

reagents may, however, raise considerable technical problems. The TLC method presented here gives a faster separation and increased sensitivity, besides permitting the use of more aggressive spray reagents for detection of the sugars.

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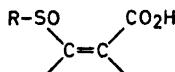
Anchimerically Assisted Sulfoxide Reactions

I. On the Reduction of 2-(Ethylsulfinyl)-cyclohexene-1-carboxylic Acid in Acidic Iodide Solution

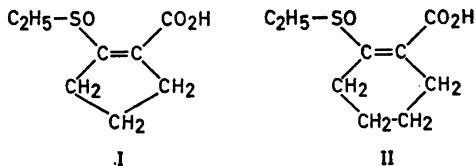
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For the study of carboxyl-assisted sulfoxide reductions¹ 1,2-disubstituted cycloalkenes are of great interest. Heretofore, only one system of this kind, 2-(ethylsulfinyl)-cyclopentene-1-carboxylic acid (I), has been kinetically investigated with respect to the reduction of the sulfoxide group by means of iodide in acid solution.² It was found that I was much more slowly reduced than open-chain compounds of the same type, as represented below:



This fact was interpreted as due to an increase of ring strain during the formation of a bicyclic acyloxysulfonium ion intermediate from I. If this interpretation were correct, we thought that the same would not occur for the reduction of the next higher homologue, *i.e.* 2-(ethylsulfinyl)-cyclohexene-1-carboxylic acid (II), and we now wish to report briefly the preparation and the kinetic study of II.



The reduction of II was carried out at $25.0 \pm 0.02^\circ\text{C}$ in 50% (v/v) acetic acid with sodium perchlorate added, $[\text{ClO}_4^-] = 0.250 \text{ M}$, to keep the ionic strength

approximately constant, *i.e.* under the same conditions as earlier used for the kinetic study of I. The initial concentration of sodium iodide was 0.200 M in both cases; only the perchloric acid concentration in the reduction of II was much lower than that used for I. In Table 1 the second-order rate constants (first-order in sulfoxide and first-order in hydrogen ion concentration³) for the reduction of I and II are given. The value of the rate constant calculated for II is rather approximate, as the reaction, even at the very low perchloric acid concentration used in the experiment, was too fast to measure with accuracy.

As can be seen in Table 1 the ratio k_{II}/k_I is of the magnitude 6000. This ratio

Table 1. Second-order rate constants found for the reduction of I and II under the conditions given above.

Compound	C_6HClO_4 in 50 % (v/v) HAc (M)	$[H^+]_0$ (M)	k (l mole ⁻¹ min ⁻¹)
I	0.50	0.50	0.023 (k_I)
II	0.010	0.018	140 (k_{II})

The zero-subscript denotes the concentration at $t = 0$.

reflects the difference in strain between the transition states through which I and II must pass in order to form the bicyclic acyloxysulfonium ion intermediates; this is because the cyclization step has earlier been shown to be rate-determining.³ It is also noteworthy that II is reduced faster than the open-chain compounds studied previously.²

Experimental. 2-(Ethylthio)-cyclopentene-1-carboxylic acid was prepared according to Ross *et al.*⁴ M.p. 174.5–175.5°. (Ref. 4: 174–175°).

2-(Ethylsulfanyl)-cyclopentene-1-carboxylic acid was obtained by oxidation of the sulfide-acid with peracetic acid as described previously.² M.p. 117.2–118.2°.

2-(Ethylthio)-cyclohexene-1-carboxylic acid. From 51 g (0.30 mole) of ethyl 2-cyclohexanone-1-carboxylate and 56 g (0.90 mole) of ethanethiol 64 g (79 %) of ethyl 2,2-bis-(ethylthio)-cyclohexane-1-carboxylate, b.p._{0.1} 134–135°, n_D^{20} 1.5161 was obtained. (Found: C 56.58; H 8.70; S 23.14. Calc. for $C_{13}H_{24}O_2S_2$: C 56.46; H 8.76; S 23.21). This ester was refluxed for 5 h with an excess of sodium hydroxide in a water-ethanol mixture. After acidification and fractional crystallization of the crude product thus obtained, two fractions were isolated. The main fraction had a m.p. of 147° and consisted of pure 2-(ethylthio)-cyclohexene-1-carboxylic acid. Chandra *et al.*⁵ report m.p. 146°. The m.p. of the smaller fraction was 87.5–89.0° and IR and elemental analyses showed it to consist of 2,2-bis-(ethylthio)-cyclohexane-1-carboxylic acid. (Found: C 53.45; H 8.12; S 25.25. Calc. for $C_{11}H_{20}O_2S_2$: C 53.19; H 8.12; S 25.82).

2-(Ethylsulfanyl)-cyclohexene-1-carboxylic acid was prepared by oxidation of the sulfide-acid with peracetic acid. Repeated recrystallizations from ethyl acetate-petroleum ether yielded an acid of m.p. 123.5–124.0°. (Found: C 53.53; H 6.97; S 15.86; equiv. wt. (NaOH) 202.9. Calc. for $C_9H_{14}O_2S$: C 53.44; H 6.98; S 15.85; equiv. wt. 202.3).

2-(Ethylsulfanyl)-cyclohexene-1-carboxylic acid was obtained when an excess of peracetic acid was used for the oxidation of the sulfide-acid. M.p. 119.0–119.5°. (Found: C 49.64; H 6.53; S 14.66; equiv. wt. 218.6. Calc. for $C_9H_{14}O_2S$: C 49.53; H 6.47; S 14.69; equiv. wt. 218.3).

The kinetic work was performed by the method described earlier.³

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