SYNTHESIS AND PROPERTIES OF sym-TRIAZENE DERIVATIVES

12.* SYNTHESIS OF 2,4-BIS(TRICHLOROMETHYL)-6-SUBSTITUTED sym-TRIAZENES CONTAINING A STERICALLY HINDERED PHENOL GROUP

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6-Substituted 2,4-bis(trichloromethyl)-sym-triazenes containing the 2,6-di-tert-butylphenol group are synthesized by simultaneous cyclotrimerization of trichloroacetonitrile with the nitrile or thiocyanate derivative of the sterically hindered phenol in the presence of gaseous HCl. Significant amounts of 2,4,6-tris(trichloromethyl)-sym-triazene are formed as a by-product.

In a continuation of studies of derivatives of sym-triazenes which incorporate a sterically hindered phenol group [2-5], we have synthesized 6-substituted 2,4-bis(trichloromethyl)-sym-triazenes containing the 2,6-di-tert-butylphenol group. Such compounds may be of interest as intermediates in the synthesis of biologically active substances, thermally stable antioxidants for hydrocarbon fuels, lubricants, and polymeric materials.

It is known [6,7] that one of the most useful methods of synthesizing sym-triazene derivatives having trichloromethyl substituents is the simultaneous cyclotrimerization of trichloroacetonitrile (TCAN) with different cyano-containing compounds. In the present work we have studied the reaction of TCAN with nitriles (I-V) and thiocyanates (VI and VII) containing 2,6-di(tert-butyl)phenyl groups in order to synthesize sym-triazene derivatives of this type.

According to [6,7], 2,4-bis(trichloromethyl)-6-aryl-sym-triazenes are formed in 90-95% yield when dry HCl is passed into a mixture of an aromatic nitrile and TCAN (1:2 mole ratio) in an inert solvent in the presence of catalytic amounts of AlBr3. However, when 4-hydroxy-3,5-di(tert-butyl)benzonitrile, I, was introduced into the reaction with TCAN under these conditions (ether, 20°C, 6 h, 5 mole % AlBr3), only starting nitrile I along with an 82% yield of the homocyclotrimerization product of TCAN, 2,4,6-tris(trichloromethyl)-sym-triazene (VIII), were isolated from the reaction mixture.

It was found that the product of the mixed cyclotrimerization, 2,4-bis(trichloromethyl)-6-[4-hydroxy-3,5-di(tert-butyl)phenyl]-sym-triazene (IX), is formed in low yield (20-27%) after prolonged (12-14 h) heating of the reaction mixture.

*For Communication 11, see [1].

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TABLE 1. Characteristics of the Synthesized Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Temp. °C</th>
<th>R_f 2</th>
<th>PMR Spectra, δ, ppm 3</th>
<th>Yield, %*4</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>C_{19}H_{21}Cl_{6}N_{3}O</td>
<td>208...210</td>
<td>0.64(a)</td>
<td>1.68 4.88 7.20  —</td>
<td>27 (45)</td>
</tr>
<tr>
<td>X</td>
<td>C_{20}H_{23}Cl_{6}N_{3}O</td>
<td>133...134.5</td>
<td>0.58(6)</td>
<td>1.56 4.92 7.32 3.65 (2H, CH_{2})</td>
<td>75 (12)</td>
</tr>
<tr>
<td>XI</td>
<td>C_{21}H_{25}Cl_{6}N_{3}O</td>
<td>Oil (μP, 1.4634)</td>
<td>0.49(6)</td>
<td>1.60 5.10 7.18 4.02...4.14 (4H, CH_{2})</td>
<td>70 (15)</td>
</tr>
<tr>
<td>XII</td>
<td>C_{20}H_{23}Cl_{6}N_{3}O</td>
<td>157...158</td>
<td>0.74(a)</td>
<td>1.70 4.95 7.34 3.92 (2H, CH_{2})</td>
<td>72 (15)</td>
</tr>
<tr>
<td>XIII</td>
<td>C_{21}H_{25}Cl_{6}N_{3}O</td>
<td>Oil (μP, 1.4805)</td>
<td>0.52(a)</td>
<td>1.52 5.02 7.24 4.08...4.16 (4H, CH_{2})</td>
<td>76 (13)</td>
</tr>
<tr>
<td>XIV</td>
<td>C_{19}H_{21}Cl_{6}N_{3}O</td>
<td>162...163.5</td>
<td>0.40(6)</td>
<td>1.50 4.86 7.27  —</td>
<td>92</td>
</tr>
<tr>
<td>XV</td>
<td>C_{20}H_{23}Cl_{6}N_{3}O</td>
<td>108...109</td>
<td>0.54(6)</td>
<td>1.65 4.98 7.15 3.90 (2H, CH_{2})</td>
<td>94</td>
</tr>
</tbody>
</table>

*Compounds recrystallized: IX from aqueous Methyl Cellosolve; X from petroleum ether; XII from aqueous ethanol; XIV from ethanol; XV from 1:3 acetone:hexane.

*2 Solvent for the system shown in parentheses.

*3 Spectra of compounds IX and XIV were taken in DMSO-D_{6}; of compounds X-XIII and XV, in CDCl_{3}.

*4 Yield of by-product sym-triazene VIII show in parentheses.

at 145-150°C. At the same time, sym-triazene VIII is formed in significant amounts (40-45% yield) along with desired sym-triazene IX.

We were not successful in increasing the yield of sym-triazene IX and lowering the yield of by-product VIII by changing the ratio of the reactants, prolonging the process, or using other catalysts (AlCl_{3} + HCl, BF_{3} etherate + HCl, ZnCl_{2} + HCl, SnCl_{4} + HCl). It should be noted that increasing the reaction temperature to 165-170°C led to the conversion of the entire reaction mixture to tar.

Presumably such a low yield of sym-triazene IX is due to the low reactivity of the cyano group in nitrile I [9].

The simultaneous cyclotrimerization of TCAN with nitriles II-V was carried out quite smoothly in the presence of gaseous HCl by the method previously developed [8] for the preparation of 6-aryl-2,4-bis(trichloromethyl)-sym-triazenes, using a TCAN:nitrile mole ratio of 1.5:1 in ether or chloroform at -5-0°C (2 h), holding the mixture at 20°C, and then heating it to 95-100°C. Under these conditions 6-substituted 2,4-bis(trichloromethyl)-sym-triazenes (X-XIII) were synthesized in 70-76% yields, although considerable amounts (12-15%) of by-product sym-triazene VIII were still isolated from the reaction mixtures. The yield of compound VIII rose to 20-25% when mixed acid catalysts (AlCl_{3} + HCl, BF_{3} etherate + HCl) were used in the reactions of TCAN with nitriles II-V.

It is known [10] that 2,4-bis(trichloromethyl)-6-alkyl(aryl)thio-sym-triazenes are readily formed by the simultaneous cyclotrimerization of TCAN with thiocyanates in the presence of AlBr_{3} and HCl gas. In the present work it was shown that thiocyanates VI and VII react with TCAN (1:2 mole ratio) in the presence of AlBr_{3} and gaseous HCl at -20-0°C to give the corresponding 2,4-bis(trichloromethyl)-6-thio-sym-triazenes (XIV, XV). Note that in the case discussed, not even a trace of by-product VIII was found in the reaction mixture.

\[ \text{Ar}-(\text{CH}_2)_n-\text{SCN} + 2 \text{Cl}_3\text{CCN} \xrightarrow{\text{HCl} + \text{AlBr}_3} \text{XIV, XV} \]

At \( n = 0 \); XIV \( n = 1 \).