tra.[14]

1-Chloro-1-(α-nitraminoethyl)cyclohexane (28). The acidification technique of Meyers and Nabeya[8] was modified for this imine reduction. To a stirred solution of 4.00 g (19.5 mmol) of methyl 1-chlorocyclohexylnitroketimine in 100 mL of dioxane, 100 mL of absolute ethanol, and 24 drops of glacial acetic acid with an ice/acetone bath for cooling was added 12.8 g of sodium borohydride in small portions to control frothing. The mixture was allowed to stir for 30 min at reduced temperature, 60 drops of glacial acetic acid was added, and stirring was continued for 60 min at reduced temperature, followed by 30 min at room temperature. The mixture was carefully diluted with 400 mL of ca. 3% aqueous acetic acid and extracted with methylene chloride. The organic extracts were dried, filtered, and concentrated in vacuo to give a yellow oil which crystallized from hexane. Recrystallization from hexane yielded 1.66 g (8.03 mmol, 41%) of 1-chloro-1-(α-nitraminoethyl)cyclohexane, mp 84–85 °C (lit.[14] mp 91–92.5 °C). Both NMR and IR were in agreement with the reported spectra.[14]

3-Chloro-3-methyl-2-nitroiminobutane. A solution of 200 g (2.85 mol) of 2-methyl-2-butene in 1200 mL of methylene chloride was stirred at 0 °C while nitrosyl chloride was slowly bubbled into the solution for 1.3 h. The resultant blue solution was stirred for 1.5 h at 0 °C and concentrated in vacuo without heating to give ca. 200 g of 3-chloro-3-methyl-2-butanone oxime as an oily blue-green solid. Further purification was not attempted.

The 200 g of 3-chloro-3-methyl-2-butanone oxime in 1600 mL of methylene chloride was stirred at 0 °C while nitrosyl fluoride was slowly bubbled into the solution for 1.25 h. The green solution was stirred at 0 °C for 3.5 h, followed by 1.5 h at room temperature. The mixture was slowly poured into saturated aqueous sodium carbonate and washed with saturated aqueous sodium carbonate, water, and brine. The organic layer was dried, filtered, and concentrated in vacuo to give a blue oil which was distilled giving 21.00 g (0.128 mol, 4% overall) of 3-chloro-3-methyl-2-nitroiminobutane, bp 48–50 °C (0.5 mm).

The spectral data for the oxime were: IR ($CHCl_3$) 3.01, 3.32, 3.81 (br), 6.36, 6.96, 7.24, 7.32, 7.76, 8.13, 8.71, 9.01, 9.86, 10.06, 10.56, 11.11 μm; NMR ($CDCl_3$) τ 0.56 (s, 1 H, C=NOH), 7.95 (s, 3 H, CH_3C=NOH), 8.23 (s, 6 H, $(CH_3)_2CCl$).

The spectral data for the nitrimine were: IR (neat) 3.40, 3.47, 6.17, 6.36 (s), 6.92, 7.34, 7.65, 7.85, 8.12, 8.72, 9.01, 9.82, 10.12, 10.52, 10.94, 11.52, 11.87, 13.32 μm; NMR ($CDCl_3$) τ 7.76 (s, 3 H, $-C(CH_3)$=N–), 8.17 (s, 6 H, $(CH_3)_2CCl$).

Anal. Calcd for $C_5H_9N_2O_2Cl$: C, 36.49; H, 5.51; N, 17.02; Cl, 21.54. Found: C, 36.30; H, 5.59; N, 17.27; Cl, 21.51.

3-Chloro-3-methyl-2-nitraminobutane (29). The acidification technique of Meyers and Nabeya[8] was modified for this imine reduction. To a stirred solution of 4.04 g (24.6 mmol) of 3-chloro-3-methyl-2-nitroiminobutane in 100 mL of dioxane, 100 mL of absolute ethanol, and 24 drops of acetic acid at 0 °C was added 5.18 g (136 mmol) of sodium borohydride as fast as possible while still controlling frothing. The mixture was allowed to stir for 20 min at 0 °C, 60 drops of glacial acetic acid were added, and stirring was continued for 1 h at 0 °C, followed by 15 min at room temperature. The mixture was carefully diluted with 400 mL of ca. 3% aqueous acetic acid and extracted with methylene chloride. The combined organic extracts were dried, filtered, and concentrated in vacuo to give a light yellow liquid which was taken up in ether, washed with water (to remove dioxane), dried, filtered, and concentrated in vacuo to give a light yellow liquid which was distilled, giving 1.73 g (10.4 mmol, 42%) of 3-chloro-3-methyl-2-nitraminobutane as a clear liquid, bp 60 °C (0.1 mm).

The spectral data were: IR ($CHCl_3$) 2.90, 3.30, 6.35, 6.88, 7.25, 7.45, 7.74, 8.23, 8.75, 8.85, 9.17, 9.68, 11.00, 12.15 μm; NMR ($CDCl_3$) τ 1.45 (br m, 1 H, >NH), 5.56 (br q, 1 H, J = 6.5 Hz, $>CHNHNO_2$), 8.33 (s, 3 H, $CH_3C(Cl)<$), 8.36 (s, 3 H, $CH_3C(Cl)<$), 8.61 (d, 3 H, J = 6.5 Hz, $>C(CH_3)NH–$).

Anal. Calcd for $C_5H_{11}N_2O_2Cl$: C, 36.05; H, 6.66; N, 16.81; Cl, 21.28. Found: C, 36.09; H, 6.52; N, 16.28; Cl, 21.49.

Registry No.—**5,** 63866-33-1; **6,** 63866-34-2; **7,** 604-35-3; **8,** 1912-54-5; **9,** 31239-32-4; **10,** 31239-36-8; **11,** 63215-89-4; **17,** 13943-77-6; **18,** 63866-35-3; **19,** 63866-36-4; **20,** 63866-37-5; **21,** 63866-38-6; **22,** 63866-39-7; **24,** 1256-31-1; **25,** 4025-59-6; **26,** 63866-40-0; **27,** 63866-41-1; **29,** 63215-91-8; nitric acid, 7697-37-2; 2-hydroxy-10-methyldecalin, 2547-28-6; 2-methyl-2-butene, 513-35-9; 3-chloro-3-methyl-2-nitriminobutane, 63215-90-7; 3-chloro-3-methyl-2-butanone oxime, 3238-16-2.

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Chirality of Nucleophilic Reactions of Axial Aldehydes and Methyl Ketones in the Diterpene Series

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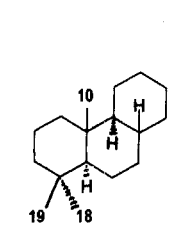
Received January 28, 1977

The conformation of the 4β aldehyde and methyl ketone groups in the podocarpane series has been reinvestigated. Felkin's hypothesis on the geometry of the most favored transition state for a nucleophilic reaction on these aldehydes and ketones combined with a calculation of the energy profile for the rotation around the C_α—C=O bond gives explanations for both chemical results and NMR data.

I. Introduction

The determination of the most stable conformation of the axial aldehyde group (4β) in the podocarpane **1** or ursane **2** series relies upon the following arguments.[1] (a) In the ^1H NMR spectra the signal associated with the aldehyde proton in a compound such as **3a** appears as a doublet (J = 1.6 Hz)[2] which has been shown to be due to long-range ^4J coupling with the 3α proton. The conformation of 3β-hydroxyaldehyde **4a**



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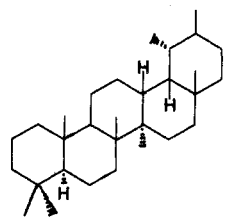

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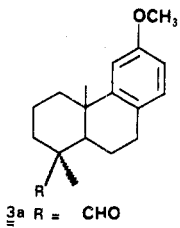
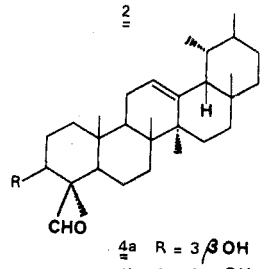
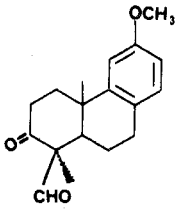


3a R = CHO
3b R = CDO
3c R = CH_2OAc
3d R = CH_2OH



4a R = 3β OH
4b R = 3α OH



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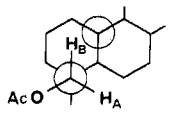
is frozen owing to strong hydrogen bonding (no "free" OH vibration in the IR spectrum). Upon irradiation of the 3α proton the aldehyde doublet merges into a singlet. No such coupling can be detected in the NMR spectra of the 3α-hydroxyaldehyde **4b** or the 3-ketoaldehyde **5**. (b) Reduction of aldehyde **3a** with $LiAlD_4$ is highly stereoselective. It gives an alcohol whose acetate A exhibits a singlet at δ 3.95 in the NMR spectrum instead of the classical quartet found in its nondeuterated counterpart (Figure 1).

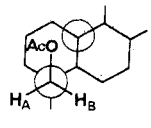
Likewise, reduction of the deuterated aldehyde **3b** is nearly stereospecific. The corresponding acetate B gives rise to a singlet at δ 4.26 (Figure 1). In order to get a deeper knowledge of the reduction mechanism, a careful study of the chirality of acetates A and B was undertaken.

II. Nuclear Overhauser Effect in the Acetates

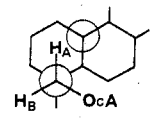
In the NMR spectrum of acetate **3c** the two protons bonded to C-19[3] are expected to appear as an AB quartet.[4,5] In fact, each of the two A lines is split into two parts of equal intensity (J = 0.5 Hz).[6] No modification of the shape of this multiplet was observed between −40 and 110 °C. Thus one of the conformations must be highly favored. A reasonable assumption is that the *most stable conformation can be represented by* **6a**.[7] Rotamer **6b** is ruled out, since the acetate moiety is too



6a



6b



6c

bulky for its having any tendency to rest close to the angular methyl group. Rotamer **6c** cannot be accepted either without violating the present status of ^4J σ coupling, i.e., upon irradiation of any of the two methyl groups no simplification of the A part of the signal taking place.

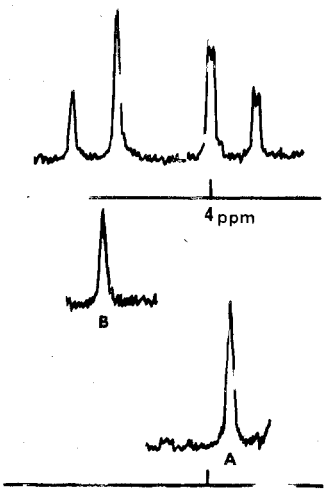


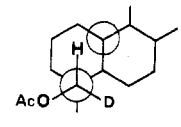
Figure 1.

Table I. Chemical Shifts of the Two CCH_3 Groups of Podocarpinol *O*-Methyl Ether 3d in Various Solvents[a]

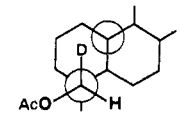
Solvent	δ Me-18, ppm	δMe-20, ppm
CCl_4	1.18	1.02
$CDCl_3$	1.19	1.04
$CCl_2{=}CCl_2$	1.15	1.01
Pyridine	1.21	1.22

[a] Me_4Si as internal reference.

If the assumption is correct, it should be easy to determine the chirality of the two previously mentioned deuterated acetates A and B, either **7** or **8**, by NMR spectroscopy. Upon



7



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irradiation of the angular methyl groups the nuclear Overhauser effect (NOE) on the italicized proton of the $CH_3COOCHD$ group should be higher in **7** than in **8**. It is therefore necessary to make sure that the designation of the two CCH_3 signals is correct.

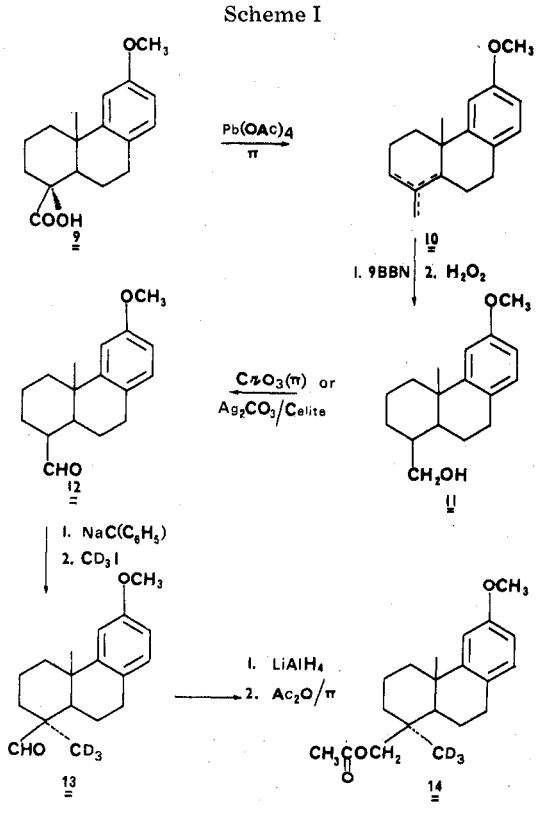
According to Wenkert[8] the peak observed at 1.20 ppm is due to the angular methyl group. However, NOE experiments, carried out on the basis of this assignment and the previously accepted reaction mechanism of aldehyde reduction, led to results inconsistent with the hypothesis of rotamer **6a** being the most stable conformer. Thus it was necessary to check Wenkert's assignment, however sound it seems to be.[9] Thus a synthesis of the deuterated acetate **14** (Scheme I) was undertaken. Decarboxylation of podocarpic acid *O*-methyl ether **9** by lead tetraacetate in pyridine[10] gives a mixture of three olefins which without separation was converted to the noralcohol **11** by hydroboration (9-BBN)[11] and then to the noraldehyde **12** on oxidation with Collins reagent or silver carbonate on Celite. The crude aldehyde was alkylated with trideuteriomethyl iodide in the presence of triphenylmethyl sodium in a mixture of diethyl ether and dimethylformamide.[12] The resulting aldehyde **13**, which has the same melting point as *O*-methylpodocarpinal,[13] exhibits in its NMR spectrum a doublet at 9.70 ppm (J = 1.5 Hz) indicative of an axial

Table II. Chemical Shifts of Podocarpane and Podocarpane-*18-d*$_3$ derivatives[a]

Registry no.			
16826-83-8	Podocarpinal *O*-methyl ether **3a**	1.05	1.07
63533-65-3	Podocarpinal-*18-d*$_3$ *O*-methyl ether **13**		1.07
16826-86-1	Podocarpinol *O*-methyl ether **3d**	1.04	1.19
63533-66-4	Podocarpinol-*18-d*$_3$ *O*-methyl ether		1.20
16826-82-7	Podocarpinol *O*-methyl ether acetate **3c**	1.04	1.20
63533-67-5	Podocarpinol-*18-d*$_3$ *O*-methyl ether acetate **14**		1.21

[a] In parts per million in $CDCl_3$ with Me_4Si as internal standard.

Scheme I



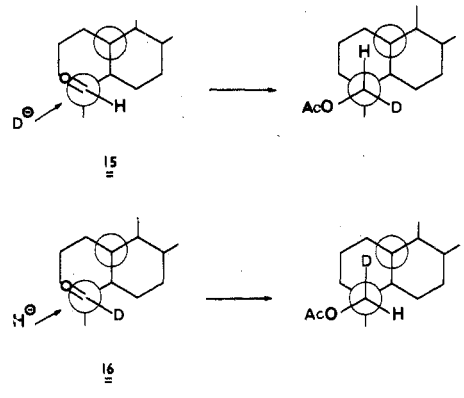
aldehyde group[1,14] and a CCH_3 singlet at 1.06 ppm, in agreement with the published data. Lithium aluminium hydride reduction of the aldehyde gave a carbinol which was converted ultimately into its acetate **14**. A comparison between the NMR spectra of the deuterated and nondeuterated acetates **4** and **3c**, respectively, shows that the signal at 1.20 ppm assigned by Wenkert to the angular methyl group had been assigned correctly (Table II). This point settled firmly, the NOE of acetates A and B was measured (Table II) and showed them to have structures **8** and **7**, respectively.

Discussion of the Experimental Results

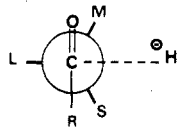
The NOE result raises a question, since the earlier interpretation of the experimental data[1] had led to opposite chiralities for the two deuterated acetates.[1] Were aldehyde **3a** to react in its most stable conformation **15** and the reducing agent to arrive from the less hindered side, acetate A (from lithium aluminium deuteride reduction of the aldehyde group, followed by acetylation) should be **7**, i.e., 19*S*.

Similarly acetate B (from lithium aluminium hydride reduction of the deuterioaldehyde group followed by acetylation) should be **8**, i.e., 19*R*.

Therefore, either the basic assumption on which the interpretation of the NOE data relies is wrong or the reduction mechanism is more subtle than interpreted. In order to check



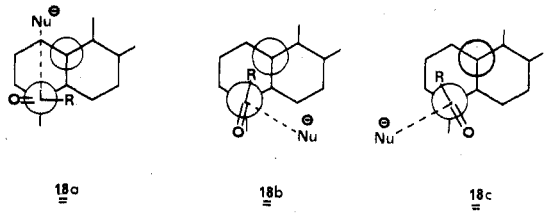
our hypothesis on the most stable acetate rotamer we have calculated the energy profile for the rotation of the C-4-axial substituent around the C-4β bond with the molecular mechanics method developed by Allinger.[15-17] The calculated rotational profile[18] is shown in Figure 2 and indicates the most stable conformation to be the predicted one. Hence the chirality of the deuterated acetates, deduced from NOE, is established. Various geometries of the transition state for the $LiAlH_4$ reduction of a carbonyl group have been proposed.[19-23] Recently the validity of Felkin's model has been established as a result of ab initio calculations.[24] The lithium aluminium hydride reagent, however, always has been considered as a bare H^- ion, neither the lithium cation nor any solvent being taken into account. The transition state has been represented by **17** (L = large, M = medium, S = small), the incipient car-



bon–hydrogen bond being antiperiplanar with respect to the bond between the α carbon and the bulkier (L) group attached to it.

In the case of aldehydes **3a** or **3b** six such transition states must be considered (**18a–f**; R = H or D, Nu = D or H, respectively). The stability of the required conformation of the aldehyde group was estimated with the "force field" program (Figure 3).[25]

Transition states **18b** and **18e** are ruled out on the basis of the high interaction energy between the angular methyl group and the oxygen or hydrogen (deuterium) of the aldehyde



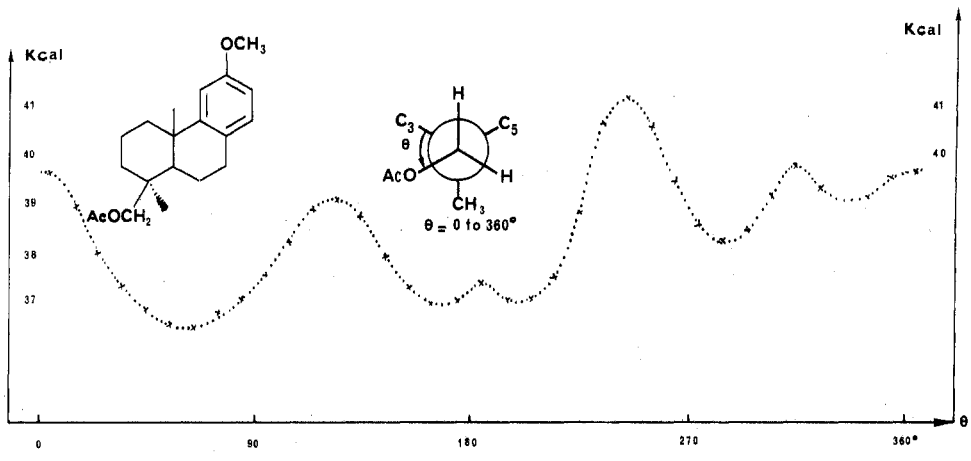


Figure 2.

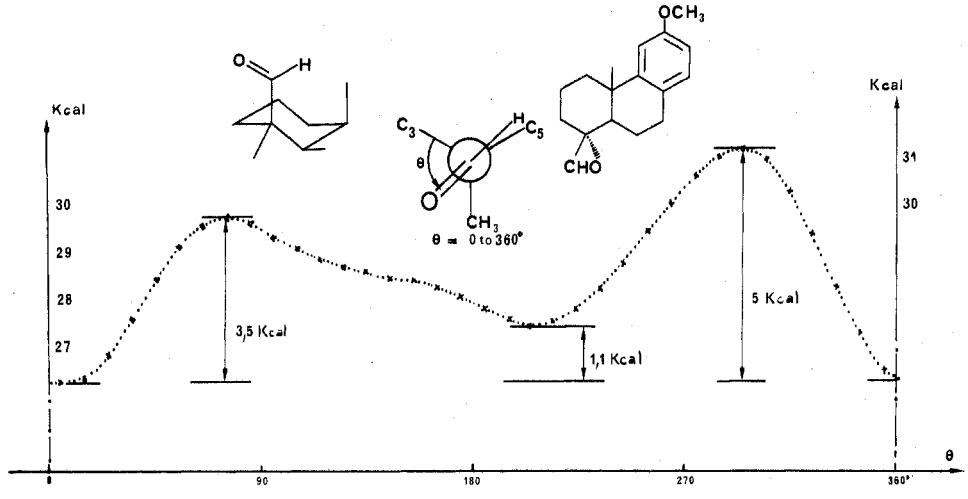
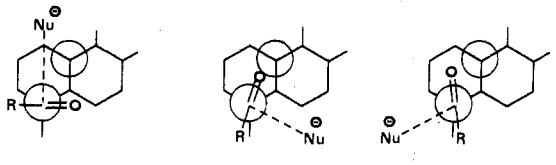


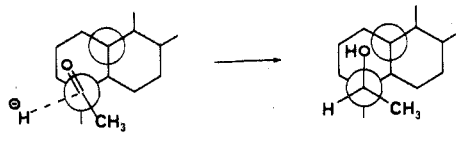
Figure 3.

(deuterioaldehyde) group. Transition states **18a** and **18d** may be excluded also, since steric hindrance impedes the required antiperiplanar attack of the deuteride (hydride) ion. The energies of the aldehyde conformations in the last two transition states **18c** and **18b** are approximately the same (although **18c** seems to be slightly more stable than **18b**).



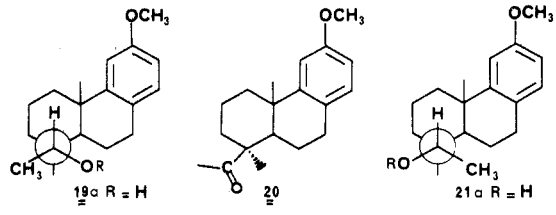
18d **18e** **18f**

Unfortunately the program cannot accommodate the presence of a solvated lithium cation in the neighborhood of the oxygen, the increase of electron density on this oxygen, and the elongation of the carbon–oxygen bond. All these factors destabilize transition state **18f**[26] and suggest the aldehyde reduction to proceed via transition state **18c**. This conclusion, the opposite of the one previously accepted, is substantiated fully by the NOE results. Similarly, a reaction of methyllithium with the aldehyde **3a** (R = H, Nu = CH_3) should give the secondary alcohol **19a** through transition state **18c**. The alcohol thus is expected to be the 19*R* isomer. Indeed this reaction has been found to be highly stereoselective.[27] Moreover, the same alcohol is the major component of the 94:6 mixture of carbinols obtained by $LiAlH_4$ reduction of the parent



18c **19a**

methyl ketone **20**. The energy profile for the internal rotation around the C-4β bond of this ketone has been calculated (Figure 4). Among the six transition states (**18a–f**; R = CH_3, Nu = H) five may be disregarded either on the basis of the high energy of the required conformation (**18b**, **18c**, and **18e**) or because of steric hindrance in the approach of the nucleophile (**18a** and **18d**). The remaining transition state **18f** is expected to lead to the 19*R* isomer **19a**, in agreement with the experimental findings. Horeau's analysis of the chirality of carbon centers shows the stereochemistry of both the major and minor secondary alcohols **19a** and **21a** to be correct.[28,29]



19a R = H **20** **21a** R = H

19b R = Ac **21b** R = Ac

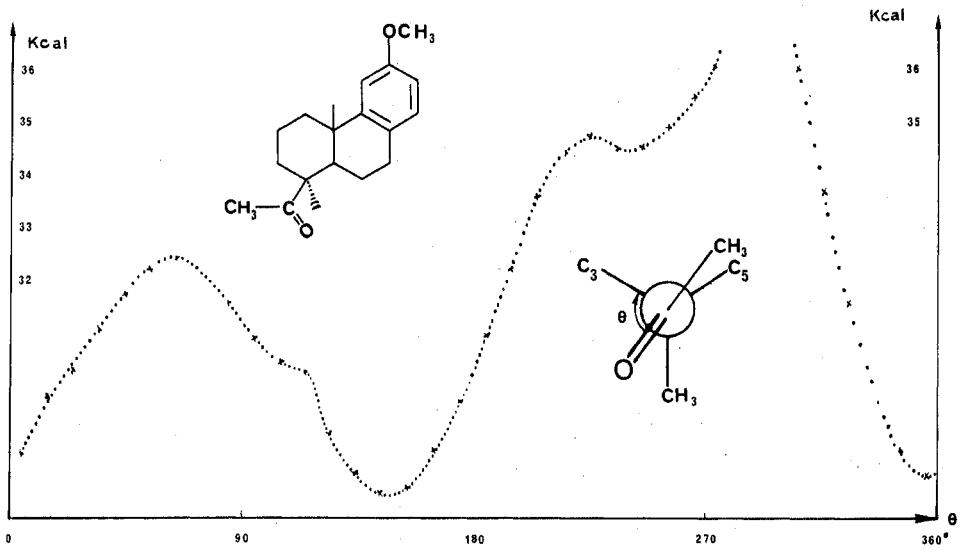


Figure 4.

It is noteworthy that NOE gives approximately the same values for the acetates **19a** and **7**, thereby confirming the chirality of the latter compound (*regardless of the stereochemistry of* **19b**). The most stable conformation of 19*S*-acetate is represented by **21b**. In both 19*R* and 19*S* isomers the C-19 proton is located the same distance from the angular methyl group.

Conclusion

Felkin's hypothesis on the geometry of the most favored transition state for the nucleophilic attack on an aldehyde or methyl ketone proved to be reliable. Therefore a combination of this assumption and of a calculation of the energy profile for the rotation around the C_α—C=O bond appears to be extremely valuable for the prediction of the course of such reactions.

Experimental Section

General. Melting points (Köfler microscope) were not corrected. The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Unless stated otherwise, the NMR spectra were obtained either on a Varian T60 or NV14 in CCl_4 or $CDCl_3$ with tetramethylsilane as internal standard. Nuclear Overhauser effects were measured on a Varian XL-100, in sealed tubes, the solution being carefully degassed.

Podocarpic Acid *O*-Methyl Ether. It was prepared from methyl podocarpate *O*-methyl ether according to a published procedure:[31] mp 154–156 °C.

Oxidative Decarboxylation of Podocarpic Acid *O*-Methyl Ether. It was carried out according to Bennett and Cambie's method:[10] 8.55 g of the acid gave 3.85 g of a mixture of the three expected olefins, which could not be separated and was used as such for the next step.

18-Nor-19-hydroxy-12-methoxypodocarpa-8,11,13-triene (11). To 3.85 g of the preceding mixture in 30 mL of dry THF, 30 mL of a 0.50 M solution of 9-BBN in THF was added dropwise at 0 °C under a dry nitrogen atmosphere. After 48 h at room temperature, the clear solution is treated with 5 mL of 6 N NaOH and 4 mL of H_2O_2 (110 vol). After the usual workup, the oily substance is separated by chromatography on silica gel. A mixture of Δ^3 and Δ^4 olefins is eluted first, followed by the expected primary alcohol **11** (2.02 g).

A careful analysis (TLC) indicated that two isomers (roughly 3:1) (R_f 0.55 and 0.58, hexane/diethyl ether, 7:3) are formed. However, they could not be separated in a preparative scale. NMR (CCl_4): 1.13 and 3.66 (minor compound), 1.01 and 3.66 ppm (major compound).

Aldehyde 12. (a) The preceding alcohol mixture (0.476 g) and 15 g of Ag_2CO_3/Celite in 100 mL of benzene are refluxed under argon for 24 h. After filtration of the solid, evaporation of benzene, and chromatography of the resulting oil, 0.242 g of aldehyde **12** (a mixture of axial and equatorial isomers) is obtained.

(B) The alcohol mixture (0.473 g) is oxidized by Collins reagent (from 1.2 g of CrO_3 and 1.9 g of pyridine in 30 mL of CH_2Cl_2) for 15 min at room temperature. After the usual workup, the mixture of the axial and equatorial aldehydes is separated by preparative thin-layer chromatography; 0.115 g are thus obtained: IR 1710 cm^{-1} (ν C=O); NMR 0.98 (s, 10-CH_3), 3.68 (OCH_3), 9.89 ppm (br s, -CHO) (major compound); NMR 1.06 (s, 10-CH_3), 3.68 (OCH_3), 9.68 ppm (d, J = 1.0 Hz, -CHO) (minor compound).

***O*-Methylpodocarpinal-*18*-d_3 (13).** A mixture of the preceding aldehydes (0.158 g) in 22 mL of dry DMF was added dropwise, under argon, to 22 mL of a solution of 0.028 M of triphenylmethyl sodium in diethyl ether.[30] Freshly distilled methyl-d_3 iodide (3 mL) was added. The reaction mixture was refluxed for 15 h, and then poured in 120 mL of 3 N hydrochloric acid. After the usual workup and chromatography on silica gel, 0.088 g of the crystalline aldehyde was isolated. It was recrystallized twice in hexane/diethyl ether: mp 135–137 °C (nondeuterated podocarpinal, mp 135–136 °C[1]); IR (CCl_4) 2214 (ν -CD_3) and 1713 cm^{-1} (ν C=O); NMR (CCl_4) 1.04 (10-CH_3), 9.70 ppm (CHO, d, J = 1.25 Hz); NMR ($CDCl_3$) 1.06 (10-CH_3), 9.65 ppm (d, J = 1.25 Hz, CHO).

Podocarpinol-*18*-d_3 *O*-Methyl Ether. Podocarpinol-*18*-d_3 (0.042 g) in 6 mL of diethyl ether was reduced at 0 °C by 0.05 g of $LiAlH_4$ in 8 mL of diethyl ether. The resulting alcohol (oil, 0.042 g) was purified by TLC and crystallized as white needles: mp 88.5–90 °C (hexane); IR (CCl_4) 3608 cm^{-1}; NMR (CCl_4) 1.19 (10-CH_3), 3.78 ppm (s, OCH_3); NMR ($CDCl_3$) 1.20 (s, 10-CH_3), 3.78 ppm (s, OCH_3).

NOE Measurements. Nuclear Overhauser effect measurements have been carried out in the CW or FT modes either on a Varian HA 100 or a Varian XL-100. The concentrations of the samples were 0.25 $\times 10^{-4}$ mol/L (FT mode) and 1×10^{-4} mol/L (CW mode). The solutions were degassed three times and the tubes were sealed.

Acknowledgments. We thank Professor N. L. Allinger for kindly sending the "force field" program, Professor R. Bell, in whose laboratory most of the NOE experiments have been carried out, and the C.N.R.S. for generous financial support.

Registry No.—**9**, 10037-26-0; Δ^3-**10**, 54168-28-4; Δ^4-**10**, 13740-16-4; **11** isomer 1, 63533-68-6; **11** isomer 2, 63533-69-7; **12** isomer 1, 63597-43-3; **12** isomer 2, 23962-85-8.

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(26) They all contribute to increasing the bulk of the oxygen of the carbonyl dipole.
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Notes

Kinetics and Mechanism of Ynamine–Isocyanate Additions[1]

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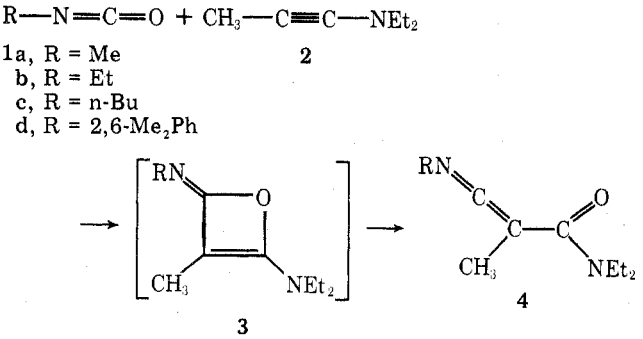
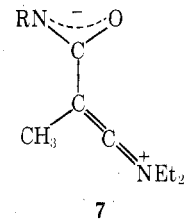
Received May 18, 1976

Alkyl isocyanates **1a–c** and the ortho-blocked aryl isocyanate **1d** react with 1-diethylaminopropyne to give ketenimines.[3] The products are easily identified by their characteristic infrared absorption bands just above 2000 cm^{-1}. Reactions with aqueous acid and acetic acid parallel those previously reported for ketenimines.[4]

In contrast to these 2 + 2 additions to the C–O π bond, aryl isocyanates typically give solvent-dependent product mixtures from competing 2 + 2 and 4 + 2 additions involving the C–N π bond,[5a] and other conjugated isocyanates undergo 4 + 2 additions.[5] The C–O π bond involvement is not unique, however. One example involving phenyl isocyanate and a cyanoynamine has been reported,[6] and a reexamination of the reaction of phenyl isocyanate with **2** indicates that in CCl_4 a ketenimine (IR 2010 cm^{-1}; NMR δ 1.92 (s)) forms and disappears in the reaction mixture. We have not been able to determine the fate of the ketenimine.



These reactions are very solvent dependent. In acetonitrile, phenyl isocyanate and **2** react rapidly to produce the 4 + 2 adduct. No intermediates are detectable by IR or NMR. Ketenimine **4d** also forms rapidly and in high yield in acetonitrile but slowly and in poor yield in CCl_4. Solvent effects are expected to be significant for reactions which proceed through zwitterionic intermediates such as **7**,[7] and ynamine reactions



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are characteristically solvent sensitive.[8] For that reason it was surprising to find that the alkyl isocyanate reactions did not show either product or significant rate dependence on solvents. The rate of the reaction of **2** with methyl isocyanate was followed by NMR and found to be first order in each reactant with rate constants as shown in Table I. The factor of 8 difference between rate constants in benzene and acetonitrile at 34 °C can be compared to factors of 10^3–10^4 for tetracyanoethylene/enol ether additions for which a zwitterionic intermediate has been established.[7] From the temperature dependence of the rate constant in benzene, values of 13 ± 2 kcal/mol and −31.5 ± 5 eu can be derived for the activation

Table I. Solvent and Temperature Dependence of Rate Constants for Formation of 4a

Solvent	*T*, °C	$k \times 10^4$, M^{-1} s^{-1}
C_6H_6	16	0.45 ± 0.05
C_6H_6	34	1.8 ± 0.1
C_6H_6	56	8.8 ± 0.5
$C_6H_5NO_2$	34	9.5 ± 1.0
C_6H_5CN	34	8.0 ± 0.5
CD_3CN	34	15.3 ± 1.6