$AgNO_3$ on ethylene glycol column,[22] retention times **70**, 2.2 min at 50 °C; **71**, 6.6 min at 50 °C; **72**, 5.6 min at 65 °C; and **73**, 15.3 min at 65 °C. Tetracyclopropylethylene was prepared by thermolysis of the sodium salt of dicyclopropyl ketone *p*-tosylhydrazone.[21] The UV maxima of the cyclopropylalkenes, determined using a Cary 118 instrument swept with N_2, were in reasonable agreement with published values.[21,23]

Kinetics. The kinetics of the alkene hydrations were followed by monitoring the decrease in absorption of the alkenes in 1-cm cells using Cary 14 and 118 instruments. Acid solutions were prepared by dilution of concentrated reagent and concentrations were determined by titration with NaOH. Concentrated D_2SO_4 (Diaprep) was diluted with D_2O.

Injections of 10-μL aliquots of 0.02 M solutions of the alkenes in 95% ethanol into the sulfuric acid solutions in the UV cell gave final concentrations of 7×10^{-4} M alkene. The decrease of the absorption at the maxima was followed for at least 2 half-lives and good first-order kinetics were observed. At least three runs were carried out at each acid concentration. The absorption decreased by at least 80% in each case, indicating large equilibrium constants for hydration.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

References and Notes

(1) (a) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976); (b) S. Y. Attia, J. P. Berry, K. M. Koshy, Y.-K. Leung, E. P. Lyznicki, Jr., V. J. Nowlan, K. Oyama, and T. T. Tidwell, *ibid.*, preceding paper in this issue; (c) W. K. Chwang, P. Knittel, K. M. Koshy, and T. T. Tidwell, *ibid.*, accompanying paper in this issue.
(2) M. Charton and B. I. Charton, *J. Org. Chem.*, **38**, 1631 (1973).
(3) R. W. Taft, unpublished results quoted in P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).
(4) (a) D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Am. Chem. Soc.*, **90**, 4633 (1968); (b) D. S. Noyce, D. R. Hartter, and R. M. Pollack, *ibid.*, **90**, 3791 (1968).
(5) A. J. Kresge and H. J. Chen, *J. Am. Chem. Soc.*, **94**, 2818 (1972).
(6) C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970.
(7) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).
(8) J. Hine and N. W. Flachskam, *J. Am. Chem. Soc.*, **95**, 1179 (1973).
(9) S. W. Benson et al., *Chem. Rev.*, **69**, 279 (1969).
(10) P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 187 (1962).
(11) V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4930 (1952).
(12) See p 194 of ref 10, footnote 13 of ref 13, and footnote *d*, Table 3, of R. M. Joshi, *J. Macromol. Sci., Chem.*, **6**, 595 (1972).
(13) S. W. Staley, *J. Am. Chem. Soc.*, **89**, 1532 (1967).
(14) T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969).
(15) (a) T. Okuyama and T. Fueno, *J. Org. Chem.*, **39**, 3156 (1974); (b) T. Okuyama and T. Fueno, *Kagaku No Ryoiki*, **29**, 633 (1975); *Chem. Abstr.*, **84**, 58041q (1976); (c) T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Am. Chem. Soc.*, **89**, 5826 (1967).
(16) A. J. Kresge, Y. Chiang, P. H. Fitzgerald, R. S. McDonald, and G. H. Schmid, *J. Am. Chem. Soc.*, **93**, 4907 (1971).
(17) L. B. Young and W. S. Trahanovsky, *J. Org. Chem.*, **32**, 2349 (1967).
(18) J. S. Meek and J. W. Rowe, *J. Am. Chem. Soc.*, 77, 6675 (1955).
(19) E. E. Schweizer, J. G. Thompson, and T. A. Ulrich, *J. Org. Chem.*, **33**, 3082 (1968).
(20) A. Maercker, *Angew. Chem., Int. Ed. Engl.*, **6**, 557 (1967).
(21) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971).
(22) M. E. Bednas and D. S. Russell, *Can. J. Chem.*, **36**, 1272 (1958).
(23) C. H. Heathcock and S. R. Poulter, *J. Am. Chem. Soc.*, **90**, 3766 (1968).

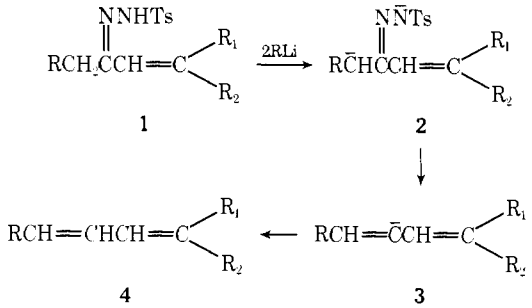
The Role of Tosylhydrazone Stereochemistry upon the Regiospecificity of Olefin Formation[1,2]

W. G. Dauben,* G. T. Rivers, and W. T. Zimmerman

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received November 8, 1976*

Abstract: The isomeric pulegone *p*-toluenesulfonylhydrazones (tosylhydrazones), **5**-*E* and **5**-*Z*, have been prepared and their structures have been established by x-ray crystallographic techniques. The alkyllithium mediated decomposition of these isomeric tosylhydrazones has been studied in order to evaluate the role of tosylhydrazone stereochemistry upon the regiospecificity of olefin formation. Significantly, decomposition of the isomeric tosylhydrazones in *N,N,N',N'*-tetramethylethylenediamine (TMEDA) leads to product where the tosylhydrazone stereochemistry seems to direct the course of the reaction while decomposition in benzene leads to the same product regardless of tosylhydrazone stereochemistry. The mechanism of this diene forming reaction has been established through the decomposition of a variety of α,β-unsaturated tosylhydrazones and through the synthesis and decomposition of specifically deuterated pulegone tosylhydrazones.

The alkyllithium mediated decomposition of *p*-toluenesulfonylhydrazones (hereafter called tosylhydrazones) of α,β-unsaturated ketones under mild conditions (0–20 °C) has been shown to yield conjugated 1,3-dienes in a regiospecific manner so that the position of the original carbon–carbon double bond

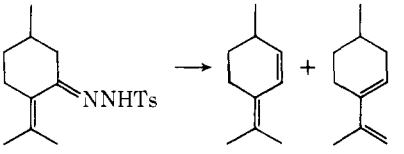


in the unsaturated ketone is maintained in the diene.[3] Such dienes were postulated to be formed by α'-proton abstraction from the tosylhydrazone monoanion to yield the dianion **2** which subsequently decomposed to the vinyl anion **3** and this intermediate, in turn, was protonated to give the diene **4**. Recently, this reaction scheme has been established in the conversion of a ketone tosylhydrazone to an olefin.[4]

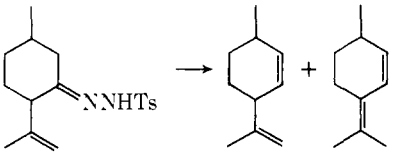
In the initial study[3] of enone tosylhydrazones, the derivative was prepared in tetrahydrofuran (trace of acid) and then this solvent was displaced by benzene prior to formation of the dianion with an ethereal solution of methyllithium. In some cases, it was found that the tosylhydrazone was thermally labile and the overall yield of the diene was decreased owing to difficulties encountered during the change in solvent or, in a few cases, during actual isolation of the derivative. To circumvent this problem, the procedure was modified and the entire reaction sequence from the unsaturated ketone to the 1,3-diene was conducted directly in tetrahydrofuran; in no case was the

tosylhydrazone isolated. This procedure was utilized to prepare a wide variety of substituted 1,3-cyclohexadienes.[5]

In the course of a continuing study of the photochemistry of 1,3-dienes, a tetrahydrofuran solution of pulegone tosylhydrazone (**5**), prepared either in situ or from crystalline pulegone tosylhydrazone, mp 143–145 °C,[6] was allowed to react with an excess of an ethereal solution of methyllithium. It was found that in contrast to the earlier studies[3] in benzene, two isomeric *p*-menthadienes were formed. The major isomer (80%) was the expected 2,4(8)-*p*-menthadiene (**6**) and the minor isomer (20%) was 3,8-*p*-menthadiene (**7**). The cor-



5 **6** **7**

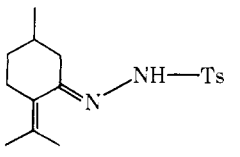


8 **9** **6**

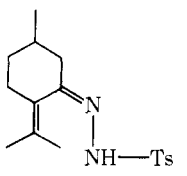
rectness of the earlier regiospecific results in benzene was confirmed by numerous repetitions of the initial procedure. Suitable control experiments showed that **6** and **7** did not interconvert under the tetrahydrofuran reaction conditions. Thus, in changing from benzene to tetrahydrofuran for the decomposition of tosylhydrazone **5** the regiospecificity of the diene formation was lost and the reasons for this loss have been investigated.

The involvement of isopulegone tosylhydrazone (**8**), the β,γ isomer of **5**, was first evaluated. A tetrahydrofuran solution of pure crystalline **8** upon reaction with an ethereal methyllithium solution gave the expected regiospecific diene **9** (80%) and the rearranged conjugated diene **6** (20%). The nonconjugated diene **9** was found to isomerize slowly to **6** under the reaction conditions but no isomerization of either of these dienes to **7** was found.[7] Thus, in this case the expected regiospecificity of the reaction of the nonconjugated tosylhydrazone **8** is consistent with earlier findings[5] of only primary or secondary proton abstraction under these olefin-forming reaction conditions.

The reasons for stereoselectivity in this olefin synthesis from a ketone tosylhydrazone have never been established, but it was suggested recently,[4a] without any experimental justification, that the stereochemistry of the tosylhydrazone derivative could be the sole controlling factor. Since the completion of the work described herein,[1] stereospecifically directed dianion formation has been demonstrated on oxime derivatives of *saturated* ketones.[8] If such be the case, then, *Z*–*E* isomerization of the tosylhydrazone of **5** could account for the formation of the isomeric dienes **6** and **7**, diene **6** arising in a directed α'-proton abstraction from the **5**-*E* isomer and the diene **7** in a directed γ-proton abstraction from the **5**-*Z* tosylhydrazone isomer.



5-*E*



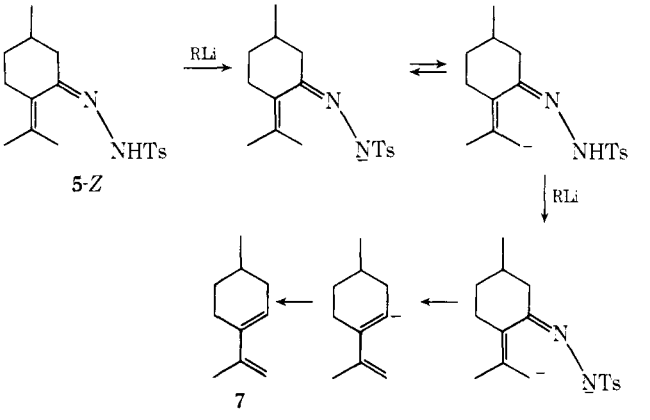
5-*Z*

During the course of this work with one pulegone tosylhydrazone isomer it was found possible to prepare the other isomeric derivative, mp 111–113 °C. The earlier prepared higher melting isomer, mp 143–145 °C, was prepared by mixing a hot saturated solution of tosylhydrazine in methanol containing a trace of hydrochloric acid with pulegone. As the solution cooled, the tosylhydrazone crystallized in excellent purity. The lower melting isomer, mp 111–113 °C, was formed by heating a 95% ethanolic solution of tosylhydrazine, pulegone, and a trace of hydrochloric acid under reflux. The two derivatives were shown to be isomeric by elemental analysis and they exhibited nearly identical infrared and NMR spectra. However, the two isomers were cleanly separated on TLC, thus providing a reliable method to ascertain purity. It also was found that when the higher melting isomer was heated under reflux in acidic ethanolic solution, isomerization to the lower melting isomer occurred. The stereochemistry of these two crystalline isomers was kindly established by Dr. J. F. Blount using x-ray crystallographic procedures. It was found that the higher melting isomer had the **5**-*E* configuration and the lower melting isomer had the **5**-*Z* configuration.

With the availability of **5**-*Z* and **5**-*E* isomers, their reactions in benzene solution with an excess of ethereal methyllithium were compared (benzene–ether, 20:1). In both cases, the ratio of dienes **6** to **7** was at least 99:1. These results demonstrated that under these exact reaction conditions, the regiospecificity of proton abstraction from a tosylhydrazone is *independent of the stereochemistry of the derivative* and α'-proton abstraction occurred to greater than 99%. However, in the case of the **5**-*Z* derivative, if the ethyl ether from the added ethereal methyllithium solution was an appreciable portion of the benzene–ether reaction mixture, the amount of diene **7**, relative to unrearranged diene **6**, increased. This solvent effect was not observed in the case of **5**-*E*. For example, in 1:1 ether–benzene solution, **5**-*E* yielded diene **6** in greater than 99% purity while **5**-*Z* gave a mixture of **6** and **7** in a ratio of 40:60. This preference for γ hydrogen in **5**-*Z* was even more pronounced in tetrahydrofuran solution. In parallel experiments in this latter solvent, **5**-*E* gave **6** and **7** in a ratio of 80:20 while **5**-*Z* gave these same dienes in a ratio of 20:80.

Combination of all the foregoing results indicates that at least two factors play a role in determining whether α' or γ proton abstraction occurs, i.e., tosylhydrazone stereochemistry and solvent. The dependency of proton abstraction upon the stereochemistry of the tosylhydrazone could be the result of an intramolecular proton abstraction by the tosylhydrazone monoanion (Scheme I, using **5**-*Z* as the example) or by a

Scheme I

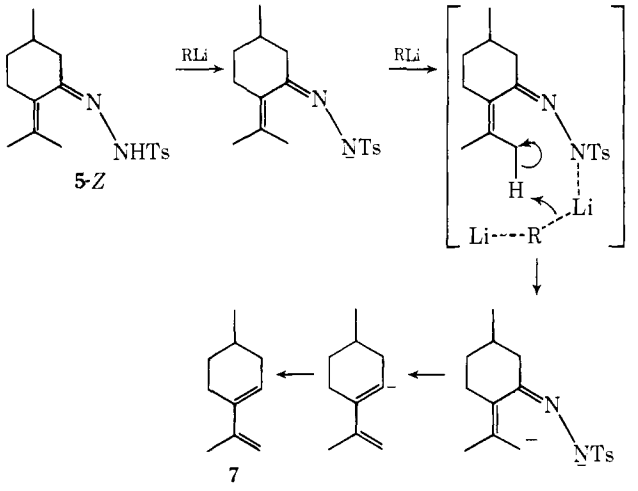


5-*Z* **7**

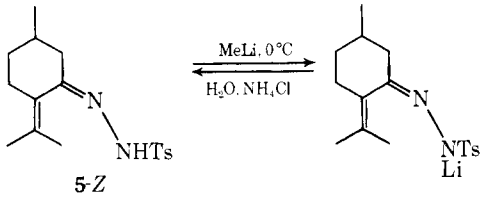
chelation effect exerted on the methyllithium by the tosylhydrazone monoanion (Scheme II).

The effect of solvent on the reaction course has no straightforward explanation. It is evident that factors dealing with the solvation of the organometallic species and with the state of aggregation of the organometallic complex must be considered. In order to locate the step(s) in which the solvent played a role, control experiments were conducted and it was

Scheme II



found that the monoanions of the two isomeric tosylhydrazones maintained their original stereochemistry. When either tosylhydrazone **5**-*Z* or **5**-*E* was treated with 1 equiv of methyl-



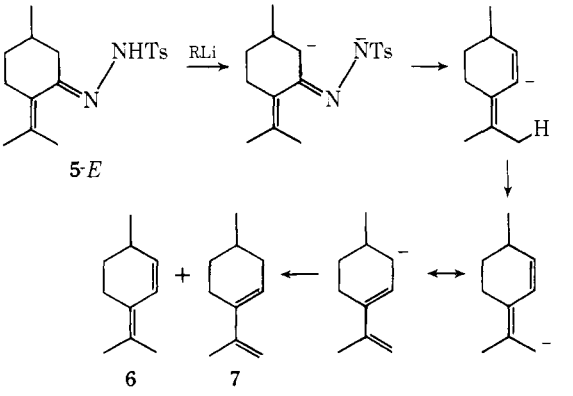
lithium in benzene or tetrahydrofuran, under comparable conditions where 2 equiv of the organometallic reagent would have led to diene formation, it was found that quenching of the reaction mixture with saturated ammonium chloride solution gave the original tosylhydrazone in excellent yield with no isomerization detectable by TLC. Thus, the loss of regiospecificity with different solvent systems cannot be due to *Z*-*E* isomerization of the tosylhydrazone in the reaction mixture.

Next, the utilization of *n*-butyllithium as the base was evaluated. In benzene, **5**-*E* gave unrearranged diene **6** in greater than 98% purity, while **5**-*Z* yielded dienes **6** and **7** in a ratio of 75:25. The same product ratios were obtained in 1:1 benzene-ether. In tetrahydrofuran, however, **5**-*E* formed dienes **6** and **7** in a ratio of 65:35 while **5**-*Z* gave the dienes in a ratio of 10:90. Thus, with this base the same general trend as found with methyllithium was observed, except that with *n*-butyllithium a slightly greater preference for γ-proton abstraction was observed. The reasons for this increased preference with *n*-butyllithium are not known, but factors which may play a role are a greater preference for the unhindered γ-proton abstraction due to a greater steric bulk or an increased basicity which, in turn, is reflected in the relative kinetic acidities of the α' and γ positions.

Significantly, when the decomposition of the tosylhydrazones was conducted in *N,N,N',N'*-tetramethylethylenediamine with *n*-butyllithium the regiospecificity of the diene formation was excellent. Under such conditions, **5**-*E* yielded diene **6** exclusively, within detectable limits, while **5**-*Z* gave a mixture of 10% diene **6** and 90% diene **7**. Thus, under these specific reaction conditions, the regiospecificity of the proton abstraction can be *largely controlled by the stereochemistry of the derivative.*

While competitive α' vs. γ proton abstraction offers one possible explanation for the formation of dienes **6** and **7**, other mechanisms must be considered. One of the most attractive possibilities is the intramolecular hydrogen transfer process shown in Scheme III. This process was evaluated by study of different deuterated pulegone tosylhydrazones. Reaction of pulegone-9,10-d_6 tosylhydrazone, prepared under conditions

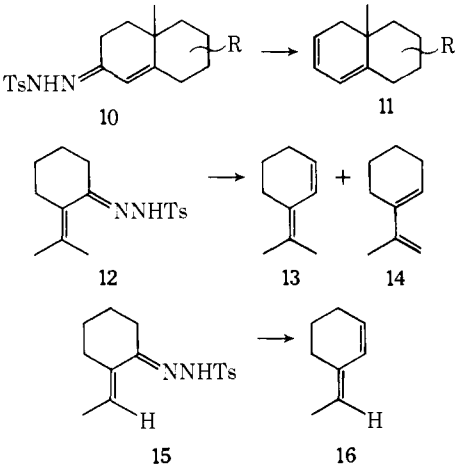
Scheme III



favorable to the formation of the **5**-*E* isomer, in tetrahydrofuran with ethereal methyllithium yielded diene **6**-d_6 and diene **7**-d_5 in a ratio of 97:3. If the hydrogen transfer mechanism had intervened, then diene **7** would have been d_6 rather than d_5. In addition, the change in product ratio from 80:20 in the undeuterated case to 97:3 in the deuterated case is consistent with a primary isotope effect,[9] where k_H/k_D is about 8.[10] In a similar study of 2-d_2-**5**-*E* under the above conditions, dienes **6**-*d* and **7**-d_2 were formed in a ratio of 45:55. The combined isotope effects clearly show that removal of the α' or γ proton resulting in dianion formation is the rate-determining step in these tosylhydrazone conversions and that **6** and **7** do not arise from a common precursor such as the postulated pentadienyl anion (Scheme III).

Utilizing the above product distribution data, the preference for α'-proton abstraction and the deuterium isotope effect for the **5**-*E* tosylhydrazone was calculated using the selectivity-reactivity relationships developed by Curtin.[11] Using this treatment, it is calculated that there is a preference for α'-proton abstraction of 6.27 and the isotope effect is 5.15.

Some factors involved in the α'- and γ-proton competitive removal process in this tosylhydrazone reaction have been investigated. Earlier studies of the tosylhydrazones of endocyclic enones, for example, octalones (**10**)[5] in tetrahydrofuran, displayed only the reaction of the α' proton to yield the endocyclic dienes **11**. First, the reaction of a tosylhydrazone of



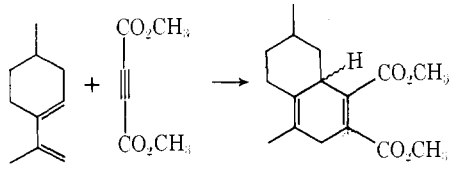
norpulegone (**12**) was studied. The stereochemistry of the derivative is not known but from the studies of the two isomeric derivatives of pulegone in tetrahydrofuran it is known that the ratio of α'- to γ-proton removal varies from 80:20 to 20:80 in the **5**-*E* and **5**-*Z* isomers. With **12** in tetrahydrofuran, it was found that the ratio of α'-derived olefin **13** to γ-derived olefin **14** was 90:10, a result which shows that the distal β'-methyl group had a small effect upon the ratio of relative reactivities of the α' and γ protons. A tosylhydrazone of (*E*)-2-ethyli-

denecyclohexanone (**15**) was prepared and its decomposition in tetrahydrofuran yielded only α'-derived olefin **16.** This result, when combined with those reported for the endocyclic derivatives, indicates that γ-proton abstraction requires an s-cis enone with a γ proton on a Z alkyl group.

To evaluate further this geometric hypothesis, specific deuterium-labeled pulegone was prepared. It was found that when the ketone was heated under reflux in deuterium oxide containing sodium carbonate, preferential exchange at the C-2 and C-9 positions occurred. Mass spectral analysis of the deuterated pulegone showed the material to be approximately 50% d_5 and 25% d_6. ^{1}H NMR analysis indicated greater than 80% incorporation of deuterium on the Z 9-methyl group (δ 1.95 ppm) and less than 20% incorporation on the E 10-methyl group (δ 1.77 ppm).[12] These combined data clearly indicate that extensive exchange had occurred at C-2. The tosylhydrazone of this deuterated pulegone was formed under conditions favorable for the formation of the **5**-E isomer. Since both α' and Z-γ positions are deuterated there should be a minimal deuterium isotope effect upon the diene ratio, providing that the E 10-methyl group does not participate in olefin formation.

Decomposition of the deuterated tosylhydrazone in tetrahydrofuran with ethereal methyllithium yielded dienes **6** and **7** in a 65:35 ratio. In a parallel experiment with nondeuterated material, **6** and **7** were again formed in a 80:20 ratio. These data establish a deuterium isotope effect and this conclusion was substantiated by GC/MS analysis. Diene **6** was found to be approximately 60% d_4 and 30% d_5, a result in agreement with loss of deuterium from the α' position. Diene **7** was found to contain 40% d_5 and 35% d_6 material. Such a result is consistent with competitive loss of hydrogen rather than deuterium and indicates that in the presence of an unfavorable deuterium isotope effect, due to the labeling on the Z 9-methyl group, proton abstraction can occur to some extent from the E 10-methyl group.

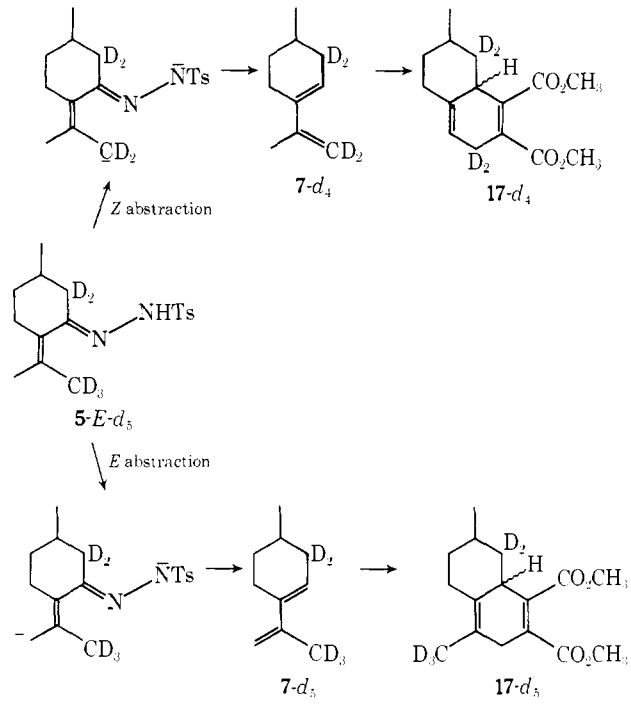
The dienes **6** and **7** were difficult to separate on a preparative scale. In order to obtain a derivative of **7** for NMR analysis the diene mixture was allowed to react with dimethyl acetylenedicarboxylate. The Diels–Alder adduct **17** was utilized to determine the position of the deuterium on diene **7.** Starting with



7 **17**

optically active diene **7,** derived from (R)-(+)-pulegone, two diastereomeric cycloadducts were obtained in approximately a 2:1 ratio. The ^{1}H NMR spectrum of the mixture of nondeuterated diastereomeric cycloadducts clearly distinguished the diallylic methylene position (δ 2.90 ppm) and the allylic methyl group (δ 1.67 ppm). The ^{1}H NMR spectrum of the deuterated material showed that the label was distributed between the diallylic methylene position and the allylic methyl group in a ratio of 25:75.

Considering the deuterium distribution in the Z and E methyl groups in the starting material, i.e., mainly in the Z group, sole formation of the dianion from the Z methyl group should yield a diene cycloaddition product with little deuterium in the allylic methyl group. On the other hand, formation of the dianion from the E methyl group should yield an adduct with a large deuterium content in the allylic methyl group. The finding of a ratio of 25:75 for the deuterium content in the diallylic methylene group and in the allylic methyl group in the derivative indicates that diene **7** was formed by generation of the dianion from the Z 9- and E 10-methyl groups. In view of



the predominant deuterium label on the Z 9-methyl group, which, due to the deuterium isotope effect, should lead to a preference for dianion formation from the E 10-methyl group, the finding of 25% deuterium labeling clearly demonstrates that in the absence of an isotope effect there is a strong preference for dianion formation from the Z 9-methyl group.

Any detailed explanation of the observed solvent dependencies or of the observed tosylhydrazone stereochemical dependencies on the course of this decomposition reaction still awaits further studies owing to the complexities of the reaction system.

Experimental Section[13]

Pulegone Tosylhydrazone (5-*E*). Pulegone (1.86 g, 12 mmol) and concentrated hydrochloric acid (0.2 mL) were added to a hot saturated solution of tosylhydrazine (2.45 g, 13 mmol, Aldrich, 97%) in 33 mL of 95% ethanol. The mixture was allowed to cool and was stirred at room temperature for 3 h. The tosylhydrazone was collected by vacuum filtration, washed with cold 95% ethanol, and recrystallized from 30 mL of 95% ethanol to give 1.68 g (44%) of white needles: mp 143–145 °C dec (lit.[6] mp 145–147 °C); NMR ($CDCl_3$) δ 7.56 (AB q, 4, $\Delta\nu$ = 35 Hz, J = 8 Hz), 7.23 (s br, 1), 3.0–0.8 (m, 7), 2.40 (s, 3), 1.63 (s, 3), 1.42 (s, 3), 0.92 (d, 3, J = 6 Hz); IR (KBr) 3180, 2860, 1380, 1320, 1180, 1170, 950 cm^{-1}.

Anal. Calcd for $C_{17}H_{24}O_2N_2S$: C, 63.71; H, 7.55; N, 8.74; S, 10.00. Found: C, 63.54; H, 7.47; N, 8,74; S, 9.86.

Pulegone Tosylhydrazone (5-*Z*). A. A mixture of 1.00 g (3.12 mmol) of (E)-pulegone tosylhydrazone (**5**-E) and 1 drop of concentrated hydrochloric acid in 6 mL of 95% ethanol was heated under reflux for 30 min, during which time the hydrazone slowly went into solution. The reaction mixture was cooled to room temperature and allowed to stand at −15 °C for 12 h. The precipitate was collected and was recrystallized from 3 mL of 95% ethanol to give 0.31 g (31%) of white, granular crystals: mp 110–112 °C dec; NMR ($CDCl_3$) δ 7.57 (AB q, 4, $\Delta\nu$ = 30 Hz, J = 9 Hz), 7.48 (s br, 1), 3.0–0.8 (m, 7), 2.42 (s, 3), 1.72 (s, 3), 1.45 (s, 3), 0.88 (d, 3, J = 6 Hz); IR (KBr) 3130, 2820, 1420, 1350, 1160, 1020 cm^{-1}.

Anal. Found: C, 63.41; H, 7.40; N, 8.94; S, 9.95.

Pulegone Tosylhydrazone (5-*Z*). B. A solution of 18.6 g (0.12 mol) of pulegone and 24.5 g (0.13 mol) of tosylhydrazine (Aldrich, 97%) in 330 mL of 95% ethanol was refluxed with 2 mL of concentrated hydrochloric acid for 3 h. The orange reaction mixture was cooled in ice and the white crystals were collected by vacuum filtration. This material was recrystallized from ethanol to give 11.3–17.1 g of **5**-Z, mp 110–112 °C dec.[14]

In many reactions, decomposition products were formed and their presence rendered the isolation of the pure derivative difficult.

Representative Decomposition Procedure. A 50-mg (0.156 mmol) portion of tosylhydrazone in 3 mL of dry solvent (benzene, 1:1 ether–benzene, THF, or TMEDA) was stirred under N_2 and 0.50 mL of 2.45 M (1.22 mmol) of *n*-BuLi in hexane or 0.70 mL of 1.56 M (1.09 mmol) of MeLi in ether was added by syringe. Aliquots of 0.10 mL were periodically withdrawn and partitioned between water and pentane (2 mL:2 mL). The pentane layer was dried over Na_2SO_4 and analyzed by VPC (10 ft × 0.125 in., 10% Carbowax 20M–10% KOH on Chromosorb W at 90 °C; relative retention times of **6** to **7** were 1 to 1.12). Actual product ratios are given in the text and were found to be essentially time independent except in the case of **5**-*Z* in 1:1 ether–benzene.

Preparation of Diene 6. A suspension of 2.00 g (6.24 mmol) of **5**-*E* in 40 mL of benzene was cooled in an ice bath and 10 mL of 1.5 M (15 mmol) ethereal methyllithium solution was added over 10 min. The mixture was stirred for 1 h while the original white suspension became a colorless solution, then an orange solution, and finally an orange suspension. The reaction was quenched with 50 mL of saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted once with ether. The combined organic layers were washed three times with water, dried over $MgSO_4$, and concentrated by rotary evaporation at ambient temperature. The residue was evaporatively distilled (oven 120 °C, aspirator vacuum) to give 0.68 g (83%) of **6** as a colorless liquid: NMR (CCl_4) δ 6.32 (dd, 1, J_1 = 10; J_2 = 3 Hz), 5.45 (dm, 1, J_1 = 10 Hz), 2.8–0.6 (m, 7), 1.72 (s, br, 6), 1.00 (d, 3, J = 8 Hz).

Preparation of Diene 7. A solution of 500 mg (1.56 mmol) of **5**-*Z* in 15 mL of TMEDA (distilled from NaH) was cooled under N_2 in a dry ice-2-propanol bath and 3 mL of 2.45 M (7.35 mmol) of *n*-butyllithium in hexane was added by syringe. The bath was removed and the red solution was stirred for 2 h. The reaction mixture was poured into water and extracted four times with pentane. The combined extracts were washed with saturated NH_4Cl and $NaHCO_3$, dried over Na_2SO_4, and rotary evaporated at ambient temperature to give 180 mg of reddish oil which was filtered through 5 g of silica gel with pentane to give 165 mg (78%) of a 9:1 mixture of **7** and **6**. The spectral data were in agreement with the published data.[15]

Stability of Diene 6 to Reaction Conditions. A stock solution of **6** in hexane (22.4% **6** by weight, 3.37 g total, 754 mg of **6**, 5 mmol) was dissolved in 25 mL of THF and 4 mL of 1.8 M (7.2 mmol) of methyllithium in ether was added. The mixture was stirred for 18 h under N_2; a positive Gilman test was obtained indicating the presence of methyllithium. The reaction mixture was quenched with water and extracted with pentane. No isomerization of the starting olefin could be detected by VPC. Similar experiments using lithium diisopropylamide failed to isomerize **6**.

Stability of Monoanions of 5-*Z* and 5-*E*. The following procedure is representative. A solution of 1.00 g (3.12 mmol) of **5**-*E* in 10 mL of dry THF was cooled in an ice bath and 1.2 mL of 2.46 M (2.95 mmol) methyllithium in ether was added. The mixture was stirred for 1 h at 0 °C under N_2. The reaction mixture was poured into saturated aqueous NH_4Cl. The THF layer was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4 and the solvents were removed to give 920 mg (92%) of recovered hydrazone. Analytical TLC (silica gel, chloroform, UV visualization, two developments) indicated the presence of only **5**-*E* (R_f 0.47) while **5**-*Z* (R_f 0.55) could not be detected. Similar results were obtained in benzene.

Also, when **5**-*Z* was subjected to the above conditions, isomerization could not be detected.

Isopulegone Tosylhydrazone (8). To a solution of 9.30 g (50 mmol) of tosylhydrazine in 25 mL of hot methanol was added 7.72 g (50 mmol) of isopulegone (prepared by Brown oxidation[16] of isopulegol (Givaudan)). The mixture was allowed to stand for 18 h at room temperature. The solid was collected and recrystallized from ethanol–water to give 10.10 g (63%) of crystalline **8**: mp 102–103 °C; NMR ($CDCl_3$) δ 7.99 (s, br, 1) 7.22 (AB q, $\Delta\nu$ = 35 Hz, J = 7 Hz), 4.62 (d, 2, J = 10 Hz), 2.80–1.20 (m, 7), 2.37 (s, 3), 1.60 (s, 3), 0.90 (d, 3, J = 4 Hz).

Decomposition of Isopulegone Tosylhydrazone (8). Dienes 6 and 9. A solution of 9.42 g (29.4 mmol) of **8** in 55 mL of THF was cooled in an ice bath and 49.0 mL of 1.8 M (88.0 mmol) ethereal methyllithium was added over 30 min. A Gilman test was positive 3 h after the addition. The ice bath was removed and the mixture was stirred for 18 h at room temperature. The dark brown suspension gave a positive Gilman test and the reaction mixture was cooled in ice and quenched by slowly adding water. The mixture was extracted three times with pentane. The extracts were washed twice with water and once with saturated NaCl, dried over $MgSO_4$, and concentrated by distillation at atmospheric pressure to give a quantitative yield of a 20:80 mixture of dienes **6** and **9** as determined by VPC. Pure samples of **6** and **9** were obtained by preparative VPC (10 ft × 0.25 in., 10% Carbowax 6M–10% KOH on Chromosorb W, 120 °C, relative retention times of **6** to **9** were 3:2) and properties were in accord with those reported in the literature.[17]

Stability of Diene 9 to Reaction Conditions. To a solution of 94 mg (0.69 mmol) of **9** in 3 mL of dry THF was added 0.38 mL of 1.8 M methyllithium in ether at 0 °C under N_2. After 21 h at room temperature, an aliquot was quenched and extracted as above. Analytical VPC indicated a 1:1 mixture of dienes **6** and **9**.

2-Isopropylidenecyclohexanone (Norpulegone). A solution of 100 mmol of lithium diisopropylamide in 160 mL of ether was cooled in a dry ice-2-propanol bath and a solution of 9.80 g (100 mmol) of redistilled cyclohexanone in 50 mL of ether was added, dropwise, over 40 min in order to maintain the temperature below −70 °C. The solution was warmed to −10 °C and 7.00 g of freshly fused zinc chloride was added in one portion against a positive nitrogen pressure. The mixture was stirred for 10 min between −15 and −5 °C and a solution of 6.00 g (103 mmol) of acetone (stored over K_2CO_3) in 20 mL of ether was added in one portion while the reaction flask was cooled in dry ice-2-propanol. The thick white suspension was stirred for 5 min at −10 °C and poured into 300 mL of cold, saturated, aqueous NH_4Cl. Sufficient water was added to dissolve the salts. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined organic extracts were washed successively with water, saturated $NaHCO_3$, and saturated NaCl, dried briefly over $MgSO_4$, and concentrated by rotary evaporation to give 12.73 g (81%) of ketol as colorless liquid: NMR (CCl_4) δ 3.51 (s br, 1), 2.60–1.00 (m, 9), 1.13 (s, 6); mass spectrum *m/e* 138 (M − H_2O). (Subsequent work showed that the use of zinc chloride was unnecessary if the aldol condensation was conducted below −65 °C.)

A mixture of 12.70 g (81.5 mmol) of crude ketol, 10 mL of Nujol, and 2.50 g (18.4 mmol) of $KHSO_4$ was heated at 120 °C for 2 h, 150–170 °C for 1 h, and 140 °C for 2 h. The distillation head was warmed with a heat gun and ca. 1.5 mL of distillate, mostly water, was collected. The mixture was cooled and distilled. Fractions were collected at 40–117 °C (20 mm), 117–121 °C (20 mm), and 100 °C (0.5 mm). The last two fractions gave 4.70 g (40%) of enone containing 2% of the β,γ isomer: NMR (CCl_4) δ 2.40 (m, 4), 1.92 (s, 3), 1.80 (m, 4), 1.75 (s, 3); mass spectrum *m/e* 138, 95, 67. (Subsequent work showed toluenesulfonic acid–benzene to be superior dehydration conditions.)

Isopropylidenecyclohexanone Tosylhydrazone (12). The tosylhydrazone was prepared by the method described for **8** and was recrystallized from methanol to give **12** in 69% yield: mp 150–151 °C; NMR ($CDCl_3$) δ 7.49 (AB q, 4, $\Delta\nu$ = 34 Hz, J = 8 Hz), 2.38 (s, 3), 2.50–2.10 (m, 4), 1.70–1.40 (m, 4), 1.62 (s, 3), 1.38 (s, 3).

Decomposition of 12. Dienes 13 and 14. A solution of 3.06 g (10.0 mmol) of **12** in 20 mL of THF was decomposed with 16.7 mL of 1.8 M (30.0 mmol) ethereal methyllithium by the procedure described for **8** to give 1.07 g (88%) of a 90:10 mixture of **13** to **14** as determined by VPC and NMR. The properties of **13** and **14** were in agreement with those reported.[18]

Ethylidenecyclohexanone Tosylhydrazone (15). To a solution of 3.18 g (17.2 mmol) of tosylhydrazine in a minimum volume of hot methanol (8–10 mL) was added 2.13 g (17.2 mmol) of (*E*)-ethylidenecyclohexanone.[19] The mixture was allowed to stand for 2 h at room temperature. TLC (silica gel, CH_2Cl_2) and infrared analysis indicated the near absence of enone and the mixture was cooled in ice and the solid collected to give 2.58 g (52%) of **15**: mp 128–130 °C; NMR ($CDCl_3$) δ 7.43 (AB q, 4, $\Delta\nu$ = 34, J = 9 Hz), 5.68 (q, 1, J = 7 Hz), 2.38 (s, 3), 2.20–2.00 (m, 4), 1.70–1.30 (m, 4), 1.58 (d, 3, J = 7 Hz).

Decomposition of 15. Diene 16. A solution of 2.50 g (8.56 mmol) of **15** in 15 mL of THF was decomposed with 15 mL of 1.8 M (25.7 mmol) ethereal methyllithium as described for **8** to give a pentane solution containing 0.88 g (95%) of **16** in greater than 99% purity as determined by VPC. A solvent-free sample was obtained by preparative VPC (10 ft × 0.25 in., 4% SF-96 on Chromosorb G, 95 °C) with properties identical with those reported.[20]

Preparation of Deuterated Pulegones. A. Pulegone-*2,2,9,9,9-d*$_5$. A mixture of 1.00 g (6.57 mmol) of pulegone and 1.00 g (9.43 mmol) of sodium carbonate in 20 mL of deuterium oxide was heated under reflux under nitrogen for 4 h. The reaction mixture was cooled and extracted four times with dichloromethane. The combined extracts were dried over sodium sulfate and concentrated by rotary evaporation. The residue was evaporatively distilled (oven 125 °C (5 mm)) to give 0.73 g (71%) of colorless liquid. This material contained approximately 10% of the β,γ isomer as determined by VPC analysis. A pure sample was obtained by chromatography on silica gel using 5% ether–pentane for elution: NMR (CCl_4) δ 3.0–1.0 (m, 5), 1.74 (s, 3), 0.98 (d, 3, J = 6 Hz); mass spectrum *m/e* (rel intensity) 82 (100), 156 (12), 157 (45), 158 (24), 159 (8).

B. Pulegone-*2,2-d*$_2$. A solution of 3.50 g (32.0 mmol) of 3-methylcyclohexanone-*2,2,6,6-d*$_4$[21] in 20 mL of ether was added to a solution of 32.3 mmol of lithium diisopropylamide in 170 mL of ether at such a rate as to maintain the internal temperature below −65 °C while the reaction flask was cooled in a dry ice–2-propanol bath. When the addition was complete, the solution was stirred for an additional 5 min, and a solution of 2.00 g (34.5 mmol) of acetone in ether was added at a rate as to maintain the internal temperature below −60 °C. After 3 min the suspension was poured into 300 mL of cold, saturated, aqueous ammonium chloride. Sufficient water was added to dissolve the salts, the ether layer was separated, and the aqueous phase was extracted three times with ether. The combined ether layers were washed with saturated sodium chloride, briefly dried over magnesium sulfate, and concentrated by rotary evaporation. The residue was distilled (bp 95–130 °C (20 mm)) to give 3.45 g (62%) of colorless 2-(2′-hydroxyisopropyl)-5-methylcyclohexanone-*2,2,6-d*$_3$: NMR (CCl_4) δ 2.90 (s br, 1), 1.80 (m, 5), 1.14 (s, 6), 1.01 (d, 3, J = 4 Hz); mass spectrum *m/e* 115 (M − CH_3COCH_3).

To a solution of the above ketol in 50 mL of dry benzene was added 0.25 g of toluenesulfonic acid monohydrate. The mixture was placed in a bath preheated at 130 °C and heated under reflux with water separation for 7 min. The reaction mixture was immediately cooled in an ice bath, and washed twice with saturated sodium bicarbonate, dried over sodium sulfate, and concentrated by rotary evaporation. The residue was evaporatively distilled (oven 150 °C (5 mm)) to give 2.63 g (84%) of pulegone-*2,2-d*$_2$: NMR (CCl_4) δ 2.80–0.80 (m, 5), 1.92 (s, 3), 1.78 (s, 3), 1.00 (d, 3, J = 6 Hz); mass spectrum *m/e* 154.

C. **Pulegone-*9,9,9,10,10,10-d*$_6$.** The ketol was prepared in the manner as above from 3-methylcyclohexanone and acetone-d_6 (99.5% D) (Stohler Isotope Chemical Co.): NMR (CCl_4) δ 2.80–0.80 (m, 8), 1.01 (d, 3, J = 4 Hz). The ketol was dehydrated as above to give pulegone-d_6: NMR δ 2.82–0.80 (m, 7), 1.00 (d, 3, J = 6 Hz); mass spectrum *m/e* 158.

Preparation of Deuterated Pulegone Tosylhydrazones. These compounds were prepared from the corresponding deuterated pulegones and tosylhydrazine by the procedure described for **15.** Pulegone tosylhydrazone *9,9,9,10,10,10-d*$_6$: mp 143–145 °C dec; NMR ($CDCl_3$) δ 7.55 (AB q, 4, $\Delta\nu$ = 37 Hz, J = 8 Hz), 2.90–1.00 (m, 7), 2.40 (s, 3), 0.84 (d, 3, J = 6 Hz). Pulegone tosylhydrazone-*2,2-d*$_2$: mp 143–144 °C dec; NMR ($CDCl_3$) δ 7.55 (AB q, 4, $\Delta\nu$ = 37 Hz, J = 8 Hz), 7.23 (s br, 1), 3.00–0.80 (m, 5), 2.40 (s, 3), 1.63 (s, 3), 1.42 (s, 3), 0.84 (d, 3, J = 6 Hz). Pulegone tosylhydrazone-*2,2,9,9,9-d*$_5$: mp 143–145 °C dec; NMR ($CDCl_3$) δ 7.55 (AB q, 4, $\Delta\nu$ = 37 Hz, J = 8 Hz), 7.23 (s br, 1), 3.00–0.80 (m, 5), 2.40 (s, 3), 1.42 (s, 3), 0.84 (d, 3, J = 6 Hz).

Decomposition of Deuterated Pulegone Tosylhydrazones. The majority of these decompositions were conducted on an analytical scale as described in the Representative Decomposition Procedure. Isomer ratios and deuterium content were determined by VPC or GC/MS analysis. Actual product ratios and deuterium content are given in the text. In the cases of pulegone tosylhydrazone-*9,9,9,10,10,10-d*$_6$ and pulegone tosylhydrazone-*2,2-d*$_2$ the decompositions were conducted on a preparative scale and samples of the deuterated dienes were isolated by preparative VPC. The following procedure is representative. To a solution of 1.70 g (5.22 mmol) of pulegone tosylhydrazone-*9,9,9,10,10,10-d*$_6$ in 30 mL of THF was added 10.4 mL of 1.5 M methyllithium in ether over 20 min while the reaction flask was cooled in an ice bath. After 1 h at 0 °C the reaction was quenched with water and worked up as described for **8.** Samples of the deuterated dienes were obtained by preparative VPC (10 ft × 0.25 in., 10% Carbowax 6M–10% KOH on Chromosorb W at 120 °C). The deuterated dienes had the following spectral data. *p*-Mentha-2,4(8)-diene-*9,9,9,10,10,10-d*$_6$ (**6**-d_6): NMR (CCl_4) δ 6.32 (dd, 1, J_1 = 1, J_2 = 10 Hz), 5.43 (dd, 1, J_1 = 3, J_2 = 10 Hz), 1.05–2.75 (m, 5), 1.03 (d, 2, J = 7 Hz); mass spectrum *m/e* 142 (M^+). *p*-Mentha-3,8-diene-*9,9,10,10,10-d*$_5$ (**7**-d_5): mass spectrum *m/e* 141 (M^+). *p*-Mentha-2,4(8)-diene-*2-d*$_1$ (**6**-d_1): NMR (CCl_4) δ 6.28 (s br, 1), 2.70–1.05 (m, 4), 1.70 (s, 6), 1.00 (d, 3, J = 7 Hz); mass spectrum *m/e* 137 (M^+). *p*-Mentha-3,8-diene-*2,2-d*$_2$ (**7**-d_2): NMR (CCl_4) δ 5.73 (s br, 1), 4.88 (s br, 1), 4.77 (s br, 1), 2.46–1.20 (m, 5), 1.85 (s, 3), 0.99 (d, 3, J = 7 Hz); mass spectrum *m/e* 138 (M^+). *p*-Mentha-2,4(8)-diene-*2,9,9,9-d*$_4$ (**6**-d_4): mass spectrum *m/e* (rel intensity) (parent ion cluster) 139 (15.6), 140 (56.5), 141 (27.8) *p*-Mentha-3,8-diene (mixture of deuterated material): mass spectrum *m/e* (rel intensity) (parent ion cluster) 139 (2), 140 (10), 141 (38), 142 (35), 143 (14), 144(2).

Preparation of 17. A solution of 165 mg (1.23 mmol) of a ca. 1:9 mixture of dienes **6** and **7** and 690 mg (4.86 mmol) of dimethyl acetylenedicarboxylate in 1 mL of benzene was heated under reflux under nitrogen for 1 h. The reaction mixture was chromatographed on 25 g of silica gel. The column was eluted with 40 mL of pentane followed by elution with 10% ether–pentane (25-mL fractions) to give 109 mg (37%) of colorless, diastereomeric cycloadducts in fractions 13–20 which partially solidified upon standing at 0 °C: NMR ($CDCl_3$, 100 MHz) δ 3.81–3.75 (three singlets due to diastereomeric cycloadducts, 6), 3.24–2.74 (m, 2), 2.74–2.34 (m, 1), 2.34–1.18 (m, 7), 1.67 (s, 3), 1.10 and 0.90 (two doublets due to diastereomeric adducts, 3, J = 7 Hz).

Preparation of 17-*d*$_5$. A solution of 4.0 mg of a mixture of deuterated dienes **6** and **7** containing approximately 1.5 mg (1.0 μmol) of diene **7** and 50 μL (57.8 mg, 407 μmol) of dimethyl acetylenedicarboxylate in 200 μL of benzene was heated under reflux under nitrogen for 1.25 h. The reaction mixture was chromatographed on 4 g of silica gel. The column was eluted with pentane (6 ml) followed by 10% ether–pentane (6 mL fractions) to give approximately 0.5 mg of cycloadduct in fractions 7–11. This material was approximately a 2:1 mixture of diastereomers as determined by analytical VPC (5 ft × 0.125 in. glass column, 3% SE-30, 165 °C): NMR ($CDCl_3$, 100 MHz) δ 3.81–3.75 (3 s, 6), 3.24–2.74 (m, ≈ 1.5), 2.74–2.34 (m, 1), 2.34–1.18 (m, 7), 1.67 (s, ≈ 0.75), 1.10 and 0.90 (2 d, 3, J = 7 Hz).

Acknowledgment. The authors are indebted to Dr. J. F. Blount of Hoffmann-La Roche, Inc., for the x-ray analyses, to Dr. Lois Durham of Stanford University for 100-MHz ^{1}H NMR spectra, and to Dr. Paul Philip of the University of California for GC/MS analyses. The authors wish to express special thanks to Professor N. C. Yang for his cooperation in the preliminary portion of this study.

References and Notes

(1) A report of preliminary results appeared: *Tetrahedron Lett.*, 2951 (1976).
(2) This work was supported by Grant AM-00709, National Institute of Arthritis, Metabolism and Digestive Diseases, and The Hoffmann-LaRoche Foundation.
(3) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).
(4) (a) R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, *Tetrahedron Lett.*, 1811 (1975); (b) J. E. Stemke and F. T. Bond, *ibid.*, 1815 (1975).
(5) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973).
(6) R. O. Hutchins, M. Kacher, and L. Rua, *J. Org. Chem.*, **40**, 923 (1975).
(7) R. B. Bates, E. S. Caldwell, and H. P. Klein, *J. Org. Chem.*, **34**, 2615 (1969).
(8) (a) W. G. Kofron and M.-K. Yeh, *J. Org. Chem.*, **41**, 439 (1976). (b) M. E. Jung, P. A. Blair, and J. A. Lowe, *Tetrahedron Lett.*, 1439 (1976). (c) Recently, this type of stereoselective metalation of the α-carbon atom of *N,N*-dimethylhydrazones has been indicated: B. J. Corey and S. Knapp, *ibid.*, 4687 (1976).
(9) This change in isomer ratio clearly illustrates the synthetic utility of the hydrogen isotope effect in the preparation of isomeric substances from reactions where the loss of the proton is the rate-determining factor.
(10) W. H. Saunder and D. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).
(11) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953). In this treatment, k_1/k_2 for *9,10-d*$_6$-**5**-*E* is 97:3 (or 32.3) and k_1'/k_2' for *2-d*$_2$-**5**-*E* is 55:45 (or 1.22). Furthermore, $S = [(k_1/k_2)(k_1'/k_2')]^{1/2}$ and $I = [(k_1/k_2)/(k_1'/k_2')]^{1/2}$.
(12) The chemical shift assignments were made by D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1973, p 81. A study of chemical shift changes with concentration of europium shift reagent corroborated the assignments.
(13) Unless otherwise noted, the following general conditions were used in all

reactions. Infrared spectra were recorded using either a Perkin-Elmer 137 Infracord or a 237 grating spectrometer. NMR spectra were obtained with a Varian T-60 spectrometer with tetramethylsilane as an internal standard. Mass spectral analyses and elemental analyses were obtained from the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

(14) This direct procedure was first reported by Professor N. C. Yang and his associates at the University of Chicago.
(15) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965).
(16) H. C. Brown and C. P. Grag, *J. Am. Chem. Soc.*, **83**, 2952 (1961).
(17) K. Gollnick and G. Schade, *Tetrahedron*, 123 (1966).
(18) G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Am. Chem. Soc.*, **90**, 173 (1968).
(19) Prepared by the method of A. S. Dreiding and S. N. Nickel, *J. Am. Chem. Soc.*, **76**, 3965 (1954). This material was shown to be the *E* isomer using NMR data of J. E. Dubois and M. Dubois, *C. R. Acad. Sci.* **256**, 715 (1963).
(20) L. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **94**, 7761 (1972).
(21) Prepared by refluxing of mixture of 3-methylcyclohexanone and NaOD in D_2O for 4 h.

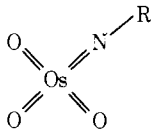
Synthesis of Dioxobis(*tert*-alkylimido)osmium(VIII) and Oxotris(*tert*-alkylimido)osmium(VIII) Complexes. Stereospecific Vicinal Diamination of Olefins[1]

Anthony O. Chong, Koichiro Oshima, and K. Barry Sharpless*

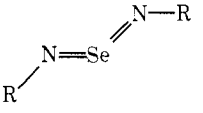
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received December 6, 1976*

Abstract: The synthesis and properties of dioxobis(*tert*-butylimido)osmium(VIII) (**5**) and oxotris(*tert*-butylimido)osmium(VIII) (**6**) are described. Other *tert*-alkylimido derivatives (*tert*-alkyl = *tert*-amyl, 1-adamantyl) were also prepared. These di- and triimido complexes were prepared by reaction of osmium(VIII) oxo compounds with *N*-*tert*-alkylphosphinimines, and are stable, yellow, crystalline compounds. Both the diimido complex **5** and the triimido complex **6** were found to react with monosubstituted and trans-disubstituted olefins to give cis vicinal diamines as the major products on reductive workup. Cyclic diamido complexes of osmium(VI) were isolated in the case of dimethyl and diethyl fumarate. Improved conditions are described for the synthesis of trioxo-*tert*-butylimidoosmium(VIII) and trioxo-*tert*-amylimidoosmium(VIII) from osmium tetroxide and the corresponding amine using water as solvent.

We have reported the vicinal oxyamination of olefins by *tert*-alkylimidoosmium(VIII) complexes **1**,[2] and the allylic amination of olefins by imido selenium reagents **2**.[3] Both



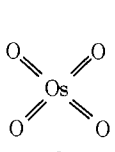
1



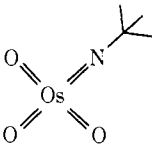
2

transformations are aza analogues of known oxygen insertion processes and represent a new class of reactions. More recently, we developed a catalytic oxyamination procedure[4] using chloramine-T and a catalytic amount of osmium tetroxide which has greatly increased the synthetic utility of the oxyamination reaction. It occurred to us that, by replacing more than one of the oxo groups of osmium tetroxide with imido groups, we might be able to extend this new class of reactions to include the direct vicinal diamination of olefins. Such a transformation is potentially of considerable value to synthetic chemists.

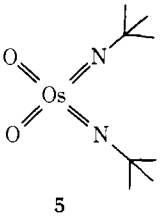
Thus, our aim was to complete the oxoimido series



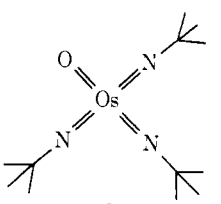
3



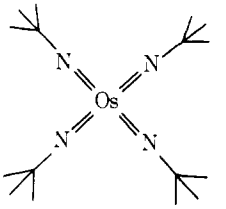
4



5



6



7

and to investigate the reactions of the new osmium imido compounds with olefins. Prior to our work, the only known members of the oxoimido series were osmium tetroxide (**3**) and the monoimido complex **4**. In this paper we report the first synthesis and characterization of dioxobis(*tert*-butylimido)osmium(VIII) (**5**) and oxotris(*tert*-butylimido)osmium(VIII) (**6**), and their reactions with olefins to give primarily vicinal diamines. We also report a simplified procedure for the preparation of the monoimido complex **4**.

Results and Discussion

Preparation and Characterization of Di- and Triimido Osmium(VIII) Complexes. The *tert*-butylimido complex **4** was first prepared from osmium tetroxide and *tert*-butylamine.[5] However, this procedure cannot be used to make the di-, tri-, and tetraimido compounds. The monoimido complex **4** is recovered unchanged after several days of exposure to neat *tert*-butylamine. It was then found that both the diimido complex **5** and the triimido complex **6** can be prepared directly from less substituted members of the oxoimido series by treatment with the appropriate number of equivalents of *N*-*tert*-butylphosphinimine (Scheme I). Although *N*-*tert*-butyltriphenylphosphinimine was satisfactory for preparing