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.

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

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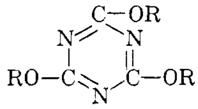
Received August 22, 1961

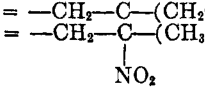
Esterification reactions of certain alcohols and phenols with cyanuric chloride to give alkoxy-*s*-triazines and aryloxy-*s*-triazines have been previously described in the literature.[2,3] The preparation of a nitroaryloxy derivative, tris(*p*-nitrophenyl) cyanurate, by the nitration of triphenyl cyanurate 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.



I

Ia. R = $—CH_2—CF_3$
Ib. R = $—CH_2—CBr_3$
Ic. R = $—CH_2—C—(CH_2ONO_2)_3$
Id. R = 
$—CH_2—\underset{\displaystyle NO_2}{\underset{|}{C}}—(CH_3)_2$

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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[5] R. Hirt, N. Nidecker, and R. Berchtold, *Helv. Chem. Acta*, **33**, 1365 (1950).

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trifluoroethanol was stirred at room temperature while 0.9 g. (0.005 mole) of cyanuric chloride was added gradually; the reaction temperature was held at 30–35°. After all the cyanuric chloride was added, the mixture was refluxed for 5 hr. A solid (potassium chloride) was separated by filtration. The filtrate was washed with water and the excess trifluoroethanol removed by distillation. The residue was washed with water and then dried. Recrystallizations from petroleum ether (b.p. 30–60°) gave colorless crystals; m.p. 45–46°; yield 1.2 g. (64%).

Anal. Calcd. for $C_9H_6F_9N_3O_3$: C, 28.80; H, 1.60; F, 45.60; N, 11.20. Found: C, 28.96; H, 1.54; F, 45.67; N, 11.60.

2,4,6-Tris(tribromoethoxy)-s-triazine (Ib). A solution of 0.9 g. (0.005 mole) of cyanuric chloride in 15 ml. of acetone was mixed with 4.4 g. (0.015 mole) of tribromoethanol in 15 ml. of acetone. A solution of 0.85 g. (0.015 mole) of potassium hydroxide in 10 ml. water was then added slowly in order to keep the reaction temperature around 45°. After all the solution was added, the mixture was continuously stirred for 20 min. The solid was separated by filtration and washed with water, alcohol, and then acetone. Repeated recrystallizations from methylene chloride and *n*-hexane yielded the product weighing 4.0 g. (86%); m.p. 280–281° dec.

Anal. Calcd. for $C_9H_6Br_9N_3O_3$: C, 11.70; H, 0.65; N, 4.56; Br, 77.89. Found: C, 11.57; H, 0.57; N, 4.64; Br, 78.38.

2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine (Ic) was prepared in a manner similar to compound Ib by the reaction of cyanuric chloride with 2,2-bis(nitroxymethyl)-3-nitroxy-1-propanol; m.p. 131–132°; yield, 88%.

Anal. Calcd. for $C_{18}H_{24}N_{12}O_{30}$: C, 24.32; H, 2.71; N, 18.91. Found: C, 24.30; H, 2.89; N, 18.79.

2-Chloro-4,6-bis(2-methyl-2-nitropropoxy)-s-triazine was prepared in a manner similar to compound Ib by the reaction of cyanuric chloride with 2-methyl-2-nitro-1-propanol; m.p. 103–104°; yield, 17%.

Anal. Calcd. for $C_{11}H_{16}N_5O_6Cl$: C, 37.76; H, 4.57; N, 20.28; Cl, 10.15. Found: C, 38.16; H, 5.27; N, 20.33; Cl, 10.52.

2,4,6-Tris(2-methyl-2-nitropropoxy)-s-triazine (Id). A solution of 1.8 g. (0.01 mole) of cyanuric chloride and 3.7 g. (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml. of acetone was added to a solution of 1.7 g. of potassium hydroxide in 15 ml. of water. The temperature rose immediately to 55° and then the mixture was allowed to reflux for 1.5 hr. Evaporization of the acetone gave a white solid which was recrystallized from a nitromethane–methanol mixture; m.p. 248–249°. Analyses indicated the formation of the triester; yield, 0.7 g. (16%).

Anal. Calcd. for $C_{15}H_{24}N_6O_9$: C, 41.64; H, 5.55; N, 19.44. Found: C, 41.98; H, 5.65; N, 19.85.

Acknowledgment. We are indebted to Dr. J. H. Boyer and Professor M. L. Wolfrom for helpful discussions. We are also grateful to Mrs. P. Wheeler for the elemental analyses.

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An Intramolecular Wittig Olefin Synthesis[1,2]

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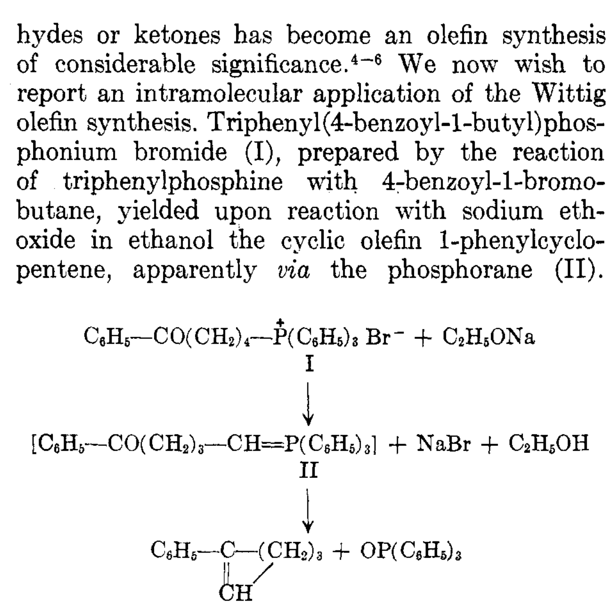
Received August 24, 1961

The Wittig reaction between phosphoranes (from phosphonium salts plus base) and aldehydes or ketones has become an olefin synthesis of considerable significance.[4-6] We now wish to report an intramolecular application of the Wittig olefin synthesis. Triphenyl(4-benzoyl-1-butyl)phosphonium bromide (I), prepared by the reaction of triphenylphosphine with 4-benzoyl-1-bromobutane, yielded upon reaction with sodium ethoxide in ethanol the cyclic olefin 1-phenylcyclopentene, apparently *via* the phosphorane (II).



The olefin thus obtained was identical with 1-phenylcyclopentene synthesized according to Bauer[7] by addition of phenyl Grignard reagent to cyclopentanone and dehydration of the resulting 1-phenylcyclopentanol with formic acid. The yield of this internal Wittig olefin synthesis was 24%. With lithium ethoxide in ethanol a comparable yield was obtained, but with phenyllithium in ether only about 1% of the cyclic olefin resulted.

Even if the intramolecular Wittig olefin synthesis inherently gives low yields of cyclic olefins, the method may prove useful in those cases where the olefinic double bond is to be located in a given position and other methods involving an elimination reaction as the final step would yield mixtures of isomers or the wrong isomer. It is to be expected that the intramolecular Wittig olefin synthesis, like the well established intermolecular kind,[6] permits specific placement of the double bond and is not complicated by subsequent isomerization.

As to the mechanism of the intramolecular Wittig olefin synthesis, there is no reason to believe that it is basically different from that suggested[4-6] for the intermolecular kind.

Reaction of I with aqueous sodium hydroxide proceeded with the normal elimination of a phenyl

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(1) Supported in part by the Faculty Research Fund of the University of Mississippi.

(2) Some of this work was presented before the Southeastern Regional Meeting of the American Chemical Society in Birmingham, Ala., November 3, 1960, Abstracts p. 10.

(3) Taken from the M.S. dissertation submitted by Eugene H. Eisman to The University of Mississippi in June 1961.

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