ISOMERIC 1,3-CYCLOPENTANEDICARBOXYLIC ACIDS FROM THE OXIDATIVE OZONIZATION OF NORBORNENE¹

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We wish to report an unexpected *cis-trans* isomerization which occurs when the ozonization product of bicyclo[2.2.1]heptene-2(norbornene), (I), is oxidized to 1,3-cyclopentanedicarboxylic acid, (II).



Several oxidative procedures have been reported to convert norbornene to pure cis-1,3cyclopentanedicarboxylic acid (norcamphoric acid). These include oxidation of norbornene with permanganate (1) as well as the action of chlorine (2) and hydrogen peroxide (3) on I-ozonization products prepared in methanol. By use of a newly developed chromatographic technique (4) for the quantitative estimation of cis II and trans II in mixtures of the isomers, it was discovered (Table I) that the procedures involving oxidation of I-ozonization product yielded small amounts of trans II, previously undetected. Isomer distribution was not influenced by ageing the ozonization product (Table I, expt. 3) or preparing it at either -70 or 25 °C (Table I, expts. 2 and 4).

TABLE I								
cis/trans	Acid	ratios						

Expt. No.	Ozonization		Oxidation		Yield (%)		-1-14
	Solvent	Temp.(°C)	Solvent	Oxidant	cis	trans	Ratio*
1† 2‡ 3‡,§	MeOH MeOH MeOH MeOH	$-70 \\ -70 \\ -70 \\ -70 \\ 25$	MeOH~H₂O 85% HCOOH 85% HCOOH	$\begin{array}{c} Cl_2 \\ H_2O_2 \\ H_2O_2 \\ H_2O_2 \end{array}$	85.5 63.3 66.4 62.6	Trace 0.9 0.9	>29 67 72 72
$\frac{4}{5}$ 6 7	MeOH MeOH t-BuOH	$-70 \\ -70 \\ 25$	85% HCOOH 85% HCOOH 85% HCOOH 85% HCOOH	$Air \parallel$ Air $Air \parallel$	$56.0 \\ 55.2 \\ 56.4$	$5.8 \\ 6.2 \\ 6.6$	$10 \\ 9 \\ 9$
8 · 9 10	<i>t</i> -BuOH–H ₂ O H ₂ O Permanganate o	25 25 xidation¶	85% HCOOH H ₂ O	Air Air	$49.5 \\ 45.2$	$5.4 \\ 4.7$	9 10 97

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*Determined by chromatography (4). †Duplication of ref. 2. †Duplication of ref. 3. \$Ozonate solution allowed to stand at room temperature 2 weeks before oxidation. \$Small amount of potassium persulfate added to oxidation mixture. ¶Duplication of ref. 1.

As much as 10% of trans II was obtained, however, when norbornene ozonization product prepared in water or an alcohol as solvent was oxidized with air (5) (Table I, expts, 5 and 6). The ratio of *cis* to *trans* obtained by this procedure was essentially the

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same over a temperature range of -70 to 25 °C during ozonization. Norcamphoric acid (*cis* II) is known to isomerize to the *trans* isomer under acidic conditions (6, 7, 8). However, extended treatment of pure norcamphoric acid under the conditions used for oxidation of the ozonization product—bubbling air through a hot formic acid solution— caused no isomerization. This experiment serves to substantiate that the *trans* acid observed in these experiments did not result from isomerization of already formed norcamphoric acid.

The isomeric ratios were determined by a liquid-liquid chromatographic technique (4) utilizing a silicic acid column. It was demonstrated that interconversion of the isomers does not occur on the column, and that elution of both acids is essentially quantitative. The chromatographic technique permitted high purity *trans* II to be obtained free from *cis* isomer. The chromatographically purified *trans* acid had a melting point of 98–99 °C, several degrees higher than previous reported values. Pospischill (6) reported m.p. 87–88.5° for *trans* II, Ingold and Mohrhenn (9) reported m.p. 89°, and Birch and Dean (8) reported m.p. 95.5–96.5°. Chromatographically pure *cis* II melted at 121.5–122.5 °C.

The equilibrium isomer composition of II under acidic conditions was also determined. In previous HCl-catalyzed isomerizations (6, 8) the crude product obtained was estimated to consist of about equal parts of the two isomers. In all cases, however, the separation of isomers was incomplete and only impure *trans* II was isolated. In this work quantitative analysis of the isomers in the product mixtures permitted determination of a definite value, for the equilibrium isomer composition of II, of 1.0:1.0 at 110 °C. The equilibrium was approached from both sides, i.e., both mixtures rich in *cis* and *trans* II were isomerized by refluxing in concentrated HCl. The rate of isomerization was slow since equilibrium was not reached in 48 h.

EXPERIMENTAL

Norbornene Ozonization

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The low temperature ozonization products were prepared as described by Perry (3). During ozonization at room temperature, if conducted by passing the ozone-oxygen stream through a solution of norbornene (I) in a solvent, there were rapid losses of the highly volatile olefin by entrainment in the gas stream. To minimize the loss of I during ozonization at 25°, norbornene dissolved in the appropriate solvent (15% solution) and ozone (2.3% in oxygen) were simultaneously added, at equimolar rates, to the reactor containing the same amount of solvent as used for the norbornene solution. The norbornene solution was metered to the reactor by means of a small pump. When water was employed as the reaction medium, an emulsion of norbornene in water was used. A solution of 66 g of norbornene in 14 ml of *n*-heptane was added slowly to 630 ml of water, containing 3.5 ml of Tergitol NP-14 and 1.5 ml of Triton X-405, with rapid stirring in a home blender. Stirring was continued for several minutes. The emulsion, which was stable for about 24 h, was added simultaneously with ozone to water in the reactor. The ozonization product formed was soluble in water.

Oxidations

The hydrogen peroxide oxidations of norbornene ozonization products were carried out as described by Perry (3). The air oxidations were performed by adding 85% formic acid (100 ml per 0.1 mole norbornene) to the ozonization solution, and then bubbling air (0.5 l/min) through the well-stirred, heated mixture (70-80° water bath) for 10 to 14 h. During this time the alcohol, if used as ozonization medium, was allowed to slowly evaporate. To maintain constant volume, the solvent loss was replenished by adding additional 85% formic acid. Finally, the solvents were removed *in vacuo* at 70 to 80° to give a residue suitable for chromatographic analysis.

Infrared Spectra of Acids

Characteristic absorption bands for cis-1,3-cyclopentanedicarboxylic acid (Nujol mull) were found at 7.76 (s), 8.01 (m), 8.25 (m), 9.78 (w), and 10.32 (w) microns. The *trans* acid has characteristic absorption bands at 8.17 (s) and 8.79 (w) microns. The absorption spectra of the *trans* acid in a Nujol mull containing water changed, particularly in the 10.3 to 11.3 micron region associated with the acid OH groups. Under these conditions, the *cis*-acid spectrum was unchanged. Apparently hydrogen bonding occurred with the *trans* acid but not with the *cis* acid which is internally bonded (4).

NOTES

Equilibration of Acids

A solution of 3.0 g of cis-1,3-cyclopentanedicarboxylic acid in 60 ml of 20.2% hydrochloric acid was refluxed for 112 h at 110°. The solvent was removed in vacuo at room temperature, and the residue was analyzed by chromatography. The cis/trans ratio was 1.00:1.00. Similarly, a mixture of 2.7 g of the trans acid and 0.5 g of the cis acid was refluxed with 60 ml of 20.2% hydrochloric acid for 112 h. The cis/trans ratio in the product was 1.04:1.00 according to chromatographic analysis. A solution of 10 g of the cis acid in 85% formic acid was heated at 85° for 28 h while air was bubbled through at about 0.5 l/min. Solvent was removed in vacuo at 80°. The residue, analyzed chromatographically, showed the presence of less than 1% trans isomer.

Chromatographic Analysis

A detailed description of the chromatographic procedure has been published (4).

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THE CHEMICAL SHIFT OF THE HYDROXYL PROTON OF PHENOLS IN DIMETHYL SULFOXIDE

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The effect of ring substituents on the spectral properties of phenols has been examined by several groups of workers (1). The infrared stretching frequency of the phenolic hydroxyl group has been shown to vary linearly with σ^- values for 4-substituents in both the simple series and the 2,6-di-t-butyl series (2). The identical ρ has been found for both series. The effect of substituents on the nuclear magnetic resonance (n.m.r.) signal of the phenolic proton might also be expected to correlate with σ^- if the chemical shift is dependent on both inductive and resonance factors. However, the observed resonance signal represents a time average of all possible phenolic aggregates at the concentration under consideration. Therefore, it is necessary to extrapolate to infinite dilution in order to obtain the chemical shift of a definable species: that of the monomeric phenol. Dilution studies on phenols have led to inconclusive results as the extrapolated values of the chemical shifts are closely similar and only a trend with σ is noted (3). The reason for this lack of a correlation is unknown at present. The introduction of bulky substituents

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