable to the mild electron-donating effect of the *p*-methyl substituents. This not only retards the rate of attack by alkoxide ion in the aromatic SN reaction, but it also shifts the equilibrium between the triarylsulfonium alkoxide and the alkoxytriarylsulfurane (of the type **1**) toward the ions. This obviously causes retardation of the radical sequence. However, the tris(*p*-tolyl)sulfur radical would be more stable (and more readily formed) than the triphenylsulfur radical (**2**) owing to hyperconjugation in the former,[3] and therefore it would have a greater tendency to be formed in a relatively free state by dissociation of the initially formed radical pair than would the triphenylsulfur radical. Thus, once a sufficient concentration of initiator radicals had been formed, the radical chain reaction of the tris(*p*-tolyl)sulfonium system would progress smoothly.

The iodide salts differ from the other sulfonium salts in that they probably exist at tight ion pairs.[3] A close association of the large iodide ion with the positive sulfur of the sulfonium salt would tend to retard the aromatic SN reaction both by a steric effect and also by decreasing the electrophilic reactivity of the sulfonium cation through induction. For the same reasons, nucleophilic attack of the alkoxide ion at sulfur to form a sulfurane intermediate would be hindered, thus causing retardation of the radical process. However, an iodide ion has a greater ability to enter into an electron-transfer process than does a bromide, chloride, or fluoroborate anion.[10,11] Thus, an electron-transfer process provides an alternative source of a triarylsulfur radical from the triarylsulfonium iodide.

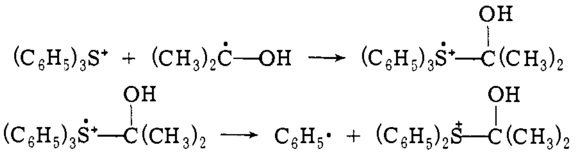
$$Ar_3S^+, I^- \longrightarrow Ar_3S\cdot, I\cdot$$

The triarylsulfur radical formed in this manner can then act as an initiator radical and set in motion the radical chain reaction leading to aromatic hydrocarbon, carbonyl compound, and diaryl sulfide. Thus, by an indirect (and somewhat slower) process, the radical sequence is favored over the aromatic SN sequence and leads to an increase in the hydrocarbon to ether ratio.

To gain an understanding of the effect of oxygen, it is important to realize that oxygen can function as either a promoter or an inhibitor in chain-transfer processes. According to Frank,[12] a chain-transfer process manifests itself in two ways (exclusive of inhibition, which is a special case of chain transfer with formation of an inactive radical) in autoxidation in polymer processes: (a) a promoting effect in which the chain-transfer agent generates a radical more capable of sustaining attack than the original initiator radical; and (b) a moderating effect in which the chain-transfer agent deactivates the "excess" radicals. Examples of promoting[13-16] and moderating[17-20] effects are extensive. In our systems, for the reactions of the sulfonium cations with ethoxide ion, oxygen apparently inhibits the radical chain process, resulting in lower yields of aromatic hydrocarbons. However, for the isopropoxide ion, owing to the lower bond dissociation energy of the carbinyl C–H bond,[9] an additional radical initiation process may become available, namely the abstraction of a hydrogen atom by oxygen. If this process were sufficiently rapid, the supply of readily available oxygen in the closed system would soon be exhausted,[21] and an "excess" of radicals would be available to initiate the chain reaction. Generally, such an effect is seen when the more stable tris(p-tolyl)sulfur radical is being formed, and this suggests that a synchronous radical β-elimination reaction may be occurring.

$$Ar_3S{-}O{-}CHRR' + O_2 \longrightarrow Ar_3S\cdot + RR'C{=}O + HOO\cdot$$

Other conceivable mechanisms for the formation of the products of the reactions of triarylsulfonium salts with sodium alkoxides have been considered in a previous publication,[3] and evidence was presented to rule out these possibilities. However, one additional, conceivable mechanism for the radical chain reaction must now be considered. This involves formation of an alkylhydroxycarbinyl radical by abstraction of a carbinyl hydrogen atom from the solvent as part of the initiation process. Then, as applied to the reaction of a triphenylsulfonium salt with sodium isopropoxide in isopropyl alcohol, the propagation steps would be:



$$(C_6H_5)_3S^+ + (CH_3)_2\dot{C}{-}OH \longrightarrow (C_6H_5)_3\dot{S}^+{-}\overset{\overset{\text{OH}}{|}}{C}(CH_3)_2$$

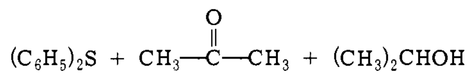
$$(C_6H_5)_3\dot{S}^+{-}\overset{\overset{\text{OH}}{|}}{C}(CH_3)_2 \longrightarrow C_6H_5\cdot + (C_6H_5)_2S^+{-}\overset{\overset{\text{OH}}{|}}{C}(CH_3)_2$$

3

$$C_6H_5\cdot + (CH_3)_2CHOH \longrightarrow C_6H_6 + (CH_3)_2\dot{C}{-}OH$$

Of course, the following reaction would subsequently destroy the newly formed sulfonium cation **3**.

$$\mathbf{3} + (CH_3)_2CH{-}O^- \longrightarrow$$



$$(C_6H_5)_2S + CH_3{-}\overset{\overset{\text{O}}{\|}}{C}{-}CH_3 + (CH_3)_2CHOH$$

That this conceivable chain process is unlikely is evident from the results of the reactions of tris(p-tolyl)sulfonium bromide with benzoyl peroxide in isopropyl alcohol solution, shown in Table V. No more than trace amounts of toluene and bis(p-tolyl) sulfide were formed. We have previously demonstrated that the reaction of diphenyliodonium salts with benzoyl peroxide in isopropyl alcohol produces high yields of benzene and iodobenzene (plus a small amount of biphenyl),[22] and therefore there can be no doubt that the decomposition of benzoyl peroxide in isopropyl alcohol will provide dimethylhydroxycarbinyl radicals. Thus, the failure of tris(p-tolyl)sulfonium bromide to undergo any significant degree of reaction with the peroxide indicates that the alternative chain process cited above is not a reasonable possibility.

We are now able to consider one additional aspect of our original formulation of the competing radical chain and aromatic SN reactions. Since the coming together of two ions with unlike charges is always a fast process,[23] the initial step of the initiation process of the radical chain reaction is almost certainly faster than the subsequent steps, those that give rise to radicals. Therefore, since there would be no marked effects of changes of solvent polarity on the rates of the radical processes, the change from 100% ethanol to an ethanol–toluene or ethanol–hexane mixed solvent system would exert no major influence on the rate of formation of benzene. However, since the aromatic nucleophilic substitution reaction involves dissipation of charges as the transition state is formed, the change from a more polar to a less polar solvent would cause acceleration of this reaction. It therefore follows that (as applied to the reaction of triphenylsulfonium bromide with sodium ethoxide), with a decrease of the polarity of the solvent, the ratio of nucleophilic aromatic substitution product (phenetole) to the radical products (benzene and acetaldehyde, which subsequently forms an aldol resin in the strongly basic medium) would increase. The data provided in Table VI support this interpretation.

Inasmuch as the presence of radical traps has been shown to inhibit the production of aromatic hydrocarbons in the reactions of triarylsulfonium[2] and diarylhalonium[24,25] salts with sodium alkoxides, and since the inhibition of other radical chain reactions by aromatic hydrocarbons has been reported,[26-28] it was deemed necessary to evaluate the possible role of toluene as a specific inhibitor of the radical chain reaction as against its effect as a relatively nonpolar component of the solvent system. As shown by the results summarized in Table VII, the presence of 1 equiv of toluene exerts no significant effect on the yield of benzene in the reaction of triphenylsulfonium bromide with sodium ethoxide in absolute ethanol. In like manner, the presence of 1 equiv of benzene or n-hexane also has no significant effect on this reaction.

Experimental Section

All of the sulfonium salts were prepared as described in a previous paper,[3] with the exception of diphenyl-p-tolylsulfonium iodide.

Diphenyl-p-tolylsulfonium Iodide. To a solution of 1.5 g (0.007 mol) of phenyl p-tolyl sulfoxide[29] in 50 ml of anhydrous benzene was added 6 g (0.0445 mol) of anhydrous aluminum chloride. The mixture became purple. The mixture was refluxed for 20 hr, cooled to room temperature, and then it was poured into 100 ml of ice–water containing 20 ml of concentrated hydrochloric acid. The resulting mixture was warmed on a steam bath for a few minutes. The aqueous layer was separated from the organic layer, and the former was washed twice with benzene. A solution of 20 g of potassium iodide in the minimum amount of water was added to the aqueous solution, and a white precipitate immediately formed. The precipitate was then extracted into three 50-ml portions of chloroform. After it had been dried over anhydrous sodium sulfate, the chloroform extract was evaporated to give a yellow solid. The solid was dissolved in acetone–chloroform (5:1) mixed solvent, and treatment of this solution with an excess of ether caused the precipitation of white crystals, which were collected by filtration to give 1.6 g. (57%) of pure diphenyl-p-tolylsulfonium iodide. The crystals were dried in a low-pressure oven at 110° overnight: mp 249–250.5° dec; nmr (CDCl$_3$) δ 2.47 (s, 3 H), 7.4–7.9 (m, 14 H).

Anal. Calcd for $C_{19}H_{17}SI$: C, 56.43; H, 4.21; I, 31.43. Found: C, 56.42; H, 4.16; I, 31.38.

Reactions of Arylsulfonium Salts with Sodium Alkoxides. All reactions, not specified otherwise, were carried out under an argon atmosphere. For these reactions, 50 ml of the respective alcohol solvent was deoxygenated and caused to react with sodium under argon. Appropriate volumes, as specified in the tables, were used for each reaction. The reaction tube, which had been flushed with argon after addition of the sulfonium salt, was again flushed after addition of the alkoxide solution, the tube then being sealed under argon. For the reactions carried out in isopropyl alcohol, the temperature of the alcohol solution was maintained just below its boiling point during its reaction with sodium in order to accelerate the reaction and prevent the precipitation of sodium isopropoxide.

The sealed tubes were placed in an oil bath for the duration of the reaction time. After completion of the reaction, the tubes were opened, neutralized with 85% phosphoric acid (usually requiring only 2 drops from a micropipet), and immediately analyzed on a F & M 609 flame ionization gas chromatograph equipped with either a 6-ft 10%-SE 30, 100–110 Anakrom or a 5-ft Carbowax 20M column.

To assure maximum reproducibility, the reactions were carried out in batches of four to eight at a time. Each batch contained the same alkoxide solution, and all reaction mixtures were deoxygenated in the same manner. The yields of the reaction products were determined by calculating the areas of the peaks observed in the vapor-phase chromatogram. Approximate peak areas were obtained by multiplying the peak height by the peak width at half-height. Three standard solutions, having compositions near the approximate value obtained from the reaction mixture, were then prepared for each component and subjected to vpc analysis; the approximate areas were obtained and plotted graphically *vs.* composition. The actual product compositions were then obtained directly from the graphs.

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