Studies Relating to the Synthesis of Cyclodecenes from Bicyclo[5.3.1]undecanediol Derivatives

JAMES A. MARSHALL,[1a] CHARLES J. V. SCANIO, AND WILLIAM J. IBURG[1b]

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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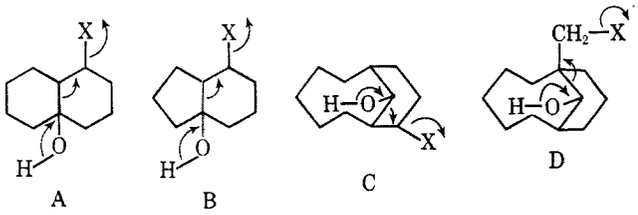
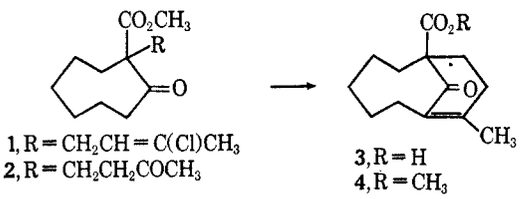
The monotosylate derivative **6** of 1-hydroxymethyl-8-methylbicyclo[5.3.1]undec-7-en-11-ol (**5**) was prepared from methyl 2-oxocyclooctanecarboxylate *via* condensation with methyl vinyl ketone, cyclization of the resulting diketo ester (**2**) in sulfuric acid, reduction of the cyclization products, acid **3** and ester **4**, with lithium aluminum hydride, and treatment of the diol thereby obtained with *p*-toluenesulfonyl chloride in pyridine. In refluxing methanolic sodium methoxide, hydroxy tosylate **6** underwent fragmentation, affording 2-methyl-5-methylene-*cis*-1-cyclodecenecarboxaldehyde (**11**). The *trans* isomer **9** was secured through oxidation of the corresponding alcohol **12** with manganese dioxide. Alcohol **12** was formed directly upon treatment of hydroxy tosylate **6** with lithium aluminum hydride in refluxing 1,2-dimethoxyethane. In refluxing acetic acid buffered with potassium acetate, hydroxy tosylate **6** afforded 8-methylbicyclo[5.4.0]undec-7-ene-1-carboxaldehyde (**14**); no cyclodecenes were detected. The structure of this aldehyde was confirmed through independent synthesis from ethyl 8-methylbicyclo[5.4.0]undec-7-en-9-one-1-carboxylate (**16**), the condensation product of ethyl 2-oxocycloheptanecarboxylate and ethyl vinyl ketone.

Few classes of compounds have provided chemists with more interesting and varied avenues for exploration than the medium-ring carbocycles.[2] Long noted for their anomalous chemical reactivity and preparative inaccessibility, these substances have more recently been implicated in terpene biosynthesis,[3] a view supported by the occurrence of medium-ring sesquiterpenes in nature.[4] The challenging synthetic problems posed by these natural products has provided much of the impetus for supplanting the classical acyloin ring closure method[5] of preparing medium-ring compounds with efficient stereoselective approaches. One alternative which has been successfully applied to a variety of substituted bicyclic compounds, including bicyclo[4.4.0]decanediols (*cf.* A),[6a] bicyclo[4.3.0]nonanediols (*cf.* B),[6b] and bicyclo[5.3.1]undecanediols (*cf.* C),[6c] is based on the heterolytic fragmentation[7] of 1,3-diol monosulfonic esters.



The work which we now describe was undertaken in order to extend our recently reported fragmentation of the bicyclo[5.3.1]undecanediol derivatives exemplified by C to other compounds with this carbon framework. We were particularly interested in examining the potential of carbinyl derivatives related to D for the synthesis of medium-ring exocyclic olefins. From a preparative viewpoint this approach offered a stereochemical advantage over the others previously examined because in D, the nucleofugal group[8] as well as the electrofugal group[8] is configurationally unrestricted.

Bicyclo[5.3.1]undecane derivatives appropriate to the present study are remarkably easy to prepare, thanks to Prelog and his co-workers,[9] who found that (γ-chlorocrotyl)cyclooctanone **1**, upon prolonged treatment with sulfuric acid,[10] afforded the keto ester **4**. Using essentially their method, we converted dione **2**, the condensation product of methyl 2-oxocyclooctanecarboxylate and methyl vinyl ketone, to a mixture of the bicyclic keto ester **4** and the corresponding acid **3** (eq 1). The latter afforded additional quantities of ester **4** upon treatment with methanolic sulfuric acid and both were readily reduced by lithium aluminum hydride to the diol **5**.



1, R = $CH_2CH{=}C(Cl)CH_3$
2, R = $CH_2CH_2COCH_3$

3, R = H
4, R = CH_3

(1)

Selective esterification of diol **5** with *p*-toluenesulfonyl chloride proceeded cleanly in pyridine, affording the monotosylate **6**. The structure of this derivative was easily ascertained from its nmr spectrum which displayed an AB quartet for the C-1 methylene protons at a downfield position relative to the chemical shift at which these protons appeared in the spectrum of the starting diol. The C-11 (carbinol) proton maintained nearly the same chemical shift in the spectra of both compounds. Upon oxidation with chromic acid, hydroxy tosylate **6** afforded a conjugated ketone, **8** (eq 2). The C-1 methylene protons of this compound gave rise to a sharp singlet in the nmr

(1) (a) Fellow of the Alfred P. Sloan Foundation; (b) National Science Foundation Undergraduate Summer Research Program participant, 1966.

(2) J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

(3) D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, 150 (1957); E. D. Brown, M. D. Solomon, J. K. Sutherland, and A. Torre, *Chem. Commun.*, No. 3, 111 (1967).

(4) F. Šorm, *Pure Appl. Chem.*, **2**, 533 (1961); F. Šorm and L. Dolejš, "Guaianolides and Germacranolides," Holden-Day, Inc., San Francisco, 1966, pp 75–99.

(5) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **30**, 1822 (1947).

(6) (a) P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, **30**, 3254 (1965); (b) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964); (c) J. A. Marshall and C. J. V. Scanio, *J. Org. Chem.*, **30**, 3019 (1965).

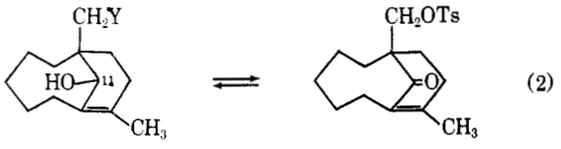
(7) C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 3 (1967); see also, A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952); R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1983 (1957).

(8) For a defintion of terms and a general survey of heterolysic fragmentation reactions, see the recent review by Grob and Schiess.[7]

(9) V. Prelog, P. Barman, and M. Zimmermann, *Helv. Chim. Acta*, **32**, 1284 (1949).

(10) *Cf.* O. Wichterle, *Collection Czech. Chem. Commun.*, **12**, 93 (1947).

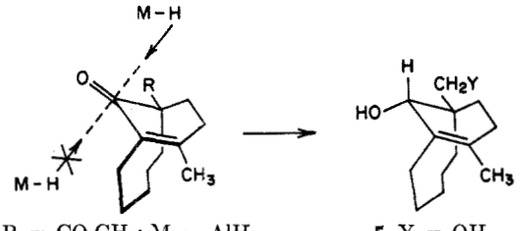
spectrum indicating their magentic equivalence. Reduction with ethanolic sodium borohydride regenerated hydroxy tosylate **6**.



(2)

5, Y = OH
6, Y = OTs
7, Y = H

Our assignment of stereochemistry to diol **5** is based on the assumption that hydridic reagents preferentially attack the less hindered face of the ketonic carbonyl grouping in keto ester **4** and keto tosylate **8**.[11]



4, R = CO_2CH_3; M = AlH_3
8, R = CH_2OTs; M = BH_3

5, Y = OH
6, Y = OTs

Models show that the pentamethylene bridge of these bicyclic ketones effectively shields approach to the carbonyl carbon. Thus attack from the cyclohexene side of the carbonyl should occur preferentially as shown below. Unfortunately, the oily and intractable nature of diol **5** and its tosylate derivative precluded accurate analysis of their stereochemical purity. However, the sharp features and clear patterns which dominate the nmr spectra of these compounds suggest that each is reasonably homogeneous. In any event, the stereochemistry of hydroxy tosylate **6**, as noted earlier, should not influence the fragmentation reaction (Scheme I).

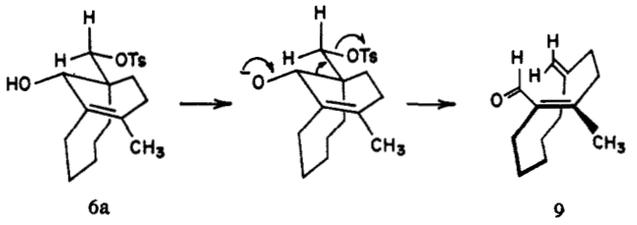
Fragmentations of 1,3-diol monotosylates have previously been effected with potassium *t*-butoxide in *t*-butyl alcohol. In order to provide more effective solvation for the tosylate grouping we chose methanolic sodium methoxide for our reaction. In this medium, at elevated temperatures, the starting material was slowly converted to a new compound whose infrared and nmr spectra indicated the presence of conjugated aldehyde, exocyclic methylene, and vinyl methyl groupings. Evidently, the desired reaction had taken place, albeit somewhat more slowly than was previously observed with related bicyclo[5.3.1]undecanediols bearing secondary tosylates as nucleofugal groups (*cf.* C). Considering the cleavage mechanism, we would expect the *trans*-cyclodecenecarboxaldehyde **9** as the kinetic product (Scheme I). However, in the strongly basic reaction medium, isomerization to a presumably more stable[12] *cis* isomer **11** could occur, conceivably *via* one of the β,γ-unsaturated aldehyde isomers (**10**). That this was indeed the case became evident from the transformations outlined in Scheme II.

We have previously shown that lithium aluminum

(11) *Cf.* J.-C. Richer, *J. Org. Chem.*, **30**, 324 (1965); J. A. Marshall and R. D Carroll, *ibid.*, **30**, 2748 (1965).

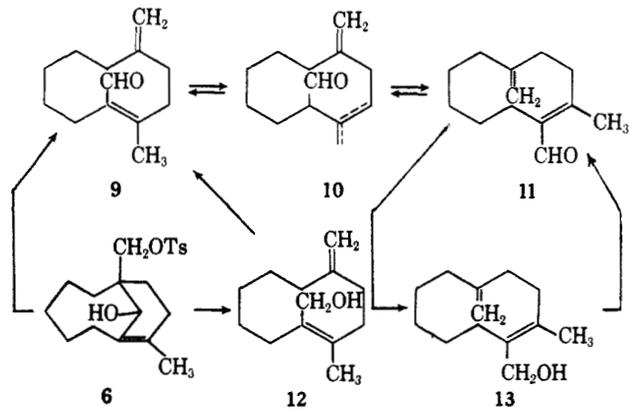
(12) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **81**, 3153 (1959).

SCHEME I



6a **9**

SCHEME II



9 **10** **11**

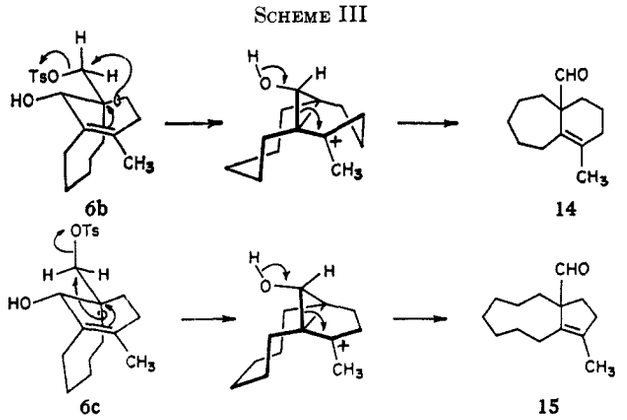
6 **12** **13**

hydride effects the fragmentation of certain bicyclo[5.3.1]undecanediol monotosylates (*cf.* C).[6c] The excess hydride employed in the reaction rapidly reduces the initially formed aldehyde and a high yield of the corresponding alcohol can thereby be realized. When applied to hydroxy tosylate **6**, this procedure afforded a mixture of isomeric alcohols readily separated by chromatography. The nmr spectrum of the earlier eluted isomer featured absorption peaks indicative of secondary alcohol, vinyl methyl, and quaternary methyl groupings in keeping with its formulation as alcohol **7**, the hydrogenolysis product of tosylate **6**. The second isomer contained peaks in its nmr spectrum arising from exocyclic methylene, primary alcohol (AB quartet), and vinyl methyl groupings, all characteristics of the cyclodecenylmethanol **12**. Since this compound was formed under conditions where reduction of the aldehyde should be much faster than isomerization of the conjugated carbon–carbon double bond, it can be formulated as the *trans* isomer **12**. Upon oxidation with manganese dioxide in benzene, alcohol **12** afforded the conjugated aldehyde **9**, an isomer of **11**, which smoothly isomerized to **11** in methanolic sodium methoxide. Alcohol **13**, an isomer of **12**, was secured through reduction of aldehyde **11**.

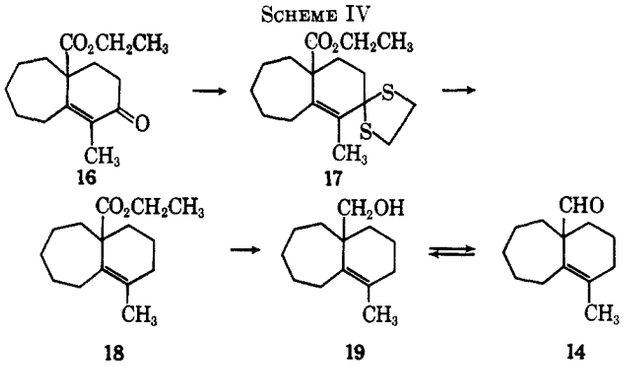
Supporting evidence for the stereochemistry of alcohols **12** and **13** came from their nmr spectra. Whereas the C-1 methylene protons of the *cis* isomer **13** appear as a singlet, the corresponding protons of the *trans* isomer **12** give rise to an AB quartet indicating magnetic nonequivalence in the latter but not the former. Furthermore, in **12** this pattern persists even at 200° where ordinary single-bond rotations should be rapid relative to the nmr time scale. Binsch and Roberts[13] have shown that while *trans*-cyclodecene is dissymmetric, the half-life of each optical form is extremely short, owing to the ease with which the vinylic hydrogens can pass beneath the octamethylene bridge, thus allowing the double bond to rotate. This rotation, which

(13) G. Binsch and J. D. Roberts, *ibid.*, **87**, 5157 (1965).

SCHEME III



SCHEME IV



interconverts an (*R*) and (*S*) series of conformers in *trans*-cyclodecene itself, should take place much more slowly with **12** where a methyl or methylol grouping must pass beneath the bridge. Thus, the nonequivalence of the methylene protons in unsaturated alcohol **12** can be attributed to the dissymmetry of the attached cyclodecene ring,[14] a situation obtaining only with the *trans* isomer.[15]

Hoping to find milder conditions for the preparation of unsaturated aldehyde **9**, we briefly explored solvolysis reactions of hydroxy tosylate **6**. In refluxing aqueous acetone containing sodium bicarbonate, essentially no reaction took place, even after prolonged heating. However, in refluxing acetic acid buffered with potassium acetate, hydroxy tosylate **6** was rapidly converted to an aldehyde whose nmr spectrum featured an unsplit formyl proton and a vinyl methyl group but completely lacked vinyl proton absorption. Apparently a reaction somewhat more involved than simple fragmentation had taken place. Two possibilities (Scheme III) leading to products (**14** and **15**) with the observed spectral properties could be visualized. The first of these (**6b** → **14**) seemed intuitively more reasonable and we therefore decided to synthesize aldehyde **14** by an unequivocal route.

To this end, the unsaturated keto ester **16** was prepared through condensation of ethyl vinyl ketone and methyl 2-oxocycloheptanecarboxylate. The thioketal derivative **17** was converted to the unsaturated ester **18** *via* desulfurization with Raney nickel in ethanol. Reduction to the alcohol **19** was accomplished with lithium aluminum hydride and oxidation of this compound with chromic acid afforded the desired aldehyde **14**. The infrared and nmr spectra of this aldehyde perfectly matched the spectra of the aldehyde secured through acetolysis of hydroxy tosylate **6**. Samples of aldehyde **14** prepared by both routes afforded alcohol **19** when treated with lithium aluminum hydride (Scheme IV).

The contrasting behavior of hydroxy tosylate **6** under basic and acidic conditions is somewhat surprising since analogous fragmentation reactions have been effected solvolytically.[16] We feel that the conformational mobility of the carbinyl tosylate grouping of **6** plays an important part in bringing about the observed disparity. Formula **6a** (Scheme I) depicts the conformation of hydroxy tosylate **6** which is best suited to the fragmentation reaction. This orientation should predominate in the conjugate base where the alternative staggered rotamers suffer from adverse dipole interactions. In acidic or neutral solution, conformer **6b** (Scheme III) should be favored because it affords the opportunity for internal hydrogen bonding. This conformer may be particularly important in the transition state of the solvolysis reaction where hydrogen bonding could assist heterolysis of the tosylate grouping. The alternative conformer **6c** leading to unsaturated aldehyde **15** cannot provide the aforementioned assistance to solvolysis.

(14) For examples of magnetic nonequivalence of methylene protons induced by an asymmetric environment, see W. L. Meyer, D. L. Davis, L. Foster, A. S. Levinson, V. L. Sarvin, D. Craig Shew, and R. F. Weddleton, *J. Am. Chem. Soc.*, **87**, 1573 (1965), and references cited therein.

(15) We plan to attempt optical resolution of this compound in the near future.

(16) *Cf.* P. S. Wharton, *J. Org. Chem.*, **26**, 4781 (1961), footnote 5.

Experimental Section[17]

Methyl 8-Methylbicyclo[5.3.1]undec-7-en-11-one-1-carboxylate (4).—To 87.5 ml of 0.1% methanolic sodium methoxide maintained at −20° was added dropwise and with stirring 65.6 g of methyl 2-oxocyclooctanecarboxylate[18] followed by 27.0 g of methyl vinyl ketone dissolved in 17.5 ml of methanol.[17a] After addition of the vinyl ketone was complete the solution was allowed to stand at −20° for 1.5 hr whereupon the base was neutralized with acetic acid and the mixture was concentrated under reduced pressure. The residue was diluted with aqueous sodium chloride and the product was isolated with ether,[17b] affording 89.9 g (100%) of diketo ester **2**, a colorless oil: λ_{max}^{film} 5.79–5.85 (ester and ketone CO), 7.98, 8.15, 8.35, 8.42, 8.90, 9.21, and 11.50 μ.

The above sample of diketo ester **2** was dissolved in 52 ml of ice cold concentrated sulfuric acid. After 1 week at room temperature, the solution was added dropwise to a vigorously stirred portion of ice water (*ca.* 1 l.). The product was isolated with ether[17b] and recrystallized from hexane, yielding 15.5 g of light yellow crystals, mp 67–68° (lit.[9] mp 70–71°). A second crop afforded 10.5 g, mp 67–68°, and a third crop gave an additional 1.5 g, mp 66–68°, for a total yield of 33.2%.

The alkaline washes from the above extraction were acidified with hydrochloric acid and extracted with ethyl acetate. The solid keto acid **3**, thereby obtained, was recrystallized from ethyl acetate–hexane, affording a first crop of 10.7 g, mp 178–180° (lit.[9] mp 175°), a second crop of 8.4 g, mp 178–179°, and a third crop of 4.5 g, mp 178–180° (30.2% yield of recrystallized acid).

A solution containing 3.3 g of keto acid **3** and 1 drop of sulfuric acid in 1.8 ml of methanol and 4.5 ml of 1,2-dichloroethane[19] was stirred at reflux for 6 hr. The mixture was diluted with water

(17) (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere over reaction mixtures. (b) The isolation procedure consisted of thoroughly extracting the reaction mixture with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. Pyridine was removed from the organic phase by washing with water and aqueous 2% sulfuric acid. Acids were removed by washing with saturated aqueous sodium bicarbonate or cold 5% aqueous sodium hydroxide. (c) Melting points were determined on a Fisher-Johns hot stage. (d) Microanalyses were done by Micro-Tech Laboratories, Inc., Skokie, Ill.

(18) Prepared from dimethyl carbonate and cyclooctanone by the procedure of S. J. Rhoads, J. C. Gilbert, A. W. Decora, T. R. Garland, R. J. Spangler, and M. J. Urbigkit, *Tetrahedron*, **19**, 1625 (1963).

(19) The procedure of R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

and extracted with ether, affording 3.0 g (86%) of solid keto ester **4**.

1-Hydroxymethyl-8-methylbicyclo[5.3.1]undec-7-en-11-ol (5).—A solution containing 4.44 g of keto acid **3** in 50 ml of 1,2-dimethoxyethane (DME) was carefully added to 3.04 g of lithium aluminum hydride in 50 ml of DME. After 24 hr at reflux, the mixture was cooled, diluted with 100 ml of ether, and cautiously treated with 6.08 ml of water and 4.86 ml of 10% aqueous sodium hydroxide. Stirring was maintained for 3 hr, the salts were removed by filtration, and the filtrate was distilled, affording 3.86 g (92%) of colorless oil: bp 105–115° (bath temperature) at 0.04 mm; λ_{max}^{film} 3.00 (OH), 8.40, 8.56, 8.67, 8.90, 9.28, 9.42, 9.58, 10.20, 10.49, 11.19, and 14.00 μ; $\delta_{TMS}^{CCl_4}$ 4.48 (OH) 2 H, 4.20 (C-11 H) 1 H, 3.47 (CH_2O– AB quartet, $\Delta\nu_{AB}$ = 19 Hz, J_{AB} = 11 Hz) 2 H, and 1.75 ppm (C-8 CH_3 doublet, J = 2 Hz) 3 H. The analytical sample, bp 141–143 (0.3 mm), was secured by redistillation.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.5; H, 10.6.

Comparable results were obtained when keto ester **4** was similarly reduced.

1-*p*-Toluenesulfonoxymethyl-8-methylbicyclo[5.3.1]undec-7-en-11-ol (6).—A solution containing 2.79 g (13.3 mmoles) of diol **5** in 13 ml of pyridine at 0° was treated portionwise with 2.78 g (14.6 mmoles) of *p*-toluenesulfonyl chloride. The mixture was allowed to stand at room temperature for 48 hr[17a] and 1 g of ice was added to destroy the excess acid chloride. After 10 min, water was added and the product was isolated with ether,[17b] affording 5.01 g (100%) of oily tosylate **6**: λ_{max}^{film} 2.82 (OH), 6.24 (aromatic C=C), 8.40, 8.50, 9.04, 9.40, 9.78, 10.40, 11.53, 11.86, 12.24, 13.90, 14.49, and 15.00 μ; $\delta_{TMS}^{CCl_4}$ 7.52 (–CH_A=CH_B– quartet, $\Delta\nu_{AB}$ = 28 Hz, J_{AB} = 8 Hz) 4 H, 4.16 (C-11 H) 1 H, 3.86 (CH_2O– AB quartet, $\Delta\nu_{AB}$ = 30 Hz, J_{AB} = 9 Hz) 2 H, 2.64 (OH) 1 H, 2.39 (aromatic CH_3) 3 H, 1.70 ppm (C-8 CH_3 doublet, J = 2 Hz) 3 H. This material was used directly without purification for subsequent experiments.

1-*p*-Toluenesulfonoxymethyl-8-methylbicyclo[5.3.1]undec-7-en-11-one (8).—A 364-mg sample of hydroxy tosylate **6** in 1 ml of acetone was cooled to 0° and treated with 0.5 ml of chromic acid reagent.[20] After 10 min, 2-propanol was added to destroy the excess oxidizing agent, the mixture was diluted with water, and the product was isolated with ether,[17b] affording 379 mg of solid ketone **8**. Recrystallization from ethyl acetate afforded 320 mg (88%), mp 106–110°. A second recrystallization gave 233 mg (64%): mp 115–117°; λ_{max}^{KBr} 5.97 (conjd CO), 6.25 (aromatic C=C), 8.38, 8.43, 9.08, 9.74, 10.11, 10.53, 10.76, 11.12, 11.82, 12.10, 12.50, 12.90, 13.72, and 14.87 μ; $\delta_{TMS}^{CCl_4}$ 7.53 (–CH_A=CH_B– quartet, $\Delta\nu_{AB}$ = 18 Hz, J_{AB} = 8 Hz) 4 H, 3.98 (CH_2O–) 2H, 2.42 (aromatic CH_3) 3H, and 1.79 ppm (C-8 CH_3) 3 H. The analytical sample, mp 118.5–120°, was secured after one additional recrystallization.

Anal. Calcd for $C_{20}H_{26}O_4S$: C, 66.27; H, 7.23; S, 8.85. Found: C, 66.4; H, 7.2; S, 8.8.

A 362-mg sample of keto tosylate **8** was allowed to stand at 40° with 38 mg of sodium borohydride in 8 ml of absolute ethanol. After 20 hr, the product was isolated with ether, affording 370 mg (100%) of oily hydroxy tosylate **6**. The infrared spectrum of this sample was identical with that of the material previously prepared from diol **6**.

2-Methyl-5-methylene-*trans*-1-cyclodecenecarboxaldehyde (9).—A solution containing 100 mg of alcohol **12** in 10.5 ml of benzene was stirred with 1.06 g of manganese dioxide[21] for 3 hr. The mixture was filtered through diatomaceous earth and the filtrate was distilled, affording 94 mg (95%) of aldehyde **9**: bp 50° (bath temperature) at 0.1 mm; λ_{max}^{film} 3.28 (vinyl CH), 3.64 (aldehyde CH), 6.01 (conjd CO), 6.18 (C=C), 8.70, 9.49, 11.19, and 13.37 μ; $\delta_{TMS}^{CCl_4}$ 10.16 (aldehyde CH) 1 H, 4.98 (C=CH_2, br) 2 H, and 2.15 ppm (vinyl CH_3) 3 H.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.9; H, 10.5.

2-Methyl-5-methylene-*cis*-1-cyclodecenecarboxaldehyde (11).

A. From Hydroxy Tosylate 6.—To a solution of sodium methoxide (from 0.5 g of sodium in 20 ml of methanol) was added 1.98 g of hydroxy tosylate **6**.[17a] The infrared spectra of aliquots removed at various times indicated that the tosylate was completely gone after 6 hr at reflux. Accordingly, the mixture was cooled, diluted with water, and the product was isolated with ether.[17b] Distillation afforded 0.89 g (85%) of colorless oily aldehyde **11**: bp 75° (bath temperature) at 0.3 mm; λ_{max}^{film} 3.28 (vinyl CH), 3.64 (aldehyde CH), 5.99 (conjd CO), 6.19 (C=C), 8.39, 8.68, 8.92, 10.70, 11.10, and 13.36 μ; $\delta_{TMS}^{CCl_4}$ 10.14 (aldehyde CH) 1 H, 4.85 and 4.71 (C=CH_2) 2 H, and 2.19 ppm (vinyl CH_3) 3 H.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.0; H, 10.7.

B. From Alcohol 13.—A solution containing 40 mg of alcohol **13** in 5 ml of benzene was stirred with 0.5 g of manganese dioxide for 3 hr. The mixture was filtered through diatomaceous earth and distilled, affording 37 mg (93%) of aldehyde **11** identical with the material prepared in part A.

Reaction of Hydroxy Tosylate 6 with Lithium Aluminum Hydride. A. 1,8-Dimethylbicyclo[5.3.1]undec-7-en-11-ol (7).—To a solution containing 0.39 g of lithium aluminum hydride in 20 ml of DME was added dropwise 1.00 g of hydroxy tosylate **6** in 15 ml of DME. After 6 hr at reflux, the mixture was cooled and cautiously treated with 0.78 ml of water and 0.62 ml of 10% aqueous sodium hydroxide. The resulting mixture was diluted with ether, stirred for 1 hr, and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on 30 g of silica gel. Elution with benzene afforded 0.21 g (40%) of oily alcohol **7**: bp 40° (bath temperature) at 0.2 mm; λ_{max}^{film} 2.87 (OH), 8.38, 8.56, 8.99, 9.22, 9.40, 9.57, 9.76, 10.17, 10.48, 10.73, and 14.02 μ; $\delta_{TMS}^{CCl_4}$ 3.78 (C-11 H) 1 H, 1.75 (vinyl CH_3) 3 H, and 1.00 ppm (C-1 CH_3) 3 H.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.41; H, 11.34. Found: C, 80.1; H, 11.2.

B. 2-Methyl-5-methylene-*trans*-1-cyclodecenylmethanol (12).—Elution of the column described in part A with 1% ether in benzene afforded 0.23 g (23%) of alcohol **12**, mp 67–69°, purified by distillation and subsequent sublimation of the solid distillate at 35° (0.1 mm): λ_{max}^{KBr} 3.10 (OH), 3.28 (vinyl CH), 6.08 (C=C), 8.37, 8.79, 9.51, 9.90, 10.21, 11.09, 11.27, 11.50, and 11.97 μ; $\delta_{TMS}^{CCl_4}$ 4.92 (C=CH_2, br) 2 H, 4.11 (CH_2O– AB quartet, $\Delta\nu_{AB}$ = 36 Hz, J_{AB} = 12 Hz) 2 H, 2.49 (OH) 1 H, and 1.85 ppm (vinyl CH_3) 3 H.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.41; H, 11.34. Found: C, 80.4; H, 11.2.

A neat sample of this alcohol showed the same AB quartet pattern at temperatures between 75 and 200°.

2-Methyl-5-methylene-*cis*-1-cyclodecenylmethanol (13).—A 218-mg sample of aldehyde **11** was stirred with 86 mg of lithium aluminum hydride in 4 ml of ether for 12 hr. Aqueous sodium hydroxide was added and, after the salts had granulated, the mixture was filtered. Distillation of the filtrate afforded 187 mg (85%) of oily alcohol **13**: bp 75–80° (bath temperature) at 0.1 mm; λ_{max}^{film} 3.03 (OH), 3.28 (C=C), 6.10 (C=C), 10.00, and 11.17 μ; $\delta_{TMS}^{CCl_4}$ 4.79 and 4.62 (C=CH_2) 2 H, 3.95 (CH_2O–) 2 H, 2.55 (OH, br) 1 H, and 1.71 ppm (vinyl CH_3) 3 H.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.41; H, 11.34. Found: C, 80.2; H, 11.0.

8-Methylbicyclo[5.4.0]undec-7-en-1-carboxaldehyde (14). A. *Via* Acetolysis of Hydroxy Tosylate 6.—A 1.09-g sample of hydroxy tosylate **6** was dissolved in 12 ml of 0.5 *N* potassium acetate in acetic acid and the solution was heated at reflux for 2 hr,[17a] cooled, and poured over 50 g of ice. The mixture was neutralized with 10% aqueous sodium hydroxide and the product was isolated with ether[17b] and distilled, affording 0.46 g (80%) of colorless oily aldehyde **14**: bp 50–60° (bath temperature) at 0.04 mm; λ_{max}^{film} 3.70 (aldehyde CH), 5.80 (CO), 6.00 (C=C), 10.42, 11.06, 14.10, and 14.39 μ; $\delta_{TMS}^{CCl_4}$ 9.42 (aldehyde CH) 1 H and 1.70 ppm (vinyl CH_3) 3 H. The gas chromatogram indicated a purity of 92%.[22] The analytical sample was secured after two successive distillations.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.5; H, 10.8.

B. *Via* Oxidation of Alcohol 19.—A solution containing 87 mg of alcohol **19** in 1 ml of acetone at 0° was treated with 0.26 ml of chromic acid reagent and the product was isolated with ether,[17b] affording 54 mg of aldehyde **19**. The infrared spectrum and vpc retention time (peak enhancement) showed it to be identical with the material prepared in part A.

Ethyl 8-Methylbicyclo[5.4.0]undec-7-en-9-one-1-carboxylate (16).—To a solution of sodium ethoxide (prepared from 50 mg of sodium and 25 ml of ethanol) was added 18.4 g of ethyl 2-

(20) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon *J. Chem. Soc.*, 39 (1956).

(21) Obtained from Beacon Chemical Co., a division of Lehn and Fink Products, Cambridge, Mass.

(22) A 13 ft × 0.25 in. column containing 16% Carbowax 20M on 60–80 mesh Diatoport S was used.

oxocycloheptanecarboxylate.[23] The solution was cooled to −20° and 12.6 g of ethyl vinyl ketone was added dropwise with stirring.[17a] After 1 hr at −20° and 1 hr of warming to room temperature, the mixture no longer gave a ferric chloride test. Accordingly, 5 ml of 3 *N* ethanolic sodium ethoxide was added and after 5 hr at room temperature, the mixture was neutralized with acetic acid and concentrated under reduced pressure. Water was added to the residue and the product was isolated with ether[17b] and distilled. The bulk of the material (18.8 g), bp 102–116° at 0.1 mm, contained mainly the conjugated ketone **16** along with some uncyclized diketo ester. A 10.3-g sample of this mixture was heated at 60° with 11.1 ml of 1.5 *N* ethanolic sodium ethoxide for 6 hr to effect complete aldol cyclization. Work-up, according to the procedure described above, afforded 5.9 g (55%) of the keto ester **16**: bp 110–120° (0.07 mm); λ_{max}^{film} 5.81 (ester CO), 6.00 (conjd CO), 6.20 (C=C), 8.01, 8.21, 8.42, 8.68, 9.09, 9.23, 9.45, 9.72, 10.06, 10.18, 10.39, 10.72, 11.25, 11.57, and 12.01 μ; $\delta_{TMS}^{CCl_4}$ 4.12 (–OCH_2– quartet, J = 7 Hz), 1.74 (C-8 CH_3), and 1.22 ppm (CH_2CH_3 triplet, J = 7 Hz). The analytical sample, bp 111–112° (0.07 mm), was secured by redistillation.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.7; H, 8.9.

Ethyl 9,9-Ethylenedithio-8-methylbicyclo[5.4.0]undec-7-ene-1-carboxylate (17).—The procedure of Fieser was employed.[24] A solution containing 2.50 g of keto ester **16**, 3 ml of 1,2-ethanedithiol, and 3 ml of boron trifluoride etherate in 30 ml of acetic acid was allowed to stand at room temperature for 1 hr.[17a] The mixture was poured into brine and the product was isolated with ether[17b] and distilled, affording 2.98 g (91%) of colorless oily thioketal **17**: bp 150–160° (bath temperature) at 0.04 mm; λ_{max}^{film} 5.80 (ester CO), 8.00, 8.39, 9.10, 9.19, 9.72, and 10.42 μ; $\delta_{TMS}^{CCl_4}$ 4.01 (–OCH_2– quartet, J = 7 Hz), 3.42–3.17 (–SCH_2–CH_2S– multiplet), 1.91 (C-8 CH_3), and 1.09 ppm (CH_2CH_3 triplet, J = 7 Hz). The analytical sample, bp 155–160° (bath temperature) at 0.04 mm, was secured by redistillation.

Anal. Calcd for $C_{17}H_{26}O_2S_2$: C, 62.53; H, 8.03; S, 19.64. Found: C, 62.4; H, 8.1; S, 19.5.

Ethyl 8-Methylbicyclo[5.4.0]undec-7-ene-1-carboxylate (18).—A 2.53-g sample of thioketal **17** in 45 ml of ethanol was stirred with 45 g of W-2 Raney nickel[25] at room temperature for 1 hr and at reflux for 5 hr.[17a] The mixture was cooled, filtered through diatomaceous earth, and the filtrate was distilled, affording 1.36 g (74%) of colorless oily ester **18**: bp 50–60° (bath temperature) at 0.04 mm; λ_{max}^{film} 5.80 (ester CO), 8.10, 8.20, 8.50, 8.62, 9.10, and 9.65 μ; $\delta_{TMS}^{CCl_4}$ 4.06 (–OCH_2– quartet, J = 7 Hz), 1.65 (C-8 CH_3), and 1.20 ppm (–CH_2CH_3 triplet, J = 7 Hz). The analytical sample was secured after two successive distillations.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 76.4; H, 10.3.

8-Methylbicyclo[5.4.0]undec-7-enylmethanol (19). A. *Via* **Reduction of Ester 18.**—A mixture containing 704 mg of ester **18** and 228 mg of lithium aluminum hydride in 10 ml of ether was stirred at room temperature for 12 hr. Water (0.46 ml) and 10% aqueous sodium hydroxide (0.37 ml) were added cautiously and, after 2 hr of continued stirring, the mixture was filtered. The ether was removed from the filtrate under reduced pressure affording 532 mg of colorless oil which readily solidified. Recrystallization from hexane gave 418 mg (72%) of crystalline alcohol **19**: mp 62–64°; λ_{max}^{KBr} 3.08 (OH), 8.23, 8.31, 8.45, 8.51, 8.79, 9.03, 9.14, 9.29, 9.70, 10.00, 10.41, 10.91, 11.48, 11.88, 12.12, 12.79, 13.12, and 14.68 μ; $\delta_{TMS}^{CCl_4}$ 3.39 (–CH_2O– AB quartet, $\Delta\nu_{AB}$ = 12.5 Hz, J_{AB} = 11 Hz), 3.11 (OH), and 1.61 ppm (C-8 CH_3). The analytical sample, mp 63–65°, was secured after two additional resrystallizations from hexane.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.4; H, 11.4.

B. *Via* **Reduction of Aldehyde 14.**—A 100-mg sample of aldehyde **14** in 1 ml of ether was stirred with 58 mg of lithium aluminum hydride for 2 hr at room temperature. Water (0.12 ml) and 10% aqueous sodium hydroxide (0.09 ml) were added and after 2 hr of continued stirring the mixture was filtered and the filtrate was concentrated, affording 95 mg of solid. Recrystallization from hexane gave 46 mg (46%) of alcohol **19**, mp 60–62°, undepressed upon admixture of the material obtained in part A. The infrared spectra of the two samples were superimposable.

Registry No.—**2**, 14320-32-2; **5**, 14320-18-4; **6**, 14233-74-0; **7**, 14233-75-1; **8**, 14233-76-2; **9**, 14233-77-3; **11**, 14233-78-4; **12**, 14233-79-5; **13**, 14233-80-8; **14**, 14233-81-9; **16**, 14233-82-0; **17**, 14233-83-1; **18**, 14233-84-2; **19**, 14233-85-3.

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(23) Prepared from cycloheptanone and diethyl carbonate.[18]

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Stereospecific Synthesis of 1,4-Dienes. II[1]

GO HATA AND DAN AOKI

Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura, Japan

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Effects of diene structure in the iron(III) acetylacetonate–triethylaluminum-catalyzed addition of ethylene to substituted 1,3-dienes have been investigated. This reaction gives exclusively *cis* isomers of 1,4-dienes. Methyl and phenyl substituents of the 1,3-dienes control the orientation of addition of ethylene. 1,3-Dienes, of which cisoid conformations are sterically unfavored, do not react with ethylene. Addition of propylene to 1,3-butadiene gives 2-methyl-1-*cis*-4-hexadiene and 1-*cis*-5-heptadiene.

In connection with catalytic behaviors of transition metals, the reaction of 1,3-dienes with ethylene has received considerable attention in recent years.[2–6] In a preliminary communication,[4] the novel synthesis of 1,4-dienes by the reaction of 1,3-dienes with ethylene in the presence of a catalyst consisting of iron(III) acetylacetonate [$Fe(AcAc)_3$] and triethylaluminum has been reported. The present paper is concerned with steric factor and orientation of the reaction by this catalyst. The reaction of substituted 1,3-dienes with ethylene and that of 1,3-butadiene with propylene have been investigated.

(1) Presented at the Seventh World Petroleum Congress, Mexico, April 1967.

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Results

Reaction of Substituted 1,3-Dienes with Ethylene.—The catalyst was prepared by mixing iron(III) acetylacetonate and triethylaluminum in 1,3-dienes. When prepared in the absence of the dienes, the catalyst showed only low activity. The reaction was carried out by stirring at 30° under ethylene pressure (40 kg/