Catalysis Letters 3 (1989) 413–420

BIS(ETHYL-3-OXO-BUTANOLATO-O^1, O^3)-BIS(2-PROPANOLATO) TITANIUM (TYZOR DC^R) AS A REACTANT AND CATALYST IN THE TRIMERIZATION OF 2-ISOCYANATOETHYL METHACRYLATE (IEM)

John C. GRAHAM, Xinmin XU and Margarita ORTICOCHEA

Eastern Michigan University, Coatings Research Institute, Ypsilanti, MI 48197, U.S.A.

Received 15 June 1989; accepted 8 August 1989

The reaction of bis(ethyl-3-oxo-butanolato-O^1, O^3)-bis(2-propanolato)titanium (Tyzor DC^R) and 2-isocyanatoethyl methacrylate (IEM) in different molar ratios, at room temperature produced the trimer of IEM in high yields with ethyl acetoacetate, isopropyl acetoacetate, and titanium dioxide, which are derived from Tyzor DC^R, as by-products. The reaction products were identified by FTIR, ^{1}H NMR, ^{13}C NMR, G.C. and M.S. procedures. The study showed that Tyzor DC^R acts as a catalyst in this reaction.

Titanium alkyl catalyst, homogeneous trimerization

1. Introduction

Insertion reactions involving metalloids, such as titanium (IV) alkoxides, with isocyanates and other cumulenes are well known yielding a variety of products involving multiple insertion reactions as outlined below [1]:

$$M(OR)_n + mR^1NCO \rightarrow (RO)_{n-m}M[N(R^1)CO_2R]_m. \qquad (1)$$

In addition, the formation of isocyanate trimers (isocyanurates) has been observed using metalloids and organo-metallic complexes as catalysts [2].

In this investigation [3], we have reacted the title compounds (I and II) varying the ratio from 1 : 4 to 1 : 32 in hexane at room temperature and recovered cyclic trimer (III) in high yields with no polymerization of the methacrylate double bond. In refluxing hexane, the nylon-1 polymer (VI) of IEM is recovered [4].

2. Experimental

The reactants, Tyzor DC^R (I) and 2-isocyanatoethyl methacrylate (II) were obtained from DuPont and Dow, respectively, and used without further purification. Hexane and chloroform were dried over $MgSO_4$ overnight and distilled before using.

A measured amount of Tyzor DC^R (I) was dissolved in dried hexane. Twenty milliliters of IEM (II) were added dropwise to this solution with stirring and the reaction temperature maintained at room temperature for 3 days. The products, which are insoluble in hexane, precipitated from the reaction medium and were removed by filtration. This solid mixture which contains cyclic trimer (III) and titanium dioxide was washed with chloroform and filtered to separate the soluble trimer from the insoluble material. Recrystallization from chloroform yielded the trimer (MP 83–5 ° C) which was characterized by FTIR, ^{1}H NMR and ^{13}C NMR. FTIR and NMR analysis were performed using IBM Model 44 and Bruker 360 MHz instruments, respectively.

3. Results and discussion

The reaction of Tyzor DC^R (I) and 2-isocyanatoethyl methacrylate (II) in ratios varying from 1 : 4 to 1 : 32 has been studied at room temperature. Unlike the work previously reported by Meth-Cohn [1c], Tyzor DC^R (I) was found to function as a catalyst at levels as low as 3% (by weight) generating cyclic trimer (III) in high yields (table 1). By-products ethyl acetoacetate (IV) and isopropyl acetoacetate (V), indicating hydrolysis and extensive scrambling of the substituent groups of the Tyzor DC^R molecule, were also observed in small amounts. The reaction is outlined in scheme 1.

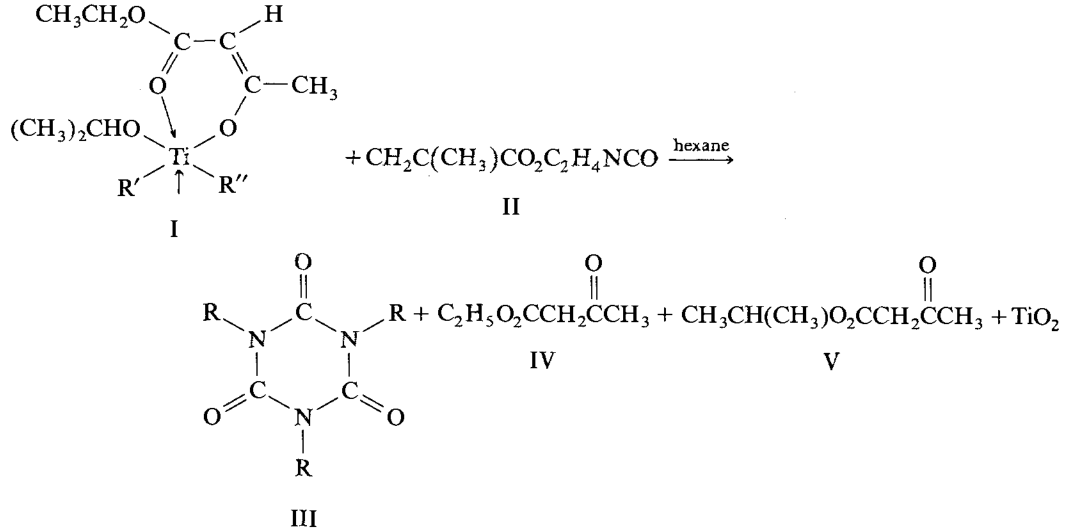
The trimer (III) has a molecular weight of 465 by chemical ionization mass spectrometry. Its infrared spectrum exhibited vibrations at 2977, 2927 and 2857 cm^{-1} due to the presence of the methyl and methylene groups, a carbonyl vibration due to the six membered ring at 1693 cm^{-1}, a carbonyl vibration

Table 1

Product yields as a function of reaction ratio for the reaction of Tyzor DC^R with 2-isocyanatoethyl methacrylate (IEM) at room temperature

Tyzor DC^R (mole)	0.035	0.0175	0.0088	0.0044
IEM (mole)	0.141	0.141	0.141	0.141
Tyzor DC^3: IEM molar ratio	1:4	1:8	1:16	1:32
Trimer (moles) [a]	0.045 (0.135)	0.046 (0.138)	0.045 (0.135)	0.044 (0.132)
Trimer yield	96%	99%	96%	94%
Ethyl aceto-acetate (moles)	0.032	0.014	0.008	0.004
Isopropyl aceto-acetate (moles)	0.023	0.010	0.006	0.004

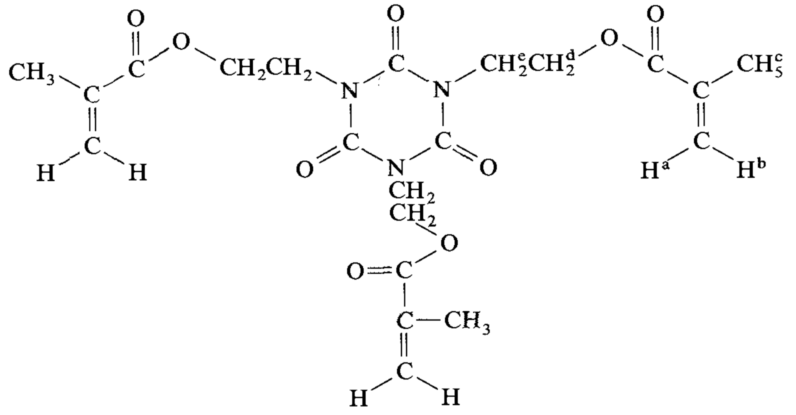
[a] Moles of isocyanate is parenthesis.



Where: $R'' = —OC(CH_3)CHCO_2CH_2CH_3$
$R' = —OCH(CH_3)_2$
$R = —C_2H_4O_2CC(CH_3)CH_2$

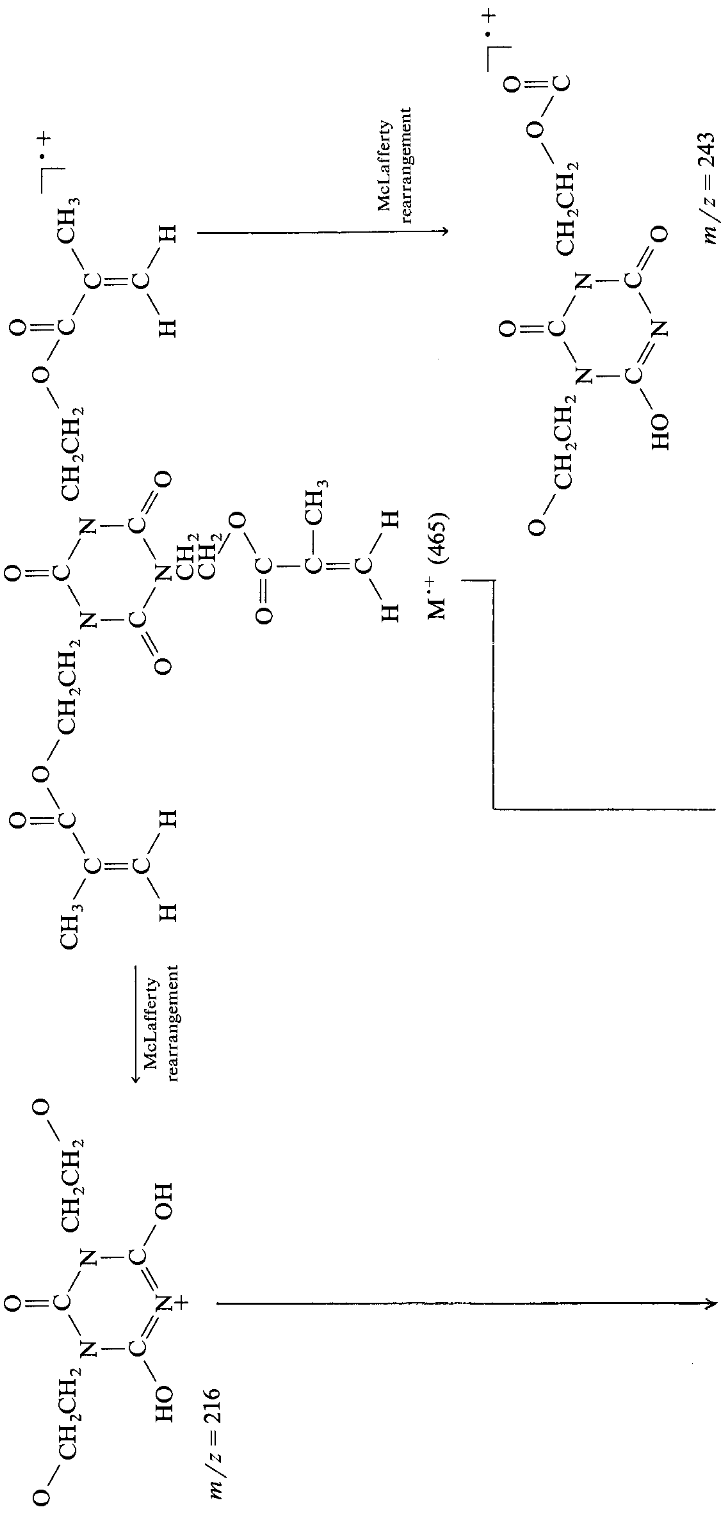
Scheme 1. Reaction of Tyzor DC^R with isocyanatoethyl methacrylate at room temperature in hexane.

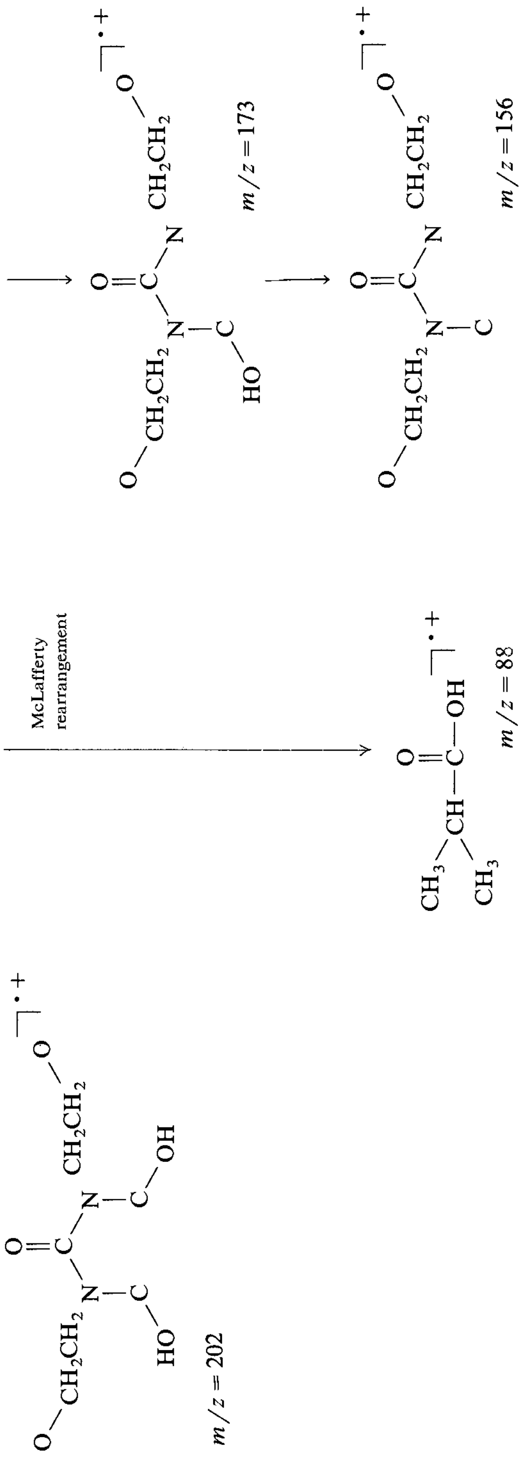
assignable to the methacrylate group at 1720 cm^{-1}, and a carbon-carbon double bond vibration at 1638 cm^{-1}. The ^1H NMR spectrum of the trimer showed the chemical shift of the methylene group downfield from the position of the isocyanatoethyl methacrylate equivalent group owing to the formation of the conjugated ring, which functions to withdraw electrons from the neighboring



Proton	Field position	Integration
a	6.07 ppm	a 0.98
b	5.56 ppm	b 1.0
c	1.90 ppm	c 2.96
d	4.35 ppm	d 2.10
e	4.23 ppm	e 2.11

Scheme 2. Interpretation of the ^1H NMR of the trimer.


McLafferty rearrangement
McLafferty rearrangement
M·+ (465)
m/z = 243
m/z = 216

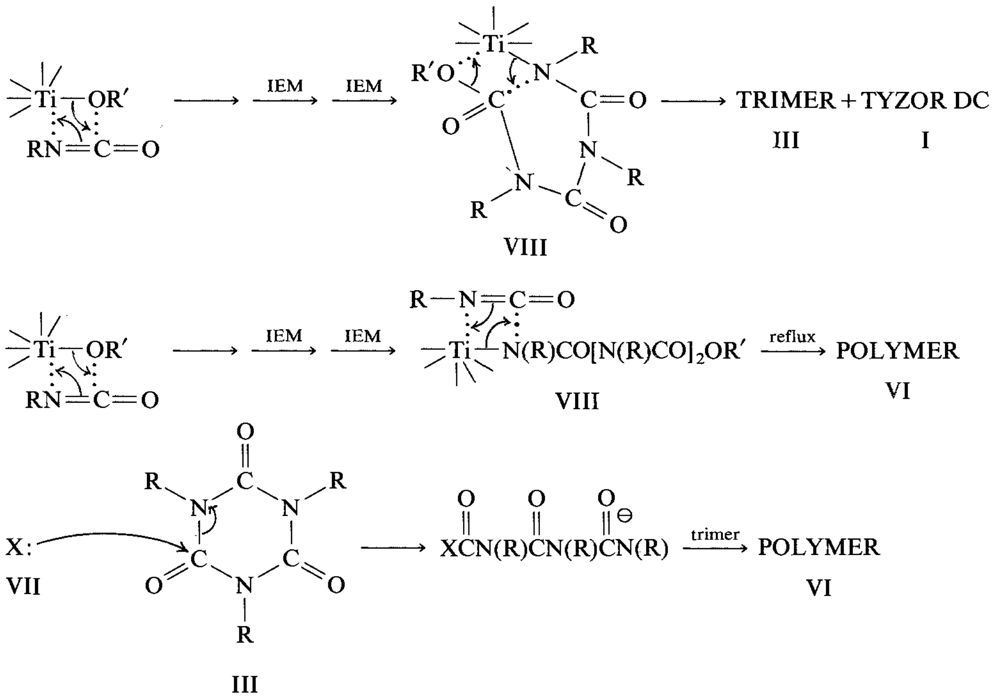


Scheme 3. Interpretation of the mass spectra of the trimer.

methylene group(s). As a result of this, the methylene proton triplet peak shifts from 3.56 ppm for IEM to 4.23 ppm for the cyclic trimer. The other methylene protons shifted from 4.28 ppm to 4.36 ppm, as the monomer is converted to trimer. An interpretation of the proton NMR spectra of the trimer in chloroform-d_1 is shown in scheme 2. An analysis of mass spectral data is shown in scheme 3.

Although initial evidence indicated that the IEM trimer (III) was thermally unstable converting to the corresponding nylon-1 polymer (VI) after refluxing in chloroform, more recent studies have shown the existence of a catalyst (VII) derived from Tyzor DC^R and atmosphere moisture which appears to function as a nucleophile in the ring opening of the trimer (III). Pure trimer (III) is observed to be stable up to 250 °C by TGA. Studies designed to identify this catalyst are currently underway.

It appears that a chain growth mechanism as suggested previously by Meth-Cohn [1c] involving insertion of the isocyanate group into Ti-O or Ti-N bonds is involved in the formation of cyclic trimer (III) or polymer (VI) (scheme 4). At room temperature, the exclusive formation of trimer (III) indicates that this product is the thermodynamically favored product. At reflux however, the yield of the trimer (III) is observed to decrease from 71% to 2% or less and the yield of



Where: X: = Nucleophile
$R' = -OCH(CH_3)_2$
$R = -CH_2CH_2O_2CC(CH_3)CH_2$

Scheme 4. Proposed mechanistic routes to the formation of IEM trimer and polymer.

Table 2
Material balance for the reactions of Tyzor DC with 2-isocyanatoethyl methacrylate at room temperature

Tyzor DC^R : IEM molar ratio	1:4	1:8	1:16	1:32
Isocyanate (moles)				
Theory	0.141	0.141	0.141	0.141
Recvd	0.135	0.138	0.135	0.132
Acetoacetate (moles)				
Theory	0.070	0.035	0.018	0.009
Recvd	0.055	0.035	0.014	0.007
Isopropyl alcohol (moles)				
Theory	0.07	0.035	0.018	0.009
Recvd	0.023	0.01	0.006	0.004

the polymer (VI) increase from 28% to 98% as the Tyzor DC^R: IEM ratio is varied from 1:4 to 1:32 [4]. This implies that polymer formation competes with trimer formation at higher temperatures especially in the presence of excess amounts of IEM (II) with both forming via a common intermediate (VIII). However, as previously mentioned recent evidence has shown that Tyzor DC^R (I) is converted in the presence of atmospheric moisture to an unknown reactive intermediate (VII) which opens the cyclic trimer (III) to form polymer (VI). As such, it is possible that the trimer (III) forms initially even at reflux but is converted to the polymer (VI) by reaction with this unknown catalyst (scheme 4). Additional studies, now in progress will hopefully elucidate this aspect of the mechanism.

Despite the complexity of the reactions, a reasonably good material balance exists in the system for acetoacetate and isocyanate (table 2). Isopropyl alcohol does not balance as well which no doubt is due to the loss of this volatile material during work-up.

4. Conclusions

2-Isocyanatoethyl methacrylate (IEM) can be converted to the cyclic trimer at room temperature in high yield (above 90%) using catalytic amounts of bis(ethyl-3-oxo-butanolato-O^1, O^3) bis(2-propanolato)titanium (Tyzor DC^R). Ethyl acetoacetate, isopropyl acetoacetate and TiO_2 were observed as by-products. The products were identified by FTIR, ^{1}H NMR, ^{13}C NMR, GC/MS and MS procedures. The material balance around the reactions was very close to theory except for isopropyl alcohol, which could easily be lost under the conditions of the reaction, and TiO_2, which was difficult to remove from the walls of the reaction flask.

References

[1] a. A.J. Pearson, *Metallo-Organic Chemistry* (John Wiley & Sons, 1985).
  b. H. Burgër, Monatsh 95 (1964) 671.
  c. O. Meth-Cohn, D. Thorpe and H.J. Twitchett, J. Chem. Soc. C. (1970) 132.
  d. K.N. Mehendra, P.C. Bharara and R.C. Mehrotra, Inorg. Chem. Acta. 25 (1977).

[2] S.R. Sandler, *Polymer Synthesis*, V. III (Academic Press, 1980) p. 129–132.

[3] X. Xu, M.S. Thesis, Eastern Michigan University, July, 1989.

[4] J.C. Graham, X. Xu, L. Jones and M. Orticochea, J. Polym. Sci., Polym. Chem. Ed. (1989) in press.