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SUBSTITUENT EFFECTS OF THE $-S(CH_3)_2^+$ GROUP IN NITRATION

H. M. Gilow and George L. Walker[1]
Southwestern at Memphis
Memphis, Tennessee 38112

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The nitration of dimethylphenylsulfonium picrate in conc. nitric and sulfuric acid has been reported by Baker and Moffitt[2] as being 100% meta. Since ortho-, meta- and para-nitrodimethylphenylsulfonium salts have very similar properties, analysis of the nitration products could have failed to observe small amounts of ortho- and para-nitration products. It is for this reason we undertook a reinvestigation of this nitration reaction.

para-Nitrodimethylphenylsulfonium methosulfate undergoes very rapid S_n reactions indicating that the dimethylsulfonium group is an excellent leaving group[3]. We have also found that at room temperature ortho-nitrodimethylphenylsulfonium methosulfate reacts very rapidly with dilute solutions of sodium methoxide in methanol to form ortho-nitroanisole. The corresponding meta-nitrosulfonium salt forms only a small amount of meta-nitroanisole under the same conditions. According to Baker and Moffitt's[2] procedure for isolation of the nitrosulfonium salts the strongly acid reaction mixture was neutralized or made weakly basic with sodium hydroxide. This could have converted the ortho- and para-nitrosulfonium salts to the corresponding anisoles leaving only the meta-isomer.

If ortho-, meta- or para-nitrodimethylphenylsulfonium methosulfate is dissolved in methanol, cooled to the temperature of dry ice in methanol, and treated with sodium methoxide only dealkylation[4] occurs, forming the corresponding *ortho*-, *meta*- or *para*-nitrothioanisoles (0.5% nitroanisoles). Known mixtures of *ortho*-, *meta*- and *para*-nitrosulfonium salts were treated in the same manner as the nitration of dimethylphenylsulfonium methosulfate. The nitration mixture is diluted with methanol, cooled to the temperature of dry ice in methanol, and a solution of sodium methoxide is added dropwise until the solution is basic. Results of two of the gas chromatographis analyses (using 2,4,7-trinitro-9-fluorenone on Chromosorb W) of these resulting solutions are given in Table I indicating good agreement with the known composition. No dinitration was observed.

Nitration of dimethylphenylsulfonium methosulfate in a mixture of 95% sulfuric and 69% nitric acid for two hours at 60° indicated that 3.6 ± 0.2% *ortho*-, 90.4 ± 0.3% *meta*- and 6.0 ± 0.2% *para*-substitution occurred, using the same analysis as above. Changing the reaction conditions from one hour at room temperature to eight hours at 60° did not have any effect on the ratio of the isomers.

Phenylmethylsulfide was nitrated under the same conditions as the sulfonium salt and no nitrothioanisoles could be detected. Further evidence indicating that all of the *ortho*- and *para*-nitration was the result of nitration of the sulfonium salt and not phenylmethylsulfide, a possible contaminant, was obtained when phenylmethylsulfide was added to the sulfonium salt and then nitrated to give essentially the same results (Table I) as the uncontaminated sulfonium salt. The sulfide is apparently oxidized to the sulfone by the nitric acid which does not interfere with the analysis of the nitrosulfonium salts.

TABLE I

Gas Chromatographic Analysis of Nitrothioanisoles

Reaction		% ortho	% meta	% para
Nitration of dimethylphenylsulfonium methosulfate		3.6 ± 0.2*	90.4 ± 0.3	6.0 ± 0.2
Nitration of dimethylphenylsulfonium methosulfate contaminated with methylphenylsulfide		3.4 ± 0.3	90.2 ± 0.4	6.4 ± 0.3
Nitration of known mixture of o-, m- and p-nitrosulfonium salts	found	6.2 ± 0.2	85.3 ± 0.3	8.5 ± 0.2
	calc.	6.44	85.22	8.34
Nitration of known mixture of o-, m- and p-nitrosulfonium salts	found	2.5 ± 0.3	91.3 ± 0.3	6.2 ± 0.2
	calc.	2.65	91.21	6.14

*Each value is an average of five g. c. analyses.

Recent investigations By Ridd and coworkers[5,6] of the directive effect of positive poles ($-\overset{|}{\underset{|}{N}}-^{+}$, $-\overset{|}{\underset{|}{P}}-^{+}$ and $-\overset{|}{\underset{|}{As}}-^{+}$) attached directly to the aromatic ring have shown that a considerable amount of para-nitration takes place. The strongly inductive withdrawing positive poles being most effective in the ortho-position and least effective in the para-position causing para-nitration but no ortho-nitration along with the normal meta-nitration. These groups have been referred to as meta-, para-directors[6].

Inductively the dimethylsulfonium group is a strong electron withdrawing group similar to the trimethylammonium group (σ_m for the dimethylsulfonium group is +1.00 and for the trimethylammonium group it is +1.02[7].) and stronger than the phosphonium group[8]. Hence inductively the ortho-position should be deactivated the most and the para-position deactivated the least towards electrophilic substitution.

A number of additional factors need to be considered in the case of sulfonium salts which need not be considered in the case of the ammonium salts. One such factor is the availability of empty d-orbitals on sulfur interacting with the π-electrons of the aromatic ring deactivating the para- and ortho-positions as is apparently the case with phosphonium salts[6]. The filled p-orbitals of sulfur, not available in the case of nitrogen, phosphorus or arsenic salts, can also contribute electrons to the aromatic ring activating the ortho- and para-positions more than the meta-positions. Since an appreciable amount of ortho-nitration is found in the case of sulfonium salts and no ortho-nitration in the case of ammonium or phosphonium salts, apparently a small interaction of the filled p-orbitals and the aromatic ring could account for the ortho-substitution. The larger amount of para-nitration could be explained in the same manner together with the fact that inductively para-substitution would be favored.

Other effects such as the size of the groups, field effects, type of electrophilic agents and etc. are presently being investigated.

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