

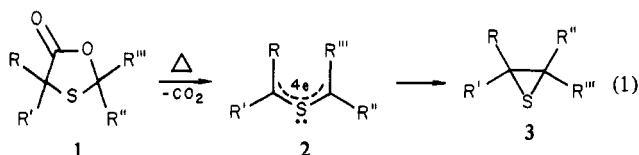
## Flash Vacuum Thermolysis of 1,3-Dioxolan-4-ones

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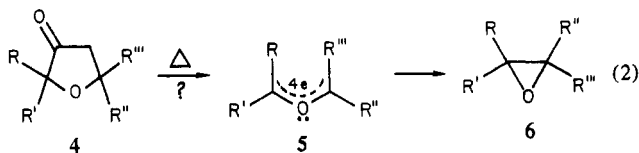
Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. Received July 11, 1980. Revised Manuscript Received January 19, 1981

**Abstract:** Flash vacuum thermolysis of 1,3-dioxolan-4-ones yields aldehydes and ketones as the major products as the result of apparent decarbonylation of  $\alpha$  lactones formed by collapse of a 1,3 dipole. When phenyl substituents are present, epoxides are also formed via the intermediacy of a carbonyl ylide.

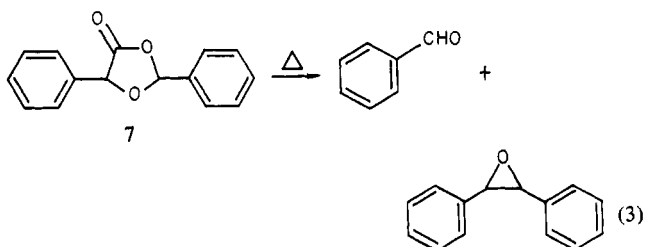
Flash vacuum thermolysis of 1,3-oxathiolan-5-ones (1) yields thiiranes (3) as the only isolated product (eq 1).<sup>2</sup> This reaction



proceeds with clean inversion of stereochemistry. This fact as well as substituent effects supports the intermediacy of thiocarbonyl ylides (2).<sup>2</sup> This paper describes the initial results in the pyrolysis of the corresponding oxygen heterocycles, the 1,3-dioxolan-4-ones (4),<sup>3</sup> in an attempt to generate the analogous carbonyl ylides (5) which would be expected to collapse to epoxides (6) (eq 2).



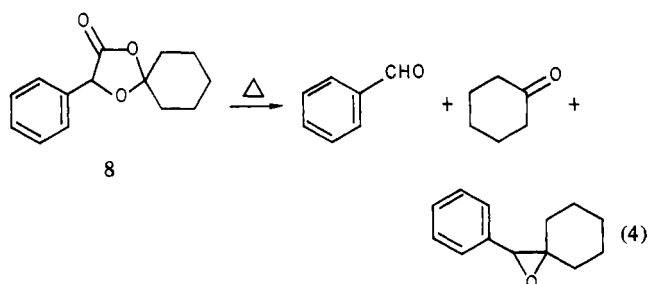
The initial system which was examined was 2,5-diphenyl-1,3-dioxolan-4-one (7). Flash vacuum thermolysis<sup>4</sup> of this material



gave a mixture of benzaldehyde and stilbene oxide<sup>5</sup> (eq 3). At 600 °C, 59% of the product was benzaldehyde and 13% was stilbene oxide while 28% of the starting material was recovered.<sup>6</sup> At a cracking temperature of 650 °C, the amounts of benzaldehyde and epoxide increased to 81% and 15%, respectively. Only a trace (4%) of starting material remained (see Table I).

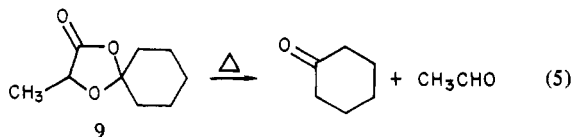
The stilbene oxide in the reaction of eq 3 was not formed stereospecifically in contrast to the results in the corresponding sulfur system.<sup>2</sup> The starting dioxolanone 7 was produced in a 63/37 cis/trans ratio<sup>7</sup> but the epoxide was present in a 16/84 cis/trans ratio.<sup>6,7</sup> Pyrolysis of pure *cis*-stilbene oxide at 650 °C gives a 27/73 cis/trans ratio<sup>7</sup> of epoxides and this shows that epoxides do indeed isomerize under flash vacuum pyrolysis conditions. This makes sense because of the known thermal conversion of epoxides into carbonyl ylides.<sup>8</sup>

Another system containing only one phenyl, 2,2-pentamethylene-5-phenyl-1,3-dioxolan-4-one (8), was also subjected to flash vacuum thermolysis and three products were obtained (eq 4). At 600 °C and 700 °C the reaction went 39% and 88% to completion, respectively, while at 750 °C no starting material



remained. The product distribution at 750 °C was 46% benzaldehyde, 47% cyclohexanone, and 7% of the epoxide.<sup>6</sup>

Pyrolysis of the heterocycle containing no phenyl substituents, 2,2-pentamethylene-5-methyl-1,3-dioxolan-4-one (9), required 800 °C for complete cracking to give cyclohexanone as the only isolated product (eq 5).<sup>6,9</sup> At 700 °C the reaction goes to 45% conversion<sup>6,9</sup> and dioxolanone 9 is stable at 600 °C.



A comparison of the extent of reaction for the three dioxolanones 7-9 shows the usual substituent effects.<sup>2</sup> For example, the 2,5-diphenyl system is 72% decomposed at 600 °C while the 2,2-pentamethylene-5-phenyl analogue is 39% cracked at this temperature. 2,2-Pentamethylene-5-methyldioxolanone is unaffected at 600 °C. Apparently, phenyl groups are more efficient than alkyl groups at stabilizing the intermediate. This is expected for carbonyl ylides which generally require phenyl substituents for ease of preparation.<sup>8</sup>

The epoxide product is missing in the systems lacking phenyl substituents and this implies that two competing reactions are probably occurring (Scheme I). Only when sufficient stabilization is present (phenyl substituents) does a carbonyl ylide form and this leads to an epoxide. Otherwise, an alternative 1,3 dipole (10) is generated by loss of the carbonyl compound 11. This dipole

(1) Taken in part from the Ph.D. dissertation of Tim. B. Cameron, University of Georgia, 1981.

(2) Cameron, T. B.; Pinnick, H. W. *J. Am. Chem. Soc.* **1979**, *101*, 4755; **1980**, *102*, 744-747.

(3) These compounds are easily prepared from  $\alpha$ -hydroxycarboxylic acids and aldehydes or ketones in the presence of an acid catalyst: Farines, M.; Soulier, J. *Bull. Soc. Chim. Fr.* **1970**, 332-340.

(4) Solution-phase thermolysis of 1,3-dioxolan-4-ones did not give clean results: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565-598.

(5) Product identification and composition were determined by comparison of <sup>1</sup>H NMR and GC data with authentic samples.

(6) All material balances are >95% as determined by weight of material and clean analysis by NMR.

(7) As determined by NMR analysis.

(8) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572-585. (b) Griffin, G. W. *Ibid.* **1971**, *10*, 537-547. (c) Hamberger, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1190-1192.

(9) Presumably, acetaldehyde was lost to the vacuum system.

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Table I. Pyrolysis of Substituted 1,3-Dioxolan-4-ones

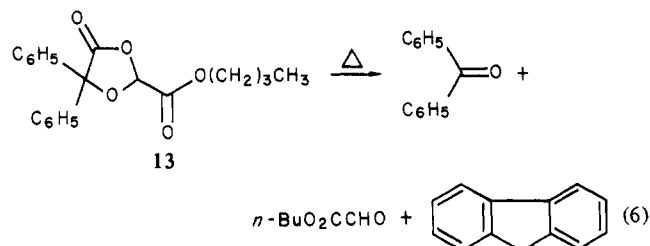
dioxolanone	temp, °C	products <sup>a</sup>		
		start-ing material	ep-oxide	carbonyl compd
	600	28	13	59
	650	4	15	81
	600	61	3	18
	700	12	8	38
	750	7	46	18 42 47
	600	98		45
	700	55		93
	800			
	600	100		<i>n</i> -BuO <sub>2</sub> CCHO
	750	55		45

<sup>a</sup> These percentages were determined by <sup>1</sup>H NMR and GC analysis and are assumed to be accurate to ±5%. All material balances are ≥95%. <sup>b</sup> Presumably, acetaldehyde is lost to the vacuum system.

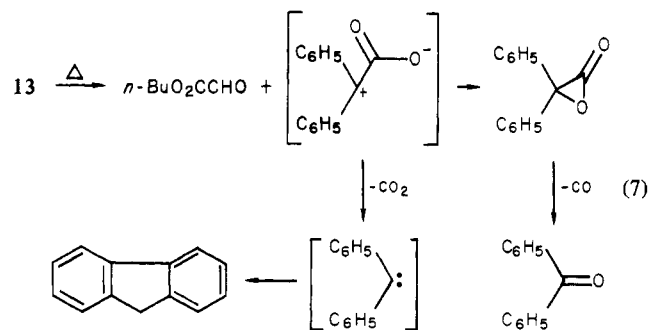
closes to the α lactone **12** which is known to suffer decarbonylation to aldehydes or ketones.<sup>10</sup>

The results of the thermolysis of 2-(*n*-butoxycarbonyl)-5,5-dimethyl-1,3-dioxolan-4-one are consistent with this hypothesis. This compound is stable at 600 °C but 45% is converted to *n*-butyl glyoxylate at 750 °C (see Table I).<sup>11</sup> None of the epoxide is obtained. This seems to imply unequal charge distribution in the transition state of the reaction.

Another system shows an interesting fragmentation pattern. Flash vacuum pyrolysis of 2-(*n*-butoxycarbonyl)-5,5-diphenyl-1,3-dioxolan-4-one (**13**) at 600 °C gives 14% benzophenone, 20% *n*-butyl glyoxylate, 13% fluorene, and 53% starting material (eq 6).<sup>6</sup> Only 4% of the starting material remains after cracking at



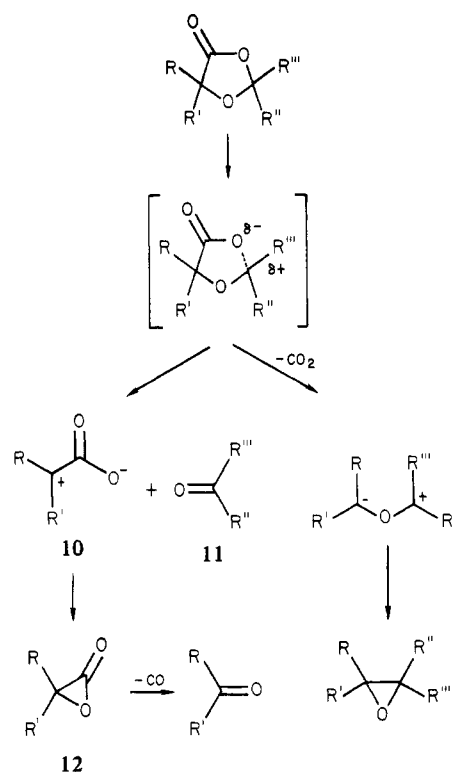
700 °C. The products are benzophenone (26%), *n*-butyl glyoxylate (46%), and fluorene (24%). The benzophenone apparently arises by α-lactone formation from dipole **10** (R = R' = C<sub>6</sub>H<sub>5</sub>) and decarbonylation as in Scheme I. Fluorene could be formed by decarboxylation of dipole **10** to give diphenylcarbene which is known to rearrange to fluorene (eq 7).<sup>12</sup>



(10) Adam, W.; Lice, J. C.; Rodriguez, O. *J. Org. Chem.* **1973**, *38*, 2269-2270.

(11) Presumably, acetone is lost to the vacuum system.

Scheme I. Proposed Mechanism



In an effort to gain some insight into the factors which determine the mode of fragmentation of dioxolanones, several substituted diaryl compounds were prepared and subjected to flash vacuum pyrolysis (see Table II). There is a dramatic substituent effect both on the extent of reaction and the product distribution. Groups at the 2 position which can better stabilize incipient positive charge enhance the reaction rate. In particular, at 570 °C the 2-(*p*-methoxyphenyl) derivative is completely decomposed while the 2-phenyl compound is 13-44% recovered and the 2-(*p*-nitrophenyl) analogue is unaffected. This is consistent with the initially formed transition state proposed in Scheme I which involves positive charge development at the 2 position.

Furthermore, replacing the 5-phenyl substituent of the dioxolanone with a *p*-nitrophenyl group causes several changes. The reaction rate is tripled and the amount of epoxide doubles. Presumably, the carbonyl ylide is stabilized better by the nitrophenyl group and this leads to a greater amount of epoxide.

Experiments to refine this mechanism are underway. Additional work is also in progress to gain direct evidence for the proposed intermediates. Synthetic applications are also being developed.

### Experimental Section

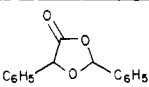
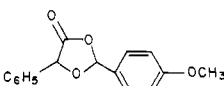
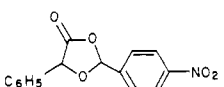
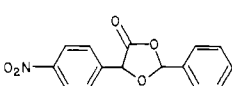
All preparations were run under nitrogen in flamed-out apparatus. Tetrahydrofuran and ether were freshly distilled from potassium and calcium hydride, respectively. <sup>1</sup>H NMR spectra were run on a Varian T-60 spectrometer. Infrared spectra were recorded on Perkin-Elmer Model 247 and 297 spectrophotometers. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Combustion analyses were conducted by M-H-W Laboratories of Phoenix, Arizona.

**Preparation of 1,3-Dioxolan-4-ones. General Procedures.** The α-hydroxy acid (100 mmol) and the aldehyde or ketone (110 mmol) are dissolved in 150 mL of dry benzene and 15 mmol of *p*-toluenesulfonic acid (*p*-TsOH) is added. The reaction mixture is refluxed until the theoretical amount of water is obtained (Dean-Stark trap), cooled to room temperature, and washed with 10% aqueous NaHCO<sub>3</sub> until the wash is just basic (pH 7.5-8.0). The organic layer is dried and concentrated and the product is distilled or recrystallized.

Alternatively, the α-hydroxy acid (100 mmol) and the aldehyde or ketone (110 mmol) are dissolved in 150 mL of dry ether and 125 mmol

(12) Myers, J. A.; Jones, R. C.; Jones, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 4740-4742.

Table II. Pyrolysis of 2,5-Diaryldioxolanones

dioxolanone	temp, °C	products <sup>a</sup>				
		st. mat.	C <sub>6</sub> H <sub>5</sub> CHO	4-MeO-C <sub>6</sub> H <sub>4</sub> CHO	4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> CHO	epoxide
	570	44	40			16
	570	8	44	44		12
	570 650	>95 8	49		51	0
	570	13	26		27	34

<sup>a</sup> All percentages were determined by <sup>1</sup>H NMR. Material balances are ≥95%.

of freshly distilled BF<sub>3</sub>·OEt<sub>2</sub> in 25 mL of ether is added dropwise over a 15-min period. Workup as before after 3 h gives the product.

**Preparation of 2,4-Diphenyl-1,3-dioxolan-4-one (7).** Mandelic acid (15.2 g, 100 mmol), benzaldehyde (10.6 g, 100 mmol), and *p*-GsOH·H<sub>2</sub>O (0.19 g, 1.0 mmol) gave 11.1 g (46.3%) of a white solid after recrystallization from benzene/hexane: mp 87–91 °C (lit.<sup>3</sup> mp 97 °C); *cis/trans* = 63/37; <sup>1</sup>H NMR (CDCl<sub>3</sub>) *cis* δ 5.46 (d, *J* = 1 Hz, 1 H), 6.63 (d, *J* = 1 Hz, 1 H), 7.53 (m, 10 H), *trans* δ 5.56 (s, 1 H), 6.76 (s, 1 H), 7.53 (m, 10 H); IR (KBr) 1790 cm<sup>-1</sup> (C=O).

**Preparation of 2,2-Pentamethylene-4-phenyl-1,3-dioxolan-4-one (8).** Mandelic acid (15.2 g, 100 mmol), cyclohexanone (11.8 g, 120 mmol), and *p*-TsOH·H<sub>2</sub>O 0.19 g, 1.0 mmol) gave 20.5 g (88.4%) of a white solid after recrystallization from benzene/hexane: mp 85–86 °C (lit.<sup>3</sup> mp 85 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.2–2.2 (m, 10 H), 5.43 (s, 1 H), 7.46 (s, 5 H); IR (KBr) 1805 cm<sup>-1</sup> (C=O).

**Preparation of 2,2-Pentamethylene-4-methyl-1,3-dioxolan-4-one (9).** Redistilled lactic acid (9.00 g, 100 mmol), cyclohexanone (11.8 g, 120 mmol), and *p*-TsOH·H<sub>2</sub>O (0.19 g, 1.0 mmol) gave 11.2 g (65.8%) of a clear liquid: bp 86–87 °C (3 mmHg) (lit.<sup>3</sup> bp 62 °C (14 mmHg)); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.2–2.2 (m, 10 H), 1.46 (d, *J* = 7 Hz, 3 H), 4.50 (q, *J* = 7 Hz, 1 H); IR (NaCl) 1800 cm<sup>-1</sup> (C=O).

**Preparation of 2-(Carbobutoxy)-5,5-dimethyl-1,3-dioxolan-4-one.** α-Hydroxyisobutyric acid (0.50 g, 4.8 mmol), *n*-butyl glyoxylate<sup>13</sup> (0.80 g, 6.1 mmol), and *p*-TsOH·H<sub>2</sub>O (0.01 g, 0.05 mmol) gave 1.19 g (89.1%) of a colorless liquid: bp 120–122 °C (3.5 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.7–2.0 (m, 7 H), 1.50 (s, 3 H), 1.56 (s, 3 H), 4.28 (t, *J* = 7 Hz, 2 H), 5.77 (s, 1 H); IR (NaCl) 1760 (C=O), 1815 cm<sup>-1</sup> (C=O).

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>5</sub>: C, 55.5; H, 7.5. Found: C, 55.23; H, 7.66.

**Preparation of 2-(Carbobutoxy)-5,5-diphenyl-1,3-dioxolan-4-one (13).** Benzilic acid (7.58 g, 33.2 mmol), *n*-butyl glyoxylate<sup>13</sup> (4.75 g, 36.6 mmol), and *p*-TsOH·H<sub>2</sub>O (0.10 g, 0.05 mmol) gave 10.4 g (92.2%) of a viscous liquid: bp 132–135 °C (0.005 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.7–2.0 (m, 7 H), 4.13 (t, *J* = 7 Hz, 2 H), 5.92 (s, 1 H), 7.46 (m, 10 H); IR (NaCl) 1760 (C=O), 1810 cm<sup>-1</sup> (C=O).

Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>: C, 70.6; H, 5.9. Found: C, 70.68; H, 6.02.

**Preparation of 2-(4-Methoxyphenyl)-5-phenyl-1,3-dioxolan-4-one.** Mandelic acid (4.56 g, 30.0 mmol), anisaldehyde (4.08 g, 30.0 mmol), and *p*-TsOH·H<sub>2</sub>O (0.01 g, 0.05 mmol) gave 3.76 g (46%) of a white solid after recrystallization from hexane/benzene: mp 75–84 °C; *cis/trans* = 69/31; <sup>1</sup>H NMR (CDCl<sub>3</sub>) *cis* δ 3.86 (s, 3 H), 5.43 (d, *J* = 1.15 Hz, 1 H), 6.55 (d, *J* = 1.15 Hz, 1 H), 7.03 (d, *J* = 8 Hz, 2 H), 7.48 (s, 5 H), 7.60 (d, *J* = 8 Hz, 2 H), *trans*, δ 3.86 (s, 3 H), 5.75 (s, 1 H), 6.70 (s, 1 H), 7.03 (d, *J* = 8 Hz, 2 H), 7.48 (s, 5 H), 7.60 (d, *J* = 8 Hz, 2 H); IR (KBr) 1780 cm<sup>-1</sup> (C=O).

**Preparation of 2-(4-Nitrophenyl)-5-phenyl-1,3-dioxolan-4-one.** Mandelic acid (1.52 g, 10.0 mmol), *p*-nitrobenzaldehyde (1.51 g, 10.0 mmol), and *p*-TsOH·H<sub>2</sub>O (0.1 g, 0.5 mmol) gave 1.9 g (67%) of a white solid after recrystallization from benzene/hexane: mp 96–105 °C; *cis/trans* = 55/45; <sup>1</sup>H NMR (CDCl<sub>3</sub>) *cis*, δ 5.50 (d, *J* = 1 Hz, 1 H), 6.71 (d, *J* = 1 Hz, 1 H), 7.50 (s, 5 H), 7.83 (d, *J* = 8 Hz, 2 H), 8.41 (d, *J* = 8 Hz, 2 H), *trans*, δ 5.55 (s, 1 H), 6.83 (s, 1 H), 7.50 (s, 5 H), 7.83 (d, *J* = 8

Hz, 2 H), 8.41 (d, *J* = 8 Hz, 2 H); IR (KBr) 1790 cm<sup>-1</sup> (C=O). Anal. Calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>5</sub>: C, 63.2; H, 3.9. Found: C, 63.49; H, 4.04.

**Preparation of 2-Phenyl-5-(4-nitrophenyl)-1,3-dioxolan-4-one.** *p*-Nitromandelic acid<sup>14</sup> (0.30 g, 1.52 mmol), benzaldehyde (0.17 g, 1.67 mmol), and BF<sub>3</sub> etherate (0.32 g, 2.28 mmol) gave 0.35 g (69%) of a white solid after recrystallization from ether/hexane: mp 109–113 °C; *cis/trans* = 84/16; <sup>1</sup>H NMR (CDCl<sub>3</sub>) *cis*, δ 5.56 (d, *J* = 1 Hz, 1 H), 6.76 (d, *J* = 1 Hz, 1 H), 7.61 (s, 5 H), 7.80 (d, *J* = 8 Hz, 2 H), 8.36 (d, *J* = 8 Hz, 2 H), *trans*, δ 5.60 (s, 1 H), 6.78 (s, 1 H), 7.61 (s, 5 H), 7.80 (d, *J* = 8 Hz, 2 H), 8.36 (d, *J* = 8 Hz, 2 H); IR (KBr) 1786 cm<sup>-1</sup> (C=O).

**Pyrolysis of 1,3-Dioxolan-4-ones. General Procedure.** The 1,3-dioxolan-4-one is slowly distilled directly into a quartz tube (ca. 1 × 15 cm), wrapped with heating ribbon, which is maintained at the desired temperature.<sup>2</sup> A slow flow of nitrogen facilitates the transfer. The pyrolysate is collected on a cold finger held ca. 2 cm from the end of the hot tube. This material is analyzed by comparison with NMR and GC data of authentic samples.

**Pyrolysis of 2,5-Diphenyl-1,3-dioxolan-4-one.** The dioxolanone (0.10 g, 0.41 mmol; *cis/trans* = 63/37)<sup>7</sup> was heated at 100 °C at 0.03 torr with the hot zone at 600 °C and 0.088 g of product was collected. This consisted of starting material (28%), benzaldehyde (59%), and stilbene oxide (13%)<sup>15</sup> as determined by NMR.

Another sample of the starting material (0.23 g, 0.96 mmol) was passed through the hot tube maintained at 650 °C to give 0.21 g of material which was analyzed by NMR as benzaldehyde (81%), stilbene oxide<sup>15</sup> (15%; *cis/trans* = 16/84), and starting material (4%).

**Pyrolysis of 2,2-Pentamethylene-5-phenyl-1,3-dioxolan-4-one.** The dioxolanone (0.40 g, 1.7 mmol) was heated to 80 °C at 0.08 torr with the hot tube at 700 °C. The pyrolysate (0.35 g) was collected and analyzed by NMR and VPC as starting material (12%), 2,2-pentamethylene-3-phenyloxirane (8%),<sup>16</sup> cyclohexanone (42%), and benzaldehyde (38%).

Another sample (0.50 g, 2.2 mmol) was heated to 80 °C at 0.05 torr with the hot zone at 750 °C. The product (0.41 g) consisted of benzaldehyde (46%), epoxide (7%),<sup>16</sup> and cyclohexanone (47%) by VPC and NMR.

**Pyrolysis of 2,2-Pentamethylene-5-methyl-1,3-dioxolan-4-one.** The dioxolanone (0.40 g, 2.4 mmol) was vaporized at 0.5 torr with a hot tube temperature of 600 °C to give 0.39 g (98%) of starting material.

Another sample (0.40 g, 2.4 mmol) was pyrolyzed at 0.5 torr and 700 °C to give 0.33 g of a mixture which consisted of starting material (55%) and cyclohexanone (45%).

The dioxolanone (0.42 g, 2.5 mmol) was cracked at 0.5 torr and 800 °C to give, after bulb-to-bulb distillation, 0.23 g (93%) of cyclohexanone: bp 150–155 °C.

**Pyrolysis of 2-(Carbobutoxy)-5,5-diphenyl-1,3-dioxolan-4-one.** The dioxolanone (0.25 g, 0.78 mmol) was heated to 120 °C at 0.005 torr and

(14) Prepared from the cyanohydrin of *p*-nitrobenzaldehyde: Ketcham, R.; Shah, V. P. *J. Org. Chem.* 1963, 28, 229–230.

(15) Authentic samples of both *cis*- and *trans*-stilbene oxide were prepared from the corresponding olefins with *m*-chloroperbenzoic acid.

(16) Prepared by *m*-chloroperbenzoic acid epoxidation of benzylidene-cyclohexane.

(13) Wolf, F. J.; Weijlard, J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 124 and 125.

passed through a hot tube maintained at 700 °C. The pyrolysate (0.23 g) was analyzed by GC/MS in addition to separation by preparative TLC on silica gel for unambiguous identification: benzophenone (51 mg, 36%; mp 46–48 °C), fluorene (46 mg, 36%; mp 114–116 °C), and *n*-butyl glyoxylate (48 mg, 47%). These products were formed in a ratio of 26:24:46 (the remaining 4% was starting material).

**Pyrolysis of 2,5-Diphenyl-1,3-dioxolan-4-one.** The dioxolanone (0.25 g, 1.04 mmol; cis/trans = 63/37)<sup>7</sup> was heated to 100 °C at 0.05 torr with the hot tube at 570 °C. The product (0.23 g) was analyzed by NMR as starting material (44%), benzaldehyde (40%), and stilbene oxide (16%, cis/trans = 16/84).

**Pyrolysis of 2-(4-Methoxyphenyl)-5-phenyl-1,3-dioxolan-4-one.** The dioxolanone (0.15 g, 0.55 mmol, cis/trans = 69/31) was vaporized at 130 °C at 0.005 torr through a hot tube at 570 °C to give 0.14 g of pyrolysate

which analyzed by NMR to be benzaldehyde (44%), anisaldehyde (44%), and 1-phenyl-2-(*p*-methoxyphenyl)oxirane (12%, >95% trans) as well as a trace of starting material.

**Pyrolysis of 2-(4-Nitrophenyl)-5-phenyl-1,3-dioxolan-4-one.** The dioxolanone (0.15 g, 0.53 mmol; cis/trans = 55/45) was heated to 150 °C at 0.005 torr with the hot tube at 650 °C. The pyrolysate (0.13 g) was benzaldehyde (49%) and *p*-nitrobenzaldehyde (51%) as well as a trace of starting material by NMR.

**Pyrolysis of 5-(4-Nitrophenyl)-2-phenyl-1,3-dioxolan-4-one.** The dioxolanone (0.10 g, 0.35 mmol; cis/trans = 84/16) was heated to 130 °C at 0.05 torr with the hot zone at 570 °C to give 84 mg of a pale yellow wet solid. This analyzed by NMR to be *p*-nitrobenzaldehyde (27%), benzaldehyde (26%), 1-phenyl-2-(*p*-nitrophenyl)oxirane (34%, cis/trans = 30/70), and 13% starting material.

## Proton-Transfer Reactions. 1. Partitioning of Carbanion Intermediates Generated by Reactions of Alkenes with Alkoxide Ions in Alcohol

H. F. Koch,\* J. G. Koch, D. B. Donovan, A. G. Toczko,<sup>1a</sup> and A. J. Kielbania, Jr.<sup>1b</sup>

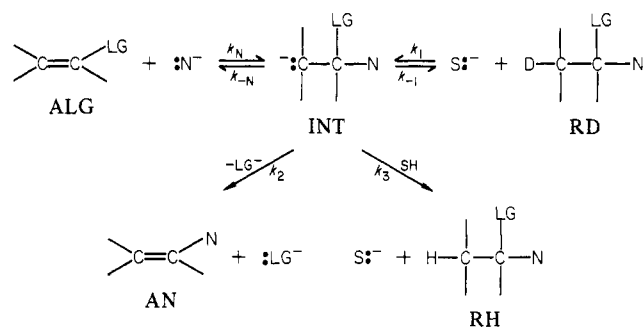
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**Abstract:** Nucleophilic reactions with sodium alkoxide in alcohol have been studied with various *gem*-difluoroalkenes of general structure C<sub>6</sub>H<sub>5</sub>CR=CF<sub>2</sub>. Rates and Arrhenius parameters [ $k \times 10^3$  (M<sup>-1</sup> s<sup>-1</sup>), at -50 °C,  $\Delta H^\ddagger$  (kcal mol<sup>-1</sup>), and  $\Delta S^\ddagger$ , (eu)] are respectively: R = -CF<sub>3</sub> (II), 105, 9, and -23; -CF<sub>2</sub>Cl (III), 135, 10, and -19; -CF<sub>2</sub>CF<sub>3</sub> (IV), 40.6, 9, and -23; -CF<sub>2</sub>H (V), 3.63, 11 and -19. Reactions proceed via carbanion intermediates, and the products from reaction with ~0.3 N sodium ethoxide in ethanol are: II, 85% vinyl ether and 15% saturated ether; III, 100% allylic ether; IV, 74% vinyl ether, 22% allylic ether, and 4% saturated ether; V, >98% allylic ether. The observed product distributions suggest the following order of leaving group ability for fluoride in different environments: -CF<sub>2</sub>H >> -CF<sub>2</sub>OR > -CF<sub>2</sub>CF<sub>3</sub> >> -CF<sub>3</sub>. Solvent protonation of the carbanion is apparently slower than fluoride ion ejection from all groups studied other than trifluoromethyl. Product isotope effects (PIE),  $k^H/k^D$ , for the protonation of the carbanion generated from II by reaction in ethanol are 1.50 (-78 °C) and 1.86 (20 °C) and by reaction in methanol are 1.22 (-78 °C).

Over the years our research efforts have gradually shifted from studies of nucleophilic reactions of alkenes<sup>2</sup> to proton exchange and elimination reactions,<sup>3</sup> and finally to an in-depth analysis of primary kinetic isotope effects applied to proton transfer occurring during dehydrohalogenation reactions.<sup>4,5</sup> The unifying theme of all our work has been the study of carbanion intermediates formed during the course of chemical reactions and the determination of products formed by the partitioning of these intermediates along alternate pathways. In order to study the partitioning of such intermediates, one must first be able to detect them directly or to design experiments whose results can best be interpreted by postulating the existence of a carbanion or the lack of one along the reaction pathway. A carbanion intermediate, INT, can be generated by the reaction of a nucleophile with an alkene, ALG, or by the base-catalyzed abstraction of hydrogen from a saturated carbon, RD, Scheme I. The intermediate can partition to form an alkene, AN, or to form the exchanged saturated compound, RH.

If the starting point of such investigations is the alkene, then the process will be the competition between a vinyl displacement reaction or the addition across a carbon-carbon double bond. On

Scheme I



the other hand, if one starts with the saturated compound, then the reactions studied are elimination vs. exchange. However, if one considers the intermediate, both studies become a competition between the ejection of a leaving group, LG, and the proton transfer from a solvent molecule, SH. Problems can arise if reversible reactions are competitive with the forward process. For example, if N is a comparable or better leaving group than LG, a study of this reaction would not give a true measure of the rate of reaction of N with ALG, nor would it give the actual partitioning of the intermediate regarding all three alternatives. The study of elimination and exchange reactions is further complicated by the possibilities of a concerted mechanism becoming the low-energy pathway for elimination reactions.

The facile reaction of nucleophiles with a *gem*-difluoroethylene group, =CF<sub>2</sub>, has been well documented in the literature, and the study of such systems is ideal for our purposes.<sup>6</sup> Miller et

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