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THE MICHAEL INDUCED RAMBERG-BACKLUND OLEFIN SYNTHESIS.[1]

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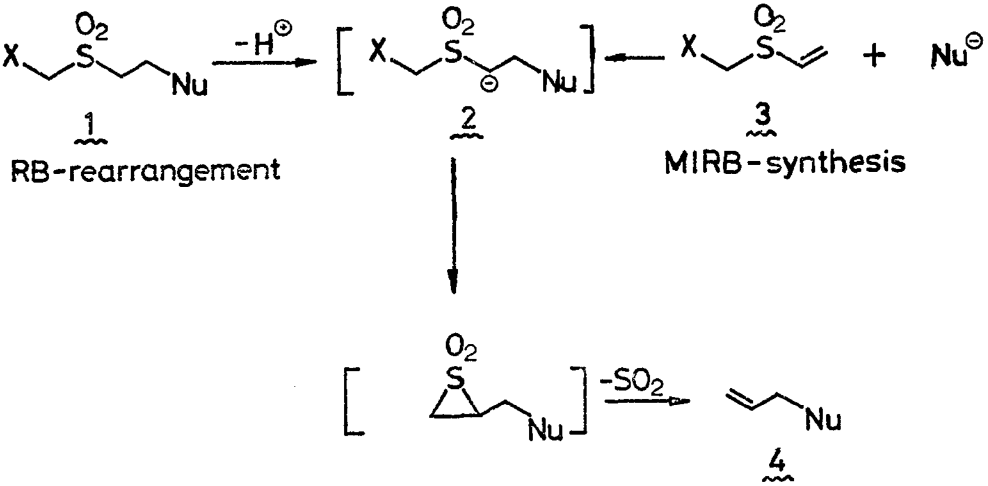
The base induced olefin synthesis starting from α-halosulfones (1), known as the Ramberg-Bäcklund[2] (RB) rearrangement, requires strong bases with high proton affinity for the formation of the sulfonyl carbanion intermediate 2. The same intermediate may also be produced upon Michael addition of a suitable anion Nu$^-$ to α-halosulfones carrying a Michael acceptor system attached to the α' position (3).

Vinyl sulfones are known to be excellent Michael acceptors, while sulfinate anions are good nucleophiles, combining high carbon affinity with low proton affinity. Thus the reaction of halomethyl vinyl sulfones with sulfinate anions can be expected to unite two chain extension methods (viz. the Michael addition and the RB rearrangement) in one operation. We have named this approach the Michael induced Ramberg-Bäcklund (MIRB) synthesis.

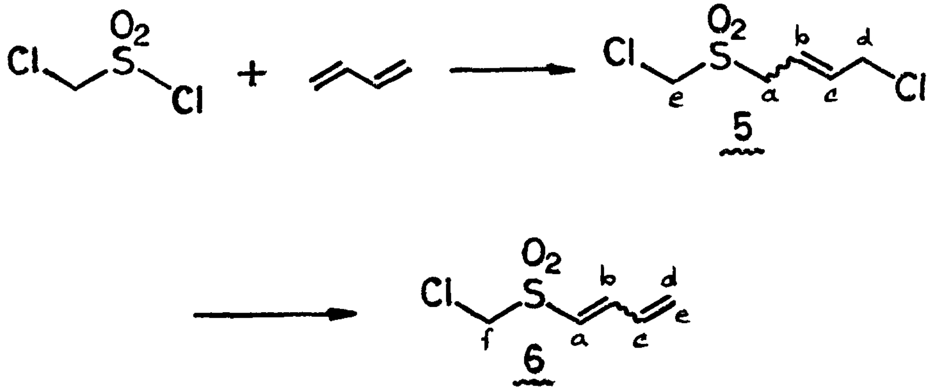


A condition for this combined reaction is that the solvation states of the Michael adduct anion and the anion formed from 1 by proton abstraction are comparable.

To test the hypothesis we have synthesized the required vinyl halomethyl sulfone in the following way. Copper catalyzed 1,4-addition[3] of chloromethylsulfonyl chloride[4] to butadiene gave the dichlorosulfone 5[5], isolated upon distillation (123°/.01 mm) after a forerun of sulfolene (74°/.01 mm). Treatment of 5 with triethylamine/ether[6] at r.t. furnished the dienyl sulfone 6.[5]

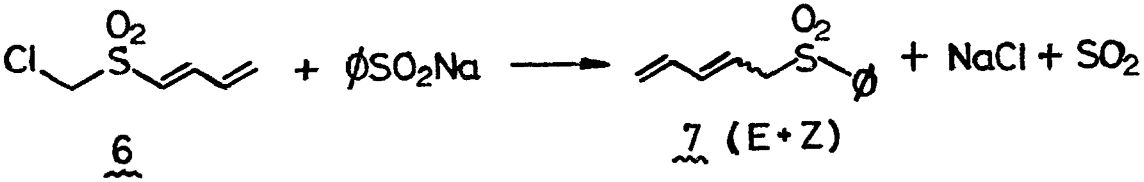
5: ^{1}H-NMR (100 MHz, $CDCl_3$), δ 3.86-422 (H_a and H_d, m, 4), 4.43 (He, s, 2), 5.65-6.30 (H_b and H_c, m, 2).

6: ^{1}H-NMR (100 MHz, $CDCl_3$), δ 4.49 (H_f, s, 2), 5.72 (H_e, d, 1), 5.86 (H_d, d, 1), 6.45 (H_a, d, 1), 6.53 (H_c, m, 1), 7.32 (H_b, dd, 1).



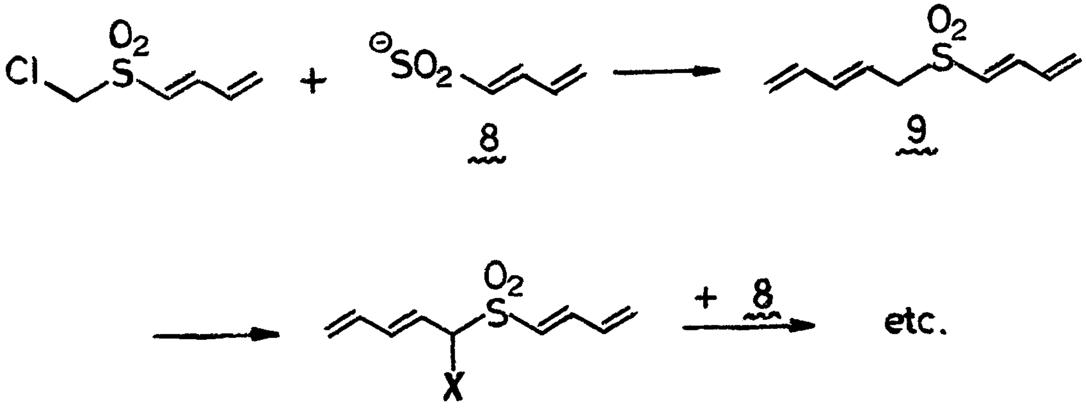
The reaction of 6 (dissolved in d_6-DMSO) with one equivalent of sodium phenylsulfinate was monitored by NMR. After 1 h all reactants had disappeared and been converted to a mixture of the (E) and (Z)-MIRB-products 7 in a 2:1 ratio. The slightly unstable isomers 7 were isolated from the reaction mixture in 44% yield by column chromatography.

7: ^{1}H-NMR (100 MHz, $CDCl_3$), δ 3.71 (E-CH_2, d, J 7.5 Hz), 3.95 (Z-CH_2, d, J 8.5 Hz), 5.0-6.5 (vinylic H), 7.38-7.95 (aromatic H).



We expect that the reaction has a more general character and may also be performed with nucleophiles other than sulfinate anions.

Preliminary experiments using dienylsulfinate anions of type 8 as a nucleophile with built-in Michael acceptor system have proved that the MIRB-synthesis can be made into a step by step polyene building approach extending the chain with four carbon atoms at a time. The repeating operations are i) introduction of chlorine[7] at the allylic position of the MIRB-product 9, ii) condensation with the next chain extending unit. To our surprise 8 and 9 hardly suffered from anionic polymerization under the reaction conditions.



REFERENCES AND NOTES.

1. Dedicated to prof. Dr. H.O. Huisman on the occasion of the 20th anniversary of his accession to office.

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