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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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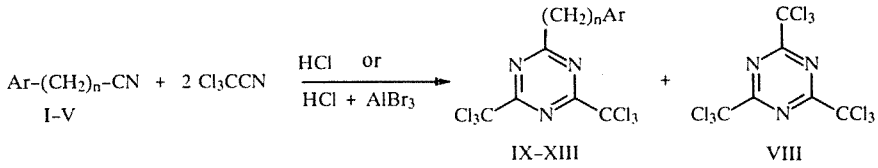
6-Substituted 2,4-bis(trichloromethyl)-sym-triazenes containing the 2,6-di-tert-butylphenol group are synthesized by simultaneous cyclotrimerization of trichloroacetonitrile with the nitrile or thiocyanate derivative of the sterically hindered phenol in the presence of gaseous HCl. Significant amounts 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 [6-8] 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.



I—III, IX—XI Ar = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$; IV, V, XII, XIII Ar = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$S; I, IX n = 0; II, IV, X, XII n = 1; III, V, XI, XIII n = 2

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 $AlBr_3$. 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 % $AlBr_3$), 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

Compound	Molecular formula	T_{mp}, °C*	R_f*2	PMR Spectra, δ, ppm*3				Yield, %*4
				t-Bu (18H, s)	OH (1H, s)	H_{arom} (2H, s)	other protons	
IX	$C_{19}H_{21}Cl_6N_3O$	208...210	0,64(a)	1,68	4,88	7,20	—	27 (45)
X	$C_{20}H_{23}Cl_6N_3O$	133...134,5	0,58(б)	1,56	4,92	7,32	3,65 (2H, с, CH_2)	75 (12)
XI	$C_{21}H_{25}Cl_6N_3O$	Oil (n_D^{20}1,4634)	0,49(б)	1,60	5,10	7,18	4,02...4,14 (4H, м, CH_2CH_2)	70 (15)
XII	$C_{20}H_{23}Cl_6N_3OS$	157...158	0,74(a)	1,70	4,95	7,34	3,92 (2H, с, CH_2)	72 (15)
XIII	$C_{21}H_{25}Cl_6N_3OS$	Oil (n_D^{20}1,4805)	0,52(a)	1,52	5,02	7,24	4,08...4,16 (4H, м, CH_2CH_2)	76 (13)
XIV	$C_{19}H_{21}Cl_6N_3OS$	162...163,5	0,40(б)	1,50	4,86	7,27	—	92
XV	$C_{20}H_{23}Cl_6N_3OS$	108...109	0,54(б)	1,65	4,98	7,15	3,90 (2H, с, CH_2)	94

*Compounds recrystallized: IX from aqueous Methyl Cellosolve; X from petroleum ether; XII from aqueous ethanol; XIV from ethanol; XV from 1:3 acetone:hexane.
*2Solvent for the system shown in parentheses.
*3Spectra of compounds IX and XIV were taken in DMSO-D_6; of compounds X-XIII and XV, in $CDCl_3$.
*4Yield of by-product sym-triazene VIII show in parentheses.

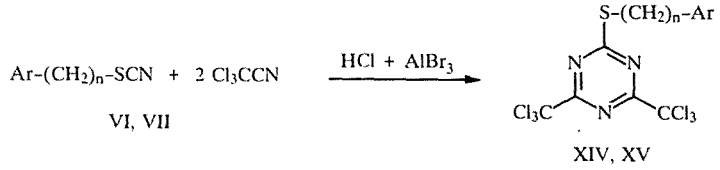
at 145-150°C. At the same time, sym-triazene VIII is formed in significant amounts (40-45% yield) along with desired sym-triazene IX.

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.



VI, VII

XIV, XV

Ar = 4-HO-3,5-*t*-$Bu_2C_6H_2$; VI, XIV n = 0; VII, XV n = 1

In the IR spectra of synthesized sym-triazenes VIII-XV, absorption maxima of varying intensities were found which could be assigned to stretching (1530-1520, 1410-1400 cm^{-1}), breathing (1110-1095, 1005-995 cm^{-1}), out-of-plane bending (805-790 cm^{-1}), and in-lane (705-685 cm^{-1}) bending vibrations of the sym-triazene ring [2-5, 8, 11, 12]. Intense absorption bands in the 780-770 cm^{-1} region correspond to the C–Cl stretching vibration [8]. Along with these vibrations, the spectra of compounds IX-XIII, XIV, and XV also have absorption bands due to the sterically hindered phenol group: a narrow band at 3655-3640 cm^{-1}, characteristic of a shielded hydroxyl [13]; two bands of medium intensity in the 1260-1210 cm^{-1} range attributed to Ar–OH stretching in shielded phenols [14], and two groups of bands in the 885-870 and 830-820 cm^{-1} region (out-of-plane bending vibrations of a tetrasubstituted benzene ring).

In the PMR spectra (see Table 1) sym-triazenes IX-XIII, XIV, and XV the signals from the hydroxyl protons occur as singlets in the 4.86-5.10 ppm range. This is characteristic of shielded phenols [13, 15]. Signals of the tert-butyl group protons are found as singlets in the 1.50-1.70 ppm region. Singlets at 7.15-7.34 ppm are due to the two magnetically shielded protons of the hydroxyaryl groups [2-5, 15].

EXPERIMENTAL

The IR spectra were taken on a Bruker IFS-48 instrument in a mineral oil suspension or in KCl tablets. The PMR spectra were obtained on a Bruker WP-80SY instrument, TMS internal standard. The course of the reactions was monitored and the purity of the compounds obtained checked by means of TLC on Brokman Al_2O_3 III st. act. in benzene–methanol solvent systems, 20:1 (a) and 30:1 (b), developed with iodine vapor. Melting points were determined on a Boetius microblock.

The elementary analyses of the compounds synthesized for C, H, Cl, and N agreed with the calculated values.

The nitriles of [3,5-di(tert-butyl)]-4-hydroxybenzoic (I) [16], [3,5-di(tert-butyl)]-4-hydroxyphenylacetic (II) [17], β-[3,5-di(tert-butyl)]-4-hydroxyphenyl]proprionic (III) [3], [3,5-di(tert-butyl)]-4-hydroxyphenylthioacetic (IV) [3], and β-[3,5-di(tert-butyl)]-4-hydroxyphenylthio]propionic (V) [3] acids as well as [3,5-di(tert-butyl)]-4-hydroxyphenylthiocyanate (VI) [18] and [3,5-di(tert-butyl)]-4-hydroxybenzylthiocyanate (VII) [3] were prepared by known methods.

6-[3,5-Di(tert-butyl)-4-hydroxyphenyl]-2,4-bis(trichloromethyl)-sym-triazene (IX). A current of dry HCl was passed into a stirred mixture of 2.88 g (12.5 mmoles) of nitrile I, 3.61 g (25 mmoles) of TCAN, and 0.33 g (1.25 mmoles) of $AlBr_3$ in 30 ml of dry ether at −10°C for 1 h. The reaction mixture was held for 12 h at 20°C, the solvent and excess HCl removed under reduced pressure, and the residue held for 12 h at 145°C. The dark mass that formed was washed with a 3% solution of $NaHCO_3$, then with water (2 × 15 ml), and extracted with hot acetonitrile (3 × 30 ml). The extract was dried with Na_2SO_4, concentrated to a volume of 10-12 ml and chromatographed on an Al_2O_3 column (110 × 5.0 cm). The initial nitrile, 0.38 g, (T_{mp} 145-146°C, 147°C according to [16]) was eluted with a benzene–acetone mixture (30:1), then 1.75 g (27%) of sym-triazene IX with a 20:1 benzene–methanol mixture and 1.62 g (45%) of sym-triazene VIII with a 5:1 benzene–methanol mixture. T_{mp} 93-94°C (from ethanol). R_f 0.77 (6). According to [8], T_{mp} is 94-95°C.

6-[3,5-Di(tert-butyl)-4-hydroxybenzyl]-2,4-bis(trichloromethyl)-sym-triazene (X). A current of dry HCl was passed into a stirred mixture of 3.67 g (15 mmoles) of nitrile II and 3.25 g (22.5 mmoles) of TCAN in 35 ml of dry chloroform at −5-0°C for 2 h. The reaction mixture was held for 12 h at 20°C, the solvent and excess HCl removed under reduced pressure, and the residue held for 2 h at 95-100°C. The reaction mixture was cooled to 20°C, extracted with ether (4 × 50 ml), and the extract washed with 3% $NaHCO_3$ (2 × 60 ml), then with water, and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the remaining oil chromatographed on an Al_2O_3 column (90 × 5.0 cm). The small amount of initial nitrile II was eluted with a 5:1 benzene–hexane mixture, then sym-triazene X is washed out with a 25:1 benzene–methanol mixture, and sym-triazene VIII with a 5:1 benzene–methanol mixture.

The sym-triazenes XI-XIII were synthesized in analogous fashion. Compounds XI and XIII were purified by further chromatography on a silica gel column with a 30:1 chloroform–acetone mixture as eluent.

6-[3,5-Di(tert-butyl)-4-hydroxyphenylthio]-2,4-bis(trichloromethyl)-sym-triazene (XIV). A current of dry HCl was passed into a stirred mixture of 4.7 g (18 mmoles) of thiocyanate VI, 5.2 g (36 mmoles) of TCAN, and 0.25 g (1 mmole) of $AlBr_3$ in 40 ml of dry ether at −20°C for 2 h. The reaction mixture was held for 12 h at 0°C, then for 24 h at 20°C. The solvent and excess HCl were removed under reduced pressure. The residue was held for 1 h at 110-120°C, cooled to 20°C, and crystallized from ethanol with the addition of activated charcoal.

In analogous fashion, 6-[3,5-di-tert-butyl)-4-hydroxybenzylthio]-2,4-bis(trichloromethyl)-sym-triazene (XV) was synthesized from thiocyanate VII.

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