Aromatic Sulphonation. Part XLIII.[1] Selenonation and Sulphonation of Polyalkylbenzenes with Selenic and Sulphuric Acids in Acetic Anhydride

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The selenonation of a series of polyalkylbenzenes with a mixture of H_2SeO_4 and acetic anhydride (*i.e.* with acetylselenic acid) at 0° has been studied. The isomer distributions of the selenonic acids are similar to those determined for sulphonation with acetylsulphuric acid as reagent. The isomer distributions indicate high selectivity for the two substitutions. The n.m.r. spectra of the polymethylbenzene-selenonic and -sulphonic acids in water are almost identical, illustrating that the shielding parameters of the SeO_3^- and SO_3^- groups on aromatic hydrogen atoms and methyl groups are about the same.

In connection with our studies on aromatic sulphonation and the properties of arenesulphonic acids,[2] it was thought of interest to study the selenonation of a series of aromatic hydrocarbons. In order to compare selenonation with sulphonation, it was desirable to study sulphonation under the same conditions as for selenonation.

Information on aromatic selenonation and areneselenonic acids is very limited,[3] in contrast to that on aromatic sulphonation and arenesulphonic acids.[2,4] This difference is in part related to the stronger oxidizing properties of selenium(VI) as compared with sulphur(VI) compounds. Direct treatment of *e.g.*, polymethylbenzenes with 96% selenic acid leads to vigorous oxidation of the substrate. The use of acetic anhydride as a solvent was found to moderate the oxidizing properties of selenic acid sufficiently to allow the preparation and subsequent isolation of alkylbenzeneselenonic acids.

By analogy with the suggestions made for the corresponding sulphur system,[5] it is proposed that the selenonating entity in the $Ac_2O-H_2SeO_4$ system is acetylselenic acid $AcOSeO_3H$, or, less likely because of its lower electrophilicity, $AcOSeO_3^-$. The possibility of concurrent acylation[6] will be less for acetylselenic acid than for acetylsulphuric acid $AcOSO_3H$, because selenium is somewhat less electronegative than sulphur.[7] Acetylsulphuric acid at room temperature gives only sulphonation of (reactive) aromatic compounds and no acylation,[8] whereas, at elevated temperatures it only acylates and rearranges with formation of sulphoacetic acid.[9]

So far acetylsulphuric acid has not been isolated as such, but its presence in the systems $Ac_2O-H_2SO_4$, Ac_2O–oleum, $Ac_2O-ClSO_3H$, AcOH–oleum, and AcOH–SO_3 has been firmly established.[5c,10]

RESULTS

The selenonation and sulphonation of the aromatic compounds with acetylselenic and acetylsulphuric acids were performed at 0° by dropwise addition of 96% H_2SeO_4 or 98% H_2SO_4 to the solution of the substrate in acetic anhydride. Product formation is shown in Table 1. Isomerisation of the selenonic and sulphonic acid products does not occur, not even after prolonged reaction, and their formation is apparently kinetically controlled. The isomer distributions for the two types of reactions are similar. In general, one of the isomers is formed in great excess, illustrating the high selectivity of the two substitutions. The reactivity of acetylselenic acid is less than that of acetylsulphuric acid, as benzene at 0° reacts very slowly with the latter reagent, but does not react at all with the former. The lower reactivity of acetylselenic acid

TABLE 1

Selenonation and sulphonation of substituted benzenes at 0°

Substituents in benzene	Isomer distribution (or main isomer)	
	Selenonation [a]	Sulphonation [b]
None	No reaction	1- [c]
Me	12 ± 2% 2-; 88 ± 2% (4- + 3-) [d,e]	8 ± 2% 2-; 92 ± 2% (4- + 3-) [c,d]
Et	4- [f]	4- [f]
Pr^i	4- [f]	4- [f]
Bu^t	4- [f]	4- [f]
1,2-Me_2	4- [f]	4- [f]
1,3-Me_2	4- [f]	4- [f]
1,4-Me_2	2-	2- [c]
1,2,3-Me_3	90 ± 2% 4-; 10 ± 2% 5- [g]	80 ± 3% 4-; 20 ± 3% 5- [d,h]
1,2,4-Me_3	5- [f]	5- [f]
1,3,5-Me_3	2-	2-
1,2,3,4-Me_4	5-	5-
1,2,3,5-Me_4	4-	
1,2-Et_2	4-	4- [c,f]
1,3-Et_2	4- [f]	4- [f]
1,3-Pr^i_2	4- [f]	4- [f]
OMe	4- [f]	4- [f] (4- + 2- [i])
OH	Explosive decomp.	4- [f] (4- + 2- [i])

[a] Reagent 96% $H_2SeO_4-Ac_2O$. [b] Reagent 98% $H_2SO_4-Ac_2O$. [c] Reaction temperature 25°. [d] The isomer distribution is independent of the substrate conversion. [e] The same result is obtained with 100% H_2SeO_4. [f] No evidence for the presence of other isomers was found. Given the limitations of the n.m.r. analysis, this implies that the sum of the other isomers is $\leqslant 5\%$. [g] With CH_2Cl_2 as co-solvent. [h] With or without CH_2Cl_2 as co-solvent. [i] H. Friese, *Ber.*, 1931, **64B**, 2109.

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would imply a higher selectivity. The lower degree of 5-substitution of 1,2,3-trimethylbenzene in selenonation as compared with sulphonation (Table 1) is in accord with this conclusion.

The nearly exclusive formation of the 4-substitution products with the three 1,3-dialkylbenzenes studied indicates that the steric effects are not predominant in the directing effect of the alkyl substituents.

The apparent chemical differences between areneselenonic acids and their salts on the one hand, and the corresponding sulphonic acids and their salts on the other, are the higher oxidizing properties of the former and their lower stability at high temperatures. Heating areneselenonic acids at temperatures >150° in general leads to decomposition. Treatment of these acids with concentrated hydrochloric acid at room temperature leads to the formation of the corresponding seleninic acids. These seleninic acids are also formed upon heating the selenonic acid with acetic anhydride at 100°, or simply by heating the $ArH-Ac_2O-H_2SeO_4$ reaction mixture at 100° after selenonation at 0° is complete. The former conversion was observed with 3,4-dimethyl- and 2,5-dimethyl-benzeneselenonic acid, the latter with toluene and ethylbenzene.

Attempts to protodeselenonate the areneselenonic acids under conditions reported for protodesulphonation [11] failed, probably because of decomposition of the selenonic acids at the high temperatures (140°).

I.r. spectra of areneselenonic acids and selenonate salts have not been reported before. The observed frequencies of the various selenonic compounds which, by comparison with the corresponding sulphur analogues,[12] are considered to be specific for the SeO_3H and SeO_3^- groups, are collected, with their assignments, in Table 2.

The n.m.r. spectra of the areneselenonic acids in D_2O strongly resemble those of the corresponding arenesulphonates, the difference in chemical shift of the corresponding signal between any set of analogues being $\leqslant 0{\cdot}2$ p.p.m.* The substituent shielding parameters $\Delta\delta$ of the SeO_3^- group on aromatic hydrogen atoms and methyl groups are thus about equal to those reported recently for the SO_3^- group [14] (*o*-H + 0·39; *m*-H + 0·13; *p*-H + 0·18; *o*-Me + 0·26; *m*-Me + 0·06; and *p*-Me + 0·05 p.p.m.).

The u.v. spectra of the areneselenonates and arenesulphonates in water are also similar (Table 3). For a given set of analogues the wavelengths of maximum absorption of the B bands are about the same. The wavelength of maximal absorption of the K band is the same for the three arenesulphonates, but increases slightly with increasing number of methyl groups for the corresponding selenonates.

TABLE 2

Specific SeO_3H and SeO_3^- i.r. frequencies

SeO_3H [a]	SO_3H[13]	Vibration assigned	SeO_3^- [b]	SO_3^-[13]	Vibration assigned
ν/cm⁻¹			ν/cm⁻¹		
965—945s	1352—1340	ν_a[S(e)=O]	910—890vs, br [c]	1220—1150	ν_a[S(e)–O]
900—880vs	1200—1100	ν_s[S(e)=O]	870—850s [c]	1120—1030	ν_s[S(e)–O]
865—855v	1100—1060	Unknown	415m, br	*ca.* 690	Unknown
730—705v	910—895	ν[S(e)–O]			

[a] I.r. spectra of selenonic acids in $CHCl_3$ or solid KBr are similar. [b] Spectra of selenonate salts taken in solid KBr. [c] Potassium octane- and decane-selenonate show a strong broad absorption at 905 cm^{-1} and two weak absorptions at 865 and 855 cm^{-1}.

TABLE 3

U.v. spectra of arene-selenonates and -sulphonates in H_2O

$\lambda_{max.}$/nm (10^{-2} ε/lmol^{-1} cm^{-1})

Substituted	$ArSeO_3^-$		$ArSO_3^-$	
$ArS(e)O_3^-$	K band	B Band	K Band	B Band
4-Me	224 (133)	260(6·7); 271(4·0)	222 (118)	261(3·80); 271(1·80)
2,4-Me_2	227 (107)	267(8·0); 275(7·6)	223 (90·1)	268(4·65); 276(4·37)
2,4,6-Me_3	231 (97·3)	274(14·6); 282(14·8)	223 (92·2)	273(8·8); 281(9·3)

EXPERIMENTAL

Selenonation.—1 Mol. equiv. of 96% selenic acid (B.D.H.) was added dropwise at 0° within 20 min to a stirred solution of 1—2 mol. equiv. of the aromatic substrate in an amount of acetic anhydride just sufficient to keep the reaction mixture homogeneous after the addition of the selenic acid (2—5 mol. equiv.).[15] The reaction must be performed at 0° in order to prevent reduction of the selenic and selenonic acids by the solvent (with formation of selenium dioxide and seleninic acids respectively). The selenonic acid(s), formed in general within a few hours, precipitate(s) in most cases quantitatively from the reaction mixture. Filtration of the precipitate, rapid washing with dry, cold ether and recrystallization from 50% aqueous ethanol yields the pure selenonic acid(s). The selenonate salts were obtained by neutralization of the aqueous selenonic acid solutions.

The structural assignment of the selenonic acids was based on the n.m.r. spectra of the isolated products in D_2O,[14,16] and by comparison with the n.m.r. spectra of the corresponding sulphonates in D_2O.[17a] The isomer distributions and substrate conversions were determined from the n.m.r. spectra of the reaction mixtures after being made homogeneous by the addition of more solvent or a co-solvent (*e.g.* CH_2Cl_2), or by warming to room temperature.

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* For instance the zero concentration n.m.r. chemical shifts of 2,4,6-trimethylbenzene selenonate in D_2O are: 2-Me, δ 2·672 (3·2); 3-H, 7·123 (−30); 4-Me, 2·306 (−22), whereas for the corresponding sulphonate they are: δ 2-Me, 2·554 (6·5); 3-H, 7·035 (−19); 4-Me, 2·265 (−14). The data in parentheses refer to the slope of δ against the concentration (in l Hz mol^{-1}).

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Some selenonations were performed with 100% H_2SeO_4–Ac_2O. 100% H_2SeO_4 was prepared from 96% H_2SeO_4 by distillation.[18] The substrate was then added at 0° to a solution of 100% H_2SeO_4 (a solid) in acetic anhydride.

Sulphonation.—To the aromatic substrate dissolved in acetic anhydride (2—6 mol. equiv.) was added at 0° dropwise within 20 min 98% H_2SO_4 (1—3 mol. equiv., depending on the substrate reactivity). If the mixture proved to be heterogeneous, homogeneity was brought about either by performing the reaction at 25° or by the addition of CH_2Cl_2 or $CHCl_3$ as co-solvent. The isomer distributions and substrate conversions were determined from the n.m.r. spectra of the reaction mixtures.

The sulphonic acids were isolated from the mixtures by three methods. (i) The acids were filtered off and washed with *e.g.* cold ether, provided that the acid(s) precipitated directly from the reaction mixture, or after evaporation of the (co)solvent. (ii) For reactions in which the sulphuric acid was completely consumed the sulphonic acids were obtained as a residue after removal of the other compounds by distillation under reduced pressure. (iii) In the remaining cases the mixture was quenched with an exess of ice–water and the non-sulphonic organic compounds were removed by extraction with ether. The aqueous solution was neutralized and the sulphonates were isolated by removal of water by distillation or by salting out.

At 25° and higher temperatures the formation of sulphoacetic acid is concurrent with or dominant over the sulphonation of the polyalkylbenzenes. This is apparent from the n.m.r. absorption at δ 4·34 (s) in D_2O, as verified for an authentic [9a] sample of sulphoacetic acid.

More detailed experimental information is given elsewhere.[17b]

Spectra.—I.r. spectra were recorded with a Perkin-Elmer 125 spectrometer, n.m.r. spectra with Varian HA100 and A60 spectrometers, and u.v. spectra with a Cary 14 spectrometer.

This investigation was supported financially by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

[3/1169 *Received, 6th June,* 1973]

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