AKLYLATION OF VINYL ETHERS OF $\beta-\text{ARYLTHIO}-\alpha-\text{CHLOROALKYL}$ ALKYL ETHERS

V. A. Smit and I. P. Smolyakova

 β -Arylthio- α -chloroalkyl alkyl ethers obtained in quantitative yield by the Ad_E reaction of arylsulfenyl chlorides with vinyl ethers (VE) in the presence of Lewis acids such as TiCl₄ and SnCl₄ smoothly alkylate vinyl ethers to give 1:1 adducts:



TABLE 1

| Number | (VE-I) | (VE-II) | Nucleo- phile | Adduct* | Yield, %† |
|--------|-----------|---------|------------------|------------------------------|-------------------------|
| 1 | MeO = | MeO | но- | ArS CHO OMe | 85 |
| 2 | Same | Same | MeO- | ArS 1 CH (OMe)2 OMe | 95 (50) |
| .3 | » | MeO | но- | ATS I I OMe O | 75 (62) |
| 4 | | () o | MeO- | MeO SAr O OMe | 90 |
| 5 | MeO | MeO | Same | ArS CH (OMe)2 | 93 |
| 6 | мео_Снме | Same | » | Ars I (OMe) ₂ | 70 |
| 7 | MeO | MeO | HO- | O.OMe | 57 |
| 8 | | MeO | MeO- | SAr CH (OMe) ₂ | 80(67) |

 $Ar = p-CH_3C_6H_4$ in all cases. The yields are given for the reactions using TiCl₄; the yields given in parentheses are for reactions with SnCl₄.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2831-2832, December, 1984. Original article submitted July 18, 1984. The products obtained are aldol-type adducts (Table 1). This reaction of VE permits us to carry out all four variants of the crossed aldol condensation with stereoselectivity: aldehyde—aldehyde (1, 2, 4, 8), aldehyde—ketone (3), ketone—aldehyde (5, 6), and ketone—ketone (7). The compounds synthesized were characterized by analytical data, mass spectra, and ¹H NMR spectroscopy.

The absence of oligomeric products in this reaction, which is a usual complication in the alkylation of vinyl ethers such as acetals [1], is apparently a result of the intermediate formation of a stable thiophene salt (TPS) [2] which is incapable of alkylating (VE-II) under the conditions for the reaction described. Hence, the preparation of either carbonyl derivatives or their acetals is possible depending on the method for treatment of the TPS.

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USE OF ¹³C-¹³C SPIN-SPIN COUPLING CONSTANTS FOR THE ESTABLISH-

MENT OF THE CONFIGURATION OF AROMATIC OXIMES

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L. B. Krivdin, G. A. Kalabin, S. E. Korostova, S. G. Shevchenko, and B. A. Trofimov

In light of the difference in the chemical properties of Z and E isomers of oximes, it is especially important to establish their configurational structure.

In order to solve this problem, we propose a new method based on the steric specificity of direct ¹³C-¹³C coupling constants. Values are given below for the coupling constants between the nuclei of the ¹³C oxime carbon and the α -carbon atom of the phenyl group of the oximes of benzaldehyde (IZ, IE), acetophenone (IIZ, IIE), and benzophenone (III) for the two extreme cases of the orientation of the unshared electron pair of the nitrogen atom relative to the coupled nuclei. The value for this constant in the corresponding carbonyl compounds is given in parentheses



This coupling constant differs by 8-9 Hz in the oxime isomers and is 52.5-54.4 Hz for the trans orientation of the unshared pair and 61.7-63.8 Hz for the cis orientation. In the former case, this constant is within about 1 Hz of the value for the corresponding aldehyde or ketone. The pronounced effect of the nitrogen unshared pair (~15% of the value of the constant) on the direct $^{13}C^{-13}C$ coupling constants for neighboring carbon nuclei may be used for the unequivocal determination of the isomers of oximes and related compounds.

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