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# SYNTHESIS OF TRIARYLSULFONIUM SALTS FROM DIARYLETHOXYSULFONIUM SALTS

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This report describes a new synthesis of triarylsulfonium salts via the reaction of diarylethoxysulfonium salts with arylmagnesium halides. However, optically active diarylethoxysulfonium salts gave only inactive triarylsulfonium salts.

The sulfonium salts prepared are listed in Table 1. The diaryl sulfoxides were converted to the diarylethoxysulfonium tetrafluoroborates using triethyloxonium tetrafluoroborate in methylene chloride (1). The methylene chloride solvent was then replaced by tetrahydrofuran and the resulting mixture added to the Grignard reagent in tetrahydrofuran at -20° to 0°. After hydrolysis, the aqueous layers were extracted with chloroform to remove the sulfonium salt. Concentration of the chloroform extracts gave the sulfonium salt, often as an oil, which was then converted to the perchlorate salt by precipitation from aqueous solution by sodium perchlorate. Addition of the Grignard reagent to the diarylethoxysulfonium salt gave similar results as did the use of dimethoxyethane-ethyl ether solvent mixtures. The yields ranged from 30 to 60%. The optical rotatory dispersion curves from 600 to 300 mμ gave no evidence of optical activity for the sulfonium salts prepared from optically active sulfoxides.

Triarylsulfonium salts have previously been synthesized from diaryl sulfoxides and arylmagnesium halides without the intermediacy of diarylethoxysulfonium salts, but only at higher temperatures (2).

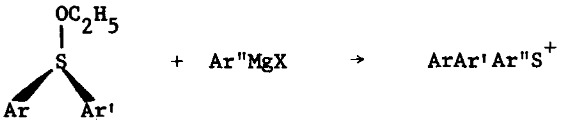
TABLE 1

| Sulfoxide | Grignard | Sulfonium Salt[a] | | m.p. |
|---|---|---|---|---|
| ArAr'SO | | ArAr'Ar"$S^+$ | $X^-$ | |
| $C_6H_5$, $C_6H_5$ | $C_6H_5MgBr$ | $(C_6H_5)_3$ | $Br^-$ | 284-286°,[b] |
| (+)-m-$CH_3C_6H_4$,<br>p-$CH_3C_6H_4$ | $C_6H_5MgBr$ | m-$CH_3C_6H_4$,<br>p-$CH_3C_6H_4$,<br>$C_6H_5$ | $ClO_4^-$ | 133-135° |
| (+)-$C_6H_5$,<br>p-$CH_3C_6H_4$ | o-$CH_3OC_6H_4MgBr$ | $C_6H_5$,<br>p-$CH_3C_6H_4$,<br>o-$CH_3OC_6H_4$ | $ClO_4^-$ | 86-88° |
| (-)-o-$CH_3OC_6H_4$,<br>p-$CH_3C_6H_4$ | $C_6H_5MgBr$ | $C_6H_5$,<br>p-CH3C6H4,<br>o-$CH_3OC_6H_4$ | $ClO_4^-$ | 85-87° |

[a] All new compounds gave satisfactory analyses.

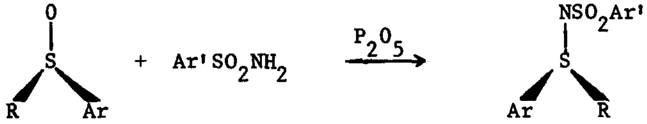
[b] Lit. m.p. 285-286° (2) and 292.5° (3).

The lack of optical activity is surprising in view of the analogy between this reaction (eq. 1) and the stereospecific syntheses of sulfoxides (4) (eq. 2) and sulfilimines (5) (eq. 3), and the stereospecific solvolysis of ethoxysulfonium salts (1) (eq. 4).

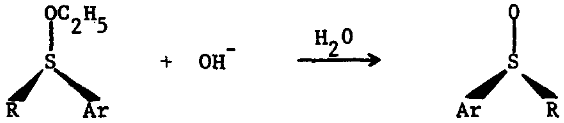


(1)

(2)



(3)



(4)

Either the reaction proceeds through a symmetrical intermediate or transition state, or the triarylsulfonium salts, presumably pyramidal about sulfur as are the trialkylsulfonium salts, have a low barrier for enantiomer interconversion analogous to the amines.

The possibility of symmetrical intermediates is unlikely in view of eqs. 2,3, and 4. Exchange of aryl groups of the sulfonium salt with the aryl group of the Grignard, a process which takes place with triarylsulfonium salts and aryllithium compounds (6) and which might lead to racemization, apparently does not take place since phenyl-p-tolyl-o-anisylsulfonium perchlorate can be prepared from two routes (Table 1).

The possibility of a low barrier to enantiomer interconversion seems the more likely explanation especially since sulfoxides can be racemized thermally (7). A steric factor has been shown to be operative here; i.e., the sulfoxides with bulky R groups racemize the most easily. By analogy, triarylsulfonium salts would be expected to have lower energy barriers for racemization than the trialkylsulfonium salts some of which have been resolved (8).

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