# Aldol Condensation of Ketones Promoted by Sterically Crowded Aryloxide Compounds of Aluminum

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The interaction of $AlEt(BHT)_2$ with 2 equiv of O=C(Me)$^t$Bu, O=C(Et)Ph, or O=$CEt_2$ yields the aluminum-β-oxo enolate complexes $\overline{AlEt(BHT)[O{=}C(^tBu)CH_2C(Me)(^tBu)O]}$ (1), $\overline{AlEt(BHT)[O{=}C(Ph)C(H)(Me)C(Et)(Ph)O]}$ (2), and $\overline{AlEt(BHT)[O{=}C(Et)C(H)(Me)C(Et)_2O]}$ (3), respectively. Compounds 1, 2, and 3 have been characterized by IR and $^1$H, $^{13}$C, and $^{27}$Al NMR spectroscopy. In addition, the structure of 1 has been confirmed by X-ray crystallography. The stereospecificities of the intramolecular alkoxide-assisted enolization and condensation reactions are discussed. Compound 1 crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions $a$ = 9.3428 (6) Å, $b$ = 14.3079 (6) Å, $c$ = 11.3322 (6) Å, $\beta$ = 91.971 (4) °, $Z$ = 2, 1907 observed data, $R$ = 0.0628, and $R_w$ = 0.0730.

The reaction of trialkylaluminum compounds with organic carbonyls, to give products of alkyl addition, reduction, and enolization, has been exhaustively studied.[2] Much of the reactivity, including the presence of multiple reaction pathways, is dependent on the dimeric nature of many organoaluminum compounds. Recent work in our laboratory has focused, therefore, on the synthesis and characterization of products from the reaction of organic carbonyls with monomeric aluminum complexes derived from the sterically hindered 2,6-di-*tert*-butyl-4-methylphenol (BHT-H, from the trivial name butylated hydroxytoluene).[3-5]

We report here the aldol condensation of pinacolone, O=C(Me)$^t$Bu, propiophenone, O=C(Et)Ph, and 3-pentanone, O=$CEt_2$, using $AlEt_x(BHT)_{3-x}$ ($x$ = 1, 2).

## Results and Discussion

The interaction of $AlMe(BHT)_2$ with O=C(Me)$^t$Bu in pentane allows the isolation of the Lewis acid–base complex $AlMe(BHT)_2[O{=}C(Me)^tBu]$ as a pale yellow crystalline solid.[5] Adduct formation is not observed under the same conditions, however, between O=C(Me)$^t$Bu and $AlEt(BHT)_2$; instead, enolization and condensation occurs to give a coordinated β-oxo enolate.

Interaction of $AlEt(BHT)_2$[6,7] with 1 equiv of O=C(Me)$^t$Bu results in an equimolar mixture of $AlEt(BHT)_2$ and $\overline{AlEt(BHT)[O{=}C(^tBu)CH_2C(Me)(^tBu)O]}$ (1). If, however, the reaction is carried out with 2 equiv of pinacolone, 1 is the only product observed (eq 1) in addition

$$AlEt(BHT)_2 + 2O{=}C(Me)^tBu \rightarrow 1 + BHT\text{-}H \quad (1)$$

$$AlEt_2(BHT) + 2O{=}C(Me)^tBu \rightarrow 1 + C_2H_6 \quad (2)$$

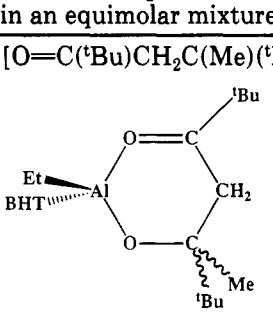
to 1 equiv of BHT-H. Compound 1 is also formed from the reaction of $AlEt_2(BHT)(OEt_2)$[8] with 2 equiv of O=C(Me)$^t$Bu, presumably via the loss of ethane in place of BHT-H (eq 2). All IR and NMR spectra (see below and Experimental Section) are consistent with the proposed structure of 1. The $^1$H (Figure 1) and $^{13}$C NMR spectra of 1 are consistent with the presence of two distinct isomers in a 2:1 ratio. The relative quantity of each isomer is independent of the synthetic route.

The interaction of O=C(Me)$^t$Bu with $AlMe_3$ has been reported[8] to yield the mixed-bridge alkoxide-β-oxo enolate complex $Me_2Al[\mu\text{-}OC(Me)_2{}^tBu][\mu\text{-}OC(Me)(^tBu)CH_2C(O)^tBu]AlMe_2$, which results from both the enolization/condensation and the alkylation of the ketone.

The molecular structures of the two isomers of 1 as determined by X-ray crystallography are shown in Figure 2; selected bond lengths and angles are given in Tables I

**Table I. Bond Lengths (Å) in $\overline{AlEt(BHT)[O{=}C(^tBu)CH_2C(Me)(^tBu)O]}$**

| | | | |
|---|---|---|---|
| Al–O(1) | 1.732 (5) | Al–O(2) | 1.911 (5) |
| Al–O(3) | 1.720 (5) | Al–C(1) | 1.962 (9) |
| O(1)–C(11) | 1.364 (8) | O(2)–C(41) | 1.242 (8) |
| O(3)–C(43)A | 1.43 (2) | O(3)–C(43)B | 1.43 (2) |
| C(1)–C(2) | 1.56 (1) | C(11)–C(12) | 1.410 (9) |
| C(11)–C(16) | 1.40 (1) | C(12)–C(13) | 1.39 (1) |
| C(12)–C(121) | 1.54 (1) | C(13)–C(14) | 1.36 (1) |
| C(14)–C(15) | 1.39 (1) | C(14)–C(141) | 1.51 (1) |
| C(15)–C(16) | 1.40 (1) | C(16)–C(161) | 1.54 (1) |
| C(41)–C(42)A | 1.51 (2) | C(41)–C(42)B | 1.57 (2) |
| C(41)–C(44) | 1.49 (1) | C(42)A–C(43)A | 1.55 (2) |
| C(42)B–C(43)B | 1.60 (3) | C(43)A–C(48)A | 1.57 (2) |
| C(43)B–C(48)B | 1.54 (3) | C(43)A–C(49) | 1.58 (2) |
| C(43)B–C(49) | 1.51 (2) | C(44)–C(45) | 1.52 (1) |
| C(44)–C(46) | 1.53 (1) | C(44)–C(47) | 1.55 (1) |
| C(49)–C(50)A | 1.80 (3) | C(49)–C(50)B | 1.54 (3) |
| C(49)–C(51)A | 1.42 (2) | C(49)–C(51)B | 1.73 (2) |
| C(49)–C(52)A | 1.68 (2) | C(49)–C(52)B | 1.50 (2) |
| C(121)–C(122) | 1.55 (1) | C(121)–C(123) | 1.55 (1) |
| C(121)–C(124) | 1.56 (1) | C(161)–C(162) | 1.55 (1) |
| C(161)–C(163) | 1.52 (1) | C(161)–C(164) | 1.56 (1) |

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(1) (a) Harvard University. (b) University of Alabama.
(2) See: Zietz, J. R.; Robinson, G. C.; Lindsay, K. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel E. W., Eds.; Pergamon: Oxford, England, 1983; Vol. 1, Chapter 46, p 365.
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(6) Starowieyski, K. B.; Pasynkiewicz, S.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1975**, *90*, C43.
(7) Healy, M. D.; Power, M. B.; Barron, A. R. *J. Coord. Chem.*, in press.
(8) Jeffery, E. A.; Meisters, A. *J. Organomet. Chem.* **1974**, *82*, 307.

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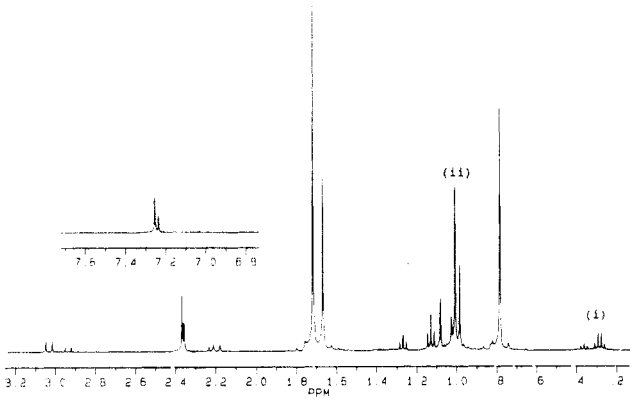



**Figure 1.** $^1H$ NMR spectrum of AlEt(BHT)[O=C($^t$Bu)-$CH_2C(Me)(^t$Bu)O showing the resonances due to the aluminum ethyl $\alpha$-protons (i) and the alkoxide *tert*-butyl group of the oxo enolate (ii).

**Table II. Bond Angles (deg) in AlEt(BHT)[O=C($^t$Bu)$CH_2$C(Me)$^t$Bu)O]**

| | | | |
|---|---|---|---|
| O(1)-Al-O(2) | 102.9 (2) | O(1)-Al-C(1) | 116.2 (3) |
| O(2)-Al-C(1) | 107.8 (4) | O(3)-Al-C(1) | 117.8 (4) |
| O(1)-Al-O(3) | 112.7 (3) | O(2)-Al-O(3) | 95.8 (2) |
| Al-O(1)-C(11) | 136.0 (4) | Al-O(2)-C(41) | 128.3 (5) |
| Al-O(3)-C(43)A | 126.7 (7) | Al-O(3)-C(43)B | 128.2 (7) |
| Al-C(1)-C(2) | 116.6 (7) | O(1)-C(11)-C(12) | 120.1 (6) |
| O(1)-C(11)-C(16) | 118.9 (6) | C(12)-C(11)-C(16) | 120.8 (6) |
| C(11)-C(12)-C(13) | 117.3 (7) | C(11)-C(12)-C(121) | 122.3 (6) |
| C(13)-C(12)-C(121) | 120.3 (7) | C(12)-C(13)-C(14) | 123.3 (7) |
| C(13)-C(14)-C(15) | 117.6 (7) | C(13)—C(14)-C(141) | 120.8 (8) |
| C(15)-C(14)C(141) | 121.6 (8) | C(14)-C(15)-C(16) | 122.9 (8) |
| C(11)-C(16)-C(15) | 117.0 (7) | C(11)-C(16)-C(161) | 123.1 (6) |
| C(15)-C(16)-C(161) | 119.9 (7) | O(2)-C(41)-C(42)A | 117.5 (9) |
| O(2)-C(41)—C(42)B | 119.9 (9) | O(2)-C(41)-C(44) | 119.0 (7) |
| C(42)A-C(41)-C(44) | 119.9 (8) | C(42)B-C(41)-C(44) | 118.9 (9) |
| C(41)-C(42)A-C(43)A | 110 (1) | C(41)-C(42)B-C(43)B | 111 (1) |
| O(3)-C(43)A-C(42)A | 110 (1) | O(3)-C(43)B-C(42)B | 108 (1) |
| O(3)-C(43)A-C(48)A | 110 (1) | C(42)A-C(43)A-C(48)A | 107 (1) |
| O(3)-C(43)B-C(48)B | 112 (1) | C(42)B-C(43)B-C(48)B | 108 (1) |
| O(3)-C(43)A-C(49) | 105 (1) | C(42)A-C(43)A-C(49) | 118 (1) |
| C(48)A-C(43)A-C(49) | 107 (1) | O(3)-C(43)B-C(49) | 108 (1) |
| C(42)B-C(43)B-C(49) | 114 (1) | C(48)B-C(43)B-C(49) | 107 (1) |
| C(41)-C(44)-C(45) | 110.7 (7) | C(41)-C(44)-C(46) | 107.9 (8) |
| C(45)-C(44)C(46) | 109.0 (8) | C(41)-C(44)-C(47) | 109.4 (7) |
| C(45)-C(44)-C(47) | 109.4 (8) | C(46)-C(44)-C(47) | 110.5 (8) |
| C(43)A-C(49)-C(50)A | 99 (1) | C(43)B-C(49)-C(50)B | 115 (1) |
| C(43)A-C(49)-C(51)A | 118 (1) | C(50)A-C(49)-C(51)A | 101 (2) |
| C(43)B-C(49)-C(51)B | 105 (1) | C(50)B-C(49)-C(51)B | 98 (1) |
| C(43)A-C(49)-C(52)A | 106 (1) | C(50)A-C(49)-C(52)A | 111 (1) |
| C(51)A-C(49)-C(52)A | 120 (1) | C(43)B-C(49)-C(52)B | 117 (1) |
| C(50)B-C(49)-C(52)B | 114 (1) | C(51)B-C(49)-C(52)B | 106 (1) |
| C(12)-C(121)-C(122) | 110.5 (6) | C(12)-C(121)-C(123) | 111.3 (6) |
| C(122)-C(121)-C(123) | 111.4 (7) | C(12)-C(121)-C(124) | 110.9 (6) |
| C(122)-C(121)-C(124) | 106.4 (7) | C(123)-C(121)-C(124) | 106.3 (6) |
| C(16)-C(161)-C(162) | 108.4 (6) | C(16)-C(161)-C(163) | 112.4 (7) |
| C(162)-C(161)-C(163) | 109.6 (7) | C(16)-C(161)-C(164) | 111.1 (7) |
| C(162)-C(161)-C(164) | 108.3 (7) | C(163)-C(161)-C(164) | 107.1 (7) |

and II, respectively. The geometry around aluminum is distorted from tetrahedral, with the angles associated with O(2), the aldol carbonyl oxygen, being the most acute. A similar distortion is observed for the benzophenone complex $AlMe(BHT)_2(O{=}CPh_2)$.[5] The Al-C bond length in **1** (1.962 (9) Å) is in the region previously reported for four-coordinate aluminum alkyl compounds.[9]

The aryloxide Al-O distance (Al-O(1) = 1.732 (5) Å) is consistent with some degree of $\pi$-bonding between the oxygen lone-pair orbitals and $\sigma$ antibonding orbitals on aluminum.[10,11] The bond from the aldol alkoxide oxygen

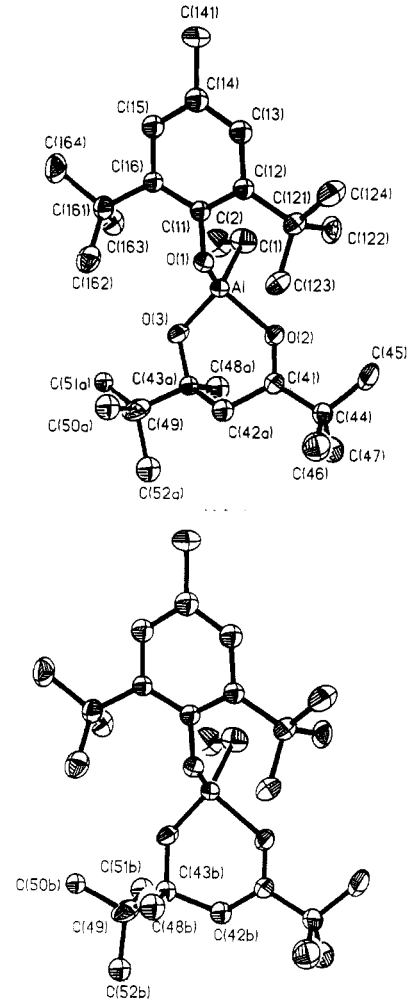



**Figure 2.** Structure of the two isomers of AlEt(BHT)[O=C-($^t$Bu)$CH_2C(Me)(^t$Bu)O]. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

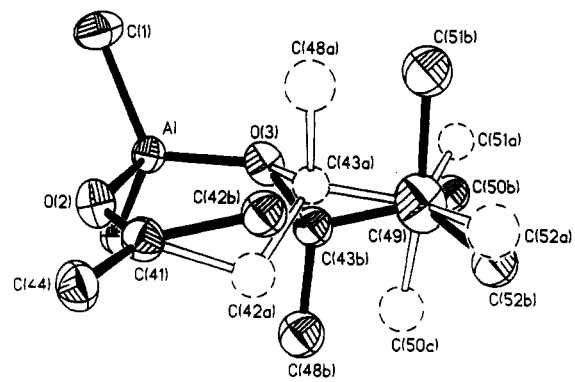



**Figure 3.** Partial coordination sphere of the $\beta$-oxo enolate ring in AlEt(BHT)]O=C($^t$Bu)$CH_2C(Me)^t$Bu)O]. The chemically minor isomer, **1a**, is indicated by open ellipsoids.

to aluminum (Al-O(3) = 1.730 (5) Å) is also in the region of possible Al-O $\pi$-interaction. In contrast the aldol carbonyl Al-O distance is comparable to that in organic carbonyl adducts of $AlMe(BHT)_2$ (1.903 (6)–1.920 (3) Å).[5]

The two isomers observed in the solid state appear as a 1:1 disorder of the six-membered ring and can be imagined as being due to inversion of the quaternary carbon (C(43)) attached to the alkoxide carbon (Figure 3). In this inversion, the oxygen (O(3)) and the ipso carbon (C(49))

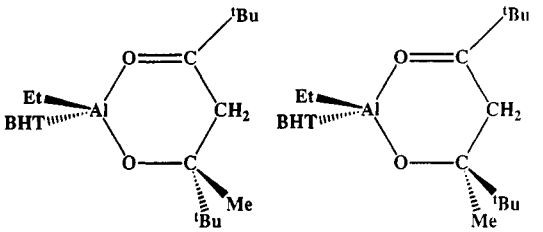
(9) (a) Wierda, D. A.; Barron, A. R. *Polyhedron* **1989**, *8*, 831. (b) Healy, M. D.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 398. (c) Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 1828.

(10) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

(11) Healy, M. D.; Ziller, J. W.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2949.

remain fixed with the resolution of the experiment, while C(43) and the methylene link of the ring (C(42)) "flip" within the ring. The results of these are 3-fold: the ring itself adopts a virtual "half-chair" conformation in one isomer, isomer a; in isomer b, the *tert*-butyl group of the alkoxide becomes considerably closer to being eclipsed with respect to the ethyl group; finally, the inversion of the alkoxide methyl group is accompanied by a "rotation" of the *tert*-butyl group so that the arrangement about the C(43)–C(49) bond remains staggered.

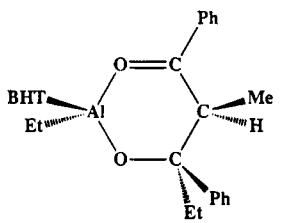
In order to determine which of the two isomers of **1** observed in the solid state is the major product from the reaction (eq 1), an NOE experiment was undertaken. Irradiation of the aluminum ethyl $\alpha$-protons of the major isomer (i) resulted in enhancement of the signal due to the alkoxide *tert*-butyl of the oxo enolate (ii) (see Figure 1). This indicates that in the major isomer, **1b**, the aluminum ethyl group is cis with respect to the alkoxide *tert*-butyl group of the oxo enolate.




**1a** **1b**

The presence of the two isomers of **1** suggested that the condensation reaction (eq 1) is nonstereospecific. It is obviously not possible, however, to ascertain if the enolization process is stereospecific. In an effort to determine the stereospecificity of the enolization, we have investigated the reaction of $AlEt(BHT)_2$ with O=C(Et)Ph and $O{=}CEt_2$.

The reaction of $AlEt(BHT)_2$ or $AlEt_2(BHT)(OEt_2)$ with 2 equiv of O=C(Et)Ph yields the $\beta$-oxo enolate complex AlEt(BHT)[O=C(Ph)CH(Me)C(Et)(Ph)O] (**2**). The $^1H$




**2**

and $^{13}C$ NMR spectra of **2** indicate the presence of a single isomer. The $^1H$–$^1H$ COSY spectrum (Figure 4) reveals the alkoxy ethyl group to be anisochronous due to its hindered rotation. Irradiation of the BHT *tert*-butyl resonance resulted in a nuclear Overhauser enhancement of the methyl and the alkoxy phenyl group of the $\beta$-oxo enolate; no enhancement of the alkoxy ethyl resonance was observed. The BHT and ring methyl and phenyl groups are therefore mutually cis. Both the enolization and condensation of O=C(Et)Ph are therefore stereospecific, as demonstrated by the presence of a single conformation at the central and alkoxide carbons of the oxo enolate. In contrast, the reaction of $AlEt(BHT)_2$ with a symmetric ketone, $O{=}CEt_2$, results in the formation of two isomers, arising from the nonstereospecific enolization of the ketone.

The reaction of $AlEt(BHT)_2$ with $O{=}CEt_2$ results in the formation of AlEt(BHT)[O=C(Et)CH(Me)C(Et)$_2$O] (**3**). The $^1H$ NMR spectrum of **3** indicates the presence of two isomers in a 3:1 ratio. The $^1H$–$^1H$ COSY spectrum of **3**

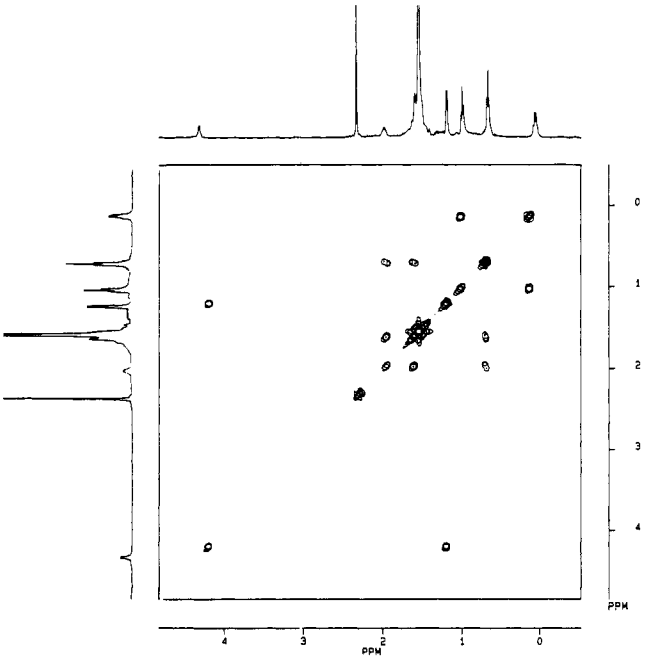



**Figure 4.** $^1H$–$^1H$ COSY spectrum of AlEt(BHT)[O=C(Ph)C(H)(Me)C(Et)(Ph)O].

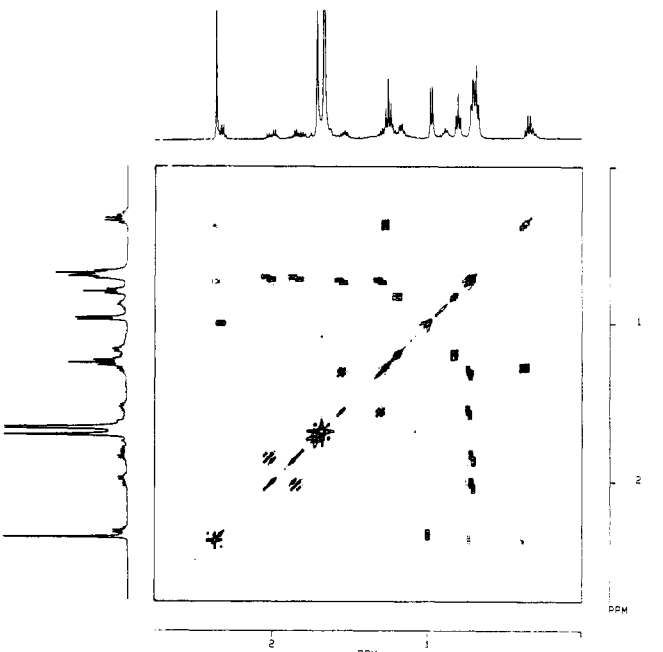


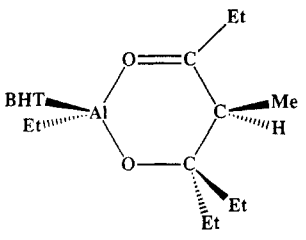

**Figure 5.** $^1H$–$^1H$ COSY spectrum of AlEt(BHT)[O=C(Et)C(H)(Me)C(Et)$_2$O].

(Figure 5) demonstrates that the $\beta$-oxo enolate alkoxy ethyls are anisochronous. This leads to a very complex $ABX_3$ $^1H$ resonance, which may be simplified by irradiation of the ethyl $CH_3$ groups.

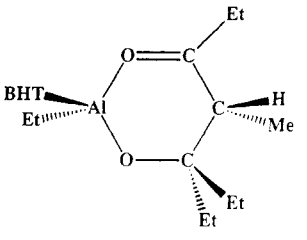
A nuclear Overhauser enhancement of the BHT *tert*-butyl resonance of the major isomer of **3** was observed when the ring methyl of the $\beta$-oxo enolate was irradiated. This indicates that in the major isomer, **3a**, the ring methyl and BHT are cis with respect to each other.

The accepted mechanism for the enolization of ketones by aluminum alkyls involves a six-membered transition state (**I**) with the concurrent loss of alkane.[12] We propose

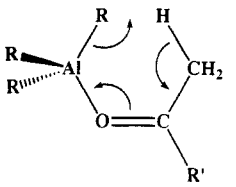
(12) (a) Pasynkiewicz, S.; Sliwa, E. *J. Organomet. Chem.* **1965**, *3*, 121. (b) Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* **1974**, *74*, 365.




3a

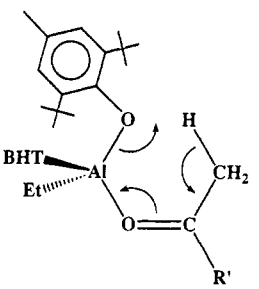



3b




I

that the reaction of $AlEt_2(BHT)$ with ketones occurs via a similar mechanism, whereby the ethyl group acts as an intramolecular base to assist in the enolization of the coordinated ketone. In direct contrast to this usual mechanism is the enolization of ketones by $AlEt(BHT)_2$, in which one of the coordinated aryloxides is lost as the phenol, BHT-H. We propose, therefore, that the reaction occurs via a unique intramolecular alkoxide-assisted enolization in which BHT acts as the base (II). It should

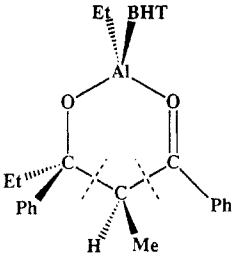



II

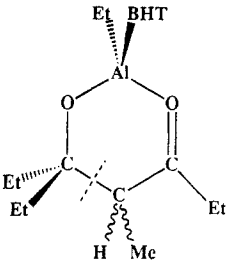
be noted that the aluminum enol compound is independent of the identity of the initial aluminum complex.

The ratio of isomers of the $\beta$-oxo enolate complexes is independent of the choice of $AlEt(BHT)_2$ or $AlEt_2(BHT)$. In addition, we have been unable to isolate the enolized products from the reaction of either aluminum species with O=C(Me)$^t$Bu, O=C(Et)Ph, or $O{=}CEt_2$ even when the aluminum compound is in vast excess. The foregoing suggests that (a) the enolization occurs prior to the coordination of the second equivalent of ketone and (b) the condensation reaction is faster than the enolization of the coordinated ketone. The implication of this for the coordination geometry of the initial aluminum ketone complex is as yet unclear; we are, however, continuing our investigations in order to more fully understand the enolization of coordinated ketones by aluminum alkoxide compounds.

Hydrolysis of 1 gives a low yield of the $\beta$-hydroxy ketone O=C($^t$Bu)$CH_2$C(Me)($^t$Bu)OH,[13] which has been characterized by IR and NMR spectroscopy (see Experimental Section). Disappointingly, a $\beta$-hydroxy ketone is not isolated from the hydrolysis of either **2** or **3**. Hydrolysis of **2** under weakly acidic conditions gives an approximately 1:1:1:1 mixture of O=C(Et)Ph, HOC(H)(Et)Ph, O=C(H)Ph, and $HOC(Et)_2Ph$. This mixture presumably results from the nonspecific cleavage of the carbon–carbon bonds in the aluminum $\beta$-oxo enolate ring (III). In contrast




III




IV

$O{=}CEt_2$ and $HOC(H)Et_2$ are formed in the hydrolysis of **3**, consistent with the cleavage of only one of the possible $\beta$-oxo enolate ring carbon–carbon bonds (IV). The products were characterized by $^1$H and $^{13}$C NMR and GC techniques by comparison with authentic samples.

While dehydration is a common side reaction in the acid- or base-catalyzed aldol condensation reactions, the facile carbon–carbon bond cleavage observed on hydrolysis of compounds **2** and **3** is unusual, given that hydrolysis of aluminum $\beta$-oxo enolates has been previously shown to give the $\beta$-hydroxy ketones.[8]

## Experimental Section

Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Melting points were determined in sealed capillaries and are uncorrected. IR spectra (4000–700 cm$^{-1}$) were recorded on a Nicolet 5ZDX FT-IR spectrometer as Nujol mulls (NaCl). NMR spectra, in $C_6D_6$ or $CDCl_3$, were recorded on Bruker AM-500 and AM-400 ($^1$H and $^{13}$C) and WM-300 ($^{27}$Al) spectrometers ($\delta$ in parts per million relative to $SiMe_4$ ($^1$H, $^{13}$C) and external $Al(H_2O)_6^{3+}$ ($^{27}$Al)). $^1$H–$^1$H COSY NMR spectra were collected by use of a standard pulse sequence[14] with a 45° mixing pulse, a 1-s relaxation delay, and a resolution of ca. 4 Hz per point. The FID's were not weighted before Fourier transformation, and the spectral matrix was symmetrized about the diagonal. All manipulations were carried out under nitrogen. Solvents and ketones were dried, distilled, and degassed before use. $AlEt(BHT)_2$ and $AlEt_2(BHT)(OEt_2)$ were prepared as previously described.[9]

**AlEt(BHT)[O=C($^t$Bu)$CH_2$C($CH_3$)($^t$Bu)O] (1). Method 1.** To $AlEt(BHT)_2$ (2.0 g, 4.04 mmol) in pentane (40 mL) at room temperature was added O=C(Me)$^t$Bu (0.7 mL, 8.7 mmol) in pentane (20 mL) dropwise. A pale yellow color resulted, which became lighter upon stirring for 1 h. After the mixture was stirred for 2 h, the resulting solution was reduced to dryness under vacuum. The resulting oily residue was dissolved in the minimum amount of pentane (~20 mL) and the solution set aside in the freezer overnight. Large crystals formed, which were filtered and dried under vacuum; yield ~75%.

**Method 2.** To $(BHT)AlEt_2(Et_2O)$ (3.0 g, 7.92 mmol) in pentane (30 mL) was added O=C(Me)$^t$Bu (1.27 mL, 15.84 mmol). An initial yellow color formed, which became paler on stirring. After the mixture was stirred for $2^1/_2$ h, the resulting reaction mixture was evaporated to dryness under vacuum to yield an oily residue. This was washed once with pentane (20 mL) and filtered, leaving a white precipitate. The filtrate was set aside overnight at −20 °C, yielding large colorless crystals. $^1$H NMR spectroscopy indicated that both the white precipitate and crystalline solid were identical: yield 85–90%; mp 147–148 °C. Anal. Calcd for $C_{29}H_{52}O_3Al$: C, 73.22; H, 11.01. Found: C, 73.55; H, 10.51. IR (Nujol, NaCl, cm$^{-1}$): 1617 (s), 1295 (sh), 1260 (s), 1230 (sh), 1210 (s), 1180 (sh), 1145 (m), 1080 (s), 1010 (s), 975 (s), 950 (w), 920 (w), 870 (w), 860 (s), 835 (w), 800 (w), 780 (m), 730 (s), 690 (m), 650 (sh), 635 (sh), 610 (s), 580 (m), 525 (w), 505 (w). $^{27}$Al NMR ($\delta$, $C_6D_6$): 73 ($\omega_{1/2}$ = 10 550 Hz).

**Isomer 1a.** $^1$H NMR ($\delta$, $C_6D_6$): 7.22 (2 H, s, $C_6H_2$, BHT), 2.94 [1 H, d, $J$(H–H) = 15.6 Hz, $CH$], 2.34 (3 H, s, $CH_3$, BHT), 2.19

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[1 H, d, $J$(H–H) = 15.6 Hz, C$H$], 1.65 [18 H, s, C($CH_3$)$_3$, BHT], 1.25 [3 H, t, $J$(H–H) = 8.29 Hz, Al—$CH_2CH_3$], 1.02 (3 H, s, $CH_3$), 0.98 [9 H, s, C($CH_3$)$_3$], 0.78 [9 H, s, C($CH_3$)$_3$], 0.35 [2 H, q, $J$(H–H) = 8.29 Hz, Al—$CH_2$]. $^{13}$C NMR ($\delta$, $C_6D_6$): 241.41 (O=$C$), 154.91 (O$C$, BHT), 138.62 (*o*-$C$, BHT), 125.91 (*m*-$C$, BHT), 125.41 (*p*-$C$, BHT), 78.10 ($CH_2$), 44.63 (O$C$), 39.59 ($CH_3$), 35.02 [$C$(CH$_3$)$_3$, BHT], 31.42 [C($CH_3$)$_3$, BHT], 25.48 [O=CC($CH_3$)$_3$], 25.38 [OCC($CH_3$)$_3$], 24.94 [OC$C$(CH$_3$)$_3$], 24.16 [O=C$C$(CH$_3$)$_3$], 21.58 ($CH_3$, BHT), 9.70 (Al—$CH_2CH_3$), 0.25 (Al—$CH_2$).

**Isomer 1b.** $^1$H NMR ($\delta$, $C_6D_6$): 7.24 (2 H, s, $C_6H_2$, BHT), 3.03 [1 H, d, $J$(H–H) = 16.4 Hz, C$H$], 2.35 (3 H, s, $CH_3$, BHT), 2.19 [1 H, d, $J$(H–H) = 16.4 Hz, C$H$], 1.70 [18 H, s, C($CH_3$)$_3$, BHT], 1.12 [3 H, t, $J$(H–H) = 8.25 Hz, Al—$CH_2CH_3$], 1.07 (3 H, s, $CH_3$), 1.00 [9 H, s, C($CH_3$)$_3$], 0.78 [9 H, s, C($CH_3$)$_3$], 0.272 [2 H, q, $J$(H–H) = 8.25 Hz, AL—$CH_2$]. $^{13}$C NMR ($\delta$, $C_6D_6$): 241.64 (O=$C$), 154.86 (O$C$, BHT), 138.75 (*o*-$C$, BHT), 125.91 (*m*-$C$, BHT), 125.38 (*p*-$C$, BHT), 75.80 ($CH_2$), 46.93 (O$C$), 39.36 ($CH_3$), 35.05 [$C$(CH$_3$)$_3$, BHT], 31.32 [C($CH_3$)$_3$, BHT], 25.60 [OC$C$(CH$_3$)$_3$], 25.48 [O=CC($CH_3$)$_3$], 25.44 [OCC($CH_3$)$_3$], 24.16 [O=C$C$(CH$_3$)$_3$], 21.58 ($CH_3$, BHT), 9.80 (Al—$CH_2CH_3$), 0.50 (Al—$CH_2$).

**AlEt(BHT)[O=C(Ph)CH($CH_3$)C(Ph)(Et)O] (2). Method 1.** O=C(Et)Ph (0.54 g, 4.04 mmol) was added to a pentane (40 mL) solution of AlEt(BHT)$_2$ (1.0 g, 2.02 mmol). A yellow-orange solution resulted. After it was stirred for 2 h, the solution was reduced under vacuum to about 10 mL and a yellow solid precipitated. This was filtered and recrystallized from pentane to yield orange crystals; yield 60%.

**Method 2.** O=C(Et)Ph (2.14 mL, 15.84 mmol) was added via syringe to AlEt$_2$(BHT)(Et$_2$O) (3.0 g, 7.92 mmol) in pentane (50 mL). A deep orange color resulted. After the mixture was stirred for 1 h, the solvent was removed, under vacuum, to leave an orange oil. The oil was left under dynamic vacuum overnight ($\sim 10^{-3}$ mmHg) and then washed with pentane, yielding a yellow precipitate. This was filtered and dried under vacuum: yield: ~75%; mp 152–153 °C. Anal. Calcd for $C_{35}H_{47}O_3Al$: C, 77.45; H, 8.72. Found: C, 76.52; H, 8.70. IR (Nujol, NaCl, cm$^{-1}$): 1600 (m), 1585 (s), 1555 (s), 1290 (sh), 1270 (s), 1260 (s), 1240 (s), 1200 (m), 1185 (m), 1160 (m), 1120 (w), 1085 (w), 1050 (m), 1000 (m), 980 (m), 925 (m), 880 (s), 860 (m), 830 (w), 800 (w), 775 (w), 745 (s), 720 (m), 700 (s), 670 (s), 620 (s). $^1$H NMR ($\delta$, $CDCl_3$): 8.59–7.45 (10 H, m, $C_6H_5$, Ph), 7.31 (2 H, s, $C_6H_2$, BHT), 4.44 [1 H, q, $J$(H–H) = 6.9 Hz, C$H$CH$_3$], 2.54 (3 H, s, $CH_3$, BHT), $\delta_A$ = 2.04, $\delta_B$ = 1.68 [2 H, ABX$_3$ spin system, $J_{AB}$ = 13.4 Hz, $J_{AX}$ = $J_{BX}$ = 7.0 Hz, $CH_2CH_3$], 1.79 [18 H, s, C($CH_3$)$_3$, BHT], 1.44 [3 H, d, $J$(H–H) = 6.9 Hz, CHC$H_3$], 1.27 [3 H, t, $J$(H–H) = 8.0 Hz, Al—$CH_2CH_3$], 0.94 [3 H, t, $J$(H–H) = 6.8 Hz, $CH_2CH_3$, OC(Ph)Et], 0.38 [2 H, q, $J$(H–H) = 8.0 Hz, Al—$CH_2$]. $^{13}$C NMR ($\delta$, $CDCl_3$): 222.03 (O=C), 154.39 (O$C$, BHT), 145.55 ($C_6H_5$, Ph), 138.62 (*o*-$C$, BHT), 134.17, 131.00, 129.84, 127.80, 126.26 ($C_6H_5$, Ph), 125.62 (*m*-$C$, BHT), 124.93 (*p*-$C$, BHT), 80.41 [O$C$(Ph)Et], 50.63 ($CHCH_3$), 37.29 (CH$CH_3$), 34.60 [$C$(CH$_3$)$_3$, BHT], 30.86 [C($CH_3$)$_3$, BHT], 21.21 ($CH_3$, BHT), 14.72 ($CH_2CH_3$), 9.03 ($CH_2CH_3$), 7.91 (Al—$CH_2CH_3$), –0.31 (Al—$CH_2$). $^{27}$Al NMR ($\delta$, $CDCl_3$): 65.3 ($w_{1/2}$ = 4380 Hz).

**AlEt(BHT)[O=C(Et)CH($CH_3$)C(Et$_2$)O] (3). Method 1.** Excess O=C$Et_2$ (~1 mL) was added to a pentane (40 mL) solution of AlEt(BHT)$_2$ (2.0 g, 4.04 mmol). A pale yellow color formed, which upon stirring for 1 h became colorless. The resulting solution was reduced in volume under vacuum, and a white microcrystalline precipitate formed. This was filtered and dried under vacuum. Cooling the filtrate overnight (–20 °C) resulted in the formation of crystalline product, yield 80%.

**Method 2.** AlEt(BHT)$_2$ (2.0 g, 4.04 mmol) was dissolved in O=C$Et_2$ (~5 mL), resulting in a yellow/green solution from which a white precipitate formed. The excess O=C$Et_2$ was removed under vacuum and the resulting crude product recrystallized from pentane; mp 130–132 °C. Anal. Calcd for $C_{27}H_{48}O_3Al$: C, 72.60; H, 10.60. Found: C, 72.73; H, 10.81. IR (Nujol, NaCl, cm$^{-1}$): 1750 (w), 1625 (s), 1330 (w), 1310 (sh), 1290 (s), 1275 (s), 1260 (s), 1230 (w), 1215 (w), 1200 (m), 1180 (w), 1160 (s), 1125 (m), 1090 (w), 1055 (s), 1010 (s), 990 (sh), 950 (w), 930 (w), 915 (w), 890 (s), 855 (s), 830 (w), 800 (w), 775 (m), 740 (m), 710 (m), 665 (m), 635 (s), 600 (s). $^{27}$Al NMR ($\delta$, $C_6D_6$): 77.3 ($w_{1/2}$ = 12 640 Hz).

**Isomer 3a.** $^1$H NMR ($\delta$, $C_6D_6$): 7.27 (2 H, s, $C_6H_2$, BHT), 2.37 (3 H, s, $CH_3$, BHT), 2.32 [1 H, q, $J$(H–H) = 7.0 Hz, C$H$CH$_3$], $\delta_A$ = 2.0, $\delta_B$ = 1.83 [2 H, ABX$_3$ spin system, $J_{AB}$ = 20.6 Hz, $J_{BX}$ = $J_{AX}$ = 7.0 Hz, $CH_2CH_3$], 1.68 [18 H, s, C($CH_3$)$_3$, BHT], $\delta_A$ = 1.61, $\delta_B$ = 1.30 [2 H, ABX$_3$ spin system, $J_{AB}$ = 20.7 Hz, $J_{BX}$ = $J_{AX}$ = 7.4 Hz, $CH_2CH_3$], 1.27 (3 H, t, $J$(H–H) = 8.0 Hz, Al—$CH_2CH_3$), 1.18 [2 H, q, $J$(H–H) = 7.5 Hz, O=CC$H_2$CH$_3$], 0.99 [3 H, d $J$(H–H) = 7.0 Hz, CHC$H_3$], 0.82 [3 H, t, $J$(H–H) = 7.5 Hz, O=CCH$_2$C$H_3$], 0.71 [6 H, m, CH$_2$C$H_3$, Al—O—C(Et)$_2$], 0.37 [2 H, q, $J$(H–H) = 8.0 Hz, Al—$CH_2CH_3$]. $^{13}$C NMR ($\delta$, $C_6D_6$): 239.77 ($C$=O), 154.78 (O$C$, BHT), 138.82 (*o*-$C$, BHT), 125.94 (*m*-$C$, BHT), 125.34 (*p*-$C$, BHT), 76.83 [O$C$(Et)$_2$], 52.28 (HC$CH_3$), 38.77 [$CH_2CH_3$, Al—O—C(Et)$_2$], 34.85 [$C$(CH$_3$)$_3$, BHT], 33.24 (O=C-$CH_2CH_3$), 31.35 [C($CH_3$)$_3$, BHT], 30.41 (Al—$CH_2CH_3$), 28.79 [$CH_2CH_3$, Al—O—C(Et)$_2$], 21.58 [$CH_3$, BHT], 12.03 (HC$CH_3$), 8.47 (O=CC$H_2CH_3$), 8.09 and 6.83 [Al—O—C(CH$_2$CH$_3$)$_2$], 0.13 (Al—$CH_2CH_3$).

**Isomer 3b.** $^1$H NMR ($\delta$, $C_6D_6$): 7.02 (2 H, s, $C_6H_2$, BHT), 2.37 (3 H, s, $CH_3$, BHT), 2.32 [1 H, q, $J$(H–H) = 7.0 Hz, C$H$CH$_3$], $\delta_A$ = 2.0 $\delta_B$ = 1.83 [2 H, ABX$_3$ spin system, $J_{AB}$ = 20.6 Hz, $J_{BX}$ = $J_{Ax}$ = 7.0 Hz, O—C($CH_2CH_3$)$_2$], 1.72 [18 H, s, C($CH_3$)$_3$, BHT], $\delta_A$ = 1.61, $\delta_B$ = 1.30 [2 H, ABX$_3$ spin system, $J_{AB}$ = 20.7 Hz, $J_{BX}$ = $J_{AX}$ = 7.4 Hz, O—C($CH_2CH_3$)$_2$], 1.27 [3 H, t, $J$(H–H) = 8.0 Hz, Al—$CH_2CH_3$], 1.18 [2 H, q, $J$(H–H) = 7.5 Hz, O—CC$H_2$], 0.99 [3 H, d, $J$(H–H) = 7.0 Hz, CHC$H_3$], 0.91 [3 H, t, $J$(H–H) = 7.5 Hz, O=CCH$_2$C$H_3$], 0.71 [6 H, m, O—C(CH$_2$C$H_3$)$_2$], 0.36 [2 H, q, $J$(H–H) = 8.0 Hz, Al—$CH_2$]. $^{13}$C NMR ($\delta$, $C_6D_6$): 239.58 ($C$=O), 155.20 (O$C$, BHT), 138.80 (*o*-$C$, BHT), 125.94 (*m*-$C$, BHT), 125.34 (*p*-$C$, BHT), 76.23 [O$C$(Et)$_2$], 52.68 (HC$CH_3$), 38.04 [$CH_2CH_3$, O—C(Et)$_2$], 35.02 [$C$(CH$_3$)$_3$, BHT], 32.57 [O=CC$H_2$], 31.40 [C-(CH$_3$)$_3$, BHT], 30.41 [Al—$CH_2CH_3$], 29.27 [O—C($CH_2CH_3$)$_2$], 21.38 [$CH_3$, BHT], 11.73 (HC$CH_3$), 9.28 [O—CC$H_2CH_3$], 7.63 and 7.10 [O—C(CH$_2$CH$_3$)$_2$], 0.13 (Al—$CH_2$).

**Table III. Summary of X-ray Diffraction Data**

| | |
|---|---|
| formula | $C_{29}H_{51}AlO_3$ |
| mol wt | 474.78 |
| space group | $P2_1$ |
| $a$, Å | 9.3428 (6) |
| $b$, Å | 14.3079 (6) |
| $c$, Å | 11.3322 (6) |
| $\beta$, deg | 91.971 (4) |
| $V$, Å$^3$ | 1513.5 (3) |
| $Z$ | 2 |
| $D$(calcd), g cm$^{-3}$ | 1.046 |
| cryst dimens, mm | 0.07 × 0.08 × 0.10 |
| temp, °C | 25 |
| radiation | Cu K$\alpha$ (1.5418 Å, graphite monochromator) |
| $\mu$, cm$^{-1}$ | 7.43 |
| $2\theta$ limit, deg | $2 < 2\theta < 110$ |
| no. of collected rflns | 2159 |
| no. of unique rflns | 2159 |
| no. of obsd data ($F > 3\sigma(F)$) | 1907 |
| no. of params | 261 |
| $R$ | 0.0628 |
| $R_w$ | 0.0730 |
| final residual, e Å$^{-3}$ | 0.33 |

**Hydrolysis of 1.** To BHT-H (13.2 g, 60.0 mmol) in pentane (60 mL) was added AlEt$_3$ (60 mL of a 1.0 M hexane solution) via syringe. After the mixture was stirred for ~1/2 h, ether (15.0 mL) was added via syringe. The resulting solution was then reduced in volume to remove any excess ether, and $^t$BuMeCO (9.62 mL, 120.0 mmol) was added via syringe. A yellow color formed, which paled after ~1/2 h of stirring. The resulting solution was hydrolyzed (0.1 M HCl solution or saturated $NH_4Cl$ solution) and subsequently extracted with ether (3 × 75 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator. The remaining colorless liquid was distilled to yield 5-hydroxy-2,2,5,6,6-pentamethylheptan-3-one: yield 30%; bp 78.5 °C (3 mm) [lit. bp 64–65 °C,[12a] 89–90 °C (5 mm),[12b] 77 °C (3 mm),[12a] 60–67.5 °C (1.6 mm)[12a]]. IR (cm$^{-1}$): 3469 (associated OH), 2969 (s), 2909 (m), 2872 (m), 1708, (s) (C=O with H bonding), 1478 (m), 1465 (m), 1393 (m), 1365 (m), 1274 (w), 1261 (m), 1222 (w), 1201 (w), 1181 (w), 1137 (s), 1099 (s), 1049 (m), 1009 (m), 991 (m), 955 (w), 913 (m), 866 (w), 843 (sh), 832 (sh), 806 (m), 731 (w), 695 (w), 672 (w), 554 (w). $^1$H NMR ($\delta$, $CDCl_3$): 3.53 [2 H, q, AB pattern,

**Table IV. Fractional Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (×10³ Å²) of the Non-Hydrogen Atoms in AlEt(BHT)[O=C(ᵗBu)CH₂C(Me)(ᵗBu)O]**

| atom | *x/a* | *y/b* | *z/c* | *U*(eqv) |
|---|---|---|---|---|
| Al | 0.3744 (2) | 0.4070 | 0.2108 (2) | 0.043 (2) |
| O(1) | 0.3458 (5) | 0.3397 (4) | 0.3348 (4) | 0.047 () |
| O(2) | 0.5223 (5) | 0.4908 (4) | 0.2639 (4) | 0.053 (1) |
| O(3) | 0.4751 (5) | 0.3502 (4) | 0.1088 (4) | 0.054 (8) |
| C(1) | 0.212 (1) | 0.4823 (7) | 0.1518 (9) | 0.076 (3) |
| C(2) | 0.170 (1) | 0.4730 (9) | 0.0173 (9) | 0.093 (13) |
| C(11) | 0.2312 (7) | 0.3182 (5) | 0.4013 (6) | 0.042 (1) |
| C(12) | 0.2100 (7) | 0.3659 (5) | 0.5082 (6) | 0.045 (1) |
| C(13) | 0.0832 (8) | 0.3484 (6) | 0.5651 (7) | 0.053 (1) |
| C(14) | −0.0155 (9) | 0.2851 (6) | 0.5259 (7) | 0.057 (2) |
| C(15) | 0.0168 (8) | 0.2320 (6) | 0.4279 (7) | 0.054 (2) |
| C(16) | 0.1421 (7) | 0.2443 (5) | 0.3660 (6) | 0.043 (1) |
| C(41) | 0.6487 (8) | 0.4940 (6) | 0.2335 (7) | 0.051 (2) |
| C(42)A | 0.710 (2) | 0.407 (1) | 0.179 (1) | 0.056 (3) |
| C(42)B | 0.693 (2) | 0.444 (1) | 0.117 (2) | 0.057 (4) |
| C(43)A | 0.614 (2) | 0.377 (1) | 0.071 (1) | 0.043 (4) |
| C(43)B | 0.627 (2) | 0.342 (1) | 0.107 (2) | 0.050 (4) |
| C(44) | 0.7464 (9) | 0.5656 (6) | 0.2880 (7) | 0.056 (4) |
| C(45) | 0.662 (1) | 0.6364 (7) | 0.3577 (9) | 0.081 (11) |
| C(46) | 0.852 (1) | 0.5152 (8) | 0.3721 (9) | 0.086 (3) |
| C(47) | 0.827 (1) | 0.6167 (8) | 0.1899 (9) | 0.090 (7) |
| C(48)A | 0.601 (2) | 0.462 (1) | −0.15 (2) | 0.073 (5) |
| C(48)B | 0.689 (2) | 0.284 (1) | 0.212 (2) | 0.071 (5) |
| C(49) | 0.665 (1) | 0.2910 (8) | −0.0043 (9) | 0.086 (13) |
| C(50)A | 0.683 (3) | 0.204 (2) | 0.111 (3) | 0.072 (7) |
| C(50)B | 0.577 (2) | 0.202 (2) | −0.031 (2) | 0.049 (5) |
| C(51)A | 0.565 (2) | 0.248 (2) | −0.083 (2) | 0.046 (5) |
| C(51)B | 0.597 (2) | 0.359 (1) | −0.119 (2) | 0.079 (5) |
| C(52)A | 0.827 (2) | 0.321 (2) | −0.053 (2) | 0.078 (6) |
| C(52)B | 0.822 (2) | 0.280 (2) | −0.026 (2) | 0.063 (5) |
| C(121) | 0.3192 (8) | 0.4369 (6) | −0.5601 (6) | 0.051 (1) |
| C(122) | 0.305 (1) | 0.5318 (6) | 0.4951 (8) | 0.064 (21) |
| C(123) | 0.4740 (7) | 0.3987 (7) | 0.5563 (7) | 0.058 (8) |
| C(124) | 0.2910 (9) | 0.4569 (7) | 0.6924 (7) | 0.072 (13) |
| C(141) | −0.1539 (9) | 0.2719 (8) | 0.5890 (9) | 0.087 (21) |
| C(161) | 0.1780 (9) | 0.1763 (6) | 0.2654 (7) | 0.055 (2) |
| C(162) | 0.3316 (9) | 0.1378 (7) | 0.2898 (8) | 0.069 (8) |
| C(163) | 0.169 (1) | 0.2230 (7) | 0.1448 (7) | 0.070 (13) |
| C(164) | 0.072 (1) | 0.0920 (7) | 0.2604 (8) | 0.082 (16) |

$J$(H–H) = 16.0 Hz, $CH_2$], 2.61 [1 H, s, OH, exchanged with $D_2O$], 2.21 (3 H, s, $CH_3$), 1.22 (9 H, s, ᵗBu), 0.97 (9 H, s ᵗBu). $^{13}C$ NMR ($\delta$, $CDCl_3$): 213.3 (*C*=O), 74.87 (*C*—OH), 43.90 [$C(CH_3)_3$, ᵗBuMeC(OH)], 34.58 ($CH_2$), 26.02 [$C(CH_3)_3$, ᵗBuMeC(OH)], 25.20 [$C(CH_3)_3$, ᵗBuC=O], 24.19 [$C(CH_3)$ ᵗBuC=O], 17.56 ($CH_3$).

**Hydrolysis of 2 and 3.** The hydrolysis was performed in a manner similar to that for compound 1; however, analysis of the crude product prior to distillation indicated that for **2** an approximately 1:1:1:1 mixture of O=C(Et)Ph, HOC(H)(Et)Ph O=C(H)Ph, and $HOC(Et)_2Ph$ was obtained, and for **3** an equimolar mixture of $O{=}CEt_2$ and $HOC(H)Et_2$ was formed. These products were characterized via $^1H$ and $^{13}C$ NMR and GC techniques in comparison with commercially available authentic samples (Aldrich).

**Crystallography.** A colorless crystal of 1 measuring 0.07 × 0.08 × 0.10 mm was sealed in a glass capillary under an inert atmosphere and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Cu radiation. Final lattice parameters, as determined by a least-squares refinement of the setting angles of 25 accurately centered reflections ($2\theta > 40°$), together with other data collection and structure solution parameters are given in Table III. Experimental details of data collection have been discussed previously.[15]

After inclusion into the data of an empirical absorption correction based on 360° $\psi$ scans of five reflections, the structure was solved by use of the direct-methods option of SHELX-89.[16] This revealed the coordinates of the aluminum, its coordination sphere, and the BHT group. Subsequent difference Fourier maps, calculated by using SHELX,[17] eventually revealed the positions of all of the other non-hydrogen atoms, with two alternative positions shown for the C(ᵗBu)MeCH₂ fragment (excluding the ipso carbon of the *tert*-butyl group). These were initially included in the refinement such that equivalent atoms were treated with linked thermal parameters and the group occupancies were constrained to total 1. The latter converged at values of 0.497 (13) and 0.503 (13) and so were fixed at 0.5 for the final refinement. This refinement was performed with use of anisotropic thermal parameters for the nonaromatic, full-occupancy, non-hydrogen atoms with appropriate "riding" hydrogens placed in calculated positions [$d$(C–H) = 1.0 Å]. Neutral-atom scattering factors were taken from the usual sources.[18] Fractional atomic coordinates are listed in Table IV.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom parameters, and torsion angles (4 pages); a table of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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