Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.8; H, 9.8.

10β-Methyl-7α-isopropyl-9β-hydroxy-2-decalone (10).—A solution of 7.76 g of ketol 9 in 70 ml of absolute ethanol was hydrogenated over 0.5 g of platinum oxide at 1 atm. Approximately 1 hr was required for the theoretical uptake of hydrogen. The catalyst was removed by filtration and the solvent was removed from the filtrate at reduced pressure. Distillation of the residue gave 7.03 g (90%) of ketol 10 as a colorless oil, bp 117° (0.2 mm) to 114° (0.1 mm), and 0.5 g (6%), bp 100–115° (bath temperature) at 0.05 mm (evaporative distillation of the residues). The material crystallized upon overnight refrigeration and was recrystallized from hexane at −78°. The material which could be recrystallized in 90% yield exhibited mp 52–56°; $\lambda_{max}^{CCl_4}$ 2.89 (OH), 5.85 (ketone CO), 7.80, 9.61, 9.94 μ; $\delta_{TMS}^{CCl_4}$ = 2.85 (O*H*), 1.19 (C*H*$_3$), 0.87 ppm (CHC*H*$_3$; doublet, *J* = 5 cps). The distilled material was found suitable for subsequent reactions. The analytical sample, mp 58–59°, was obtained by recrystallization from a small volume of hexane at −10°.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.0; H, 10.8.

10β-Methyl-7α-isopropenyl-1(9)-octal-2-one (11).—A mixture of 500 mg of 10β-methyl-7α-isopropenyl-9β-hydroxy-2-decalone (9) and 5 ml of 10% aqueous potassium hydroxide solution was stirred at reflux under nitrogen for 8 hr[12b] and cooled; the product was isolated with ether.[12c] The crude octalone was distilled giving 436 mg (96%) of product: bp 85–95° (bath temperature) at 0.05 mm; λ_{max}^{film} 3.24 (vinyl H), 5.99 (ketone CO), 6.19 (C=C), 8.01, 11.19 μ. The analytical sample, λ_{max}^{EtOH} 245 mμ (ε 12,700), mp 35°, was obtained by recrystallization from hexane at −20°.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.5; H, 10.0.

The dinitrophenylhydrazone derivative, mp 133–134°, was prepared in 73% yield.

Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29; N, 14.57. Found: C, 62.8; H, 6.4; N, 14.4.

10β-Methyl-7α-isopropyl-1(9)-octal-2-one (12).—A mixture of 7.0 g (0.031 mole) of ketol 10 and 70 ml of 10% aqueous oxalic acid was heated at reflux under nitrogen[12b] for 5 hr and cooled; the product was isolated with ether.[12c] Distillation of the residue afforded 6.05 g (94%) of octalone 12: bp 83–84° (0.07 mm); λ_{max}^{film} 6.00 (ketone CO), 6.20 (C=C), 7.92, 10.18, 11.65 μ; $\delta_{max}^{CCl_4}$ = 5.63 (C=CH), 1.28 (CH$_3$), 0.90 ppm (CHC*H*$_3$; doublet, *J* = 5 cps); λ_{max}^{EtOH} 242 mμ (ε 13,800) [lit.[6] 239 mμ (ε 16,100)]; [α]D +48° (*c* 0.23, dioxane)[20] {lit.[6] [α]D +65° (*c* 1.44, methanol)}. The 2,4-dinitrophenylhydrazone, mp 149–150°, was recrystallized from methanol-ethyl acetate. We did not observe the mp (195–197°) reported for this derivative.[6]

Anal. Calcd for $C_{20}H_{26}N_4O_4$: C, 62.16; H, 6.78; N, 14.50. Found: C, 62.4; H, 6.9; N, 14.65.

Vpc of octalone 12 on a 10-ft, 20% Carbowax 20M on Gaspack F column at 195° indicated that the material was over 90% pure. The infrared spectrum was superimposable with that of the material prepared by Djerassi, *et al.*[6,21]

Attempted 1,4 Addition of Methylmagnesium Iodide to Octalones 11 and 12.—The Grignard reagent, prepared from 1.08 g (50 mg-atoms) of magnesium turnings and 7 g of methyl iodide in 40 ml of anhydrous ether, was cooled to −10°, and a solution of 3.09 g (15 mmoles) of octalone 12 and 0.52 g (3 mmoles) of cupric acetate monohydrate in 56 ml of anhydrous tetrahydrofuran was added over 0.5 hr.[12b] The dark reaction mixture was allowed to warm to room temperature over 2 hr and was refluxed for 15 min. The cooled mixture was carefully treated with excess aqueous ammonium chloride and extracted thoroughly with ether. The pale green aqueous phase became deep blue upon shaking in air. The organic layer was washed with aqueous sodium thiosulfate, brine, and dried over anhydrous sodium sulfate. Removal of the solvent at reduced pressure afforded 3.19 g (96%) of yellow-green oil: λ_{max}^{film} 3.00 μ (OH); $\delta_{TMS}^{CCl_4}$ = 5.20 (C=CH), 3.09–3.43 (OH), 1.20 (C-10 CH$_3$), 1.11 (C-2 CH$_3$), 0.88 ppm (CHC*H*$_3$; doublet, *J* = 6 cps). The spectra indicated only a trace (5%) of saturated ketone carbonyl (5.85 μ). Evaporative distillation gave 2.81 g (85%) of 2,10β-dimethyl-7α-isopropyl-1(9)-octal-2-ol (16): bp 75–85° (bath temperature) at 0.25 mm; λ_{max}^{film} 3.00 (OH), 6.02 (C=C), 7.23, 7.32, 8.87, 9.14, 9.60, 9.95, and 10.61 μ. Chromatography of 1.0 g of distilled material on 100 ml of alumina (Fisher) afforded 0.75 g of alcohol mixture 16 which was distilled twice affording the analytical sample.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.9; H, 11.7.

The experiment described above was repeated using 3.06 g of isopropenyloctalone 11 and 3.31 g of oil was obtained. The infrared spectrum of this substance showed a strong band at 3 μ (OH) but was devoid of bands in the 5.8-μ region expected for a cyclohexanone carbonyl and was therefore not investigated further.

Acknowledgment.—We wish to thank the Public Health Service for a Research Grant (AI-04965) and a Predoctoral Fellowship (1-Fl-GM-29,696 to H. R.) in support of this work.

(21) We are indebted to Professor Djerassi for a copy of his spectrum.

Oxygenation of 1,10-Dimethyl-1(9)-octalin

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1,10-Dimethyl-1(9)-octalin (4), prepared from 1,10-dimethyl-1(9)-octal-2-one *via* the alcohol 2 and acetate 3, was subjected to chemically and photochemically excited oxygen. The principal product, 1-methylene-*trans*-10-methyl-9-decalyl hydroperoxide (5), was characterized through its hydrogenation product, *cis*-1,10-dimethyl-*trans*-9-decalol (13), independently synthesized from 10-methyl-*trans*-1(9)-oxidodecalin (19) and methylmagnesium bromide. The oxygenation products were converted to a mixture of allylic alcohols by treatment with lithium aluminum hydride. Gas chromatography and nmr analysis indicated a similar mixture of products from both photosensitized and chemical oxygenation of olefin 4.

In recent years, several naturally occurring sesquiterpenes possessing oxygen functions at bridgehead positions have been identified (*e.g.*, telekin,[1] β-agarofuran[2]). These compounds pose some intriguing synthetic problems whose solution we felt might be available, in part, through the selective photooxygenation[3] of appropriately substituted 1,10-dimethyl-1(9)-octalins. That such selectivity might indeed be possible first became evident during studies which culminated in the total synthesis of racemic alantolactone.[4] In the course of that work we found that unsaturated lactone I afforded allylic hydroperoxide II as the predominant photo-

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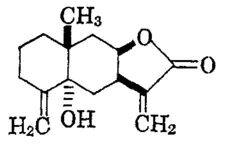
(1) V. Benešová, V. Herout, and W. Klyne, *Collection Czech. Chem. Commun.*, **27**, 498 (1962); V. Benešová, V. Herout, and F. Šorm, *ibid.*, **26**, 1350 (1961).

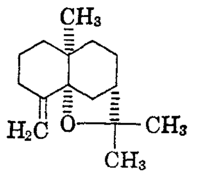
(2) M. L. Maheshwari, T. C. Jain, R. B. Bates, and S. C. Bhattacharyya, *Tetrahedron*, **19**, 1079 (1963).

(3) G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

(4) J. A. Marshall and N. Cohen, *J. Am. Chem. Soc.*, **87**, 2773 (1965).

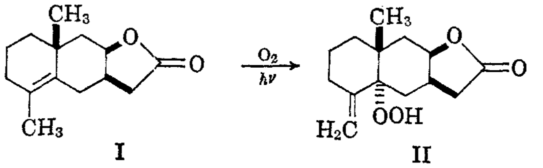


telekin



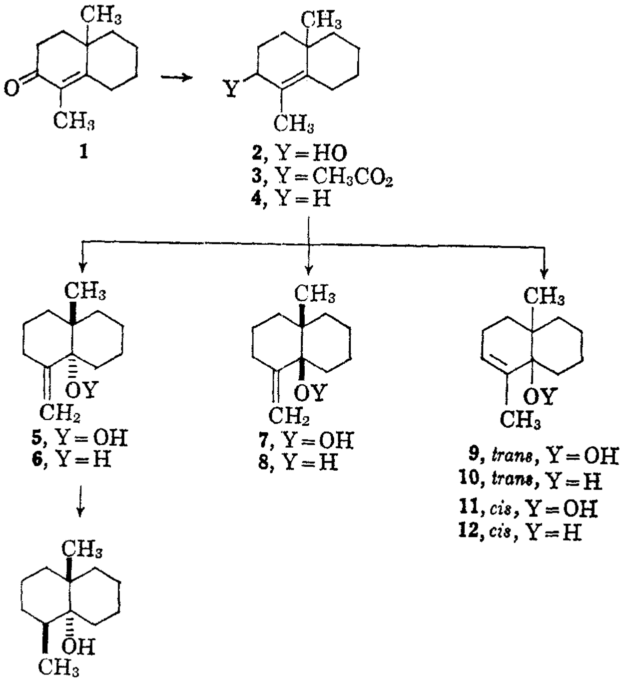
β-agarofuran

oxygenation product. In order to appraise the potential utility of related transformations and gain additional information concerning their stereochemical and positional selectivity, we undertook the study described in this report.



We chose 1,10-dimethyl-1(9)-octalin (**4**) as the substrate because of its close relationship to the systems of interest, its ready availability, and the ease of identifying the expected reaction products. Scheme I outlines the pertinent reactions.

SCHEME I

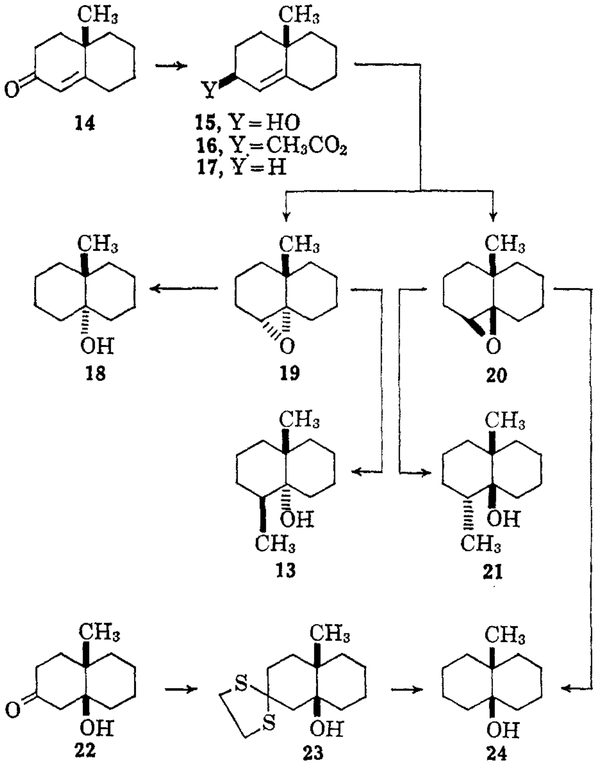


The chosen olefin was prepared from 1,10-dimethyl-1(9)-octal-2-one (**1**), the condensation product of 2-methylcyclohexanone and ethyl vinyl ketone.[5] Reduction with lithium aluminum hydride gave the allylic alcohol **2** as a mixture of stereoisomers which was directly converted to the acetate derivative **3**. Hydrogenolysis of allylic acetate **3** occurred readily upon treatment with lithium in ethylamine[6] and octalin **4** was thereby secured in 67% over-all yield based on octalone **1**. The material obtained in this manner contained a small quantity of an isomeric olefin (most likely 1,10-dimethyl-1-octalin) as evidenced by absorption between 5.2 and 5.4 ppm in the nmr spectrum. A gas chromatogram indicated less than 6% contamination and the material was accordingly used for subsequent experiments without additional purification.

Octalin **4** readily underwent photooxygenation with hematoporphyrin as the sensitizer according to the procedure of Nickon and Bagli.[7] Oxygen uptake was remarkably rapid and within 3.5 hr the reaction was complete. The product displayed strong infrared absorption bands at 6.1 and 11.2 μ characteristic of a C=CH_2 grouping. Therefore, a primary allylic hydrogen appears to have been preferentially abstracted from octalin **4**, a result which parallels our previous finding with olefinic lactone I. The spectrum contained no bands at 5.9–6.0 μ to indicate the formation of a conjugated ketone (*e.g.*, **1**).[8]

Chromatography of the hydroperoxide mixture yielded, in the early fractions, a crystalline isomer (**5**) isolated in 20–30% yield. This material, on reduction with lithium aluminum hydride, gave allylic alcohol **6** which was homogeneous according to gas chromatography. The exocyclic methylene grouping was easily identified through its characteristic infrared and nmr peaks. Catalytic hydrogenation of either the crystalline hydroperoxide **5** or the corresponding allylic alcohol **6** afforded *cis*-1,10-dimethyl-*trans*-9-decalol (**13**). This substance was identified through comparison with an authentic sample synthesized by the route outlined in Scheme II. We defer a detailed account of this sequence to a subsequent part of this discussion.

SCHEME II



Later chromatographic fractions yielded an oily material consisting of the *cis*- and *trans*-decalyl hydroperoxides **5** and **7**. This mixture was cleanly reduced

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[5] F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952).

[6] *Cf.* A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *ibid.*, 1969 (1957).

[7] A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961).

[8] *Cf.* A. Nickon and W. L. Mendelson, *Can. J. Chem.*, **43**, 1419 (1965).

to the corresponding alcohols **6** and **8** upon treatment with lithium aluminum hydride. The exocyclic methylene protons of the resulting *cis*- and *trans*-decalol isomers appeared at differing chemical shifts, and the composition of this mixture could therefore be determined from the integrated nmr spectrum. The gas chromatogram likewise indicated two decalol components in a ratio which agreed with that obtained from the nmr analysis. We were thus able to identify positively and estimate quantitatively 1-methylene-*cis*-10-methyl-9-decalol (**8**) and its epimer **6** by a method which accurately related these substances to their hydroperoxide progenitors **7** and **5**.

Reduction of the crude photooxygenation reaction product with lithium aluminum hydride gave a mixture of unsaturated alcohols in 82% yield. This mixture was recovered virtually unchanged after treatment with manganese dioxide in chloroform.[9] Therefore, only minor amounts of primary or secondary allylic alcohols could be present. In addition to the characteristic peaks due to the exocyclic methylene protons of decalols **6** and **8**, the nmr spectrum of the alcohol mixture displayed two broad peaks at 5.7–5.5 and 5.4–5.2 ppm which seem best accommodated by the olefinic protons of octalols **10** and **12**. Evaluation of the integration trace led to an estimate for the composition of this mixture as 45% **6**, 25% **8**, 20% **10**,[10] and 10% **12**. Since the crystalline hydroperoxide **5** gave the corresponding alcohol **6** in high yield, even after prolonged exposure to lithium aluminum hydride, we surmise that side reactions, such as hydrogenolysis, do not occur under the reducing conditions.

The gas chromatogram of the alcohol mixture showed peaks due to *trans*- (45%) and *cis*- (22%) decalols **6** and **8** along with a third peak (28% of the total mixture) of comparable retention time due to two components (indicated by peak width), most likely **10** and **12**. Unfortunately, these last two materials could not be separated sufficiently to allow an estimate of each. Therefore, we must depend upon the nmr integral for evaluation of the formation of hydroperoxides **9** and **11**. The remarkably close agreement between the nmr and gas chromatographic analyses of the *trans*- and *cis*-decalols **6** and **8** tends to justify this application of the former method to **10** and **12**.

In order to ascertain the stereochemistry of hydroperoxide **5**, the major oxygenation product, we undertook an unequivocal synthesis of its hydrogenation product, decalol **13**. Scheme II outlines the transformations related to this project. 10-Methyl-1(9)-octal-2-one (**14**) yielded 10-methyl-1(9)-octalin (**17**) *via* the corresponding alcohol **15** and acetate **16** along the lines described earlier for the conversion of octalone **1** to octalin **4**. Oxidation of octalin **17** with *m*-chloroperoxybenzoic acid gave a mixture of oxiranes **19** and **20**. Although gas chromatography failed to separate the constituents of this mixture, we were able to gauge its composition (60% **19** and 40% **20**) by evaluating the relative areas of nmr peaks due to the respective angular methyl groups of **19** and **20**. Our initial preference for the α-oxide **19** as the major component was based on the expectation that the angular methyl group of octalin **17** would hinder the peroxy acid in its approach to the double bond. The correctness of this assumption was demonstrated as follows.

Reduction of the oxide mixture with lithium aluminum hydride gave two decalols (**18** and **24**) whose structures were confirmed by the nmr spectrum which lacked absorption between 4 and 5 ppm (CHOH) and showed peaks at 1.02 and 0.96 ppm due to the angular methyl group of each component. The ratio obtained from the integrated spectrum (60:40) agreed with that secured by gas chromatography (57:43). The minor component was identified as *cis*-10-methyl-9-decalol (**24**) by comparison with an authentic sample synthesized *via* desulfurization of the thioketal **23** derived from the known ketol, *cis*-10-methyl-9-hydroxy-2-decalone (**22**).[11] Therefore, the major decalol isomer must be *trans*-10-methyl-9-decalol (**18**) and the corresponding oxirane **19** must likewise predominate in the mixture derived from octalin **17**.

Oxiranes **19** and **20**, upon prolonged exposure to methylmagnesium bromide in refluxing tetrahydrofuran, yielded a mixture of 1,10-dimethyl-9-decalols **13** and **21**, along with unchanged starting material. In order to analyze this mixture we treated a portion of the distilled material (70% yield) with lithium aluminum hydride and subjected the resulting 10-methyl- and 1,10-dimethyl-9-decalols to gas chromatography. The components were identified as **18** (0.4%), **24** (8.8%), **21** (17.8%), and **13** (73%) in the order of their elution. The last assignment can be made with certainty since this substance represents over 50% of the starting oxirane mixture and must therefore originate from the predominant isomer **19**. Interestingly, this oxirane appears more vulnerable to cleavage by methylmagnesium bromide than the *cis* isomer **20**.

The dimethyl-*trans*-decalol **13**, purified by column elution chromatography, and the material obtained *via* hydrogenation of the crystalline hydroperoxide **5** (or the corresponding allylic alcohol **6**) gave identical infrared and nmr spectra.

With the stereochemistry of our photooxygenation products satisfactorily established and a method at hand for determining the relative amount of each, we next investigated the oxygenation of octalin **4** using chemically generated oxygen ($NaOCl-H_2O_2$). The procedure of Foote and Wexler[12] yielded a mixture of allylic hydroperoxides in 20% yield. Lithium aluminum hydride reduced this mixture to the corresponding allylic alcohols which were formed in nearly the same ratio (36% **6**, 18% **8**, and 34% **10** and **12**) as was previously obtained *via* the photochemical process (Table I). This finding lends support to the proposal that singlet-state oxygen intervenes in photooxygenation reactions.[13] The low yield and somewhat greater preference of this reaction to give products

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[9] *Cf.* P. J. Neustaedter in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, pp 104–110.

[10] We base our assignment of **10** as the major octalol stereoisomer on the established preference for steroidal olefins to undergo oxygenation on the α face. *E.g.*, A. Nickon and W. L. Mendelson, *J. Org. Chem.*, **30**, 2087 (1965), and references cited therein. Our assumption regarding the gross structure of **10** and **12** is supported by the finding that upon catalytic hydrogenation these materials afford four isomeric 1,10-dimethyl-9-decalols. Three of these isomers were independently synthesized and related to the hydrogenation products through spectroscopic and gas chromatographic comparison.

[11] J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964).

[12] C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879 (1964).

[13] C. S. Foote and S. Wexler, *ibid.*, **86**, 3880 (1964); E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

TABLE I

OXYGENATION OF 1,10-DIMETHYL-1(9)-OCTALIN

	Product composition, %^{a}					
	trans					
	Primary H	*cis*		Secondary H		
Method	**5**	**7**	**11**	**9**	**2**	Yield, %^{a}
Photochemical	45^b	22^b	9^c	19^c	4	82
Chemical	36^b	18^b	34^b		11	20

^{a} Based on the corresponding alcohol mixture after distillation. ^{b} Obtained from the gas chromatogram. ^{c} The total percentage is based on the gas chromatogram and the relative percentage is derived from the nmr spectrum.

derived from abstraction of secondary allylic hydrogens rendered the chemical oxygenation less interesting to us from a synthetic viewpoint. We therefore did not attempt to determine the ratio of **11** to **9**.

Table I summarizes the oxygenation experiments conducted with 1,10-dimethyl-1(9)-octalin (**4**). We consider as noteworthy two points which emerge from this study. First, abstraction of a primary allylic hydrogen atom leading to the exocyclic olefins **5** and **7** constitutes the principal reaction pathway. Investigations on steroidal olefins by Nickon and his coworkers[7,8,10,14] have clearly demonstrated that allylic hydrogens must be unhindered and possess a bond which is perpendicular to the olefinic plane in order to participate in the oxygenation reaction. With octalin **4**, the quasi-axial hydrogen at C-2 and one of the C-1 methyl hydrogens meet this requirement; the axial hydrogen at C-8 is essentially excluded because of steric hindrance by the C-10 methyl group. Conformational changes would alter the stereoelectronic availability of the allylic hydrogens and allow participation by the quasi-equatorial C-2 hydrogen through a boat conformation of the cyclohexane ring.[8] The participating methyl hydrogen can attain the required perpendicular orientation with the olefinic bond through a relatively free rotation of the methyl group. In fact, Dreiding models show that a more favorable alignment can be achieved between a methyl hydrogen and the double bond than between the C-2 quasi-axial hydrogen and the double bond (assuming the optimum cyclohexene conformation). This latter point could explain the observed preference for exocyclic olefinic products in the present study.[15a] Other workers have noted a similar moderate to high preference for abstraction of methyl hydrogens by photochemically excited oxygen.[15b-d] In at least one case[15b] steric factors may govern the reaction course.

The second point of interest in the present study concerns the formation of *trans*- and *cis*-fused hydronaphthalene oxygenation products. Although the ratio 64:31 for the *trans*:*cis* preference (Table I) must be considered approximate because of the uncertainty in measuring **9** and **11**, the ratio 45:22 accurately reflects the stereoselectivity of pathways leading to the exocyclic olefinic products **5** and **7** (Table I). These figures show that the angular methyl group of octalin **4** exerts less stereochemical control over the oxygenation reaction than the analogous angular methyl group of its steroidal counterpart, 4-cholestene, where *trans* products (α attack) override *cis* products (β attack) by a factor of 3 or 4. The data presented in Table I support the contention[8] that steric interactions with the developing C–O bond more effectively control the oxygenation reaction than interactions with the allylic hydrogen atoms. Were this latter factor product determining, the ratios **5**:**7** and **9**:**11** would differ because the allylic hydrogens, which must be abstracted from olefin **4** to give these products, have differing steric environments. On the other hand, the double bond (C-9) offers the exact same environment, insofar as the process leading to **5** and **9** (α attack) and likewise **7** and **11** (β attack) is concerned and therefore comparable ratios of *trans* to *cis* products would result if the developing C–O bond were product determining. The observed ratios (**5**:**7** = 2.0 and **9**:**11** = 2.1) agree with the latter premise and therefore support this point.[8]

Experimental Section[16]

Melting points were determined on a Fisher-Johns hot stage. Nmr spectra were obtained with a Varian A-60 spectrometer. A Beckman IR-5 spectrophotometer was used for infrared spectra. Vpc analyses were performed on an F & M Model 720 instrument employing helium as the carrier gas. Retention times are reported in minutes from the time of injection. The method of J. C. Bartlet and D. M. Smith [*Can. J. Chem.*, **38**, 2057 (1960)] was used to evaluate peak areas. Combustion analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

1,10-Dimethyl-1(9)-octal-2-one (**1**).—The procedure of Marshall and Fanta[11] was followed. A solution containing 3.7 ml of 3 *M* ethanolic sodium ethoxide in 35 g of 2-methylcyclohexanone maintained at −10° was efficiently stirred under a nitrogen atmosphere[16a] while 25.6 g of ethyl vinyl ketone in 36 g of 2-methylcyclohexanone was added over 6 hr. After an additional 6 hr at −10°, the mixture was treated with saturated brine and the product was isolated with ether[16b] and distilled, affording 44.3 g of 2-methylcyclohexanone, bp 56° (14 mm), and 39.1 g of a mixture of ketol and octalone **1**: bp 108–118° (0.25 mm); $\lambda_{\max}^{\text{film}}$ 2.86 (OH), 5.84 (CO), 5.99 (conjugated CO), 6.19 μ (C=C).

The above mixture was efficiently stirred with 300 ml of 10% aqueous potassium hydroxide at reflux for 8 hr.[16a] The product was isolated with ether[16b] and distilled, affording 31.6 g (58%) of octalone **1**: bp 73–74° (0.15 mm); $n^{25}\text{D}$ 1.5252 (lit.[5] $n^{20}\text{D}$ 1.5260); $\lambda_{\max}^{\text{film}}$ 5.99 (conjugated CO), 6.19 μ (C=C). The gas chromatogram[17] showed a single peak at t_R (retention time) 12.9 min.

1,10-Dimethyl-1(9)-octal-3-yl Acetate (**3**).—To a stirred solution containing 6.8 g of lithium aluminum hydride in 450 ml of anhydrous ether was added 31.5 g of octalone **1** in 50 ml of ether over a 20-min period. The mixture was allowed to stir for 4 hr, then carefully treated with 13.6 ml of water and 10.9 ml of 10% aqueous sodium hydroxide. Stirring was maintained for an additional 4 hr, the granulated salts were filtered, and the ether was removed under reduced pressure, affording 31.4 g (98%) of crude octalol **2**.

This alcohol was dissolved in 180 ml of dry pyridine, 50 ml of acetic anhydride was added, and the solution was allowed to stand under nitrogen[16a] at room temperature for 20.5 hr. The reaction mixture was poured into 1 l. of saturated aqueous sodium chloride and thoroughly extracted with ether. The ether extracts were successively washed with water, 2% aqueous sulfuric acid, and saturated aqueous sodium chloride. Distil-

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[14] A. Nickon, N. Schwartz, J. B. DiGiorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965).

[15] (a) We are grateful to a referee for suggesting this possibility. (b) E. Klein and W. Rojahn, *Tetrahedron*, **21**, 2173 (1965); (c) G. O. Schneck, S. Schroeter, and G. Ohloff, *Chem. Ind.* (London), 459 (1962); (d) G. O. Schenck, H. Eggert, and W. Denk, *Ann.*, **584**, 177 (1953).

[16] (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere. (b) The isolation procedure consisted of thorough extraction and back-extraction with the specified solvent, washing the extracts with saturated brine, and drying over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts on a steam bath under reduced pressure.

[17] A 13 ft × 0.25 in. column containing 16% Carbowax 20-M on 60–80 mesh Diatoport S was employed at 210° with a helium flow rate of 90 cc/min.

lation of the solution after drying over magnesium sulfate afforded 37.2 g (94%) of acetate **3**: bp 74–76° (1.0 mm); $n^{25}\text{D}$ 1.4950; $\lambda_{\max}^{\text{film}}$ 5.75 (ester CO), 8.03, 9.81 μ.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.94. Found: C, 75.6; H, 9.9.

1,10-Dimethyl-1(9)-octalin (4).—A 30.1-g sample of acetate **3** was dissolved in 500 ml of ethylamine and treated with 5.6 g of lithium wire according to the procedure of Hallsworth, Henbest, and Wrigley.[6] A deep blue color developed after 50 min and the solution was allowed to stir for an additional 15 min. Solid ammonium chloride was cautiously added to neutralize the lithium salts and decompose the excess metal. The reaction mixture was poured into 1 l. of saturated aqueous sodium chloride and thoroughly extracted with ether. The combined organic extracts were successively washed with water, 2% aqueous sulfuric acid, and saturated sodium chloride solution, and dried over magnesium sulfate. Distillation afforded 16.2 g (73%) of octalin **4**: bp 100–101° (15 mm); $n^{25}\text{D}$ 1.4996; $\lambda_{\max}^{\text{film}}$ 8.72, 10.17 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 1.04 (C-10 methyl), 1.59 (C-1 methyl), and a trace of vinyl hydrogen absorption at 5.33 ppm.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 88.0; H, 12.4.

The gas chromatogram[18] gave peaks at 9.7 (1.1%), 10.9 (94.4%), and 12.8 min (4.5%).

Photooxygenation of Octalin 4. A. Isolation of 1-Methylene-*trans*-10-methyl-9-decalyl Hydroperoxide (5).—The procedure of Nickon and Bagli[7] was followed. A 30-mm Pyrex tube surrounded by three 15-w fluorescent lamps placed approximately 1 cm from its walls was charged with a solution of 2.02 g of octalin **4** and 88 mg of hematoporphyrin in 200 ml of anhydrous pyridine. Oxygen was admitted through a gas dispersion tube and the mixture was irradiated during 3.5 hr. The solution was diluted with ether, warmed briefly with decolorizing carbon, and filtered. Removal of solvent under reduced pressure afforded 2.35 g of crude hydroperoxide, which was immediately chromatographed on 200 ml of Florisil. The early 2% ether–hexane fractions afforded 0.47 g (19.5%) of white crystalline hydroperoxide: mp 72–75°; $\lambda_{\max}^{\text{KBr}}$ 3.02 (OOH), 3.25, 6.06 and 11.15 ($C{=}CH_2$), 8.55, 11.38, 11.67 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 5.05 ($H{-}C{=}C$, triplet, J = 2 cps), 4.78 ($HC{=}C$, triplet, J = 1.5 cps), 0.95 ppm (C-10 CH_3).

Sublimation at 45° (0.07 mm) afforded the analytical sample, mp 76–77°.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.4, H, 10.2.

The later 2% ether–hexane fractions afforded an additional 0.45 g (18.5%) of an oil which slowly crystallized on standing. This material was shown to be a mixture of *trans*- and *cis*-decalyl hydroperoxides **5** and **7** (2:1) by gas chromatography of its reduction products.

The fractions eluted with ether (0.93 g) showed a strong band at 5.85 μ (CO) in the infrared spectrum. This band was not present in the spectrum of the crude product before chromatography and must therefore arise from a decomposition product of the hydroperoxides which is formed on the chromatographic absorbent. The cleavage of allylic hydroperoxides is well documented[3] and this finding is therefore not surprising. However, the facility of this side reaction in the present case prevented our realization of optimum yields of the hydroperoxides.

B. Reduction of the Crude Hydroperoxide Mixture with Lithium Aluminum Hydride.—The previously outlined photooxygenation procedure was followed using 2.01 g of octalin **4**. The crude hydroperoxide mixture (2.48 g) was immediately dissolved in 20 ml of anhydrous ether and added to a stirred solution containing 1.87 g of lithium aluminum hydride in 80 ml of anhydrous ether. The solution was stirred for 5 hr, carefully treated with 3.7 ml of water and 3.0 ml of 10% aqueous sodium hydroxide, and stirred overnight. Filtration and removal of solvent afforded 1.80 g (82%) of oil, bp 65–72° (bath temperature) at 0.1 mm. The nmr spectrum displayed peaks at 5.7–5.55, 5.4–5.2, 4.9, 4.7, and 4.6 ppm due to the various olefinic protons. The integral suggested 45% **6**, 25% **8**, 20% **10**, and 10% **12**.

The gas chromatogram[19] gave peaks at 32.2 (**8**, 22.2%), 34.4 (**10** and **12**, 28.4%), 39.3 (**6**, 45.4%), and 54.6 min (**2**, 4.0%). Peak enhancement with a 65:35 mixture of **6** and **8** led to the assignment of the first and third peaks. The last peak was similarly identified as alcohol **2**. A 0.36-g sample of this mixture was dissolved in 50 ml of chloroform, 2.0 g of activated manganese dioxide[20] was added, and the mixture was stirred at room temperature for 6 hr. The solution was filtered and distilled affording 0.30 g, bp 65–72° (bath temperature) at 0.1 mm. The infrared spectrum showed slight carbonyl absorption at 6.00 μ indicating the formation of a conjugated ketone. The peak due to allylic alcohol **2** was replaced by a new peak due to octalone **1** in the gas chromatogram of the distilled mixture, which was otherwise identical with that of the starting material.

The stability of decalols **6** and **8** to the reduction conditions was tested as follows. To a stirred solution containing 0.3 g of lithium aluminum hydride in 20 ml of anhydrous 1,2-dimethoxyethane was added 113 mg of a 65:35 mixture of decalols **6** and **8**. The solution was heated at reflux for 15 hr, cooled, diluted with 30 ml of ether, and carefully treated with 0.60 ml of water and 0.54 ml of 10% aqueous sodium hydroxide. The solution was stirred for an additional 3 hr, filtered, and distilled, affording 103 mg of material whose infrared spectrum was superimposable upon that of the starting material. The gas chromatogram was likewise unchanged.

Chemical Oxygenation of 4 Followed by Reduction Using Lithium Aluminum Hydride.—The Foote and Wexler[12] method was employed with slight procedural modifications. A 595-mg sample of octalin **4** in 20 ml of ethanol was treated with 1.55 ml of 30% hydrogen peroxide. The solution was efficiently stirred while 9 ml of a 14% solution of sodium hypochlorite was introduced (during 1.8 hr) beneath the liquid surface by means of a pipet with a capillary tip. The product was isolated with ether[16b] and reduced using 0.26 g of lithium aluminum hydride in 50 ml of ether. After 5 hr, the mixture was decomposed as previously outlined and the product was distilled, affording 403 mg of material, bp 40–55° (bath temperature) at 0.08 mm. The gas chromatogram[21] showed peaks at 8.4 (**4**, 80%), 31.2 (**8**, 3.6%), 34.3 (**10** and **12**, 6.9%), 39.0 (**6**, 7.1%), 53.4 [**2** (α-OH), 0.6%], and 60.2 min [**2** (β-OH), 1.7%].

1-Methylene-*trans*-10-methyl-9-decalol (6).—To a stirred solution containing 140 mg of lithium aluminum hydride in 12 ml of anhydrous ether was added 170 mg of hydroperoxide **5**. The solution was stirred for 5 hr, carefully treated with 0.24 ml of water and 0.22 ml of 10% aqueous sodium hydroxide, and stirred for an additional 3 hr. Filtration and distillation afforded 135 mg (87%) of an oil: bp 52–56° (bath temperature) at 0.06 mm; $n^{25}\text{D}$ 1.5088; $\lambda_{\max}^{\text{film}}$ 2.89 (OH), 6.08 and 11.15 ($C{=}CH_2$), 8.56, 10.07, 10.41, 11.31 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 4.72 ($HC{=}C$, triplet, J = 2 cps), 4.58 ($HC{=}C$, triplet, J = 1.5 cps), 0.87 ppm (C-10 CH_3).

The gas chromatogram[22] gave peaks at 14.4 (3.5%) and 17.0 min (96.5%).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.75; H, 11.25.

***cis*-1,10-Dimethyl-*trans*-9-decalol (13).**—A 131-mg sample of hydroperoxide **5** was hydrogenated over 100 mg of reduced platinum oxide in 18 ml of acetic acid. Hydrogen uptake (2 equiv) was complete within 1 hr and the mixture was filtered, poured into cold 10% sodium hydroxide, and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and distilled affording 102 mg (84%) of oil, bp 65–70° (bath temperature) at 0.3 mm. This material showed a weak absorption at 5.85 μ and was therefore chromatographed on 25 ml of Florisil. The fractions eluted with 2% ether–hexane afforded *trans*-decalol **13** with an infrared spectrum and gas chromatographic retention time which exactly matched those of the major decalol isomer obtained from the oxirane **19** as described below.

The same product was obtained upon hydrogenation of alcohol **6** using reduced platinum oxide in methanol.

***cis*-1,10-Dimethyl-*trans*-9-decalol (13) and *trans*-1,10-Dimethyl-*cis*-9-decalol (21).**—To a solution of 1.80 g of oxide mixture (57% **19** and 43% **20**) in 20 ml of anhydrous tetrahydrofuran was added 25 ml of 5 *M* methylmagnesium bromide in tetrahydrofuran.[16a] After stirring at reflux for 32 hr, the mixture was allowed to cool and treated with 5 ml of saturated aqueous

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[18] The 13-ft Carbowax 20-M column[17] was employed at 134° with a helium flow rate of 77 cc/min.

[19] A 19 ft × 0.25 in. column of 1:4 KOH–Carbowax 20-M on 60–80 mesh Chromosorb W was employed at 160° with a helium flow rate of 100 cc/min.

[20] Beacon Chemical Industries, Inc., Cambridge 40, Mass.

[21] The KOH–Carbowax 20-M column[19] was employed at 161° with a helium flow rate of 100 cc/min.

[22] A 10 ft × 0.25 in. column containing 10% Ucon 75H, 90,000 Polar on 60–80 mesh Gaspack-W was employed at 154° with a helium flow rate of 71 cc/min.

ammonium chloride, and the product was isolated with ether[16b] and distilled, affording 1.36 g (69%), bp 65–69° (0.2 mm). The gas chromatogram[23] gave peaks at 6.5 (**19** and **20**, 9.2%), 13.2 (**21**, 17.8%), and 14.8 min (**13**, 73.0%).

A 0.35-g sample was chromatographed on 150 ml of Florisil. The fractions eluted with 50% benzene–hexane afforded the *trans*-decalol **13**: bp 60° (bath temperature) at 0.2 mm; $\lambda_{\max}^{\text{film}}$ 2.90 (OH), 9.32, 10.50, 10.85, 11.30 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 1.10 (C-10 methyl), 1.03 ppm (C-1 methyl, doublet, J = 8 cps).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 79.06; H, 12.16. Found: C, 78.8; H, 12.1.

A 0.15-g sample of the distilled mixture of decalols and unreacted oxide was reduced with 0.11 g of lithium aluminum hydride and the product was isolated as described previously. Distillation afforded 0.14 g of oil, bp 50–60° (bath temperature) at 0.07 mm. The gas chromatogram[24] gave peaks at 6.7 (0.4%, **18**), 7.3 (8.8%, **24**), 8.7 (17.8%, **21**), and 9.7 min (73%, **13**), identified by peak enhancement.

10-Methyl-1(9)-octalin (17).—To a stirred solution containing 5.0 g of lithium aluminum hydride in 500 ml of anhydrous ether was added 20.4 g of octalone **14** in 20 ml of ether over a 15-min period. After stirring for 3 hr, the mixture was cautiously treated with 10.0 ml of water and 8.0 ml of 10% aqueous sodium hydroxide. After an additional 3 hr of stirring, the granulated salts were filtered and the ether was distilled from the filtrate under reduced pressure.

A 6.65-g sample of the resulting octalol **15** was dissolved in 42 ml of dry pyridine, and 11.4 ml of acetic anhydride was added.[16a] After 21 hr, saturated aqueous sodium chloride (300 ml) was added and the mixture was thoroughly extracted with ether. The combined extracts were washed successively with water, 2% aqueous sulfuric acid, and saturated aqueous sodium chloride. After drying over magnesium sulfate, the solution was distilled, affording 7.60 g (91%) of acetate **16**: bp 62–63° (0.08 mm); $\lambda_{\max}^{\text{film}}$ 5.76 (ester CO), 6.00 (C=C), 8.02, 9.79 μ.

A 6.86-g sample of the acetate **16** was dissolved in 250 ml of ethylamine and treated with 2.36 g of lithium wire according to the procedure of Hallsworth, Henbest, and Wrigley.[6] After a deep blue coloration developed (1 hr), the mixture was stirred for an additional 20 min and solid ammonium chloride was cautiously added to neutralize the lithium salts and decompose the excess metal. The reaction mixture was poured into 400 ml of saturated aqueous sodium chloride and thoroughly extracted with ether. The combined extracts were washed with water, 2% aqueous sulfuric acid, and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Distillation gave 3.45 g (68%) of the octalin **17**: bp 86–88° (26 mm); $n^{25}\text{D}$ 1.4942; $\lambda_{\max}^{\text{film}}$ 6.01 (C=C), 9.95, 10.15, 12.40 μ [lit. bp 92–94 (35 mm),[25] 76–77° (10 mm)[26]; $n^{22}\text{D}$ 1.4929,[25] $n^{24}\text{D}$ 1.4926;[26] $\lambda_{\max}$ 6.03, 12.41 μ[25]].

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.9; H, 12.1.

The gas chromatogram[27] gave peaks at 7.4 (2%) and 9.3 min (98%).

***trans*-10-Methyl-9-decalol (18) and *cis*-10-Methyl-9-decalol (24).**—To a stirred solution containing 0.1 g of lithium aluminum hydride in 15 ml of anhydrous ether was added 0.15 g of oxide mixture **19** and **20**. The mixture was allowed to stir for 5 hr, then cautiously decomposed with 0.19 ml of water and 0.17 ml of 10% aqueous sodium hydroxide. After an additional 3 hr of stirring, the salts were filtered and the product was distilled, affording 0.14 g (89%) of liquid: bp 50–55° (bath temperature) at 0.1 mm; $\lambda_{\max}^{\text{film}}$ 2.88 (OH), 8.48, 9.95, 10.56, 11.36 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 1.02 (60%), 0.96 ppm (40%) (C-10 methyl of **18** and **24**, respectively).

The gas chromatogram[28] gave peaks at 11.5 (57%, **18**) and 12.7 min (43%, **24**). Admixture with a pure sample of *cis*-decalol **24** enhanced the latter peak.

10-Methyl-*trans*-1(9)-oxidodecalin (19) and 10-Methyl-*cis*-1(9)-oxidodecalin (20).—A stirred solution of 7.2 g of *m*-chloroperoxybenzoic acid[29] in 300 ml of benzene was chilled to 10° and 2.82 g of octalin **17** was added. The cooling bath was removed and the solution was allowed to stand for 2.5 hr. The reaction mixture was washed with 10% aqueous potassium hydroxide and saturated aqueous sodium chloride, and the benzene solution was dried over anhydrous magnesium sulfate. Distillation afforded 2.60 g (83.5%) of oxide mixture: bp 47–48° (0.2 mm); $n^{25}\text{D}$ 1.4958; $\lambda_{\max}^{\text{film}}$ 10.83, 11.16, 11.66, 11.93, 13.42 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 2.86–2.72 (H-1), 1.12 (60%), 1.06 (40%) ppm (C-10 methyl of **19** and **20**, respectively).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.3; H, 10.8.

Ethylene Thioketal Derivative of *cis*-10-Methyl-9-hydroxy-2-decalone (23).[30]—The procedure of Fieser was employed.[31] A solution of 5.0 g of ketol **22**[11] in 100 ml of glacial acetic acid, 7.8 ml of 1,2-ethanedithiol, and 7.8 ml of boron trifluoride etherate was allowed to stand at room temperature for 1 hr.[16a] The solution was diluted with saturated aqueous sodium chloride and extracted with ether. The combined extracts were washed with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether was distilled and the residue crystallized from hexane, affording 3.15 g (45%) of thioketal **23**, mp 94–95°. The analytical sample, mp 96–97°, was obtained by recrystallization from hexane.

Anal. Calcd for $C_{13}H_{22}OS_2$: C, 60.82; H, 8.58; S, 24.81. Found: C, 61.0; H, 8.5; S, 24.8.

***cis*-10-Methyl-9-decalol (24).**[30]—A solution of 3.00 g of thioketal **23** in 250 ml of absolute ethanol was stirred with 100 g of freshly prepared W-2 Raney nickel at room temperature for 2 hr and at reflux for 4 hr. The cooled mixture was filtered and the ethanol was distilled from the filtrate at atmospheric pressure. The residue was dissolved in hexane, washed with saturated aqueous sodium chloride, and dried. The hexane was removed by distillation, affording 1.63 g (84%) of liquid: bp 45–48° (bath temperature); $n^{25}\text{D}$ 1.4997; $\lambda_{\max}^{\text{film}}$ 2.88 (OH), 8.66, 9.55, 10.00, 10.23, 10.70 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 0.96 ppm (C-10 methyl).

Anal. Calcd for $C_{11}H_{20}O$: C, 77.51; H, 11.98. Found: C, 77.3; H, 11.8.

The gas chromatogram[32] showed a single peak at 13.0 min.

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[23] The Ucon column[22] was employed at 159° with a helium flow rate of 69 cc/min.

[24] The Ucon column[22] was employed at 165° with a helium flow rate of 82 cc/min.

[25] F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

[26] J. W. Rowe, A. Melera, D. Arigoni, O. Jager, and L. Ruzicka, *Helv. Chem. Acta*, **40**, 1 (1957).

[27] The Carbowax column[17] was employed at 99° with a helium flow rate of 97 cc/min.

[28] The Ucon[22] column was employed at 153° with a helium flow rate of 70 cc/min.

[29] FMC Corp., Inorganic Chemical Division, Carteret, N. J.

[30] We are indebted to Miss Heide Roebke for performing this experiment.

[31] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[32] The Ucon column[22] was employed at 151° with a helium flow rate of 71 cc/min.