

REACTION OF *TERT*-BUTYL ALUMOXANE WITH KETONES

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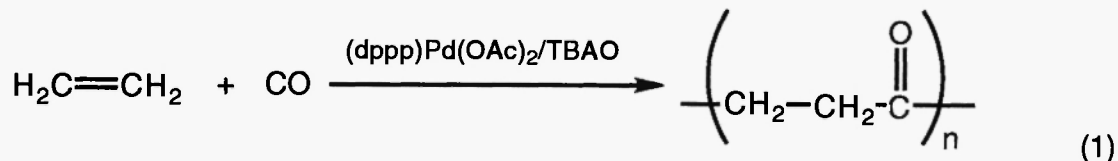
Abstract

The reaction of *tert*-butyl alumoxane ($[(^t\text{Bu})\text{AlO}]_n$, TBAO), with the enolizable ketones, $\text{O}=\text{CEt}_2$ and $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ has been investigated by NMR spectroscopy and GC-mass spectrometry. TBAO promotes the aldol condensation of $\text{O}=\text{CEt}_2$ to yield the β -hydroxy ketone, $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{OH})\text{Et}_2$, which upon acid work-up is converted to $\text{O}=\text{C}(\text{Et})\text{C}(\text{Me})=\text{CEt}_2$ and *E* and *Z* $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{Et})=\text{C}(\text{H})\text{Me}$. In contrast the reaction of TBAO with $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ results in the intra- and inter-molecular aldol condensation to give $\text{OC}(\text{OH})(\text{Me})\text{CH}_2\text{C}(\text{H})=\text{C}(\text{Me})$ and $\text{O}=\text{C}(\text{Me})\text{C}_2\text{H}_4\text{C}(\text{O})\text{CH}_2\text{C}(\text{OH})(\text{Me})\text{C}_2\text{H}_4\text{C}(\text{O})\text{Me}$. The relevance of these reactions to the alumoxane co-catalyzed polyketone, $[\text{CH}_2\text{CH}_2\text{C}(\text{O})]_n$, formation is discussed.

Introduction

We have recently demonstrated that *tert*-butyl alumoxane ($[(^t\text{Bu})\text{AlO}]_n$, TBAO¹) is a suitable co-catalysts for the palladium catalyzed co-polymerization of ethylene and carbon monoxide (Eq. 1). However, since the reaction of alkyl aluminum compounds with ketones has been exhaustively studied,² and depending on the ketone and/or the aluminum alkyl group, is known to result in either alkylation,³ reduction,⁴ or enolization⁵ of the ketone, it is possible that the polyketone polymer will also be susceptible to attack from the TBAO.

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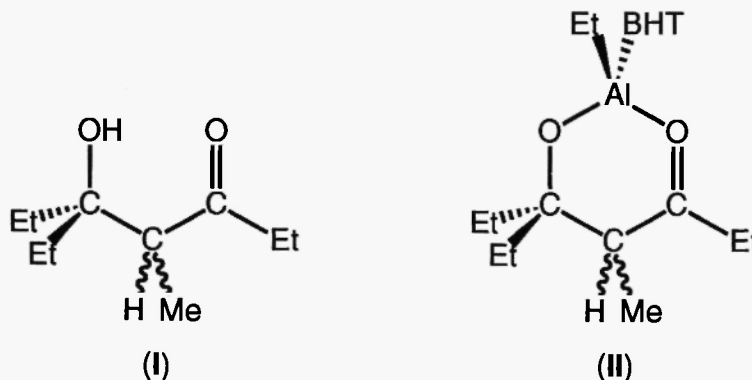
In order to study the possible reactions between polyketone polymers and residual TBAO we have investigated the products formed from the reaction of TBAO with two low molecular weight model compounds: 3-pentanone ($\text{O}=\text{CEt}_2$) and 2,5-hexanedione [$\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$].

Results and Discussion

Reaction of TBAO with 3-pentanone

The reaction of TBAO with $\text{O}=\text{CEt}_2$ in refluxing hexane results in the formation of the β -hydroxy ketone, $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{OH})\text{Et}_2$ (I), as confirmed by GC-mass spectrometry [$m/z = 172$ (M^+)] of the crude reaction mixture. The formation of $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{OH})\text{Et}_2$ is as a consequence of the enolization/condensation of two molecules of $\text{O}=\text{CEt}_2$. We have previously observed a similar product from the reaction of $\text{AlEt}(\text{BHT})_2$ (BHT-H = butylated hydroxytoluene) with $\text{O}=\text{CEt}_2$, i.e., II.^{5b}

While $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{OH})\text{Et}_2$ is formed as the exclusive condensation product, upon acidic work-up the ^1H NMR of the product mixture shows a complex pattern, see Figure 1, which may be assigned from the associated ^1H - ^1H COSY spectrum (Figure 2) as a mixture of the dehydration products of the β -hydroxy ketone ($m/z = 154$), i.e., $\text{O}=\text{C}(\text{Et})\text{C}(\text{Me})=\text{CEt}_2$ (III) and the *E* and *Z* isomers of $\text{O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{Et})=\text{C}(\text{H})\text{Me}$ (IV and V). From the ^1H NMR spectrum the *E* isomer is the more abundant ($E/Z = 2.6$). Full ^1H NMR spectroscopic assignments are given in Table 1.



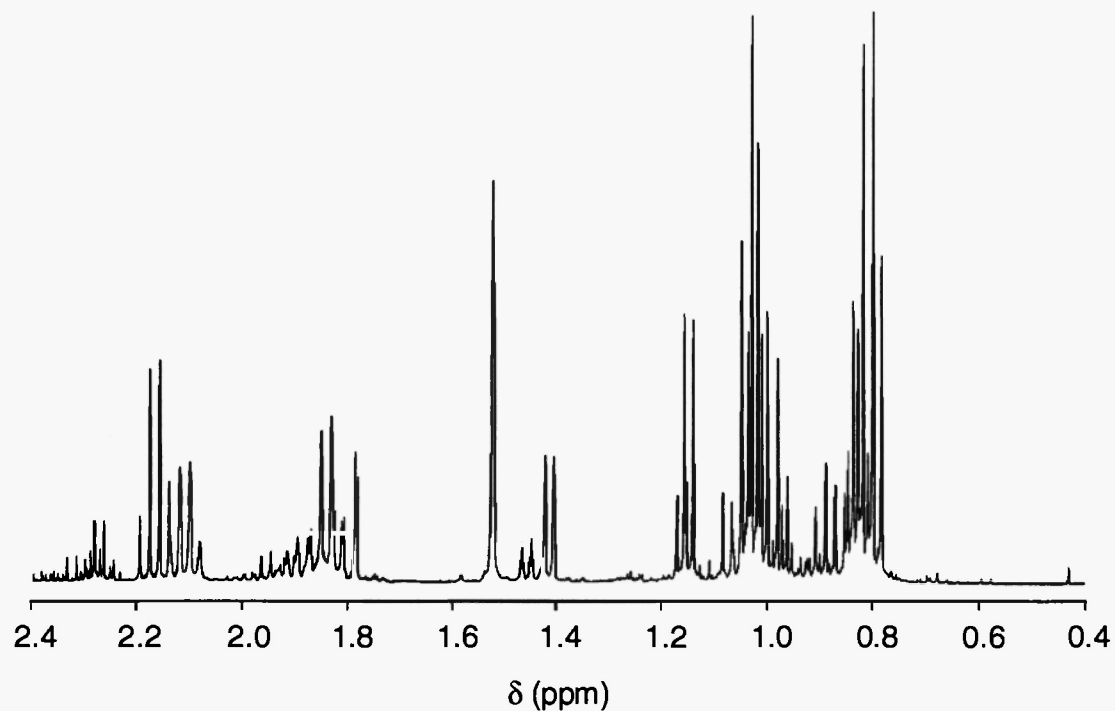


Figure 1. ^1H NMR spectrum of the aldol condensation products from the reaction of TBAO with $\text{O}=\text{CEt}_2$.

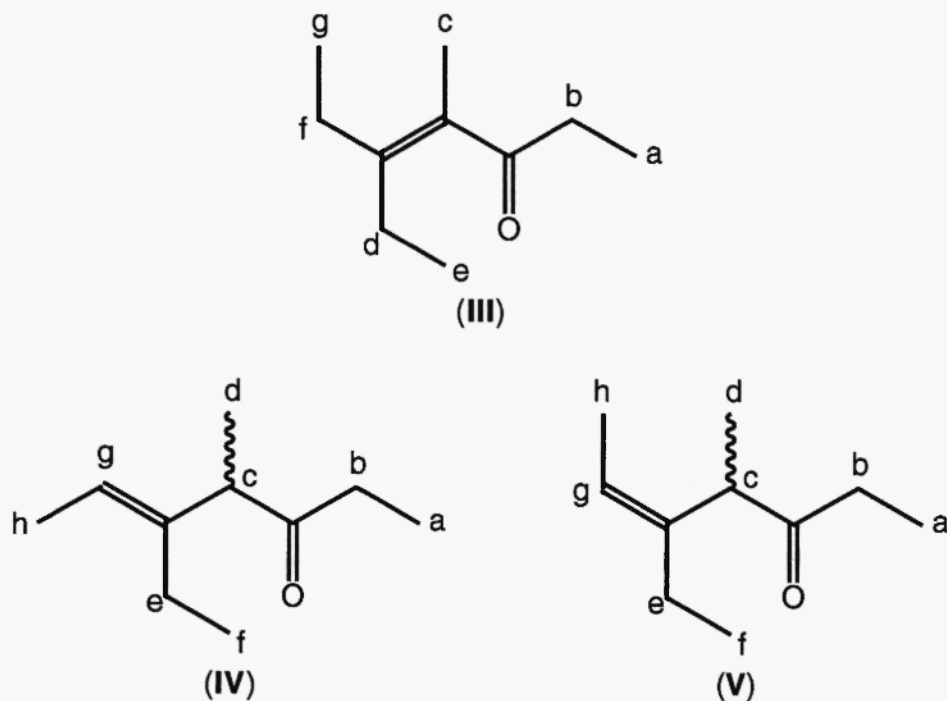


Table 1. ^1H NMR of aldol condensation products from the reaction of TBAO with $\text{O}=\text{CEt}_2$.

Compound	δ (ppm)	integration	multiplicity*	coupling constant (Hz)	assignment†
$\text{O}=\text{C}(\text{Et})\text{C}(\text{Me})=\text{CEt}_2$ (III)					
	2.17	2H	q	7.3	f
	2.17	2H	q	6.8	b
	1.84	2H	q	7.5	d
	1.52	3H	s	-	c
	1.03	3H	t	6.8	a
	1.02	3H	t	7.3	g
	0.82	3H	t	7.5	e
$E\text{-O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{Et})=\text{C}(\text{H})\text{Me}$ (IV)					
	5.17	1H	q	6.6	g
	2.28	2H	q	7.1	b
	1.92	2H	q	7.4	e
	1.47	3H	d	6.6	h
	1.15	3H	d	6.8	d
	0.98	3H	t	7.1	a
	0.83	3H	t	7.4	f
$Z\text{-O}=\text{C}(\text{Et})\text{C}(\text{H})(\text{Me})\text{C}(\text{Et})=\text{C}(\text{H})\text{Me}$ (V)					
	5.17	1H	q	6.6	g
	2.25	2H	q	7.1	b
	1.95	2H	q	7.4	e
	1.47	3H	d	6.6	h
	1.16	3H	d	6.8	d
	0.97	3H	t	7.1	a
	0.85	3H	t	7.4	f

* s = singlet, d = doublet, t = triplet, q = quartet.

† See III, IV, V for letter assignment.

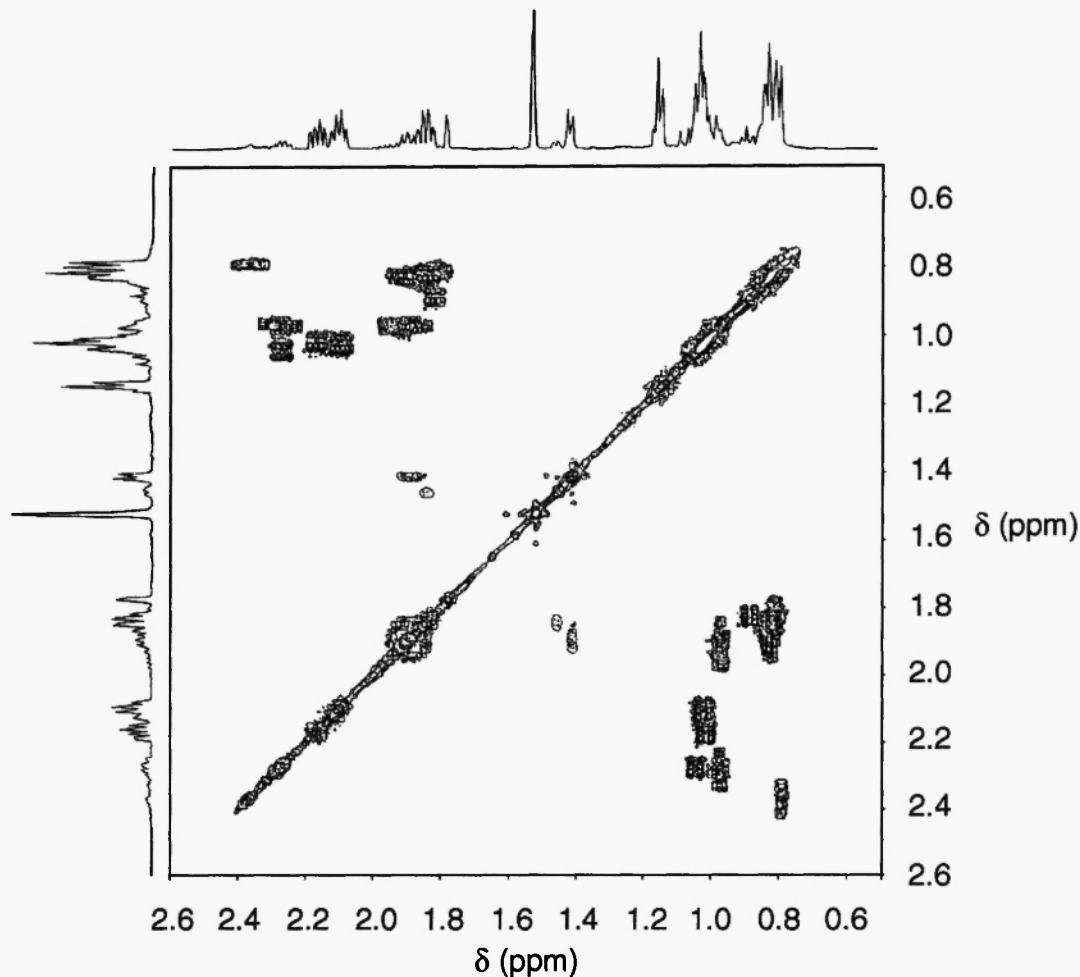
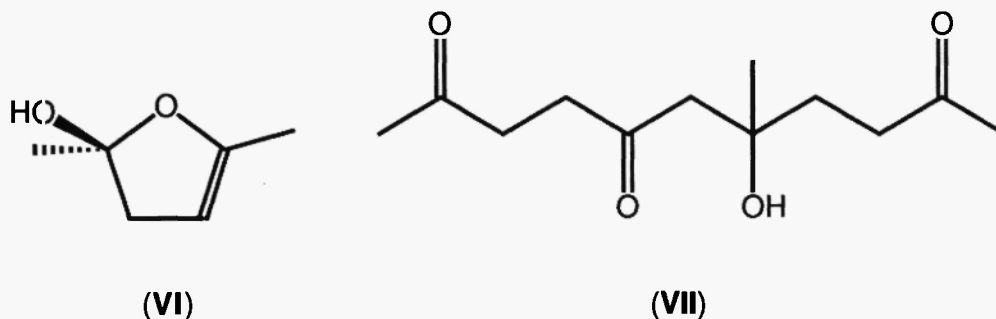


Figure 2. ^1H - ^1H COSY spectrum of the aldol condensation products from the reaction of TBAO with $\text{O}=\text{CET}_2$.

Reaction of TBAO with 2,5-hexanedione

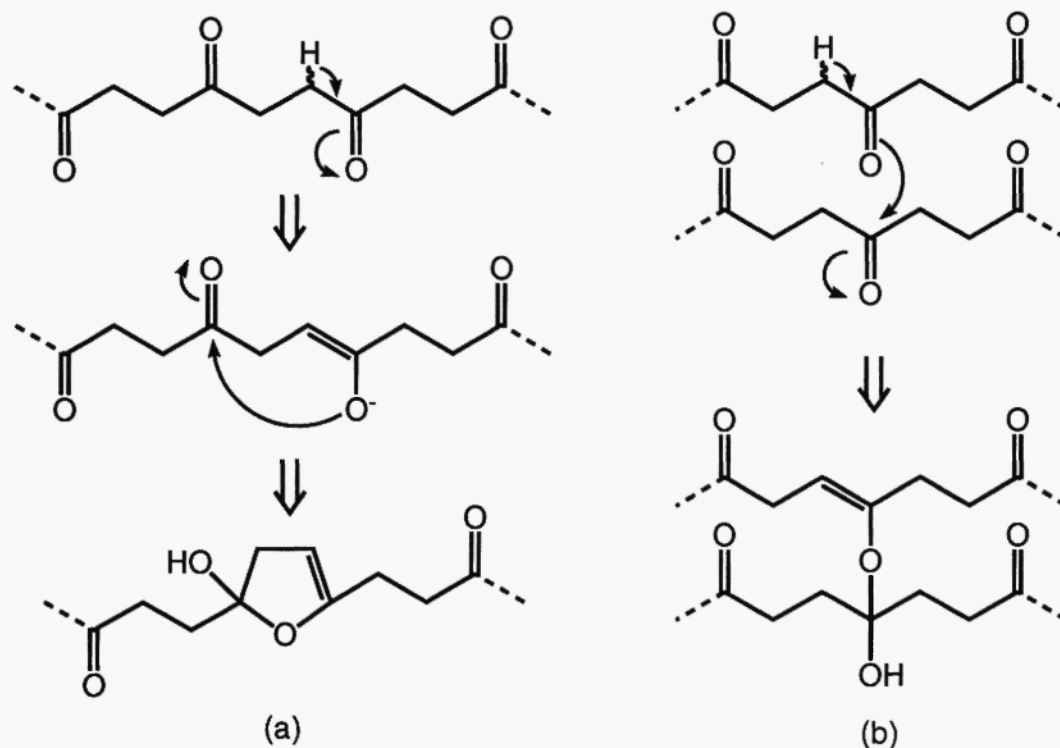
GC-MS analysis of the crude product mixture from the reaction of TBAO with $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ indicates the formation of the hydroxy furan ($m/z = 114$), $\text{OC}(\text{OH})(\text{Me})\text{CH}_2\text{C}(\text{H})=\text{C}(\text{Me})$ (VI), formed by the intra-molecular aldol condensation. The inter-molecular condensation products were insufficiently volatile for GC analysis, however, the dimerization product $\text{O}=\text{C}(\text{Me})\text{C}_2\text{H}_4\text{C}(\text{O})\text{CH}_2\text{C}(\text{OH})(\text{Me})\text{C}_2\text{H}_4\text{C}(\text{O})\text{Me}$ (VII) could be isolated, and the trimerization product was characterized by MS ($m/z = 342$).



Reaction of TBAO with polyketone

Based upon the forgoing, it is possible that under extended reaction times TBAO is sufficiently basic to cause enolization of the polyketone polymer. In order to test this a hexane suspension of polyketone polymer was refluxed in the presence of an excess of TBAO. After a set reaction time the polymer was isolated (see Experimental) and characterized by TGA and solution ^1H NMR spectroscopy. The reaction with TBAO was repeated for a total of 72 hours. The TG/DTA of the polyketone thus treated showed a broadening of the melting range. Furthermore, the melting temperature increases with increasing reaction times. This observation is consistent with the degradation of the polymer, possibly via either furanization (Scheme 1a, *c.f.*, **VI**) or cross linking (Scheme 1b, *c.f.*, **VII**); possibly in combination with dehydration. While the as formed polymer is completely soluble in $\text{HOC(H)(CF}_3)_2$, after refluxing for 72 hours only *ca.* 20 % of the sample is soluble. Furthermore, the M_w of the soluble fraction had increased only slightly, from 120,000 to 160,000.

The $\text{HOC(H)(CF}_3)_2$ soluble fraction showed no additional peaks in the ^{13}C NMR spectra, consistent with no significant chemical changes and the molecular weight measurements. The insoluble fraction was characterized by ^{13}C CPMAS NMR spectroscopy and showed, in addition to those resonances observed for the as synthesized polyketone polymer, resonances consistent with the cross linked polymer, see Figure 3. No new resonances consistent with furanization, or its accompanying dehydrated product are observed. The spectroscopic and solubility characteristics are therefore consistent with cross-linking of the polyketone polymer, in contrast to the thermally induced furinization reaction previously observed.



Scheme 1. Possible degradation of polyketone polymer via aldol condensation resulting in either (a) furanization or (b) cross linking.

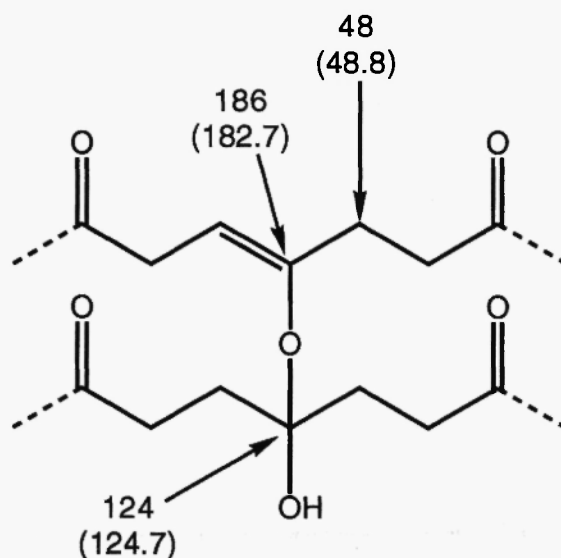
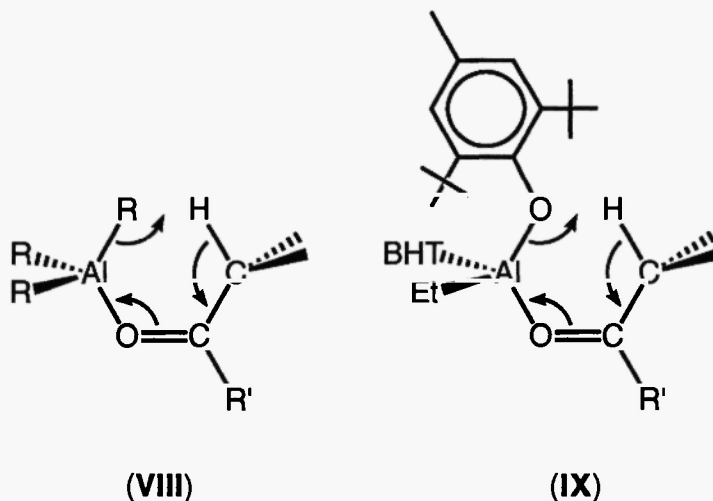


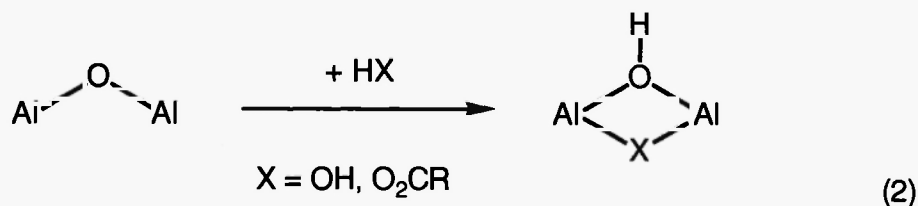
Figure 3. Observed ^{13}C CPMAS NMR spectral shifts associated with cross-linked polyketone polymer. Calculated⁶ values given in parenthesis.

Enolization via *Tert*-Butyl or Oxo Ligands?

The accepted mechanism for the enolization of ketones by aluminum alkyls involves a six-membered transition state (VIII) with the concurrent loss of alkane.⁷ We have previously reported that the reaction of aluminum aryloxy compounds, e.g., $\text{AlEt}(\text{BHT})_2$, with ketones occurs via an intramolecular aryloxy-assisted enolization in which the aryloxy oxygen acts as the base (IX).^{5b}



We have recently shown that TBAO, in common with other alkyl alumoxanes, consists of cage compounds of the general formula $[(^t\text{Bu})\text{AlO}]_n$ ($n = 6, 7, 8, 9, 12, \dots$). A trend observed in the chemistry of these cage compounds is that reactions occur at the oxo-ligands and not the *tert*-butyl groups.⁸ For example, reaction of $[(^t\text{Bu})\text{AlO}]_6$ with either water or carboxylic acids results in the protonation of the Al-O-Al group, e.g., Eq. 2.



Thus, it is clear that the most basic reaction center on the alumoxanes is the oxo-ligand and not the aluminum alkyl. It is reasonable, therefore, that the

enolization of $\text{O}=\text{CEt}_2$ and $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ by TBAO most probably occurs via an oxo-ligand acting as the base.

Experimental

All synthetic procedures were performed under purified nitrogen using standard Schlenk techniques or in an argon atmospheric VAC glovebox unless otherwise mentioned. Solvents were distilled and degassed prior to use. $[(^t\text{Bu})\text{Al}(\text{O})]_n$ was prepared as previously reported.¹ $\text{O}=\text{CEt}_2$ and $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ (Aldrich) were distilled prior to use.

GC-mass spectra were obtained on a JEOL AX-505 H mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. Ammonia was used as the reagent gas for CI experiments unless otherwise mentioned. Solution NMR spectra were obtained on a Bruker AM-500 spectrometer using C_6D_6 or $\text{C}_6\text{D}_6/\text{HOC}(\text{H})(\text{CF}_3)_2$ (9:1). Solid state ^{13}C CPMAS spectra were obtained on a Bruker instrument. Thermogravimetric analyses were obtained on a Seiko 200 TG/DTA instrument using an argon carrier gas.

Reaction of TBAO with $\text{O}=\text{CEt}_2$. To a solution of TBAO (8.0 g, 80.0 mmol) in hexane (50 mL) was added $\text{O}=\text{CEt}_2$ (12 mL, 0.12 mol). The solution was refluxed overnight. The volatiles were removed in vacuo to leave a light-yellow solid residue. The residue was dissolved in Et_2O (50 mL) and cold (ca. 0 °C) water (20 mL) was added (CAUTION: reaction of TBAO with H_2O liberates iso-butane). The solution was stirred vigorously until the light-yellow color was disappeared. Following addition of a few drops of a HCl (1.0 N solution in water), the solution was stirred additional 8 hours. The Et_2O layer was separated using a separation funnel and then dried over MgSO_4 for 24 hours. The Et_2O solution was used directly for GC-MS, while removal of Et_2O allowed for characterization by ^1H NMR spectroscopy.

Reaction of TBAO with $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$. To a solution of TBAO (2.0 g, 20.0 mmol) in toluene (10 mL) was added by $\text{MeC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Me}$ (1.2 mL, 10 mmol), and the resulting solution was refluxed overnight. The volatiles were removed in vacuo to leave an orange-red oily residue. The residue was dissolved in Et_2O (30 mL) and cold (ca. 0 °C) water (10 mL) added. The solution was allowed to stir vigorously for 6 hours.

The ether layer was separated using a separation funnel and then dried over MgSO_4 for 24 hours. The Et_2O solution was used directly for GC-MS, while removal of Et_2O allowed for characterization by NMR and MS.

Reaction of TBAO with $[\text{CH}_2\text{CH}_2\text{C}(\text{O})]_n$. To a suspension of previously characterized sample of polyketone (50 mg, 0.9 mmol) in hexane (10 mL) was added TBAO (50 mg, 5.0 mmol). The resulting mixture was refluxed overnight. The solvent was removed by filtration and the residue was washed with hexane (10 mL). The polymer was dried under vacuum, and analyzed by TG/DTA.

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