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

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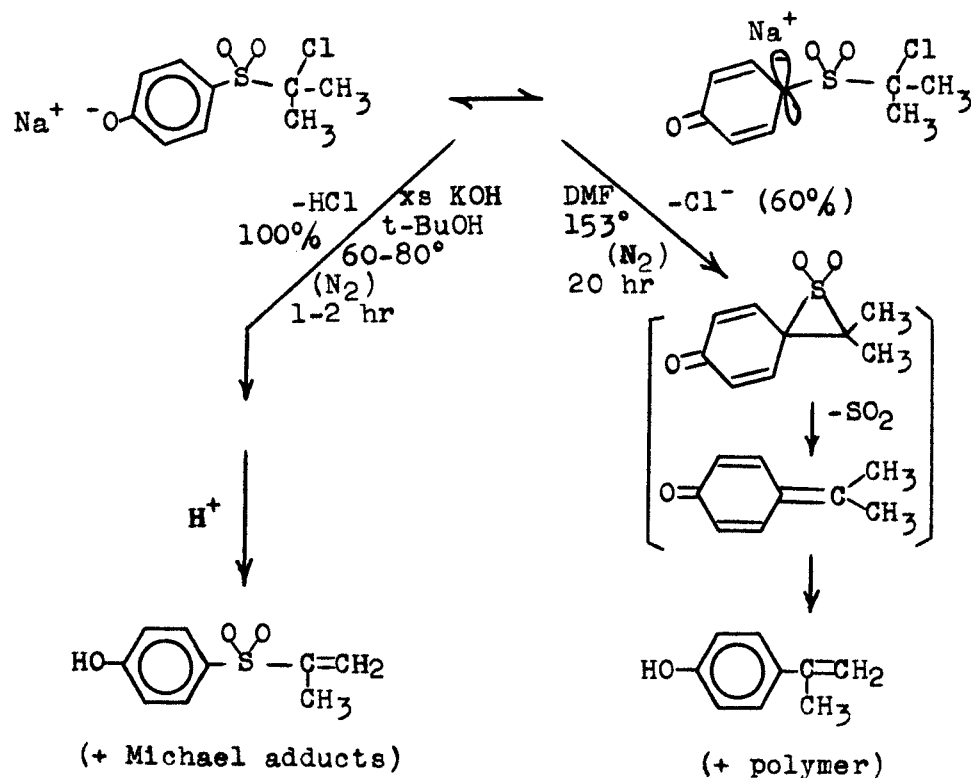
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1,7-RAMBERG-BÄCKLUND REACTIONS AND OTHER ANOMALOUS REACTIONS OF *p*-HYDROXYPHENYL α -HALO SULFONES

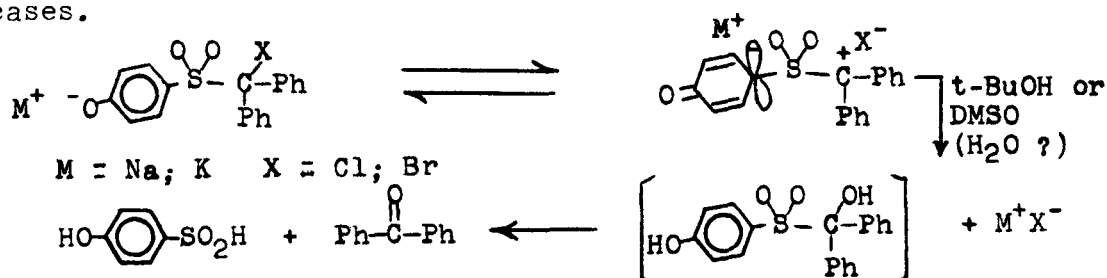
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p-Hydroxyphenyl α -halo sulfones are unusual in several respects. For example, *p*-hydroxyphenyl α -chloroisopropyl sulfone has no α' -H; however, when heated with one equivalent of base it undergoes a 1,7-elimination reaction via a pathway usually 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.

