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Study Leading to the Development of Polymers for Use in High Temperatures

by

Therald Moeller and Antonio Vandi
University of Illinois, Urbana, Illinois

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I. Abstract

Reactions of bis-trichlorophosphazosulfone and of the dialkylamides of trichlorophosphazosulfuric acid with organo-metallic compounds have been completed during this synthesis period. Phenylmagnesium bromide and p-tolylmagnesium bromide have been employed as typical Grignard reagents and have been caused to react with the corresponding chlorides, leading to eleven new completely substituted compounds never reported before in the literature. According to the yields in which these compounds were obtained, substitutions appear to be more facile in introducing a phenyl radical than in the case of p-tolyl group.

The compounds have been characterized in terms of analysis, melting point, and infra-red spectrum. Their thermal stabilities at 200°C. and 250°C. have been evaluated also.

II. Thermal Characteristics of Bis-triarylphosphazosulfones and of N,N-Dialkyl-triarylphosphazosulfones

A. Results and Discussion

The thermal stabilities of the compounds synthesized during this period have been evaluated according to the method described in an early report (1). Thermal stability measurements were carried out by heating in an inert atmosphere for 10 hours at 200°C. 0.2-0.5 g. of the sample and determining the loss of weight after that period. The compounds which gave a loss of weight less than 0.3 per cent at that temperature, underwent further heating at 250°C., for the same length of time, and their loss of weight was redetermined. Experimental data, in terms of uncorrected temperatures and of increasing weight loss, are given in Table I.

Inasmuch as in our early studies on N-substituted sulfamides, promising results in respect to thermal stability could not be achieved, we have attempted the synthesis of a new category of compounds in which the nitrogen atoms of sulfamide and of its N-substituted derivatives are linked to phosphorus atoms and the study of their behavior towards heat. Furthermore, typical aryl radicals such as phenyl and p-tolyl groups, have been placed on the phosphorus atoms by reaction with Grignard reagents.

Data from Table I, show clearly that at least at 200°C. almost all the compounds can be considered as stable thermally since the loss of weight is less than or of the order of 0.3 percent. Raising the temperature, however, gives remarkably increasing weight losses, which means that substantial thermal decomposition takes place rapidly at 250°C.

III. Reactions of Bis-trichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric acid with Grignard Reagents

Study of the previously reported (2) complete replacement of the chlorine atoms in bis-trichlorophosphazosulfone and in the dialkylamides of trichlorophosphazosulfuric acid by Grignard reagents has been continued during this synthesis period. Besides phenylmagnesium bromide, p-tolylmagnesium bromide has been caused to react with the starting chlorides, leading to the corresponding arylated derivatives. According to our data, these nucleophilic substitutions are not at all facile. In order to obtain completely substituted derivatives refluxing up to 12 hours was required and even so the yields of the pure compounds were rather slow. In any instance, yields were higher with phenylmagnesium bromide than when p-tolylmagnesium bromide was employed.

The general reaction is illustrated by the following equation:

$$\begin{matrix}R\\R'\end{matrix}\!\!>NSO_2N{=}PCl_3 + 3ArMgBr \xrightarrow{\text{ether}} \begin{matrix}R\\R'\end{matrix}\!\!>NSO_2N{=}P(Ar)_3 + 3MgClBr$$

Where: R=R', may be CH_3, C_2H_5, C_3H_7, C_4H_9, and C_3H_8O (from morpholine) and Ar = C_6H_5 , p-$CH_3C_6H_4$.

The following compounds were prepared by this type of reaction:

I. Bis-triphenylphosphazosulfone
II. N,N-dimethyl-triphenylphosphazosulfone
III. N,N-diethyl-triphenylphosphazosulfone
IV. N,N-dipropyl-triphenylphosphazosulfone
V. N,N-dibutyl-triphenylphosphazosulfone
VI. N,N-morpholine-triphenylphosphazosulfone
VII. Bis-tri-p-tolylphosphazosulfone
VIII. N,N-dimethyl-tri-p-tolylphosphazosulfone
IX. N,N-diethyl-tri-p-tolylphosphazosulfone
X. N,N-dipropyl-tri-p-tolylphosphazosulfone
XI. N,N-dibutyl-tri-p-tolylphosphazosulfone
XII. N,N-morpholine-tri-p-tolylphosphazosulfone

B. Physical Properties

All the compounds here synthesized are white, crystalline, non-hygroscopic materials with reasonably high melting points. They are insoluble in cold and boiling water; insoluble in ether, petroleum ether, and n-heptane; fairly soluble in hot ethanol, carbon tetrachloride, and benzene; soluble in acetone and chloroform. Their purification is best effected by several recrystallizations from ethanol.

The infra-red spectra of chloroform solution and KBr pellets show an intense absorption in the 1140-1145 $cm.^{-1}$ region, which is associated with the symmetrical S-O vibration in the $-SO_2-$ grouping. The asymmetrical vibration, which usually occurs in the 1320-1340 $cm.^{-1}$ region disappears, while a new strong absorption band in the 1270-1300 $cm.^{-1}$ is constantly present. We attribute this vibration rather than to the pure $-N{=}P\lessdot$ stretch due to the

$[-\overset{O}{\underset{O}{S}}-N{=}P\lessdot]$ group. The reason for this assumption lies in the fact that

in all our spectra the peaks in the 1300 $cm.^{-1}$ region are not well resolved and present a shoulder. This would indicate that there might be a coupling between the $-SO_2-$ asymmetric stretch and the pure $-N{=}P\lessdot$ vibration, thus giving rise to the strong vibration in the 1300 $cm.^{-1}$ region.

C. Experimental

1. p-tolylmagnesium Bromide. Magnesium turnings (3.648 g., 0.15 mole), previously treated with a small crystal of iodine, were placed in a well-dried, 500-ml., 3-necked flask, equipped with a reflux condenser, with a drying tube on top, and a dropping funnel. Some 70 ml. of dry ether was placed in the flask. While the mixture was stirred magnetically, p-bromotoluene (25.65 g., 0.15 mole) in 150 ml. of ether was added dropwise to the magnesium. After a short heating to overcome the period of induction, the reaction starts and proceeds smoothly until all the magnesium is dissolved.

2. N,N-diethyl-triphenylphosphazosulfone. Fourteen and thirty-seven hundreths grams (0.05 mole) of N,N-diethyltrichlorophosphazosulfone in 50 ml. of ether, was slowly added to an ether solution of phenyl-magnesium bromide (27.19 g., 0.15 mole) at room temperature over a period of 2 hours. After the addition was completed, the mixture was gently refluxed for 12 hours. The reaction mixture was then slowly poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which was separated was extracted with benzene and the organic layer dried over calcium chloride. The excess of benzene was driven off under vacuum and the solid, which was obtained, purified by recrystallization from ethanol. The pure compound was a white, crystalline solid, melting at 127°C. Yield: 13.60 g. (66.0% of the theoretical).

Anal. Calcd. for $C_{22}H_{25}N_2O_2PS$: C, 64.07; H, 6.11; N, 6.79.
Found : C, 63.90; H, 6.17; N, 6.89.

3. N,N-dimethyl-triphenylphosphazosulfone. Twelve and ninety-seven hundreths grams (0.05 mole) of N,N-dimethyltrichlorophosphazosulfone in 150 ml. of benzene was slowly added, with stirring, to an ether solution of phenylmagnesium bromide (27.19 g., 0.15 mole) at room temperature. After the addition of the chloride, gentle refluxing was held for an additional 12 hours. The mixture was then decomposed by slowly pouring it into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which separated was extracted with benzene and the organic layer dried over calcium chloride the excess of benzene was distilled under reduced pressure and the solid which was left purified by recrystallization from ethanol. The pure compound was a white, crystalline material, which melted at 156-158°C. Yield: 7.0 g. (36.8% of theory).

Anal. Calcd. for $C_{20}H_{21}N_2O_2PS$: C, 62.49; H, 5.50; N, 7.28
Found : C, 62.52; H, 5.33; N, 7.18

4. N,N-dibutyl-triphenylphosphazosulfone. Eight and six-tenths grams (0.025 mole) of N,N-dibutyltrichlorophosphazosulfone in 50 ml. of ether was slowly added to an ether solution of phenylmagnesium bromide (13.59 g., 0.075 mole) at room temperature. After the addition was completed, the mixture was stirred and gently refluxed for 12 hours. The reaction mixture was then poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which was separated was extracted with benzene and the organic layer dried over calcium chloride. Upon distillation of the excess of benzene, a solid material was left. It was purified by recrystallization from ethanol, yielding the pure compound which melted at 149°C. Yield: 6.0 g (51.3% of the theoretical).

Anal. Calcd. for $C_{26}H_{33}N_2O_2PS$: C, 66.65; H, 7.10; N, 5.98
Found: C, 66.76; H, 7.10; N, 6.21

5. N,N-dibutyl-tri-p-tolylphosphazosulfone. Eight and six-tenths grams (0.025 mole) of N,N-dibutyltrichlorophosphazosulfone in 50 ml. of ether was added at small portions to a well-stirred solution of p-tolylmagnesium bromide (14.64 g., 0.075 mole) at room temperature. After the addition of the chloride, the mixture was stirred and refluxed for 12 hours. The reaction mixture was then decomposed by pouring it into a flask containing 200 g. of crushed ice and 50 ml. of 12 M hydrogen chloride. The solid which separated, was extracted with benzene and the organic layer dried over calcium chloride. After the removal of the excess of solvent, the solid material which was left was purified by recrystallization from ethanol. The pure

compound was a white, crystalline solid, that melted at 155°C. Yield: 6.0 g. (48.0% of theory).

Anal. Calcd. for $C_{28}H_{39}N_2O_2PS$: C, 68.21; H, 7.70; N, 5.48
Found : C, 68.34; H, 7.59; N, 5.55

6. N,N-dimethyl-tri-p-tolylphosphazosulfone. Twelve and ninety-seven hundreths grams (0.05 mole) of N,N-dimethyltrichlorophosphazosulfone in 150 ml. of benzene was slowly added to an ether solution of p-tolyl magnesium bromide (29.29 g., 0.15 mole) at room temperature with stirring. After the addition was completed, the reaction mixture was gently refluxed for 12 hours. The mixture was then slowly poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M hydrochloric acid. The solid which separated was extracted with benzene and the benzene layer dried over calcium chloride. The excess of solvent was removed under reduced pressure, and the crude product which was left was purified by recrystallization from ethanol. The pure compound was a white, crystalline material which melted at 196°C. Yield: 6.45 g. (30.0% of the theoretical).

Anal. Calcd. for $C_{23}H_{27}N_2O_2PS$: C, 64.77; H, 6.38; N, 6.56
Found : C, 64.68; H, 6.43; N, 6.26

7. Bis-tri-p-tolylphosphazosulfone. Nine and sixteen-hundreths grams (0.025 mole) of bis-trichlorophosphazosulfone in 30 ml. of ether was slowly added to an ether solution of p-tolylmagnesium bromide (29.29 g., 0.15 mole) at room temperature over a period of 2 hours. After the addition was completed, gentle refluxing was continued for an additional 12 hours. The mixture was then cooled and slowly poured into a flask containing crushed ice and 50 ml. of 12 M poured into a flask containing crushed ice and 50 ml. of 12 M hydrochloric acid solution. A solid, insoluble in water, separated. It was extracted with benzene and the benzene layer dried over calcium chloride. After the removal of the solvent, the solid which was left was purified by several recrystallizations from ethanol. The pure compound melted at 226°C. Yield: 5.0 g. (29.4% of theory).

Anal. Calcd. for $C_{42}H_{42}N_2O_2P_2S$: C, 72.02; H, 6.04; N, 4.00
Found : C, 71.79; H, 6.10; N, 3.94

8. N,N-dipropyl-tri-p-tolylphosphazosulfone. Fifteen and seventy-eight hundreths grams (0.05 mole) of N,N-dipropyltrichlorophosphazosulfone in 50 ml. of ether were slowly added to an ether solution of p-tolylmagnesium bromide (29.29 g., 0.15 mole) at room temperature. The mixture was gently refluxed and stirred vigorously for 12 hours after the addition was completed. The crude compound was then obtained by pouring the reaction mixture into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which separated was extracted with benzene and the organic layer dried over calcium chloride. After the removal of the excess of benzene by distillation under vacuum, the solid was purified by recrystallization from ethanol. The pure compound was a white, crystalline material, melting at 175°C. Yield: 9.6 g. (40.0% of theory).

Anal. Calcd. for $C_{27}H_{35}N_2O_2PS$: C, 67.19; H, 7.31; N, 5.80
Found : C, 66.99; H, 7.30; N, 5.93

9. N,N-morpholine-tri-p-tolylphosphazosulfone. Seven and five-tenths grams (0.025 mole) of N,N-morpholinetrichlorophosphazosulfone in 80 ml. of benzene were added at small portions to an ether solution of p-tolylmagnesium bromide (14.64 g., 0.075 mole) at room temperature with wtirring. The mixture was then gently refluxed for 12 hours after the addition was completed. The reaction product was poured into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M. hydrochloric acid, from which a solid separated. It was extracted with benzene and the organic layer dried over calcium chloride. The solid which was left after removal of the solvent was purified by recrystallization from ethanol, and the pure compound was a white, crystalline material melting at 129°C. Yield: 2.3 g. (20.0% of theory)

Anal. Calcd. for $C_{25}H_{29}N_2O_3PS$: C, 64.09; H, 6.24; N, 5.98
Found : C, 64.36; H, 6.26; N, 5.91

D. Discussion

Reactions of bis-trichlorophosphazosulfone and of the dialkylamides of trichlorophosphazosulfuric acid with phenylmagnesium bromide and p-tolylmagnesium bromide have been shown to yield completely substituted products where all the chlorine atoms are replaced by corresponding aryl groups. However, the non-sharp melting points of the crude materials and the fact that they can be obtained in high purity only after several recrystallizations from ethanol lead us to believe that these nucleophilic substitutions are not facile and that partially substituted compounds are always obtained as by-products. This would account also of the low yields in which they are very often obtained.

IV. Outline of Future Work

It is proposed to devote our time to the synthesis of the trimer of sulfanuric chloride and consequently to accomplish some solvolytic processes with that interesting material as soon as it will become available in workable quantities. For this purpose, the synthesis of sulfanuric chloride will be attempted, either according to the Kirsanov procedure, i.e., by thermal decomposition of trichlorophosphazosulfonyl chloride, or by the Goehring procedure, which consists in the decomposition of a mixture of sulfuryl chloride and thionyl chloride with gaseous ammonia at low temperatures.

In addition, exchange reactions of bis-trichlorophosphazosulfone by metathesis with sodium fluoride in acetonitrile or nitrobenzene as solvents will be under study. In all instances, the underlying obejctive will be the improvement of thermal stabilities in model compounds for polymer synthesis.

V. References

1. T. Moeller and A. Vandi: Quarterly Progress Report No. 2, Contract DA-11-022-2956, Nov. 30, 1959.

2. T. Moeller and A. Vandi: Quarterly Progress Report No. 8, Contract DA-11-022-2956, May 31, 1961.

Table I

Properties of Bis-triarylphosphazosulfones and N,N-dialkyl-triarylphosphazosulfones

Compound	Weight loss after 10 hrs. at 200°C.(%)	Weight loss after 10 hrs. at 250°C.(%)	M.p., °C.
Bis-tri-p-tolylphosphazosulfone	0	3.2	226
Bis-triphenylphosphazosulfone	0	12.1	240-244
N,N-dimethyl-triphenylphosphazosulfone	0.13	8.0	156-158
N,N-morpholine-triphenylphosphazosulfone	0.16	8.4	181-182
N,N-dipropyl-triphenylphosphazosulfone	0.18	1.8	178-179.5
N,N-dimethyl-tri-p-tolylphosphazosulfone	0.25	1.63	196
N,N-dibutyl-triphenylphosphazosulfone	0.31	-	149
N,N-dipropyl-tri-p-tolylphosphazosulfone	0.40	-	175
N,N-morpholine-tri-p-tolylphosphazosulfone	1.20	-	129
N,N-diethyl-triphenylphosphazosulfone	2.40	-	127
N,N-dibutyl-tri-p-tolylphosphazosulfone	2.50	-	155