

this yellow product melts at 184°. Like all the other addition products of the anhydro compound it is readily hydrolyzed to phenyl dibenzoyl methane.

Anal. Calcd. for $C_{28}H_{20}O_8N_4$: C, 62.2; H, 3.7. Found: C, 61.9; H, 3.8.

Summary

This paper contains the results of the study of the pseudo base 2-methyl-3,4,5-triphenyl-3-hydroxy isoxazoline and its salts. It is shown that this substance, in addition to the usual reactions of pseudo bases, undergoes a novel irreversible transformation into an open chained anhydro compound, the behavior of which has been explored. The results obtained in this work provide a basis for the formulation of a mechanism which correlates the behavior of all pseudo bases of the isoxazole series.

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PREPARATION OF ALIPHATIC AND AROMATIC SULFONES WITH SODIUM HYPOCHLORITE¹

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This paper represents a study of the conditions best suited for the oxidation of pure alkyl and aromatic sulfides. Birch and Norris² have made some observations relevant to the oxidation of organic sulfides previously dissolved in a light petroleum distillate. Birch and Norris reported the complete oxidation of ethyl, *n*-propyl, *isobutyl* and *iso-amyl* sulfides to the corresponding sulfones. Under similar conditions, Wood, Greene and Provine³ reported the oxidation of ethyl, *n*-propyl and phenyl sulfides to the corresponding sulfones.

Experimental

Eastman's ethyl, *n*-propyl, *n*-butyl, *n*-heptyl, phenyl and benzyl sulfides were used without further purification.

Hypochlorite solutions 1, 2 and 3 were prepared by passing chlorine into solutions of pure sodium hydroxide. Hypochlorite solutions 4, 5 and 6 were prepared by passing chlorine into solutions containing both pure sodium hydroxide and pure sodium carbonate. The chlorinating solutions were kept below 27°. The alkalinity was determined by decomposing the sodium hypochlorite with hydrogen peroxide and titrating against standard hydrochloric acid with phenolphthalein and methyl orange as indicators. The available chlorine was determined by titrating the iodine liberated from potassium iodide against 0.1 *N* sodium thio-

¹ A preliminary version of this paper was received on May 3, 1927.

² Birch and Norris, *J. Chem. Soc.*, 127, 1934 (1925).

³ Wood, Greene and Provine, *Ind. Eng. Chem.*, 18, 823 (1926).

sulfate solution. The compositions of the hypochlorite solutions are indicated in Table I.

TABLE I
COMPOSITIONS OF SODIUM HYPOCHLORITE SOLUTIONS

NaOCl soln.	NaOH, %	Na ₂ CO ₃ , %	Avail. Cl per liter, g.
1	2.00	0.00	93
2	0.20	.00	23
3	.11	.00	91
4	.00	.12	23
5	.00	.23	23
6	.00	.61	23

In carrying out the experiments, from 0.2 to 0.3 g. of the organic sulfide was added to 50 cc. of the sodium hypochlorite solution previously placed in a small, glass-stoppered bottle and shaken for predetermined periods of time. The sulfones were recovered, recrystallized and identified by melting point determinations.

Results

The results with the different hypochlorite solutions are indicated in Table II.

TABLE II
RESULTS WITH DIFFERENT SOLUTIONS

NaOCl soln.	Ethyl sulfide	<i>n</i> -Propyl sulfide	<i>n</i> -Butyl sulfide	<i>n</i> -Heptyl sulfide	Phenyl sulfide	Benzyl sulfide
1	Completely oxidized in two hours	Partially oxidized in two hours	No appreciable effect at the end of a two-hour treatment			
2	Oxidized instantly	Oxidized within thirty minutes	Oxidized within three hours	Slight effect	Oxidized within three hours	
4	All organic sulfides investigated except <i>n</i> -heptyl were almost instantly converted to the corresponding sulfones. With the <i>n</i> -heptyl sulfide small amounts of the sulfone were formed but the oxidation was principally to the sulfoxide.					

An examination of Table II indicates that ethyl, *n*-propyl, *n*-butyl and *n*-heptyl sulfides are reactive in the order named and that phenyl and benzyl sulfides have about the same order of reactivity as the *n*-butyl sulfide. Table II also indicates the effects of hydroxyl concentrations on the reactivity of sodium hypochlorite solutions. Sodium hypochlorite solution 1 was apparently reactive only with ethyl and *n*-propyl sulfides. Solutions 2 and 3 were apparently only slightly reactive with *n*-heptyl sulfide but were reactive with the other alkyl sulfides investigated in an inverse ratio to the molecular weights. The aromatic sulfides investigated were reactive with solutions 2 and 3. Solutions 4, 5 and 6 were most reactive, readily converting all the sulfides investigated except *n*-heptyl

to the corresponding sulfones. These last sodium hypochlorite solutions converted *n*-heptyl sulfide principally to the sulfoxide, forming at the same time small amounts of the *n*-heptyl sulfone.

It is also interesting to note that the alkalinity of sodium hypochlorite solutions 4, 5 and 6 is due to sodium carbonate, thereby stabilizing the solution for use and at the same time reducing the hydroxyl concentration to a minimum and promoting the formation of free hypochlorous acid in accord with the theory of Kauffmann.⁴ These facts are also in agreement with the results obtained by Cullen and Hubbard,⁵ who state that hypochlorite solutions may be stabilized for use by the addition of 0.5% of borax, by the addition of 1% of sodium carbonate, or by the addition of 0.2% of sodium hydroxide.

Conclusions

These results indicate that sodium hypochlorite solutions of low alkalinity may be effectively used in the preparation of aromatic sulfones and low molecular weight alkyl sulfones from the corresponding sulfides.

Summary

This work represents a study of the action of solutions of sodium hypochlorite on a number of selected organic sulfides. Ethyl, *n*-propyl, *n*-butyl, *n*-heptyl, phenyl and benzyl sulfides were used. Sodium hypochlorite solutions of varying degrees of alkalinity and available chlorine were employed. These results indicate that the oxidizing effects of solutions of sodium hypochlorite are dependent on the alkalinity of the hypochlorite solution and on the type and molecular weight of the organic sulfide employed. With hypochlorite solutions of low alkalinity (about 0.2% of free sodium hydroxide) ethyl and *n*-propyl sulfide were readily and completely converted to the corresponding sulfones; butyl, phenyl and benzyl sulfides were less readily converted to the corresponding sulfones; and heptyl sulfide was the least reactive, being converted principally to the sulfoxide.

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⁴ Kauffmann, *Z. angew. Chem.*, **37**, 364 (1924).

⁵ Cullen and Hubbard, *J. Biol. Chem.*, **37**, 511 (1919).