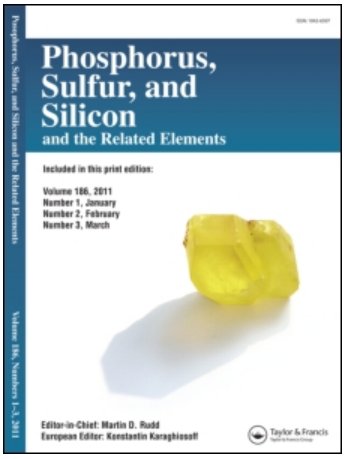

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1,7-RAMBERG-BÄCKLUND REACTIONS AND OTHER ANOMALOUS REACTIONS OF P-HYDROXYPHENYL α-HALO SULFONES

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1,7-RAMBERG-BÄCKLUND REACTIONS AND OTHER ANOMALOUS REACTIONS OF p-HYDROXYPHENYL α-HALO SULFONES

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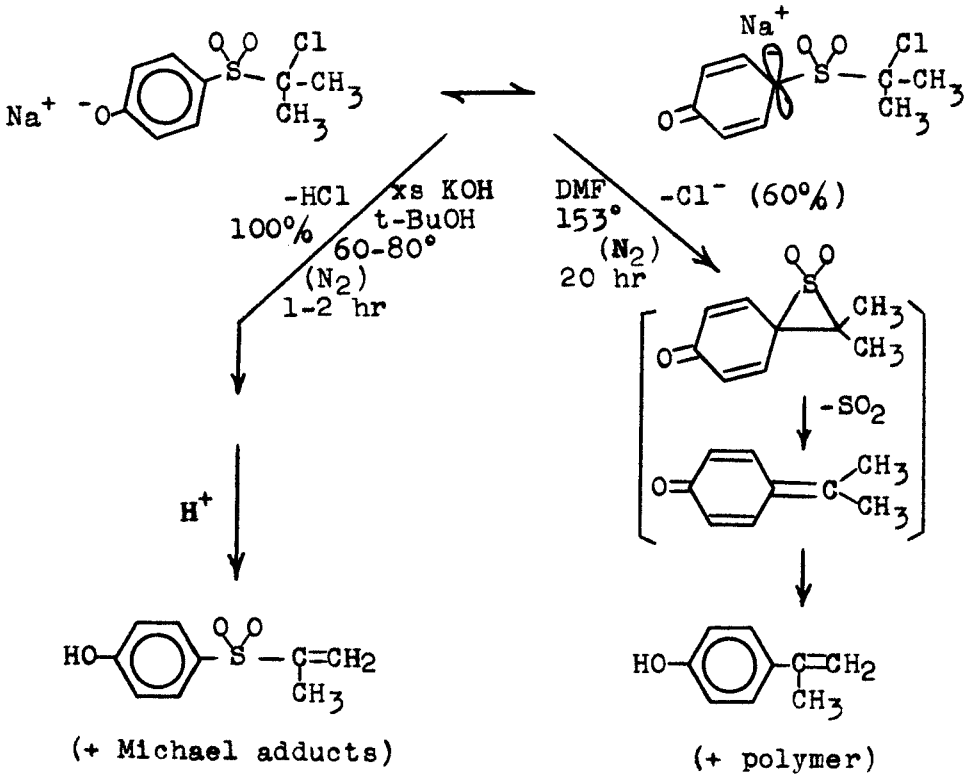
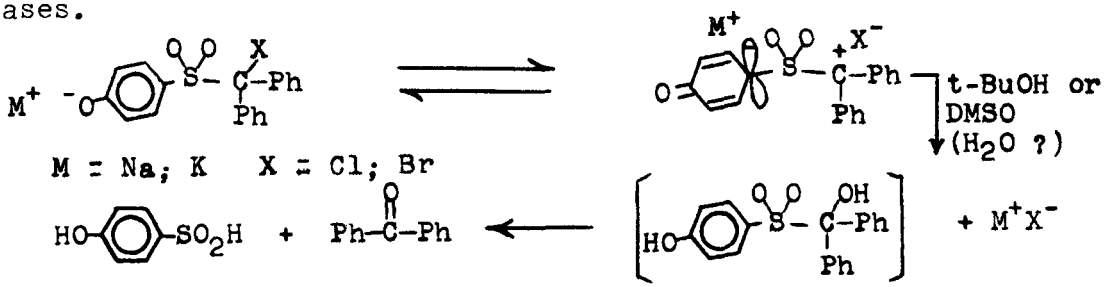
p-Hydroxyphenyl α-halo sulfones are unusual in several respects. For example, p-hydroxyphenyl α-chloroisopropyl sulfone has no α'-H; however, when heated with one equivalent of base it undergoes a 1,7-elimination reaction via a pathway usually associated with the 1,3-elimination step of Ramberg-Bäcklund reactions. The 1,7-elimination process is energetically unfavorable, however; in the presence of excess base this α-chloro sulfone more rapidly undergoes α,β-dehydrochlorination, and the 1,7-elimination products are not detected.



These results suggested that p-hydroxyphenyl α-halobenzhydryl sulfones should exclusively undergo the 1,7-elimination reaction. In reality, however, while the phenolic α-chlorobenzhydryl sulfone was unchanged by treatment with excess KOH-t-BuOH at 25°, its monosodium salt was fragmented into benzophenone and p-hydroxybenzenesulfinic acid when heated in t-BuOH or DMSO. The corresponding α-bromo sulfone was even more sensitive to fragmentation and rapidly provided these products almost quantitatively when treated with alkali-t-BuOH at 25°. Ironically, little if any evidence for 1,7-elimination was detected in these cases.



α-Halo sulfones are generally very resistant to solvolytic halide displacement reactions because of the electronegativity of the sulfonyl group. Evidently this characteristic is greatly reduced by p-O^- substitution which permits the inherent stability of the benzhydryl cation to be manifested. Under better solvolysis conditions such fragmentations were induced by p-HO or MeO substitution, observations which lend support to this explanation.