ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 1, p. 149. © Pleiades Publishing, Ltd., 2007. Original Russian Text © A.P. Zaraiskii, L.I. Velichko, N.A. Zaraiskaya, N.M. Anikeeva, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 1, p. 159.

> LETTERS TO THE EDITOR

Exhaustive Direct Methylthiomethylation of Mesitylene and Durene

A. P. Zaraiskii, L. I. Velichko, N. A. Zaraiskaya, and N. M. Anikeeva

Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, ul. R. Lyuksemburg 70, Donetsk, 83114 Ukraine

Received August 30, 2006

DOI: 10.1134/S1070363207010239

We previously showed [1] that the use of methylsulfanylmethyl acetate as reagent under acidic conditions ensures direct introduction of a MeSCH₂ group into aromatic ring. Oda and Yamamoto [2] reported on the methylthiomethylation of anisole, but the yield of the product was poor. As a rule, the procedures for the synthesis of MeSCH₂-substituted derivatives implied treatment of highly nucleophilic substrates (phenols, naphthols, anilines) with appropriately activated sulfur-containing reagents (DMSO, sulfides, thiols), and the reaction conditions were difficult to maintain (liquid ammonia, low temperature, etc [1]). A general method for the preparation of such compounds is based on the reaction of the corresponding chloromethyl derivative with alkali metal thiolates. Serious disadvantages of most known procedures include a large number of steps, often poor yields, and formation of by-products. Using mesitylene and durene as examples we now demonstrate a modified procedure [1] for the direct and exhaustive methylthiomethylation at the aromatic ring.

1,3,5-Trimethyl-2,4,6-tris(methylsulfanylmethyl)benzene. A heterogeneous mixture of 0.7 ml of mesitylene, 3.3 ml of methylsulfanylmethyl acetate, 2.5 ml of *n*-nonane, and 2.5 ml of 45% sulfuric acid was stirred at 115°C. After 3 h, the mixture was cooled, 10 ml of chloroform and 5 ml of water were added, the organic phase was separated and washed with 5 ml of water, 5 ml of sodium hydrogen carbonate, and 5 ml of water again and dried over anhydrous calcium chloride, and the solvent was distilled off. Yield 1.29 g (85%), mp 178–180°C (from CCl₄). ¹H NMR spectrum (CD₂Cl₂, TMS), δ , ppm: 2.09 s (9H, SCH₃), 2.41 s (9H, CH₃), 3.74 s (6H, CH₂). Found, %: C 60.72; H 8.59; S 30.61. C₁₅H₂₄S₃. Calculated, %: C 59.94; H 8.05; S 32.01.

1,2,4,5-Tetramethyl-3,6-bis(methylsulfanylmethyl)benzene. Following an analogous procedure, from 0.66 g of durene, 2.7 ml of methylsulfanylmethyl acetate, 2.5 ml of *n*-nonane, and 2.5 ml of 45% sulfuric acid we obtained 1.0 g (80%) of the product. mp 166°C (from *n*-nonane). ¹H NMR spectrum (acetone- d_6 , TMC), δ , ppm: 2.12 s (6H, SCH₃), 2.28 s (12H, CH₃), 3.78 s (4H, CH₂). Found, %: C 66.30; H 8.79; S 25.00. C₁₄H₂₂S₂. Calculated, %: C 66.08; H 8.72; S 25.20.

Under the above conditions, no more than two methylsulfanylmethyl groups can be introduced into the naphthalene ring. A mixture of 0.25 g naphthalene, 1.1 g of methylsulfanylmethyl acetate, 2.5 ml of *n*-octane, and 2.5 ml of 45% sulfuric acid was heated for 4 h at 115°C under stirring. The product was 1,4-bis(methylsulfanylmethyl)naphthalene. Yield 0.34 g (68%), mp 104°C (from *n*-octane). ¹H NMR spectrum (acetone- d_6 , TMC), δ , ppm: 2.06 s (6H, SCH₃), 4.21 s (4H, CH₂), 7.40 s (2H, 2-H, 3-H), 7.52 d (2H, 5-H, 8-H), 8.26 d (2H, 6-H, 7-H). Found, %: C 67.75; H 6.53; S 25.72. C₁₄H₁₆S₂. Calculated, %: C 67.69; H 6.49; S 25.81.

The fact that two *peri* positions in the naphthalene molecule remained unoccupied indicates strong paraorienting effect of methylsulfanylmethyl group and considerable steric requirements of the reagent. However, the relative ease of formation of exhaustively substituted derivatives from mesitylene and durene is not completely clear from the above viewpoint.

The ¹H NMR spectra were recorded on a Varian Gemini-200 instrument (200 MHz).

REFERENCES

- 1. Zaraiskii, A.P. and Kachurin, O.I., *Russ. J. Org. Chem.*, 2003, vol. 39, no. 11, p. 1572.
- 2. Oda, R. and Yamamoto, K., *Chem. Abstr.*, 1963, vol. 59, no. 4, p. 3806.