(in most cases Methyl Cellosolve, mixtures of Methyl Cellosolve and ethanol, or acetic acid) gave N-acylacetylaminobenzenesulfonates with a purity of 97–99.5%. Small amounts (1 to 3%) of sodium fluoride or acetate which were found to be present by titration with perchloric acid in acetic acid, could only be removed by repeated recrystallizations.

Acknowledgment.—We wish to thank Prof. Dr. A. Van Dormael, Director of the Chemical Research Department, for his kind interest in this work. We are indebted to Dr. L. Moelants, Head of the Analytical Department, for the analyses.

The Chemistry of Bi(phosphine sulfides). II. A Convenient Method for Preparing Phosphine Oxides and Phosphine Sulfides Containing Different Groups[1a]

H. JAMES HARWOOD[1b] AND KENNETH A. POLLART

The Central Research Department, Monsanto Chemical Company, St. Louis 66, Missouri

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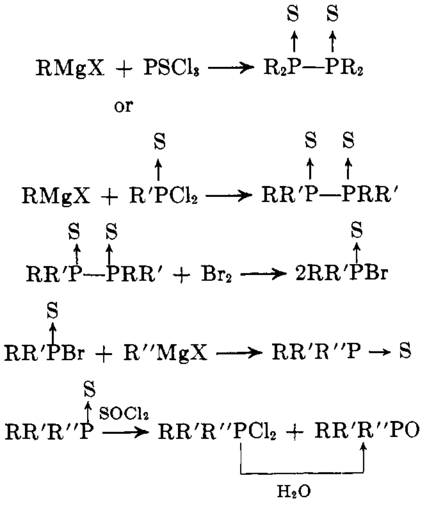
Dialkyl- and alkylarylthiophosphinic halides react with Grignard reagents to form phosphine sulfides in good yield, whereas thiophosphoryl chloride and alkyl- or arylthiophosphonic dichlorides are known to react with Grignard reagents to yield bi(phosphine sulfides). On the basis of these findings, a stepwise procedure for preparing phosphine sulfides and oxides has been developed.

Although a considerable number of symmetrical phosphines, phosphine oxides, and phosphine sulfides are described in the chemical literature, only a few of such compounds containing different groups have been reported.[2] Until recently, the preparations of unsymmetrically substituted phosphines, phosphine oxides, etc., were based, in one or more of the reactions utilized, upon reactions of halophosphines, phosphonic dihalides, or phosphinic halides with organometallic compounds. Since the degree of substitution realized in these reactions could not be selectively controlled, mixtures resulted, and intermediates necessary for preparing the unsymmetrical compounds were not obtained in high over-all yields.

In recent years, improved routes to unsymmetrical phosphines and their derivatives have been developed. The stepwise alkylation of phosphines has been refined considerably[3–5] and a number of new techniques have been developed for the synthesis of unsymmetrical phosphinic acids and their derivatives.[6–8] Unsymmetrical phosphinic halides obtained *via* these recently developed procedures may be converted to unsymmetrically substituted phosphine oxides by reaction with Grignard reagents or metal alkyls, although such reactions are sometimes difficult[2b] and may require forcing conditions.

The cleanest routes to unsymmetrically substituted phosphines, etc., however, seem to be those in which tertiary phosphines containing benzyl,[9] β-cyanoethyl,[10] or hydroxymethyl groups[11] react with alkylating agents. The quarternary phosphonium salts, thus obtained in high yield, are then degraded to new tertiary phosphines. Repetition of the alkylation–degradation sequence provides a convenient method for preparing unsymmetrically substituted phosphines. Since most of the phosphine sulfides prepared in the past have been obtained by the addition of sulfur to phosphines, the alkylation–degradation reactions can be utilized in the synthesis of unsymmetrically substituted phosphine sulfides as well. The alkylation–degradation procedure cannot be used to place aryl substituents on phosphorus, however, and aryl phosphines must be available as starting materials if unsymmetrical arylphosphines or aryl substituted phosphine sulfides are to be prepared.

This paper describes a route to unsymmetrical phosphine derivatives which seems to complement the synthetic methods discussed. For example, this route may be used to prepare phosphine derivatives which contain one or two aromatic substituents. In special cases it may perhaps also be applicable to the preparation of unsymmetrically substituted triarylphosphine derivatives. Our synthesis is based on the following series of reactions.



$$RMgX + PSCl_3 \longrightarrow R_2\overset{\overset{S}{\uparrow}}{P}\text{—}\overset{\overset{S}{\uparrow}}{P}R_2 \qquad (1)$$

or

$$RMgX + R'\overset{\overset{S}{\uparrow}}{P}Cl_2 \longrightarrow RR'\overset{\overset{S}{\uparrow}}{P}\text{—}\overset{\overset{S}{\uparrow}}{P}RR' \qquad (2)$$

$$RR'\overset{\overset{S}{\uparrow}}{P}\text{—}\overset{\overset{S}{\uparrow}}{P}RR' + Br_2 \longrightarrow 2RR'\overset{\overset{S}{\uparrow}}{P}Br \qquad (3)$$

$$RR'\overset{\overset{S}{\uparrow}}{P}Br + R''MgX \longrightarrow RR'R''P \rightarrow S \qquad (4)$$

$$RR'R''\overset{\overset{S}{\uparrow}}{P} \xrightarrow{SOCl_2} \underbrace{RR'R''PCl_2 + RR'R''PO}_{H_2O} \qquad (5)$$

Bi(phosphine sulfides), the key intermediates in the synthesis, are usually prepared in good yield by treating thiophosphoryl chloride (eq. 1) or phosphinothioic

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[1] (a) Presented in part before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959; (b) The University of Akron, Akron 4, Ohio.

[2] (a) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950; (b) for a recent review of the synthesis of phosphine oxides, etc., see K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

[3] F. Pass, E. Steiniger, and H. Schindlbauer, *Monatsh. Chem.*, **90**, 792 (1959).

[4] M. M. Rauhut, H. A. Curries, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5138 (1951).

[5] K. Issleib and D. Jacob, *Chem. Ber.*, **94**, 107 (1961), and other papers in this series.

[6] T. P. Dawson and K. C. Kennard, *J. Org. Chem.*, **22**, 1671 (1957).

[7] P. C. Crofts and I. S. Fox, *J. Chem. Soc.*, 2995 (1958).

[8] D. C. Morrison, *J. Am. Chem. Soc.*, **73**, 4820 (1950).

[9] (a) W. J. Bailey and S. A. Buckler, *ibid.*, **79**, 3567 (1957); (b) W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, **25**, 1996 (1960).

[10] M. Grayson, P. T. Keough, and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959).

[11] H. Hellman and O. Schumacher, *Angew. Chem.*, **72**, 211 (1960).

dihalides (eq. 2) with Grignard reagents. The bi(phosphine sulfides) react quantitatively with bromine[12] or chlorine[13] to yield phosphinothioic halides (eq. 3). The phosphinothioic halides are subsequently converted to phosphine sulfides in high yield by reaction with Grignard reagents (eq. 4).

The depicted synthetic sequence was utilized in this work to prepare dimethylphenylphosphine sulfide, dimethylphenylphosphine oxide, trimethylphosphine sulfide, ethylmethylphenylphosphine sulfide, and ethylmethylphenylphosphine oxide. In the synthesis of dimethylphenylphosphine sulfide, tetramethyl bi(phosphine sulfide), obtained in nearly quantitative yield from the reaction of methylmagnesium bromide with thiophosphoryl chloride, was treated with bromine to yield dimethylthiophosphinic bromide in 95% yield. The bromide then reacted with phenylmagnesium bromide to form dimethylphenylphosphine sulfide in 88% yield. Trimethylphosphine sulfide was similarly prepared from dimethylthiophosphinic bromide or from the corresponding chloride in 90 and 79% yields, respectively.

In the preparation of ethylmethylphenylphosphine sulfide, phenylthiophosphonic dichloride reacted with ethylmagnesium bromide to yield a mixture[13] of the racemic and *meso* forms of diethyldiphenyl bi(phosphine sulfide). The bi(phosphine sulfide) was then chlorinated to give ethylphenylphosphinothioic chloride in 90% yield. The chloride then reacted with excess methylmagnesium bromide to form ethylmethylphenylphosphine sulfide in 84% yield. On an over-all basis, the yield of this product was 31%, starting from phenylphosphonothioic dichloride. The poor step in this sequence was the reaction in which the bi(phosphine sulfide) was prepared (41% yield). However, it was found that the acidic byproducts of this reaction could also be utilized for the preparation of ethylphenylphosphinothioic chloride. The over-all yield of ethylmethylphenylphosphine sulfide ultimately obtainable from this series of reactions is therefore considerably greater than 31%.

Conversion of the phosphine sulfides into the corresponding oxides was accomplished by treatment with thionyl chloride followed by hydrolysis (eq. 5). The phosphine oxides thus formed, were obtained in essentially quantitative yields. When the hydrolysis step was omitted, mixtures of phosphine oxide and phosphine dichloride were obtained. The relative quantities of these materials formed depended primarily upon the amount of thionyl chloride used and on the reaction temperature. For example, refluxing dimethylphenylphosphine sulfide with excess thionyl chloride yielded dimethylphenylphosphine dichloride in 94% yield. This product was subsequently converted to the corresponding oxide in high yield. Triphenylphosphine sulfide, when treated with a stoichiometric amount of thionyl chloride at room temperature, yielded a mixture of triphenylphosphine oxide (69%) and triphenylphosphine dichloride (24%). Triphenylphosphine oxide was shown in this work to react with thionyl chloride at 80° to yield triphenylphosphine dichloride in 93% yield. It thus appears that the phosphine oxides are intermediates in the formation of trisubstituted phosphine dichlorides.[14]

The synthesis outlined in this paper rests critically on the unusual circumstance that phosphinothioic halides react with Grignard reagents to yield substitution products, whereas coupling products, bi(phosphine sulfides), often result when phosphinothioic dihalides or thiophosphoryl chloride are reacted with Grignard reagents. The reaction of phosphinothioic halides with Grignard reagents occurs smoothly and in excellent yield.[15] There is no reason, at this point, to believe that this reaction will not be completely general. In contrast, the reactions of Grignard reagents with phosphonothioic or phosphoryl halides may take several paths. Thus, low molecular weight, sterically unhindered Grignard reagents react with thiophosphoryl chloride or phosphonothioic dihalides to yield bi(phosphine sulfides), whereas high molecular weight (*e.g.*, cetyl[16]) or sterically hindered (*e.g.*, cyclohexyl[17]) aliphatic Grignard reagents react with thiophosphoryl halides to yield phosphine sulfides and other products. Obviously, only those reactions which lead to bi(phosphine sulfides) in reasonable yield can be employed in the synthetic scheme outlined in this paper.

The reactions of aromatic Grignard reagents with thiophosphoryl halides have not been studied appreciably, but it has been established that these reactions may also proceed in several ways. Thiophosphoryl chloride has been reported to yield triarylphosphine sulfides when treated with aromatic Grignard reagents. However, Maier[18] observed that a bi(phosphine sulfide) formed when phenylmagnesium bromide reacted with methylphosphonothioic dibromide. This reaction introduces the possibility that our synthesis may be applicable to the preparation of trisubstituted phosphine derivatives which contain two or three aromatic residues. Should aromatic Grignard reagents yield bi(phosphine sulfides) when treated with arylphosphonothioic dihalides, the stepwise synthesis of unsymmetrical triarylphosphine derivatives by our procedure should be possible. The over-all applicability of the synthetic approach outlined herein cannot be fully accessed until a better understanding of the scope and mechanism of bi(phosphine sulfide) formation is achieved.

Finally, the fact that coupling products are not found in the reactions of phosphinothioic halides with Grig-

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[12] W. Kuchen and H. Buchwald, *Angew. Chem.*, **71**, 162 (1959).

[13] K. A. Pollart and H. J. Harwood, *J. Org. Chem.*, **27**, 4444 (1962).

[14] One of the referees, quite reasonably, questioned the validity of this statement since we were comparing the reactions of thionyl chloride with triphenylphosphine oxide at 80° and with triphenylphosphine sulfide at 25°. Thus we reinvestigated the reaction of thionyl chloride with triphenylphosphine oxide. We found that a 1:1 mole ratio of reactants gave a 17% yield of the triphenylphosphine dichloride after one hour at 25°. When excess thionyl chloride is used (2:1 mole ratio) the dichloride is obtained in 31% yield after one hour at 25° and in 51% yield after eight hours at 25°.

Attempts to treat SCl_2 and S_2Cl_2, the most likely sulfur- and halogen-containing by-products from the thionyl chloride–phosphine sulfide reaction, with triphenylphosphine oxide resulted in a maximum yield of triphenylphosphine dichloride of 7% even under reflux conditions. These results tend to substantiate our original conclusion that the phosphine dichloride is formed by reaction of the thionyl chloride with the phosphine oxide. However, we cannot rule out the possibility that some dichloride is being formed by direct reaction of thionyl chloride with phosphine sulfide.

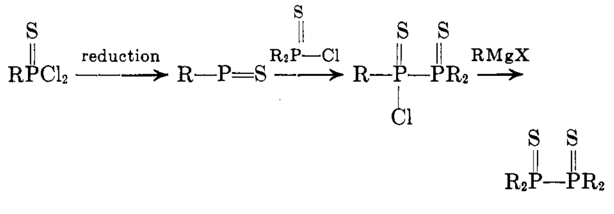
[15] It is worthwhile to note that the corresponding reactions of phosphinic halides with Grignard reagents are not always entirely satisfactory.

[16] W. Kuchen, H. Buchwald, K. Strolenberg, and J. Metten, *Ann.*, **652**, 28 (1962).

[17] H. Niehergall and B. Lagenfeld, *Chem. Ber.*, **95**, 64 (1962).

[18] L. Maier, *ibid.*, **94**, 3043 (1961).

nard reagents is of theoretical as well as of synthetic importance. The requirement that at least two halogen atoms be attached to phosphorus if bi(phosphine sulfide) formation is to take place is consistent either with a process where phosphorus becomes reduced prior to the coupling step or with a process where the phosphorus atom must have a certain threshold electronegativity before the coupling reaction can occur. A mechanism involving metal–halogen interchange could fall into this latter category. While the experimental results of this paper must be accommodated by any mechanism which attempts to explain bi(phosphine sulfide) formation, little more can be said at present about the nature of this process.



Experimental

Dimethylphosphinothioic Bromide.—A solution of bromine (0.35 mole) in 400 ml. of carbon tetrachloride was added dropwise to a well stirred mixture of tetramethyl bi(phosphine sulfide)[13] (0.35 mole), and 300 ml. of carbon tetrachloride while the temperature was maintained below 0°. After stirring at room temperature for a few hours, the mixture was distilled to yield 0.66 mole (94% yield) of the desired product, b.p. 87–88° (14 mm.). The compound solidified on standing.

Anal. Calcd. for C_2H_6PSBr (173.0): C, 13.88; H, 3.50; P, 17.90; Br, 46.19. Found: C, 13.60; H, 3.79; P, 18.11; Br, 46.54.

Trimethylphosphine Sulfide.—Dimethylphosphinothioic bromide (0.058 mole) in 15 ml. of ether was added dropwise to 0.1 mole of 3 *M* methylmagnesium bromide solution. The reaction mixture was maintained below 10° during the addition and was then allowed to warm to room temperature and stirred overnight. The reaction mixture was hydrolyzed by pouring into a mixture of ice and hydrochloric acid. Part of the product was obtained by evaporation of the ether layer, but most of it was isolated by ether extraction of the aqueous layer. The product, trimethylphosphine sulfide, was recrystallized from cyclohexane, m.p. 155–156° (5.6 g., 90% yield). Its infrared spectra and melting point were identical with the literature.[19]

The same reaction was repeated using dimethylphosphinothioic chloride[11] (0.076 mole) and methylmagnesium bromide (0.15 mole). This procedure gave a 79% yield of trimethylphosphine sulfide, m.p. 155–156°.

Dimethylphenylphosphine Sulfide.—A solution of dimethylphosphinothioic bromide, (16.4 g., 0.095 mole) in 75 ml. of ether was added during 15 min. to a solution of phenylmagnesium bromide (0.10 mole) in 110 ml. of anhydrous ether at 0–10°.

The mixture was allowed to stand overnight and then poured into ice-cold 10% sulfuric acid. The light green ether solution was separated, and the sulfuric acid solution was extracted with fresh ether. The combined ether extracts were washed with water, dried over sodium sulfate, and concentrated to a light yellow oil. On cooling and scratching, the oil solidified, m.p. 44–46.9°. It was recrystallized from hexane–benzene to form white needles, m.p. 47.0–47.7° (14.2 g., 88% yield), which were shown by analysis to be dimethylphenylphosphine sulfide.

Anal. Calcd. for $C_8H_{11}PS$ (170.2): C, 56.45; H, 6.52; S, 18.84. Found: C, 56.45; H, 6.55; S, 19.12.

Ethylmethylphenylphosphine Sulfide.—Methylmagnesium bromide (0.085 mole) in 75 ml. of anhydrous ether was added dropwise to a stirred solution of ethylphenylphosphinothioic chloride[13] (15 g., 0.071 mole) in 75 ml. of anhydrous ether while the temperature was maintained below 15°. After the addition was complete, the mixture was stirred at 25° for 0.5 hr. and then refluxed 1 hr. The mixture was hydrolyzed by the dropwise addition of 15 ml. of saturated ammonium chloride solution. The ether layer was decanted and dried over anhydrous magnesium sulfate. Distillation gave ethylmethylphenylphosphine sulfide (11 g., 84% yield), b.p. 103–105° (0.04 mm.), m.p. 33–34°.

Anal. Calcd. for $C_9H_{13}PS$ (184.2): C, 58.67; H, 7.11; S, 17.41. Found: C, 58.67; H, 6.99; S, 17.27.

Reaction of Dimethylphenylphosphine Sulfide with Thionyl Chloride.—A solution of dimethylphenylphosphine sulfide (6.33 g., 0.037 mole) in 35 ml. benzene was chilled in an ice bath. Thionyl chloride (10 ml., 0.140 mole) was then slowly added with stirring. A mild exothermic reaction was noted, the mixture became turbid, and a yellow precipitate formed. The reaction mixture was refluxed for 1 hr. and filtered under nitrogen. The light yellow precipitate proved to be dimethylphenylphosphine dichloride contaminated with a small amount of sulfur. Sulfur was separated by dissolving the product in chloroform and filtering. Concentration of the chloroform yielded the dimethylphenylphosphine dichloride as large colorless cubic crystals, 7.37 g. (94% yield), m.p. 173.9–176.0°. The product was hygroscopic and strongly acidic.

A sample of the dichloride was dissolved in water and titrated with standard alkali. The equivalent weight thus determined was 111.5 (calcd. for $C_8H_{11}PCl_2$, 105).

Sulfur recovered from the chloroform extraction and from the reaction mixture filtrate amounted to 0.73 g. (0.023 mole).

A sample of dimethylphenylphosphine dichloride was hydrolyzed in distilled water. The hydrolysis solution was evaporated to dryness, redissolved in distilled water, and then passed through a column of Amberlite IR-410 (hydroxide form) to remove the residual traces of acid. Evaporation of the water solution gave dimethylphenylphosphine oxide, m.p. 113–116°, as cubic crystals. Melting points of 100°, 107–109°, and 121–122° have been previously reported for this material.[20–22] The considerable range of these values is probably due to the hygroscopic nature of the compound.

Reaction of Ethylmethylphenylphosphine Sulfide with Thionyl Chloride.—Thionyl chloride (0.033 mole) in 30 ml. of benzene was added dropwise to a stirred solution of ethylmethylphenylphosphine sulfide (0.03 mole) in 70 ml. of benzene, while the temperature was kept below 30°. A large quantity of yellow solid (presumably sulfur) rapidly separated. The mixture was maintained at room temperature for 2 hr. and was then refluxed for 15 min. The mixture was then filtered through glass wool and concentrated, using a rotary evaporator to remove excess thionyl chloride or any other low boiling material. The semisolid residue was redissolved in 50 ml. of benzene, and 5 ml. water was added. After this mixture was refluxed for 1 hr., the water layer was removed by azeotropic distillation. Distillation of the residue gave ethylmethylphenylphosphine oxide (4.1 g., 81% yield), b.p. 102–104° (0.07 mm.), m.p 55–56° (very hygroscopic); lit.[23] m.p. 50°.

Anal. Calcd. for $C_9H_{13}PO$ (168.2): C, 64.28; H, 7.79; P, 18.42. Found: C, 64.38; H, 7.64; P, 18.32.

Reaction of Triphenylphosphine Sulfide with Thionyl Chloride.—Thionyl chloride (4.1 g., 0.034 mole) was slowly added to a stirred solution of triphenylphosphine sulfide (10 g., 0.034 mole) in 100 ml. of benzene at room temperature. The solution slowly turned yellow, and a small amount of a heavy oil separated, but there was no temperature rise. After stirring for 1 hr. at room temperature, the insoluble oil was separated and the clear yellow solution evaporated under reduced pressure with a minimum of heat. The resulting light yellow solid was washed with hot water (this wash water was found to contain only a very slight trace of acid) and recrystallized from dilute ethanol to give 6.5 g. (69% yield) of triphenylphosphine oxide, m.p. 158°; m.m.p. 158° with an authentic sample.

The insoluble oil, which was separated, was boiled with distilled water for 3 min. After cooling, the precipitate was filtered. Titration of the filtrate showed that it contained 0.018 moles of HCl. Recrystallization of the precipitate (from dilute ethanol)

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(19) F. N. Hooge and P. J. Christen, *Rec. trav. chim.*, **77**, 911 (1958).

(20) J. Meisenheimer, J. Casper, M. Horning, W. Lanter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

(21) R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).

(22) H. Hoffmann and R. Grunewald, *ibid.*, **94**, 186 (1961).

(23) J. Meisenheimer and L. Lichtenstadt, *ibid.*, **44**, 356 (1911).

gave 2.4 g. (0.0085 mole, 25% yield) of triphenylphosphine oxide, m.p. 157–158°. Thus, the insoluble oil was triphenylphosphine dichloride.

The total yield of triphenylphosphine oxide was 94%.

Reaction of Triphenylphosphine Oxide with Thionyl Chloride.—Thionyl chloride (0.07 mole) was added dropwise to a stirred solution of triphenylphosphine oxide (0.036 mole). The mixture was heated at reflux for 1 hr. As the mixture reached its boiling point, a rapid evolution of gas ensued, lasting about 0.5 hr. The reaction mixture, which had separated into two layers, was vacuum stripped at 120° (0.1 mm.). The residual oil was washed with four 50-ml. portions of benzene, two 50-ml. portions of ether, hydrolyzed with hot water, and titrated with standard base (0.067 mole to phenolphthalein end point). On the basis of this result, it was concluded that the oil contained 0.0335 mole (93% yield) of triphenylphosphine dichloride.

The Cycloaddition of Potassium Diazomethanedisulfonate to Activated Olefins

A. P. KOTTENHAHN

Contribution No. 130 from the Elastomer Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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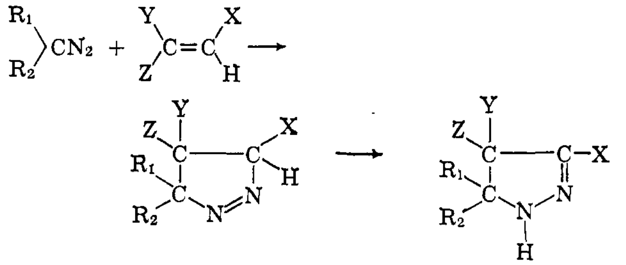
Potassium diazomethanedisulfonate in aqueous solution reacts with a variety of activated olefins to form 1:1 addition products for which the structure of disulfonated pyrazoline derivatives is proposed. Treatment with acid or base converts these products into monosulfonated pyrazole derivatives, which are readily N-alkylated.

Potassium diazomethanedisulfonate, $(KO_3S)_2CN_2$, was first prepared in 1895 by von Pechmann[1] who also studied some decomposition and addition reactions of this unusually stable diazo compound.[1,2] After von Pechmann's early work the compound apparently received little attention, since, aside from occasional mention in review articles,[3] only a few papers[4] appeared describing some of its reactions and physical properties. This is in striking contrast to other diazoalkanes which have been under continued extensive study ever since their discovery.

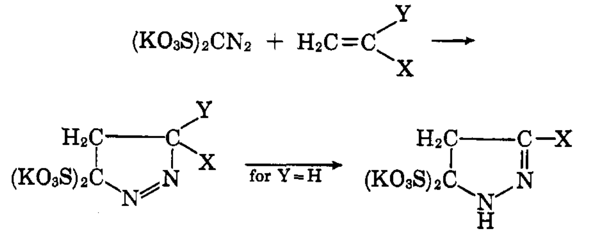
The addition of diazoalkanes to olefins with formation of pyrazolines is well known in the literature.[5] The reaction first yields Δ^1-pyrazolines, which readily rearrange to Δ^2-pyrazolines if a hydrogen substituent is present in the 3-position.



We have found that potassium diazomethanedisulfonate reacts readily with a variety of activated olefins to give disulfonated pyrazoline derivatives in a manner entirely analogous to other diazoalkanes such as diazomethane or diazoacetates. Because of the insolubility of potassium diazomethanedisulfonate in organic solvents, these reactions are most conveniently carried out in aqueous solution and, therefore, the olefinic reaction partner should have at least a moderate solubility in water. This requirement somewhat limits the applicability of this synthetic route. The solubility of the olefins and thereby the ease of reaction can be improved to some extent, however, by the addition of small quantities of methanol or other mutual solvents to the aqueous solution of the diazo compound.

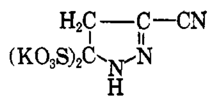
When activated olefins such as acrylonitrile, methacrylonitrile, methyl vinyl ketone, or ethyl acrylate, are added to an aqueous solution of potassium diazomethanedisulfonate, an exothermic reaction occurs and the yellow color of the diazo compound disappears more or less rapidly without evolution of nitrogen.

The reaction products can be precipitated with an excess of methanol and recrystallized from water. The elemental analyses of these products correspond to those of 1:1 adducts of potassium diazomethanedisulfonate and the respective olefins. These products are formulated as disulfonated pyrazolines in analogy with the structures of the adducts of such olefins with other diazoalkanes.



The infrared spectra of these adducts show that the functional groups X are preserved during the addition reaction.

Support for the proposed cyclic structure of these compounds is obtained from a comparison of the infrared and ultraviolet spectra of the addition products from acrylonitrile and methacrylonitrile. The proposed structures for these two products are as follows.



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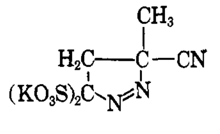

II

X

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(1) H. v. Pechmann and P. Mank, *Ber.*, **28**, 2374 (1895).

(2) H. v. Pechmann, *ibid.*, **29**, 2161 (1896).

(3) *E.g.*, R. Huisgen, *Angew. Chem.*, **55**, 439 (1955).

(4) H. J. Backer, *Rec. trav. chim.*, **48**, 619 (1929); A. Hantsch and J. Lifschitz, *Ber.*, **45**, 3023 (1912); F. Nesh, *J. Phys. Chem.*, **62**, 566 (1958); A. O. Rogers and M. A. Stevens (to Du Pont), U. S. Patent 2,825,747 (March 4, 1958).

(5) Summary in R. C. Elderfield, "Heterocyclic Chemistry," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957; H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.