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REACTIONS OF α-DIAZOSULFONES IN SOME APROTIC SOLVENTS IN THE PRESENCE OF PERCHLORIC ACID. ISOLATION OF COVALENT PERCHLORATES[1].

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In connection with our studies[2,3] on the mechanism of the acid-catalysed hydrolysis of α-diazosulfones[4], we became interested in the behaviour of these diazo compounds in aprotic solvents in the presence of strong acids. A detailed kinetic study[2,3] on the hydrolysis reaction of α-diazosulfones in aqueous solutions has shown that the reaction exhibits specific hydrogen ion catalysis. Strong evidence has been presented for a bimolecular rate determining step with a rather low participation of the nucleophile in the transition state:

$$RSO_2CHN_2 + H_3O^{\oplus} \rightleftarrows RSO_2CH_2N_2^{\oplus} + H_2O$$

$$RSO_2CHN_2^{\oplus} + H_2O \xrightarrow{slow} RSO_2CH_2OH + H^{\oplus} + N_2$$

The present communication deals with the reaction of the α-diazosulfones RSO_2CHN_2 Ia ($R = p\text{-}CH_3C_6H_4$) and Ib ($R = C_6H_5CH_2$) in the presence of a 70% aqueous perchloric acid solution using 1,2-dichloroethane, acetonitrile and propionitrile as the solvents.

Reaction in 1,2-dichloroethane.

In this case a rapid and quantitative evolution of nitrogen was observed and from both α-diazosulfones a white crystalline solid was isolated in a reasonable yield. The products were characterized as the covalent perchlorates IIa and IIb:

$$RSO_2CHN_2 + HClO_4 \longrightarrow RSO_2CH_2OClO_3 + N_2$$

IIa, R = p-$CH_3C_6H_4$, yield 49%, m.p. 92-94°

IIb, R = $C_6H_5CH_2$, yield 44%, m.p. 120.5-121.5°

In addition, the normal hydrolysis products[2] RSO_2CH_2OH were isolated in minor quantities (about 10%).

The structural assignment of the perchloric esters was based on correct elemental analyses, infrared absorptions at 1250 cm^{-1} (tentatively assigned to the $-CH_2OClO_3$ group) and the absence of a broad and strong absorption around 1100 cm^{-1} as found in ionic perchlorates[5]. The low field PMR signals at τ 4.73 ppm for IIa and τ 4.97 ppm for IIb (both in deuterochloroform) are characteristic for methylene protons flanked by two electronegative groups. The compounds IIa and IIb are readily soluble in organic solvents as ether or chloroform but are decomposed by water and ethanol[6]. Although these perchloric esters are thermally rather stable in comparison with the very explosive ethyl perchlorate[7], and can be handled in small quantities without spontaneous decomposition, they detonate when struck with a hammer. The enhanced stability is presumably the result of a decreased leaving ability of the perchlorate anion due to the presence of the strongly electron attracting sulfone group.

The formation of the perchloric ester may be explained by assuming attack of a tight ion pair of perchloric acid[8] on the α-diazosulfone. Reaction of the α-diazosulfone with dissociated perchloric acid (if present at all in this solvent of low polarity) would require recombination of the sulfonylmethyldiazoniumion $RSO_2CH_2N_2^{\oplus}$ with the stable perchlorate anion and seems highly improbable.

Ehret and Winstein[9] have presented evidence for the intermediacy of a covalent perchlorate in the perchloric acid-catalyzed isomerisation of iso-cholesteryl acetate but isolation of this intermediate was not possible. In our case, the high energy content of the protonated α-diazosulfone permits the collaps of an intimate ion pair $RSO_2CH_2N_2^{\oplus}ClO_4^{\ominus}$ to the covalent perchlorate with simultaneous liberation of nitrogen. This collaps is also favoured by the low polarity of the solvent and the absence of appreciable amounts of other nucleophiles in the solvation shell. The isolation of small quantities of the hydroxymethylsulfones, RSO_2CH_2OH, demonstrates that water introduced into the system by the concentrated perchloric acid solution competes with perchlorate anion in the nucleophilic attack on the diazonium ion. The compounds RSO_2CH_2OH did not react with perchloric acid under the reaction conditions described above and thus this route to the perchloric esters could be definitely excluded.

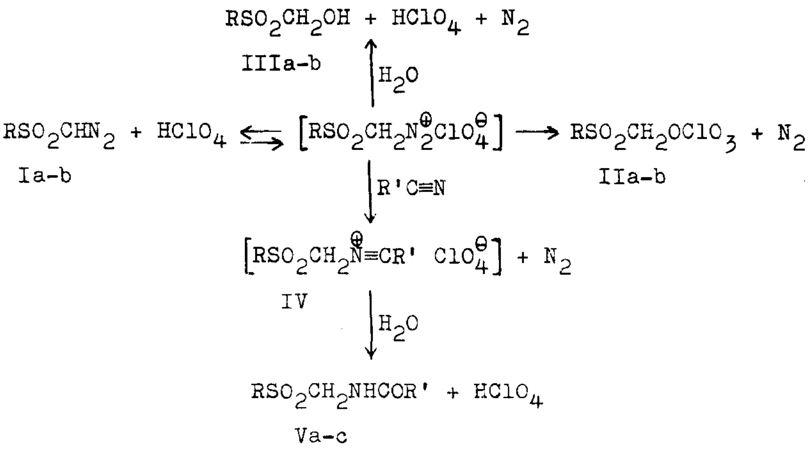
The use of anhydrous p-toluenesulfonic acid instead of perchloric acid in the reaction with Ia resulted in a 72% yield of the tosylate $p\text{-}CH_3C_6H_4SO_2CH_2OSO_2C_6H_4CH_3\text{-}p$ (m.p. 109-112°).

Reaction in acetonitrile and propionitrile.

The reaction of Ia and Ib in acetonitrile or propionitrile in the presence of perchloric acid took a different course. In addition to minor amounts of the perchloric esters IIa-b and of the hydroxymethylsulfones IIIa-b, the sulfonylmethylcarbonamides Va-c were isolated. This behaviour of the α-diazosulfones is in strong contrast to that of diaryldiazomethanes[10] which gave under similar conditions tetraarylethenes.

In the following scheme the formation of the products from the α-diazosulfones is rationalized:

SCHEME



In the table the yields of the products are summarized.

TABLE

Compound	R	R'	Yield (%)	m.p.(°C)	By-products
Va	p-$CH_3C_6H_4$	CH_3	52	133-136	13% IIa; 13% IIIa
Vb	$C_6H_5CH_2$	C_2H_5	41	126.5-128	37% IIb; 10% IIIb
Vc	p-$CH_3C_6H_4$	C_2H_5	45	115-116	11% IIa; 7% IIIa

The amides Va-c were characterized by correct elemental analyses and by their infrared and PMR spectral properties. Furthermore, the compounds Va and Vc were shown to be identical (mixed m.p. and infrared spectra) with those prepared by an alternate synthesis, e.g. the condensation of p-methylbenzene sulfinic acid with formaldehyde and acetamide or propionamide, respectively[11,12].

Although the products Va-c could possibly arise from a reaction of the perchloric esters II with the nitrile, good evidence for a direct interaction of the nitrile with the diazonium ion was found in the observation that the perchloric esters could be recovered unchanged from an attempted reaction with acetonitrile under conditions used for the reaction with the diazo compound.

The presence of the conjugate acid of the nitrile is unlikely because of the extremely weak basic character of the nitrile function[14]. Therefore, protonation of the α-diazosulfone by this acid can be left out of consideration, and the perchloric acid ion pairs are again the protonating species. Apparently solvation of the diazonium perchlorate $RSO_2CH_2N_2^{\oplus}ClO_4^{\ominus}$ by the rather polar solvent molecules decreases the tightness of this ion pair and consequently attack of the weak nucleophilic nitrile can compete effectively with the reaction with perchlorate anions or water.

Because less than equimolecular quantities of perchloric acid are sufficient to liberate nitrogen quantitatively from the α-diazosulfone, it must be concluded that water present in the reaction mixture hydrolyses the nitrilium salt IV [13] to the amide V with regeneration of perchloric acid.

All reactions were carried out[15] by adding a 70% aqueous perchloric acid solution to a stirred solution of the α-diazosulfone in the respective solvent. Nitrogen was rapidly evolved and its volume was measured as a control for a complete reaction. After additional stirring for thirty minutes, water was added and the mixture was neutralized carefully with sodium bicarbonate. The water layer was extracted with dichloromethane and the combined organic solvents were dried. Removal of the solvent in vacuo gave the crude reaction products. The covalent perchlorates IIa-b were purified by recrystallization from ether-n-hexane with considerable loss of material. Dioxane-water was used for the recrystallization of the amides Va-c. Separation of the perchloric esters and the amides was accomplished by chromatography over silicagel. From the aqueous layer the hydroxymethylsulfones[16] were isolated after acidification with hydrochloric acid and extraction with dichloromethane. All reported yields are of analytically pure compounds. The melting points were determined on a hot stage microscope.

Acknowledgment.

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