Steric Effect of Neopentyl Groups in the Reaction of Olefins with Peracids[1]

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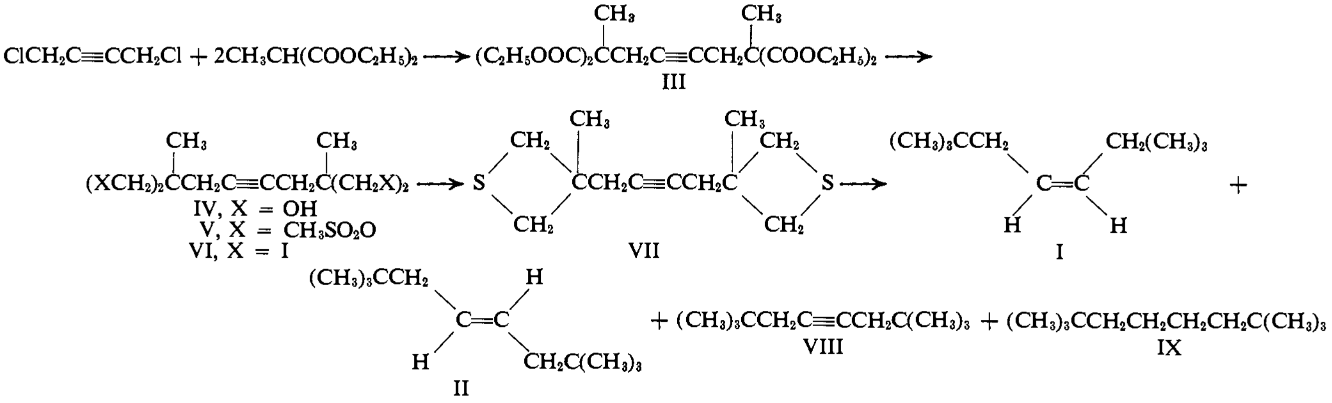
Abstract: The synthesis and reactions of *cis*- and *trans*-1,2-dineopentylethylenes with *m*-chloroperbenzoic acid are described, as are the reactions of 1-pentene, 4-methyl-1-pentene, and neopentylethylene with perbenzoic acid. Comparison of the rates shows that the steric effect of neopentyl groups in these reactions of olefins are less than the effect in reactions involving addition to carbonyl groups.

The objective of the research herein reported was to find out more about steric effects on the reaction of peracids with olefins. In particular, we wished to see how sensitive the rate of epoxidation would be to neopentyl groups attached to the olefinic function. Since one objective was to study *cis*-1,2-dineopentylethylene (I) and *trans*-1,2-dineopentylethylene (II) not only with regard to difference in rate of epoxidation but also to have the differences in heat of hydrogenation determined,[4] the synthesis of these unknown hydrocarbons was effected as is shown in Scheme I.

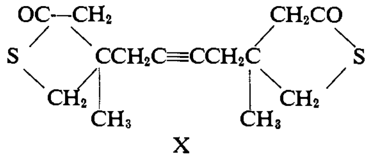
Scheme I



The condensation of 1,4-dichloro-2-butyne[5] with sodio diethyl methylmalonate in ethanol afforded about 70% yields of III, but only tars were obtained when the alkylation was tried with potassium *t*-butoxide in dimethyl sulfoxide. Reduction of III to IV followed by successive conversion to the tetramesylate (V) was carried out as in similar cases.[6] Attempts to convert the tetramesylate (V) to bisthietane (VII) resulted in a mixture of bisthietane (VII) and a compound similar to VII but containing an oxetane ring.[2] The tetraiodide (VI) was converted into bisthietane (VII) in 85% yield.

The desulfurization of VII by reaction with Raney nickel yielded mixtures of I, II, 1,2-dineopentylacetylene (VIII), and dineopentylethane (IX) whose composition varied with catalyst age and other reaction variables (see Experimental Section). The mixtures produced could not be completely separated by distillation on any column at hand. However, small pure samples of each were obtained by preparative gas chromatography and were identified by analysis (except for IX as too little was obtained) and nmr spectroscopy. With the aid of glpc analysis the yields of the four components could be determined in various runs, and thus approximate yields determined. The best yields of I were in the 66–72% region and the best yield of II was 37%.

In one experiment in which VII was treated in boiling acetone with Raney nickel a 15% yield of a pure compound believed to be the bis(γ-thiolactone) of 3,8-bismercaptomethyl-3,8-dimethyl-5-decynedioic acid (X) was obtained. The structure is advanced entirely on the basis of elemental analyses and infrared and nmr spectral data (see Experimental Section). We have no explanation to offer for the formation of X in this reaction.



X

On equilibration of I and II by heating at 195–198° over a rhodium-on-alumina catalyst, the equilibrium

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(2) Holder of a PEO International Peace Scholarship, 1961–1963. The work dealing with the dineopentylethylenes formed part of the Ph.D. thesis of N. Gill presented to the Ohio State University, 1965.

(3) The epoxidation of olefins with perbenzoic acid was taken from the M. S. thesis of D. W. Thomson presented to the Ohio State University, 1964.

(4) Professor R. B. Turner, Rice University, has found that the heat of hydrogenation of I and II are 26.90 ± 0.06 and 26.04 ± 0.15 kcal/mole, respectively. He will report his results in a separate paper.

(5) We thank Antara Chemicals, General Aniline and Film Corp., for a generous gift of this reagent.

(6) M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrad, *J. Am. Chem. Soc.*, **86**, 868 (1964).

ratio of II to I was shown to be 4.8 ± 0.2. This corresponds to a free-energy difference of 1.47 ± 0.05 kcal/mole. The hydrogenation of I ($H = -26.90 \pm 0.06$ kcal/mole)[4] is 0.86 kcal/mole more exothermic than that of II ($H = -26.04 \pm 0.15$ kcal/mole)[4] at room temperature. On the assumption that the enthalpy contents of I and II differ by the same amount at 195° (as would be expected if I and II have similar heat capacities),[7] the entropy of isomerization of I to II is calculated to be 1.3 ± 0.4 eu.[8]

After sufficient amounts of I and II had been purified for the hydrogenation studies,[4] very little remained for determination of the rates of reaction. Hence the rates of epoxidation were determined by a method involving nmr measurement (see Experimental Section). The rate constants for the reactions of the monosubstituted olefins with perbenzoic acid (see below) were determined by conventional means.[9]

Relatively little systematic work with regard to steric factors has been carried out on the measurement of rates of addition of reagents to mono- and polyalkylated olefins. The addition of bromine to olefins in acetic acid at 25° was shown to proceed at the following relative rates:[10] 1-hexene, 1.05; *t*-butylethylene, 0.70; neopentylethylene, 0.10; 2-methyl-1-butene, 30; methyl oleate (as typical of a *cis*-dialkylethylene), 30. Thus the rate of bromination of neopentylethylene is about one-tenth that of 1-hexene. Furthermore, the rate for a *cis*-1,2-di-*n*-alkylethylene is about 30 times that for 1-hexene. 1,1-Dineopentylethylene, although readily epoxidized with perbenzoic acid,[11] is not readily attacked by neutral or alkaline permanganate[11] or by chromic acid,[12] and does not add bromine but reacts with evolution of hydrogen bromide.

Since trifluoroacetic acid adds to 1-hexene only about three times more rapidly than to neopentylethylene,[13] the addition of acidic reagents to acyclic olefins is apparently less affected by steric factors than addition reactions involving carbonyl functions.[14]

The rates of reaction of olefins with peracetic acid in acetic acid have been studied.[15] In these cases, the rates for monosubstituted olefins were about 1/20th those of 1,1- or 1,2-disubstituted olefins, but no highly branched olefins were studied.

We have found that the rates of epoxidation of 1-pentene, 4-methyl-1-pentene, and 4,4-dimethyl-1-pentene (neopentylethylene) with perbenzoic acid[3] in benzene at 30° are 10.3×10^{-4}, 6.8×10^{-4}, and 4.6×10^{-4} l. mole^{-1} sec^{-1}. These results show that the rate of epoxidation is little affected by steric factors as the six-number[16] for these olefins varies as 3:6:9. Interestingly, the rate of epoxidation of monosubstituted olefins seems less affected by steric factors than the rate of bromination, as judged by the fact that neopentylethylene is brominated at one-tenth the rate of 1-hexene.[10] The rates of reaction of *cis*-1,2-dineopentylethylene (I) and *trans*-1,2-dineopentylethylene (II) with *m*-chloroperbenzoic acid in chloroform at 40° are 12.4×10^{-2} and 4.7×10^{-2} l. mole^{-1} sec^{-1}, respectively. The rate ratio, *ca.* 2.6, is slightly higher than those found for oleic and elaidic acids,[17] *ca.* 1.1, and for ricinoleic and ricinelaidic acids,[17] *ca.* 1.6. The rates for I and II are greater than that for epoxidation of *t*-butylethylene, 11.0×10^{-3} l. mole^{-1} sec^{-1}, as is generally the case for 1,2-disubstituted ethylenes compared to monosubstituted ethylenes.

If it is correct to assume that in general addition of acidic reagents to olefins is less affected by steric factors than additions to carbonyl functions,[18] the explanation probably lies in the hypothesis that the rate-determining step in olefin additions involves the addition of the reagent to that carbon of the double bond which is farthest removed from the chain branching in the chain attached to the other carbon of the double bond[19] (or perhaps to both, as in the case of a bromonium ion), whereas in carbonyl additions the rate-determining step involves the formation of an sp^3 carbon atom (*i.e.*, the carbon of the carbonyl group). The steric factor for the latter process would be expected to be greater than that involved in olefin additions, as examination of models reveals.

Experimental Section[20]

Tetraethyl 4-Octyne-2,2,7,7-tetracarboxylate (III). To a solution at room temperature (in a 1-l. three-necked flask equipped with a stirrer) containing the sodium ethoxide prepared from 15.5 g (0.67 g-atom) of sodium and 220 ml of absolute ethanol was added 170.0 g (0.98 mole) of diethyl methylmalonate (one component by glpc analysis). After this solution was warmed to 80° for 3 hr and cooled to 30°, the addition of 40.0 g (0.325 mole) of 1,4-dichloro-2-butyne[5] was made during 2 hr as the reaction was highly exothermic. After stirring for 1.5 hr, the deep yellow mixture was neutralized with acetic acid and the sodium chloride was just dissolved by addition of water. This mixture was worked up as usual[21] to yield 94.0 g (72%) of III, bp 148.0–148.1° (0.5 mm) through a

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[7] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 549 (1958).

[8] We thank Professor Jack Hine for these calculations and consultation during the writing of this manuscript.

[9] B. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[10] P. W. Robertson, J. K. Heyes, and B. E. Swedlund, *ibid.*, 1014 (1952).

[11] P. D. Bartlett, G. L. Fraser, and R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 495 (1941). No rate was determined.

[12] F. C. Whitmore and J. D. Surmatis, *ibid.*, **63**, 2200 (1941).

[13] P. E. Peterson and G. Allen, *ibid.*, **85**, 3608 (1963).

[14] See M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 4.

[15] Perhaps the most exhaustive study is that by D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947); see also D. Swern, *Chem. Rev.*, **45**, 1 (1949); *Org. Reactions*, 7, 378 (1953).

[16] See ref 14, p 243, for a description of the six-number.

[17] M. W. C. Smit, *Rec. Trav. Chim.*, **49**, 686 (1930).

[18] For example, the ratio of the rate of esterification of butanoic acid to 3,3-dimethylbutanoic acid with methanol at 40° is about 21: ref 14, p 205.

[19] For a recent discussion of the mechanism of olefin epoxidation with peracids, see H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966); and K. D. Bingham, G. D. Meakins, and G. H. Whitham, *Chem. Commun.*, 445 (1966).

[20] Melting points were determined in a stirred silicone bath equipped with a calibrated thermometer, but are uncorrected. Most infrared spectra were taken on a Perkin-Elmer Infracord but, in important cases, on a P-E Model 21 double-beam instrument. Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane (TMS) as an internal standard. δ values are given in parts per million downfield from the TMS resonance (0 ppm). Near-infrared spectra were recorded on a Cary 14 spectrometer. Microanalyses marked "a" were by Schwarzkopf Laboratory, Woodside, N. Y., and those, marked "b" by Microanalysis, Wilmington, Del. Vapor phase chromatographic analyses were carried out on a Model 609 (F & M Scientific Corp.) flame ionization instrument equipped with a disk chart integrator. Preparative gas chromatography was done on a Model A-700 Wilkens Instrument Inc., preparative gas chromatograph. We thank the National Science Foundation and a special fund of the Ohio State University for enabling us to purchase these instruments.

[21] The term "worked up as usual" means that an ether–benzene extract of the reaction products was washed with water, dilute acid, and/or base, and saturated sodium chloride solution. All washings were reextracted with ether–benzene and these extracts added to the original solution. The ether–benzene layer was then filtered through a pad of anhydrous magnesium sulfate and the solvent removed by distillation, if advisable through a packed column to avoid loss of volatile constituents (important near the end). The residue was then crystallized or distilled.

glass-helice-packed 30 × 2.5 cm column. The product was pure by glpc analysis on a 2 ft × 0.25 in. 10% SE-30 on 60–80 P column (column A); infrared band at 5.75 μ (1739 cm^{-1}); nmr (CCl_4), δ 1.23 (triplet, 12 H, $J \approx 7$ cps, CH_3 of ethyl group), 1.40 (singlet, 6 H, CH_3C–), 2.63 (singlet, 4 H, $CH_2C{\equiv}C$), and 4.13 ppm (quartet, 8 H, $J \approx 7$ cps, $-COOCH_2-$).

Anal. Calcd for $C_{20}H_{30}O_8$: C, 60.3; H, 7.6. Found^a: C, 60.1; H, 7.4.

2,2,7,7-Tetrakis(hydroxymethyl)-4-octyne (IV). In the best of several runs a solution of 38.4 g of III in 150 ml of dry ether was added during 1.5 hr to a slurry of 28.5 g of lithium aluminum hydride in 500 ml of dry ether. After stirring at reflux for 12 hr, the mixture was treated with 140 ml of 10% sulfuric acid, made neutral with sodium bicarbonate, saturated with sodium chloride, and continuously extracted with ether. The crude product was recrystallized from benzene–ethanol to yield 19.2 g (86%) of IV, mp 150–151°. When tetrahydrofuran was used instead of ether, a 70% yield of IV was obtained: nmr (d_6-DMSO), δ 0.83 (singlet, 6 H, CH_3C–), 2.07 (singlet, 4 H, $CH_2C{\equiv}C$), 3.30 (doublet, 8 H, $J_{CH_2OH} \approx 5$ cps, $-CH_2O-$), and 4.37 ppm (triplet, 4 H, $J_{CH_2OH} \approx 5$ cps, –OH).[22]

Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.6; H, 9.6. Found: C, 62.8; H, 9.6.

2,2,7,7-Tetrakis(hydroxymethyl)-4-octyne Tetramethanesulfonate (V). To a stirred mixture of 29.0 g (0.126 mole) of IV and 350 ml of chloroform at −10° was added 104.0 g (0.908 mole) of methanesulfonyl chloride in one portion. During 2.3 hr was added 110.0 g (0.908 mole) of collidine with the temperature being kept below 5°. After the addition of the collidine a clear, light yellow solution was at hand. The temperature was held at 0° for 2 hr and then allowed to rise to room temperature, whereupon the color deepened and finally after 12 hr was black. The mixture was treated with 250 ml of water and filtered through fiberglass filter paper. The chloroform solution was then treated as usual. The brown solid thus obtained was triturated with a little ether (discarded) and recrystallized from chloroform–methanol (charcoal) to yield 63.0 g (92%) of V: mp 121–122°; nmr ($CDCl_3$), δ 1.15 (CH_3C–), 2.35 ($CH_2C{\equiv}C$), 3.05 (CH_3SO_3–), and 4.15 ppm ($-CH_2O-$), all singlets of relative areas 6:4:12:8, respectively

Anal. Calcd for $C_{16}H_{30}O_{12}S_4$: C, 35.4; H, 5.5; S, 23.6. Found^a: C, 35.6; H, 5.7; S, 23.5.

2,2,7,7-Tetrakis(iodomethyl)-4-octyne (VI). A mixture of 206.0 g of sodium iodide, 62.0 g of V, and 400 ml of Ethyl Cellosolve (monoethyl ether of ethylene glycol) was heated under nitrogen at 110–120° and finally at 125° for 24 hr. After the addition of 200 ml of water, the mixture was worked up as usual (one washing with sodium thiosulfate) to yield a light brown solid. Recrystallization from benzene–methanol yielded 70.0 g (91%) of VI: mp 63–64°, nmr, δ 1.19 (6 H, CH_3C–), 2.39 (4 H, $CH_2C{\equiv}C$), and 3.36 ppm (8 H, $-CH_2I$), all singlets.

Anal. Calcd for $C_{12}H_{18}I_4$: C, 21.5; H, 2.7; I, 75.8. Found^a: C, 21.7; H, 2.6; I, 75.8.

3,3′-(2-Butynylene)bis(3-methylthietane) (VII). In this step, the importance of using pure dry sodium sulfide cannot be overemphasized. We purified sodium sulfide nonahydrate by two crystallizations from ethanol and dried the product to constant weight over P_2O_5. To a stirred solution of 30.0 g of VI in 800 ml of freshly distilled Ethyl Cellosolve at 110° under nitrogen was added a solution of 43.0 g of sodium sulfide in 800 ml of Ethyl Cellosolve during 1 hr. The mixture was held at 125° for 6 hr and then concentrated under reduced pressure to remove most of the solvent. After addition of water and ether, the usual work-up afforded 8.6 g (85%) of VII: bp 129–131° (0.3 mm), shown to be homogeneous by glpc (column A); nmr (CCl_4), δ 1.35 (singlet, 6 H, CH_3C–), 2.41 (singlet, 4 H, $CH_2C{\equiv}C$), 2.83, and 3.05 ppm (AB quartet, 8 H, $J_{AB} \approx 9$ cps, $\delta_A - \delta_B = 13.23$ cps, CH_2S–).[23]

Anal. Calcd for $C_{12}H_{18}S_2$: C, 63.7; H, 7.9; S, 28.3. Found^a: C, 63.6; H, 7.7; S, 28.0.

cis-**1,2-Dineopentylethylene (I).** In the best of several experiments a solution of 8.3 g of VII in 50 ml of pure methanol was added all at once without stirring to a mixture of 165 g of Raney nickel,[24] W-2, and 90 ml of methanol under nitrogen in a three-necked 500-ml flask equipped with a stirrer and a condenser cooled with ice–water. On stirring the contents caused the methanol to reflux. After 30 min the exothermic reaction had subsided and the contents was stirred for 5 hr at room temperature. The mixture was then filtered through an inert cellulose filtering bed (Hypo-flo Supercel) and the nickel washed with 400 ml of pentane. The filtrate and nickel cake were worked up separately.

On addition of 5 ml of water to the filtrate two layers separated. The lower aqueous methanol layer was extracted twice with 100 ml of pentane and the combined pentane solution worked up as usual except that the pentane was slowly distilled through a 30-cm helices-packed column. Distillation of the residue yielded 4.7 g (77%) of a colorless liquid, bp 100–103° (78 mm), which was collected in a Dry Ice cooled receiver. Gas chromatographic analysis on an 8 ft × 0.25 in. 30% Carbowax 20M on 60–80 mesh Chromosorb P column (column B) showed three components in the ratio 8.3:24:1 in order of increasing retention times.

The first two components were separated by preparative gas chromatography on a 20 ft × $^3/_8$ in. 30% Carbowax 20M on 60–80 Chromosorb P column (column C) using on-column injection and programming the A-700 instrument[20] from 100 to 145° (helium flow rate 133 ml/min and sample size, 75 μl). Component A, retention time 21 min, and component B, retention time 24 min, were obtained.

Examination of A on a 100-ft squalane capillary column (colunn D) showed two components in the ratio 1:1.3. Nmr analysis of this mixture showed that the components were 1,2-dineopentylethane (IX) and II in the ratio of 1:1.4 (see below for a separation of IX and II).

Component B proved to be pure I by glpc (column D) and also by mass-spectrographic analysis.[25] The near-infrared spectrum of I exhibited a combination band at 2.140 μ characteristic of *cis* unsaturation.[26] The nmr spectrum (CCl_4) exhibited signals at δ 0.91 ppm (singlet, 18 H, $(CH_3)_3C$–), 1.93 (two quartets of lines of the AB portion, 4 H, $J_{vic} \approx 4.5$ cps, $J_{al} \approx 1.3$ cps, $CH_2C{=}$,[27] and 5.55 ppm (triplet of triplets, 2 H, $J_{vic} \approx 4.5$ cps, $J_{al} \approx 1.3$ cps, CH=).

Anal. Calcd for $C_{12}H_{24}$: C, 85.6; H, 14.4. Found^b: C, 85.8; H, 14.4.

Analysis by glpc of five similar runs showed that I was present in 66–72% yield in the filtrate components.

After Soxhlet extraction (pentane) of the nickel cake and a similar work-up, there was obtained 0.6 g of colorless liquid, bp 102–104° (79 mm), which showed on gas chromatography that components A and B, similar to those obtained in the filtrate (see above), were present in the ratio 1.1:1.0.

trans-**1,2-Dineopentylethylene (II) and 1,2-Dineopentylethane (IX).** On reacting 8.3 g of VII and 181 g of Raney nickel (which had been kept under ethanol for 30 days) in 140 ml of methanol for 16 hr at room temperature (no violent exothermic reaction as described above under I) followed by a work-up similar to that described above, there was obtained 4.5 g (74%) of liquid, bp 99–102° (76–77 mm). Analysis of this on a 20 ft × $^3/_8$ in. 30% tetracyanoethylated pentaerythritol on 60–80 mesh Chromosorb P column (column E)[28] at a column temperature of 100° and helium flow rate of 90 ml/min showed the presence of three components in the ratio 1.0:1.60:1.74 with retention times of 19, 21, and 25 min, respectively. Separation by preparative gas chromatography on column E with 25-μl samples, on column injection as just described, showed that the components were IX, II, and I, respectively.

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(22) As in D_2O the hydroxyl proton resonance disappeared; the presence of exchangeable protons in IV was confirmed.

(23) For calculation of parameters $\delta_A - \delta_B$, δ_A, and δ_B of the AB system, see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1959, p 89; N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 42.

(24) The Raney nickel was prepared as described in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181, except that the reaction with alkali was done at 35 to 40° and the catalyst was washed with 36 5-l. portions of distilled water during 27 hr and allowed to stand under ethanol for 7 days. Just before use the ethanol was removed and the catalyst was washed twice with methanol.

(25) We thank Dr. Maynard Hamming, Continental Oil Co., Ponca City, Okla., for this analysis.

(26) R. T. Holman, S. Ever, and P. R. Edmondson, *Arch. Biochem. Biophys.*, **80**, 72 (1959); R. F. Goddu, *Anal. Chem.*, **29**, 1790 (1957).

(27) The magnitude of the geminal coupling constant (J_{AB}) cannot be determined from the 60-Mc spectrum, where satellites due to A and B protons are barely visible. Allylic couplings were observed only for the four central lines of the AB portion. Vicinal (J_{vic}) and allylic (J_{al}) coupling constants were determined from the spectra recorded at a sweep rate of 0.1 cps sec^{-1}.

(28) We thank Dr. Earl Taft of Wilkens Instrument and Research, Inc. Walnut Creek, Calif., for suggesting this column and for his aid in our behalf.

Pure II had strong infrared absorption at 10.3 μ (970 cm^{-1}; =CH out-of-plane vibration) characteristic of *trans* olefins.[29] The nmr spectrum (CCl_4) showed resonance signals at δ 0.89 (singlet, 18 H, $(CH_3)_3C$–), 1.90 (two quartets of lines of the AB portion, 4 H, $J_{vic} \approx 4.5$ cps, $J_{al} \approx 1.9$ cps, CH=),[27] and 5.43 ppm (triplet of triplets, 2 H, $J_{vic} \approx 4.5$ cps, $J_{al} \approx 1.9$ cps, CH=).

Anal. Calcd for $C_{12}H_{24}$: C, 85.6; H, 14.4. Found[b]: C, 85.6; H, 14.6.

Glpc analysis of the hydrocarbon mixture showed that the proportion of II in the material obtained from the nickel cake was higher (40%) than that in the material obtained from the filtrate (15–17%).

Assignment of structure to the isomeric olefins I and II was made on the basis of nmr[30]. The olefinic proton resonance occurred farther upfield in the *trans* isomer (II) (δ 5.43 ppm) than in the *cis* isomer (I) (δ 5.55 ppm). The observed chemical shift difference of 0.12 ppm between the olefinic protons of the geometrical isomers is in accord with the anticipated long-range shielding effect associated with the diamagnetic anistropy of the carbon–carbon single bonds.[30] The allylic coupling constant for the *cis* isomer (I) ($J_{transoid} \approx 1.3$ cps) is lower, numerically, than that of the *trans* isomer (II) ($J_{cisoid} \approx 1.9$ cps), in agreement with the observation reported[31] that the magnitude of J_{cisoid} is slightly higher than that of $J_{transoid}$. The methyl and methylene protons of the neopentyl groups of the *cis* isomer (I) resonate at a higher frequency, by 1.5[32] and 2 cps,[32] respectively, than those of the *trans* isomer (II). This small paramagnetic shift is probably associated with the steric interaction of the *cis*-oriented neopentyl groups.

Pure IX was a colorless solid, mp 25–26°, which had a very high vapor pressure and was not analyzed for C and H as the nmr spectrum was considered conclusive. The nmr spectrum in CCl_4 showed resonance signals at δ 0.88 (singlet, 18 H, $(CH_3)_3C$–) and 1.20 ppm (singlet, 8 H, –CH_2–); infrared bands at 3.45 (shoulders at 3.40, 3.49, and 3.52), 6.80 (s), 7.20, 7.35 (s), and 8.05 μ (m).

Dineopentylacetylene (VIII). When a mixture of 8.2 g of VII, 148 g of Raney nickel catalyst (which was much less reactive than those used above), and 145 ml of methanol was stirred at room temperature for 4 hr and worked up as described, a product was obtained which was separated by distillation into 1.2 g (20%) of liquid, bp 100–103° at 80 mm, and 4.0 g (50%) of VII. Analysis of the liquid on column E showed that an appreciable amount of a component having a retention time of 40 min was present. By preparative glpc on column E about 12 mg of VIII was isolated. The structure was established only by nmr as insufficient material was available for C and H analysis after the spectrum was taken. The nmr spectrum (CCl_4) showed singlets at δ 0.98 (18 H, $(CH_3)_3C$–) and 2.01 ppm (4 H, $CH_2C{\equiv}C$).

The olefins, 1-pentene and 4-methyl-1-pentene, were commercial samples. The neopentylethylene used was prepared as described.[33] The above olefins were greater than 99% pure by glpc analysis. The rates of reaction with perbenzoic acid in benzene at 30° were determined essentially as described for other cases.[34]

Kinetic Procedure for the Epoxidation of Olefins.[35] To an nmr tube flushed with nitrogen was added 0.20 ml of a 0.50 *M* solution of olefin in $CHCl_3$ (spectral-quality) with a calibrated syringe. The nmr tube was kept in the probe at ~40° for at least 5 min, and the instrument resolution was optimized. To the olefin solution was added 0.20 ml of a 0.50 *M* solution of *m*-chloroperbenzoic acid[36] in $CHCl_3$ and the timer started. Measurements were taken at appropriate time intervals by sweeping through the *t*-butyl region. Kinetic runs followed second-order plots up to 85% of the reaction. After the completion of the epoxidation reaction, the sample was scanned and the nmr spectrum of the epoxide agreed with the expected result in each case.

Equilibration Procedure. The equilibration experiments were done in special all-glass containers. In a typical run 0.80 g of a mixture containing 52.5% I, 27.6% II, and 19.9% IX (by glpc analysis) and 0.40 g of 5% rhodium-on-alumina (dried for 48 hr at 80° under vacuum) were sealed in the apparatus and heated at 195–198° for 20 hr.[37] The contents were cooled to room temperature and the inner tip of the tube was broken with a glass-covered magnet. Distillation of the equilibrated olefinic mixture (carried out in the same apparatus) yielded 0.73 g of a colorless liquid which was collected in a Dry Ice cooled receiver. The equilibrated sample was analyzed twice by glpc on column E. The peaks were symmetrical, and the equilibrium constant was calculated from the ratio of peak areas which were calculated from peak height and width at half-height measurements. The isomerization equilibrium constant ($K_{eq} = 4.8 \pm 0.2$) is an average of three determinations.

Bis(γ-lactone) of 3,8-Bismercaptomethyl-3,8-dimethyl-5-decynedioic Acid. (X). Raney nickel, 72 g, prepared as described,[24] was rinsed by decantation with acetone, then suspended in 100 ml of acetone. After holding at reflux for 1 hr and cooling to room temperature, 60 ml of acetone was removed by decantation. A solution of 3.0 g of VII in 40 ml of acetone was added; the mixture was stirred for 30 min and then held at reflux for 3 hr. After filtration through Hypo-flo Supercel,[38] the nickel was washed with 200 ml of hot pentane. The reaction mixture was then worked up as usual and the pentane removed by careful fractionation. When the volume was about 5 ml, a solid crystallized. This was recrystallized from chloroform to yield 0.50 g (15%) of colorless crystals, mp 105–107°, strong infrared band at 5.90 μ (1695 cm^{-1}). The nmr spectrum ($CDCl_3$) had signals at δ 1.34 (singlet, 6 H, CH_3C–); 2.46 (singlet, 4 H, $CH_2C{\equiv}C$); 2.38, 2.63 (AB quartet, 4 H, $J_{AB} \approx$ 17.5 cps, $CH_2C{=}O$);[23] 3.16, 3.43 (AB quartet, 4 H, $J_{AB} \approx 11.5$ cps, CH_2S–).[23] This experiment was not repeated.

Anal. Calcd for $C_{14}H_{18}S_2O_2$: C, 59.6; H, 6.4; S, 22.7; O, 11.3. Found[b]: C, 59.8; H, 6.4; S, 22.6; O, 11.2.

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[29] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 45.

[30] Reference 23, pp 115–119.

[31] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); D. J. Collins, J. J. Hobbs, and S. Sternhell, *Australian J. Chem.*, **16**, 1030 (1963), and references cited therein.

[32] These values were confirmed by scanning the spectrum four to five times on both samples of identical concentration.

[33] F. C. Whitmore and A. H. Homeyer, *J. Am. Chem. Soc.*, **55**, 4555 (1933).

[34] Details may be found in the M. S. thesis of D. W. Thomson.[3]

[35] I, II, and *t*-butylethylene were allowed to react with *m*-chloroperbenzoic acid in $CHCl_3$ at 40°. Ultrapure samples of I and II were obtained by preparative glpc. The purity of I, II, and *t*-butylethylene were checked by glpc and nmr.

[36] The *m*-chloroperbenzoic acid used in the rate measurements was standardized with $Na_2S_2O_3$.

[37] Equilibrium was reached in 20 hr. The ratio of II to I did not change on heating for 70 hr.

[38] Hypo-flo Supercel is an inert cellulose filter aid.