the acetylene signal and the increase in intensity of the product signals relative to neopentane as an inert reference.

It appears that the reaction of acetylene is only with the 1:1 complex since the intensity of the low field signal relative to that of the inert reference does not change during the course of the reaction.

From the totality of these results we may conclude that acetylene forms a weak, labile complex with both the monomeric and trimeric forms of the $SbCl_5 \cdot CH_3COCl$ complex. The compound $SbCl_5 \cdot CH_3COCl \cdot HC{\equiv}CH$ then reacts further to give the final product. No stereochemical information about this ternary complex can be deduced from the present results.

Experimental Section

Chemicals. Aluminum chloride, acetyl chloride, and sulfur dioxide were purified as previously reported.[8] Antimony pentachloride was vacuum distilled into a storage container on the vacuum line. Acetylene, propyne, and neopentane were transferred directly from the supplier's cylinders to storage vessels on the vacuum line or to NMR sample tubes. 4-Chloro-3-penten-2-one was prepared from equilmolar quantities of $AlCl_3$, acetyl chloride, and propyne in CCl_4 at 0 °C. The reaction mixture was decomposed with an ice–water–HCl mixture. After separation the aqueous layer was further extracted with CCl_4. The combined organic layer was washed with water until free of HCl and dried over $CaCl_2$. The solvent was removed and the residue distilled under reduced pressure (bp 74 °C at 7.2 torr). The product was identified, via proton NMR, as 87% *E* and 13% *Z* isomers of 4-chloro-3-penten-2-one.

Sample Preparation. Some $AlCl_3$ was transferred, in a drybox, into an NMR tube closed with a Teflon high vacuum stopcock and weighed. Then the appropriate quantities of sulfur dioxide, neopentane, and acetyl chloride, all measured as vapors, were condensed into the NMR tube. The contents were thawed and mixed, and then the walls of the tubes were washed by distillation of solvent from the solution in the lower part. Finally, a known quantity of the alkyne (also measured as vapor) was condensed into the sample tube, which was then sealed under vacuum. Thawing and mixing of the sample was done in a dry ice–methanol bath. It was immediately transferred to the chilled NMR probe and its spectrum taken at low temperature. A similar procedure was followed with the $SbCl_5$-containing samples except that the $SbCl_5$ was vacuum-transferred and the quantities of all reagents, except acetylene, were verified by weighing the sample tube.

Rate Measurements. Proton and carbon-13 resonance spectra of the $AlCl_3$-containing samples were obtained in the Fourier transform mode on a Varian Associates XL-100 spectrometer equipped with a Nicolet 1180 computer and associated pulsing and power amplifier components. Spectra of the $SbCl_5$-containing samples were obtained with a Bruker AM-400 spectrometer. The variable temperature controllers were calibrated with a methanol sample for each series of spectra. Neopentane, which is inert under the experimental conditions, was used as internal reference and chemical shifts were converted to tetramethylsilane as zero with corrections of δ 0.92 for protons and δ 31.4 for ^{13}C. Concentrations are reported as mole fractions and all calculations are in this unit.

Samples were equilibrated for each reaction period and then the spectra were taken at low temperature as previously described.[8] The concentrations of the various species were calculated from the integrals of their resonance signals and the initial compositions of the samples. Rates of reactions occurring on the NMR time scale were obtained by comparison of spectra at several temperatures with theoretical spectra calculated by a stochastic method.[13]

Registry No. $AlCl_3$, 7446-70-0; antimony pentachloride, 7647-18-9; acetylene, 74-86-2; acetyl chloride, 75-36-5; propyne, 74-99-7; (*E*)-4-chloro-3-penten-2-one, 49784-51-2; (*Z*)-4-chloro-3-penten-2-one, 49784-64-7.

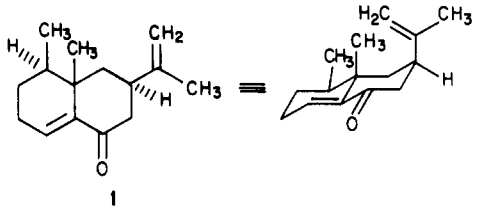
Supplementary Material Available: Proton and carbon-13 chemical shifts for the various species, and characteristic proton resonance spectra (6 pages). Ordering information is given on any current masthead page.

Communications

Stereoselective Insertion of the Isopropenyl Functionality

Summary: A new method of stereoselectively introducing the isopropenyl functionality in the axial orientation on a *trans*-9-methyldecalin ring system by the thermal decomposition of a diazene intermediate is described.

Sir: The isopropenyl moiety can be found widespread throughout terpene chemistry.[1] Classic Wittig methodology applied to methyl ketones can easily generate isopropenyl groups; however, this procedure necessitates the predefined stereochemistry of the precursor.[2] This approach therefore finds most of its utility in the preparation of the more thermodynamically stable products. In certain members of the sesquiterpene class, like the compound eremophilone 1,[3] the isopropenyl group displays an axial orientation on a decalin skeleton. To relieve the 1,3-diaxial



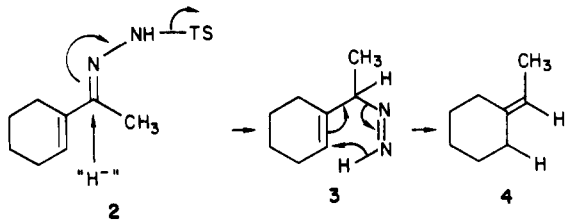
1

interaction, eremophilone would be expected to adopt a twist-boat conformation. Several efficient solutions to the problem of producing the less stable isomer have been reported.[4] We have been interested in this problem and the general problem of placing the isopropenyl group in a sterically more hindered position.

Several years ago, Hutchins and co-workers[5] demonstrated that (*p*-tolylsulfonyl)hydrazones of α,β-unsaturated ketones react with $NaBH_3CN$ to produce olefinic products with double-bond migration. The proposed mechanism

(1) (a) Simonsen, J. L.; Owen, L. N. "The Terpenes"; University Press: 1947; Vol. 1–5. (b) Devon, T. K.; Scott, A. I.; et al. Academic Press: New York, 1972; Vol. II.
(2) McGuire, H. M.; Odom, H. C.; Pinder, A. R. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1879.
(3) Pinder, A. R. *Fortschr. Chem. Org. Naturst.* **1977**, *34*, 81.
(4) (a) Coates, R. M.; Shaw, J. E. *J. Org. Chem.* **1970**, *35*, 2592. (b) Van der Gen, A.; van der Linde, L. M.; Witteveen, J. G.; Boelens, H. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 1034. (c) McMurry, J. E.; Musser, J. H.; Ahmad, M. S.; Blaszczak, L. C. *J. Org. Chem.* **1975**, *40*, 1829.
(5) Hutchins, R. O.; Kacher, M.; Rua, L. *J. Org. Chem.* **1975**, *40*, 923.

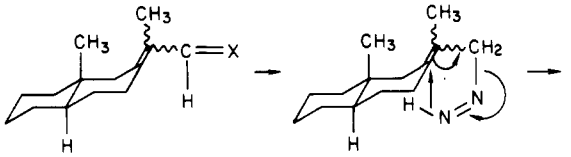
0022-3263/85/1950-2798$01.50/0



2 3 4

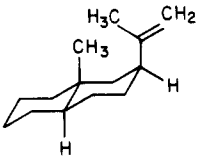
suggests that hydride reacts via 1,2 addition to the tosylhydrazone to produce a diazene intermediate which collapses with a 1,5-sigmatropic shift of hydrogen to produce an olefin with a transposed double bond. We recognized that a stereocenter could be formed by application of this reaction to a suitably substituted α,β-unsaturated aldehyde but also questioned whether the steric bulk in the molecule would direct the decomposition of the diazene intermediate.

To test this hypothesis, the α,β-unsaturated aldehyde **7** was chosen as a model. We envisioned that the corresponding *p*-tosylhydrazone **8** would react with hydride to produce the diazene intermediate **9**, which would decom-



7, X = O
8, X = NNHTS

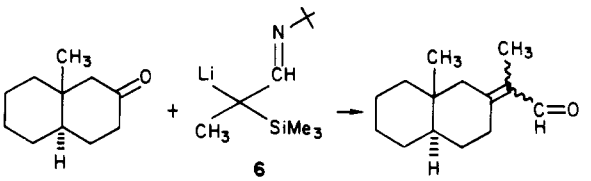
9



10

pose with the delivery of hydrogen to the equatorial face of the ring. The delivery of hydrogen to the less hindered side of the molecule would thus push the newly forming isopropenyl group into the desired axial orientation of the olefin **10**.

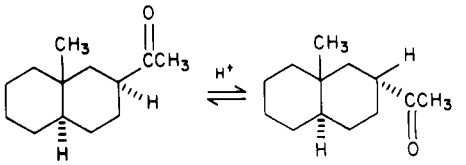
trans-9-Methyl-2-decalone (**5**)[6] was treated with 1.1 equiv of α-(trimethylsilyl)propionaldehyde *tert*-butylimine **6**, under the influence of LDA/THF, according to the



5 **6** **7**

procedure of Corey et al.[7] Quenching with tartaric acid and purification on silica gel (5% EtOAc/petroleum ether) produced the α,β-unsaturated aldehyde **7**, as a 2:1 mixture of *E*/*Z* isomers: mass spectrum, *m*/*e* 206 (M^+); IR ($CDCl_3$) 1670, 1625 cm^{-1}; NMR ($CDCl_3$) δ 10.30 and 10.20 (two singlets, 1 H), 1.75 (s, 3 H), 0.73 (s, 3 H); 80% yield. Treatment of the aldehydes **7** with (*p*-tolylsulfonyl)hydazide in EtOH yielded the *p*-tosylhydrazones **8**: purification on silica gel (20% EtOAc/petroleum ether), 75% yield; mp 65–110 °C; NMR ($CDCl_3$) δ 7.80 (d, 2 H), 7.30 (d, 2 H), 2.40 (s, 3 H), 0.60 and 0.55 (two singlets, 3 H each). Hydrazones **8** were treated with 4 molar equiv of $NaBH_3CN$ in a 1:1 sulfolane/DMF solvent at pH <3 which gave the olefinic product **10** as a 3:1 mixture of isomers:[5] silica gel chromatography (cyclohexane), 80% yield; mass spectrum, *m*/*e* 194 (M^+); NMR ($CDCl_3$) δ 4.82 and 4.70 (two multiplets, 2 H), 1.80 and 1.70 (two singlets, 3 H each), 0.86 (s, 3 H).

To show that the major isopropenyl product was the axial isomer, the olefinic mixture **10** was subjected to ozonolysis. The resultant methyl ketones **11** and **12** were



11 **12**

allowed to equilibrate in deuteriochloroform with a catalytic amount of concentrated HCl. Inspection of the proton NMR revealed that the mixture rapidly equilibrated to the more stable trans-axial, equatorial isomer **12**: cis isomer **11**, mass spectrum, *m*/*e* 194 (M^+); IR ($CHCl_3$) 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.18 (s, 3 H), 0.68 (s, 3 H); trans isomer **12**, mass spectrum, *m*/*e* 194 (M^+); IR ($CHCl_3$) 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.10 (s, 3 H), 0.82 (s, 3 H).

The generality of this procedure is further being explored on other substituted ring systems and terpene synthesis. We are also investigating some of the interesting mechanistic questions that have been raised in the discovery of this reaction.

Registry No. **5**, 1197-95-1; **6**, 96791-23-0; **7** (isomer 1), 96791-24-1; **7** (isomer 2), 96791-25-2; **8** (isomer 1), 96791-26-3; **8** (isomer 2), 96791-27-4; **10** (isomer 1), 96791-28-5; **10** (isomer 2), 96791-29-6; **11**, 96791-30-9; **12**, 96791-31-0; (*p*-tolylsulfonyl)hydrazide, 1576-35-8.

Michael G. Silvestri,* Patrick J. Bednarski
Department of Chemistry
California Polytechnic State University
San Luis Obispo, California 93407

Ernest Kho
Natural Sciences Division
University of Hawaii at Hilo
Hilo, Hawaii 96720-4091

Received October 16, 1984

(6) Nagata, W.; Kikkawa, I. *Chem. Pharm. Bull.* **1963**, *11*, 289.
(7) Corey, E. J.; Endres, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, 7.

Oxidation of 2,2′-Dihydroxy-1,1′-binaphthyl by Periodic Acid. Structure of the Product

Summary: Oxidation of 2,2′-dihydroxy-1,1′-binaphthyl with periodic acid gives a new nine-membered keto lactone. The implication of this result on the mechanism of oxidation of phenols by periodic acid has been pointed out.

Sir: Oxidation of aromatic substrates like hydrocarbons, phenols, etc., by periodic acid presents a confused mechanistic picture,[1-4] None of the published mechanistic proposals are consistent with a large body of facts and observations. In connection with an extended study of an

(1) Adler, E.; Anderson, G.; Edman, E. *Acta Chem. Scand., Ser. B* **1975**, *29*, 909.
(2) Fatiadi, A. J. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72a*, 341.
(3) Becker, H. D.; Gustafson, K. *J. Org. Chem.* **1979**, *46*, 428.
(4) Fatiadi, A. J. *Synthesis* **1974**, 229.

0022-3263/85/1950-2799$01.50/0