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Application of the Study of Reactivity of Alkaline Salts of Isocyanuric Acid to the Synthesis of Mono- and Trisubstituted Isocyanurates

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APPLICATION OF THE STUDY OF REACTIVITY OF ALKALINE SALTS OF ISOCYANURIC ACID TO THE SYNTHESIS OF MONO AND TRISUBSTITUTED ISOCYANURATES

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Abstract : Reactivity of alkaline salts of isocyanuric acid has been studied. It has been established that the nucleophilic substitution is not selective because of the protonic exchanges between salts and substituted derivatives. The synthesis of mono or trisubstituted derivative is due to secondary reactions and to solvent effects. With this study, it has been possible to settle a method to prepare mono and trisubstituted derivatives of isocyanuric acid.

Isocyanuric acid derivatives have found a number of industrial applications. Thus N-chlorination of isocyanuric acid (ICA) leads to products that have gained wide acceptance as dry bleaches and sanitizers for use in dishwater formulations, industrial cleansers and in swimming pool desinfection.[1-3] The triallyl-[4-9] and tris(2-hydroxyethyl)[4,10,11] derivatives are employed as additives to impact

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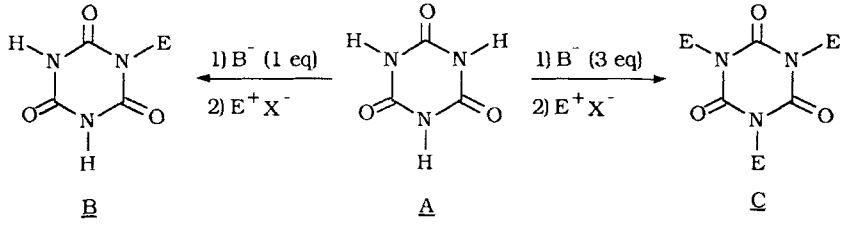
special properties to polyester resins. Tris(2,3-epoxypropyl) isocyanurate[12-16] is used in weather-resistant powder coatings.

From the literature data it appears that trisubstituted isocyanuric derivatives may be obtained by trimerization of the corresponding isocyanates[17-20] or by substitution, often under harsh conditions, of the unexpensive and easily handled ICA.[1,2,21] On the other hand monosubstitutions of isocyanuric acid are scarce.[4,22-25]

In the present publication we wish to report a number of results dealing with the selective condensation of electrophiles with alkali metal salts of ICA according to the reactions reported on the Scheme.



B A C

A systematic study,[26] which details are not reported here, led to the following conclusions.

- Compounds B may be obtained either from salts preformed in water and then added to an organic solvent (see experimental part) or from salts *in situ* prepared. Compounds C were conveniently obtained from *in situ* prepared salts.

- The formation of B or C did not take place in solvents such as tetrahydrofuran, dioxane, toluene, acetonitrile, diphenylsulfoxide or sulfolane.

- Aprotic solvents such as DMF, NMP, DMSO, TMU, DMAC and above all HMPA considerably favor acid-base reactions in such a way that mono salts of A easily abstract the protons of substituted derivatives such as B. In other words, starting from a mono salt in dipolar aprotic solvent, a very large amount of C was formed even in the presence of one equivalent of electrophile.

As a corollary HMPA appeared as well suited for the synthesis of C.

- Protic solvent such as acetamide and above all formamide did not favor acid-base exchanges and favor the formation of B from mono salt.

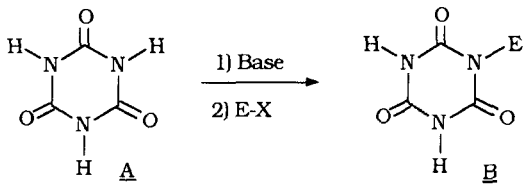
- The nature of the cation of the salts plaid also an important part in the selectivity of the condensations. Mono lithium salt appeared as weaker base than the corresponding sodium or potassium derivatives, and thus more prone to lead to B.

Taking in account the above observations a number of mono-substituted isocyanuric acid derivatives were prepared as reported in the Table I.

From these unprecedented results it appears that mono-substituted derivatives B may be obtained in reasonable yields under our conditions.

In a number of condensations a cosolvent was necessary in order to increase the rate of the condensation. In such cases the

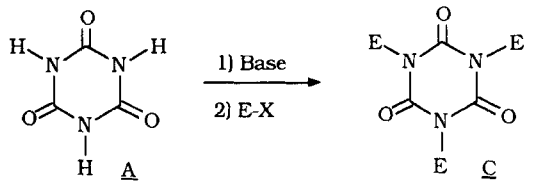
TABLE I



Base[a] or salt[b]	Solvent[c]	EX[d]	T°C	t (h)	Condensed ICA %	**B** %[e] Isolated	Purity %
LiOH, H_2O	FA	n-C_4H_9-I	100	1	63	**1** 59	~100
LiOH, H_2O	FA	n-C_6H_{13}-I	100	3	55	**2** 60	~100
LiOH, H_2O	FA	n-C_8H_{17}-I	100	12	67	**3** 31	~100
LiOH, H_2O	FA-HMPA	$C_6H_5CH_2Cl$	65	5	70	**4** 40	100
MLIC	NMF-FA	CH_2=C(CH_3)CH_2Cl	65	5	60	**5** 30	~100
LiOH, H_2O	FA	CH_2=CH-(CH_2)$_6$Br	100	6	67	**6** 36	90
MLIC	FA-HMPA	NC-(CH_2)$_6$-Br	65/85	5/1	78	**7** 21	~100
MLIC	FA-HMPA	MeOCO-(CH_2)$_4$-Cl	65/85/100	5/5/5	77	**8** 6	85
MLIC	NMF-FA	Me-CO-CH_2Cl	65	1	45	**9** 11	~100
LiOH, H_2O	FA	HO-(CH_2)$_8$-Br	100	6	60	**10** 20	~100

[a] Base/ICA = 1. [b] MLIC = Monolithium isocyanurate (1 eq.). [c] FA = Formamide, NMF = N-Methylformamide, HMPA = Hexamethylphosphoramide. [d] EX/ICA or salt = 1.2. [e] Calculated relatively to the non recovered ICA.

TABLE II



A C

Base	Solvent	EX	T°C	t (h)	C % Isolated	
NaH	HMPA	n-C_8H_{17}-Br	100	5	**11**	88
NaH	HMPA	n-C_8H_{17}-I	100	5	**11**	80
NaH	HMPA	$C_6H_5CH_2Cl$	100	3.5	**12**	80
LiOH, H_2O	HMPA	$C_6H_5CH_2Cl$	25	5	**12**	88
NaH	HMPA	CH_2=CH-CH_2Cl	100	3	**13**	70
LiOH, H_2O	HMPA	CH_2=CH-CH_2Cl	50	5	**13**	64
NaH	HMPA	CH_2=C(CH_3)-CH_2Cl	100	4	**14**	78
LiOH, H_2O	HMPA	CH_2=C(CH_3)-CH_2Cl	70	5.5	**14**	93
NaH	HMPA	HO-$(CH_2)_2$-Cl	100	7	**15**	56
NaH	HMPA	NC-CH_2-Cl	60-65	7	**16**	41
NaH	HMPA	EtO-CO-CH_2Cl	100	3	**17**	54
NaH	NMP	EtO-CO-CH_2Br	60-65	4.5	**17**	80

nature and above all the amount of the cosolvent must be chosen in such a way that acid-base reactions were not favored.

Finally we also prepared a number of trisubstituted derivatives C as reported in the Table II.

Compared with the literature data the yields obtained are good while sometimes a little bit lower. However the conditions used presently are generally less drastic.

EXPERIMENTAL

Materials. Fluka sodium hydride (60-65 %) in oil was titrated by standard techniques. It was used after three washings with heptane under nitrogen. $LiOH,H_2O$, halogenated sustrates and solvents were purchased from commercial source (Fluka) and were used without further purification. Isocyanuric acid was supplied by Elf-Atochem.

General methods. All melting points were determined with a Buchi 530 melting point apparatus. Infrared spectra were recorded on a Nicolet FTIR 730 spectrophotometer. ^1H and ^{13}C NMR were obtained on a Bruker AC 200 instrument (200 MHz for ^1H and 50 MHz for ^{13}C). HPLC analysis were performed on a Waters 501 apparatus (UV detector) equipped with a Lichrospher 60 RP-Select B (5 mm) with water-acetonitrile mixture as eluent. Molecular masses were determined on a Finnigan Mat 95Q apparatus, by direct introduction and chemical ionization with isobutane.

Yields of mono, di and trisubstituted derivatives were determined by ^{13}C NMR analysis before further isolation and purification.

Synthesis of monosubstituted derivatives

Method A. A 0.1 mole $LiOH,H_2O$ was added to a suspension of ICA (0.1 mole) in water (50 ml) at 60°C. The reaction medium was stirred at 100°C for 3 hours, then cooled to room temperature, filtered, and the solid dried 24 hours at 110°C. 0.1 mole lithium monosalt was added to 150 ml of formamide or a mixture formamide-HMPA or formamide-N-methylformamide (75/25) and the suspension stirred at the desired temperature (Table I). The electrophile was added to the reaction medium and the reaction monitored by HPLC analysis of small aliquots and pH measurement after hydrolysis. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue washed with cold water.

Method B. 0.1 mole $LiOH,H_2O$ was added to a suspension of ICA (0.1 mole) in 150 ml of formamide or a mixture formamide-HMPA or N-methylformamide and the mixture stirred for 1 hour at 65°C. The condensation of the electrophile was then pursued like in method A.

Products 1, 2, 7, 8, 9, and 10. The reaction products were extracted with acetone. After evaporation of the solvent it was extracted with hot water and filtered. Water was then evaporated, and the product extracted with diethyl ether. We proceded then to the evaporation of diethyl ether.

Products 3 and 6. They were extracted with diethyl ether and recrystallized from water.

Product 4. The reaction product was washed with acetone. The acid fonctions of ICA, mono and dibenzylisocyanurates were neutralized with NaOH in water. HCl 1N was then slowly added. As soon as a precipitate appeared, it was filtered and neutralized if necessary. We added HCl till the pH of the medium was less than 6. Monobenzyl isocyanurate was thus separated.

Product 5. The reaction product was extracted with acetone and recrystallized from water.

Monobutyl isocyanurate (**1**): mp 226°C (lit; 226). ^{1}H NMR (DMSO-D_6) (δ ppm): 0.86 (t, 3 H); 1.25 (m, 2 H); 1.47 (m, 2 H); 3.61 (t, 2 H); 11.24 (s, 2 H). ^{13}C NMR (DMSO-D_6) (δ 1ppm): 149.9 (C=O); 148.8 (C=O); 40 (CH_2N); 29.5 (CH_2); 19.5 (CH_2); 13.6 (CH_3). IR (KBr): 3440-3085 cm^{-1} (ν NH); 2962-2793 cm^{-1} (ν CH_3, CH_2); 1771-1684 cm^{-1} (ν CO); 1465 cm^{-1} (δ CH_3, CH_2); 1417 cm^{-1} (δ NH). Experimental mass: 186.0878 (theo. 186.0515).

Monohexyl isocyanurate (**2**): mp 226°C (lit; 226). ^{1}H NMR (DMSO-D_6) (δ ppm): 0.84 (t, 3 H); 1.6-1.1 (m, 8 H); 3.6 (t, 2 H); 11.14 (s, 2 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 150.1 (C=O); 149.1 (C=O); ~40 (CH_2N); 31.0 (CH_2); 27.5 (CH_2); 25.9 (CH_2); 22.0 (CH_2); 13.9 (CH_3). IR (KBr): 3417-3086 cm^{-1} (ν NH); 2960-2829 cm^{-1} (ν CH_3, CH_2); 1768-1691 cm^{-1} (ν CO); 1462 cm^{-1} (δ CH_3, CH_2); 1414 cm^{-1} (δ NH). Experimental mass: 214.1189 (theo. 214.1192).

Monooctyl isocyanurate (**3**): mp 217°C. ^{1}H NMR (DMSO-D_6) (δ ppm): 0.85 (t, 3 H); 1.2-1.45 (m, 12 H); 3.58 (t, 2 H); 11.35 (s, 2 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 149.7 (C=O); 148.5 (C=O); 42.6 (CH_2N); 31.5 (CH_2); 28.9 (2 CH_2); 27.5 (CH_2); 26.4 (CH_2); 22.4 (CH_2); 13.7 (CH_3). IR (KBr): 3200-3088 cm^{-1} (ν NH); 2960-

2850 cm^{-1} (ν CH_3, CH_2); 1772-1684 cm^{-1} (ν CO); 1463 cm^{-1} (δ CH_3, CH_2); 1418 cm^{-1} (δ NH). Experimental mass: 242.1505 (theo. 242.1505).

Monobenzyl isocyanurate (**4**): mp 263°C (lit. 245°C). ^1H NMR (DMSO-D_6) (δ ppm): 4.81 (s, 2 H); 7.3 (m, 5 H); 11.48 (s, 2 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 43.5 (CH_2N); 127.3 (CH arom.); 127.4 (CH arom.); 128.4 (CH arom.); 136.8 (C arom.); 148.7 (C=O); 150 (C=O). IR (KBr): 3241 cm^{-1} (ν NH); 3100 cm^{-1} (ν =C-H); 2963 cm^{-1} (ν CH_2); 1771-1692 cm^{-1} (ν C=O); 1467-1424 cm^{-1} (ν C=C); 740 and 698 (δ CH monosubstitution).

Monomethallyl isocyanurate (**5**): mp 232°C. ^1H NMR (DMSO-D_6) (δ ppm): 11.5 (s, 2 H); 4.76 (m, 1 H); 4.66 (m, 1 H); 4.11 (s, 2 H); 1.67 (s, 3 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 149.8 (C=O); 148.7 (C=O); 139.6 (C=); 109.9 (CH_2=); 45.2 (CH_2N); 20.2 (CH_3). IR (KBr): 3213 cm^{-1} (ν NH); 3091 cm^{-1} (ν =CH); 2990 cm^{-1} (ν CH_3, CH_2); 1765-1692 cm^{-1} (ν C=O); 1460 cm^{-1} (δ CH_3, CH_2); 1410 cm^{-1} (δ NH). Experimental mass: 184.0721 (theo. 184.0722).

Mono(octene-8)isocyanurate (**6**): mp 187-9°C. ^1H NMR (DMSO-D_6) (δ ppm): 1.2 (m, 6 H); 1.45 (m, 2 H); 2.0 (m, 2 H); 3.6 (t, 2 H); 4.9 (m, 2 H); 5.75 (m, 1 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 149.0 (C=O); 150.1 (C=O); 138.9 (CH=); 114.7 (CH_2); 40.3 (CH_2N); 34-26 (5 CH_2). IR (KBr): 3440-3086 cm^{-1} (ν NH et ν =CH_2); 2923-2995 cm^{-1} (ν CH_2); 1773-1665 cm^{-1} (ν CO); 1467 cm^{-1} (δ CH_2); 1417 cm^{-1} (δ NH). Experimental mass: 240.1344 (theo. 240.1348).

Mono(heptyl-7-nitrile)isocyanurate (**7**): mp 173°C. ^1H NMR (DMSO-D_6) (δ ppm): 11.37 (s, 2 H); 3.61 (t, 2 H); 2.46 (t, 2 H); 1.7-1.1 (m, 8 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 149.9 (C=O); 148.9 (C=O); 120.8 (CN); 40.3 (CH_2N); 27.8 (CH_2); 27.2 (CH_2); 25.4 (CH_2); 24.7 (CH_2); 16.16 (CH_2). IR (KBr): 3208-3086 cm^{-1} (ν NH); 2939-2793 cm^{-1} (ν CH_2); 2200 cm^{-1} (ν CN); 1771-1687 cm^{-1} (ν C=O);

1468 (δ CH_2); 1419 cm^{-1} (δ NH). Experimental mass: 239.1143 (theo. 239.1144).

Mono(methylvalerate)isocyanurate (**8**): mp 166°C. ^1H NMR (DMSO-D_6) (δ ppm): 11.3 (s, 2 H); 3.61 (m, 2 H); 3.56 (s, 3 H); 2.31 (m, 2 H); 1.5 (m, 4 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 173.4 (COO); 150.1 (C=O); 148.9 (C=O); 51.4 (OCH_3); 40.2 (CH_2N); 33.0 (CH_2-COO); 27.0 (CH_2CH_2N); 21.7 (CH_2CH_2OO). IR (KBr): 3441-3086 cm^{-1} (ν NH); 2958-2788 cm^{-1} (ν CH_3, CH_2); 1768-1666 cm^{-1} (ν C=O); 1466 cm^{-1} (δ CH_3, CH_2); 1415 cm^{-1} (δ NH); 1200 cm^{-1} (ν C-O). Experimental mass: 244.0932 (theo. 244.0933).

Mono(2-ketopropyl)isocyanurate (**9**): mp 288°C (decomp.). ^1H NMR (DMSO-D_6) (δ ppm): 11.6 (s, 2 H); 4.54 (s, 2 H); 2.16 (s, 3 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 202.2 (C=O); 150.0 (C=O); 149.1 (C=O); 49.9 (CH_2N); 27.2 (CH_3). IR (KBr): 3432-3089 cm^{-1} (ν NH); 2959-2795 cm^{-1} (ν CH_3, CH_2); 1716 cm^{-1} (ν C=O); 1471 cm^{-1} (δ CH_2, CH_3); 1411 cm^{-1} (δ NH); 1357 cm^{-1} (ν C-C of $COCH_3$); 1179 cm^{-1} (δ CH_3 of $COCH_3$). Experimental mass : 186.0510 (theo. 186.0515).

Mono(octanol-8)isocyanurate (**10**): mp : 177-9°C. ^1H NMR (DMSO-D_6) (δ ppm): 11.3 (s, 2 H); 4.31 (t, 1 H); 3.60 (t, 2 H); 3.32 (m, 2 H); 1.7-1.0 (m, 12 H). ^{13}C NMR (DMSO-D_6) (δ ppm): 149.7 (C=O); 148.5 (C=O); 60.7 (CH_2OH); ~40 (CH_2N); 32.4 (CH_2); 28.7 (CH_2); 28.6 (CH_2); 27.2 (CH_2); 26.0 (CH_2); 25.3 (CH_2). IR (KBr): 3409 cm^{-1} (ν OH); 3212-3087 cm^{-1} (ν NH); 2931-2854 cm^{-1} (ν CH_2); 1769-1691 cm^{-1} (ν C=O); 1462 cm^{-1} (δ CH_2); 1415 cm^{-1} (δ NH); 1057 cm^{-1} (ν C-O). Experimental mass: 258.1453 (theo. 258.1454).

Synthesis of trisodium isocyanurate. ICA (0.05 mole) was added to a suspension of NaH (0.15 mole) in 200 ml HMPA or 150 ml NMP under N_2 atmosphere at room temperature. After stirring for 1 hour, the reaction medium was heated at 100°C for 3 hours.

Synthesis of trilithium isocyanurate. LiOH, H_2O (0.15 mole) was added to a suspension of ICA (0.05 mole) in 150 ml HMPA at 65°C and then stirred for 4 hours at 100°C.

Reaction with the electrophile. 0.15 mole of the electrophile was added slowly at the desired temperature and the reaction monitored with HPLC analysis and pH measurement. Upon completion of the reaction, the solvent was evaporated under vacuum.

Product 11. The reaction product was dissolved in CH_2Cl_2 and filtered. The organic phase was washed with water, dried over Na_2SO_4 and evaporated.

Product 12. The residue was washed with water. It was extracted with acetone and filtered. Acetone was then evaporated.

Product 13. Same procedure than for **11**, CH_2Cl_2 being replaced by trichlorethylene.

Product 14. Same procedure than for **11**, CH_2Cl_2 being replaced by diethyl ether, and recrystallization from MeOH.

Product 15. The residue was washed with diethyl ether and extracted with hot isopropyl alcohol. After cooling, the precipitate was filtered, washed with cold isopropyl alcohol and dried.

Product 16. The residue was washed with hot water, diethyl ether, and recrystallized from DMF or acetonitrile.

Product 17. The residue, washed with water, diethyl ether, was extracted with acetone, fltered, evaporated and recrystallized from EtOH.

Trioctyl isocyanurate (**11**): ^{1}H NMR (DMSO-D6) (δ ppm): 0.7-1 (t, 9 H); 1.1-1.5 (m, 30 H); 1.5-1.8 (m, 6 H); 3.2-3.9 (m, 6 H). ^{13}C NMR (DMSO-D6) (δ ppm): 148.7 (C=O); 42.6 (CH_2-N); 31.5 (CH_2); 28.9 (CH_2); 27.5 (CH_2); 26.4 (CH_2); 22.4 (CH_2); 13.7 (CH_3). IR (KBr): 1693 cm^{-1} (ν C=O); 2955-2856 cm^{-1} (ν CH_3, CH_2); 1463 cm^{-1} (δ CH_3, CH_2).

Tribenzyl isocyanurate (**12**): mp : 162°C (lit. 161-3°C). ^{1}H NMR (DMSO-D6) (δ ppm): 5.0 (s, 6 H); 7.3 (m, 15 H). ^{13}C NMR (DMSO-D6) (δ ppm): 45.4 (CH_2N); 127.1-128.0 (CH arom.); 136.1 (C arom.); 148.9 (C=O). IR (KBr): 3080-3033 cm^{-1} (ν =CH); 2967-2852 cm^{-1} (ν CH_2); 1687 cm^{-1} (ν C=O); 1452 cm^{-1} (ν C=C); 748, 695 cm^{-1} (δ CH monosubstitution).

Triallyl isocyanurate (**13**): mp : 20°C (lit. 19-22°C). ^{1}H NMR (DMSO-D6) (δ ppm): 5.83 (m, 3 H); 5.19 (m, 3 H); 5.10 (m, 3 H); 4.34 (d, 6 H). ^{13}C NMR (DMSO-D6) (δ ppm): 44.2 (CH_2N); 116.7 (CH_2=); 131.9 (CH=); 148.3 (C=O). IR (KBr): 3085 and 3017 cm^{-1} (ν =CH); 2956 cm^{-1} (ν CH_2); 1510-1456 cm^{-1} (δ CH_2); 1691 cm^{-1} (ν C=O); 993 and 933 cm^{-1} (δ CH).

Trimethallyl isocyanurate (**14**): mp : 83-4°C (lit. 85-6°C). ^{1}H NMR ($CDCl_3$) (δ ppm): 1.75 (s, 9 H); 4.44 (s, 6 H); 4.88 (m, 3 H); 4.72 (m, 3 H). ^{13}C NMR ($CDCl_3$) (δ ppm): 20.2 (CH_3); 47.5 (NCH_2); 111.1 (CH_2=); 138.8 (C=); 149.5 (C=O). IR (KBr): 3084 cm^{-1} (ν =CH); 2989-2856 cm^{-1} (ν CH_3 and CH_2); 1686 cm^{-1} (ν C=O); 1454-1374 cm^{-1} (δ CH_3, CH_2).

Tris(2-hydroxyethyl)isocyanurate (**15**): mp : 135°C (lit. 134-6°C). ^{1}H NMR (DMSO-D6) (δ ppm): 3.8 (t, 6 H); 3.5 (m, 6 H); 4.76 (t, 3 H). ^{13}C NMR (DMSO-D6) (δ ppm): 149.2 (C=O); 57.6 (CH_2-OH); 44.3 (-CH_2-). IR (KBr): 3481-3264 cm^{-1} (ν OH); 2972-2884 cm^{-1} (ν CH_2); 1684 cm^{-1} (ν C=O); 1468 cm^{-1} (δ CH_2); 1059 cm^{-1} (ν C-O).

Tricyanomethyl isocyanurate (**16**): mp : 174°C. ^{1}H NMR (DMSO-D6) (δ ppm): 4.88 (s). ^{13}C NMR (DMSO-D6) (δ ppm): 30.6 (CH_2); 114.9 (CN); 147.3 (C=O). IR (KBr): 2987 cm^{-1} (ν CH_2); ~2200 cm^{-1} (ν CN); 1700 cm^{-1} (ν C=O); 1452 cm^{-1} (δ CH_2).

Tris(carbethoxymethyl)isocyanurate (**17**): mp : 75°C (lit. 71-8°C). ^{1}H NMR (DMSO-D6) (δ ppm): 4.58 (s, 6 H); 4.14 (q, 6 H); 1.19 (t, 9 H). ^{13}C NMR (DMSO-D6) (δ ppm): 166.9 (C=O); 148.0 (N-C=O); 61.3 (O-CH_2); 43.4 (N-CH_2); 13.8 (CH_3). IR (KBr): 2985 cm^{-1} (ν CH_3, CH_2); 1755-1700 cm^{-1} (ν C=O); 1474 cm^{-1} (δ CH_2); 1211 cm^{-1} (ν C-O).

References

1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley, New York, **1983** *7*, 397.
2. Weigert, W.; Duesing, G.; Kriebitzsch, N.; Pfleger, H., *Ullmanns Encykl. Tech. Chem.*, **1975**, *9*, 647-54.
3. Westfall, R.H. *US Pat* 2,969,360, 24 Jan. 1961.
4. Frazier, T.C.; Little E.D.; Lloyd, B.E., *J. Org. Chem.*, **1960**, *58*, 1944.
5. Frazier, T.C.; Sherman, B.H. *US Pat* 3,065,231, 20 Nov. 1962.
6. Tazuma, J.J.; Miller, R. *US Pat* 3,075,979, 29 Jan. 1963.
7. Sugai Kioyoshi, Takeuchi Ichiro, *Japan* 68 29,395, 17 Dec. 1968.
8. Kitano Hisao, Tamimoto Fumio, *Chem. Econ. Eng. Rev.* ***1971***, *3(3)*, 42-5, 52.
9. Kojima Shigeki, *Japan Kokai* 73 23,790, 27 May 1973.
10. Saygh, A.A., Ulrich, H., *J. Chem. Soc.*, **1961**, 3148.

11. Cummins, R.W., *J. Org. Chem.*, **1963**, *28*, 85-89.

12. Cooke, H.G., *US Pat* 2,809,942, 15 Oct. 1957.

13. Price, H.P.; Schroll, G.E., *J. Org. Chem.*, **1967**, *32*, 2005.

14. Price, H.P., *US Pat* 3,910,908, 7 Oct. 1975.

15. Aramaki Masato, Nakano K. Kazuo, Fujita Takao, *Japan Kokai* 76 13,784, 3 Fev. 1976.

16. Wende, A.; Priebe, H., *Brev. Fr.* 1,394,438, 2 avril 1965.

17. Juenge, F.C.; Francis, W.C., *J. Org. Chem.*, **1961**, *26*, 3334-7.

18. Bortnick, N.; Luskin, L.S.; Hurwitz, M.D.; Rytina, A.W., *J. Amer. Chem. Soc.*, **1956**, *78*, 4358-61.

19. Kaiser, D.W.; Greenwich, O., *Us Pat* 2,536,849, 2 Jan. 1951.

20. Etienne, A.; Bonte, B.; Druet, B., *Bull. Soc. Chim. Fr.*, **1972**, 251-7.

21. Smolin, E.M.; Rapoport, L., *The Chemistry of Heterocyclic Compounds*, vol. 13, A. Weissberger, ed., Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1967, 17-146.

22. Milstein, N., *Chem. Eng. Data*, **1968**, *13*, 275.

23. Meis, H.; Sauer, H., *Us Pat* 2,830,051, 8 avril 1958.

24. Winkley, M.W.; Robins, R.K., *J. Org. Chem.*, **1970**, *35*, 491-5.

25. Richard, B.; Richard, M.; Lenzy, M., *Bull. Soc. Chim. Fr.*, **1990**, *127*, 461-7.

26. Chiron-Charrier, M.; *Thèse de Doctorat de l'Université de Nancy I en chimie et physicochimie moléculaires*, 1992.

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