SYNTHESIS OF THE DIARYLACETYLENES BEARING ELECTRON WITHDRAWING GROUP VIA THE SMILES REARRANGEMENT

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Substituted acetylenes are widely used as starting materials in modern organic synthesis, especially for synthesis of indoles and antraniles [1].

Diarylacetylenes are usually prepared by Sonogashira reaction. Jorgensen described synthesis of the diarylacetylenes via the Smiles rearrangement of the enolates of benzothiazolyl dinitroarylketones in similar manner to Julia – Kocienski olefination [2]. The ketosulfones (the key-intermediates) were obtained by $S_{N}Ar$ reaction. Unfortunately, Jorgensen approach is limited to dinitroaryl acetylenes

We extended this methodology. Ketosulfones 2 were synthesized in the reaction of sulfones 1 with acyl chlorides (Scheme). The Smiles rearrangement of carbanions of the compounds 2 resulted in formation of diaryl acetylenes bearing one electron withdrawing group.

Using this methodology we synthesized nitroaryl acetylenes in 50 – 60 % overall yield (75 % per step) and diarylacetylenes bearing CF$_3$ or CN group (46 % per step).

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