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Method for synthesis of triarylisocyanurates from aryl isocyanates using triazaprophosphatrane catalysts

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Method for synthesis of triaryl isocyanurates from aryl isocyanates using triazaprophosphatrane catalysts

Abstract
A method is provided to prepare triaryl isocyanurates from aryl isocyanates by using triazaprophosphatrane catalysts

Keywords
Chemistry

Disciplines
Chemistry
METHODOLOGY FOR SYNTHESIS OF TRIARYLISOCYANURATES FROM ARYL ISOCYANATES USING TRIAZAPOPHOSPHATRANE CATALYSTS

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Related U.S. Application Data
Continuation-in-part of Ser. No. 948,168, Sept. 21, 1992, abandoned.

References Cited
U.S. PATENT DOCUMENTS
5,051,533 9/1991 Verkade 564/13
FOREIGN PATENT DOCUMENTS
1226878 9/1989 Japan
3109382 5/1991 Japan

OTHER PUBLICATIONS

Primary Examiner—John M. Ford
Attorney, Agent, or Firm—Merchant, Gould, Smith, Edell, Welter & Schmidt

ABSTRACT
A method is provided to prepare triaryl isocyanurates from aryl isocyanates by using triazaprophosphatranate catalysts.

17 Claims, No Drawings
METHOD FOR SYNTHESIS OF TRIARYLISOCYANURATES FROM ARYL ISOCYANATES USING TRIAZAPROPHOSPHATRANE CATALYSTS

This is a continuation-in-part of our copending application, Ser. No. 07/948,168, filed Sep. 21, 1992.

BACKGROUND OF THE INVENTION

This invention has been made with the support of National Science Foundation Grant No. CHE-8908136. The U.S. Government has certain rights in the invention.

Triaryl isocyanurates of general formula 1:

\[
R\begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

\[
\text{N-} \begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

\[
\text{N-} \begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

wherein \(\text{C}_6\text{H}_4\) is 1,4-phenylene, 1,2-phenylene or 1,3-phenylene and \(R\) is, for example, 2-, 3- or 4-halo, \(H\), methyl or methoxy, are useful as activators for the continuous anionic polymerization and post-polymerization of \(\varepsilon\)-caprolactam to nylon-6. These activators yield a final product having a low content of unreacted monomer and a highly stable melt viscosity. See, for example, Z. Bukac et al., Czech. CS 227,247 (Chem. Abstr. 105, 173224r (1986)); Z. Bukac et al., Chem. Prum., 35, 361 (1985) (Chem. Abstr., 103, 123978c (1984)), J. Horsky et al., Int. Polym. Sci. Tech., 9, 65 (1982). Recently, the superior thermal and hydrolysis stability of triphenyl isocyanurate-based foams and plastics have generated considerable interest in the development of methods to produce trimers of general formula 1. See, H. Ulrich, J. Cellular Plastics, 17, 31 (Jan./Feb. 1981), P.I. Kordomenas et al., Macromolecules, 14, 1434 (1981) and D.K. Hoffman, J. Cellular Plastics, 20, 129 (1984).

Since impurities in the activators of formula 1 lower the quality of nylon-6, attempts have been made to develop purification methods for these trimers. However, due to the complexity of the processes which have been used, only relatively low yields of pure products have been obtained. See, Z. Bukac et al., cited above.

Several catalytic methods to prepare triaryl isocyanurates have been reported. For example, Y. Taguchi et al., Bull. Chem. Soc. Japan, 63, 3486 (1990) reported the trimerization of phenyl isocyanate in the presence of amine catalysts in 22-100% yield using high pressures. S. Kato et al., J. Organometallic Chem. 51, 167 (1973) trimerized phenyl isocyanate to yield 1 \((R=H)\) in 82% yield, using [\(\alpha\)-(trimethylstannyl)phenacyl]triphenyolphosphonium ylide. E. Martilli et al., J. Molec. Catal., 22, 89 (1983) reported the use of (\(\eta^5\)-\(\text{C}_3\text{H}_6\text{Me})\text{Mn(CO)}\)) and photolysis to catalyze the same reaction in 80% yield. J. Mizuya et al., J. Polymer Sci: Part A: Polymer Chem. 29, 1545 (1991) accomplished the same reaction in relatively low yields (72-80%) using large amounts of alkoxalkenes as catalysts. However, the more electrophilic isocyanate, 4-methylphenyl isocyanate, did not cyclotrimerize under these conditions. K. Ashide, EPA 169,708 (Chem. Abstr., 107, 134825j (1987)) trimerized phenylisocyanate to 1 \((R=H)\) in only 63% by using 10% silicates as the catalyst.

Therefore, a continuous need exists for methods to prepare triaryl isocyanurates in high yields, which require little or no purification of the final product. A further need exists for methods to prepare triisocyanurates under mild reaction conditions using non-toxic, non-metallic catalysts.

SUMMARY OF THE INVENTION

The present invention provides a method for preparing triaryl isocyanurates comprising reacting an aryl isocyanate of the general formula 3:

\[
\text{RAN-\text{C}=\text{O}}
\]

wherein \(\text{Ar}\) is 1,3-phenylene, 1,2-phenylene or 1,4-phenylene and \(R\) is \(H\), halo \((F, Cl, Br or I)\), \((\text{C}_1-\text{C}_5)\text{alkyl}\) or \((\text{C}_1-\text{C}_5)\text{alkoxy with or without a solvent in the presence of catalytic amount of a compound of the general formula 2:}

\[
\text{R'N-P...N-R''}
\]

wherein \(\text{R'}\), \(\text{R''}\) and \(\text{R'''}\) are each \(H\), \((\text{C}_1-\text{C}_5)\text{alkyl}, \((\text{C}_6-\text{C}_9)\text{aryl}, \text{or (alk)}_3\text{Si, wherein each alk is (C}_1-\text{C}_5)\text{alkyl, preferably to yield a compound of the general formula 1:}

\[
\text{R-\begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

\[
\text{N-} \begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

\[
\text{N-} \begin{array}{c}
\text{C}_6\text{H}_4-\text{N}=\text{C} \\
\text{O}
\end{array} 
\]

wherein \(R\) is as defined above.

\(R\) can be in the 2, 3 or 4 position of the Ar \((\text{C}_6\text{H}_4)\) ring. Preferably, \(R', R''\) and \(R'''\) are the same substituents. The term "aryl" includes alkaryl or aralkyl and is preferably benzyl. The term "(C\(_1\)C\(_5\))alkyl" includes branched or straight-chain alkyl, as well as \((\text{C}_3-\text{C}_5)\text{cycloalkyl}\) or \((\text{C}_3-\text{C}_5)\text{cycloalkylalkyl}\), and is preferably \((\text{C}_1-\text{C}_2)\text{alkyl, e.g., methyl or ethyl. The catalyst can catalyze the reaction with or without solvent in the reaction mixture. Preferably, a solvent is used. A wide range of organic solvents can be employed and include ethers (tetrahydrofuran, diethyl ether), alkanes (hexane, pentane), aromatic solvents (toluene, benzene), dimethyl formamide (DMF), dimethylsulfoxide (DMSO), or acetonitrile. Preferably, the solvent is selected so that the reactants are soluble therein at the temperature at which the trimerization is carried out, but the product 1 is insoluble in the solvent, preferably below 25°C. Thus, only simple filtration is needed to obtain highly pure, solid triaryl isocyanurates.

The temperature can also be varied widely, e.g., from room temperature \((20-25^\circ C)\) to the refluxing temperature of the selected organic solvent \((i.e., 150°-200^\circ C)\). Preferably, the trimerization reaction is carried out at about 60°-70°C, in an aromatic solvent.
For example, in accord with the present method triaryl isocyanurates of formula 1 have been prepared from aryl isocyanates in 95–96% yield with 100% purity by using 0.33% trimethyl-triazaprophosphatrane as the catalyst and by using benzene as the solvent. No purification except filtration of the reaction products is necessary to obtain highly pure compounds of formula 1.

Thus, the catalyst 2 used in the present invention catalyzes trimerization of aryl isocyanates effectively under mild conditions to yield the desired triaryl isocyanurates 1 in high yield and without any by-products. Electron-donating groups on the phenyl group in aryl isocyanates make them very difficult to trimerize. Thus, as found by Mizuya et al., cited above, compounds such as alkyllylkenones with weak catalytic properties cannot catalyze trimerization of even the weakly electron-donating p-methyl-substituted phenyl isocyanate to its corresponding isocyanate. Compound 2 used in this invention is, however, strongly catalytic. Thus, it almost quantitatively catalyzes the trimerization not only of phenyl isocyanate, but also of the strongly electron-donating p-methoxy substituted phenyl isocyanate to the corresponding trimers 1 (R=H, p-MeO, respectively).

The method in the present invention also is advantageous in that the reaction may be carried out without a solvent, and that it uses a very small amount (i.e., about 0.25–5 mol-%) of the catalyst as a mol-% of the isocyanate and produces triisocyanurates in high yields (90%) in relatively short reaction times.

**DETAILED DESCRIPTION OF THE INVENTION**

As illustrated in the examples and in J.G. Verkade (U.S. Pat. No. 5,051,533), the compounds of formula 2 can be made by a straightforward pair of reactions. In the first step a trisubstituted tris-N-alkyl-2-aminoethylamine (trisalkyl-TREN) is reacted, preferably with an equimolar amount of bis-dimethylaminochlorophosphine, to provide the phosphatranyl chloride in Scheme 1.

**Scheme 1**

![Chemical structure](image)

It is possible to accomplish the reaction in the absence of a solvent, or in the presence of an organic solvent, with no criticality of temperature. Suitable solvents include chlorinated hydrocarbons, aromatic hydrocarbons, and ethers. A highly preferred solvent is methylene chloride. This reaction proceeds in an essentially stoichiometric fashion. The starting compound, TREN, wherein $R'=R''=R'''=H$, is commercially available from Aldrich Chem. Co. or W.R. Grace and Company, and can be converted to trimethyl-TREN as described in Example 1. In the second step of the synthesis, the phosphatranyl chloride is converted to the phosphophosphate in the presence of an organic base such as potassium tert-butoxide in acetonitrile solvent at room temperature.

The invention will be further described by reference to the following detailed examples.

**EXAMPLE 1**

**Synthesis of Trimethyl-TREN((HCH$_3$NCH$_2$CH$_2$)$_3$N)**

In accord with the procedure of H. Schmidt et al., *Z. anorg. allg. Chem.*, 578, 75 (1989), ethylchloroformate (33.4 g, 0.310 mol) was added dropwise to a solution of tris(2-aminoethyl)amine (TREN) (29.2 g, 0.20 mol) dissolved in a mixture of benzene (225 mL) and water (100 mL) cooled to 5°C. After the addition was completed, KOH (36.4 g, 0.650 mol) dissolved in water (35 mL) was added dropwise simultaneously with more ethylchloroformate (33.4 g, 0.310 mol). The reaction mixture was stirred for 2 hr. at 5°C and then for 8 hr. at room temperature. The benzene layer was separated and the water layer extracted with chloroform (2×100 mL). The combined organic fractions were dried over MgSO$_4$, decanted and the decantate evaporated to dryness to give the intermediate tris(2-carboxyethyl)amine (5) in 85% yield as a thick oil which was used in subsequent reactions without further purification (1H NMR (CDCl$_3$)δ1.27 (9H, t, $\delta_{JHH}=7.1$ Hz), 82.60 (6H, t, $\delta_{JHH}=5.7$ Hz), 83.23 (6H, br), 64.10 (6H, $\delta_{JHH}=7.1$ 5.50 (3H, br), 1R 3300, 1720, 1530, 1250 cm$^{-1}$).

A solution of 5 (61.3 g, 0.170 mmol) in THF (250 mL) was added dropwise to a suspension of LiAlH$_4$ (30.0 g,
5

0.79 mol) in THF (700 mL). The reaction mixture was heated at reflux temperature overnight. Water (50 mL) and a solution of KOH (50 g) in water (50 mL) were carefully added. The solution was decanted from the inorganic gel. Removal of the solvent from the decantate yielded a yellow oil which upon distillation yielded product 4 in 88% yield as a colorless liquid (m/e 189.2082 (calcd. 189.20793 for M + H)); 31C NMR (CDCl3) δ541 (CH2), 849.6 (CH2), 836.3 (CH3). 1H NMR (CDCl3) δ1.30 (3H, br. NH), 82.39 (9H, s, CH3), δ1.48 (6H, m, J13JH=6.1 Hz) δ1.52 (6H, m). J1J2H=6.1 Hz).

EXAMPLE 2

P(CH2=NC6H5)2N (2a)

Method A: P(NMe2)3 (8.8 g, 54 mmol) and 4 (10 g, 53 mmol) were dissolved in dry xylene (60 mL) and heated at reflux for 21 days. The solvent was removed under vacuum. Sublimation of the resulting thick oil at 105° C./0.05 mm Hg afforded 2a in 46% yield (5.3 g, 24.5 mmol) as a colorless waxy solid (m/e 216.15085 (calcd. 216.15039 for M)); IR 332 s, 1303 m, 1244 s, 1226 s, 1197 m, 1145 s, 1128 s, 1053 s, 1004 s, 960 w, 887 m, 850 s, 767 w, 650 s, 634 s cm−1. Method B: A solution of 4 (1.67 g, 11.4 mmol) in CH2Cl2 (20 mL), is added over a period of 5 min to a stirred solution of CIP(NMe2)2B (1.76 g, 11.4 mmol) and Et3N (1.5 g, 15 mmol) in CH2Cl2 (30 mL). Stirring at room temperature for 1 hr., followed by removal of the solvent and Et3N afforded the phosphoranyl chloride in essentially quantitative yield. The salt was recrystallized from hexane/chloroform at −20 °C. to give an 82% yield of the product as a colorless crystalline solid. Treatment of the compound (Cl−) with AgBF4 in CH2Cl2 gave the BF4− salt in quantitative yield. X-ray crystallography of the BF4− salt confirmed the presence of the phosphoranyl cation phosphorane wherein R1, R2 and R3 are methyl.

The chloride was converted to the corresponding phosphoraphosphate by adding 0.87 g (3.4 mmol) of the salt dissolved in 10 mL of acetonitrile to a suspension of potassium tertiary butoxide (0.41 g, 3.7 mmol) in acetonitrile (20 mL). After stirring the reaction mixture for 30 minutes at room temperature, the solution was removed under vacuum and the residue extracted with 2×30 mL of hexanes. The white residue was purified by vacuum sublimation (60° C./0.01 mm Hg) to give the phosphoraphosphate 2a (R1=R2=R3=Me) in 82% yield.

EXAMPLE 3

To a solution of 2a (0.11 g, 0.50 mmol) in dry benzene (10 mL) was added by syringe phenyl isocyanate (18.03 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred at room temperature. A white precipitate formed rapidly after 3 minutes of stirring. Then the mixture solidified into a solid mass in a few seconds. The solid mass was cooled to room temperature and evaporated under vacuum (with oil pump) to remove the solvent. The residue was ground to powder and then stirred with 30 mL of dry benzene for 2 hr, filtered in vacuo, further washed with 15 mL of dry benzene and finally dried in vacuo to give 17.24 g (96.6%) of TLC-pure triphenyl isocyanurate (1, R=H); m.p. of 279.0°−14 279.5° C. The structure and purity of 1 (R=H) were confirmed by 1H NMR, IR and HRMS analyses.

EXAMPLE 4

To 0.11 g (0.50 mmol) of 2a was added by syringe phenyl isocyanate (18.03 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred at room temperature. A white precipitate formed rapidly after 2 minutes of stirring. A solid mass appeared in a few seconds. The solid mass was ground to powder and then stirred with 30 mL of dry benzene, filtered in vacuo, further washed with 10 mL of dry benzene and finally dried in vacuo to give 16.86 g (94.4%) of TLC-pure triphenyl isocyanurate (1, R=H); m.p. of 279.0°−279.5° C. The structure and purity of 1 (R=H) were confirmed by 1H NMR, IR and HRMS analyses.

EXAMPLE 5

To a solution of 2a (0.06 g, 0.3 mmol) in dry benzene (5 mL) was added by syringe p-methoxyphenyl isocyanate (11.30 g, 99% pure, 75 mmol, Aldrich). The mixture was stirred at room temperature. After 3 minutes of stirring, a white precipitate formed gradually. The mixture solidified in another 5 minutes. The solid was cooled to room temperature, evaporated under vacuum to remove the solvent. The residue was ground to powder and then stirred with 50 mL of dry benzene, filtered in vacuo, further washed with 30 mL of dry benzene and finally dried in vacuo in 50° C. to give 11.05 g (98.7%) of TLC-pure p-methoxyphenyl isocyanurate (1, R=−p-methoxy); m.p. of 261.0°−261.5° C. The structure and purity of 1 (R=H) were confirmed by 1H NMR, IR and HRMS analyses.

EXAMPLE 6

To 0.06 g (0.3 mmol) of 2a was added by syringe p-methoxyphenyl isocyanate (11.30 g, 99% pure, 75 mmol, Aldrich). The mixture was stirred at room temperature. After 5 minutes of stirring, a white precipitate formed very rapidly. The mixture solidified in a few seconds. The solid was cooled to room temperature, ground to powder and then stirred with 50 mL of dry benzene. The solids were filtered in vacuo, further washed with 30 mL of dry benzene and finally dried in vacuo in 50° C. to give 10.5 g (93.8%) of TLC-pure p-methoxyphenyl isocyanurate (1, R=−p-methoxy); m.p. of 261.0°−261.5° C. The structure and purity of 1 (R=−p-methoxy) were confirmed by 1H NMR, IR and HRMS analyses.

EXAMPLE 7
EXAMPLE 8

\[ \text{[HP(N(CH_2)Ph)CH_2CH_2]NCl} \]

5c-HCl(2HCl, R' = R'' = -CH_2Ph)

A solution containing 0.233 g (1.70 mmol) of PCl_3 in 5 mL of CH_2Cl_2 was added all at once to a solution containing 0.555 g (3.41 mmol) of P(NMe_2) in 10 mL of CH_2Cl_2. To this solution was slowly added a solution containing 2.12 g (5.11 mmol) of tris-(N-benzyl-2-aminoethylamine in an additional hour. The mixture was evaporated to dryness, the residue was washed with hexanes giving 2.40 g (98% yield) of spectroscopically pure 2c-HCl.

EXAMPLE 9

P[N(CH_2)Ph]CH_2CH_2]N, 2d (2, R' = R'' = -CH_2Ph)

To a solution containing 0.572 g (5.11 mmol) of KO-t-Bu in 20 mL of THF was added a solution containing 2.21 g (4.64 mmol) of 2c-HCl in 20 mL of THF. After stirring the reaction mixture at room temperature for one hour, the volatiles were removed in vacuo. The residue was extracted with several 100 mL portions of hexanes for 3 hours. The extracts were collected and the hexanes removed in vacuo to give an oily residue which was spectroscopically pure 2d. (31P NMR (Et_2O)) 6128.3 (s): 31H NMR (CD_3OD) 6 7.30 (15 H, m, CH_2), 64.04 (6 H, d, _3J_F-H = 12.1 Hz), 82.71 (12 H, br, NCH_3), 11C NMR (CD_2Cl) 6 80.6 (d, PhCH_2), _3J_F-H = 15.2 Hz), 850.2 (s, N_2CH_2), 654.7 (s, N_2CH_2), 6128.0 (s, CH_2), 6128.3 (s, CH_2), 6129.4 (s, CH_2), 6138.1 (s, CH_2).

HRMS: m/e (calculated) 444.24374, m/e (measured) 444.24429 for C_2H_22N_4P.

EXAMPLE 10

[HP(N(SiMe_3)]CH_2CH_2]N (6)

In accord with the procedure of D. Gudat et al., Organometallics, 8, 2772 (1989), a solution of 2.00 g (13.7 mmol) of TREN in 35 mL of THF was cooled to -50°C, and 20.5 mL of 2 M solution of n-butyl lithium in hexanes was slowly added. The mixture was allowed to warm to room temperature and was stirred for 15 minutes. The mixture was evaporated to dryness and the residue was suspended in 50 mL of ether and was stirred for 30 minutes. After filtration and evaporation of the solvent, the residue was distilled, afford- ing 2.66 g of 6 as a colorless liquid (bp 80°-90°C, yield 54%).

EXAMPLE 11

HP[N(SiMe_3)CH_2CH_2]N, 2c-HCl(2-HCl, R' = R'' = R''' = SiMe_3)

A solution containing 1.22 g (8.85 mmol) of PCl_3 in 5.0 mL of CH_2Cl_2 is added at once to a solution containing 2.89 g (17.70 mmol) of P(NMe_2) in 25 mL of CH_2Cl_2. This solution is then cooled to 5°C and 9.62 g (26.55 mmol) of 6 is added over a period of 15 minutes. The resulting precipitate is separated by filtration and washed with 25 mL of CH_2Cl_2 to yield the title compound.
wherein R is as defined above; wherein the improvement comprises carrying out the reaction in the presence of a catalytic amount of a compound of the general formula (2):

wherein R', R'' and R''' are each H, (C1–C4)alkyl, (C6–C9)aryl or (alk)3Si, wherein each alk is (C1–C4)alkyl.

2. The process of claim 1 wherein the improvement further comprises carrying out the reaction without solvent.

3. The process of claim 1 wherein C6H4 is 1,4-phenylene.
4. The process of claims 1 or 3 wherein R is halo.
5. The process of claim 4 wherein R is 4'-chloro.
6. The process of claims 1 or 3 wherein R is (C1–C3)alkyl.
7. The process of claim 6 wherein R is 4'-CH3.
8. The process of claim 1 wherein R is H.
9. The process of claim 1 or 8 wherein R', R'' and R''' are each (C1–C4)alkyl.
10. The process of claim 9 wherein R', R'' and R''' are CH3.
11. The process of claims 1 or 8 wherein R', R'' and R''' are benzyl.
12. The process of claims 1 or 8 wherein R', R'' and R''' are trimethylsilyl.
13. The process of claim 1 wherein the reaction is carried out in an organic solvent.
14. The process of claim 13 wherein the reaction is carried out at about 60°–70° C. in an aromatic solvent.
15. The process of claim 14 wherein the solvent is benzene.
16. The process of claims 13 wherein the compound of formula 1 is separated by filtration from the organic solvent, the compound of formula 2 and the compound of formula 3.
17. The process of claim 1 wherein about 0.25–5 mol-% of the compound of formula 2 is used.

* * * * *
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 2, line 19, please insert --a-- after the word “of”

In column 2, line 33, please insert --CH₃-- after the word “preferably”

In column 2, line 49, please delete “cyclyalkylalkyl” and insert --cycloalkylalkyl--

In column 4, line 13, please delete “(2)” and insert --(2a)--

In column 3, line 46, please delete “(90%)” and insert --(≥ 90%)--

In column 4, line 47, please delete “anoro alql” and insert --anorg. allg--

In column 4, line 65, please insert --Hz), δ-- after the numeral “7.1”

In column 5, line 9, please delete “54 1” and insert --54.1--

In column 5, line 23, please delete “332s” and insert --1332s,--

In column 5, line 37, please delete “quantiative” and insert --quantitative--

In column 5, line 66, please delete “14” after “279.0°”

In column 6, line 3, please delete “(0.50Q mmol)” and insert --(0.50 mmol)--

In column 6, line 14, please delete “we firmed” and insert --were confirmed--

In column 7, line 13, please delete “0 555” and insert --0.555--

In column 7, line 36, please delete “3J” and insert “2J"
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 8, line 2, please delete “p” and insert --P--