acid either to the bromphenol blue end point or potentiometrically.

Product Analysis.—The products formed under the conditions of the kinetic measurements were determined for each of the compounds studied. The products represented a normal product distribution (large excess of inversion over retention, predominant formation of olefin) for a typical solvolysis of cyclohexyl compounds. The detailed results are presented in Table V.

Registry No.—**2**, 19556-66-2; **3**, 19556-67-3; **4**, 19556-68-4; **4** (3,5-dinitrobenzoate derivative), 19556-69-5; **5**, 19556-70-8; **6**, 19556-71-9; **8**, 19556-72-0; **9**, 19556-73-1; **10**, 19556-74-2; **10** (3,5-dinitrobenzoate derivative), 19594-76-4; **11**, 19556-75-3; **12**, 19556-76-4; *trans*-4-chlorocyclohexyl acetate, 19556-77-5; *trans*-4-chlorocyclohexyl 3,5-dinitrobenzoate, 19556-78-6; *trans*-4-bromocyclohexyl 3,5-dinitrobenzoate, 19556-96-8; *cis*-4-carboxamidocyclohexanol, 19556-97-9; *cis*-4-carboxamidocyclohexyl acetate, 19556-98-0; *cis*-4-cyanocyclohexyl tosylate, 19556-99-1; *trans*-4-carboxamidocyclohexyl acetate, 19557-00-7; *trans*-4-cyanocyclohexyl tosylate, 19557-01-8; *cis*-3-carboxamidocyclohexanol, 19557-02-9; *cis*-3-carboxamidocyclohexyl acetate, 19557-03-0; *cis*-3-cyanocyclohexyl acetate, 19557-04-1; *cis*-3-cyanocyclohexyl tosylate, 19557-07-4; *trans*-3-carboxamidocyclohexyl acetate, 19557-05-2; *trans*-3-cyanocyclohexyl tosylate, 19557-06-3.

Polarity Effects on the Acetolysis of Substituted 1-Decalyl Methanesulfonates[1]

DONALD S. NOYCE AND BYRON E. JOHNSTON

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

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All four stereoisomers of 4-cyano-1-decalol containing the *trans*-decalin moiety have been synthesized and characterized. The rates of acetolysis of the methanesulfonates of these compounds have been measured. *trans*-4α-Cyano-1β-decalyl methanesulfonate (equatorial cyano and equatorial methanesulfonate) solvolyzes 3.2 times faster than *trans*-4α-cyano-1β-decalyl methanesulfonate (axial cyano and equatorial methanesulfonate) in agreement with calculations based on a direct field effect model. In contrast, an inductive effect operating through the bonds would predict identical rates for these two compounds. The field effect model, based upon 70% charge separation at the transition state, predicts the reaction rates quite well for three of the four compounds in this study. The fourth compound, *trans*-4β-cyano-1α-decalyl methanesulfonate (axial cyano and axial methanesulfonate), reacts about twice as rapidly as predicted; this is probably the result of a complex mechanism for the axial methanesulfonate, as has been postulated in similar systems, involving participation of the adjacent ring juncture hydrogen (which is tertiary, axial, and in an antiperiplanar orientation to the leaving sulfonate group).

In the preceding paper, we have shown that the solvolysis of 4-halocyclohexyl methanesulfonates is most satisfactorily explained on the basis of a field effect.[2] However, the conformational mobility of simple cyclohexane systems adds an additional degree of uncertainty to this conclusion, and it seemed desirable to examine the effect of the polarity of substituents on reaction rate in conformationally rigid systems. For this purpose we have chosen to investigate the reactivity of a selected group of *trans*-decalin derivatives.

Condensation of 1-(1-acetoxyvinyl)cyclohexene with acrylonitrile produced a mixture of 4α-cyano- and 4β-cyano-1-acetoxy-$\Delta^{1,10}$-octalins. Mild hydrolysis afforded a mixture of four isomeric 4-cyano-1-decalones. The two major components of this mixture, *trans*-4α-cyano-1-decalone (**1**,[3] 65%), and *trans*-4β-cyano-1-decalone (**2**, 33%), were separated and purified. The two minor components (2% of the total mixture) were assigned the *cis*-4-cyano-1-decalone structures by virtue of their conversion into a mixture of **1** and **2**. The structure of **1** and **2** was established by hydrolysis to the known *trans*-4α-carboxy-1-decalone (**3**) and comparison with an authentic sample prepared by the method of Nazarov, Kucherov, and Segal.[4] This establishes that the cyano group is in the 4 position rather than the 3 position, which would have resulted from addition in the reverse direction in the Diels–Alder reaction. The assignment of configuration to **1** and **2**, respectively, comes from a consideration of their nmr spectra. *trans*-4β-Cyano-1-decalone has a peak for one proton at δ 2.93, in good agreement with the δ 2.91 chemical shift observed for the equatorial hydrogen atom adjacent to the cyano group in *cis*-4-*t*-butyl-1-cyanocyclohexane.[5] The peak for the hydrogen atom adjacent to the cyano group in **1** is not separated from the complex multiplet due to the ring protons. The corresponding peak for the axial hydrogen atom adjacent to the cyano group in *trans*-4-*t*-butyl-1-cyanocyclohexane is also obscured by the ring protons.[5]

Pure samples of *trans*-4α- and *trans*-4β-cyano-1-decalones were each reduced with aluminum isopropoxide; from **1** a 50:50 mixture of two alcohols was obtained, and from **2**, a 70:30 mixture of two different alcohols was formed. The mixtures of alcohols were separated by chromatography on alumina. The structures of these alcohols were established on the basis of their origins and their nmr spectra. The chemical shifts of the nmr peaks are listed in Table I with the chemical shifts of the peaks for known compounds in the cyclohexane series which are "conformationally pure." The methanesulfonates of these alcohols were then formed by standard methods. The structures of

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[1] Supported in part by grants from the National Science Foundation, GP-1572 and GP-6133X.

[2] D. S. Noyce, B. N. Bastian, P. T. S. Lau, R. S. Monson, and B. Weinstein, *J. Org. Chem.*, **34**, 1247 (1969).

[3] Nomenclature in this paper will use the steroid conventions and numbering, with the hydrogen at C-10 in the β orientation. All the compounds in the present study are *dl* mixtures. Only one enantiomorph is shown in Scheme I for convenience.

[4] I. N. Nazarov, V. F. Kucherov, and G. M. Segal, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1241 (1956).

[5] N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962).

TABLE I

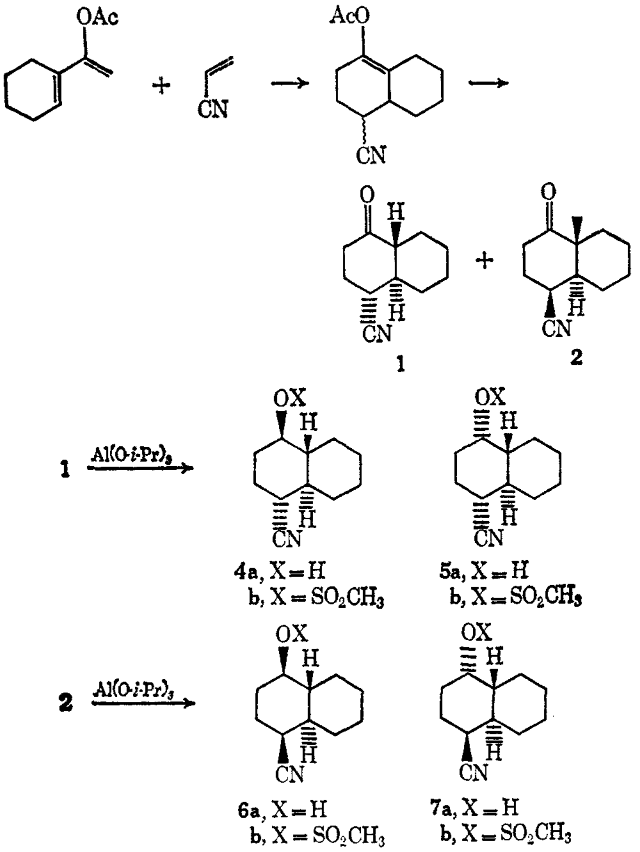
SIGNIFICANT NMR PEAKS FOR ASSIGNMENT OF STRUCTURE

Compd	Confign[a] CN	Confign[a] OX	δ[b] Eq H (CHCN)	Eq H (CHOH)	Ax H (CHOH)	Eq H (CHOMs)	Ax H (CHOMs)
2	Ax		2.93 (7)				
4a	Eq	Eq			3.21 (15)		
4b	Eq	Eq					4.29 (16)
5a	Eq	Ax		3.73 (7)			
5b	Eq	Ax				4.70 (7)	
6a	Ax	Eq	2.73 (7)		3.17 (15)		
6b	Ax	Eq	2.77 (7)				4.28 (16)
7a	Ax	Ax	2.95 (7)	3.78 (7)			
7b	Ax	Ax	2.83 (7)			4.73 (7)	
cis-4-*t*-Butyl-1-cyanocyclohexane[c]	Ax		2.91				
trans-1β-Decalol		Eq			3.13 (15)		4.17 (16)
cis-4-*t*-Butylcyclohexanol[d]		Ax		3.93 (7)		4.88 (7)	
trans-4-*t*-Butylcyclohexanol[d]		Eq			3.37 (15)		4.45 (16)

[a] Axial or equatorial, OH or OSO_2CH_3 (OMs). [b] The values are chemical shifts in parts per million from TMS (internal) in chloroform solution. Values in parentheses are peak widths at half-height in cycles per second. [c] Reference 5. [d] From ref. 8.

the methanesulfonates were also supported by comparison of the nmr spectra with the nmr spectra of known compounds in the cyclohexane series (see Table I). These reactions are summarized in Scheme I.

SCHEME I



Kinetic Results.—The four isomers all solvolyzed smoothly in acetic acid giving good first-order behavior. The rates of solvolysis are substantially less than the rates of solvolysis of the corresponding decalols as would be expected. The rates of acetolysis of both *trans*-1α-decalyl tosylate and *trans*-1β-decalyl tosylate have been measured.[6,7] Extrapolation of these measured rates to 90°, in conjunction with our previous comparisons of tosylates and methanesulfonates,[8] predicts a rate for *trans*-1α-decalyl methanesulfonate (axial sulfonate) of 3.2×10^{-3} sec^{-1} and for *trans*-1β-decalyl methanesulfonate (equatorial sulfonate) of 7.8×10^{-5} sec^{-1}. The rate ratio (axial/equatorial) of 40 is not the usual factor of about 3. However, other instances of axial sulfonates with an adjacent equatorial substituent showing accelerated rates are well documented. The rate ratio in the menthyl series ($k_{\text{neomenthyl}}/k_{\text{menthyl}}$) is 77,[9] presumably revealing an enhanced rate due to participation by the neighboring axial hydrogen; for the 2-methylcyclohexyl tosylate, the rate ratio is 71.[6]

Our rate measurements are summarized in Table II and derived thermodynamic data are given in Table III.

Discussion

Observed Reaction Rates.—The kinetic results listed in Table II indicate that the orientation of the cyano substituent does affect the reaction rates, as predicted if a field effect were important. The relative rates for the isomeric compounds in this study are listed in Table IV. The relative rates of the equatorial methanesulfonates differ by a factor of 3, while the relative rates of the axial methanesulfonates differ by only 20%. To a first approximation these ratios should be independent of the leaving group, depending only on the relative energies of the carbonium ions.

The solvolysis of **5b** and **7b** may well be complicated by participation, and therefore this ratio is less instructive. The equatorial methanesulfonate solvolyses (*i.e.*, **4b** and **6b**) should not be complicated by participation.

The similar compound, menthyl *p*-toluenesulfonate, reacts through a normal solvolysis.[9] Therefore, the solvolysis rates of the *trans*-4-cyano-1-decalyl methanesulfonates, which have equatorial methanesulfonate groups, should be useful for studying polar effects on acetolysis rates. The resulting rate ratio for this pair of compounds, k_{4b}/k_{6b} (Table IV) shows that there is a substantial difference in the rates due to the change in the orientation of the substituent dipole.

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(6) W. Hückel and H. D. Säurland, *Ann.*, **592**, 190 (1955).

(7) I. Moritani, S. Nishida, and M. Murakami, *J. Amer. Chem. Soc.*, **81**, 3420 (1959).

(8) D. S. Noyce, B. E. Johnston and B. Weinstein, *J. Org. Chem.*, **34**, 463 (1969).

(9) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

Table II

Kinetics of the Acetolyses of 4-Substituted *trans*-1-Decalyl Methanesulfonates

Compd[a]	Confign[b] -CN	Confign[b] -OMs	Temp, °C	$k_1 \times 10^5$, sec^{-1}
4b	Eq	Eq	90.00	2.64 ± 0.04
			110.00	23.0 ± 0.8
6b	Ax	Eq	90.00	0.813 ± 0.020
			110.00	7.25 ± 0.020
5b	Eq	Ax	70.00	5.65 ± 0.34
			90.00	51.7 ± 0.5
7b	Ax	Ax	70.00	7.27 ± 0.32
			90.00	64.7 ± 0.8

[a] **4b** is *trans*-4α-cyano-1β-decalyl methanesulfonate. **6b** is *trans*-4β-cyano-1β-decalyl methanesulfonate. **5b** is *trans*-4α-cyano-1α-decalyl methanesulfonate. **7b** is *trans*-4β-cyano-1α-decalyl methanesulfonate. [b] Axial or equatorial configuration of methanesulfonate group (-OMs) or cyano group (-CN).

Table III

Activation Parameters

Compd[a]	ΔH‡, kcal	ΔS‡, eu
4b	29.2 ± 0.3	−4.1 ± 0.7
6b	29.5 ± 0.3	−5.5 ± 0.7
5b	26.7 ± 0.2	−5.0 ± 0.6
7b	26.4 ± 0.2	−5.5 ± 0.7

[a] **4b** is *trans*-4α-cyano-1β-decalyl methanesulfonate. **6b** is *trans*-4β-cyano-1β-decalyl methanesulfonate. **5b** is *trans*-4α-cyano-1α-decalyl methanesulfonate. **7b** is *trans*-4β-cyano-1α-decalyl methanesulfonate.

Table IV

Relative Acetolysis Rates of the *trans*-4-Cyano-1-decalyl Methanesulfonates

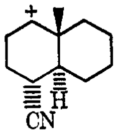
Temp, °C	Equatorial -OMs k4b/k6b	Axial -OMs k5b/k7b
70.00		0.80
90.00	3.25	0.78
110.00	3.17	

Calculated Reaction Rates.—Interaction energies between the substituent dipole and the reaction center were calculated as in the Kirkwood-Westheimer treatment.[10] The dipoles were treated as point charges on the cyano carbon atom and nitrogen atom rather than as point dipoles[10] since the length of the dipole is the same order of magnitude as distances between the dipoles and the reaction centers. This type of treatment predicts that the interaction will have a $1/R$ dependence rather than $1/R^2$ dependence as in the point dipole approximation. The use of the point charge models has been suggested elsewhere,[11-13] but has not been used extensively because of the increased complexity of the calculations. Calculations which have been carried out applying both point charge and point dipole models to a system do not produce appreciably different results.[11,14]

The choice of a model for the cavity is somewhat more difficult. Ideally the cavity should have a shape and volume which are similar to the shape of the molecule and the volume which it occupies in the solvent. In order to treat the problem mathematically a simplified model for this cavity must be chosen. Kirkwood and Westheimer[10] treat this cavity as an ellipsoid with the point dipole and the reactive center at the foci. The volume of the cavity can be approximated using Traube's rules,[15] based on extensive studies of the volume changes associated with the solution of compounds. Tanford[16] has suggested the use of a spherical model with a radius which is 1.0 Å greater than the distance from the center of the molecule to the furthest point charge. This type of treatment centers the cavity at the center of the molecule, while still maintaining all substituents within the cavity. This 1.0-Å distance has been comprised to the minimal distance between the substituent and the nearest solvent molecule.

The Traube radius for a cyanodecalyl methanesulfonate is 4.62 Å, compared with the Tanford radius (relative to the center of the ring) of 5.15 Å for a compound with an equatorial cyano group and 4.46 Å for a compound with an axial cyano group. The Traube radius for cyclohexyl methanesulfonate is 4.16 Å. This latter model is impractical since it would place the equatorial nitrogen atom on the surface of the sphere, when in reality, the solvent molecules are limited in their approach by steric interactions.

The dipole moments used in this study were taken from standard sources. The calculated interaction energies for the ground states and carbonium ions (**8** and **9**) of the compounds in this study, based on these models, are listed in Table V. The corresponding calculations for the 4-hydrogen compounds are included, since corrections for the effect of the hydrogen dipole should be applied if the calculated rates for the unsubstituted compounds are to be used as standards for the reaction rates in the absence of a dipole effect. As seen in Table V the calculated interactions are quite insensitive to the model for the cavity and the radius. The effective dielectric constants are very close to 2.0, the internal dielectric constant, as can be seen by comparing the calculated interaction energies using cavity models, with the corresponding energies for a continuous medium with a dielectric constant of 2.0. Therefore, the medium effect is small (relative to a solvent such as water, $D = 78$) and the choice of a model for the cavity is less important. Methods E and F place the limits of the cavity at or very near the nitrogen atom. This type of treatment is impractical for two reasons: the



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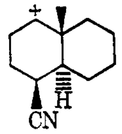

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(10) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(11) H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5188 (1964).

(12) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(13) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539 (1962).

(14) H. D. Holtz and L. M. Stock, *ibid.*, **87**, 2404 (1965).

(15) J. Traube, *Samml. Chem. Chem.-Tech. Vortr.*, **4**, 225 (1899).

(16) C. Tanford, *J. Amer. Chem. Soc.*, **79**, 5348 (1957).

TABLE V

CALCULATED FIELD EFFECT ENERGIES[a]

Compd[b]	Method[c]					
	A	B	C	D	E	F
8	6.09	5.45	5.37	5.26	5.04	5.03
9	6.53	6.12	6.01	6.16	5.98	6.02
4b	0.51	0.60	0.58	0.60	0.60	0.59
6b	0.75	0.75	0.75	0.75	0.75	0.77
5b	0.28	0.28	0.27	0.28	0.27	0.28
7b	0.37	0.52	0.52	0.52	0.52	0.54

[a] These calculations were carried out using the FIELD computer program, supplied to us by Professor C. F. Wilcox of Cornell University, to whom we are indebted. This program evaluates the first eleven Legendre polynomials for each interaction (see ref 10). The values are listed in kilocalories. [b] Compounds **4b**–**7b** are the 4-cyano-1-decalyl methanesulfonates, as depicted in Scheme I. Compounds **8** and **9** are the two carbonium ions derived from these compounds. [c] Method A is calculated on the basis of a continuous medium, $D = 2.0$; methods B and C use Tanford radii, centered at the middle of the ring and the middle of the C_9–C_{10} bond, respectively. Methods D and E use the Traube radii for decalin compounds centered in the middle of the ring and in the middle of the C_9–C_{10} bond. Method F used the Traube radii for the cyclohexane molecules centered in the ring.

bulk of the substituent prevents the solvent continuum from beginning near the center of charge, and the mathematical treatment used for these calculations begins to break down when a charged species is placed near the surface of the cavity, owing to nonconvergence of the Legendre polynomial function.

All of the calculation methods listed in Table V predict that *trans*-4β-cyano-1-decalyl carbonium ion **9** is less stable than *trans*-4α-cyano-1-decalyl carbonium ion **8**. These calculations predict that 4α-cyano compounds will react faster than the 4β-cyano compounds, as has been observed for the equatorial methanesulfonates.

For quantitative calculations the charge separation in the transition state has been treated as a variable between 50 and 100%. The effect of the negatively charged ion on the transition state energy has been assumed to be negligible. This assumption is based on the predicted lengthening of the carbon–oxygen bond in the transition state and the spreading of the developing charge over the three oxygen atoms of the sulfonate group and over the solvent, through hydrogen bonding. Methods B, C, and D in Table V are probably the most valid treatments. The calculated interaction energies for these methods are essentially equivalent, so subsequent calculations have been carried out for only method B, which is based on Tanford spheres centered at the center of the substituted ring.

The calculated interaction for these compounds are listed for a range of charge separations in Table VI. The calculated rates relative to the unsubstituted decalin methanesulfonates are listed in Table VII.

TABLE VI

ELECTROSTATIC ACTIVATION ENERGIES[a]

Compd[b]	X[c]			
	1.0	0.85	0.70	0.50
4b	4.04	3.36	2.68	1.78
6b	4.95	4.11	3.26	2.14
5b	4.34	3.66	2.98	1.98
7b	5.11	4.27	3.42	2.30

[a] Energies in kilocalories. [b] Compounds as listed in Table I. [c] Fractional charge separation in transition state.

TABLE VII

CALCULATED k_{CN}/k_H[a] AT 90°

Compd[b]	X[c]			
	1.0	0.85	0.70	0,50
4b	0.0037	0.0095	0.0244	0.0849
6b	0.0011	0.0034	0.0192	0.0512
5b	0.0008	0.0063	0.0161	0.0643
7b	0.0008	0.0027	0.0088	0.0413

[a] Calculated acetolysis rates of 4-cyano-1-decalin methanesulfonates relative to the unsubstituted 1-decalin methanesulfonates. [b] These compounds are depicted in Scheme I. [c] X is the fraction of charge separation in the transition state.

Using the rates for *trans*-1β-decalyl methanesulfonate and *trans*-1α-decalyl methanesulfonate mentioned earlier (*vide supra*), directly calculated rates of acetolysis may be derived from the information in Table VII. The most satisfactory agreement is achieved using a charge separation of 0.70 in the transition state; this leads to the comparison in Table VIII.

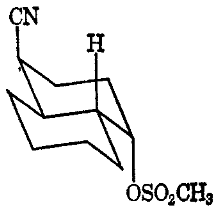
TABLE VIII

COMPARISON OF CALCULATED AND EXPERIMENTAL RATE CONSTANTS

Compd[a]	Calculated rate[b] × 10^7	Experimental rate[c] × 10^7
4b	19.3	26.4
6b	8.63	8.13
5b	522	517
7b	284	642

[a] The compounds are depicted in Scheme I. [b] Calculated acetolysis rates at 90° assuming 70% charge separation in the transition states. [c] Experimental acetolysis rates at 90°.

The agreement between the calculated and experimental rate constants in Table VIII is quite good except for *trans*-4β-cyano-1α-decalyl methanesulfonate (**7b**). A possible reason for the disagreement in this case may be related to the possibility of participation by the tertiary axial hydrogen atom, which has been discussed above. In particular, for **7b**, the cyano group has a direct steric interaction with this axial hydrogen atom. The presence of an axial leaving group creates an ideal geometrical relationship for participation of the axial hydrogen atom, and subsequent relief of the strain between the cyano group and hydrogen atom. The "*A* value" for the cyano group in cyclohexyl system is relatively small (approximately 0.2 kcal),[5,17] but with the increased steric crowding of a decalin system this interaction may become sufficient to produce a significant rate acceleration.



7b

(17) F. R. Jensen and B. Rickborn, *J. Org. Chem.*, **27**, 4606 (1962).

Experimental Section[18]

1-Acetoxy-4-cyano-$\Delta^{1,10}$-octalin.—A fresh sample of 1-(1-acetoxyvinyl)cyclohexene (60.7 g), prepared from acetylcyclohexene by the method of Ansell and Brooks,[19] was placed in a steel autoclave with acrylonitrile (24.2 g), hydroquinone (0.2 g), and 120 ml of dry toluene. The autoclave was heated to 145 ± 5° and then shaken for 16 hr. After cooling, the dark liquid was distilled under vacuum. After removal of the solvent and excess reagent, 45.3 g (57%) of a mixture of adducts was collected, bp 130–145° (1.5 mm). This mixture solidified on cooling to form a solid, mp 50–68°. Analysis on a 5 ft × 0.25 in. SE-30 on 80/100 mesh Chromosorb W column indicated that the solid was a mixture of two compounds in the ratio of 68:32. These compounds were assigned the structures 1-acetoxy-4α-cyano-$\Delta^{1,10}$-octalin and 1-acetoxy-4β-cyano-$\Delta^{1,10}$-octalin, respectively: ir (CCl_4) 2220, 1710, 1650 cm^{-1}; nmr (CCl_4) δ 1.0–2.8 (m), 2.22 (s).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81; N, 6.39. Found: C, 71.36; H, 7.66; N, 6.10.

***trans*-4α- and *trans*-4β-Cyano-1-decalones.**—A portion of the mixed 1-acetoxy-4-cyano-$\Delta^{1,10}$-octalins was stirred at 25° for 64 hr with a solution of 0.3 *N* sodium hydroxide (485 ml). The oil and water mixture was extracted three times with 120-ml portions of ether and the ether extracts were dried ($MgSO_4$). The ether was removed by distillation leaving a viscous oil (22.6 g, 88%) which crystallized slowly on standing. Vpc analyses indicated that this solid was a mixture of two major components and two minor components. The two minor components, about 2% of the total, were easily removed by recrystallization from ethanol–water, leaving an oily solid, mp 30–65°, containing the two major components. The minor components are the *cis*-decalone isomers (see below). The two major components, present in a ratio of about 2:1, were more difficult to separate. Samples enriched in one of the two compounds were obtained by distillation using a spinning-band column or by elution chromatography on Woelm grade III aluminum oxide. Enriched samples were fractionally recrystallized from ethanol–water to obtain the pure isomers.

The chief component, mp 69.5–70.0°, was assigned the structure of *trans*-4α-cyano-1-decalone (1) on the basis of the following spectral information: ir (CCl_4) 2257 (C≡N), 1720 cm^{-1} (C=O); nmr (CCl_4) δ 1.0–2.9 (m).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.83; H, 8.26; N, 7.87.

The other component, mp 71.0–71.5°, was assigned the structure of *trans*-4β-cyano-1-decalone (2) on the basis of the following spectral information: ir (CCl_4) 2237 (C≡N), 1718 cm^{-1} (C=O); nmr (CCl_4) δ 1.1–2.9 (m), 2.94 (broad, 7 cps width at half-height).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.80; H, 8.48; N, 8.04.

Partial Equilibration of *trans*-4α-Cyano-1-decalone.—Pure ketone 1 (20 mg) was stirred for 64 hr in 7 ml of a 0.30 *N* sodium hydroxide solution. The mixture was then extracted with ethyl ether. The ether extracts were dried over anhydrous magnesium sulfate and analyzed by vpc. About 15% of the material had been converted into *trans*-4β-cyano-1-decalone, and about 2% had been converted into one of the minor components of the enol acetate hydrolysis.

Partial Equilibration of *trans*-4β-Cyano-1-decalone.—Pure ketone 2 (20 mg) was stirred for 40 hr in 7 ml of a 0.30 *N* sodium hydroxide solution. The mixture was then extracted with ethyl ether. The ether extracts were dried over anhydrous magnesium sulfate and analyzed by vpc. About 30% of the material had been converted into *trans*-4α-cyano-1-decalone (1) and about 4% had been converted into the same minor component which was obtained from the partial equilibration of the *trans*-4α-cyano-1-decalone.

Partial Equilibration of Mixture Enriched in *cis*-4α- and *cis*-4β-Cyano-1-decalones.—A mixture of the 4-cyano-1-decalones (20 mg), enriched in the *cis* isomers (50%), was obtained from the mother liquors of the original crystallization. This mixture was stirred for 40 hr in 7 ml of a 0.30 *N* sodium hydroxide solution. The ether extracts were dried over anhydrous magnesium sulfate and analyzed (vpc) showing that about 80% of the ketone mixture was now the *trans*-4β- and *trans*-4α-cyano-1-decalones.

***trans*-4α-Cyano-1α-decalol (5a) and *trans*-4α-Cyano-1β-decalol (4a).**—*trans*-4α-Cyano-1-decalone (20.6 g) and aluminum isopropoxide (143 g) were mixed with 500 ml of anhydrous ethyl ether. The mixture was refluxed with vigorous stirring for 24 hr. The mixture was shaken with 10% hydrochloric acid to decompose aluminum salts, and the organic layer then dried over anhydrous magnesium sulfate. The ether and isopropyl alcohol were removed on a rotary evaporator, leaving 20.5 g (98%) of a mixture of two compounds in a ratio of approximately 52:48 as determined by vpc analysis.

A portion of this mixture (9.6 g) was chromatographed on 741 g of grade III Woelm neutral aluminum oxide. The column was eluted, first with *n*-pentane and then with *n*-pentane and ethyl ether mixtures. The 48% component, *trans*-4α-cyano-1α-decalol (5a, 4.00 g), was collected in the fractions eluted with 2:1 ether–pentane. This was followed by incompletely separate mixtures (1.21 g) eluted with the same solvent. The solvent was changed to 3:1 ether–*n*-pentane, and *trans*-4α-cyano-1β-decalol (4a, 2.47 g) was collected.

The 1α isomer (5a) crystallized immediately, forming colorless needles, mp 101–102°. Recrystallization from ethanol–water afforded a pure sample of 5a: mp 101.5–102.5°; ir ($CHCl_3$) 3509 (OH), 2247 (C≡N) 1040, 1021, 943 cm^{-1}; nmr ($CHCl_3$) δ 0.6–2.4 (m) 3.73 (broad, 7 cps width at half-height).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.71; H, 9.61; N, 8.03.

The 1β isomer (4a) was obtained as a clear viscous oil, which crystallized very slowly. Recrystallization was successful with seeding to give a pure sample of 4a: mp 74–75°; ir ($CHCl_3$) 3509 (OH), 2247 (C≡N), 1064, 1042, 1026 cm^{-1}; nmr ($CHCl_3$) δ 0.2–2.4 (m), 3.21 (broad, 15 cps width at half-height).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.88; H, 9.70; N, 8.02.

***trans*-4β-Cyano-1α-decalol (7a) and *trans*-4β-Cyano-1β-decalol (6a).**—*trans*-4β-Cyano-1-decalone (20.3 g) and aluminum isopropoxide (142.5 g, 0.70 mol) were mixed with 494 ml of anhydrous ethyl ether. The mixture was refluxed while stirring for 30 hr. The mixture was shaken with 700 ml of 10% hydrochloric acid to decompose the excess aluminum isopropoxide and then dried over anhydrous magnesium sulfate. The ether and isopropyl alcohol were removed on a rotary evaporator, leaving 21.3 g (93%) of a mixture of two compounds in a ratio of approximately 70:30, as determined by vpc analysis.

A portion of this product mixture (10.1 g) was chromatographed on grade III Woelm neutral aluminum oxide. The column was eluted, first with *n*-pentane and then with ether–pentane mixtures. The 70% component, *trans*-4β-cyano-1α-decalol (7.07 g, 7a), was collected in the fractions eluted with a 60:40 ethyl ether–*n*-pentane. This was followed by mixtures of both components (0.28 g) eluted with the same solvent mixture. The solvent was changed to pure ethyl ether and *trans*-4β-cyano-1β-decalol (6a, 2.64 g) was collected.

The 1α isomer (7a) formed white crystals: mp 90.5–91.5°; ir ($CHCl_3$) 3534 (OH) 2247 (C≡N), 1064, 1006, 971 cm^{-1}; nmr ($CHCl_3$) δ 1.0–2.2 (m) 2.95 (broad, 7 cps width at half-height), 3.78 (broad, 7 cps width at half-height).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.98; H, 9.38; N, 7.65.

The 1β isomer (6a) crystallized slowly: mp 89–90°; ir ($CHCl_3$) 3472 (OH), 2242 (C≡N), 1136, 1064, 1032, 961 cm^{-1}; nmr ($CHCl_3$) δ 0.5–2.4 (m), 2.73 (broad, 7 cps width at half-height), 3.17 (broad, 15 cps width at half-height).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.86; H, 9.39; N, 9.58.

***trans*-4α-Cyano-1β-decalyl methanesulfonate (4b)** was prepared in the same manner in 52% yield: mp 162.5–163.5°; ir ($CHCl_3$) 2252 (C≡N), 953, 932, 914 cm^{-1}; nmr ($CHCl_3$) δ 0.6–2.6 (m), 3.02 (s, 3, CH_3SO_2), 4.29 (broad, 15 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 56.17; H, 7.22; N, 5.20; S, 12.33.

***trans*-4α-Cyano-1α-decalyl Methanesulfonate (5b).**—Methanesulfonyl chloride (1.13 g) and *trans*-4α-cyano-1α-decalol (2.00 g) were mixed with 30 ml of dry ethyl ether. The solution was stirred at 25° while a solution of triethylamine (1.02 g) in 20 ml of ethyl ether was added over 30 min. The stirring was continued

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[18] All melting points and boiling points are uncorrected. Melting points were determined on a Fischer-Johns melting point apparatus. Infrared spectra were determined on a Perkin-Elmer Model 237 Infracord spectrophotometer. The nmr spectra were recorded on a Varian Associates Model A-60 or HA-100 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.

[19] M. F. Ansell and G. T. Brooks, *J. Chem. Soc.*, 4518 (1956).

for 15 min. A white solid precipitated and was collected. The solid was shaken with water to remove the triethylamine hydrochloride and with cold ethyl ether to remove any occluded organic impurities [unreacted alcohol (0.8 g, 40%) was recovered from these ether washings] leaving 1.6 g (56%) of *trans*-4α-cyano-1α-decalyl methanesulfonate (**5b**): mp 141.5–142.5°; ir ($CHCl_3$) 2242, 970, 917 cm^{-1}; nmr ($CHCl_3$) δ 0.6–2.5 (m, 15), 3.00 (s, 3, CH_3SO_2), 4.70 (broad, 7 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 55.68; H, 7.28; N, 5.26; S, 12.36.

***trans*-4β-Cyano-1β-decalyl methanesulfonate (6b)** was prepared similarly from 3.4 g of **6a** in 76% yield, mp 152–153°. Spectral characteristics of **6b** are ir ($CHCl_3$) 2232 ($C\equiv N$), 969, 934, 897 cm^{-1}; nmr ($CHCl_3$) δ 0.8–2.4 (m), 2.77 (7 cps width at half-height, 1, CHCN), 3.02 (s, 3, CH_3SO_2), 4.28 (broad, 16 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 56.28; H, 7.28; N, 5.42; S, 12.40.

***trans*-4β-Cyano-1α-decalyl Methanesulfonate (7b).**—From 2.5 g of **7a** there was obtained 2.0 g (**7b**) of *trans*-4β-cyano-1α-decalyl methanesulfonate, mp 138–139°. Spectral properties of **7b** are ir ($CHCl_3$) 2237 ($C\equiv N$), 968, 924 cm^{-1}; nmr ($CHCl_3$) δ 1.0–2.3 (m), 2.83 (7 cps width at half-height, 1, CHCN), 3.02 (s, 3, CH_3SO_2) 4.73 (7 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.00; H, 7.44; N, 5.44; S, 12.46. Found: C, 55.75; H, 7.26; N, 5.28; S, 12.33.

***trans*-1β-Decalol** was prepared by sodium and alcohol reduction of *trans*-1-decalone[20] and crystallization of the crude product from hexane: mp 61.5–62.0° (lit.[20,21] mp 58–59.5°, 63°); nmr ($CHCl_3$) δ 0.6–2.4 (m), 3.13 (15 cps width at half-height, 1, CHO). From this alcohol, ***trans*-1β-decalyl methanesulfonate** was prepared and purified by crystallization from hexane: mp 44.5–45.0°; nmr ($CHCl_3$) δ 0.5–2.5 (m), 2.90 (s, 3, CH_3SO_2), 4.17 (16 cps width at half-height, 1, CHO).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.85; H, 8.68; S, 13.80. Found: C, 56.98; H, 8.62; S, 13.66.

Kinetic Measurements.—The usual sealed ampoule technique was used. The concentration of the sulfonate ester was 0.012 *M* in anhydrous acetic acid containing sodium acetate (0.025 *M*) and acetic anhydride (0.022 *M*). At appropriate time intervals 5-ml samples were titrated with perchloric acid in acetic acid using a Metrohm Model 336 recording Potentiograph equipped with a 5-ml automatic delivery buret.

Rate constants were calculated using a nonlinear least-squares program.[22] Precision was generally better than ±1%, always better than ±3%.

Registry No.—1, 19556-82-2; 2, 19556-83-3; **4a**, 19556-84-4; **4b**, 19556-85-5; **5a**, 19556-86-6; **5b**, 19556-87-7; **6a**, 19556-88-8; **6b**, 19556-89-9; **7a**, 19556-90-2; **7b**, 19556-91-3; *trans*-1β-decalol, 6549-76-4; 1-acetoxy-4α-cyano-$\Delta^{1,10}$-octalin, 19556-93-5; 1-acetoxy-4β-cyano-$\Delta^{1,10}$-octalin, 19556-94-6; *trans*-1β-decalyl methanesulfonate, 19556-95-7.

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[20] W. Hückel, *Ann.*, **441**, 1 (1925).

[21] W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Amer. Chem. Soc.*, **76**, 4420 (1954).

[22] LSKIN2, written by C. E. DeTar and D. F. DeTar, Florida State University, as modified by Dr. H. A. Hammond.

Resin Acids. XV. Oxidative Transformations of the Levopimaric Acid–Acetylenedicarboxylic Ester Adduct[1,2]

WERNER HERZ AND R. C. BLACKSTONE[3]

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

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The oxidation of certain Diels–Alder adducts of levopimaric acid was investigated with a view to preparing intermediates suitable for the synthesis of polycyclic molecules. Oxidation proceeded satisfactorily only in the presence of a 1a–4a double bond. Because of its accessibility the adduct of levopimaric acid and acetylenedicarboxylic ester was used as model for studying the oxidative transformations of such compounds and was found to undergo a number of unusual reactions.

Diels–Alder adducts of levopimaric acid such as **1**[4] are potential starting materials for the synthesis of naturally occurring polycyclic systems if a way can be found to degrade the five-carbon bridge across ring C. Unfortunately the *endo* configuration of the most useful adducts appears to render the double bond inaccessible to the common oxidizing agents,[5-11] ozonolysis and permanganate oxidation proceeding normally only in the case of those adducts where R_1 and R_2 are *trans*, as in **3**,[1,12,13] or where R_1 = H.[1,12] In the present paper we describe our work on the oxidative transformations of some derivatives of **1** and of **4**,[14] which was undertaken with a view toward overcoming this difficulty (Chart I).

Our first efforts were directed at **5**,[4] **6**,[4] and **7**.[4,15] None of these substances was attacked by ozone or by potassium permanganate under conditions which effected smooth oxidation of compounds of type **3**; more drastic conditions led to intractable mixtures. More-

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[1] Previous paper: W. Herz, R. N. Mirrington, H. Young, and Y. Lin, *J. Org. Chem.*, **33**, 4210 (1968).

[2] Supported in part by a grant from the National Science Foundation (GP-6362).

[3] U. S. Public Health Service Fellow, 1962–1965; Ethyl Corp. Fellow, 1964–1965.

[4] W. Herz, R. C. Blackstone, and M. G. Nair, *J. Org. Chem.*, **32**, 2992 (1967). The numbering of **1** and its transformation products is discussed in ref 15 of this reference. Compounds of type **4** are numbered as shown according to the usual convention. The *Chemical Abstracts* name for **4** is 5a,8-dimethyl-12-isopropyl-1,2,8-tricarboxymethyl-4,4a,5,5a,6,7,8,8a,-9,10-decahydro-3,10a,-ethenophenanthrene.

[5] The only compounds of this type which have been studied are maleopimaric acid (**2**) and some of its derivatives.[6-11]

[6] L. Ruzicka and St. Kaufmann, *Helv. Chim. Acta*, **23**, 1346 (1940); **24**, 939 (1941).

[7] L. Ruzicka and W. A. Lalande, *ibid.*, **23**, 1357 (1940).

[8] L. H. Zalkow, R. A. Ford, and J. P. Kutney, *J. Org. Chem.*, **27**, 3535 (1962).

[9] L. H. Zalkow and N. Girotra, *ibid.*, **28**, 2033 (1963).

[10] Le-Van-Thoi and C. P. Ngoc-Son, *C.R. Acad. Sci., Paris*, **257**, 2495 (1963).

[11] L. H. Zalkow, M. V. Kulkarni, and N. Girotra, *J. Org. Chem.*, **30**, 1679 (1965).

[12] N. Halbrook, R. V. Lawrence, R. L. Dressler, R. C. Blackstone, and W. Herz, *ibid.*, **29**, 1017 (1964). This paper contains an unfortunate misprint. On p 1019, in column 1, lines 45 and 47, and in column 2, line 4, XV should be replaced by XVI. The numbering of adducts of type **3** and **4** is given in this reference.

[13] L. H. Zalkow and D. R. Brannon, *ibid.*, **29**, 1296 (1964).

[14] W. Herz, R. C. Blackstone, and M. G. Nair, *ibid.*, **31**, 1800 (1966).

[15] The preparation of **7** from **1** is relatively tedious and proceeds in poor over-all yield.[4] Several attempts to prepare **6** and/or **7** more directly by inducing a diene condensation between methyl levopimarate and cyclohexenone failed. This provides another example of the sluggishness of cyclohexenone as a dienophile since the lower homolog cyclopentenone affords a mixture of adducts, albeit in only mediocre yield (W. Herz, R. C. Blackstone, and M. G. Nair, to be published).