

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

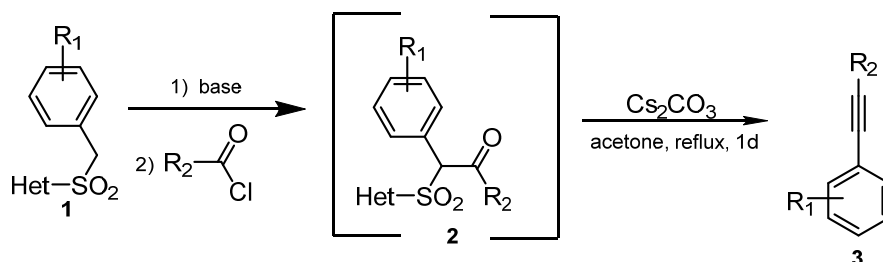
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Substituted acetylenes are widely used as starting materials in modern organic synthesis, especially for synthesis of indoles and antraniles [1].

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_NAr 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.



Het=benzothiazol-2-yl or 1-phenyl-1H-tetrazol-5-yl

$R_1 = \text{NO}_2, \text{CF}_3, \text{CN}$ $R_2 = 4\text{-CF}_3\text{C}_6\text{H}_4, 3\text{-CF}_3\text{C}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 2\text{-BrC}_6\text{H}_4, \text{Ph}, 4\text{-MeOC}_6\text{H}_4, 2\text{-naphthyl}, 2\text{-furyl}$

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).

[1] (a) Wang, H.; Li, Y.; Jiang, L.; Zhang, R.; Jin, K.; Zhao, D.; Duan, C. *Org. Biomol. Chem.* **2011**, 9, 4983. (b) Inamoto, K.; Asano, N.; Nakamura, Y.; Yonemoto, M.; Kondo, Y. *Org. Lett.* **2012**, 14, 2622. (c) Asao, N.; Sato, K.; Yamamoto, Y. *Tetrahedron Lett.* 2003, 44, 5675.

[2] Pruger, B.; Hofmeister, G. E.; Jacobsen, C. B.; Alberg, D. G.; Nielsen, M.; Jorgensen, K. A. *Chem. Eur. J.* 2010, 16, 3783.