

The enthalpy of activation for rearrangement of oxetenes is *ca.* 10 kcal/mol less than for cyclobutenes, presumably because the oxetene rearrangement to product is more exothermic. Use of Franklin group equivalents with equal strain for the tetramethyloxetene and cyclobutene<sup>9</sup> shows that the oxetene rearrangement liberates *ca.* 23 kcal/mol more energy than the cyclobutene rearrangement. The results show that approximately half of this extra product stabilization is reflected in a lower transition energy for reaction.

**Acknowledgment.** The authors wish to thank the National Science Foundation for support of this work and the Computing Center of the University of Rochester for use of their facilities.

(9) In general, rings containing oxygen have the same strain as their all-carbon analogs; see A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, 71 (1965).

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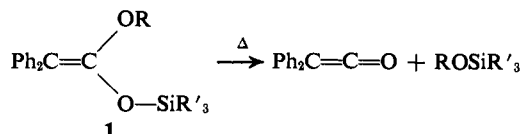
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### Pyrolysis Studies of Ketene Alkyl Trialkylsilyl Acetals

Sir:

We have found that diphenylketene methyl trimethylsilyl acetal<sup>1</sup> (**1**, R = R' = Me), at reflux at *ca.* 180° and 30 Torr for 30 min, is converted<sup>2</sup> to diphenyl-



ketene in 85% yield. Indeed, the synthetic sequence methyl diphenylacetate to **1** to diphenylketene can be rapidly accomplished in 80% overall yield and it seems to be the method of choice for the synthesis of this compound.<sup>3</sup> Other diarylketenes including *p*-tolyl and fluorene have been similarly prepared. Compound **1** (R = R' = Et) on pyrolysis gave diphenylketene in 35% yield.<sup>4</sup>

To elucidate the mechanism of this reaction a mixture of **1** (R = R' = Me) and **1** (R = R' = Et) was thermolyzed and the ether fraction was shown to contain only MeOSiMe<sub>3</sub> and EtOSiEt<sub>3</sub>. This negative crossover result eliminates free-radical and intermolecular mechanisms and is compatible with an intramolecular pathway. To answer the question as to which oxygen bond was cleaved in the process, the <sup>18</sup>O-SiMe<sub>3</sub> acetal was pyrolyzed and <sup>18</sup>O-diphenylketene was exclusively obtained.<sup>5</sup> Thus, the mechanism is consistent with a four-center one<sup>6</sup> featuring a methoxyl migration to

(1) Y. N. Kuo, F. Chen, C. Ainsworth, and J. J. Bloomfield, *Chem. Commun.*, 136 (1971).

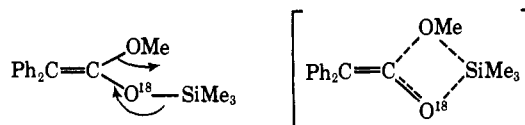
(2) For a reference concerning the pyrolysis of ketene acetals see S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *J. Amer. Chem. Soc.*, **64**, 2525 (1942). Ketene diethyl acetal heated at 200° gave ethyl acetate and ethylene.

(3) L. I. Smith and H. H. Hoehn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 356.

(4) The major product of the reaction is triethylsilyl diphenylacetate and ethylene. See ref 2.

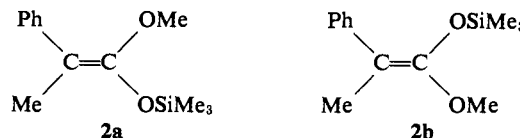
(5) Determined by mass spectral analysis. The mass spectrum of **1**, R = R' = Me, showed an equal distribution of heavy oxygen in diphenylketene and ether.

(6) A heterolytic cleavage involving a tight ion pair is not excluded.



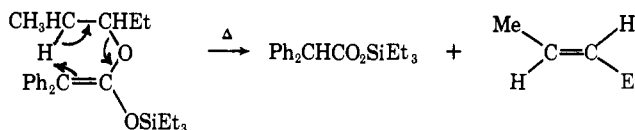
silicon with concomitant ketene formation. The transition state is probably accommodated by the ability of silicon to increase its coordination number involving 3d orbitals.<sup>7</sup>

The pyrolysis of the isomers **2a** and **2b** shown below



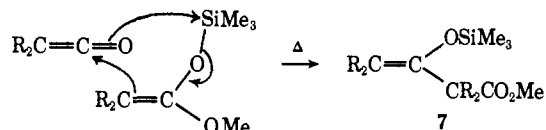
proved to be of special interest. The *cis* isomer **2b** (phenyl and trimethylsilyl)<sup>8</sup> was stable at 190° and 150 Torr for 0.5 hr but at 220° for 2 hr was converted to methylphenylketene.<sup>9</sup> The *trans* isomer **2a** at 190° for 0.5 hr formed methylphenylketene.<sup>9</sup> Thus **2b** with the methoxyl group *trans* to phenyl is more stable.<sup>10</sup>

The thermolysis of **1**, R = 3-pentyl, R' = Et, took a different course<sup>2</sup> yielding triethylsilyl diphenylacetate and *trans*-2-pentene. These products may form *via*



the indicated six-center transition state.

Pyrolysis studies were also carried out using hydrogen aryl and dialkylketene acetals of the type RR'C=C(OMe)OSiMe<sub>3</sub>; **3**, R = H, R' = Ph; **4**, R = R' = Me; **5**, R = R' = (CH<sub>2</sub>)<sub>4</sub>; and **6**, R = R' = (CH<sub>2</sub>)<sub>5</sub>. Several of these compounds gave products represented by **7** which are called ketene-ketene acetal addition products. Their formation is visualized as arising from a six-center reaction involving initially formed ketene and starting material.<sup>11</sup> Such a reaction would be



expected to have rigid stereochemical requirements. Thus, where R = phenyl the reaction failed to occur and diphenylketene was the product of pyrolysis. Pyrolysis of compound **3** at 180° and 30 Torr gave a 90% yield of **7a**,<sup>12</sup> the stereochemistry of which is established as having phenyl and OSiMe<sub>3</sub> *cis*.<sup>13</sup> This reaction is in accord with **3** having phenyl and *O*-trimethylsilyl groups *trans* as shown below.

Compound **4** heated in a sealed tube at 210° for 4 hr gave a 90% yield of product consisting of 20% di-

(7) F. P. Boer and F. P. van Remoortere, *J. Amer. Chem. Soc.*, **92**, 801 (1970), and references cited.

(8) Y. N. Kuo, F. Chen, and C. Ainsworth, *Chem. Commun.*, 137 (1971).

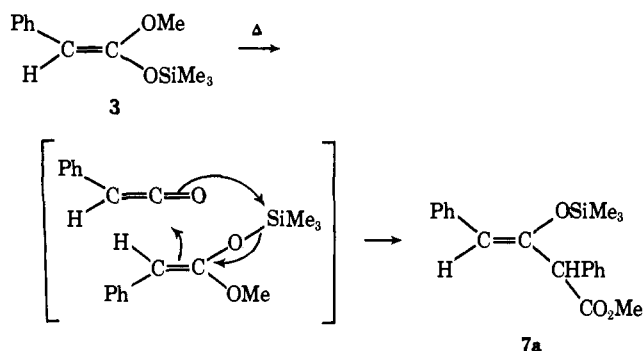
(9) The yield was about 30% accompanied with dimer and polymer.

(10) Experiments which have a bearing on this finding are in progress.

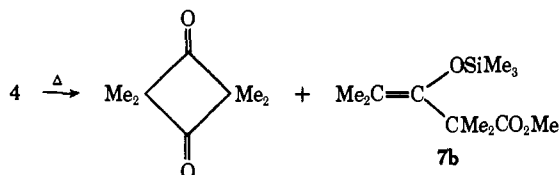
(11) (a) G. S. Burlachenko, Y. I. Baukov, and I. F. Lutsenko, *J. Gen. Chem. USSR*, **40**, 88 (1970); (b) R. Scarpati, *Rend. Accad. Sci. Fis. Mat., Naples*, 154 (1962).

(12) New compounds gave acceptable elemental analyses and molecular peaks in mass spectral analysis.

(13) The SiMe<sub>3</sub> signal was at δ 0.0 (CCl<sub>4</sub>); see ref 8.



methylketene dimer (tetramethyl-1,3-cyclobutadione,  $\delta$  1.28) and 80% ketene-ketene acetal addition product **7b**.



Compounds **5** and **6** gave similar results.

The pyrolysis study of ketene bis(trialkylsilyl) acetals is currently in progress.

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### The Reaction of Ester Enolates with Copper(II) Salts. A Synthesis of Substituted Succinate Esters

Sir:

The dimerization of carbon anions in the presence of copper salts is a well-established reaction of organic chemistry.<sup>1</sup> Nevertheless, there are relatively few examples of the copper-promoted dimerization of enolate anions.<sup>2</sup>

We wish to report that lithium ester enolates, prepared according to eq 1,<sup>3</sup> undergo a facile reaction with copper(II) salts to provide the corresponding dimerized esters in satisfactory yields (eq 2).

Addition of 1 equiv of copper(II) bromide to a tetrahydrofuran solution of lithio *tert*-butyl acetate maintained at a temperature of  $-78^\circ$  results in a series of color changes starting with green and proceeding through deep red. At the end of 15 min, the reaction mixture is dark brown and becomes completely homogeneous on warming to room temperature. Work-up produces an 85% yield of di-*tert*-butyl succinate. Use

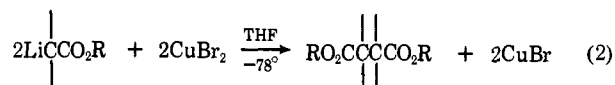
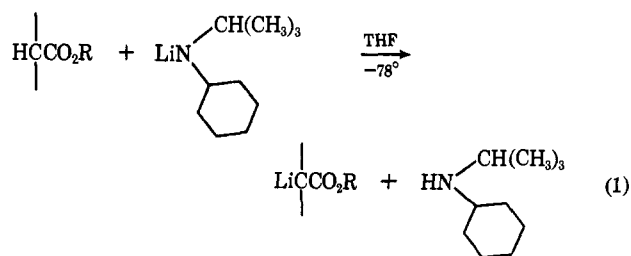
(1) Cf. T. Kauffmann and D. Berger, *Chem. Ber.*, **101**, 3022 (1968).

(2) The dimerization of the sodium enolate of acetophenone promoted by copper(II) chloride has been described by Kauffmann.<sup>3</sup> The formation of dimers as side products from the copper-catalyzed oxidation of  $\alpha,\beta$ -unsaturated aldehydes and ketone enolates has been reported by Volger, *et al.*<sup>4</sup>

(3) T. Kauffman, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **7**, 540 (1968).

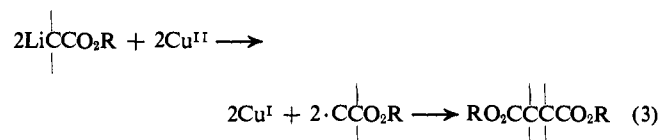
(4) H. C. Volger, W. Brackman, and J. W. F. M. Lemmers, *Recl. Trav. Chem. Pays-Bas*, **84**, 1203 (1965).

(5) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).



of reduced amounts of the copper salt produces a corresponding reduction in the yield of product; consequently the stoichiometry of the reaction is as shown by eq 2.

A minor side product of the reaction is *tert*-butyl bromoacetate. However, the major path for the formation of the succinate ester does not involve coupling of the bromo ester with the ester enolate.<sup>6</sup> Addition of authentic *tert*-butyl bromoacetate to a solution of lithio *tert*-butyl acetate produces only negligible yields (10%) of di-*tert*-butyl succinate. Furthermore, the dimerization reaction proceeds equally well (95%) with the halogen-free copper salt, copper(II) valerate.<sup>8</sup> For the present, all of our data can be accommodated by a radical-coupling mechanism (eq 3).



Results obtained with a variety of esters using either copper(II) bromide or copper(II) valerate are illustrated in Table I. The yield of dimer appears to decrease

Table I. Dimerization of Esters Using Copper(II) Salts

Ester	Product <sup>a</sup>	Yield, % <sup>b</sup>	
		CuBr <sub>2</sub>	Cu(O <sub>2</sub> -C <sub>5</sub> H <sub>9</sub> ) <sub>2</sub>
<i>tert</i> -Butyl acetate	Di- <i>tert</i> -butyl succinate	85	95
Ethyl propionate	Diethyl 2,3-dimethylsuccinate	81	50
Ethyl hexanoate	Diethyl 2,3-di- <i>n</i> -butylsuccinate	63	
Ethyl isobutyrate	Diethyl tetramethylsuccinate	25	20
Ethyl isovalerate	Diethyl 2,3-diisopropylsuccinate	20	20
Ethyl phenylacetate	Diethyl 2,3-diphenylsuccinate	75	60

<sup>a</sup> Usually obtained as a mixture of stereoisomers. The identity of all products was verified by spectral analysis or by comparison with published physical properties. <sup>b</sup> Isolated yields based on starting ester.

with increasing alkyl substitution adjacent to the carbonyl grouping of the ester (see entries for ethyl isobutyrate and ethyl isovalerate in Table I). This is attended with an increase in the production of the corresponding  $\alpha$ -bromo ester when copper(II) bromide

(6) The reaction of  $\alpha$ -bromo esters with ester enolates has been described by Hauser.<sup>7</sup>

(7) B. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, **63**, 3161 (1941).

(8) The preparation of copper(II) valerate was essentially that described by Lieben.<sup>9</sup>

(9) A. Lieben and A. Rossi, *Justus Liebigs Ann. Chem.*, **159**, 66 (1871).