

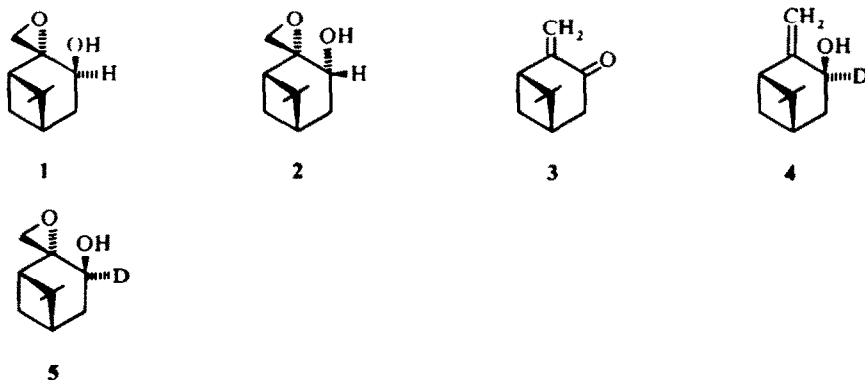
THE BASE-CATALYSED REARRANGEMENT OF 2,10-EPOXY-10 β -PINAN-3-OLS

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Abstract—Kinetic evidence is presented in support of a carbanion mechanism for the base-catalysed rearrangement of 2,10-epoxy-10 β -pinan-3-ols to give pinocarvone.

REACTION of both 2,10-epoxy-10 β -pinan-3-ols (1 and 2) with NaOH in aqueous MeOH have been reported¹ to give pinocarvone (3) in essentially quantitative yield (> 98%, GLC). We now report the results of a kinetic study of this novel base-catalysed rearrangement of epoxides (1 and 2).



EXPERIMENTAL

2,10-Epoxy-10 β -pinan-3-ols (1 and 2). These materials were prepared as reported earlier.²

3 α -Deutero-pin-2(10)-en-3 β -ol (4). A soln of pinocarvone (5.1 g) in dry Et₂O (50 ml) was added dropwise to a stirred suspension of LiAlD₄ (1 g; > 99% D) in dry Et₂O (150 ml). The mixture was stirred at 20° for 16 hr. Isolation by means of Et₂O gave a crude product shown (GLC) to contain pinocarvone (39%), *trans*-pinocarveol (4%), and 4 (57%). The mixture was adsorbed onto alumina (250 g). Elution with pentane-Et₂O (3:1) gave fractions containing pinocarvone. Elution with Et₂O gave pure (GLC) 4 (1.9 g). ν_{\max} 3425, 888 cm⁻¹. NMR (60 Mc, CDCl₃) δ 5.08, 4.76 ($\text{>C}=\text{CH}_2$); 1.26 (C⁸H₃); 0.73 ppm (C⁹H₃).

3 α -Deutero-2,10-epoxy-10 β -pinan-3 β -ol (5). 3 α -Deuteropin-2(10)-en-3 β -ol (360 mg) was added to an ice-cold soln of *m*-chloroperoxybenzoic acid (1 g) in Et₂O (12 ml). The mixture was kept at 4° for 2 days. Isolation by means of Et₂O gave the deuterated epoxide (280 mg), pure by GLC, NMR (CCl₄) δ 3.23, 2.40

(AB quartet, J_{AB} 5 c/s; $\text{>C}-\text{CH}_2$); 0.92 ppm (C⁹H₃), 3 α -deutero- content > 98% by NMR.

Kinetics. The reactions were studied at 60° for H₂O—MeOH solutions (10:1) with [OH⁻] in the range 0.06–0.50 M and [epoxide] $\sim 3 \times 10^{-4}$ M. The rate of formation of pinocarvone was recorded by measuring the optical density of reaction mixtures at 252 m μ , the absorption maximum for pinocarvone.

RESULTS AND DISCUSSION

The optical density readings for the kinetic runs, which were followed to *ca* 75% reaction, were plotted by the Guggenheim³ method and gave excellent linear plots. The pseudo first order rate constant (k_1) was derived from the slope of each plot. The second order rate constants (k_2) for the reactions of epoxide (1; $k_2 = 33 \times 10^{-4}$ l mole⁻¹ sec⁻¹) and epoxide (2; $k_2 = 3.0 \times 10^{-4}$ l mole⁻¹ sec⁻¹) were evaluated from the plot of k_1 vs $[\text{OH}^-]$ for each epoxide (Fig 1).

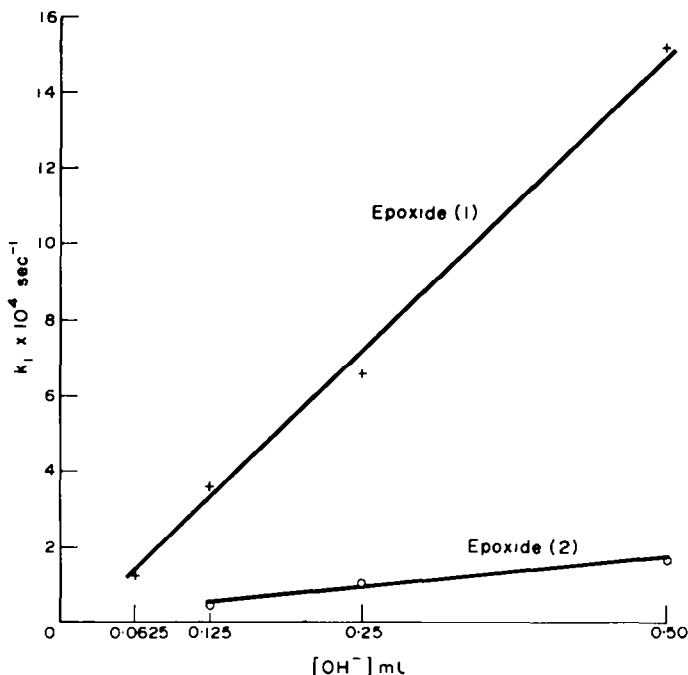


FIG 1. Plot of pseudo-first order rate constant (k_1) vs. $[\text{OH}^-]$

The rearrangement of each epoxide (1 and 2) is approximately first order in both [epoxide] and $[\text{OH}^-]$. The relative rates of rearrangement of epoxide 1: epoxide 2 *ca* 10:1 may be rationalised in terms of the relative accessibility of the C³-H in the epoxides (1 and 2) to attack by hydroxide ion. The mechanistic scheme (Fig 2), involving slow, irreversible proton abstraction by hydroxide ion followed by rapid reaction of the carbanion (6) is consistent with the kinetic data above. Further support

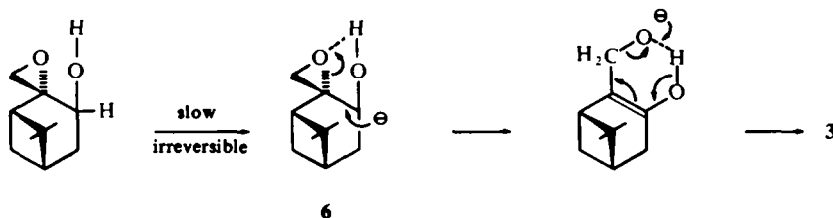


FIG 1

for this reaction scheme was afforded by data obtained for the rearrangement of 3 α -deutero-2,10-epoxy-10 β -pinan-3 β -ol (**5**). Comparison of the pseudo first order constants for the undeuterated (**1**) and deuterated (**5**) epoxides allowed the evaluation of the primary isotope effect, $k_H/k_D = 1.56 (\pm 0.04)$, for the reaction. Furthermore, isolation, and examination of unchanged epoxide at ca 50% reaction showed that no C³—D exchange had occurred, thus excluding reversibility in the initial proton abstraction step.

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