[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VISKING CORPORATION]

THE CHEMISTRY OF ALIPHATIC NITROSULFONATES. V. NITROSULFONYL CHLORIDES

MARVIN H. GOLD[1] AND LEONARD J. DRUKER[2]

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Although a wide variety of aromatic nitrosulfonyl chlorides are well known, the literature shows no reference to an aliphatic nitrosulfonyl chloride. The present reports describe the preparation of a number of such aliphatic nitrosulfonyl chlorides.

There is reason to suspect that the compounds described here might be relatively unstable and be incapable of a normal shelf life. The reasoning behind such a statement is that since both primary and secondary nitro groups are readily converted to the enolate, they might react in that form with the sulfonyl chloride group or the chlorinating agent. It was rather surprising therefore, to find that stable nitrosulfonyl chlorides could be isolated from reactions involving very vigorous chlorinating conditions (1). The stability of the compounds is not dependent upon the type of nitro group, however, but rather upon the sulfonyl chloride group. Only nitrosulfonates containing a primary sulfonate group can be converted to a stable nitrosulfonyl chloride. Where the sulfonate group is secondary or tertiary the sulfonyl group apparently loses sulfur dioxide quite rapidly or in other ways gives lower degradation products.

In general the reaction was carried out in a straightforward manner by treating an aliphatic nitrosulfonate (2) or a halogenated aliphatic nitrosulfonate (3) with phosphorus pentachloride. However, it was found that direct mixing of the two solid reagents leads to an uncontrollable reaction. This could be readily modified by suspending the nitrosulfonate in a diluent such as phosphorus oxychloride, adding an equivalent amount of phosphorus trichloride, and then bubbling in chlorine gas to oxidize the trichloride to the pentachloride (4). In this way the reaction could be kept under complete control by regulating the flow of chlorine admitted to the reaction mixture.

EXPERIMENTAL

In general the reaction is conducted in a 3-necked flask equipped with a sealed stirrer. reflux condenser, and a gas inlet tube leading to the bottom of the flask. About 150 ml. of phosphorus oxychloride is used for every 100 g. of the nitrosulfonate and to this mixture is added exactly one mole of phosphorus trichloride for each mole of nitrosulfonate. Stirring is started and dry chlorine gas is admitted through the gas inlet tube. There is a rapid evolution of heat and the reaction mixture soon reaches the reflux temperature. The rate of chlorine admission is then adjusted to a point where rapid reflux is maintained. When the reaction is about half completed there appears to be a change of phase in the suspension of salt in the phosphorus halides and stirring becomes quite difficult. However, as the

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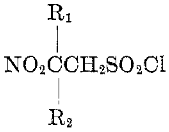
[1] Present Address: Aerojet Engineering Corp., Azusa, California.

[2] Present Address: Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

reaction is allowed to proceed, the slurry becomes less pasty and stirring is easily maintained. After one or two hours the yellow color of free chlorine gas appears in the condenser. The flow of chlorine is discontinued and the reaction is stirred and refluxed for an additional 30–60 minutes. Then the mixture is filtered through a large sintered-glass funnel to remove inorganic salts and the salts washed with a little phosphorus oxychloride. The washings and filtrate are combined and distilled under reduced pressure to remove the phosphorus halides. The salts left on the filter are then dissolved in water and the small amount of oil which separates is extracted with benzene. This benzene extract is used to dilute the distillation residue, and the dark solution washed repeatedly with cold water. The benzene solution is then rapidly dried with sodium sulfate, filtered, and then shaken thoroughly with potassium carbonate. After allowing to stand several hours, the solution is filtered and the benzene removed under reduced pressure. The residue is then distilled under the full vacuum of an oil-pump. Once the nitrosulfonyl chloride has been distilled it offers no problem in redistillation and is quite stable. However, the crude product often contains traces of impurities which tend to catalyze thermal decomposition. In this laboratory the problem has been overcome by the use of a falling film still (5) so that the sulfonyl chloride is exposed to distillation temperatures for a very short time. The yields of nitrosulfonyl chlorides obtained by this method range from 25 to 75%.

TABLE I

β-NITROSULFONYL CHLORIDES



$NO_2\overset{R_1}{\underset{R_2}{C}}CH_2SO_2Cl$

R₁	R₂	B.P., °C. (MM.)	M.P., °C.	n_D^{24}	d_4^{24}	ANALYSIS			
						Calc'd		Found	
						S	Cl	S	Cl
H	H	120–125 (2)	9–10°	1.4980	1.618	18.1	20.4	17.9	20.9
CH_3	H	105–106 (3)	5–6°	1.4840	1.502	17.1	18.9	16.8	18.8
C_2H_5	H	105–106 (2)	9–11°	1.4800	1.418	15.9	17.6	16.2	17.5
C_2H_5	Cl	108–109 (1)	—	1.4955	1.511	13.6	30.1	13.8	29.9
C_2H_5	Br	120–125 (2)	24–25°	1.5157	1.744	11.4	41.2[a]	11.1	40.7[a]

[a] Calculated and determined values for total halogen.

Solvents such as carbon tetrachloride and chlorobenzene have been tried in place of phosphorus oxychloride but the results are very poor. Apparently the nitrosulfonates are too insoluble in the organic solvents. The reaction has also been carried out by mixing phosphorus pentachloride directly with the nitrosulfonate. This method leads to an extremely vigorous and uncontrollable reaction which often exceeds the boundaries of the reaction vessel. Some of the desired product can be isolated by this procedure but a good deal is unavoidably lost. The reaction has also been carried out by an eight- to ten-hour reflux with phosphorus oxychloride. The yields by this method were quite inferior to those obtained by the preferred technique.

Similar reactions were tried with potassium 2-nitro-1-phenylethane-1-sulfonate and potassium 1-nitropentane-2-sulfonate. In both cases the sulfonate group is secondary and the corresponding sulfonyl chloride could not be isolated. Only lower-boiling oily products were obtained which qualitatively showed the presence of chlorine and nitrogen but no sulfur.

SUMMARY

Aliphatic nitrosulfonyl chlorides are produced by the treatment of the corresponding nitrosulfonates with the elements of phosphorus pentachloride. Only those nitrosulfonyl chlorides in which the sulfonyl group is primary are stable compounds.

CHICAGO 38, ILLINOIS

REFERENCES

(1) GOLD AND DRUKER, U. S. Patent 2,467,028 (April 12, 1949).
(2) GOLD, *et al.*, *J. Org. Chem.*, **16**, this issue, Paper I.
(3) GOLD, LEVINE, AND POLEN, *J. Org. Chem.*, **16**, this issue, Paper III.
(4) KOSOLAPOFF AND HUBER, *J. Am. Chem. Soc.*, **68**, 2540 (1946).
(5) GOLD, *Anal. Chem.*, **21**, 636 (1949).