METHYLATION OF THE SULFOLANE RING AT THE 2 AND 2, 5 POSITIONS

T. E. Bezmenova and N. M. Kamakin

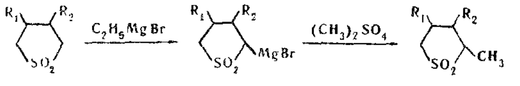
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 4, pp. 618–620, 1967

UDC 547.732.733:542.951'957

The possibility of alkylating sulfolane and its derivatives is investigated. A new method of introducing a methyl group at positions 2 and 2, 5 in the sulfolane ring, using sulfolanylmagnesium bromide is put forward.

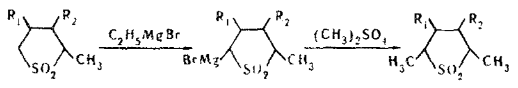
It was previously shown [1] that, depending on the reaction conditions, mono- and dibromomagnesium derivatives are formed when the active hydrogen in the position α to the sulfonyl group of sulfolane reacts with a Grignard reagent. The present paper studies the possibility of using sulfolanylmagnesium bromide as an intermediate for alkylating the sulfolane ring at the 2 and 2, 5 positions. Dimethyl sulfate was used for the alkylation. Under similar conditions alkyl halides did not react, probably because of the decreased nucleophilicity of the magnesium derivatives of the sulfones.

The sulfolanylmagnesium bromides were prepared by reaction of sulfolane (I), 3-methylsulfolane (II), and 3, 4-dimethylsulfolane (III) with ethyl magnesium bromide [1]. Equimolecular proportions of reagents gave monobromomagnesium derivatives, which with excess dimethyl sulfate gave, respectively, 2-methylsulfolane (IV), 2, 4-dimethylsulfolane (V), and 2, 3, 4-trimethylsulfolane (VI).



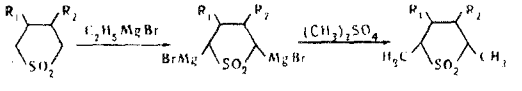
I $R_1=R_2=H$
II $R_1=CH_3$; $R_2=H$.
III $R_1=R_2=CH_3$.
IV $R_1=R_2=H$
V $R_1=CH_3$; $R_2=H$
VI $R_1=R_2=CH_3$

In the case of compound II, formation of two isomers, 2, 3-dimethyl and 2, 4-dimethylsulfolane, could be assumed. It was shown by pyrolytic opening of the sulfolane ring [2] that the reaction product is in fact 2, 4-dimethylsulfolane (practically no butenes in the pyrolysis gases). Repeated methylation of compounds IV–VI led to the synthesis of, respectively, 2, 5-dimethylsulfolane (VII), 2, 4, 5-trimethylsulfolane (VIII), and 2, 3, 4, 5-tetramethylsulfolane (IX).



IV $R_1=R_2=H$
V $R_1=CH_3$; $R_2=H$
VI $R_1=R_2=CH$
VII $R_1=R_2=H$
VIII $R_1=CH_3$; $R_2=H$
IX $R_1=R_2=CH_3$

2, 5-Dimethyl-substituted sulfolanes VII–IX are also obtained directly from I–III via the dibromomagnesium derivatives.



I $R_1=R_2=H$
II $R_1=CH_3$; $R_2=H$
III $R_1=R_2=CH_3$
VII $R_1=R_2=H$
VIII $R_1=CH_3$; $R_2=H$
IX $R_1=R_2=CH_3$

Formation of 2, 2-dibromomagnesium derivatives and of the corresponding 2, 2-dimethyl-substituted sulfolanes was not observed, probably due to the lowering of the acidic properties of the hydrogen atom remaining at position 2.

The properties of the compounds IV–IX prepared corresponded to substances synthesized by hydrogenating methylsulfolenes [3].

EXPERIMENTAL METHOD

a) Introduction of one methyl group. The monobromomagnesium derivative was prepared from 0.1 mole of the appropriate sulfolane and 120 ml 0.85 M solution of EtMgBr in tetrahydrofuran or benzene, and 25 ml dimethyl sulfate in 25 ml benzene was added to it with stirring. The reaction mixture was heated until the precipitate of bromomagnesium derivative vanished, then 50 ml 10% HCl added at 0–5°. The resultant two layers were separated. The aqueous layer was extracted with $CHCl_3$, the $CHCl_3$ extracts combined with the organic layer, and the whole washed with Na_2CO_3 solution, then with water. After drying over $MgSO_4$ and distilling off solvent and unreacted Me_2SO_4, the residue was vacuum fractionated.

b) Introduction of two methyl groups. 50 ml Dimethyl sulfate and 50 ml benzene were added to the dibromomagnesium derivative made from 0.1 mole of the appropriate sulfolane and 250 ml 0.8 M EtMgBr. The product was isolated by vacuum distillation.

The table gives the compounds synthesized.

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12 November 1965

Institute of the Chemistry
of High-Molecular Compounds, AS UkrSSR,
Kiev

Table

Products Obtained by Methylating Sulfolanes

Reaction product	Starting sulfolane	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D
IV	I	92—93 (2)	1.2082	1.4808	31.61
V	II	110—112 (2)	1.1362	1.4732	36.41
VI	III	119 (2)	1.1282	1.4803	40.89
VII	IV I	107—108 (2)	1.1535	1.4780	36.41
VIII	V II	88—89 (0.5)	1.1139	1.4718	40.78
IX	VI III	115—117 (2)	1.0967	1.4790	45.57

Table (cont'd)

Formula	Found %			Calculated %			Yield, %	Reference
	C	H	S	C	H	S		
$C_5H_{10}O_2S$	44.65	7.18	23.62	44.77	7.46	23.88	59.7	4
$C_6H_{12}O_2S$	48.31	8.34	21.39	48.71	8.11	21.62	48.0	5
$C_7H_{14}O_2S$	51.80	8.40	19.92	51.85	8.64	19.75	54.3	—
$C_6H_{12}O_2S$	48.82	7.94	21.44	48.71	8.11	21.62	64.2 43.9	6
$C_7H_{14}O_2S$	51.58	8.91	19.85	51.85	8.64	19.75	42.0 29.6	—
$C_8H_{16}O_2S$	54.21	9.13	18.36	54.55	9.09	18,18	42.7 30.6	7