

# Carbonyl Ylides and the Rearrangement of (+)-*trans*-2,3-Diisopropenyloxirane

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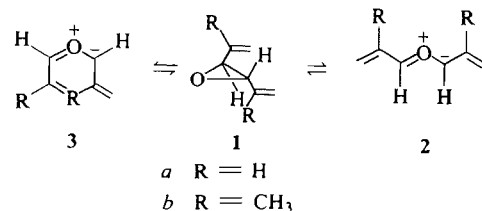
The kinetics of the gas phase racemization and rearrangement of 2,3-diisopropenyloxirane have been determined. Comparison with the kinetic data for 2,3-divinyloxirane allows us to exclude the mechanism for the formation of vinylidihydrofuran wherein an inward conrotatory ring opening comprises the first step. The mechanism proposed consists of an isomerization about the carbon-oxygen bond of the carbonyl ylide to form an isomeric intermediate which then undergoes a disrotatory five-centered ring closure to produce 2-isopropenyl-4-methyl-2,3-dihydrofuran.

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La cinétique en phase gazeuse de la racémisation du diisopropényl-2,3-époxyde (+), et de sa conversion en isopropényl-2-méthyl-4-dihydro-2,3-furanne a été étudiée et comparée à celle du divinyl-2,3-époxyde. La formation du dihydrofuranne pourrait s'expliquer par une suite de deux réactions électrocycliques concertées, ou par un mécanisme comportant trois étapes dont l'une impliquerait la rotation non concertée autour de la liaison C—O des ylures de carbonyle intermédiaires. Les résultats que nous avons obtenus sont en accord avec cette dernière hypothèse.

## Introduction

In a recent study on the racemization and rearrangement of (+)-2,3-divinyloxirane we observed that all of the products were racemic (1). Our results on the formation of vinylidihydrofuran were in agreement with the proposal of Paladini and Chuche (2) that isomerization of the carbonyl ylide intermediate followed by an electrocyclic ring closure represented a feasible path. We report, herein, a study of (+)-*trans*-2,3-diisopropenyloxirane. In using the isopropenyl group we expect a minimal change in electronic factors affecting the stability of the reactants and the carbonyl ylide intermediate (the methyl groups are at the nodes of the highest occupied molecular orbital of the carbonyl ylide). It is anticipated that steric factors will significantly destabilize those forms of the carbonyl ylide (e.g. **3b**)<sup>1</sup> produced by moving the bulkier isopropenyl group inward as opposed to those forms produced by moving them outwards (e.g. **2b**). Form **3** can readily undergo disrotatory ring closure to dihydrofuran (**6**) whereas **2** cannot. As a consequence if dihydrofuran forma-



tion occurs by oxirane ring opening as **1** → **3** then, on going from **1a** to **1b**, we would expect the ratio  $k_1/(k_2 + k_3)$  to increase dramatically.

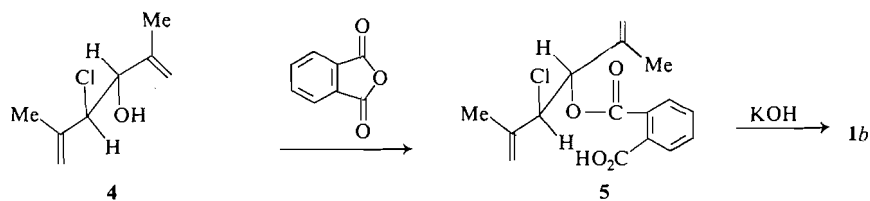
## Results

Chiral **1b** was prepared from *erythro*-4-chloro-2,5-dimethyl-1,5-hexadien-3-ol (**4**) by conversion to the half ester of phthalic acid followed by resolution of its brucine salt and the formation of **1b** by alkaline saponification of the chloro half ester (**5**) (Scheme 1).

### Kinetics of the Racemization and Conversion of **1b** to **6** and **7** (Scheme 2)

Samples of **1b** were degassed and sealed into ampoules in a manner such that at 200° the pressure would not exceed 700 Torr. The samples were then heated for the appropriate times and then analyzed by gas chromatography using a Hewlett Packard 3370A electronic integrator. Table 1 gives the data and the observed product

<sup>1</sup>Other conformations of **2** and **3** produced by the thermally allowed conrotatory ring opening of the oxirane **1** exist and the same considerations apply. The forms **2** and **3** are merely chosen as representative.



SCHEME 1

TABLE 1. Rate constants and product proportions for the reactions of 1b

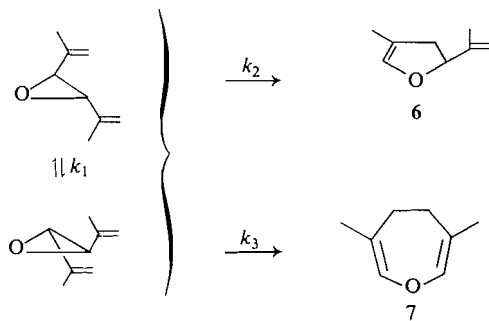
Temperature ( $\pm 0.04^\circ$ )	$10^5 (k_2 + k_3)$ ( $s^{-1}$ )	% 6	% 7
180.53		$77.6 \pm 0.2^*$	$22.4 \pm 0.2$
199.55	$2.35 \pm 0.03$	$76.8 \pm 0.2$	$23.6 \pm 0.2$
210.41	$5.80 \pm 0.06$	$76.1 \pm 0.2$	$23.9 \pm 0.2$
221.55	$15.2 \pm 0.2$	$75.5 \pm 0.3$	$24.5 \pm 0.3$
240.16		$74.4 \pm 0.3$	$25.6 \pm 0.3$

\*The error quoted is the standard deviation of five analyses.

TABLE 2. Rate constants for the racemization of (+)-1b

Temperature ( $\pm 0.03^\circ$ )	$10^5 k_a$ ( $s^{-1}$ )	$10^5 (k_2 + k_3)^*$ ( $s^{-1}$ )	$10^5 k_1$ ( $s^{-1}$ )
156.72	$2.47 \pm 0.03$	0.035	1.22
165.12	$5.21 \pm 0.06$	0.086	2.56
171.63	$9.80 \pm 0.09$	0.168	4.81
181.02	$21.7 \pm 0.2$	0.432	10.6

\*Extrapolated from plot of rate data in Table 1.



SCHEME 2

proportions. A sample run is given in the experimental section.

Samples of (+)-1b were degassed in Pyrex break-seals in a manner analogous to that described earlier (1). The rate constants for the observed racemization,  $k_a$ , and that for the rate of interconversion of enantiomers,  $k_1$ , where  $2k_1 = k_a - (k_2 + k_3)$ , are recorded in Table 2. The activation parameters for  $k_1$ ,  $k_2$ , and  $k_3$  are given in Table 3.

## Experimental

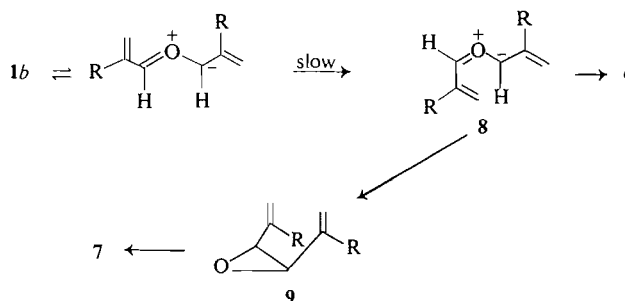
The i.r. spectra were obtained on a Perkin-Elmer 421 Spectrophotometer and the n.m.r. spectra were obtained using a Varian A-60. All rotations were measured in a thermostated cell on a Perkin-Elmer Model 141 Polarimeter. Preparative gas chromatography (g.c.) was carried out using a Nester Faust Model 850 Prepchromat.

### Preparation of erythro-4-Chloro-2,5-dimethyl-1,5-hexadien-3-ol (4)

A stream of dry hydrogen chloride was passed through a solution of 2,3-diisopropenyloxirane (1b) (3) (9.74 g, 78.5 mmol) in ether (300 ml) cooled to  $-50^\circ$ . The reaction was followed by t.l.c. Upon completion of the reaction the excess hydrogen chloride was removed by a stream of nitrogen. The solution was then neutralized with cold aqueous sodium bicarbonate and the product isolated by drying over magnesium sulfate followed by removal of the ether. The product was not distilled lest it undergo an allylic rearrangement. Proton magnetic resonance of 4 (10% w/w in carbon tetrachloride)  $\delta$ : 1.75 (3H, triplet); 1.85 (3H, triplet); 2.5 (H, removed with  $D_2O$ ); 6.08 ( $H_3$ , doublet); 6.30 ( $H_4$ , doublet);  $H_{1,6}$  4.9 to 5.11 (4H, multiplet);  $J_{3,4} = 9$  Hz. Infrared spectrum (carbon disulfide)  $cm^{-1}$ : 3540 s (OH), 3080 s ( $CH_2$ ), 1630 ms ( $C=C$ ).

TABLE 3. Activation parameters for the reactions of **1b** and (+)-**1b** as in Scheme 2

	log <i>A</i>	<i>E<sub>a</sub></i> (kcal mol <sup>-1</sup> )	Δ <i>H</i> <sup>‡</sup> (kcal mol <sup>-1</sup> )	Δ <i>S</i> <sup>‡</sup> (cal deg <sup>-1</sup> mol <sup>-1</sup> )
<i>k</i> <sub>1</sub>	12.74	34.7 ± 0.5	33.8 ± 0.5	-3 ± 1*
<i>k</i> <sub>2</sub>	13.30	39.0 ± 0.9	38.1 ± 0.9	0 ± 1
<i>k</i> <sub>3</sub>	13.58	40.7 ± 0.7	39.8 ± 0.7	1 ± 1

\*At *T* = 150° for comparison with data in ref. 1.*Resolution of 4 by the Phthalate Half Ester (5)*

A solution of phthalic anhydride (12.58 g, 85 mmol) in 17 ml of pyridine was allowed to stand for 12 h with the chlorohydrin **4** (13.6 g, 85 mmol). After heating for 1 h at 80°, the solution was cooled in an ice water bath and ether added. After washing with concentrated hydrochloric acid the ether layer was separated and the solvent evaporated. The remaining syrup was taken up in a sodium carbonate solution extracted with ether, cooled, and then acidified. After extraction with chloroform the solvent was removed and the half ester **5** was recrystallized from benzene and pentane; yield 54%, m.p. 102°.

Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>ClO<sub>4</sub>: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.27; H, 5.60; Cl, 11.51.

Bucine (27.62 g, 65 mmol) was added to a refluxing solution of the half ester **5** (36 g, 116 mmol) in dry acetone (100 ml). The solid residue was removed by rapid filtration and the filtrate cooled to produce the bucine salt (51.2 g). After three further recrystallizations from boiling acetone the salt had a constant m.p. 162–168°. Upon treatment of the salt with hydrochloric acid (100 ml of 5%) the solution was extracted six times with ether. Upon evaporation to dryness the ester **5** was produced, [α]<sub>D</sub><sup>20</sup> -2.315°; yield 6.6 g (19%).

A solution of the half ester (3.18 g, 10.29 mmol) in ethylene glycol was added dropwise, under reduced pressure (15 Torr), to a solution of potassium hydroxide (6 g, 105 mmol) in hot (60°) ethylene glycol (75 ml). The organic material in the vacuum trap was dried over potassium carbonate to yield **1** g (85%) of *trans*-2,3-diisopropenyloxirane. The oxirane was further purified by preparative gas chromatography (15% Carbowax 1500 on Chromosorb W, 80–100 mesh, 200 × 0.9 cm, 50°) [α]<sub>D</sub><sup>22.5</sup> +4.133°, [α]<sub>D</sub><sup>36.5</sup> +40.627° (*c* 4.8185 g/100 g of solution, 2-propanol).

*Kinetics of Racemization of (+)-1b*

The procedure used to observe the racemization of (+)-**1b** is the same as that described earlier for that of (+)-2,3-divinyloxirane (**1**). A sample run at 165.12 ± 0.03° consists of the following data: 10<sup>4</sup> s, [α]<sub>t</sub>/[α]<sub>0</sub>; 0.450, 0.7676; 0.744, 0.6534; 0.840, 0.6136; 1.08, 0.5615; 1.32, 0.4893; 1.536, 0.445; 1.812, 0.3812; 2.046, 0.3317; infinity tube 3 days, 0.000°. These results yield *k<sub>a</sub>* = (5.21 ± 0.06) × 10<sup>-5</sup> s<sup>-1</sup>.

*Kinetics of the Rearrangement of 1b to 6 and 7*

The procedure used is the same as that described earlier for **1a** (**1**). A sample run at 199.55 ± 0.02° for the rate of disappearance of **1b** is: 10<sup>4</sup> s, [1b]<sub>t</sub>/[1b]<sub>0</sub>; 1.44, 0.723; 1.98, 0.635; 2.52, 0.556; 3.07, 0.498; 3.60, 0.433; 4.14, 0.379; 4.67, 0.341; 5.05, 0.307. These results yield *k*<sub>2</sub> + *k*<sub>3</sub> = (2.35 ± 0.03) × 10<sup>-5</sup> s<sup>-1</sup>.

**Discussion**

A possible mode of formation of the vinylidenehydrofuran, **6**, consists of **1b** undergoing the preferred (4,5) conrotatory ring opening of the oxirane ring to produce **3b** then by a five-centered disrotatory ring closure to produce **6**. The intermediate **2b** cannot lead directly to **6** since the groups R and H are *trans* and must have a *cisoid* arrangement (as in **3**) to produce **6**. As a consequence we would expect that the rate of racemization via **2b** should be decreased only slightly but that the rate of formation of **6**, if it requires the inward conrotatory ring opening as exemplified by **3**, should decrease very sharply. From Table 3 we can calculate that at 150° the

rate constant ratio  $k_1/k_2$  is 42.4 for **1b** compared with 19.4 for **1a**. There is no significant difference between these rate ratios ( $\delta\Delta G^\ddagger \approx 0.6$  kcal mol<sup>-1</sup>) and thus we can conclude that the mode of conrotatory ring opening exemplified by **3** cannot be of significance in forming **6**. The racemization rate constant for **1a**, at 150°, is only 4.7 times greater than that for **1b**, again suggesting that substitution has had little effect. It is more likely that a path, similar to that suggested by Paladini and Chuche (2) for the rearrangement of 2-phenyl-3-vinyloxirane, is operative for **1a** and **1b**; such a path is outlined in Scheme 3. Support for this comes from the observation that the intermediate **8** by a conrotatory three-centered closure gives rise to the *cis* oxirane **9** which is known to rearrange rapidly to **7** (3). In such a case the substitution of hydrogen by methyl on going from **1a** to **1b** should not greatly affect the ratio  $k_1/(k_2 + k_3)$ ,

which is 10.7 for **1a** and 33.8 for **1b**. We conclude that the rate-determining step in the sequence is the isomerization about the carbon-oxygen bond of the carbonyl ylide to form **8**.

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1. V. VUKOV, H. TOKUNAGA, and R. J. CRAWFORD. *Can. J. Chem.* **51**, 3718 (1973).
2. J. C. PALADINI and J. CHUCHE. *Tetrahedron Lett.* 4383 (1971).
3. J. C. POMMELET, N. MANISSE, and J. CHUCHE. *Tetrahedron*, **28**, 3929 (1972).
4. H. J. H. MACDONALD and R. J. CRAWFORD. *Can. J. Chem.* **50**, 428 (1972).
5. H. HAMBERGER and R. HUISGEN. *Chem. Commun.* 1190 (1971); A. DOHMEN, H. HAMBERGER, R. HUISGEN, and V. MARKOWSKI. *Chem. Commun.* 1192 (1971).