

United States Patent

Poziomek et al.

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[54] CHEMICAL DETECTOR

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[51] Int. Cl.G01n 21/12, G01n 31/22

[58] Field of Search23/230; 252/408; 260/465 A, 260/465.2

[56] References Cited

UNITED STATES PATENTS

3,567,382 3/1971 Crabtree et al.23/230

3,405,160 10/1968 Eholzer et al.260/465 A

OTHER PUBLICATIONS

Hertler, W. R. et al., Journal of Organic Chemistry, Vol. 23, pp. 1221-2 (1958) (P.O.S.L.).

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[57] ABSTRACT

Electrophile compounds used as intermediates or pesticides can be detected by forming volatile derivatives of said compounds by treatment with N-alkylformamides producing isocyanide ions which contact an inert support medium, then treating said medium and its contents with a detector agent for said ions thus producing the color detector signal for said ions.

6 Claims, No Drawings

CHEMICAL DETECTOR

DEDICATORY CLAUSE

The invention described herein may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

SPECIFICATION

This invention is directed to the detection of electrophilic compounds which can be useful as intermediates in preparing other compounds or use in the agricultural field for detecting pesticides.

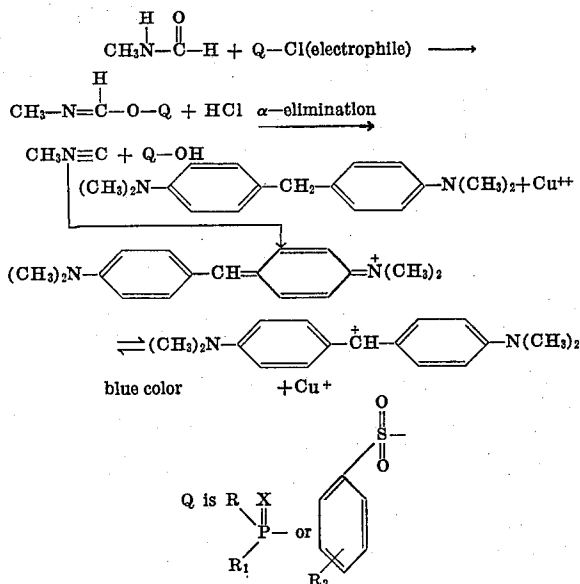
The object of this invention is the conversion of nonvolatile electrophiles to a more readily detectable volatile derivative of the electrophiles.

A general disadvantage of the former methods resides in that procedures require the determination to be carried out in liquid media, thus necessitating rather large masses of supporting equipment for solution detection and the manual handling of the sample containing the suspected compounds. The sample would have to be scraped or physically removed from the surface into a proper container for subsequent analysis in a solution procedure.

The advantage of our system lies in the minimum amount of handling the sample in view of the fact that the nonvolatile component is converted into a detectable volatile derivative. Thus the sample is no longer required to be removed from the surface for testing. The surface comprising the compound can be directly treated with the volatilizing solution forming a volatile component which is readily analyzed. Thus our system does not require physical handling of the sample, i.e., no scraping steps, and avoids any further contamination and can give greater weight to the validity of the results. In addition, inexperienced personnel can be employed since the usual chemical handling methods are no longer required.

A surface comprising about 0.1 to 1.0 μg . of an electrophile is treated with about 10–100 μl . of 1 normal N-loweralkylformamide and 100 μl . of a solvent, if desired, thus giving rise to the isocyanide ion in about 1 to 5 minutes. The isocyanide is adsorbed upon an inert support medium which is subsequently treated with a detector agent selected from the group consisting of benzidine and tetra base, producing a blue color detecting signal. If desired the inert support medium can be impregnated with the detector agent prior to exposure of the isocyanide ions, thus the support medium's blue color can be seen directly on the apparatus. The scheme, below, sets forth the general reaction of an electrophile with the α -elimination giving rise to the corresponding isocyanide which is subsequently tested.

GENERAL SCHEME



Wherein R or R₁ is an alkyl group, O-alkyl, S-alkyl or combinations thereof with the alkyl group containing from C₁ to C₅ carbon atoms.

X is oxygen or sulfur.

R₂ is hydrogen or an alkyl group from C₁ to C₃ carbon atoms.

The more specific electrophiles are benzene sulfonyl chloride, toluene sulfonyl chloride, 0,0-dimethyl phosphorochloridothionate and diethylphosphorochloridate.

10 An interesting result from our studies is that all electrophiles do not give isocyanides in the presence of N-alkylformamides. Hoy et al., J. Org. Chem., 33, 4050 (1968) disclose the reaction between N-alkylformamide and electrophilic chemicals producing the imide. For example, a reaction N-butylformamide and acetyl chloride leading to N-(butyl)-N-formylacetamide.

As a result of our new method phosphorus-containing insecticide 0,0-dimethyl phosphorochloridothionate is readily detected in the field.

20 Tetra base reagent comprises mixing solutions of equal volumes of (a) 80–120 mg. of p,p'-tetramethyldiaminodiphenylmethane and 400–600 mg. of salicylic acid in 100 ml. acetone and (b) 1.2–1.8 g. of cupric sulfate in 100 ml. of water. The preferred range is 100 mg. p,p'-tetramethyldiphenylmethane, 500 mg. salicylic acid and 1.5 g. cupric sulfate.

The benzidine reagent is mixed just prior to use, comprises equal volumes of (a) aqueous cupric acetate solution, 2.945–3.43 g./l. and (b) 675 ml. of benzidine acetate solution, saturated at room temperature, mixed with 525 ml. of water. The solutions (a) and (b) are best stored separately and in dark bottles. The preferred range for the aqueous cupric acetate is 2.86 g./l.

The use of silica gel tubes and the detecting apparatus for the isocyanide ion are well established in the open literature and may be employed according to the colorimetric method utilizing the described tetra base reagent or the benzidine reagent, Shepard, Anal. Chem., 19, 77, 1947; Williams et al., Anal. Chem., 34, 225, 1962; Crabtree et al., Talanta, 14, 857, 1967.

40 In general the silica gel tube is constructed as follows: A glass tube about 4 inches in length (3 mm. i.d.) containing an inert support medium, the untreated silica gel or treated silica gel, and then sealing off both ends of the glass tubing. The filling operations are those conventional in the art such as
45 tamping the silica gel into the tube. Prior to use, each end of the filled tube is broken off and inserted in the various sampling apparatus.

When an unimpregnated silica gel detector tube is used, the isocyanide vapor is collected on the silica gel, the detector tube is removed from the apparatus, and the silica gel is moistened with a drop of either the benzidine or tetra base reagent. The appearance of a blue color is a positive test for the isocyanide.

55 The apparatus and the reagents we employed for the isocyanide detection are disclosed in copending patent application Ser. No. 723,487, filed 23 Apr. 1968. Now U.S. Pat. No. 3,567,382.

A solvent may be used, if desired, such as quinoline to facilitate the process, however, care must be taken that ethanol or dioxane are not employed since they interfere or inhibit the detection system.

EXAMPLE 1

a. A sample in a test tube comprising at least 0.2 g. of 0,0-dimethyl phosphorochloridithionate, 100 μ l. of N-methylformamide or N-butylformamide and 100 μ l. quinoline. After about a 1-to-5-minute time lapse the detector tube and an aspirator bulb, was placed over the test tube so that the isocyanide ion could impregnate the silica gel in the detector tube. The latter tube is treated with about one drop (0.05 ml.) of the tetra base turning the silica gel blue indicating the presence of an isocyanide, thus demonstrating the original presence of an electrophile 0,0-dimethyl phosphorochloridithionate.

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Higher concentrations of the phosphorus compounds are more readily detected and give rise to the isocyanide ion in a short time.

b. The above procedure was repeated with the exception of utilizing the benzidine for the tetra base reagent.

EXAMPLE 2

The procedure according to Example 1 was followed with the exception of substituting other electrophiles of benzene sulfonyl chloride, toluene sulfonyl chloride or diethylphosphorochloridate for the phosphorochloridothionate giving rise to similar results, that is, a blue color with either the benzidine or tetra base reagent thus demonstrating the presence of electrophiles.

EXAMPLE 3

A surface comprising at least 0.2 μ g. of 0,0-dimethylphosphorochloridothionate was treated with about 100 μ l. of an amide of N-methylformamide or N-butylformamide and 100 μ l. quinoline. After about 1 to 5 minutes time lapse a detector tube was placed about the surface and the generated isocyanide was drawn into the detector tube. The latter tube was treated with a drop of either the benzidine reagent or tetra base reagent and the silica gel turned blue indicating the presence of an electrophile as in Example 1.

EXAMPLE 4

The procedure according to Example 3 was followed with the exception of substituting other electrophiles of benzene sulfonyl chloride, toluene sulfonyl chloride or diethylphosphorochloridate for the 0,0-dimethylphosphorochloridothionate giving rise to similar blue color detecting signal, thus indicating the presence of the electrophiles.

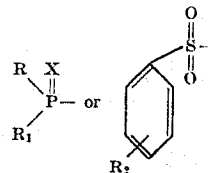
We claim:

1. The method of detecting electrophiles of the formula:

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Q-Cl

Wherein Q is



R or R₁ is an alkyl group, O-alkyl, S-alkyl or combinations thereof with the alkyl group containing from C₁ to C₃ carbon atoms.

X is oxygen or sulfur.

R₂ is hydrogen or an alkyl group from C₁ to C₃ carbon atoms. In a reaction mixture comprising adding N-alkylformamide to produce volatile isocyanide ions, contacting an inert support medium with said isocyanide ions, treating said support medium and its contents with a detector agent for said isocyanide ions, producing the detector signal for said isocyanide ions and thereby indicating the presence of electrophiles.

2. The method according to claim 1, wherein Q is



3. A method according to claim 1, wherein the N-alkylformamide is N-methylformamide or N-butylformamide.

4. The method according to claim 1, wherein the detector agent is a tetra base reagent comprising mixing solutions of equal volumes of (a) p,p'-tetramethyldiaminodiphenylmethane and salicylic acid in acetone and (b) cupric sulfate in water or benzidine reagent comprising mixing solutions of equal volumes of (a) aqueous cupric acetate and (b) aqueous solution containing saturation benzidine acetate solution.

5. A method according to claim 1, wherein the reaction mixture comprises a solvent.

6. A method according to claim 5, wherein the solvent is quinoline.

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