Heck reactions of arenediazonium salts with phenyl vinyl sulfone: A new synthesis of styryl sulfones

Saumitra Sengupta,* Subir Kumar Sadhukhan & Rajkumar Sunil Singh

Department of Chemistry, Jadavpur University, Calcutta 700 032, India
Fax: 91-033-4734266; E-mail: jusaumitra@yahoo.co.uk

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A facile new synthesis of styryl sulfones via Heck reactions of arenediazonium salts with phenyl vinyl sulfone is described.

Palladium catalyzed arylation of olefins, the Heck reaction, has found widespread use in organic synthesis. In addition to the conventional acrylates and styrenes, a number of heterosubstituted olefins e.g. vinyl ethers, -acetates, enamines, vinyl silanes, vinyl phosphine oxides/phosphonates and vinyl sulfoxides have also been used in Heck reactions. However, there are no reports on Heck reactions of vinyl sulfones, except for an isolated example of an intramolecular Heck arylation of a cyclic vinyl sulfone. Heck reaction of vinyl sulfones promised a facile new synthetic route to styryl sulfones under mild and neutral conditions which led us to investigate the Heck arylation of phenyl vinyl sulfone.

Heck reaction of 1 was first investigated with iodobenzene under Jeffery's conditions (5% Pd(OAc)\textsubscript{2}, Bu\textsubscript{4}NBr, NaHCO\textsubscript{3}, DMF) which gave rise to phenyl styryl sulfone 3\textsubscript{a} in 67% yield after 8 hr at 80°C. In search of milder reaction conditions, we then decided to use the arenediazonium salts in place of iodoarenes because of the superior Heck-reactivity of the former vis-à-vis aryl halides. Heck reactions of 1 with the arenediazonium salts 2a–d were carried out under our previously described alcoholic reaction conditions (2% Pd(OAc)\textsubscript{2}, MeOH, reflux) which led to typically fast reactions (45 min to 1 hr) to produce the corresponding styryl sulfones 3a–d in good yields (Scheme I, Table I). Only in the case of 3d, the yield is somewhat lowered, perhaps due to the steric effect of the ortho-CO\textsubscript{2}Me substituent. Further increase in the steric crowding, as in the case of 2,6-dimethyl benzenediazonium salt, led to no reactions at all, even after prolonged heating. Notably, all the styryl sulfones 3a–d were produced exclusively as the trans-isomers as evident from the large coupling constants (J > 16 Hz) between their vinyl protons.

Two-fold Heck reactions of 1 with the bis-arenediazonium salts 4a–d also led to the bis-styryl sulfones 5a–d in 50–58% yields under identical conditions as above (Scheme II, Table I). Again, the bis-styryl sulfones 5a–d were all produced as the trans, trans-isomers.

In summary, Heck reactions of arenediazonium salts with phenyl vinyl sulfones have given rise to a facile new synthesis of styryl sulfones. The methodology, by virtue of its mild and neutral conditions, is superior to the anionic condensation routes usually used to prepare styryl sulfones and hence should find widespread synthetic applications.

**Heck Reactions of 1 with the arenediazonium Salts: General procedure.** Pd(OAc)\textsubscript{2} (0.005 g, 0.02 mmole for 2a–d; 0.01 g, 0.04 mmole for 4a–d) was added to a mixture of the arenediazonium salt (1.0 mmole) and 1 (0.80 mmole for 2a–d; 2.50 mmol for 4a–d) in MeOH (10 mL) and the mixture heated under reflux for 1 hr. It was then diluted with water, extracted with CH\textsubscript{3}Cl\textsubscript{2} and the combined

Note

Dedicated to Prof. U. R. Ghatak on his 70th birthday.
organic layer was dried. Removal of solvent under reduced pressure followed by preparative thin layer chromatography (silica gel, 5-25% ethyl acetate in pet. ether) gave the styryl sulfones 3a-d or 5a-d (Table I).

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References:
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