refluxed for 45 min. A solution of 17.3 g. (0.1 mole) of benzyl bromide in 60 ml. of tetrahydrofuran was then added dropwise. After refluxing for 1 hr., the reaction mass was added to 1000 ml. of water and the precipitate filtered off. Trituration with cold 95% ethanol gave 6.5 g. (34%) of white solid, m.p. 209–211°. Recrystallization from ethanol and water produced a crystalline solid, m.p. 220–221°, exhibiting an infrared spectrum identical to that of the material produced by the addition of benzyl chloride to a mixture of lithium diphenylphosphide and phenyllithium. Mixed melting point determinations were undepressed.

Preparation of (1,2-diphenylethyl)diphenylphosphine oxide from benzyldiphenylphosphine. Phenyllithium was prepared from 8.42 g. (0.06 mole) of bromobenzene and 0.84 g. (0.12 g.-atom) of lithium metal in 100 ml. of ether. A solution of benzyldiphenylphosphine was prepared from 26.5 g. (0.1 mole) of triphenylphosphine, 1.4 g. (0.2 g.-atom) of lithium metal, 9.3 g. (0.1 mole) of *tert*-butyl chloride, and 7.6 g. (0.06 mole) of benzyl chloride in 300 ml. of tetrahydrofuran.[7] The phenyllithium was added to the benzyldiphenylphosphine maintaining the nitrogen atmosphere. After refluxing for 2 hr. at 56°, 7.6 g. (0.06 mole) of benzyl chloride was added and the mass refluxed for 5 hr. After returning to ambient temperature, the reaction mass was added to 1000 ml. of water containing one pint of 3% hydrogen peroxide. The dried precipitate weighed 28.4 g., m.p. 161–170°. Acetone trituration followed by trituration with 95% ethanol gave a white solid 16.4 g., (m.p. 173–177°, which, after repeated recrystallization from ethanol and water, had a melting point of 220–221° and an infrared spectrum identical to (1,2-diphenylethyl)diphenylphosphine oxide. Mixed melting point determinations were undepressed.

Reaction of lithium diphenylphosphide with trans-stilbene. Lithium diphenylphosphide was prepared from 13.1 g. (0.05 mole) of triphenylphosphine, 0.7 g. (0.1 g.-atom) of lithium metal, and 4.64 g. (0.05 mole) of *tert*-butyl chloride in 50 ml. of tetrahydrofuran as described previously. Addition of 9.0 g. (0.05 mole) of *trans*-stilbene followed by refluxing for 1 hr. produced no color change. Addition to 1000 ml. of water containing 0.5 pint of 3% hydrogen peroxide produced 9.0 g. of *trans*-stilbene as shown by infrared spectrum comparison and mixed melting point determinations. Acidification of the filtrate produced 8.0 g. of diphenylphosphinic acid identified by infrared spectrum comparison and mixed melting point determinations with an authentic sample.

Preparation of (1,2-diphenylethyl)diphenylphosphine sulfide. The addition of benzyl chloride was carried out as described above, but instead of pouring into peroxide, 17 g. (0.1 mole) of thiophosphoryl chloride in 100 ml. of ether was slowly added. The reaction mass was allowed to stand for a few weeks and then filtered. The residue was repeatedly recrystallized from ethyl alcohol and water producing 8.0 g. of white solid (m.p. 182–183°) with an infrared spectrum of a chloroform solution expected for a modified benzyl diphenylphosphine sulfide.

Anal. Calcd. for $C_{26}H_{23}PS$: C, 78.39; H, 5.78; P, 7.79; S, 8.04. Found: C, 77.92; H, 5.65; P, 8.15; S, 8.15.

The filtrate was stripped of solvent and the residual semisolid crystallized from ethyl alcohol and water to give more of this product as well as some benzyl diphenylphosphine sulfide.

Oxidation of (1,2-diphenylethyl)diphenylphosphine sulfide. Treatment of the above sulfide with dilute hydrogen peroxide in base or sodium peroxide led to the quantitative recovery of the starting material as shown by melting points and infrared spectra.

A suspension of 5.0 g. of this solid in a mixture of 200 ml. of glacial acetic acid and 75 ml. of 30% hydrogen peroxide was slowly heated to 90°. After standing at room temperature overnight, the solution was added to excess water and the suspension thus produced filtered. This produced (1,2-diphenylethyl)diphenylphosphine oxide by mixed melting point and infrared comparison.

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DEPARTMENT OF CHEMISTRY
FAIRLEIGH DICKINSON UNIVERSITY
MADISON, N. J.

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[7] Described in a forthcoming paper.

Preparation of 2,1,3-Benzothiadiazoles Using Dimethylformamide-Sulfur Dioxide Reagent[1]

WALTER T. SMITH, JR., AND WEN-YEAN CHEN

Received August 21, 1961

2,1,3-Benzothiadiazoles have been prepared by treatment of *o*-phenylenediamines with thionyl chloride,[2] *N*-sulfinylaniline,[3] and with sulfurous acid under pressure.[4]

In the latter method Hinsberg reported that *o*-phenylenediamine could be converted to 2,1,3-benzothiadiazole by heating with sulfurous acid at 180° for five to six hours and that there was no reaction under milder conditions. We have investigated the use of solutions of sulfur dioxide in dimethylformamide in place of sulfurous acid and have found this to be a convenient method for preparing 2,1,3-benzothiadiazole, 5-methyl- and 5-chloro-2,1,3-benzothiadiazole, and 2′,3′-naphtho-2,1,3-thiadiazole in yields of 15–40%. While the yields are not high, the method has the convenience of being carried out in ordinary, open apparatus at temperatures of 70–115° and of being easy to work up.

From 3,3′-diaminobenzidine no bis-2,1,3-benzothiadiazole was obtained but 5-(3′,4′-diaminophenyl)-2,1,3-benzothiadiazole was isolated in 2.5% yield. This compound is of particular interest since it represents an important type of starting material for preparing certain heterocyclic analogs of steroids.

EXPERIMENTAL[5]

2,1,3-Benzothiadiazoles. To 70 ml. of a saturated solution of sulfur dioxide in dry dimethylformamide was added 0.03

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-49. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[5] Melting points were determined with the Fisher-Johns apparatus and are corrected.

mole of the appropriately substituted o-phenylenediamine. The mixture was stirred at 70–75° for 8 hr. The cooled mixture was filtered to remove a small amount of insoluble material. The filtrate was diluted with an equal volume of water and extracted with two 50-ml. portions of benzene. The combined benzene extracts were washed with 50 ml. of water to remove dimethylformamide and then evaporated. The residue was recrystallized from 95% alcohol if purification was required. The above procedure gave 2,1,3-benzothiadiazole (40%), m.p. 42–43° (lit.[2] 44°), 5-chloro-2,1,3-benzothiadiazole (17%), m.p. 54–55° (lit.[3] 57.5°), 5-methyl-2,1,3-benzothiadiazole (35%), m.p. 28–30° (lit.[3] 34°).

2′,3′-Naphtho-2,1,3-benzothiadiazole, m.p. 99–100° was prepared as above in 15% yield.

Anal. Calcd. for $C_{10}H_6N_2S$: N, 15.05; S, 17.24. Found: N, 14.85; S, 17.19.

5-(3′,4′-Diaminophenyl)-2,1,3-benzothiadiazole, m.p. 150–153° was prepared as above in 2.5% yield.

Anal. Calcd. for $C_{12}H_{10}N_4S$: N, 23.14; S, 13.23. Found: N, 23.20; S, 13.41.

The yield of 2,1,3-benzothiadiazole was increased from 40% to 49% by passing a stream of sulfur dioxide into the reaction mixture during the heating period.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KENTUCKY
LEXINGTON, KY.

Some Reactions of Cyanuric Chloride with Negatively Substituted Alcohols[1]

A. J. MATUSZKO AND M. S. CHANG

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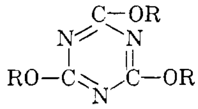
Esterification reactions of certain alcohols and phenols with cyanuric chloride to give alkoxy-s-triazines and aryloxy-s-triazines have been previously described in the literature.[2,3] The preparation of a nitroaryloxy derivative, tris(p-nitrophenyl) cyanurate, by the nitration of triphenyl cyanurate has also been reported.[4,5] However, attempts at a more direct method of preparing this same compound from cyanuric chloride and sodium p-nitrophenoxide have led only to partial replacement of the chlorine atoms.[6] This report describes the results of an investigation involving the reactions of cyanuric chloride with several negatively substituted primary alcohols in which the electronegative substituents were fluoro, bromo, nitro, or nitroxy groups.

Our first reactions with trifluoroethanol and tribromoethanol were designed to determine the effect of electron-withdrawing groups on the reaction without having to be concerned with steric effects or secondary reactions which might involve the nitro and nitroxy alcohols. Both trifluoroethanol and tribromoethanol reacted with cyanuric chloride in basic media to give products whose structures are assigned the corresponding tris(trifluoroethoxy)-s-triazine (Ia) and tris(tribromoethoxy)-s-triazine (Ib).

The synthesis of 2,4,6-tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine (Ic) was accomplished in an aqueous alkaline and acetone solution containing a mixture of cyanuric chloride and 2,2-bis(nitroxymethyl)-3-nitroxy-1-propanol. The product was obtained in good yield indicating that steric effects and side reactions were of minor importance.



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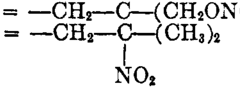
Ia. R = $—CH_2—CF_3$
Ib. R = $—CH_2—CBr_3$
Ic. R = $—CH_2—C—(CH_2ONO_2)_3$
Id. R =

$—CH_2—\underset{NO_2}{C}—(CH_3)_2$

Esterifications with cyanuric chloride were tried on several nitro alcohols. The alcohols used were primary with nitro substituents located on primary, secondary, or tertiary carbon atoms on the molecule. Cyanurate esters were not obtained from nitroethanol or 2-nitro-1-butanol. This behavior may be explained by considering the known ability of primary and secondary nitro compounds to exist in their tautomeric *aci*-forms in basic solution. Hence, it is proposed that the base introduced as the hydrogen chloride acceptor in the acid chloride–alcohol esterifications may have reacted with the *aci*-hydrogens to form nitronic esters which decomposed on attempted isolation. When a nitro alcohol with a tertiary nitro group was the reactant, as in the case of 2-methyl-2-nitro-1-propanol, both di- and trisubstituted derivatives were obtained. The 2-methyl-2-nitro-1-propanol has no hydrogen atom that is alpha to the nitro group and hence has no tautomeric *aci*-form.

Reaction conditions were limited with trinitroethanol due to its decomposition in basic solution at high temperatures. Hence, it was not possible to carry out the reaction with cyanuric chloride in solution with a base as the acid acceptor or to fuse the two reactants at elevated temperatures. Attempted fusions at lower temperatures yielded oils which were difficult to characterize.

EXPERIMENTAL

All melting points are uncorrected.

2,4,6-Tris(trifluorethoxy)-s-triazine (Ia). A suspension of 0.85 g. (0.015 mole) of potassium hydroxide in 10 ml. of

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[1] Published with the permission of the Bureau of Naval Weapons, Navy Dept. The opinions and conclusions are those of the authors.

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