Synthesis of Dimers and Trimers of Benzyl Isocyanates

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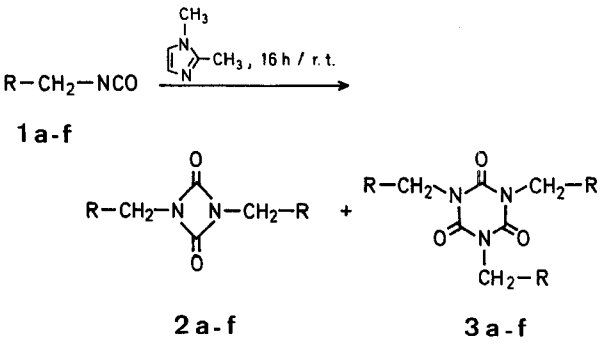
Aromatic isocyanates are known to dimerize readily in the presence of certain specific catalysts to give 1,3-diaryldiazetidine-2,4-diones[1]. Similar dimerizations of aliphatic isocyanates are not common and have so far only been described in a patent claiming the tributylphosphine-catalyzed conversion of certain aliphatic isocyanates into dimers and trimers in low yield (below 10%)[2]. Other aliphatic isocyanate dimers and mixed dimers of aliphatic and aromatic isocyanates have been synthesized via different routes[3,4].

We now wish to report that a number of benzyl isocyanates can readily be converted to mixtures of dimers and trimers in an approximate ratio of 8 : 2, using 1,2-dimethylimidazole[5] as the catalyst. On standing of a mixture of benzyl isocyanate (**1a**) and catalyst (ratio of 10 : 1) at room temperature for 16 h, complete conversion of **1a** and formation of 76% 1,3-dibenzyldiazetidine-2,4-dione (**2a**) and 24% 1,3,5-tribenzyl isocyanurate (**3a**) is observed. Other 2-, 3- and 4-substituted benzyl isocyanates give similar mixtures.

Monitoring the conversion of 4-chlorobenzyl isocyanate (**1e**) to **2e** and **3e** by I.R. (disappearance of the OCN band) revealed that the oligomerization is complete after 2 h, while 3-methoxybenzyl isocyanate (**1d**) is not completely converted even after 40 h.

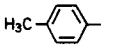
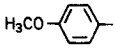
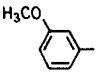
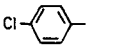
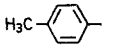
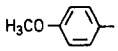
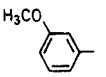
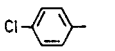
The reaction mixtures can readily be separated into dimers and trimers by repeated recrystallization from isopropyl alcohol and chloroform or *n*-hexane. Yields of all products **2** and **3**, as given in the Table, are determined by gel permeation chromatography and are approximate[6].

The I.R. spectra (in chloroform) of the benzyl isocyanate dimers **2a–f** show one characteristic carbonyl band at 1765 to



1775 cm^{-1}; aryl isocyanate dimers also absorb in this region. Molecular weight determination by vapor pressure osmometry gave the expected values for the dimers. The I.R. spectra of the trimers **3a–e** show one carbonyl absorption at 1680 to 1685 cm^{-1}; only **3f** shows a band at 1700 cm^{-1} with a weaker shoulder at 1685 cm^{-1}.

Table. Dimerization and Trimerization of Benzyl Isocyanates (**1a–f**)

Pro	R	M.p.	Yield (%)	I.R. (cm^{-1})[c] $\nu_{C=O}$	M.W.[d] (calc.)
Dimers					
2a		92–93°	76	1770	264 (266.3)
2b		140°	87	1765	300 (294.3)
2c		93–94°	82	1770	— (326.3)
2d		57–58°	40[a]	1775	330 (326.3)
2e		162–163°	81[b]	1775	350 (335.2)
2f		108–109°	80	1775	— (335.2)
Trimers					
3a		165°	24	1685	
3b		220–222°	13	1680	
3c		135–136°	18	1685	
3d		125–127°	32[a]	1685	
3e		221–222°	19[b]	1680	
3f		172–173°	20	1700/ 1685 (sh)	

[a] Measured after 40 h, remainder **1d**.
[b] Measured after 2 h.
[c] In $CHCl_3$.
[d] Determined by vapor pressure osmometry in $CHCl_3$.

On extending the reaction duration beyond the arbitrarily chosen 16 h, slow conversion of the dimers into trimers is observed (by G.P.C. and I.R.). Thus the yield of the benzyl isocyanate dimer **2a** drops from 76% after 16 h to 71% after 48 h, with a corresponding increase of yield of the trimer **3a**. A similar increase in the amount of the trimer **3d** in relation to **2d** was observed on monitoring the oligomerization of **1d**.

General Procedure for the Preparation of 1,3-Dibenzyl-diazetidine-2,4-diones (2a–f) and 1,3,5-Tribenzyl Isocyanurates (3a–f):

A mixture of the benzyl isocyanate, **1a–c, e,** and **f,** (5 g) and 1,2-dimethylimidazole (0.5 g) is kept for 16 h at room temperature. Crystals soon start to separate from the mixture, finally resulting in a complete solidification of the reaction mixture. The progress of the oligomerization can be followed by monitoring the disappearance of the NCO band at ~2270 cm^{-1} in the infrared spectrum.

G.P.C. analyses of reaction products[6] are used for yield determination, since separation of the compound mixtures by recrystallization leads to considerable loss of material.

The solid reaction products are recrystallized from a small amount of isopropyl alcohol, giving crude dimers **2a–c, e,** and **f,** which can be further purified by crystallization from the same solvent or a small amount of chloroform. The trimers **3a–c, e,** and **f** are enriched in the mother liquor and can be purified, after solvent evaporation, by recrystallization from chloroform/methanol.

The *3-methoxybenzyl isocyanate* (**1d**) oligomerization is much slower and was terminated after 48 h, giving a syrupy, semi-solid reaction mixture which is recrystallized from isopropyl alcohol. A crude oligomer mixture containing about equal amounts of **2d** and **3d** is obtained which on repeated recrystallination from methanol gives pure **3d**, leaving a mother liquor from which crude **2d** is isolated and purified by recrystallization from *n*-hexane.

Melting points, yields and carbonyl absorptions of **2a–f** and **3a–f** are listed in the table.

All pure dimers (colorless plates) and trimers (colorless needles)[7] gave satisfactory elemental analyses[8] and the dimers show correct values in the molecular weight determination by vapor pressure osmometry in chloroform.

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[1] See H. Ulrich, *Cycloaddition Reactions of Heterocumulenes*, Academic Press, New York, 1967, page 122.
[2] *French Patent* 1532054 (1968) to Farbenfabr. Bayer A.G.; *C.A.* **71**, 81328 (1969).
[3] H. Helfert, E. Fahr, *Angew. Chem.* **82**, 362 (1970); *Angew. Chem. Internat. Edit.* **9**, 372 (1970).
[4] J. C. Stowell, F. D. Green, W. R. Bergmark, *J. Org. Chem.* **36**, 3056 (1971).
[5] This compound was also found to be an excellent catalyst for the dimerization of aromatic isocyanates.
[6] The response of each pure dimer and trimer is used as standard for the yield calculation in the mixtures.
[7] Samples of each of the benzyl isocyanate trimers **3a–f** can also conveniently be prepared by potassium *t*-butoxide catalyzed trimerization of **1a–f**.
[8] Elemental analysis and molecular weight determination were made by Galbraith Laboratories Inc., Knoxville, Tenn.