Cyclohexyl diphenylphosphinate (14.45 g., 0.048 mole) was placed in a flask which was part of a system containing a thermometer and a delivery tube leading to a series of three traps with a drying tube at the exit. The entire system was swept with anhydrous nitrogen and the receivers were then immersed in Dry Ice–acetone traps. With a slow stream of nitrogen passing through the entire system, the material was melted and the temperature was raised quickly to 195° with rapid stirring. Condensate could be observed in the delivery tube. After holding the temperature at 200–205° for approximately 15 min. at which time no additional condensate was observed forming in the delivery tube, the temperature was increased to 230° during a period of 20 min. The distillate was filtered immediately into a capped vial: yield of cyclohexene, 3.56 g. (90.2%). Identification was completed by g.l.c., infrared analysis, and refractive index measurement ($n^{22}\mathrm{D}$ 1.4462, lit.[23] $n^{15.1}\mathrm{D}$ 1.44921). In a similar run on a larger scale (36.7 g., 0.122 mole of ester) the yield was 96.6%. The pyrolysis residue melted at 189–92° and was only slightly discolored. This was taken up in 10% aqueous sodium hydroxide solution and extracted with benzene. Upon acidification of the solution, diphenylphosphinic acid was deposited as a finely divided solid which, after filtering and drying, gave 10.47 g. (99.7%) of the acid, m.p. 192–193.5°. No depression was found on a mixture melting point determination with an authentic sample.

In the case of the cholesteryl ester, no material distilled from the flask. Cold aqueous sodium hydroxide removed diphenylphosphinic acid while ether dissolved the residual material. Concentration of the ether gave an oil which was chromatographed on 200 g. of acid-washed alumina. Elution with petroleum ether (b.p. 30–60°) gave 9.60 g. (96% based on theoretical diene) of an uncrystallizable, viscous material which showed a positive rotation chloroform, $[\alpha]^{24}\mathrm{D}$ +13°. Ultraviolet absorption maxima were visible at 237 mμ (shoulder at 230 mμ) and at 245 mμ (shoulder at 255 mμ) in cyclohexane (3,5-cholestadiene has a maximum at 235 mμ in isopropyl alcohol[21]). Thin layer chromatography on silica using petroleum ether for elution showed two spots. The reported rotation for 3,5-cholestadiene is $[\alpha]^{20}\mathrm{D}$ −129.6° ($HCCl_3$).[24]

**G.l.c. Analysis of Pyrolysis Products.**—All analyses were obtained using a 6 ft. × 0.125 in. column packed with 5% silicone 30 on 60–80-mesh acid-washed Chromosorb G, DMCS. Several other columns were tested but gave poorer results. Samples were taken from capped vials and injected neat. Areas under peaks were determined from averages of several injections by measurement of peak height times width at half-height.[25] In the analysis of the octenes it was shown that the areas represented by the different isomers were equivalent when equal weights of isomers were injected. From this information, analysis of these olefins consisted of taking the ratio of the area of each peak to total area of all three peaks to obtain per cent distribution.

**Attempted Isomerization of 1-Octene.**—Diphenylphosphinic acid (0.830 g., 0.0038 mole) and 1-octene (4.98 g., 0.0445 mole) were mixed (heterogenous mixture) and distilled through a small Vigreux column. Four cuts were taken (112–130°), all of which were shown to be identical by g.l.c. and to contain only 1-octene.

**Attempted Isomerization of *cis* 2-Octene.**—Diphenylphosphinic acid (0.604 g., 0.0027 mole) and *cis*-2-octene (6.036 g., 0.0538 mole) were mixed and the heterogenous mixture was heated at reflux (125°) for 2.5 hr. G.l.c. analysis indicated only one peak for *cis*-2-octene.[26]

**Acknowledgment.**—The authors wish to thank Dr. E. J. Eisenbraun for helpful discussions and the American Petroleum Institute Research Grant 58A for supplying samples of some of the hydrocarbons needed in this work.

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[23] E. Beckmann and H. Eickelberg, *Ber.*, **29**, 418 (1896).

[24] F. S. Spring and G. Swain, *J. Chem. Soc.*, 83 (1941).

[25] R. P. W. Scott and D. W. Grant, *Analyst*, **89**, 179 (1964). This article gives a thorough review of methods used for measuring chromatograms and indicates that the method used above is preferred.

[26] Two months after this paper was submitted, Dr. Paul Haake informed us he had found the same pyrolytic elimination. Different examples of alkyl diphenylphosphinates were studied but results were similar to ours.

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# Reduction of Alkylidenecyanoacetates with Sodium Borohydride

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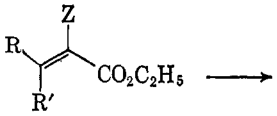
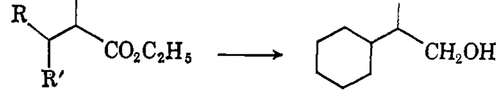
*Received March 23, 1965*

Reduction of diethyl isopropylidenemalonate (**1**), ethyl cyclohexylidenecyanoacetate (**2**), and the decalylidenecyanoacetates **7** and **22** with sodium borohydride proceeds readily with saturation of the carbon–carbon double bond. The ratio of epimers at C-2 in cyanoacetates **8** and **9** depends upon the solvent and nature of the hydride species employed. Reduction of unsaturated cyanoacetate **22** affords the axial dihydro compound **23**. Stereochemical results suggest the reduction is controlled by approach of the reducing agent rather than product stability.

We were confronted in our pursuit of certain synthetic objectives with the problem of selective double-bond reduction in alkylidenemalonic and alkylidenecyanoacetic esters. Our search for a satisfactory solution to this problem prompted us to examine the potential of sodium borohydride as a reducing agent for such carbon–carbon double bonds. We now report initial results to demonstrate the feasibility of this reaction and reveal, for the first time, its stereochemical outcome.



**1**, R = R′ = $CH_3$; Z = $CO_2C_2H_5$
**2**, R = R′ = $(CH_2)_5$; Z = CN



**3**, R = R′ = $CH_3$; Z = $CO_2C_2H_5$ **5**
**4**, R = R′ = $(CH_2)_5$; Z = CN

Addition of ethanolic sodium borohydride to a solution of diethyl isopropylidenemalonate (**1**)[1] or ethyl cyclohexylidenecyanoacetate (**2**)[2] resulted in complete reduction of the carbon–carbon double bonds within 4 hr. Reduction of the latter compound was particularly facile and required only 1 hr. at 0° with 1 molar equiv. of sodium borohydride. The respective products, diethyl isopropylmalonate (**3**)[3] and ethyl cyclohexylcyanoacetate (**4**),[4] were obtained in 72 and 85% yield (Table I, entries 1 and 2). Prolonged reaction

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[1] A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2644 (1938).

[2] A. C. Cope, C. M. Hofmann, C. Wykoff, and E. Hardenbergh, *ibid.*, **63**, 3452 (1941).

[3] E. Voliviler, *ibid.*, **47**, 2239 (1925).

[4] E. R. Alexander and A. C. Cope, *ibid.*, **66**, 886 (1944).

TABLE I

OLEFIN REDUCTIONS

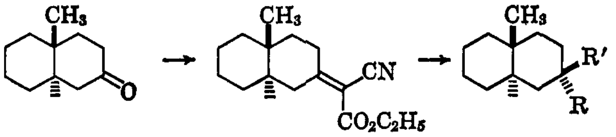
| Entry | Olefin | Reaction conditions[a] | Product(s) | Yield, % |
|---|---|---|---|---|
| 1 | 1 | $NaBH_4$ in ethanol, 25° for 4 hr. | **3** | 72 |
| 2 | 2 | $NaBH_4$ in ethanol, 0° for 1 hr. | **4** | 85 |
| 3 | 2 | $NaBH_4$ in DME, 0° for 1 hr. | **4** | .. |
| 4 | 2 | $NaBH_4$ in ethanol, 25° for 12 hr. | **5** | 54 |
| 5 | 7 | $H_2$–Pd–C in ethanol | **8**:**9** = 0.7 | 94 |
| 6 | 7 | $LiAl(O\text{-}t\text{-}Bu)_3H$, 0° for 1 hr. | **8**:**9** = 0.5 | 60 |
| 7 | 7 | $NaBH_4$ in ethanol, 0° for 1 hr. | **8**:**9** = 1 | 74 |
| 8 | 7 | $NaBH_4$ in DME 0° for 1 hr. | **8**:**9** = 2.3 | 71 |
| 9 | 7 | $NaBH_4$ in THF, 0° for 2 hr. | **8**:**9** = 2.7 | 70 |
| 10 | 22 | $H_2$Pd–C in ethanol | **23** | 91 |
| 11 | 22 | $NaBH_4$ in DME, 0° for 1 hr. | **23** | 76 |
| 12 | 22[b] | $NaBH_4$ in DME, 0° for 1 hr. | **23** | 80 |

[a] DME = 1,2-dimethoxyethane, THF = tetrahydrofuran. [b] Crystalline isomer, m.p. 82–83°.

time (Table I, entry 4) allowed the further reduction of ethyl cyclohexylidenecyanoacetate (**2**) to cyano alcohol **5**. Apparently, chemical reduction of the alkylidene double bond occurs with remarkable ease.[5] The relatively facile reduction of the ester grouping of ethyl cyclohexylcyanoacetate (**4**) leading to cyano alcohol **5** is also noteworthy.[6]

We next directed our attention to the stereochemical course of alkylidene double-bond reduction with particular interest in the configuration at the β-carbon atom of the dihydro compounds. For this study the decalylidenecyanoacetate **7** seemed well suited. The required compound was prepared in 75% yield *via* condensation[2] of ethyl cyanoacetate with *trans*-10-methyl-2-decalone (**6**).[7]

Reduction of unsaturated cyanoacetate **7** with ethanolic sodium borohydride (Table I, entry 7) afforded a 1:1 mixture of epimeric cyanoacetates **8** and **9**.[8] A significant increase in the ratio of equatorial **8** to axial cyanoacetate **9** was observed when 1,2-dimethoxyethane was employed instead of ethanol as a solvent in the borohydride reduction (Table I, entry 8). Essentially the same ratio of stereoisomers was obtained using tetrahydrofuran as a solvent. Smooth reduction of **7** was also effected with lithium tri-*t*-butoxyaluminohydride.[9] In this case, a mixture predominating in axial cyanoacetate **9** was isolated (Table I, entry 6). A similar preponderance of the axial isomer **9** resulted from hydrogenation of **7** over palladium on carbon (Table I, entry 5).



**6** **7**[a] **8–11**

**8**, R = H; R′ = $*CH(CN)CO_2C_2H_5$[b]

**9**, R = $*CH(CN)CO_2C_2H_5$;[b] R′ = H

**10**, R = H; R′ = $CH_2CO_2CH_3$

**11**, R = $CH_2CO_2CH_3$; R′ = H

[a] Isomers with CN and $CO_2C_2H_5$ interchanged. [b] Epimeric mixture at *C.

Quantitative analysis of cyanoacetate **8** and **9** mixtures and tentative assignment of stereochemistry (at C-2) was possible through n.m.r. measurements (Table II). The cyanoacetates **8** and **9** exhibit distinct doublets in the 3.5-p.p.m. region of the spectrum due to the α-methine hydrogen of the cyanoacetate grouping. The coupling constant of the higher field doublet was 5 c.p.s. in good agreement with that of the analogous doublet ($J$ = 5 c.p.s.) observed for ethyl cyclohexylcyanoacetate (**4**). The lower field doublet displayed a coupling constant of 11.5 c.p.s.[10] The assumption that the higher field doublet resulted from the equatorial isomer **8** was later validated. The position of these doublets shifted to higher field upon dilution indicating intermolecular hydrogen bonding.[11] Integration of n.m.r. spectra provided estimates of the isomer ratios (**8**:**9**) resulting from decalylidenecyanoacetate **7** under various reduction conditions. Isomer ratios obtained from gas chromatographic analyses substantiated these estimates.

TABLE II

N.M.R. OF DECALYLACETIC ESTERS[a]

| Ester | $HC(CN)CO_2Et$ or $H_2CCO_2CH_3$ resonance, p.p.m. | Multiplicity | $J$, c.p.s. | Angular $CH_3$ resonance, p.p.m. |
|---|---|---|---|---|
| **4** | 3.36[b] | Doublet | 5.5 | ... |
| **8** | 3.40[b] | Doublet | 5 | 0.88 |
| **9** | 3.66[b] | Doublet | 11.5 | 0.88 |
| **23** | 3.62[b] | Doublet | 11.0 | 0.98[c]<br>0.94[c] |
| **10** | 2.10 | Unresolved | ... | 0.82 |
| **11** | 2.36 | Unresolved | ... | 0.85 |

[a] A Varian A-60 spectrometer was used. Tetramethylsilane was the internal standard and carbon tetrachloride was the solvent. [b] Obtained from a 30% (w./v.) solution. The chemical shift is concentration dependent. [c] Two methyl peaks are observed due to $*CH(CN)CO_2Et$ epimers.

The stereochemistry assigned to decalylcyanoacetates **8** and **9** received confirmation through degradation to decalylacetates **10** and **11** and comparison of the resulting mixtures with authentic specimens of **10** and **11**. Degradation of the cyanoacetates was achieved by saponification and decarboxylation in refluxing ethylene glycolic potassium hydroxide. The resulting epimeric acids **14** and **18** were treated with

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(5) (a) In contrast, arylidenecyanoacetates are reduced slowly and arylidenemalonates afford complex mixtures with potassium borohydride: H. LeMoal, R. Carrie, and M. Bargain, *Compt. rend.*, **251**, 2541 (1960). (b) A comprehensive review of reductions with complex borohydrides summarizes the relatively few reports of carbon–carbon double-bond reduction: E. Schenker, *Angew. Chem.*, **73**, 81 (1961).

(6) Some examples wherein the ester grouping and double bond of arylacrylates are reduced with sodium borohydride have been reported: M. S. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963); J. A. Meschino and C. H. Bond, *ibid.*, **28**, 3129 (1963).

(7) M. Yanagita and K. Yamakawa, *ibid.*, **21**, 500 (1956).

(8) Each of these C-2 epimers is undoubtedly comprised of $*CH(CN)CO_2C_2H_5$ epimers. However the techniques used to measure the composition of these materials only allowed a distinction between the C-2 epimers.

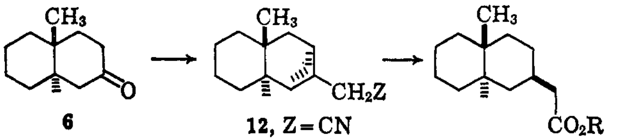
(9) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958).

(10) It is possible to predict this trend in coupling constants for **8** and **9** using the Karplus dihedral angle relationship and some reasonable assumptions regarding conformational preferences of the axial *vs.* equatorial side chain: *cf.* L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1962, p. 99 ff.

(11) *Cf.* L. M. Jackman, ref. 10, p. 66.

ethereal diazomethane affording the corresponding epimeric esters **10** and **11** in high over-all yield. Numerous attempts to analyze these mixtures by gas chromatography failed, but an estimate of their composition was possible through n.m.r. spectroscopy. Both the $\alpha$-methylene protons and the angular methyl protons of esters **10** and **11** appeared at differing chemical shifts (Table II), and the intensities of these peaks provided a measure of each isomer which coincided with the composition of the respective cyanoacetate mixtures. Thus, the 1:1 mixture of **8** and **9** (Table I, entry 7) afforded a 1:1 mixture of **10** and **11**. Similarly, the 7:3 mixture of **8** and **9** (Table I, entry 8) gave a 2:1 mixture of **10** and **11**, and the 7:10 mixture of **8** and **9** (Table I, entry 5) gave **10** and **11** in the ratio 2:3.

We now consider independent stereoselective syntheses of esters **10** and **11**. The unsaturated nitrile **12** (presumed to be a mixture of double-bond isomers) was obtained in 54% yield *via* condensation of decalone **6** with cyanoacetic acid followed by decarboxylation.[12] Conversion to the equatorial ester **10** was accomplished in 60% yield by means of hydrolysis followed by hydrogenation over platinum and esterification with diazomethane. The peaks at 2.10 and 0.82 p.p.m. previously assigned to the equatorial component of the various mixtures of **10** and **11** corresponded exactly with peaks exhibited by pure ester **10**. The method of preparation described above defines the stereochemistry of ester **10** which, in turn, affirms the stereochemistry assigned to the corresponding component **8** of the cyanoacetate mixtures.

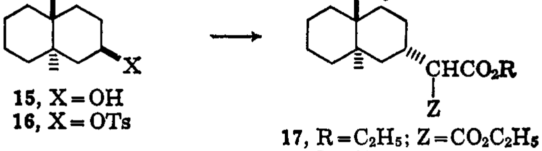


**6**

**12**, Z=CN
**13**, Z=CO$_2$H

**14**, R=H
**10**, R=CH$_3$

Authentic ester **11** was prepared by alkylation of diethyl malonate with *trans*-10$\beta$-methyl-2$\beta$-decalyl *p*-toluenesulfonate (**16**)[13] followed by hydrolysis and decarboxylation of malonate **17** and esterification of the resulting acid **18** with diazomethane. The n.m.r. spectrum of this ester exhibited peaks at 2.36 and 0.85 p.p.m. in agreement with those previously assigned to the axial component of the various epimeric mixtures of **10** and **11**.

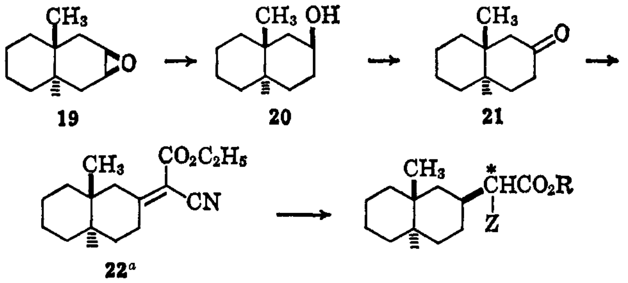


**15**, X=OH
**16**, X=OTs

**17**, R=C$_2$H$_5$; Z=CO$_2$C$_2$H$_5$
**18**, R=Z=H
**11**, R=CH$_3$; Z=H

Unsaturated cyanoacetate **22** was synthesized in order to evaluate the importance of product stability to the stereochemical outcome of alkylidenecyanoacetate double-bond reduction. The treatment of $\beta$-oxide **19** with lithium aluminum hydride followed by oxidation of the resulting alcohol **20** afforded ketone **21**. Condensation of ketone **21** with ethyl cyanoacetate proceeded slowly under the usual conditions[2] but the use of toluene and a large excess of the catalyst allowed isolation of the desired product (**22**) in 78% yield.

An authentic sample of axial cyanoacetate **23** was prepared by catalytic hydrogenation of decalylidenecyanoacetate **22**. The dihydro compound **23** was a mixture of isomers as evidenced by a sharp peak at 0.98 and 0.94 p.p.m. in the n.m.r. spectrum (Table II). That this mixture consisted of epimers at the side-chain carbon atom was confirmed by subsequent hydrolysis and decarboxylation, whereupon the crystalline acid **24** was obtained in 80% yield. A crystalline isomer of unsaturated cyanoacetate **22** gave the same epimeric mixture of saturated cyanoacetates **23** upon catalytic hydrogenation.[14] Molecular models of **22** clearly show that the angular methyl group should control the stereochemistry of catalytic hydrogenation to give axial cyanoacetate **23** as the predominant stereosiomer. Additional support for this assignment is gathered from the n.m.r. spectrum of the hydrogenation product which distinctly reveals the $\alpha$-methine proton of the side chain as a doublet at 3.62 p.p.m. ($J$ = 11 c.p.s.) in close agreement with the chemical shift and coupling constant observed for the analogous axial cyanoacetate **9** (Table II).[10]



**19** **20** **21**

**22**[a]

**23**,[b] Z=CN; R=C$_2$H$_5$
**24**, Z=R=H

[a] Isomers with CN and CO$_2$C$_2$H$_5$ interchanged. [b] Epimeric mixture at *C.

Reduction of the oily decalylidenecyanoacetate **22** with sodium borohydride in DME was complete within 1 hr. at 0°. The resulting cyanoacetate **23** yielded infrared and n.m.r. spectra which were identical with those of the material prepared by hydrogenation of **22**. The same epimeric mixture was obtained when the crystalline isomer of cyanoacetate **22** was reduced under these conditions (Table I, entry 12). The reduction of alkylidenecyanoacetates with sodium borohydride therefore appears to involve an enolate.

Analysis of the isomeric decalols (Table III) obtained by reducing decalone analogs (**6** and **21**) of decalylidenecyanoacetates **7** and **22** reveals some striking differences between the action of sodium

TABLE III

KETONE REDUCTIONS

| Entry | Ketone | Reaction conditions | Product(s) | Yield, % |
|---|---|---|---|---|
| 1 | 6 | NaBH$_4$ in C$_2$H$_5$OH | 15:25 = 6 | ~80 |
| 2 | 6 | NaBH$_4$ in (CH$_3$OCH$_2$)$_2$ | 15:25 = 6 | ~80 |
| 3 | 21 | NaBH$_4$ in (CH$_3$OCH$_2$)$_2$ | 26:20 = 0.7 | 82 |
| 4 | 21 | Na in *i*-PrOH | 20 | 75 |

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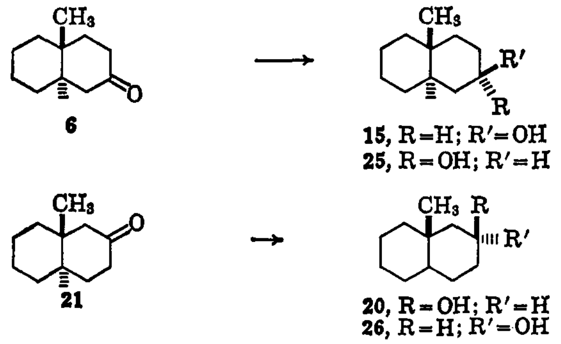
[12] D. E. Whiye and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1999 (1943).

[13] R. H. Baker, L. S. Minckler, and A. S. Hussey, *ibid.*, **81**, 2379 (1959).

[14] A 1,4-addition mechanism is evidently operative here: *cf.* R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

borohydride toward carbonyl groups and conjugated olefins in similar molecular environments. The stereochemistry attending reduction appears less sensitive to solvent and structural changes where decalones are involved (compare Table I entries 7, 8, 9, and 11 with Table III, entries 1, 2, and 3).[15]



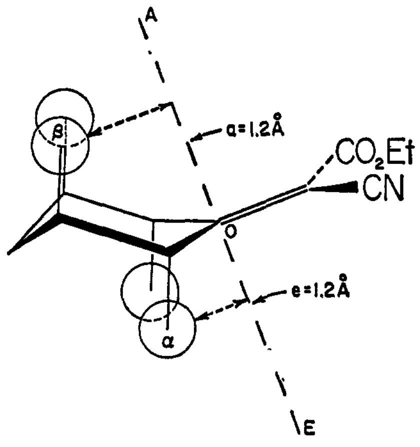
6

15, R=H; R'=OH
25, R=OH; R'=H

21

20, R=OH; R'=H
26, R=H; R'=OH

Figure 1 presents some measurements taken from a Dreiding model of ethyl cyclohexylidenecyanoacetate. The line AOE is perpendicular to the plane of the double bond. Distances from O on the AO portion of this line are designated "aO." The "a$\beta$" terms indicate distances between these points and the terminus of an axial $\beta$-CH bond. The terms "eO" and "e$\alpha$" have the same significance relative to an axial $\alpha$-CH bond. Assuming a reagent such as sodium borohydride attacks point O along line AOE (minimum transition state energy) we conclude that the relative importance of axial $\alpha$ and $\beta$ substituents in controlling such an approach will be determined not only by the size of these substituents but also by the distance from O at which the transition state is reached. If $\alpha$ and $\beta$ are identically substituted, attack will be more effectively blocked by the axial $\alpha$ group at a short distance from O and more effectively blocked by the axial $\beta$ group at a longer distance from O. The stereochemistry of alcohols resulting from the reduction of unhindered ketones with metal hydrides can thus be explained on a kinetic basis[16,17] only if the assumption is made that the hydride species closely approaches the carbonyl carbon in the transition state. Unhindered cyclohexanones afford higher proportions of axial alcohols with Grignard reagents[18] than with metal hydrides. Therefore according to the above hypothesis the transition state for additions of Grignard reagents must occur at a somewhat greater distance from the carbonyl carbon than analogous additions of hydrides. This results in greater control by axial $\beta$ substituents in the Grignard case. Reductions of alkylidenecyanoacetates appear to be likewise influenced by axial $\beta$ substituents. Our studies suggest the transition state is reached at greater distance from the cyclohexylidene carbon atom with lithium tri-*t*-butoxyaluminohydride in THF (Table I, entry 6) than with sodium borohydride in ethanol (Table I, entry 7) or sodium borohydride in DME (Table I, entry 8.)



| aO or eO | a$\beta$ | e$\alpha$ |
|---|---|---|
| 1.2 Å | 2.2 Å | 1.8 Å |
| 1.6 | 2.0 | 2.0 |
| 2.0 | 1.9 | 2.1 |
| 2.4 | 2.0 | 2.3 |
| 2.8 | 2.1 | 2.6 |
| 3.2 | 2.2 | 2.9 |
| 3.6 | 2.4 | 3.2 |
| 4.0 | 2.7 | 3.6 |
| 4.4 | 3.0 | 4.0 |

Figure 1.—Relative shielding of a cyclohexylidene carbon atom by $\alpha$ and $\beta$ substituents.

The above analogy between ketone and alkylidenecyanoacetate reductions ignores such potentially important factors as conformational distortion and entropy effects. However, this simplified picture explains many observations concerning the stereochemistry of additions to cyclohexanone carbonyl groupings[17,18] and adds a new dimension to mechanistic thinking regarding these reactions.

## Experimental[19]

**Diethyl Isopropylmalonate (3).**—To a solution of 13.0 g. (0.065 mole) of diethyl isopropylidenemalonate (1) in 10 ml. of ethanol was added a solution containing 2.60 g. (0.065 mole) of sodium borohydride in 30 ml. of ethanol at a rate to maintain the temperature of the reaction mixture below 40°.[19c] After an additional 3.5 hr., the mixture was diluted with saturated brine and isolated with ether.[19b] Distillation afforded 9.3 g. (72%) of diethyl isopropylmalonate, b.p. 49–50° (0.3 mm.), lit.[3] b.p. 105° (15 mm.), $n^{29}_{D}$ 1.4190, $\lambda^{film}_{max}$ 5.76 $\mu$ (CO).

**Ethyl Cyclohexylcyanoacetate (4). A. Ethanol Solvent.**—A solution of 12.0 g. (0.062 mole) of ethyl cyclohexylidenecyanoacetate in 10 ml. of ethanol was cooled to 0° and a solution of 0.72 g. (0.018 mole) of sodium borohydride in ethanol was added, with stirring, over a 25-min. period.[19c] After an additional 15 min. at 0°, the mixture was poured into saturated brine and the product was isolated with ether and benzene.[19b] Distillation gave 10.1 g. (85%) of colorless liquid: b.p. 112–113° (1.8 mm.), lit.[4] b.p. 138–139° (8 mm.); $n^{25}_{D}$ 1.4574; $\lambda^{film}_{max}$ 4.43 (CN) and 5.73 $\mu$ (CO); $\delta^{CCl_4}_{TSM}$ = 4.23 (OC$H_2$CH$_3$, quartet, $J$ = 7

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[15] For a survey of ketone reductions with sodium borohydride, see Schenker.[6b] The following papers are of particular interest: W. G. Dauben and R. E. Bozak, *J. Org. Chem.*, **24**, 1596 (1959); H. Haubenstock and E. E. Eliel, *J. Am. Chem. Soc.*, **84**, 2368 (1962).

[16] Figure 1 can also be used as a model for cyclohexanones.

[17] A similar kinetic argument for the reduction of unhindered ketones with lithium tri-*t*-butoxyaluminohydride has been advanced: J. C. Richer, *J. Org. Chem.*, **30**, 324 (1965). However, this explanation does not consider the effect of transition-state geometry on the stereochemistry of ketone reduction.

[18] H. O. House and W. L. Respess, *ibid.*, **30**, 301 (1965), and references therein.

[19] (a) Melting points were determined on a Fisher-Johns hot stage. (b) The isolation procedure consisted of thorough extraction and back-extraction with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous sodium sulfate or magnesium sulfate. The solvent was removed under reduced pressure on a steam bath after separation from the drying agent by filtration. (c) 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. (d) The prefix "*dl*" is omitted from names of racemic substances. The prefixes "$\alpha$" and "$\beta$" are used to designate relative configuration in racemic substances. (e) Microanalyses were performed by Micro Tech Laboratories, Inc., Skokie, Ill.

c.p.s.), 3.36 [C*H*(CN)CO$_2$Et, doublet, $J = 5.5$ c.p.s.], 1.32 p.p.m. (OCH$_2$C*H*$_3$, triplet, $J = 7$ c.p.s.).

**B. 1,2-Dimethoxyethane Solvent.**—A solution of 0.50 g. (2.6 mmoles) of ethyl cyclohexylidenecyanoacetate in 1.0 ml. of dry 1,2-dimethoxyethane (DME) was added to a stirred nearly homogeneous mixture of 30 mg. (0.8 mmole) of sodium borohydride and 6 ml. of DME at 0°.[19c] The mixture was stirred at 0° for 1 hr. and poured into water, and the product was isolated with ether.[19b] The infrared spectrum of this material was identical with that of authentic ethyl cyclohexylcyanoacetate prepared according to part A above.

**2-Cyano-2-cyclohexylethanol (5).**—A stirred solution containing 2.5 g. (0.065 mole) of sodium borohydride in 25 ml. of ethanol at 0° was treated dropwise with a solution of 12.0 g. (0.065 mole) of ethyl cyclohexylidenecyanoacetate in 25 ml. of ethanol.[19c] The mixture was allowed to stir at room temperature for 18 hr. and poured into saturated brine, and the product was isolated with ether and benzene.[19b] Distillation afforded 5.0 g. (54%) of colorless oil: b.p. 115–117° (0.5 mm.); $n^{29}$D 1.4743; $\lambda_{\max}^{\text{film}}$ 2.88 (OH), 4.43 (CN), 6.87 $\mu$; $\delta_{\text{TMS}}^{\text{CCl}_4} = 3.91$ (O*H*), 3.71 p.p.m. (CHC*H*$_2$O, doublet, $J = 6.5$ c.p.s.).

*Anal.* Calcd. for $C_9H_{15}NO$: C, 70.55; H, 9.86; N, 9.13. Found: C, 70.8; H, 9.9; N, 9.2.

**Ethyl *trans*-10β-Methyl-2-decalylidenecyanoacetate (7).**[19d]—The procedure of Cope, *et al.*,[2] was employed using 15.0 g. of decalone **6**, 12.0 g. of ethyl cyanoacetate, and 0.3 g. of ammonium acetate in 130 ml. of benzene.[19c] Cyanoacetate **7**, b.p. 115–116° (0.04 mm.), $n^{28}$D 1.5089, was obtained in 75% yield (17.5 g.): $\lambda_{\max}^{\text{film}}$ 4.48 (CN), 5.76 (CO), 6.23 $\mu$ (C=C).

*Anal.* Calcd. for $C_{16}H_{23}NO_2$: C, 73.52; H, 8.87; N, 5.36. Found: C, 73.8; H, 9.0; N, 5.3.

**Reduction of Decalylidenecyanoacetate 7. A. Sodium Borohydride in Ethanol.**—A solution containing 10.0 g. (0.039 mole) of cyanoacetate **7** in 20 ml. of ethanol was added over a 45-min. period to a stirred solution of 0.44 g. (0.01 mole) of sodium borohydride in 30 ml. of ethanol at 0°.[19c] After an additional 15 min., the mixture was poured into saturated brine and isolated with ether and benzene.[19b] Distillation afforded 7.35 g. (74%) of cyanoacetates **8** and **9**: b.p. 109–110° (0.04 mm.); $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO); $\delta_{\text{TMS}}^{\text{CCl}_4} = 4.20$ (OC*H*$_2$CH$_3$, quartet, $J = 7$ c.p.s.), 3.66 (C*H*CN of **9**, doublet, $J = 11.5$ c.p.s.), 3.40 (C*H*CN of **8**, doublet, $J = 5$ c.p.s.), 1.3 (OCH$_2$-C*H*$_3$, triplet, $J = 7$ c.p.s.), 0.88 p.p.m. (angular CH$_3$). The ratio **8**:**9** = 1 was found by integration of the peaks at 3.40 and 3.66 p.p.m. This ratio was in agreement with that found (**8**:**9** = 1.0) from gas chromatographic analysis of the distilled material.[20]

*Anal.* Calcd. for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.56; N, 5.32. Found: C, 73.1; H, 9.5; N, 5.5.

**B. Sodium Borohydride in 1,2-Dimethoxyethane.**—A solution of 41 mg. (1.1 mmoles) or sodium borohydride in 10 ml. of anhydrous 1,2-dimethoxyethane (DME) was cooled to 0° and 1.00 g. (3.8 mmoles) of cyanoacetate **7** in 1.0 ml. of anhydrous DME was added dropwise over a 5-min. period.[19c] After 1 hr. at 0° the mixture was poured into water and the product was isolated with ether.[19b] Distillation afforded 0.71 g. (71%), b.p. 115° (bath temp.) (0.2 mm.), $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO). The ratio of the n.m.r. peaks at 3.4 and 3.7 p.p.m. due to **8** and **9** was 2:1. Gas chromatography revealed 70% **8** and 30% **9** (**8**:**9** = 2.3) in agreement with the ratio determined using the n.m.r. spectrum.

**C. Sodium Borohydride in Tetrahydrofuran.**—The procedure outlined in part B was followed using 38 mg. (1 mmole) of sodium borohydride in 7 ml. of tetrahydrofuran (THF) and 0.50 g. (1.9 mmoles) of cyanoacetate **7** in 3 ml. of THF over a period of 2 hr. at 0°.[19c] Distillation gave 0.35 g. (70%) of colorless oil, b.p. 135° (bath temp.) (0.3 mm.), $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO). The infrared and n.m.r. spectra were identical with those of material prepared according to part B above. Gas chromatographic analysis[22] revealed 73% **8** and 27% **9**.

**D. Lithium Tri-*t*-butoxyaluminohydride in Tetrahydrofuran.**—To a solution containing 0.50 g. (1.9 mmoles) of cyanoacetate **7** in 10 ml. of anhydrous tetrahydrofuran (THF) at 0° was added 5.8 ml. of 0.35 *M* lithium tri-*t*-butoxyaluminohydride[9] in THF.[19c] After 1 hr. at 0°, the mixture was poured into water and the product was isolated with ether[19b] to give 0.30 g. (60%) of oil, b.p. 120–125° (bath temp.) (0.3 mm.), $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO). The ratio **8**:**9** = 0.5 was determined from the n.m.r. spectrum and gas chromatography.[20]

**E. Hydrogen Over Palladium–Carbon.**—A solution of 0.75 g. of cyanoacetate **7** in 25 ml. of ethanol was stirred under 1 atm. of hydrogen with 0.25 g. of 5% palladium on carbon. The theoretical volume of hydrogen (73 ml.) was absorbed in 1.1 hr. The mixture was filtered and the filtrate was distilled to give 0.70 g. (94%) of oil, b.p. 105–110° (bath temp.) (0.2 mm.), $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO). The ratio **8**:**9** = 0.7 determined from the n.m.r. spectrum agreed with the gas chromatographic[20] analysis (41% **8** and 59% **9**).

**Hydrolysis, Decarboxylation, and Esterification of Cyanoacetate 8 and 9 Mixtures.**—The following experiment is typical. A solution of 0.36 g. of cyanoacetate mixture (**8**:**9** = 1; from part A of the above experiment) and 0.2 g. of potassium hydroxide in 5 ml. of ethylene glycol was stirred under reflux for 12 hr.[19c] The cooled solution was poured into water washed with ether, and acidified with concentrated hydrochloric acid. The acidic product was isolated with ether and benzene[19b] and esterified with ethereal diazomethane to give 0.28 g. (90% over-all yield) of ester mixture **10** and **11**: b.p. 95° (bath temp.) (0.3 mm.); $\lambda_{\max}^{\text{film}}$ 5.73 $\mu$ (CO); $\delta_{\text{TMS}}^{\text{CCl}_4} = 3.62$ (OCH$_3$), 2.36 (C*H*$_2$CO of **11**), 2.10 (C*H*$_2$CO of **10**), 0.85 (angular CH$_3$ of **11**), 0.82 p.p.m. (angular CH$_3$ of **10**). We were unable to find conditions which would allow separation of this mixture by gas chromatography. However, analysis by integration of the peaks at 2.36 and 2.10 (CH$_2$CO) and 0.85 and 0.82 p.p.m. (angular CH$_3$) in the n.m.r. spectrum of this mixture showed that these esters were present in equal amount. Analogous results were obtained by identical treatment of the cyanoacetate mixtures **8** and **9** obtained in parts B–E above. In all cases the ratio of **10**:**11** found in the product agreed with the ratio of **8**:**9** in the starting material.

**Methyl (*trans*-10β-Methyl-2β-decalyl)acetate (10).**[19d]—The procedure of Cope, *et al.*,[21] was followed using 7.5 g. of decalone **6**, 11.5 g. of cyanoacetic acid, and 0.1 g. of ammonium acetate in 50 ml. of dry benzene at reflux for 37 hr.[19c] The yield was 4.4 g. (52%) of nitrile **12**, b.p. 97–100° (0.3 mm.), $n^{28}$D 1.5007, $\lambda_{\max}^{\text{film}}$ 4.43 $\mu$ (CN).

*Anal.* Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.11; N, 7.39. Found: C, 82.5; H, 10.2; N, 7.5.

The nitrile **12** (4.0 g.) was refluxed for 8 hr. with 0.6 g. of potassium hydroxide in 30 ml. of ethylene glycol.[19c] The cooled solution was poured into water, washed with ether, and acidified with concentrated hydrochloric acid. The acid **13** was isolated with ether[19b] and a 3.0-g. sample of the crude material (3.2 g. total) was dissolved in 30 ml. of acetic acid and reduced in a Parr hydrogenation apparatus at 50 p.s.i. of hydrogen over 0.3 g. of platinum oxide. After 5 hr., the mixture was filtered and the filtrate was concentrated. The residue was esterified with ethereal diazomethane affording 2.7 g. (31% yield based on decalone **6**) of ester **10**: b.p. 94–95° (0.4 mm.); $n^{28}$D 1.4774; $\lambda_{\max}^{\text{film}}$ 5.73 (CO), 7.86, 8.11, 8.63 $\mu$; $\delta_{\text{TMS}}^{\text{CCl}_4} = 3.62$ (OCH$_3$), 2.10 (C*H*$_2$-CO), 0.82 p.p.m. (angular CH$_3$).

*Anal.* Calcd. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.0; H, 10.8.

**Methyl (*trans*-10β-Methyl-2α-decalyl)acetate (11).**[19d]—To a mixture containing 12.8 g. of diethyl malonate and potassium *t*-butoxide (from 3.12 g. of potassium) in 150 ml. of *t*-butyl alcohol was added 11.5 g. of tosylate **16**[13] in portions under a positive nitrogen pressure. The reaction mixture was stirred under reflux for 24 hr.,[19c] most of the alcohol was removed by distillation, and the cooled residue was diluted with water and ether. The product was isolated with ether and benzene[19b] giving 3.5 g. of ester **17**, b.p. 140–150° (1.5 mm.). The residue began to decompose during distillation. Heating was therefore discontinued, and the remaining residue was evaporatively distilled affording an additional 3.5 g. of malonate **17**, b.p. 135° (bath temp.) (0.3 mm.), $n^{25}$D 1.4736. The combined yield was 7.0 g. (65%): $\lambda_{\max}^{\text{film}}$ 5.70, 5.76 (ester CO), 6.87, 7.29, 7.65, 8.11, 9.62 $\mu$.

*Anal.* Calcd. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.4; H, 9.7.

A solution containing 1.0 g. of ester **17** and 0.3 g. of potassium hydroxide in 25 ml. of ethylene glycol was heated at reflux for 15 hr.[19c] The cooled mixture was dissolved in water, washed with ether, and acidified with concentrated hydrochloric acid. The acid was isolated with ether and benzene[19b] affording 0.60 g. (90%) of acid **18**, m.p. 71–72°, after crystallization from aqueous

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(20) An 8 ft. × 0.25 in. column packed with 8% Silicone 550 oil on 60–80-mesh Chromosorb-W was used at 215°. Helium flow was 100 cc./min.

(21) A. C. Cope, A. A. D'Addieu, D. E. Whyte, and S. A. Glickman, *Org. Syn.*, **31**, 25 (1951).

methanol. The analytical sample, m.p. 71.5–72°, was obtained after an additional crystallization from aqueous methanol.

*Anal.* Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.1; H, 10.5.

A 0.50-g. sample of the above acid **18** was esterified with etheral diazomethane affording 0.46 g. (84%) of ester **11**: b.p. 95° (bath temp.) (0.2 mm.); $n^{28}$D 1.4800; $\lambda_{\max}^{\text{film}}$ 5.72 (CO), 7.24, 7.65, 7.90, 8.55, 8.86 $\mu$; $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 3.62 ($OCH_3$), 2.36 ($CH_2CO$), 0.85 p.p.m. (angular $CH_3$).

*Anal.* Calcd. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.0; H, 10.6.

***trans*-9β-Methyl-2β-decalol (20).**[19d,22]—A solution of 0.50 g. of oxide **19** and 0.25 g. of lithium aluminum hydride in 30 ml. of anhydrous ether was stirred for 16 hr. at room temperature and cautiously decomposed with 0.51 ml. of water and 0.41 ml. of 10% aqueous sodium hydroxide. The granular salts were removed by filtration and the filtrate was concentrated affording 0.56 g. of oily alcohol **20** which crystallized. This material was chromatographed on 60 ml. of silicic acid[23] and the crystalline fractions obtained by elution with 10% ether in benzene were combined giving 0.44 g. (87%) of material: m.p. 54–58°; $\lambda_{\max}^{\text{CCl}_4}$ 2.75, 2.95 (OH), 7.22, 7.35, 8.77, 9.77, 10.01, 10.10, 10.26, 10.53, 11.14 $\mu$. A sample, m.p. 57.5–58.5°, after two recrystallizations from pentane, was sublimed (50–60° at 0.02 mm.) prior to combustion analysis.

*Anal.* Calcd. for $C_{11}H_{20}O$: C, 78.49; H, 12.00. Found: C, 78.4; H, 12.0.

***trans*-9β-Methyl-2-decalone (21).**[19d]—A solution of 5.9 g. of oxide **19** in 150 ml. of anhydrous ether was reduced using 1.4 g. of lithium aluminum hydride as described above. The crude decalol **20** was dissolved in 75 ml. of acetone, the solution was cooled to 0°, and 10 ml. of Jones reagent[24] was added to the stirred solution over a 45-min. period. The excess oxidizing agent was destroyed with 2-propanol and the supernatant was concentrated under reduced pressure, diluted with water, and extracted with ether. The residual chromium salts were dissolved in water and extracted with ether. The combined extracts were dried over anhydrous magnesium sulfate, the solvent was removed under reduced pressure, and the residue was distilled giving 4.25 g. (72%) of the decalone **21**: b.p. 83–84° (1.5 mm.); $n^{25}$D 1.4892; $\lambda_{\max}^{\text{film}}$ 5.82 (CO), 6.84, 7.18, 7.67, 7.71, 8.08, 8.37, 8.52, 8.62, 10.06 $\mu$.

*Anal.* Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.6; H, 10.8.

**Ethyl *trans*-9β-Methyl-2-decalylidenecyanoacetate (22).**[19d]—A solution of 4.0 g. of decalone **21** and 4.5 g. of ethyl cyanoacetate in 75 ml. of toluene containing 2.0 g. of ammonium acetate was stirred at reflux with continuous removal of water *via* a Dean-Stark trap.[19c] After 12 hr. 1.5 ml. of water had accumulated in the trap and the mixture was allowed to cool. Water was added and the product was isolated with ether.[19b] Fractionation of the residue afforded 4.9 g. (78%) of cyanoacetate **22**: b.p. 122–126° (0.06 mm.); $n^{28}$D 1.5100; $\lambda_{\max}^{\text{film}}$ 4.48 (CN), 5.77 (CO), 6.23 $\mu$ (C=C).

*Anal.* Calcd. for $C_{16}H_{23}NO_2$: C, 73.52; H, 8.87; N, 5.36. Found: C, 73.3; H, 8.8; N, 5.8.

The n.m.r. spectrum showed $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 4.28 ($OCH_2CH_3$, quartet, $J$ = 7 c.p.s.), 1.33 ($OCH_2CH_3$, triplet, $J$ = 7 c.p.s.), 0.73, 0.79 p.p.m. (angular $CH_3$). Apparently the chemical shift of the angular methyl group differs for each of the two geometric isomers (about the C=C) comprising the cyanoacetate mixture **22**. The validity of this assumption was proven as follows.

The distilled mixture of isomeric cyanoacetates **22** upon standing formed a semicrystalline mass from which one isomer, m.p. 81–82°, was obtained by trituration with pentane and recrystallization of the triturated solid from pentane. The angular methyl peak in the n.m.r. spectrum of this substance appeared as a singlet at 0.79 p.p.m. The analytical specimen, m.p. 82.5–83°, was obtained after several recrystallizations from pentane.

*Anal.* Calcd. for $C_{16}H_{23}NO_2$: C, 73.52; H, 8.87; N, 5.36. Found: C, 73.4; H, 9.1; N, 5.4.

Catalytic hydrogenation of either the semisolid mixture or the recrystallized cyanoacetate **22** gave the identical mixture of diasterisomeric (at the $^*CH(CN)CO_2C_2H_5$ carbon) cyanoacetates **23** (see below) as evidenced by the infrared and n.m.r. spectra.

When the condensation of ketone **21** with ethyl cyanoacetate was attempted under the usual conditions using the benzene azeotrope procedure and a catalytic quantity of ammonium acetate,[2] essentially all of the starting ketone was recovered after 15 hr.

**Ethyl (*trans*-9β-Methyl-2β-decalyl)cyanoacetate (23).**[19d] **A. Catalytic Hydrogenation.**—A 0.50-g. sample of cyanoacetate **22** in 15 ml. of ethanol was stirred with 0.10 g. of 5% palladium on carbon under 1 atm. of hydrogen. After 1 hr. the theoretical quantity of hydrogen had been absorbed and the mixture was filtered. The filtrate was distilled affording 0.46 g. (91%) of cyanoacetate **23**: b.p. 115–120° (bath temp.) (0.2 mm.); $n^{28}$D 1.4835; $\lambda_{\max}^{\text{film}}$ 4.43 (CN) and 5.72 $\mu$ (CO); $\delta_{\text{TMS}}^{\text{CCl}_4}$ = 4.27 ($OCH_2CH_3$, quartet, $J$ = 7 c.p.s.), 3.62 (CHCHCN, doublet, $J$ = 11 c.p.s.), 1.30 ($OCH_2CH_3$, triplet, $J$ = 7 c.p.s.), 0.98, 0.94 p.p.m. (angular $CH_3$).[25]

*Anal.* Calcd. for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.56; N, 5.32. Found: C, 73.2; H, 9.7; N, 5.5.

The same result was obtained using the crystalline isomer of **22**, m.p. 82–83°.

**B. Sodium Borohydride in 1,2-Dimethoxyethane.**—The procedure described for reduction of the isomeric cyanoacetate **7** was followed using 0.50 g. of cyanoacetate **22**. Distillation gave 0.38 g. (76%) of cyanoacetate **23**, b.p. 110–115° (bath temp.) (0.25 mm.). The infrared and n.m.r. spectra of this cyanoacetate were identical with those of material prepared according to part A.

The same result was obtained using the crystalline isomer of **22**, m.p. 82–83°.

**(*trans*-9β-Methyl-2β-decalyl)acetic Acid (24).**[19d]—A solution containing 0.25 g. of cyanoacetate **23** and 0.2 g. of potassium hydroxide in 10 ml. of ethylene glycol was refluxed for 16 hr.[19c] The cooled solution was diluted with water, washed with ether, and acidified with concentrated hydrochloric acid. The acidic product was isolated with ether and benzene[19b] and crystallized from aqueous methanol. The first crop gave 0.10 g. (50%), m.p. 103–104.5°. A second crop yielded 0.06 g. (30%), m.p. 101–103.5°. The first crop was recrystallized from aqueous methanol to give the analytical sample, m.p. 103.5–104.5°.

*Anal.* Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.1; H, 10.7.

**Reduction of *trans*-10β-Methyl-2-decalone.**[19d]—A solution containing 1.0 g. of decalone **6** and 0.24 g. of sodium borohydride in 8 ml. of ethanol was stirred at room temperature for 4.5 hr.[19c] The product was isolated with ether and benzene.[19b] Analysis by gas chromatography[26] revealed 85% of the β alcohol **15** and 15% of the α alcohol **25**.[19d] The peaks were identified by peak enhancement using authentic samples of the two alcohols.

The above reduction was repeated using 1,2-dimethoxyethane as the solvent. The product isolated after 10 hr. contained 85% of the β alcohol **15** and 15% of the α alcohol **25**.[19d]

**Reduction of *trans*-9β-Methyl-2-decalone.**[19d]—A solution containing 0.28 g. of decalone **21** and 0.06 g. of sodium borohydride in 10 ml. of ethanol was stirred at room temperature for 5 hr.[19c] The mixture was poured into saturated brine and the product was isolated with ether and benzene.[19b] Distillation gave 0.23 g. (82%) of colorless oil, b.p. 82° (bath temp.) (0.2 mm.). Analysis by gas chromatography[26] revealed a mixture containing 60% of the β-decalol **20** and 40% of the α-decalol **26** identified by comparing retention times (7.8 and 9.0 min., respectively) with those of authentic samples determined under identical conditions (helium flow rate of 90 cc./min. at 175°).

***trans*-9β-Methyl-2α-decalol (26).**[19d]—The procedure of Johnson and co-workers[27] was employed using 0.10 g. of decalone **21** and 1.5 g. of sodium in 25 ml. of 2-propanol. Distillation afforded 0.05 g. (50%): b.p. 140° (bath temp.) (0.4 mm.); $\lambda_{\max}^{\text{film}}$ 2.99 (OH), 6.86, 8.72, 9.60, 10.10 $\mu$. Analysis by gas chromatography[26] revealed a single peak whose retention time differed from a sample of authentic β-decalol **20** and corresponded to one of the peaks observed in the decalol mixture obtained from decalone **21**.

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(22) Experiment was performed by Noal Cohen.

(23) Prepared according to H. Brockmann and H. Muxfeldt, *Ber.*, **89**, 1379 (1956).

(24) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(25) The chemical shift of the angular methyl group apparently depends upon the configuration at the $^*CH(CN)CO_2Et$ carbon. The composition of this epimeric mixture is estimated to be 1.7:1 from integration of the peaks at 0.98 and 0.94 p.p.m.

(26) A 20 ft. × 0.25 in. column packed with 10% Ucon 75-H, 90,000 Polar on 60–80-mesh Gas Pack-W was used. The temperature was 185° and the flow rate was 100 cc./min. of helium.

(27) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frish, L. Dreger, and V. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).

*Anal.* Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.97. Found: C, 78.65; H, 11.81.

**Acknowledgment.**—We thank the Public Health Service for support of this work through a research grant (AI-04965) from the National Institute of Allergy and Infectious Diseases. We are indebted to Professor A. S. Hussey for a sample of decalol 25 and to Mr. Joel Williams and Dr. Frederick Schappel for their generous assistance with gas chromatographic analyses.

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# Synthetic Studies in The Resin Acids Series. VI[1]

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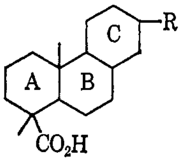
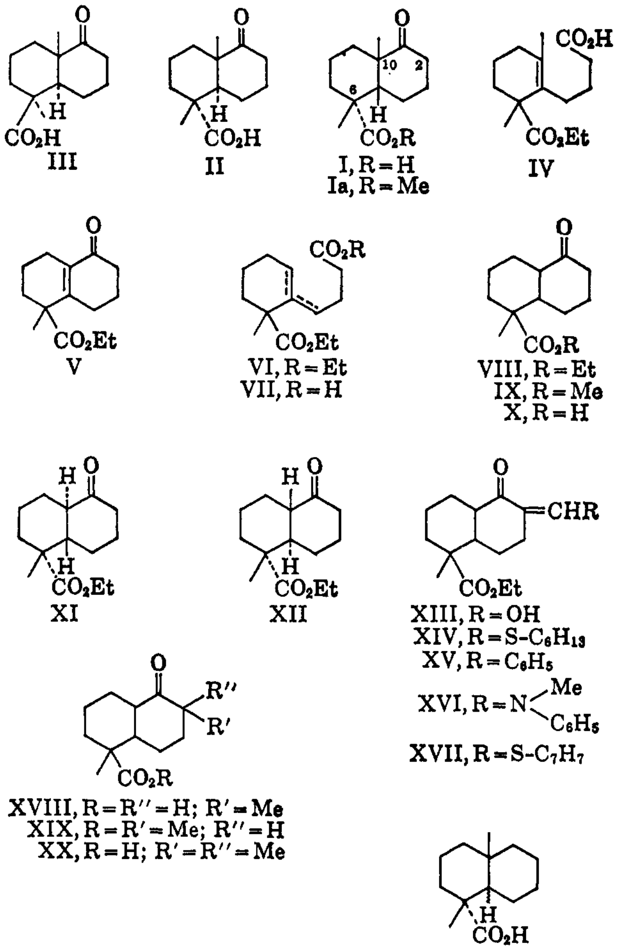
*Received March 17, 1965*

A synthesis of a stereoisomer of the bicyclic keto acid I is described, and this compound has been utilized for developing new syntheses for two isomers of methyl desisopropyldehydroabietate. A novel method for converting an A/B *cis* isomer to the corresponding A/B *trans* isomer of tricarbocyclic resin acids through treatment with palladium on charcoal at elevated temperature has been developed.



Several pathways for the synthesis of resin acids have been reported from this[3,4] and other laboratories.[5] While some investigators have constructed bicyclic intermediates with ring A and C bearing suitable substituents for the closure of ring B, others have constructed rings C and B at the start, leaving ring A to be built up in the latter stages of the synthesis. None of the methods reported so far have followed the sequence of constructing rings A, B, and C in that order. In addition, all reported syntheses have invariably utilized compounds with an aromatic ring which ultimately becomes ring C of the acids. No approach has been reported which utilizes a tricarbocyclic intermediate with a hydroaromatic ring C. After a short communication on our present work had been published,[1b] Spencer[6] reported the synthesis of methyl desisopropyldehydroabietate through the route just discussed.

CHART I



Our immediate aim was to construct a bicyclic system with all the required structural details so that it would be possible to develop it into a tricarbocyclic system. Compounds II and III (Chart I) seemed to satisfy all these requirements. Having failed to achieve the cyclization of IV[7] which would ultimately have afforded II or III, attention was turned to the possibility of synthesizing V and introducing the angular methyl group at a later stage. Dehydration of the saturated hydroxy ester[8] corresponding to VI was effected with phosphorus pentoxide, potassium bisulfate being found unsatisfactory. This was partially hydrolyzed and afforded VII. Cyclization of VII with polyphosphoric acid[5a] proceeded smoothly furnish-

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[1] (a) Paper V: M. Sharma, U. R. Ghatak, and P. C. Dutta, *Tetrahedron*, **19**, 985 (1963); (b) C. T. Mathew and P. C. Dutta, *Proc. Chem. Soc.*, 135 (1963); (c) C. T. Mathew, G. Sengupta, and P. C. Dutta, *ibid.*, 336 (1964).

[2] To whom all communications regarding this paper may be made.

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