5.88 (1 H, s), 4.86 (1 H, s), 4.42 (1 H, s), 4.20 (1 H, m), 3.82–4.02 (6 H, m), 3.77 and 3.57 (2 H, AB quartet, J = 12 Hz), 3.46 (1 H, br s) and 1.50–2.60 (9 H, m); electron impact mass spectrum, m/e 432 (M^+).

(±)-(14α)-4,5-Epoxy-3-methoxy-6,6-(ethylenedioxy)-10-methylene-17-cyanomorphinan (52b). To a solution of the ketal **52a** (112.0 mg, 0.26 mmol) in chloroform (5 mL) were added cyanogen bromide (41.0 mg, 0.39 mmol) and anhydrous K_2CO_3 (380.0 mg, 2.75 mmol), and the resulting suspension was heated at reflux temperature for 7 h. The reaction mixture was diluted with chloroform, washed with water and brine, dried, and evaporated to give **52b** (90.0 mg, 95%). Flash column chromatography (SiO_2, hexane–ethyl acetate, 1.5:1) afforded **52b** (70.0 mg, 74%). An analytical sample was prepared: mp 214–215 °C dec (ethyl acetate/hexane); IR ($CHCl_3$) 4.55, 6.17, 6.67 μm; ^1H NMR ($CDCl_3$) δ 7.10 and 6.80 (2 H, AB quartet, J = 8 Hz), 5.90 (1 H, s), 5.48 (1 H, s), 4.38 (1 H, s), 3.80–4.20 (8 H, m), 3.20 (2 H, m), 1.60–2.30 (7 H, m); electron impact mass spectrum, m/e 366 (M^+).

Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.83; H, 6.06. Found: C, 68.10; H, 5.72.

(±)-(14α)-4,5-Epoxy-3-methoxy-10-oxo-17-cyanomorphinan-6-one (52c). To a solution of **52b** (23.0 mg, 0.06 mmol) THF–H_2O (2 mL, 1:1) was added 23 μL of 2.5 wt % solution of osmium tetraoxide in *tert*-butyl alcohol, and to the resulting rapidly darkening solution was added sodium periodate (46.0 mg, 0.22 mmol). After being stirred at room temperature for 12 h, the pale yellow solution was diluted with methylene chloride (15 mL), washed with water and brine, dried, and evaporated to give crystalline **52c** (23.0 mg, 99%). An analytical sample was prepared: mp 208–210 °C dec (ethyl acetate/hexane). IR ($CHCl_3$) 4.52, 5.92, 6.19 μm; ^1H NMR ($CDCl_3$) δ 7.50 and 6.91 (2 H, AB quartet, J = 8 Hz), 4.46 (1 H, s), 4.18 (1 H, m), 3.91–3.98 (6 H, m with a sharp s at 3.98), 3.71 (1 H, d, J = 2.8 Hz), 3.34–3.41 (2 H, m), 2.64–2.80 (2 H, m), 2.04–2.40 (2 H, m), 1.80–2.00 (4 H, m); electron impact mass spectrum, m/e 368 (M^+).

Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.20; H, 5.48. Found: C, 65.03; H, 5.30.

Acknowledgment. We thank the National Institute on Drug-Abuse (NIDA) for support of this work through Grant DA02357.

Registry No. (±)-**1a**, 93757-87-0; (±)-**1b**, 93757-86-9; (±)-**1c**, 93757-88-1; (±)-**2a**, 93859-96-2; (±)-**2b**, 94061-98-0; (±)-**2c**, 93859-99-5; (±)-**5**, 93757-83-6; (±)-**7**, 93757-84-7; **8**, 93757-85-8; (±)-**10a**, 93859-95-1; (±)-**10b**, 93757-89-2; (±)-**10c**, 93757-90-5; (±)-**11**, 93859-97-3; (±)-**12**, 93757-91-6; (±)-**13a**, 93757-92-7; (±)-**14**, 93757-93-8; (±)-**15a**, 93757-94-9; (±)-**15b**, 93757-96-1; (±)-**16**, 93757-95-0; (±)-**17a**, 93757-97-2; (±)-**17b**, 93757-98-3; (±)-**17c**, 93757-99-4; (±)-**22a**, 93758-44-2; (±)-**22b**, 93758-45-3; (±)-**22c**, 93758-46-4; (±)-**23a**, 93758-02-2; (±)-**23b**, 93758-04-4; (±)-**23c**, 93758-06-6; **24a**, 93758-03-3; **24b**, 93758-05-5; **24c**, 93758-07-7; (±)-**25a**, 93758-08-8; (±)-**25b**, 93758-09-9; (±)-**25c**, 93758-11-3; (±)-**25d**, 93758-12-4; (±)-**25e**, 93758-14-6; **26b**, 93758-10-2; **26d**, 93758-48-6; **28**, 18167-91-4; (±)-**29**, 93758-00-0; **30a**, 93758-01-1; **30b**, 62787-67-1; **30c**, 93758-47-5; (±)-**31a**, 93758-15-7; (±)-**31b**, 93758-16-8; (±)-**31c**, 93758-17-9; (±)-**31d**, 93758-19-1; (±)-**32a**, 93758-49-7; (±)-**32b**, 93758-18-0; (±)-**33a**, 93758-50-0; (±)-**33b**, 93781-86-3; (±)-**33c**, 93758-20-4; (±)-**33d**, 93781-87-4; **34a**, 93758-51-1; (±)-**35a**, 93781-85-2; (±)-**35b**, 93758-21-5; (±)-**36a**, 93758-22-6; (±)-**36b**, 93758-24-8; (±)-**36c**, 93758-23-7; (±)-**36d**, 93758-25-9; (±)-**36e**, 93758-27-1; (±)-**37a**, 93758-26-0; (±)-**37b**, 93758-28-2; (±)-**37c**, 93758-31-7; (±)-**38a**, 93859-98-4; (±)-**40a**, 93758-29-3; (±)-**40b**, 93758-30-6; (±)-**47a**, 93758-52-2; (±)-**47b**, 93758-32-8; (±)-**47e**, 93758-33-9; (±)-**47f**, 93758-34-0; (±)-**47g**, 93758-37-3; (±)-**48a**, 93758-53-3; (±)-**49a**, 93758-35-1; (±)-**49b**, 93758-39-5; (±)-**49c**, 93758-38-4; **50**, 93758-36-2; (±)-**51a**, 93758-40-8; (±)-**52a**, 93758-41-9; (±)-**52b**, 93758-42-0; (±)-**52c**, 93758-43-1; isovanillic acid methyl ester, 6702-50-7; 2-[(methoxymethyl)oxy]-1-(benzyloxy)benzene, 93758-13-5; 2-[(methoxymethyl)oxy]phenol, 52702-30-4; 3-hydroxy-4-methoxybenzonitrile, 52805-46-6; 2-(benzyloxy)phenol, 6272-38-4; vinyl bromide, 593-60-2; methyl vinyl ketone, 78-94-4; 2-methoxyphenol, 90-05-1; chloromethyl methyl ether, 107-30-2.

Mechanisms of Epoxidation during Ozonation of Carbon–Carbon Double Bonds

Philip S. Bailey,* Hank H. Hwang, and Chin-Yun Chiang

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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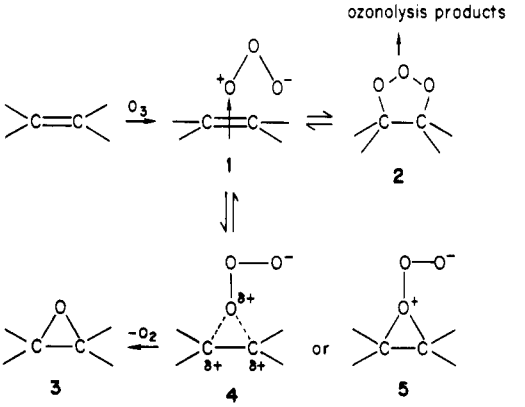
Epoxidation of several highly hindered olefins with ozone is stereospecific in all solvents, nucleophilic or nonnucleophilic. This is in agreement with expectations based on the initial formation of a π rather than an open σ complex.

Epoxidation and other "partial cleavage" reactions have long been known as reactions competitive with ozonolysis during ozonation of alkenes, olefins with various other functional groups, and related substances such as allenes and ketenes.[1,2] In many cases the epoxide itself is the product, whereas in other cases substances are obtained which could be derived from the epoxide by rearrangement, reactions with other functional groups in the molecule, or reactions with the solvent etc. Yields vary from less than 10% to nearly 100%. In many cases molecular oxygen has been observed as a product in approximately equal molar quantities with the epoxides.[1-4]

Scheme I

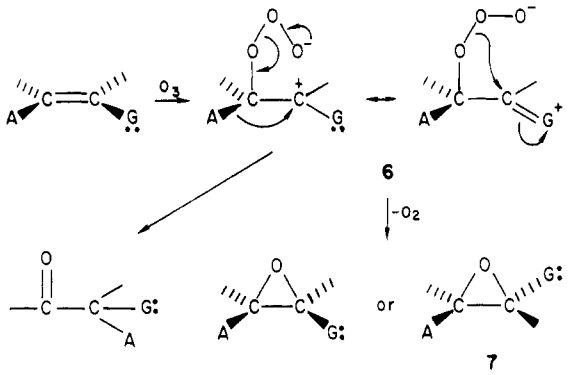


The various examples can roughly be divided into two groups: sterically hindered and unhindered olefins.[1] In the first category the degree of "partial cleavage" appears

(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1, Chapters XI and X.
(2) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1982; Vol. II, Chapter XII.
(3) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473.
(4) Bailey, P. S.; Ward, J. W.; Hornish, R. E.; Potts, F. E., III *Adv. Chem. Ser.* **1972**, *No. 112*, 1.

0022-3263/85/1950-0231$01.50/0

Scheme II



to increase with the bulk of the groups around the double bond.[1,3,4] These reactions also appear to be stereospecific, with retention of configuration.[1] For example, Murray and Suzui[5] showed that the *Z* and *E* isomers of 1-(1-naphthyl)-1-phenylpropene gave the corresponding *Z* and *E* epoxide isomers, respectively, uncontaminated with the other isomer. However, the yield in each case was only 24–31%.

For these reactions the mechanism of Scheme I was proposed.[1,3] The initial species, a π complex (**1**), was suggested to be produced first in any case. It, then, in general, tends to complete a 1,3 dipolar cycloaddition on the way to ozonolysis products. With increasing bulk around the double bond, however, such a process becomes more and more hindered and loss of molecular oxygen, via **4** (a transition state) or **5** (a σ complex), to yield an epoxide (or rearrangement etc. products thereof) becomes more and more important. The route through **4** was favored since at −150 °C the π complex (**1**) of 1-mesityl-1-phenylethene was observed, but it decomposed directly to **3** without proceeding through any observable (by NMR) intermediate.[1,4,6] Also, rearrangement products were more easily rationalized through **4**, although they also could be produced from **3**.[1,3]

The unhindered olefins that afforded epoxides or rearrangement products thereof possessed, for the most part, electron-rich groupings attached to a double-bond carbon.[1] In the cases studied, epoxide formation was not stereospecific and there was, generally, a solvent effect. For example, ozonation of both *cis*- and *trans*-1,2-difluoroethylene afforded only the cis epoxide; it was the major product in methyl chloride, whereas ozonolysis products were major in isobutane solvent.[1,7] In many of these cases, only rearranged products were obtained. For these reasons, it was suggested[1] that the intermediate in the partial cleavage reaction was a σ complex of type **6**, which would be stabilized by the electron-rich attachment, as illustrated in Scheme II.[1] With such, there should be no stereospecificity in epoxide **7** formation. Allenes and ketenes also have been assumed to belong to this category in regard to epoxide formation.[1]

A third mechanism also has been suggested for epoxide formation during ozonation. This involves epoxidation by a carbonyl oxide intermediate, or its isomeric dioxirane structure.[1,2,7-11] This could only occur, however, in cases where the epoxide yield is less than 50% (since equal amounts of olefin and carbonyl oxide would be required) and molecular oxygen is not obtained in equal amounts with the epoxide. It seems unlikely that the mechanism of this epoxidation involves 1,3 dipolar cycloaddition between the carbonyl oxide and the olefin, as once suggested by Kwart and co-workers,[12] since Gillies[10] has ozonized mixtures of the isomeric 1,2-difluoroethylenes and their deuterio analogues and has found no isotopic mixing in the epoxide produced.[2] Murray and co-workers[13] have demonstrated that carbonyl oxides, separately synthesized, actually can epoxidize olefins, but, unlike the reactions of Gillies,[7,10] epoxide formation was stereoselective.[2]

At the time of some of the earlier work,[1-4] there was some hint in the literature that solvent effects exist in the epoxide–ozonolysis competition with hindered olefins. For example, the yields of epoxide and/or rearrangement products from ozonation of 1-mesityl-1-phenylethene appeared to vary from 75 to 85% in solvents like pentane and methylene chloride to 91% in methanol.[1,3,4] For this reason we decided to study the yields and stereochemistry of epoxide formation with hindered olefins in various solvents, in order to determine whether or not there was a switch from the mechanism of Scheme I to that of Scheme II with solvents that could stabilize a carbocation intermediate. For this study we have utilized 4,4-dimethyl-2-neopentyl-1-pentene (or 1,1-dineopentylethylene),[3,4] 4-neopentyl-2,2,6,6-tetramethyl-3-heptene (or 1,1-dineopentyl-2-*tert*-butylethylene),[4,14,15] (*Z*)- and (*E*)-1-(1-naphthyl)-1-phenylpropene,[5] (*Z*)- and (*E*)-1-mesityl-1-phenylpropene,[16] and (*Z*)- (or (*E*)-) 4-*tert*-butyl-2,2,6,6-tetramethyl-3-heptene (or 1-neopentyl-1,2-di-*tert*-butylethylene),[14,15] all of which are known compounds. The principal solvents utilized were methanol, diethyl ether, methylene chloride, and pentane. The results are outlined in Table I.

It can be seen from examples 1–4 and 7 of Table I that in all solvents epoxide formation was entirely stereospecific, with retention of configuration (see footnote *m* of Table I). Only minor solvent effects regarding the competition between epoxide formation and ozonolysis occurred with the olefins bearing aromatic substituents (examples 1–4), while these effects were much larger with the purely aliphatic olefins (examples 5–7). It is curious, however, that there is no consistency of results regarding whether a nucleophilic solvent, such as methanol or diethyl ether, or a solvent such as methylene chloride affords the highest epoxide yields. It is also interesting that the epoxide yields from (*E*)-1-mesityl-1-phenylpropene are much lower than those from the *Z* isomer. This appears to be consistent with the general theory that the greater the steric hindrance of bulk around the double bond the greater the epoxide yield.[3]

Most importantly, it can be concluded that no switch over between the mechanisms of Schemes I and II occurs with increasing ability of the solvent to stabilize a carbo-

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(8) Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 6876; **1976**, *98*, 6578.
(9) Griesbaum, K.; Brüggemann, J. *Adv. Chem. Ser.* **1972**, *No. 112*, 50. Griesbaum, K.; Brüggemann, J. *Chem. Ber.* **1972**, *105*, 3638. Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 2877.
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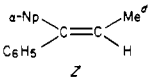
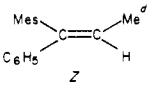
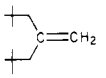
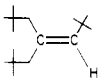
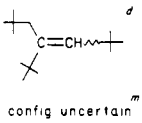
(16) (a) van der Linde, R.; Korver, O.; Korver, P. K.; van der Haak, P. J.; Veenland, J. U.; de Boer, T. J. *Stereochim. Acta* **1965**, *21*, 1893. (b) van der Linde, R.; Veenland, J. U.; de Boer, T. J. *Stereochim. Acta, Part A* **1969**, *25A*, 487.

Table I. Percentage of Epoxide from Ozonation of Hindered Olefins in Various Solvents[a,b]

expt no.	olefin[c]	MeOH, %	Et_2O, %	CH_2Cl_2, %	isopentane, %	other
1	 *Z*	20 (64–69)	22 (70–89)	13[e] (65)	16 (63)	
2	*E* isomer of above[d]	22 (68)	23 (74)			
3	 *Z*		94 (99)	86 (98)	94 (99)	
4	*E* isomer of above[d]		61 (90)		55 (85)	
5		16 (70)	9 (80)	27 (99)	4 (85)	*f* (*g*)
6		82 (99)	70 (90)	77[h] (99)	40[i] (80)	*j* (*k*)
7	 config uncertain[m]	23 (96)	4 (68)	12 (78)	3 (77)	*l*

[a] In each case 1 molar equiv of ozone was employed with oxygen as a carrier. The percentages shown without parentheses are the epoxide yields, while those in parentheses are for epoxide plus ketone (from left side of molecule); no epoxide rearrangement products were detected. Experiment 5 is an exception; see footnote *g*. Yields are based on olefin actually reacting. [b] In the first four experiments the reaction temperature was 0 °C, while for the last three experiments it was −78 °C. In several experiments it was shown that there was little or no temperature effect. See footnotes *e* and *h*. [c] The configurations indicated in experiments 1–4 are those designated in the original literature[5,16] and are based on consistent considerations. [d] In all of these examples epoxide formation occurred with 100% retention of configuration. [e] This is the value for experiments at 0 and −40 °C; the value for −78 °C was 12%. [f] For 1:1 CH_2Cl_2–CH_3OH at −78 °C, glacial acetic acid at 25 °C, and 9:1 acetic acid–water at 25 °C, the epoxide yields were 13%, 22%, and 25%, respectively. [g] In these experiments, the products isolated, in addition to the epoxide, were the corresponding ozonide (14% from methylene chloride, 37% from diethyl ether, and 52% from isopentane), dimeric ketone peroxide (3–5% from isopentane and diethyl ether), and ketone (24% from isopentane, 31% from diethyl ether, 58% from methylene chloride, and 54% from methanol). [h] This is the value for −78 °C. For −40 °C, it was 70%. [i] This is the value for −78 °C. For −40 °C, it was 42%. [j] For 1:1 CH_2Cl_2–CH_3OH at −78 °C, nitromethane of 0 °C, dimethyl formamide at 0 °C, glacial acetic acid at 25 °C, and 9:1 acetic acid–water at 25 °C, the epoxide percentages were 82%, 61%, 67%, 63%, and 75%, respectively. [k] Pivaldehyde also was identified, but not included in the total percentage yield, since it would be formed simultaneously with dineopentyl ketone by ozonolysis. [l] Also obtained was a 1% yield of pivaldehyde (right side by ozonolysis). [m] Although the configuration of the olefin is uncertain, there is no doubt that epoxide formation is stereospecific since the epoxide obtained by ozonation is identical with that obtained by the stereospecific peracid method.

cation (**6**) intermediate. Since epoxide yields in examples 1, 2, 5, and 7 were considerably less than 50%, it is possible that some, or all, of the epoxidation occurred via a carbonyl oxide intermediate. However, since the epoxide formation was 100% stereospecific, this appears unlikely. Murray and co-workers[13] found these reactions to be only stereoselective, not 100% stereospecific. The best rationalization of results appears to be the mechanism of Scheme I and a transition state such as **4**. In examples 1–4, there already is stabilization of the partial positive charges of **4**, via resonance involving the aromatic substituents. Therefore, solvent stabilization is of little importance. With examples 5–7, however, there is no resonance stabilization, and solvent stabilization plays a greater role. In all three of these cases the lowest epoxide yield was in isopentane. No explanation is readily apparent, however, for the facts that in examples 5–7 the next lowest epoxide yields occurred in ether solvent and that in experiment 6 the epoxide yield was only slightly higher in ether than in nitromethane, dimethyl formamide, and glacial acetic acid solvents and no appreciable increases occurred with aqueous acetic acid as solvent.

Experimental Section

General Procedures. Ozonation procedures were performed as described previously,[6,17] using 1 molar equiv of ozone in the solvents and at the temperatures shown in Table I. GLPC determinations were made with an Aerograph Model A-90-P_3.

(*Z*)- and (*E*)-1-(1-Naphthyl)-1-phenylpropene were prepared as described by Murray and Suzui[5] and were *ozonized* in 0.1–0.2 M solutions, using 1.5 mmol of olefin. Workup and identification of products were as described previously.[5] The results are shown in experiments 1 and 2 of Table I.

Preparation of (*Z*)- and (*E*)-1-Mesityl-1-phenylpropene. Twenty millimoles of 1-mesityl-1-phenylethene[3] was converted to the corresponding epoxide by treatment with an equivalent amount of *m*-chloroperbenzoic acid in chloroform at 0 °C overnight. The colorless crystalline product was identical with the epoxide obtained by ozonation.[3] The epoxide (18 g) was converted to **1-mesityl-1-phenyl-1-propanol** by treatment with 2 molar equiv of methylmagnesium bromide in anhydrous ether; 150 mL of toluene was then added, the ether was slowly distilled off, and the toluene reaction mixture was refluxed overnight. Workup and purification by distillation gave the crude alcohol as a viscous syrup in 94% yield. The alcohol was dehydrated to a mixture of the *Z* and *E* olefins by treatment with 2 molar equiv of *p*-bromobenzenesulfonyl chloride in pyridine (10 mL/g of the alcohol) at 0 °C for 3 h and overnight at room temperature. The reaction mixture was worked up by the usual procedures. The crude reddish brown viscous liquid product was passed through an alumina column and eluted with acetone, after which it was separated into *Z* and *E* isomers by GLPC, using a 10 ft × $^1/_4$ in. 30% SE 30 (silicon gum rubber) on Chromasorb 10 column at 250 °C. The *Z* isomer (mp 70–71 °C, 53% yield) came off first. Its NMR spectrum showed peaks at δ 7.20 (five benzene ring protons), 6.85 (two mesitylene ring protons), 6.35 (q, one olefinic proton), 2.10 (nine mesitylene methyl protons), and 1.50 (d, three protons of double-bond-attached methyl group). The *E* isomer (29% yield) melted at 40–41 °C and showed identical NMR peaks except for the olefinic proton (δ 5.55) and the protons of the olefinic methyl group (δ 1.80). The chemical shifts for the double-bond proton and the methyl group are the same as reported by Van der Linde and co-workers.[16a]

(17) Reader, A. M.; Bailey, P. S.; White, H. M. *J. Org. Chem.* **1965**, *30*, 784.

Ozonations of (*Z*)- and (*E*)-1-mesityl-1-phenylpropene were carried out with 0.1–1.1-mmol quantities in 5–15 mL of solvent. Major product determinations were made on the 30% SE 30 column at 280 °C, using triphenylmethane as an internal standard and authentic samples of the *Z* epoxide (preparation follows) and mesityl phenyl ketone (Friedel–Crafts reaction between benzoyl chloride and mesitylene; bp 102 °C (0.10 mm), 72% yield.) The results are shown in Table I, experiments 3 and 4.

(*Z*)-1-Mesityl-1-phenylpropene oxide was prepared from the corresponding olefin using *m*-chloroperbenzoic acid in chloroform at 0 °C. It was purified by GLPC as described in the preceding experiment and was shown to be identical with the peroxide obtained by ozonation of the *Z* olefin: mp 93–94 °C; NMR bands at δ 7.25 (five phenyl protons), 6.80 (two mesityl ring protons), 3.35 (m, epoxide ring proton), 2.20 (nine mesityl methyl protons), 1.03 (three protons of the methyl group attached to the epoxide ring).

(*E*)-1-Mesityl-1-phenylpropene oxide was isolated by GLPC from the ozonation reaction mixture of the olefin. Its NMR was essentially identical with that of the *Z* epoxide except for the epoxide ring proton (δ 3.20) and the protons of the methyl group attached to the epoxide ring (δ 1.15). This difference is similar to the difference found with the corresponding olefins regarding the olefinic hydrogen and methyl groups.

Ozonations of 4,4-dimethyl-2-neopentyl-1-pentene (or 1,1-dineopentylethylene, Chemical Samples Co.) were performed with 0.37 mmol of olefin in 15 mL of solvent. Product determinations were made at 100 °C on a 11 ft by $^1/_4$ in. column of 20% XF 1150 cyanosilicone on Chromosorb P (60/80) with *p*-xylene as an internal standard. Product identifications were as previously described.[3] The results are shown in Table I, experiment 5.

4-Neopentyl-2,2,6,6-tetramethyl-3-heptene (or 1,1-dineopentyl-2-*tert*-butylethylene) was synthesized from trineopentylcarbinol[14] by use of thionyl chloride and pyridine.[18] Into a solution of 3.1 g (13 mmol) of trineopentylcarbinol in 5 mL of dry pyridine was added dropwise 2.1 g (18 mmol) of thionyl chloride at 0 °C. The resulting mixture was stirred at 0 °C for 3 h, at room temperature for 1 h, at reflux temperature for 1 h, and, finally, at room temperature for overnight. It was then poured onto crushed ice, acidified with dilute hydrochloric acid, and extracted with ether. The ether extract was washed, dried, and evaporated, and the residue was distilled at 10 mm. The yield of 99% pure (GLPC) olefin boiling at 90–96 °C ranged 50–89%. The material exhibited the same IR and NMR bands previously reported.[14,15]

Ozonations of 1,1-dineopentyl-2-*tert*-butylethylene were carried out with 0.1-mmol quantities in 10–15 mL of solvent at the desired temperature (Table I). Major product determinations were by GLPC at 260 °C, using a 10 ft × $^1/_4$ in. column of 30% SE 30 (silicone gum rubber) on Chromosorb W. Isodurene was used as an internal standard. Authentic samples of dineopentyl ketone[3] and 1,1-dineopentyl-2-*tert*-butylethylene epoxide (see below) were employed in the calibrations. The results are shown in experiment 6, Table I.

1,1-Dineopentyl-2-*tert*-butylethylene epoxide was prepared from the corresponding olefin using *m*-chloroperbenzoic acid in chloroform at 0 °C. The material boiled at 75 °C at 1 mm. The mass spectrum showed major peaks at *m/e* 240 (parent) and 241 (probably protonated epoxide). NMR exhibited singlets at δ 0.97, 1.03, and 1.08 (Me_3C), singlets at δ 1.67 (CH_2 trans to *tert*-butyl) and 2.27 (ring H), and doublets at δ 2.27 and 0.94 (AB, J = 15 Hz, CH_2 cis to *tert*-butyl). At a higher temperature the singlet at δ 2.27 moved downfield relative to the doublet at the same position. Irradiation resulted in decoupling of the doublets at δ 2.27 and 0.94 and establishing the presence of the latter which was somewhat obscured by the singlet at 0.97 ppm. The two AB type doublets result from steric interactions of the *tert*-butyl and neopentyl groups cis to each other causing the methylene protons to be nonequivalent.

Anal. Calcd. for $C_{16}H_{32}O$: C, 79.93; H, 13.42. Found: C, 80.19; H, 13.25.

4-*tert*-Butyl-2,2,6,6-tetramethyl-3-heptene (or 1-neopentyl-1,2-di-*tert*-butylethylene) was prepared from dineopentyl-*tert*-butylcarbinol[16] by the same general procedure just described for the synthesis of 1,1-dineopentyl-2-*tert*-butylethylene from trineopentylcarbinol. The two isomers were separated and identified as previously described.[14,15] Attempts to isomerize the major isomer (87%) to the minor isomer by various standard methods failed. Not enough of the minor isomer was obtained to study. Configurational assignments have not been made.

Ozonation of 1-neopentyl-1,2-di-*tert*-butylethylene (major isomer) was performed by using 1–2.5-mmol quantities in 20 mL of solvent. GLPC analyses were made under the same conditions employed for the products of ozonation of 1,1-dineopentyl-2-*tert*-butylethylene, using authentic samples of the ketone[19] and of the epoxide of the olefin. The latter was prepared by the stereospecific *m*-chloroperbenzoic acid epoxidation of the olefins in 97–99% yield; bp 67–69 °C (1.5 mmHg).

Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36; O, 7.06. Found: C, 79.50; H, 13.18; O, 7.26.

The NMR spectrum showed peaks at δ 1.00, 1.09, and 1.10 (the 27 *tert*-butyl protons), 1.87 (CH_2 group), and 2.42 (one epoxide ring proton).

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Registry No. O_3, 10028-15-6; (*Z*)-1-(1-naphthyl)-1-phenylpropene, 41801-92-7; (*E*)-1-(1-naphthyl)-1-phenylpropene, 41801-93-8; (*Z*)-1-mesityl-1-phenylpropene, 4332-16-5; (*E*)-1-mesityl-1-phenylpropene, 4332-15-4; 4,4-dimethyl-2-neopentyl-1-pentene, 141-70-8; 4-neopentyl-2,2,6,6-tetramethyl-3-heptene, 34235-29-5; 4-*tert*-butyl-2,2,6,6-tetramethyl-3-heptene, 34235-30-8; 4,4-dimethyl-2-neopentyl-1-pentene ozonide, 94089-35-7; 3,3,6,6-tetraneopentyl-1,2,4,5-tetroxane, 94089-36-8; pivaldehyde, 630-19-3; dineopentyl ketone, 4436-99-1; *cis*-1-(1-naphthyl)-1-phenylpropene epoxide, 41801-97-2; *trans*-1-(1-naphthyl)-1-phenylpropene epoxide, 41801-98-3; *cis*-1-mesityl-1-phenylpropene epoxide, 94089-37-9; *trans*-1-mesityl-1-phenylpropene epoxide, 94089-38-0; 4,4-dimethyl-2-neopentyl-1-pentene epoxide, 4737-48-8; 4-neopentyl-2,2,6,6-tetramethyl-3-heptene epoxide, 94089-39-1; 4-*tert*-butyl-2,2,6,6-tetramethyl-3-heptene epoxide, 94089-40-4.

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