preparation of other carbazoles was used. A 0.5-g. portion of 5-chloro-1-(2-chlorophenyl)benzotriazole (X) was heated in a small open tube for 10 min. at 355° and the residue was dissolved in ethanol and treated with boneblack. The product was precipitated from the ethanolic solution by addition of water and was twice recrystallized from petroleum ether (b.p. 60–110°) to give 0.1 g. (22%) of white crystalline 1,6-dichlorocarbazole, m.p. 123–124°.

Anal. Calcd. for $C_{12}H_7Cl_2N$: C, 61.0; H, 3.0; N, 5.9. Found: C, 60.8; H, 2.9; N, 5.8.

This material did not depress the melting point of the 1,6-dichlorocarbazole derived from 1,6-dinitrocarbazole, thus establishing the structure of the latter compound.

Acknowledgment.—The authors are indebted to the Southern Dyestuff Company Division of Martin-Marietta Corporation for permission to publish this work conducted under their sponsorship.

The Preparation of *trans*-4-*t*-Butylcyclohexene Oxide

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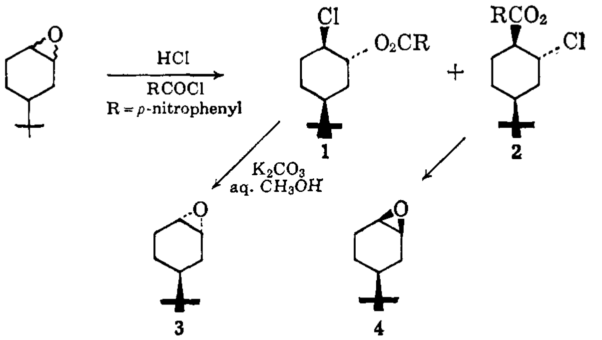
The preparation of isomerically pure liquid epoxides of substituted cycloalkenes has been a major problem in the study of the stereochemistry of oxide ring-opening reactions. Direct fractional distillation is often impossible; *e.g.*, a mixture of *cis* and *trans*-4-*t*-butylcyclohexene oxides on distillation through a 60-cm. spinning band column gives no evidence of fractionation.

Routes to the isomeric 4-*t*-butylcyclohexene oxides have been devised by two groups[1,2]; both sequences are multistep and involve either column chromatography or ion-exchange chromatography which limits their usefulness in large-scale preparations.

We wish to report a simple, rapid method of separating pure *trans*-4-*t*-butylcyclohexene oxide from a mixture with its geometric isomer. Treatment with anhydrous hydrochloric acid in the presence of *p*-nitrobenzoyl chloride in chloroform solution gave a mixture of chloroesters from which 1 was readily isolated by recrystallization. The identity of 1 follows from C and H analysis, infrared and n.m.r. spectra, expectation of *trans* diaxial opening[3] in formation, and from the observation that *trans*-4-*t*-butylcyclohexene oxide is regenerated from it in high yield. While a number of other isomers could conceivably be formed in the initial ring-opening reaction, 1 and 2 must be by far the major products, as the mixed epoxide is recovered in good yield on facile basic hydrolysis of the crude chloro ester mixture.[4]



Recrystallization from methanol of the combined second crops rapidly gave sharp-melting material which appeared to be isomer 2. However, the reformed epoxide from this material (high yield) was composed of approximately 80% *cis*- (4) and 20% *trans*-4-*t*-butylcyclohexene oxide (3). Exhaustive recrystallization from aqueous acetic acid gave a poor yield of the chloro ester 2 of approximately 95% purity. This product was used for analysis and n.m.r. spectrum determination.

The procedure described here promises to be of general utility in the separation of epoxides and, with the methods already available[1a] for stereospecific interconversion of these isomers, offers a straightforward pathway to both *trans* and *cis* forms.

Experimental

4-*t*-Butylcyclohexanol.—A 1-l. high-pressure hydrogenation bomb was charged with 342 g. (2.20 mole) of 4-*t*-butylphenol (recrystallized from aqueous methanol), 300 ml. of glacial acetic acid, and 2.5 g. of 5% rhodium-on-alumina catalyst. At ambient temperature and an average hydrogen pressure of 1800 p.s.i., reduction was complete in approximately 2.5 hr. The product, obtained in essentially quantitative yield, was composed of 60% *cis*- and 40% *trans*-4-*t*-butylcyclohexanol.

4-*t*-Butylcyclohexene was prepared in high yield by the method of Sicher,[2] b.p. 70–72° (20 mm.).

***cis*- and *trans*-4-*t*-Butylcyclohexene Oxide.**—The olefin, 105 g. (0.76 mole), was taken up in 1.5 l. of anhydrous ether, and 160 g. of commercial *m*-chloroperbenzoic acid[5] was added in portions over a period of about 2 hr. Occasional cooling was required. The mixture was allowed to stand 24 hr., washed with 10% sodium sulfite solution and dilute base, and dried over anhydrous magnesium sulfate; the solvent was evaporated. Distillation of the residue gave 107 g. (92%) of the epoxide mixture, b.p. 68–69° (4 mm.).

This mixture, which was identical with that formed by the action of either perbenzoic or monoperphthalic acid on the olefin, was comprised of 60% *cis* and 40% *trans* epoxide.[6]

***trans*-2-Chloro-*trans*-5-*t*-Butylcyclohexyl *p*-Nitrobenzoate.**—The epoxide mixture, 97 g. (0.63 mole) was dissolved in 500 ml. of chloroform, and 140 g. (0.75 mole) of *p*-nitrobenzoyl chloride (recrystallized from petroleum ether, b.p. 90–110°) was added. With magnetic stirring, a slow stream of anhydrous hydrochloric acid was passed into the solution over a period of 6 hr.; the reaction was very slightly exothermic. The chloroform solution was washed with water to remove excess acid and evaporated to give a residue which was taken up in pyridine. A few chips of ice were added to decompose the excess acid chloride, after which the mixture was taken up in ether, washed extensively with 5% hydrochloric acid, then with dilute bicarbonate and water. After drying, evaporation of the ether gave 215 g. of solid material (essentially quantitative crude yield).

Recrystallization was effected from methanol solution, with rapid purification rather than high recovery being stressed. Five recrystallizations gave 24 g. (28%), m.p. 124.5–126°.

Anal. Calcd. for $C_{17}H_{22}ClNO_4$: C, 60.1; H, 6.5. Found: C, 60.4; H, 6.8.

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[1] (a) N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, **26**, 4768 (1961); (b) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

[2] J. Sicher, F. Šipoš, and M. Tichý, *Collection Czech. Chem. Commun.*, **26**, 847 (1961).

[3] For a review of the stereochemistry of epoxide-opening reactions, see R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

[4] D. Y. Curtin and R. J. Harder, *J. Am. Chem. Soc.*, **82**, 2357 (1960).

[5] FMC Corporation, 85% minimum assay material was used.

[6] Analysis was by vapor phase chromatography.

The n.m.r. spectrum of this material (15%, CCl_4) showed two fairly well-resolved quartets ($J \sim 3$ c.p.s.), as expected for the equatorial protons at C-1 and C-2; these absorptions were centered at 4.29 and 5.33 p.p.m. (tetramethylsilane = 0).

trans-4-*t*-**Butylcyclohexene Oxide**.—The chloro ester 1, 3.4 g. (0.01 mole), was dissolved in 50 ml. of refluxing methanol. To this solution was added 4 g. of potassium carbonate dissolved in approximately 5 ml. of water. The mixture was refluxed with occasional swirling for 1 hr., after which the contents were taken up in water and extracted twice with pentane. The pentane was dried with potassium carbonate and evaporated; the residue was flash distilled to give 1.4 g. of *trans*-4-*t*-butylcyclohexene oxide (91%). The infrared spectrum was essentially identical with that of the mixed *cis* and *trans* epoxides, and showed no carbonyl absorption. Vapor phase chromatography (DEGS) indicated a purity of >99%.

trans-2-**Chloro**-*cis*-4-*t*-**Butylcyclohexyl** *p*-**Nitrobenzoate**.—The second crops from the three initial recrystallizations of isomer 1 were combined and recrystallized four times from methanol to give 44 g. of material, m.p. 71–72°. This was found to be a mixture of about 80% 2 and 20% 1 by examination of the epoxides obtained on base-catalyzed hydrolysis. Repeated recrystallization from methanol failed to change this ratio appreciably, indicating the probable formation of a mixed compound. Recrystallization from aqueous acetic acid gave poor yields of material with a wide melting point range; 1.5 g. of product, m.p. 60–81°, was obtained after numerous recrystallizations and found to be about 95% 2, 5% 1 by hydrolysis to epoxide. The melting point range is indicative of a eutectic containing a high per cent of 2. Because of the poor yields, additional efforts along these lines were abandoned, and this slightly impure material was used for analysis.

Anal. Found: C, 60.2; H, 6.5.

The n.m.r. spectrum of 2 was very similar to that of 1, two quartets centered at 4.40 and 5.22 p.p.m., indicating again equatorial protons attached to the carbon atoms bearing polar substituents.

Configuration of the Epoxides.—The *trans* epoxide was identified by lithium aluminum hydride reduction, which gives as the major product *trans*-3-*t*-butylcyclohexanol, as expected by diaxial opening of the epoxide. In analogous manner, the *cis* epoxide gave mainly *cis*-4-*t*-butylcyclohexanol. A more extensive discussion of this reaction is reserved for a later communication.

Acknowledgment.—The authors are indebted to the American Chemical Society Petroleum Research Fund for support of this work.

Identification and Separation of the Isomeric 2-Methylpyrazine Mono-N-oxides[1]

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Oxidation of 2-methylpyrazine with an equivalent of hydrogen peroxide in acetic acid was reported by Koelsch and Gumprecht[2a] to lead to two isomeric mono-N-oxides, the 1-oxide (I) and the 4-oxide (II). The 1-oxide was identified[3] by rearrangement with acetic anhydride[4] to yield, after saponification, pyrazinemethanol. The sample thought to have been the 4-oxide, under the same conditions, gave a compound (m.p. 68–69°) assumed to be 5-methyl-2(1H)-pyrazinone.[2b]

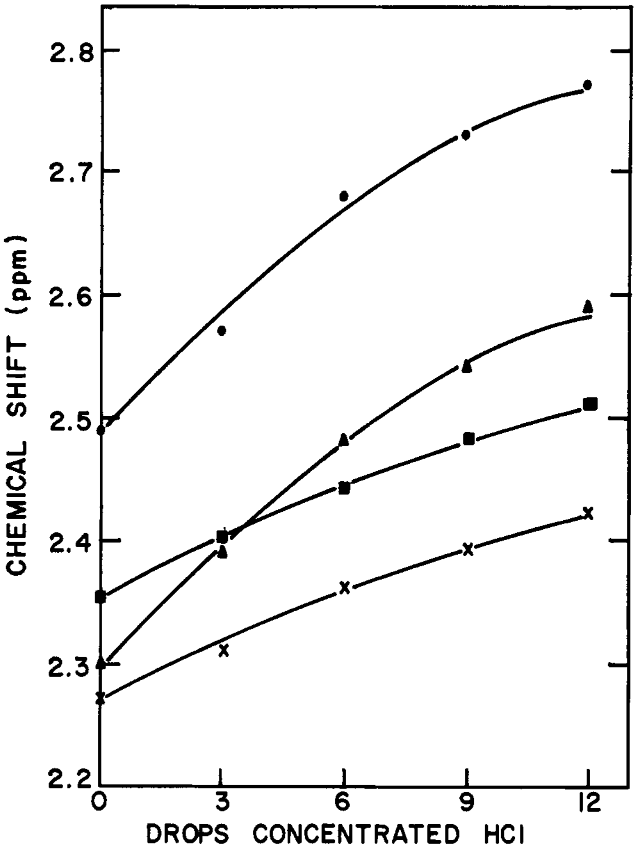
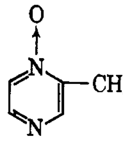


Fig. 1.—Effect of protonation on the chemical shifts for the methyl group in the n.m.r. spectra of pure 2-methylpyrazine 4-oxide (●), 2-methylpyrazine 1-oxide (■), and a eutectic mixture of the 1- and 4-oxides (×, ▲).



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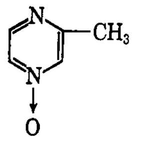

II

Klein and Berkowitz[5a] have questioned the existence of 2-methylpyrazine 1-oxide in concluding that the two samples that they obtained from the mono-N-oxidation were actually polymorphs of the 4-oxide melting at 45 and 80–82°.[5b] Their chemical evidence for polymorphism was the preparation of the same *picrate* from the two samples, and conversion of both in the low yields to 3-chloro-2-methylpyrazine.[6] The exist-

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[1] Presented in part at the 4th Omnibus Conference on Experimental Aspects of NMR Spectroscopy, Pittsburgh, Pa., March 2, 1963.

[2] (a) C. F. Koelsch and W. H. Gumprecht, *J. Org. Chem.*, **23**, 1603 (1958). (b) At the time, the authors were unaware of the melting point of 126–128° reported for this pyrazinone by G. Karmas and P. E. Spoerri [*J. Am. Chem Soc.*, **74**, 1580 (1952)].

[3] See also M. Asai, *J. Pharm. Soc. Japan*, **79**, 1273 (1959); *Chem. Abstr.*, **54**, 4607*i* (1960).

[4] V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).

[5] (a) B. Klein and J. Berkowitz, *ibid.*, **81**, 5160 (1959). (b) Selective N-oxidation at one of the two heteronitrogens in 2-methylpyrazine would be surprising, especially since the formation under the same conditions of both possible mono-N-oxides of 2,6-dimethylpyrazine is reported in this reference. The described separation of the polymorphs by distillation also must be considered unusual since molecular interaction in the vapor phase would not be expected to have a significant influence on orientation in the crystal lattice.

[6] If it is recalled that their higher melting sample melted 10° lower than that reported by Koelsch and Gumprecht, then it would seem likely that their 2-methylpyrazine 1-oxide was contaminated, probably with the 4-oxide.