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Sulfonation of chlorine-containing polymers: Sulfonation of various model *tert*-alkyl chlorides

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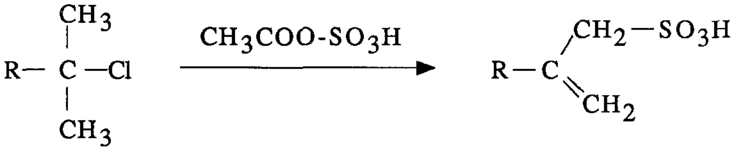
SUMMARY

tert-Alkyl chlorides of the structure R-$C(CH_3)_2Cl$, where R = methyl, ethyl, *tert*-butyl, and *neo*-pentyl, were reacted with a stoichiometric quantity of acetyl sulfate at room temperature in methylene chloride diluent. Reaction conversion was monitored as a function of time using ^1H NMR; structure of the sulfonated products was characterized using ^1H and ^{13}C NMR. Reactivity toward sulfonation increased with increasing size of the R group. In all cases the structure of the products was the same as would be expected from sulfonation of the olefin which results from dehydrochlorination of the *tert*-chloride. The observed behavior was consistent with a mechanism involving dehydrochlorination followed by addition of SO_3 to yield a zwitterionic intermediate. Depending upon structure, the zwitterion may either eliminate a proton to form one or more isomeric β,γ-unsaturated sulfonic acids, or it may rearrange to form a five-membered γ-sultone. This chemistry, which is particularly useful in the synthesis of ionomers, represents a direct route to alkyl sulfonic acids when the alkyl halide is the natural starting point in the synthesis.

INTRODUCTION

We have recently described a new synthetic route toward telechelic, polyisobutylene (PIB) ionomers which involves the direct sulfonation of *tert*-chloride end groups which are obtained from the controlled cationic polymerization isobutylene.[1,2] We are actively researching sulfonation as a general polymer modification tool, and we have discovered that a variety of *tert*-alkyl chlorides are susceptible to sulfonation by SO_3/Lewis base adducts such as acetyl sulfate,[3] and probably by SO_3 itself. The general reaction, shown below for the reaction of a *tert*-chloride with acetyl sulfate, yields the β,γ-unsaturated sulfonic acid shown and/or isomers of this compound depending on the structure of R.



$$R-C(CH_3)_2-Cl \xrightarrow{CH_3COO\text{-}SO_3H} R-C(=CH_2)-CH_2-SO_3H$$

The precise details of the mechanism of this reaction are presently not known with certainty; however, when sulfonation is carried out instead on the parent olefin, i.e., the olefin obtained by dehydrochlorination of the *tert*-chloride, precisely the same products are obtained. This suggests that the chloride serves simply to provide an equilibrium concentration of olefin for sulfonation. Certain details of the mechanism remain obscure, however, because even though the same products are obtained, they are generally *not* obtained in the same relative ratios. In this report, we describe further experiments involving *tert*-chlorides of differing structure which have been carried out to gain information about the mechanism of sulfonation.

EXPERIMENTAL

Materials

2,3,3,-Trimethyl-1-butene (TM1B), 2,4,4-trimethyl-1-pentene (TM1P), *tert*-butyl chloride (TBC), and 2-chloro-2-methylbutane (CMB) (Aldrich) were used as received. Methylene chloride ($MeCl_2$) was freshly distilled over CaH_2 before use. Acetic anhydride (Aldrich) and sulfuric acid (Fisher) were used as received.

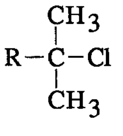
2-Chloro-2,3,3-trimethylbutane (TMCB) and 2-chloro-2,4,4-trimethylpentane (CTMP) were produced by hydrochlorination of TM1B and TM1P, respectively, as described previously.[2]

Procedures

All sulfonation reactions were conducted at room temperature using $MeCl_2$ diluent and acetyl sulfate, which was prepared *in situ* from a 1.33-fold molar excess of acetic anhydride and a stoichiometric quantity of concentrated sulfuric acid. Reaction progress was monitored by quantitative ^1H NMR spectroscopy. A representative procedure was as follows: To a 50 ml three-neck, round-bottomed flask equipped with magnetic stir-bar and condenser was charged 0.02 mole of the model compound, 2.716 g (0.0266 mole) acetic anhydride and 20 ml $MeCl_2$. While stirring, and with cooling, 1.926 g (0.02 mol) sulfuric acid was slowly added to commence the sulfonation reaction. Upon complete addition, aliquots of the reaction mixture were removed at regular intervals, diluted with $CDCl_3$ or d_6-DMSO, and immediately subjected to quantitative ^1H NMR characterization. Conversion of the model compound was obtained by monitoring the decrease in intergrated peak area of a suitable resonance assigned to the model compound compared to the area of the $MeCl_2$ peak, which was used as internal standard. ^1H and ^{13}C NMR spectra were taken using a 300 MHz Brucker AC-300.

RESULTS AND DISCUSSION

The four model compounds examined form a series, as shown below, in which the R group was increased in size from methyl to *neo*-pentyl:

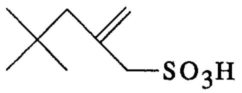


$$R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl$$

R = methyl (TBC)
ethyl (CMB)
tert-butyl (TMCB)
neo-pentyl (CTMP)

As shown in Figure 1, the sulfonation reactions appear to be equilibrium reactions. Using a stoichiometric ratio of sulfonating reagent and model compound, the conversion tended toward an asymptotic value of 0.5 - 1.0, depending on model compound. When the sulfonating reagent was used in excess, the equilibrium could be shifted to yield virtually 100% conversion to sulfonated product for all of the models except the relatively unreactive TBC. It is also clear from the data that the larger the R group, the higher the equilibrium conversion. This is logical since the larger group should impart a greater driving force toward trigonal geometry *via* loss of HCl.

As reported earlier,[2] sulfonation of the most bulky *tert*-chloride above, CTMP, yields a mixture of the two isomeric β,γ-unsaturated sulfonic acids shown below.



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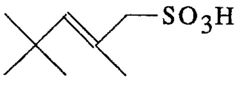

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The same two products were obtained by us upon sulfonation of the precursor olefin, 2,4,4-trimethyl-1-pentene using acetyl sulfate, and as well by Boyer et al.[4] who used liquid SO_3, and who, in addition, positively identified product 2 as possessing the (*E*)-configuration, which places the two bulky groups on opposite sides of the double bond. The two isomers result from the fact that the postulated zwitterionic intermediate can eliminate a β-proton from either the methylene or the methyl group to yield the *endo* or *exo* double bond, respectively. We were thus quite interested in the sulfonation of TMCB since it could only yield one product by this mechanism. Indeed, it was found to yield only one product, but that product was the γ-sultone 3 which results from the rearrangement reaction shown in Figure 2. Boyer et al.[4] obtained the same γ-sultone upon sulfonation of 2,3,3-trimethyl-1-butene with liquid SO_3. The ^{13}C NMR spectrum of 3 is shown in Figure 3. The obvious rearrangement which occured in this case gives strong support for the participation of a zwitterionic intermediate in the reaction of acetyl sulfate with *tert*-alkyl chlorides.

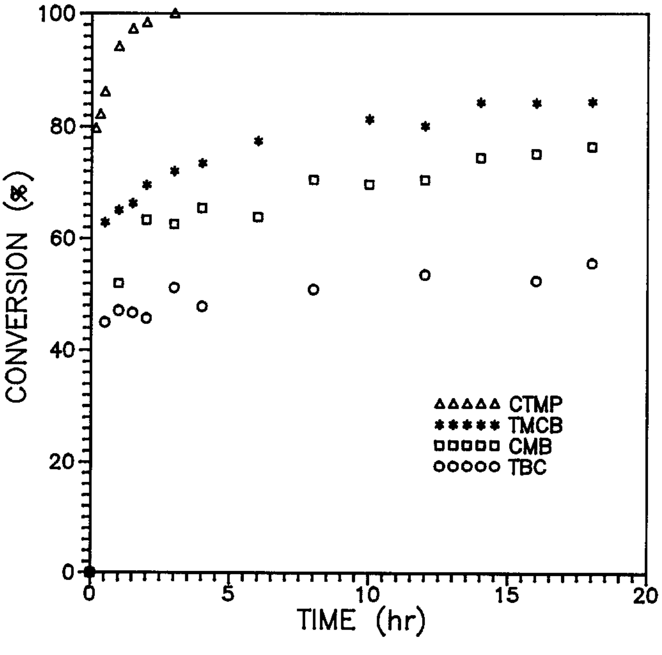

Figure 1.
Conversion vs. time for the sulfonation of model *tert*-alkyl chlorides using a stoichiometric quantity of acetyl sulfate and methylene chloride diluent.

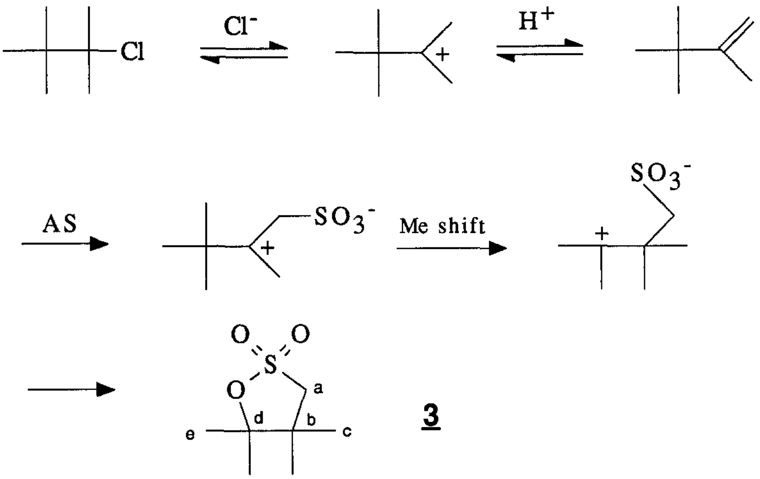

Figure 2. Mechanism of sulfonation of 2-chloro-2,3,3-trimethylbutane using acetyl sulfate.

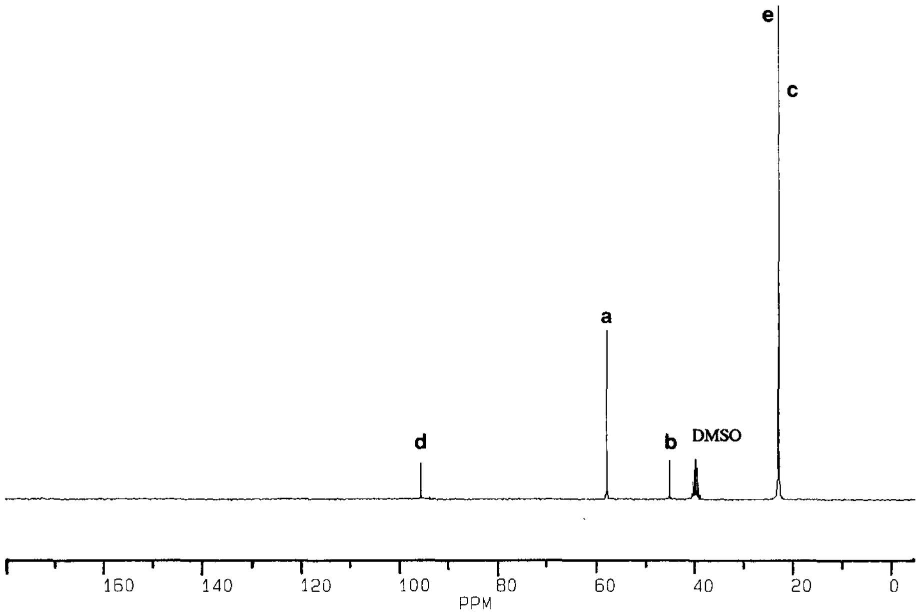

Figure 3. ^{13}C NMR spectrum of γ-sultone 3 obtained from the sulfonation of 2-chloro-2,3,3-trimethylbutane.

Sulfonation of CMB should lead to three principle isomers, as shown in the reaction scheme presented in Figure 4. In addition, isomer 5 could exist as two different geometrical isomers denoted as (**a**) and (**b**), and in fact, the presence of both isomers would lend further support to the proposed zwitterionic intermediate. The ^{13}C NMR spectrum of the CMB sulfonation reaction mixture is shown in Figure 5. Experience has shown that carbons bonded directly to sulfonic acid appear in the range 57-68 ppm, and there are exactly four resonances within this range in Figure 5. We feel these represent the four possible structures described above, and detailed analysis of the remaining resonances yielded the assignments shown in Figure 4. One of the two geometrical isomers of 5 is apparently produced in low yield, and thus only two of its five resonances could be resolved from the baseline.

It is interesting that sulfonation of the CTMP model, which theoretically can produce an analogous pair of geometrical isomers, yields only one isomer of the two within the limits of detection by 300 MHz ^{13}C NMR. This can be rationalized by steric considerations; to produce both geometrical isomers, the intermediate zwitterion must freely rotate about the bond which joins the carbocation to the methylene carbon which loses the proton during elimination. In the CTMP model this carbon carries a *tert*-butyl group which would be expected to severely hinder rotation about this bond. In fact, molecular models of the two isomers clearly show a great deal of interference between the *tert*-butyl and sulfonic acid groups in the (Z)-isomer. On the other hand, in the CMB model the methylene carbon carries only a methyl group, and it is easier to understand the formation of both isomers.

Tert-butyl chloride was found to be the most sluggish toward sulfonation of the models studied; this was expected since it should be most resistant toward loss of HCl. It also produced the most complex and diverse mixture of products. However, as in all the other cases, the products obtained were the same as might be expected from the sulfonation of the precursor olefin, in this case isobutylene. The structures of the four major sulfonated products thought to be formed are shown in Figure 6, and the ^{13}C NMR spectrum of the sulfonation reaction mixture is shown in Figure 7. Suter and Malkemus[5] showed that the sulfonation of isobuylene using dioxane/SO_3 yielded the unsaturated mono- (7) and disulfonic acid (8), and the formation of the β-sultone (9) as a primary sulfonation product is well known in olefin sulfonation.[6,7] The presence of six distinct resonances within the olefinic region of the ^{13}C NMR spectrum indicated the existence of a third unsaturated product which we have postulated to be the sulfonic anhydride (10).

CONCLUSIONS

The reaction of *tert*-chlorides with SO_3 adducts such as acetyl sulfate is a general reaction which is facilitated by the presence of at least one bulky substituent bonded to the tertiary carbon. In all cases studied, the products of sulfonation have been the same as would be obtained upon sulfonation of the olefin derived by dehydrochlorination of the *tert*-chloride. The rate of reaction of the chloride, however, is much lower than the rate of reaction of the olefin. This suggests that the *tert*-chloride, in the presence of the sulfonating agent, slowly eliminates HCl to provide a low concentration of olefin which is rapidly sulfonated.

The use of a stoichiometric amount of acetyl sulfate generally results in less than quantitative conversions to sulfonated products, except for the case of the most reactive *tert*-chloride studied, CTMP, which undergoes virtually 100% sulfonation under these conditions. However, an excess of acetyl sulfate can be used to obtain quantitative conversion even with the less reactive compounds.

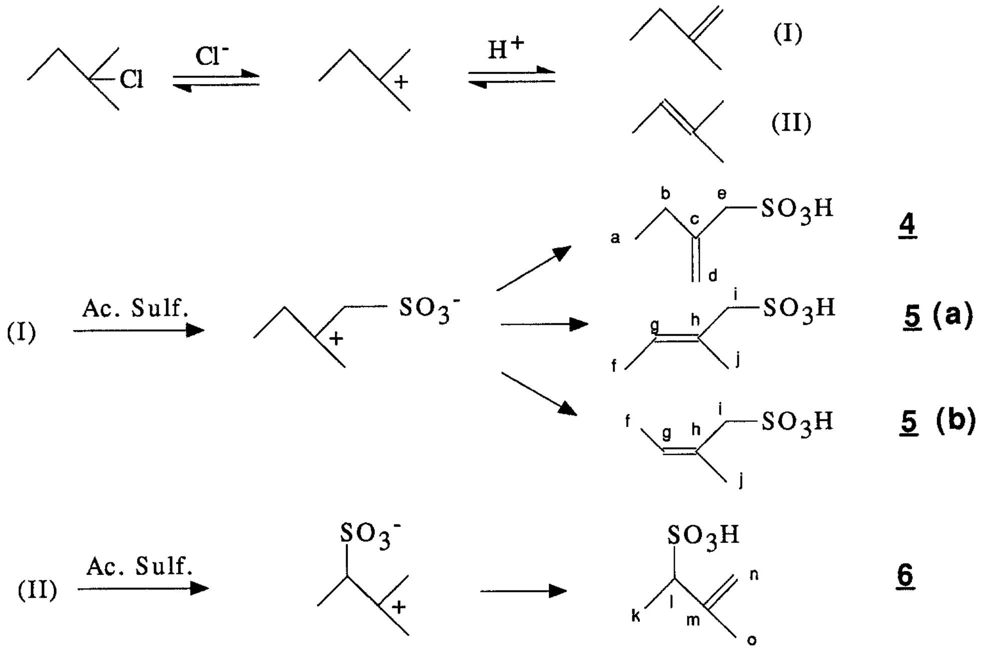

Figure 4. Mechanism of sulfonation of 2-chloro-2-methylbutane using acetyl sulfate.

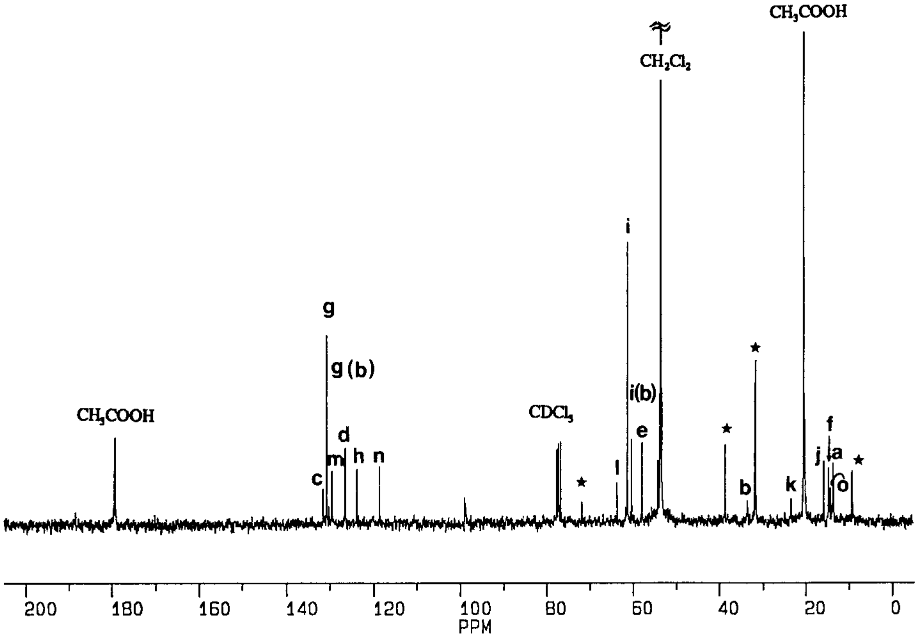

Figure 5. ^{13}C NMR spectrum of products from the sulfonation of 2-chloro-2-methylbutane.

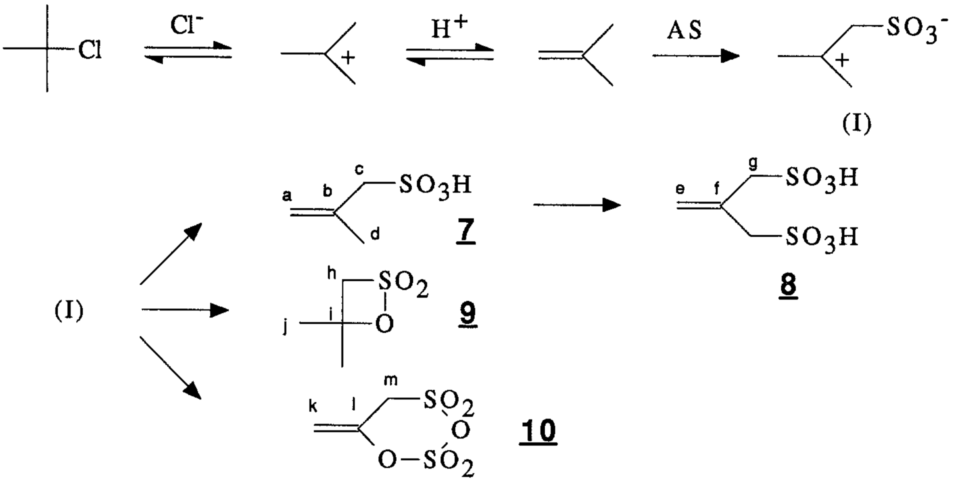

Figure 6. Mechanism of sulfonation of *tert*-butyl chloride using acetyl sulfate.

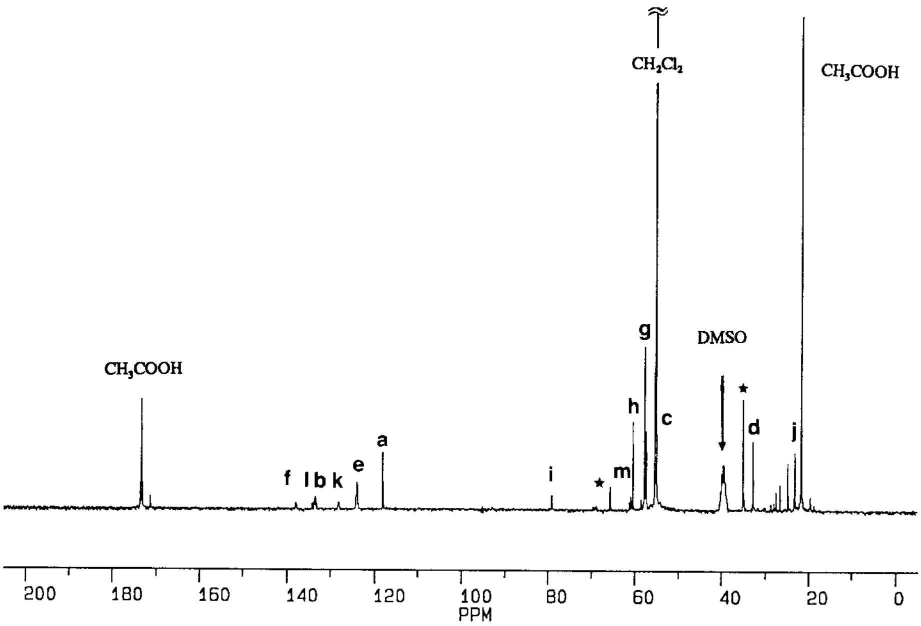

Figure 7. ^{13}C NMR spectrum of products from the sulfonation of *tert*-butyl chloride.

By all appearances, acetyl sulfate acts simply as a source of SO_3, which then adds to the olefin in such a manner as to form a zwitterionic intermediate in which the positive charge resides on the tertiary carbon. Then, depending upon structure, the carbocation may rearrange to form a γ-sultone, or a β-proton may be eliminated to yield one or more isomeric unsaturated sulfonic acids.

This chemistry can provide a direct route toward alkyl sulfonic acids in situations where the alkyl halide is the natural starting point in the synthesis. For example, *tert*-chloride end groups naturally derive from the controlled cationic polymerization of isobutylene. Also, hydrocarbon polymers such polypropylene, hydrogenated polydienes, and poly(ethylene-*co*-propylene) may be readily chlorinated to yield *tert*-chloride structures which may be sulfonated by this method to produce a variety of new ionomers.

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