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RESEARCH ON 1, 2, 4-TRIAZOLES

VI. Hydrolysis of Sulfides and Sulfones Prepared from 1-Aryltetrazolinethiones-5 and 4-Aryl-1, 2, 4-Triazolinethiones-3*

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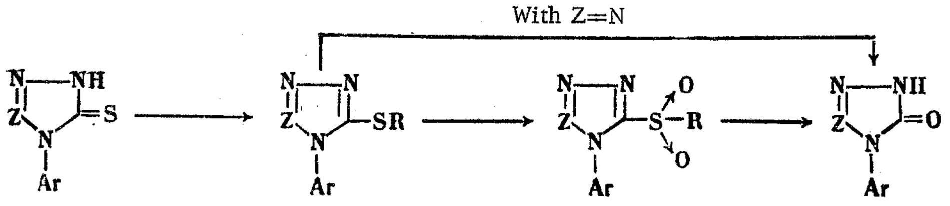
The stability of sulfides and sulfones of 1-aryltetrazoles and 4-aryl-1, 2, 4-triazoles depends on the acceptor character of the heterocyclic ring. Unlike tetrazole sulfides, triazole sulfides do not undergo hydrolysis. Tetrazole sulfones are more readily hydrolyzed than triazole ones. When an electron-donor substituent is introduced into the p-position of the phenyl ring, the rate of hydrolysis is cut. Neither triazole nor tetrazole sulfides and sulfones, not arylated at a nitrogen atom, are hydrolyzed by alkali, because of a partial decrease in positive charge at the carbon atom of the sulfoazomethine group through formation of an anion with a sextet of π-electrons in the ring. Hydrolysis of sulfides and sulfones can conveniently be used to prepared 1-aryltetrazolinones-5 and 4-aryl-1, 2, 4-triazolinones-3.

From previous papers it is evident that compounds containing the sulfoazomethine group $-N=C-SO_2R$, readily undergo hydrolysis at the C—S bond [1, 2]. In continuing a comparative study of the reactivities of 1-aryl-tetrazolinethiones-5 (TETT) (I), and 4-aryl-1, 2, 4-triazolinethiones 3 (TRIT) (II), two analogs differing by the number of nitrogen atoms in the ring, it was of interest to examine the behavior of the sulfones V, VI and sulfides III, IV of these heterocyclic systems, under alkaline hydrolysis conditions.

The stability of the C—S bond to alkaline hydrolysis is a function of the effects of electron-accepting groups at this bond. It was previously established that the more powerfully the heterocyclic ring pulls electrons, the weaker becomes the C—S bond [1].



I, II III, IV V, VI VII, VIII

I, III, V, VII Z=N; II, IV, VI, VIII Z=CH

Since tetrazole derivatives are more acid compounds than triazole compounds, and since the tetrazole ring exhibits greater electron-accepting character than the 1, 2, 4 triazole ring, it is to be expected that the TETT sulfides (III) and sulfones (V) will be more easily hydrolyzed than the corresponding TRIT derivatives (IV, VI). Actually, while the sulfides derived from TETT (III) are hydrolyzed when boiled for a few hours with 2 N sodium hydroxide solution, their analogs, the sulfides derived from TRIT (IV), are generally not hydrolyzed by sodium hydroxide solution even after boiling for two days. While sulfones of the tetrazole series (V) are even hydrolyzed by sodium hydroxide solution at room temperature (20-25°), the corresponding sulfones of the triazole series (VI) hydrolyze only on heating (at 80° hydrolysis takes 3 hr).

The relative rate of hydrolysis of sulfides and sulfones is cut when an electron-donor substituent is introduced at the p- position of the phenyl ring. Thus the ethoxy group, acting as an electron-donor cuts the relative positive charge at the carbon of the C—S link, and so considerably cuts the speed of hydrolysis. Introduction of a chlorine atom at the same position has practically no effect on the rate of hydrolysis. The hydrolysis products are 1-aryltetrazolinone-5 (VII) and 4-aryl-1, 2, 4-triazolinone-3 (VIII) obtained in good yield. Hydrolysis of the sulfones is a convenient method for preparing the azolinones VII, VIII.

A gravimetric method was used, in studying the rates of hydrolysis of sulfides and sulfones, and it was accurate enough for the investigation of comparative stabilities of the products. Sulfone hydrolysis rate can also be checked by a determination on the secondary reaction product, methylsulfinic acid. This determination is effected by titrating an acidified solution with potassium permanganate.

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*For Part V see [8].

To determine the effect of the phenyl portion on the stability of the C—S link, a study was made of the stabilities of sulfides and sulfones of unsubstituted tetrazole and triazole, i. e., of 5-methylthiotetrazole [3], 3-methylthio-1, 2, 4-triazole [4], tetrazolyl-5-methylsulfone [3], and 1, 2, 4-triazolyl-3-methylsulfone, and both sulfides and sulfones were found to exhibit considerable resistance to alkaline hydrolysis*. 3-Methylthio-1, 2, 4-triazole is alkali-insoluble, and the similar arylated methylsulfide of triazole is inert to alkali. 1, 2, 4-triazolyl-3-methylsulfone, 5-methylthiotetrazole, and tetrazolyl-5-methylsulfone have more acidic properties, and give sodium salts when dissolved in alkali. There the anion is formed having a π-electron sextet, and it must be assumed that in this anion, the negative charge is distributed over all the atoms in the heterocyclic ring, leading to decrease in the positive charge on the carbon atom linked to sulfur, and this is apparently the reason for the instability of unsaturated sulfides and sulfones when subjected to alkaline hydrolysis.

Experimental

Triazolyl-3-methylsulfone. 3. 7 g 3-methylthio-1, 2, 4-triazole was refluxed for 20 hr with 20 ml acetic acid and 6 ml 30% hydrogen peroxide. The precipitate of 1, 2, 4-triazolyl-3-methylsulfone which separated after cooling was filtered off, yield 3. 7 g (78%), mp 196-197° (prisms from water). After evaporation, the filtrate gave a further 0. 5 g (10%) sulfone. Found: N 28. 38; S 21. 30%. Calculated for $C_3H_5N_3O_2S$: N 28. 56; S 21. 79%.

1-Aryltetrazolinones-5 (VII).

a) 20 g 1-phenyl-5-methylthiotetrazole was refluxed for 3 hr with 200 ml 2 N sodium hydroxide solution, when the precipitate of sulfide gradually disappeared (mercaptan separated). After cooling, the solution of the sodium salt of 1-phenyltetrazolinone-5 was made acid with concentrated hydrochloric acid, the precipitate filtered off, and washed with cold water, quantitative yield, mp 186-187° ([5, 6] gives 186-187°).

1-p-Chlorophenyl-5-methylthiotetrazole was hydrolyzed quantitatively with 2 N sodium hydroxide solution in 4 hr, mp 1-p-chlorophenyltetrazolinone-5 200-203° (prisms from dilute alcohol). Found: N 28. 65%. Calculated for $C_7H_5ClN_4O$: N 28. 49%.

1-p-Ethoxyphenyl-5-methylthiotetrazole [7] was 80% hydrolyzed with 2 N sodium hydroxide solution, after 50 hr; mp 1-p-ethoxyphenyltetrazolinone-5 169-170° (prisms from dilute alcohol). Found: N 27. 24%. Calculated $C_9H_{10}N_4O_2$: N 27. 18%.

b) 1-Phenyl-tetrazolyl-5-methylsulfone [7] was hydrolyzed by 2 N sodium hydroxide solution even at 20-25°. After 2 hr 30 min a 90% yield of 1-phenyltetrazolinone-5 was isolated by neutralizing with hydrochloric acid.

At the same temperature 1-p-ethoxyphenyltetrazolyl-5-methylsulfone [7] was 90% hydrolyzed in 6 hr, while 1-p-ethoxyphenyltetrazolyl-5-methylsulfone [7] was 45% hydrolyzed in 6 hr.

4-Aryl-1, 2, 4-triazolinone-3 (VIII). 4-Phenyl-1, 2, 4-tetrazolyl-3-methylsulfone [8] was heated for 3 hr at 80° with 2 N sodium hydroxide solution. The reaction products were acidified, filtered, and the solid washed with cold water. A sample was titrated with potassium permanganate. Hydrolysis was 90% complete. The product was 4-phenyl-1, 2, 4-triazolinone-3, mp 185-186° ([9] gives 185-186°).

4-p-Chlorophenyl-1, 2, 4-triazolyl-3-methylsulfone [8] was 85% hydrolyzed at the same temperature in 3 hr. The product was 4-phenyl 1, 2, 4-triazolinone-3, mp 199-200° ([9] gives 200°).

4-p-Ethoxyphenyl-1, 2, 4-triazolyl-3-methylsulfone [8] was 66% hydrolyzed in 3 hr, to give 4-p-ethoxyphenyl-1, 2, 4-triazolinone-3 mp 181-182° ([9] gives 182°).

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*The considerable resistance of tetrazoline-5-methylsulfone to the action of alkali has previously been observed [3].