

(d), 129.94 (d), 134.51 (s), 215.81 (s); MS  $m/e$  85 (100). Anal. Calcd for  $C_{18}H_{28}O_2$ : C, 78.21; H, 10.21. Found: C, 78.23; H, 10.19.

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**Registry No.** 1a, 97190-47-1; 1b, 97234-22-5; 1c, 97234-23-6; 1d, 97234-24-7; 1e, 97234-25-8; 1f, 97234-26-9; 1g, 97234-27-0; 1h, 97234-28-1; 1i, 97234-29-2; 4a, 97234-30-5; 4b, 97234-31-6; 4c, 97234-32-7; 4d, 97234-33-8; 4e, 97234-34-9; 4f, 97234-35-0; 4g, 97234-36-1;

4h, 97234-37-2; 4i, 97234-38-3; 4j, 97234-39-4; 4k, 97234-40-7; 4l, 97234-41-8; 4m, 97234-42-9; 4n, 97234-43-0; 7, 14113-94-1; 8, 97234-44-1; 11, 97234-45-2; 12, 97234-46-3; 13, 97234-47-4; 14a (isomer 1), 97234-48-5; 14a (isomer 2), 97234-55-4; 14b (isomer 1), 97234-49-6; 14b (isomer 2), 97234-56-5; 14c (isomer 1), 97234-50-9; 14c (isomer 2), 97234-57-6; 14d (isomer 1), 97234-51-0; 14d (isomer 2), 97234-58-7; 14e (isomer 1), 97234-52-1; 14e (isomer 2), 97234-59-8; 14f (isomer 1), 97234-53-2; 14f (isomer 2), 97234-60-1; 14g (isomer 1), 97234-54-3; 14g (isomer 2), 97234-61-2; BHT, 128-37-0; MeLi, 917-54-4; BuLi, 109-72-8; BzLi, 766-04-1; phenyllithium, 591-51-5; cyclohexanecarbonyl chloride, 2719-27-9; isobutyryl chloride, 79-30-1; cyclopentanecarbonyl chloride, 4524-93-0; cyclobutanecarbonyl chloride, 5006-22-4; cyclopropanecarbonyl chloride, 4023-34-1; 2-methylbutyryl chloride, 5856-79-1; 2,3-dimethylbutyryl chloride, 51760-90-8; 2-ethylbutyryl chloride, 2736-40-5; 2,3,3-trimethylbutyryl chloride, 52912-50-2; benzaldehyde, 100-52-7; lithiophenylacetylene, 4440-01-1; butanal, 123-72-8; diethylamine, 109-89-7; trimethylsilyl chloride, 75-77-4.

## Structures of Three Lithium Ester Enolates by X-ray Diffraction: Derivation of Reaction Path for Cleavage into Ketene and Alcoholate<sup>1</sup>

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**Abstract:** Crystal structure analyses have been carried out for lithium enolates of the following three esters: *tert*-butyl propionate ((*Z*)-1), *tert*-butyl 2-methylpropionate (2), and methyl 3,3-dimethylbutanoate ((*Z*)-3). Enolates (*Z*)-1 and 2 are dimeric (with one TMEDA per Li atom), whereas (*Z*)-3 is tetrameric (with one THF per Li atom). The *Z* configuration of 1 and 3 established by X-ray analysis is in agreement with that assigned by Ireland. From a detailed analysis of the geometry of the ester enolate grouping, the reaction path trajectory for the breakdown of this type of molecule can be derived. The implication of ketenes as intermediates, suggested by this analysis, could be confirmed chemically.

In spite of the central importance of ester enolates as reactive intermediates in synthetic organic chemistry, very little is known about the actual structures of the metallated species involved. This lack of information is largely attributable to the low stability of ester enolates in general. In fact, the structures of only two metal derivatives of esters have been established by X-ray analysis: one is the Reformatsky reagent derived from *tert*-butyl bromoacetate,<sup>2</sup> and the other is a lithium derivative of the highly acidic pentakis(methoxycarbonyl)cyclopentadiene.<sup>3</sup> Nevertheless, it has been more than 10 years since the Lochmann<sup>4</sup> and Rathke<sup>5</sup> groups described the isolation of pure lithium derivatives of esters as solid substances. The analysis of these compounds was at that time limited to what could be achieved by IR and NMR spectroscopy; the deduction was that they are to be formulated as enolates. Deprotonation of esters of the type  $RR'CH-COOR''$  with LDA (lithium diisopropylamide) gives in principle (*E*)- or (*Z*)-configured enolates, shown as (*E*)-1 and (*Z*)-1 for the example of *tert*-butyl propionate (Scheme I).

Ireland and his co-workers<sup>6</sup> have shown that these are obtainable as distinct species by deprotonation in different media and were

Scheme I

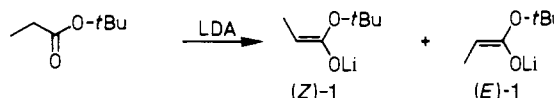


Table I. Crystallographic Data for (*Z*)-1-TMEDA, 2-TMEDA, and (*Z*)-3-THF

	( <i>Z</i> )-1-TMEDA	2-TMEDA	( <i>Z</i> )-3-THF
formula	$C_{13}H_{29}N_2O_2Li$	$C_{14}H_{31}N_2O_2Li$	$C_{11}H_{21}O_3Li$
formula wt	252.33	266.35	208.23
space group	$C2/c$	$C2/c$	$P\bar{1}$
temp, °C	-130	-140	-170
<i>a</i> , Å	20.050 (9)	19.91 (1)	10.454 (2)
<i>b</i> , Å	8.773 (4)	9.172 (3)	10.679 (2)
<i>c</i> , Å	18.75 (1)	18.94 (1)	24.959 (4)
$\alpha$ , °	90	90	77.04 (1)
$\beta$ , °	103.66 (4)	95.35 (5)	78.60 (2)
$\gamma$ , °	90	90	67.94 (2)
<i>V</i> , Å <sup>3</sup>	3205.6	3442.9	2496.6
<i>Z</i>	8	8	8
$\sin \theta_{max}/\lambda$ , Å <sup>-1</sup>	0.724	0.504	0.538
$d_{calcd}$ , g/cm <sup>3</sup>	1.05	1.03	1.11
no. of unique data			
total	5090	1843	6524
with $I > 3\sigma_I$	2522	1125	3482
<i>R</i> , %	4.2	4.7	4.1
<i>R</i> <sub>w</sub> , %	4.9	4.7	4.2

able to assign their configurations by identification of the Claisen rearrangement products of all four crotyl propionate enolates under the assumption that the [3,3]-sigmatropic shift proceeds via a chair-like transition state.

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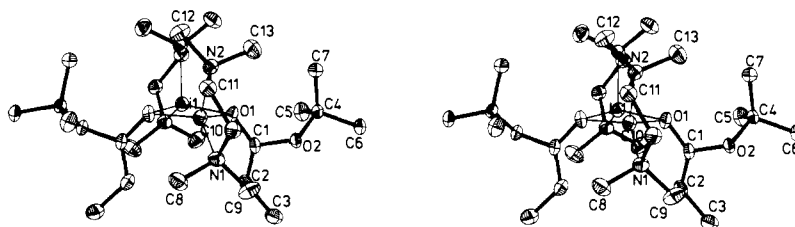
(2) (a) Dekker, J.; Boersma, J.; van der Kerk, G. J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 553. (b) Dekker, J.; Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L. *Organometallics* **1984**, *3*, 1403.

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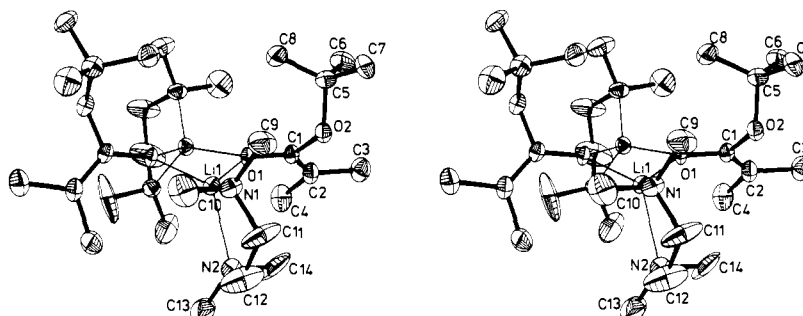
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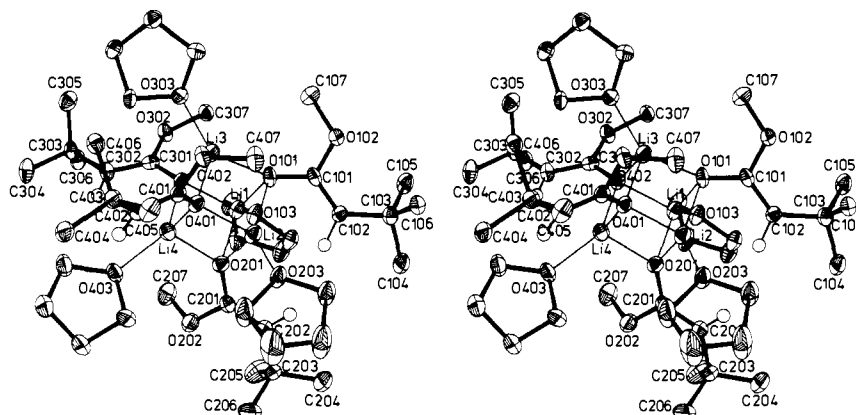
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**Figure 1.** ORTEP<sup>13</sup> stereoview of [2(*Z*)-1-2TMEDA]. The two halves of the dimer are related by crystallographic  $C_2$  axis. Displacement ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms are omitted.



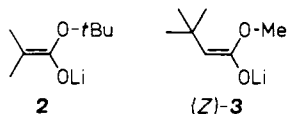
**Figure 2.** ORTEP<sup>13</sup> stereoview of [2-2-2TMEDA]. The two halves of the dimer are related by a crystallographic  $C_2$  axis. Displacement ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms are omitted.



**Figure 3.** ORTEP<sup>13</sup> stereoview of the tetramer [4(*Z*)-3-4THF]. Displacement ellipsoids are drawn at the 50% probability level. Only the vinylic hydrogen atoms are shown.

The reaction rate of the so-called "self-condensation" of ester enolates has been studied by Woodbury and Rathke,<sup>7</sup> who showed that ester enolates are less stable than amide enolates. As a possible explanation, cleavage into ketene and alcoholate has been proposed.<sup>8</sup>

In order to obtain definitive information about the structures of ester enolates, we have now determined the structures of the lithium enolates of *tert*-butyl propionate ((*Z*)-1), *tert*-butyl 2-methylpropionate (2), and methyl 3,3-dimethylbutanoate ((*Z*)-3) (see Table I).



With the help of the structure correlation principle,<sup>9,10</sup> the results of these analyses together with other structural information have

allowed us to define certain details of the reaction path trajectory leading from ester enolates to ketenes and alcoholates. Finally, the intermediacy of such ketenes has been demonstrated by trapping experiments.<sup>11</sup>

#### Description of the Structures

**Aggregation.** All three lithium ester enolates described here form aggregates in the crystalline state. Solvent molecules as well as enolate anions are attached to the lithium cations. In the crystal the aggregates appear to be held together only by van der Waals interactions. Compound (*Z*)-3 forms tetramers of the composition [4(*Z*)-3-4THF], similar to the aggregates formed by lithium ketone enolates,<sup>12</sup> whereas (*Z*)-1 and 2 form dimers with the compositions [2(*Z*)-1-2TMEDA] and [2-2-2TMEDA] (see Figures 1-3; THF = tetrahydrofuran; TMEDA = *N,N,N',N'*-tetramethylethylenediamine).

Although the  $Li_4O_4$  cube in the tetramer has no crystallographic symmetry, the twelve Li-O distances cover only the relatively small range of 1.90 to 2.04 Å; the average Li-O distance of 1.96 Å is

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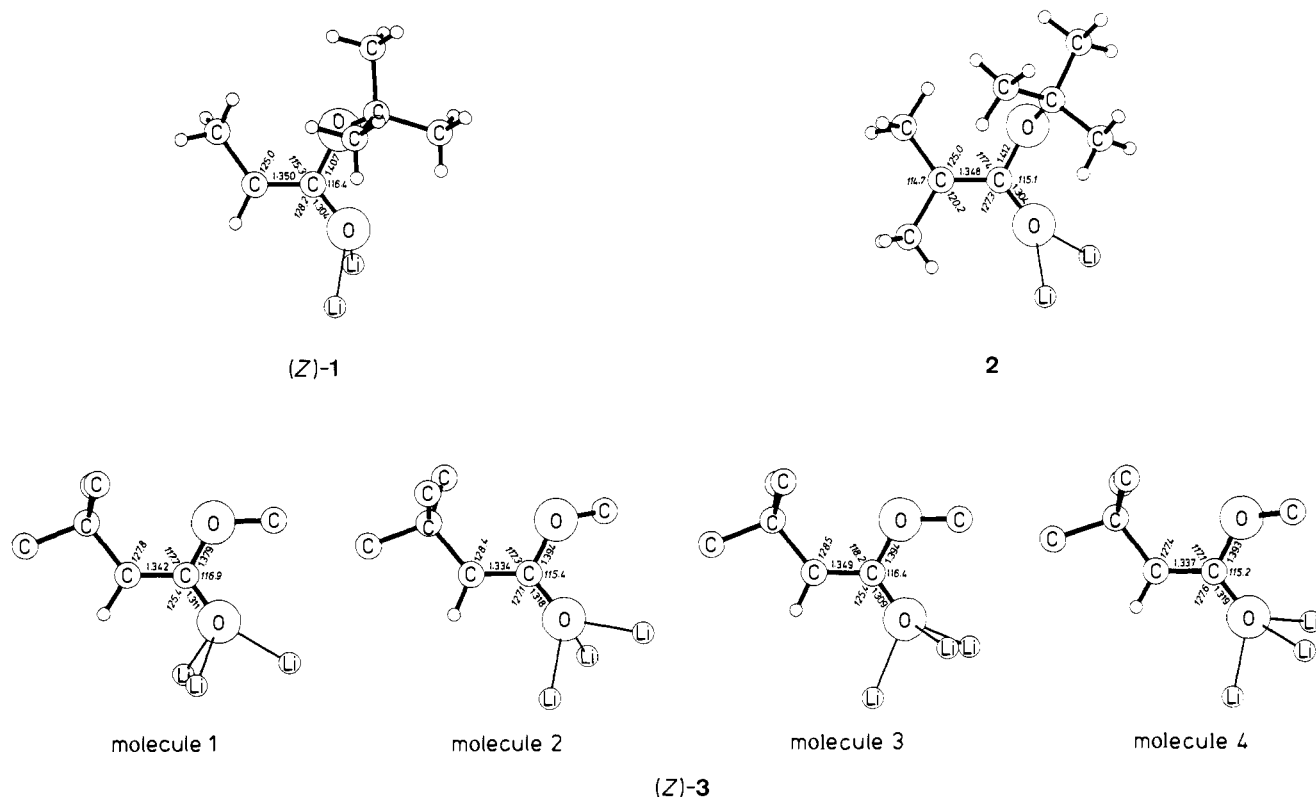


Figure 4. Comparison of some structural parameters of the six crystallographically independent ester enolate molecules (see also Table II).

practically the same as that in the pinacolone and cyclopentanone lithium enolates described previously.<sup>12</sup> This building block thus seems to have a rather well-defined structure. Each lithium atom in the tetramer is also coordinated to the oxygen atom of a THF molecule. As found in a number of other structures,<sup>14</sup> the Li···O(ether)-direction coincides closely with the C–O–C bisector, i.e., it is an  $sp^2$ -like lone pair on O rather than a  $sp^3$ -like lone pair that is involved in the bonding to lithium.

The dimeric aggregates [2(*Z*)-1·2TMEDA] and [2 2·2TMEDA] are based on  $Li_2O_2$  four-membered rings, in which the Li–O distances lie in the range 1.90 to 1.95 Å, i.e., somewhat shorter than in the tetramer. In both crystals, the four-membered ring has a crystallographic dyad axis and is approximately square, slightly folded ( $9.2^\circ$ ,  $22.0^\circ$ ) about the Li···Li diagonal, in contrast to the  $Li_2C_2$  four-membered rings in dimers derived from carbanionoid species,<sup>15</sup> where the Li···Li diagonal is much shorter than the C···C one.

In the dimers each Li attains tetrahedral coordination by bonding to the two nitrogen atoms of a TMEDA molecule. In (*Z*)-1 the Li···N distances are 2.180 (3) and 2.176 (3) Å, and in 2 they are 2.147 (8) and 2.309 (8) Å. In (*Z*)-1 the dimensions of the TMEDA unit are close to the standard dimensions recently derived for this fragment,<sup>15</sup> whereas in 2 there are quite large deviations. These features suggest that the TMEDA units in the crystal structure of 2 are actually slightly disordered (even at 133 K), and the abnormally large and anisotropic Gaussian displacement ellipsoids observed for some of the carbon atoms of this group (see Figure 2) are further indications for this. The long Li···N distances in 2 and the apparent disorder affecting the atoms of the TMEDA group in this compound may both be consequences of local overcrowding in this structure (the shortest contact distances are C14···C1 3.314 (8) Å, C14···C2 3.546 (8) Å, C13···C4' 3.567 (8) Å, C14···C4 3.686 (8) Å).

**Configuration of the C=C Double Bond.** On mechanistic grounds, Ireland and his co-workers have assigned the (*Z*) con-

figuration to the lithium ester enolates of the type  $RHC=C(OLi)(OR'')$  prepared in neat THF and the (*E*) configuration to those obtained in THF/HMPA (hexamethylphosphoramide). We were not able to crystallize 1 from neat THF (in which it was generated according to Ireland's prescription) but only through the following procedure: TMEDA was added to the THF solution of the ester enolate 1 and the resulting solution was evaporated to dryness at  $-40^\circ C$  in high vacuum (as a chelating ligand, TMEDA displaces monodentate ligands such as THF and diisopropylamine). The complexed TMEDA in the dry product is not removed by this treatment. Crystals suitable for X-ray analysis were obtained by recrystallizing the residue from hexane to which a little TMEDA had been added. The crystalline product from a parallel run was redissolved in neat THF at  $-78^\circ C$  and quenched with TBDMSCl (*tert*-butyldimethylsilyl chloride) as described by Ireland (Scheme II).

The mixture of silyl ketene acetals 5 obtained by the above procedure has approximately the same composition of isomers (ca. 20:1, by  $^1H$  NMR) as that obtained in neat THF according to Ireland.<sup>6</sup> Thus the finding of the (*Z*) configuration in the crystal of 1 constitutes a confirmation of the correctness of Ireland's assignment.

**Ester Enolate Fragments Compared and Contrasted.** The ester enolate anions in all three crystals show an approximately coplanar arrangement of bonds connected to the  $C=C$  double bond ( $C=C$  distance 1.33 to 1.35 Å, see Table II); the bulkier substituent is cis to the alkoxy group.

The largest deviations from planarity involve the alkoxy O atom, which deviates in 2 by as much as 0.11 Å from the mean plane of the other atoms. In contrast to esters,<sup>18</sup> where also the alkoxy bond *a* lies in the ester plane, all six crystallographically independent ester enolates observed by us are markedly nonplanar; the alkoxy bond *a* tends to be anticlinal with respect to the  $C=C$  double bond *c*, i.e., synclinal with respect to the former carbonyl bond *d*. Some of these out-of-plane deviations are evident from inspection of Figures 1–3. The length of bond *d* lies in the range 1.30 to 1.32 Å and is thus 0.1 Å longer than a typical carbonyl bond and approximately 0.04 Å shorter than the C–O bond in the pinacolone enolate<sup>12</sup> (Table II). In contrast, the other vinylic C–O bond (*b*) lies in the range 1.38 to 1.41 Å and is thus markedly

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Scheme II

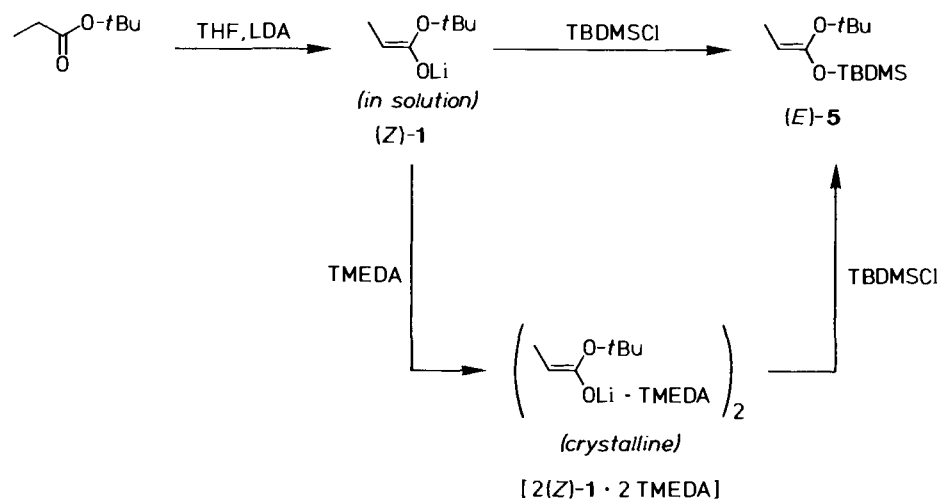


Table II. Some Structural parameters of (Z)-1, 2, (Z)-3, and Other Molecules with Comparable Fragments

com- pound	R	R'	$\bar{R}$	X	n	a	b	c	d	bc	cd	bd	ce	cf	abc	ref
(Z)-1	CH <sub>3</sub>	H	CH <sub>3</sub>	O	1	1.450 (2)	1.407 (2)	1.350 (3)	1.304 (2)	115.3 (1)	128.2 (2)	116.4 (1)		125.0 (2)	+120.4 (1)	this work
2	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	O	1	1.456 (5)	1.412 (5)	1.348 (6)	1.304 (5)	117.4 (3)	127.3 (4)	115.1 (3)	120.2 (4)	125.0 (4)	+102.9 (4)	this work
(Z)-3	<i>t</i> -Bu	H	H	O	1	1.411 (4)	1.379 (3)	1.342 (4)	1.311 (4)	117.7 (3)	125.4 (3)	116.9 (3)		127.8 (3)	+167.4 (3)	this work
						1.429 (6)	1.394 (4)	1.334 (5)	1.318 (3)	117.3 (3)	127.1 (3)	115.4 (3)		128.4 (3)	-135.9 (3)	
						1.431 (4)	1.394 (5)	1.349 (4)	1.309 (5)	118.2 (4)	125.4 (4)	116.4 (2)		128.5 (4)	+158.9 (3)	
						1.428 (4)	1.393 (5)	1.337 (4)	1.319 (4)	117.1 (3)	127.6 (3)	115.2 (3)		127.4 (3)	+140.7 (3)	
av values						1.425 (5)	1.390 (4)	1.341 (3)	1.314 (2)	117.6 (2)	126.4 (6)	116.0 (4)		128.0 (3)	151 (7)	
 4	lone pair	PPh <sub>3</sub> <sup>+</sup>		O			1.378 (6)	1.314 (7)	1.345 (6)	123.0 (5)	127.5 (5)	109.4 (4)				16
pinacolone enolate	H	H	H	C	3		1.521 (9)	1.338 (9)	1.347 (1)	122.7 (4)	122.3 (3)	115.0 (4)				12
enol ether				O	1		1.34	1.32		125. (7)						17
methyl ester			H	O	1	1.448 (8)	1.329 (9)									
esters of <i>t</i> -alcohols			C	O	1	1.473 (7)	1.34 (1)	1.50 (2)	1.195 (7)	111 (1)	125. (1)	123.4 (9)			170-180	18

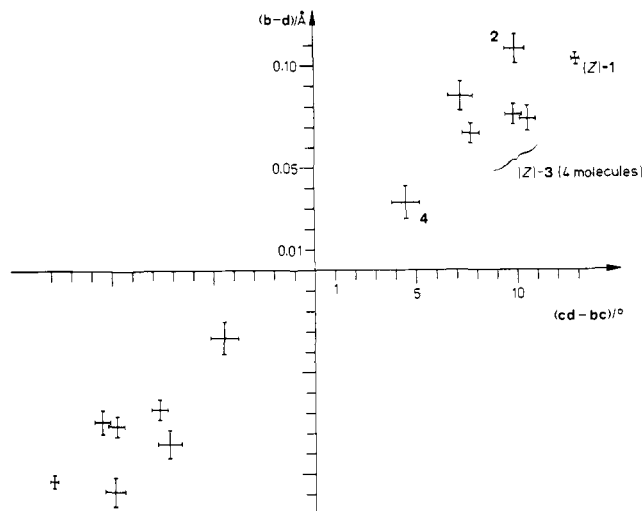


Figure 5. Bond length differences  $b-d$  plotted against bond angle differences  $cd-bc$  for the ester enolates 1-3 and the diethylketene acetal 4. Standard deviations (data from Table II) are indicated by crosses.

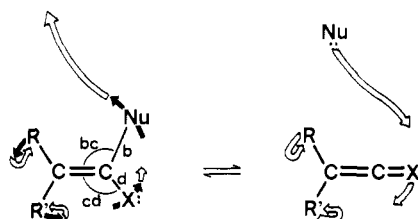


Figure 6. Sketch of the suggested reaction path for cleavage of a molecule with a trigonal center into a molecule with a digonal center and a leaving group  $\text{Nu}^-$ , or equivalently for the reverse reaction, nucleophilic attack on a digonal center (in the case of ester enolates:  $\text{X} = \text{O}^-$ ,  $\text{Nu} = \text{OR}''$ ). Bonds and angles are labeled as in Table II. The black arrows describe in an exaggerated way the movement of the atoms as deduced from the ester enolate structures, and the white arrows are estimated from the corresponding trajectory for the cleavage at tetrahedral centers.

longer than that in enol ethers (see Table II and Figure 4).

## Discussion

**Interpretation of the Enolate Fragment Geometry.** More detailed scrutiny reveals that there is a correlation between the *difference* of the two C—O bond distances ( $b-d$ ) and the *difference* of the two C=C—O bond angles ( $cd-bc$ ), as shown in Figure 5.

An analogous correlation between differences of C—O bond lengths and of C—C—O bond angles in acetals and other similar molecules was noted several years ago and interpreted as a manifestation of a displacement along the reaction coordinate for the incipient stage of the breakdown of a tetrahedral center (acetal) into a trigonal center (ketone) and a leaving group (alcohol or alcoholate).<sup>19,20</sup> In an analogous way, the correlation found here can be given an immediate interpretation in terms of the breakdown of a trigonal center (ester enolate) into a digonal center (ketene) and a leaving group (alcoholate). As bond  $d$  shortens and bond  $b$  lengthens, the shortening bond makes a larger angle with the C=C double bond and so moves toward the direction characteristic of the ketene. Similarly, as bond  $b$  begins to lengthen, the angle it forms with the C=C double bond  $c$  decreases. Thus the leaving group does not depart along the initial direction of bond  $b$ , but rather the angle of departure is continually adjusted to maintain an approximately equal angle with the incipiently forming carbonyl bond. This scenario is depicted schematically

## Scheme III

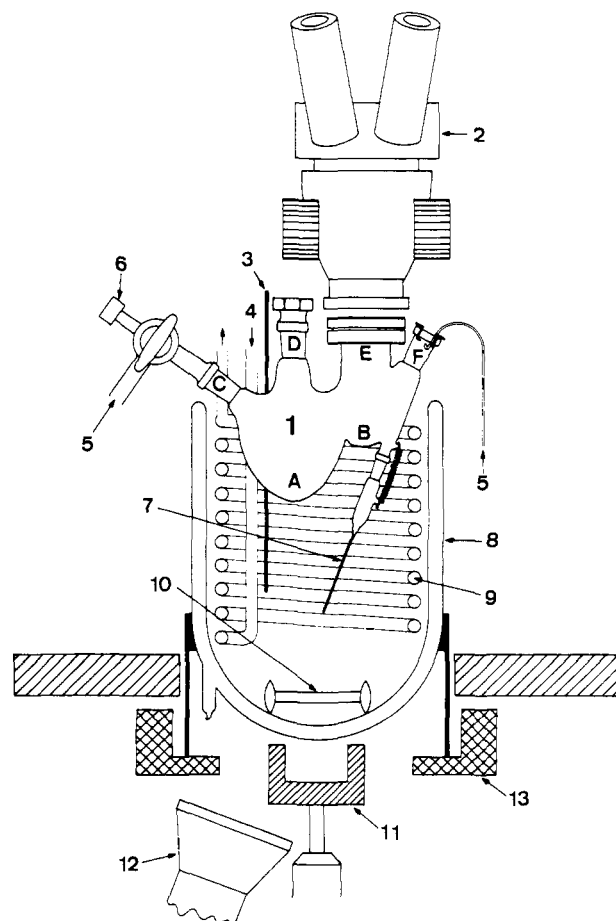
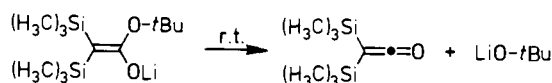


Figure 7. Apparatus for mounting temperature-sensitive crystals in a controlled atmosphere at low temperature: (1) flask for growing and manipulating the crystals, A crystal growth region, B crystal manipulation region, C joint for the connection to the argon-line and for operations with syringes, D joint for the connection to the argon-frit, E neck with observation window, F joint for the manipulation of dry crystals with needles (argon-flushed); (2) microscope; (3) Pt-100 temperature sensor; (4) liquid nitrogen inlet; (5) argon inlet; (6) serum stopper; (7) thin-walled capillary tube with joint (2 pieces); (8) transparent Dewar vessel (filled with acetone); (9) copper coil; (10) magnetic stirring bar; (11) magnet; (12) lamp with variable power; (13) support for the Dewar vessel.

in Figure 6 both for the breakdown of the trigonal structure and for the reverse reaction (nucleophilic attack on a digonal center).

Also noteworthy is the consistently large value of the C=C—C bond angle  $cf$  (cis to the alkoxy group) even in the tetrasubstituted enolate 2, suggestive of a steric interaction between the leaving group and the cis substituent R (see Table II).

It may not be entirely fortuitous that the displacement along the "reaction coordinate" observed for the three ester enolates corresponds to the observed order of stabilities. We found, for example, that (*Z*)-1 had to be handled at temperatures below  $-50^\circ\text{C}$  and decomposed rapidly at temperatures higher than  $-30^\circ\text{C}$ . By contrast, (*Z*)-3 could be handled without serious problems at

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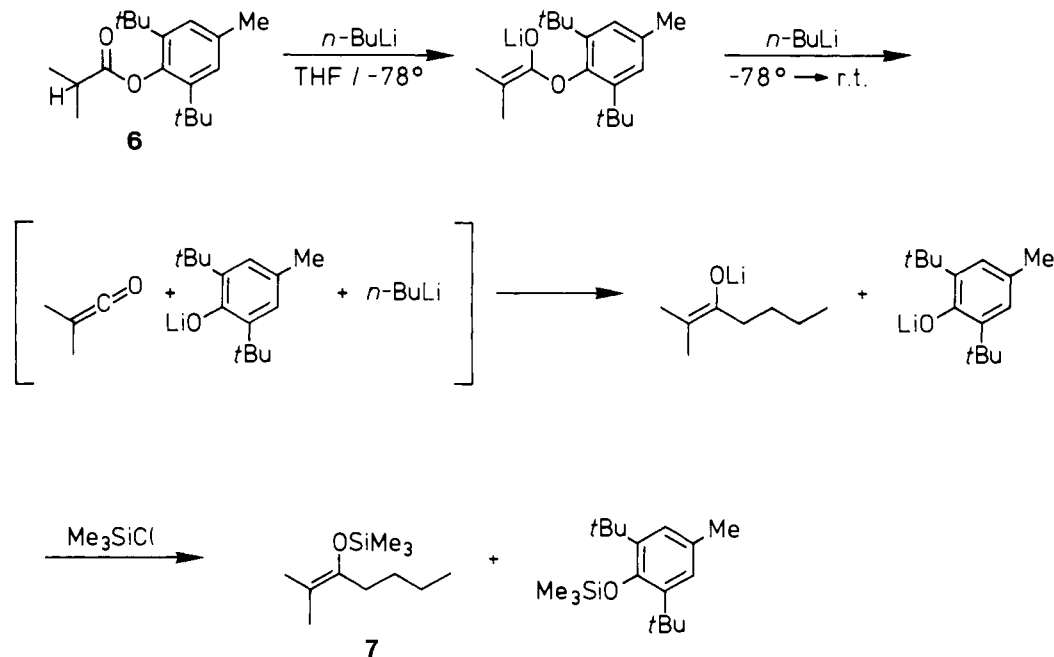
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(22) From the limited data available it would appear that for a given angular deviation from a supposed equilibrium structure the difference between the two bond lengths is larger for a trigonal center than for a tetrahedral one.

Scheme IV



room temperature, and crystals of **2** could be manipulated at 0 °C.<sup>23</sup>

The profound importance of quite small relative displacements on reaction rate has recently been demonstrated in an elegant series of experiments by Kirby and co-workers<sup>24</sup> for the breakdown of cyclic acetals with leaving groups locked in the axial position.<sup>25</sup>

**Ketenes or Ketene-like Intermediates in the decomposition of Ester Enolates.** The interpretation of the above-mentioned correlation in terms of a reaction path involving the intermediacy of such ketenes raises the question of the actual involvement of ketene intermediates in the decomposition of ester enolates. This question was taken up by Rathke and Woodbury<sup>7</sup> some time ago for different reasons. They attempted to prove the presence of ketenes as intermediates in several ways (addition of diethylamine; removal by an inert gas stream and subsequent trapping; IR spectroscopy, etc.) but without notable success. One of their best indications<sup>8</sup> is perhaps the formation of bis(trimethylsilyl)ketene from a corresponding lithium ester enolate (Scheme III).

In our own work,<sup>11</sup> we have tried to obtain similar evidence by cleavage of various lithium alkyl ester enolates in the presence of *n*-BuLi as trapping reagent, but we were unable to isolate cleanly interpretable reaction products. A more successful outcome was eventually attained by the use of (2,6-di-*tert*-butyl-4-methylphenyl) 2-methylpropanoate (**6**), whose lithium enolate<sup>26</sup> could be prepared in THF with *n*-BuLi and then cleaved by warming to room temperature in the presence of excess *n*-BuLi. Thanks to the better leaving group, good yields of the ketone enolate could be trapped with TMSCl (trimethylsilyl chloride) to give the silyl enol ether **7** as shown below (Scheme IV).<sup>27</sup>

This experiment constitutes a demonstration (although hardly a proof) of the transient existence of ketenes or ketene-like intermediates in the decomposition of ester enolates.<sup>28-30</sup>

(23) In a similar way the remarkable large displacement along the reaction coordinate for acetal breakdown found in a hydroxy lactone<sup>19</sup> can be regarded as an expression of the extremely high rate observed in the unimolecular hydroxy lactone  $\rightleftharpoons$  keto acid isomerization. The Arrhenius activation energy for this reaction is around 24–28 kJ/mol.

(24) (a) Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 288. (b) Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.* **1984**, *106*, 6200. (c) Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6207.

(25) The longer they are, the faster they break.

(26) For the use of similar ester enolates in diastereoselective aldol reactions see: Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H.; Lampe, J. *Tetrahedron* **1981**, *37*, 4087.

(27) For the reaction of diethylketene with *n*-BuLi see: Tidwell, T. T. *Tetrahedron Lett.* **1979**, 4615.

## Experimental Section

**General.** All intensity measurements were carried out with an ENRAF NONIUS CAD4 diffractometer equipped with a graphite monochromator (Mo K $\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ) and a cooling device. The structures were solved by MULTAN80<sup>31</sup> and refined by blocked full-matrix least-squares analysis with use of SHELX76<sup>32</sup> and the X-RAY72<sup>33</sup> system. The final refinements were based on experimental weights, modified for (*Z*)-1-TMEDA and (*Z*)-3-THF by an exponential function<sup>34</sup>  $w_M = w \exp(rs^2)$  with  $r = 5 \text{ \AA}^2$ .

**Preparation and Crystal Structure Analysis of (*Z*)-1.** A 100-mL three-necked flask was connected to a three-way stopcock, to a cool trap, and to an argon frit with the crystal-mounting apparatus (no. 1 in Figure 7, connected via joint D; joint F stoppered; caps instead of capillaries 7) as receiver. In the flask 10.0 mmol of LDA was generated in 30 mL of THF at  $-78^\circ \text{C}$ . During 10 min, 1.225 g of *tert*-butyl propionate (9.4 mmol) was added dropwise. After the mixture was stirred for 20 min at  $-78^\circ \text{C}$  1.429 g of TMEDA (12.3 mmol) was added and the solvent pumped off in high vacuum at  $-35^\circ \text{C}$ . To the yellowish residue 20 mL of hexane and 2 mL of TMEDA were added. After filtration, the solution was cooled from  $-40$  to  $-60^\circ \text{C}$  during 12 h. After removal of the mother liquor with a syringe at  $-60^\circ \text{C}$ , washing with  $2 \times 5 \text{ mL}$  of hexane, and drying in high vacuum at  $-50^\circ \text{C}$ , the caps at the small joints were substituted by the capillary tubes 7. Part A of the apparatus was cooled during this procedure. The apparatus 1 was then set into the Dewar vessel 8 (filled with acetone; temperature  $-55^\circ \text{C}$ ). Crystal cutting, selection, and mounting in the tubes 7 with octane as adhesive was carried out through the argon-flushed joint F. The capillaries were then transferred to a cold methylene chloride bath, sealed with a small burner, and adjusted on the diffractometer with a thermally insulating holder.

(28) Similar deviations from the ideal local  $C_{2v}$  symmetry have been observed in  $\alpha$ -substituted enamines: Van Meerssche, M.; Germain, G.; Declercq, J. P.; Molhant, N. *Cryst. Struct. Commun.* **1979**, *8*, 45. Van Meerssche, M.; Germain, G.; Declercq, J. P.; Colens, A. *Acta Crystallogr.* **1979**, *B35*, 907. Ghosez, L.; Marchand-Brynaert, J. *Adv. Org. Chem.* **1976**, *9* (Pt. 1), 421. (29) MOM ester enolates are cleaved on warming: Schultz, A. G.; Berger, M. H. *J. Org. Chem.* **1976**, *41*, 585.

(30) For the in situ generation of ketene imines see: Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567. Meyers, A. I.; Mihelich, E. D. *Angew. Chem.* **1976**, *88*, 321; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270.

(31) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN80. A system of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; University of York: York, England, 1980.

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**Preparation and Crystal Structure Analysis of 2.** LDA (20 mmol) was generated in 30 mL of hexane at 0 °C in a 100-mL three-necked flask connected to a three-way stopcock, to a cool trap, and to an argon frit with a 50-mL two-necked flask with three-way stopcock as receiver. On cooling to -78 °C 2.765 g (19.2 mmol) of *tert*-butyl 2-methylpropanoate was added during 10 min. After 1 h of stirring at -78 °C, the hexane and the diisopropylamine were distilled off at a bath temperature of -25 °C. To the resultant white powder, 20 mL of hexane and 5 mL of TMEDA were added at -30 °C. After being stirred for 5 min, the suspension was quickly filtered through the argon frit by turning the apparatus. The cooled receiver with the clear filtrate was removed in an argon stream and quickly stoppered. The solution was cooled from -40 to -60 °C during 12 h. After removal of the mother liquor at -60 °C, the crystals were washed with 4 × 7 mL of hexane, dried in high vacuum at -40 °C, and mounted at 0 °C in capillary tubes with dodecane as adhesive.

**Preparation and Crystal Structure Analysis of (Z)-3.** Methyl 3,3-dimethylbutanoate (650 mg, 5 mmol) was added at -78 °C to a solution of 5 mmol of LDA (generated at -20 °C) in 5 mL of THF. After the mixture was stirred for 30 min, the solvent was removed in high vacuum. The resultant white powder was redissolved in 3.2 mL of hexane and 0.8 mL of THF. On slow cooling from -20 to -80 °C, beautiful crystals were obtained. After removal of the mother liquor, these were mounted at room temperature in capillary tubes with hexadecane as adhesive.

**Trapping Experiment.** A solution of **6** (5.799 g, 20.0 mmol) in 35 mL of THF was added slowly to a solution of 41 mmol of BuLi (hexane solution,  $c = 1.60$  mol/L) in ca. 200 mL of THF at -78 °C. The clear

solution was allowed to warm to room temperature overnight. The mixture was cooled again to -78 °C, then a solution of TMSCl (4.6 g, 42 mmol) in 15 mL of THF was added. After the mixture was slowly warmed to room temperature (3 h), the solvent was evaporated and the residue quickly worked up with ice-cold NaHCO<sub>3</sub> solution/pentane. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated, and the residue was distilled in a micro-distillation apparatus. After a small forerun, 2.6 g of **7** was obtained as a colorless oil (yield: 65%). The crystalline residue is the silylated phenol.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of **7**: 0.162 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.902 (t,  $J = 7.2$ , 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.25-1.40 (m, 2 H, CH<sub>2</sub>), 1.40-1.50 (m, 2 H, CH<sub>2</sub>), 1.579 (s, 3 H, C=C-CH<sub>3</sub>), 1.595 (s, 3 H, C=C-CH<sub>3</sub>), 2.090 (t,  $J = 7.5$ , 2 H, C=C-CH<sub>2</sub>-).

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**Registry No.** [2(Z)-1,2TMEDA], 97210-50-9; [2(Z)-2TMEDA], 97210-51-0; [4(Z)-3,4THF], 97210-52-1; **6**, 97190-47-1; **7**, 97190-48-2; TMSCl, 75-77-4; *tert*-butyl propionate, 20487-40-5; *tert*-butyl 2-methylpropanoate, 16889-72-8; methyl 3,3-dimethylbutanoate, 10250-48-3; (2,6-di-*tert*-butyl-4-methylphenoxy)trimethylsilane, 18510-49-1.

**Supplementary Material Available:** Tables of atomic coordinates and displacement parameters for (Z)-1-TMEDA, 2-TMEDA, and [4(Z)-3,4THF] (10 pages). Ordering information is given on any current masthead page.

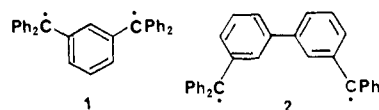
## *m*-Quinodimethane, Parent Hydrocarbon of the *m*-Quinonoid Non-Kekulé Series. Low-Temperature Isolation and Solution-Phase Chemical Reactivity

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**Abstract:** The syntheses of several precursors to 2,6-dimethylenebicyclo[3.1.0]hex-3-ene (**11**) are described. Photochemical decomposition of 2,6-dimethylene-4-(2-oxopropyl)bicyclo[3.1.0]hexane (**17a**), 4-(2-oxo-2-phenylethyl)-2,6-dimethylenebicyclo[3.1.0]hexane, 4-(benzoyloxy)-2,6-dimethylenebicyclo[3.1.0]hexane, or base-induced elimination from 4-[(methanesulfonyl)oxy]-2,6-dimethylenebicyclo[3.1.0]hexane all gave [2.2]metacyclophane. In the presence of conjugated dienes (butadiene, 2,3-dimethylbutadiene, 2,4-hexadiene, and isoprene), photochemical decomposition of **17a** leads to cycloadducts (40-60%) empirically derived from 1 mol each of a C<sub>8</sub>H<sub>8</sub> hydrocarbon and olefin. From butadiene, the major products are the (4Z)-bicyclo[6.3.1]dodeca-1(12),4,8,10-tetraene and a 13:1 mixture of 7- and 5-methyl-1-ethenylindans, respectively. The product distribution of cycloadducts is unaffected by dilution or oxygen, which is consistent with only one reactive intermediate. Mechanistic parsimony suggests that the decomposition of the above substrates initially gives the bicyclic hydrocarbon **11** which undergoes cyclopropyl ring cleavage to form the reactive diradical *m*-quinodimethane (*m*-xylylene, **3**) which then dimerizes or reacts with the included trapping reagent. Evidence for the initial formation of hydrocarbon **11** in the photochemical approaches is outlined. The intermediacy of the diradical **3** is suggested by (i) the observation of the previously identified electron paramagnetic resonance spectrum of the triplet state of **3** from the photolysis of **17a** at 77 K and (ii) the deuterium distribution in the cycloadduct from butadiene and 4-(2-oxopropyl)-2-(dideuteriomethylene)-6-methylenebicyclo[3.1.0]hexane which requires the reactive intermediate to have static or time-averaged bilateral symmetry. Stereochemical studies on the reaction of biradical **1** with 2,4-hexadienes indicate a two-step cycloaddition mechanism involving a long-lived adduct biradical.

Although *m*-quinonoid "non-Kekulé" compounds<sup>1a</sup> have been known and recognized for 70 years,<sup>1b-c,2,3</sup> the early examples, such as the Schlenk hydrocarbon **1**<sup>b</sup> and the Schlenk-Brauns hydrocarbon **2**,<sup>1c</sup> are so heavily substituted by phenyl groups that their



uniquely *m*-quinonoidal properties are veiled.<sup>4</sup>

*m*-Quinodimethane (*m*-xylylene, **3**) is the parent hydrocarbon of the *m*-quinonoid non-Kekulé series. The present paper<sup>5</sup> reports

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