2.82 (OH), 7.44, 7.50, 8.53, 10.80, 11.45, 12.00, 12.71, and 13.63 μ.

The crude mesylate (366 mg.) in 15 ml. of acetone was cooled to 0° and treated with 0.33 ml. of Jones reagent.[18] Isolation with ether[12b] as described above for keto tosylate **17** afforded 304 mg. of crude crystalline keto mesylate **19**: $\lambda_{max}^{CHCl_3}$ 5.90 (cyclooctanone CO), 7.40, 7.50, 8.52, 10.56, 10.82, and 11.47. Recrystallization from ethyl acetate–heptane afforded 230 mg. (65%) of white solid, m.p. 127–129°. Prolonged heating during the recrystallization procedure caused decomposition of this material as evidenced by deep yellow coloration of the solution. The analytical specimen, m.p. 128–129°, was obtained after three recrystallizations from ethyl acetate–heptane: $\delta_{max}^{CCl_4} = 4.57$ (H-8, X of ABX, $J_{AX} = 10$ c.p.s., $J_{BX} = 6$ c.p.s.),[11] 3.08 (CH_3SO_3), and 1.16 p.p.m. (C-1 CH_3).

Anal. Calcd. for $C_{13}H_{22}O_4S$: C, 56.91; H, 8.08; S, 11.69. Found: C, 57.1; H, 8.0; S, 11.6.

cis-**5-Methyl-4-cyclodecenylmethanol (10)**.—The mesylate **8** was prepared from 792 mg. of diol **7** (m.p. 95–105°) as described above. A solution containing the entire crude mesylate and 0.30 g. of lithium aluminum hydride in 24 ml. of anhydrous 1,2-dimethoxyethane was stirred under reflux for 10 hr. The mixture was treated carefully with 0.6 ml. of water and 0.48 ml. of 10% aqueous sodium hydroxide and the salts were removed by filtration after addition of ether. Distillation gave 0.64 g. (88%) of alcohol **10**: b.p. 85–90° (bath temperature) at 0.05 mm.; λ_{max}^{film} 2.98 (OH), 6.76, 6.90, 9.48, 9.85, 10.30, 11.76, and 12.54 μ; $\delta_{TMS}^{CCl_4} = 5.05$–5.4 (H-4, multiplet centered at 5.25), 3.5 (HO), 3.37 ($CHCH_2OH$, doublet, $J = 5$ c.p.s.), and 1.67 p.p.m. ($CH_3C{=}C$).

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.8; H, 12.2.

The methanesulfonate derivative, m.p. 50–52° (after crystallization from ether-hexane), was prepared[17] in 70% yield.

Anal. Calcd. for $C_{13}H_{24}O_3S$: C, 59.96; H, 9.29; S, 12.31. Found: C, 60.0; H, 9.2; S, 12.1.

Acknowledgment.—We acknowledge with pleasure the financial support of a National Science Foundation Institutional Grant. C. J. V. S. expresses gratitude to the National Science Foundation for a summer fellowship (1964) and to the Ethyl Corporation for a fellowship (1963–1964).

Products from the Hydroformylation of Cyclohexene Oxide[1]

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Received March 30, 1965

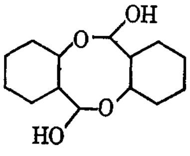
The major product resulting from the stoichiometric hydroformylation of cyclohexene oxide is not the expected 2-hydroxycyclohexanecarboxaldehyde but its dimer. A study of the chemical and spectroscopic properties of the dimer and its conversion products showed it to be a cyclic hemiacetal of structure II with all-*trans* stereochemistry. The hemiacetal was shown to be in equilibrium with the open hydroxycarboxaldehyde III. Catalytic hydroformylation under optimum conditions gave over a 40% yield of II.

The hydroformylation of epoxides has been reported to result in the formation of β-hydroxy esters, β-hydroxyaldehydes, and cobalt β-hydroxycarbonyls.[3-8] The only product reported to be formed from the hydroformylation of cyclohexene oxide is 2-hydroxycyclohexylcarbonylcobalt tetracarbonyl, which was isolated as the triphenylphosphine derivative; cleavage of this complex with iodine and methanol gave only methyl *trans*-2-hydroxycyclohexanecarboxylate.[5] Our investigation of this reaction, which was underway when the literature report appeared, indicated that the reaction was more complex, and that under certain conditions the major product was not the reported one. Furthermore, because yields were not reported and because other work[9] indicated *cis* addition, conclusions regarding the stereochemical course of the reaction are open to question.

Results and Discussion of the Stoichiometric Hydroformylation

When cyclohexene oxide was treated with cobalt hydrocarbonyl under the usual conditions of the stoichiometric hydroformylation,[10] a slow uptake of carbon monoxide was observed, followed by the precipitation of a brown material. Recrystallization of this material led to a white needlelike crystalline compound, the analysis of which corresponded to that expected for the hexahydrosalicylaldehyde. However, the molecular weight of this material in benzene showed it to be dimeric; furthermore, the infrared spectrum of a halocarbon mull showed no carbonyl band. Since no mention of either hexahydrosalicylaldehyde or its dimer appears in the literature,[11] we decided to study the chemistry and the structure of this compound.

The molecular weight of the compound, the absence of carbonyl, its ultimate analysis, and the nature of the hydroformylation reaction suggested at least two structures. Although two hydroxyl groups are present



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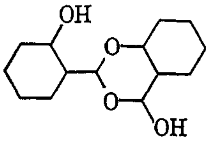

II

in each structure, those of structure II are nonequivalent. The n.m.r. and infrared spectra show the presence of two hydroxyl groups in totally different environments. A Stuart model indicates considerable steric interference in structure I, and thus the skeletal structure of II appears most likely.

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[1] This work was performed in part under a grant (APSP-16,461) from the Division of Air Pollution, Bureau of State Services, U. S. Public Health Service.

[2] (a) Public Health Service Predoctoral Fellow, 1962–1965; (b) to whom inquiries should be addressed.

[3] J. L. Eisenmann, R. L. Yarmartino, and J. F. Howard, Jr., *J. Org. Chem.*, **26**, 2102 (1961).

[4] J. L. Eisenmann, *ibid.*, **27**, 2706 (1962).

[5] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1460 (1963).

[6] Y. Takegami, C. Yokokawa, Y. Watanabe, and H. Masada, *Bull. Chem. Soc. Japan*, **37**, 672 (1964).

[7] C. Yokokawa, Y. Watanabe, and Y. Takegami, *ibid.*, **37**, 677 (1964).

[8] C. Yokokawa, Y. Takegami, and Y. Watanabe, *ibid.*, **37**, 935 (1964).

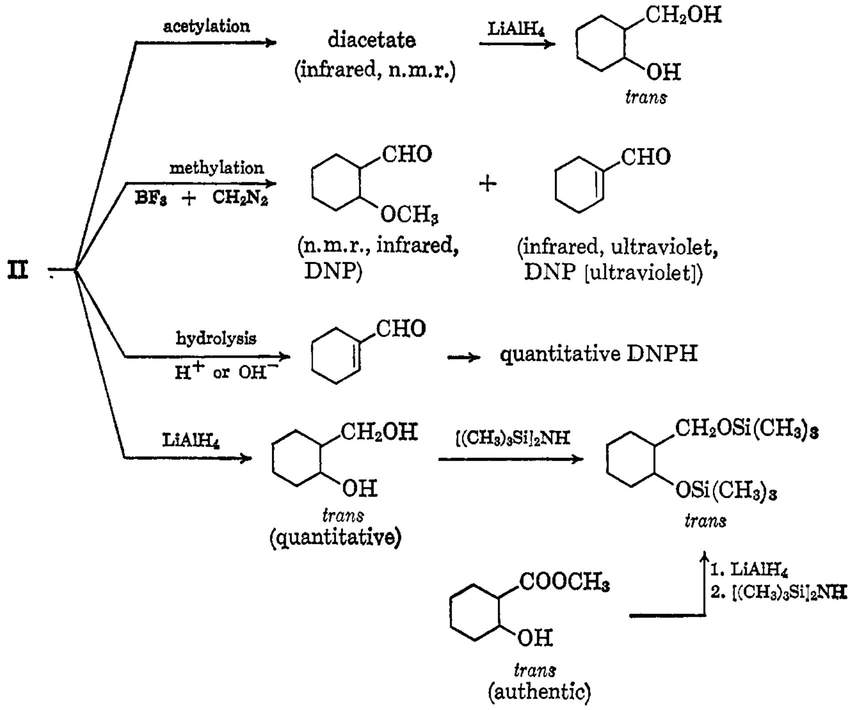
[9] A. Rosenthal and D. Abson, *Can. J. Chem.*, **42**, 1811 (1964).

[10] G. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

[11] A compound having very similar physical and chemical properties, but described as 1-hydroxyhexahydrobenzaldehyde, appears in the literature: E. D. Venus-Danilova, *J. Gen. Chem. USSR*, **6**, 1863 (1936); *Chem. Abstr.*, **31**, 4281 (1937).

CHART I

PROOF OF STRUCTURE II



The structure of II and its all-*trans* stereochemistry at the indicated linkages was shown by the series of reactions outlined in Chart I.

Acetylation.—The infrared spectrum of the white crystalline compound isolated from the acetylation of II shows two very strong carbonyl stretching bands. The n.m.r. spectrum, in agreement with the infrared data, showed the presence of two different acetate groups. However, the rest of the spectrum was very complex and could not be successfully interpreted. The attempt to substitute bromine on the anomeric carbon atom by treatment with hydrobromic acid in acetic anhydride[12] was unsuccessful.

Methylation.—Methylation of the dimer with diazomethane gave two compounds which were separated by vapor phase chromatography. The first compound to be eluted was 1-cyclohexenecarboxaldehyde. The more strongly adsorbed compound was shown to be the hitherto unknown 2-methoxycyclohexanecarboxaldehyde. Its infrared spectrum shows the presence of the carbonyl group and the methyl ether. The n.m.r. spectrum shows a doublet for the aldehydic proton and a singlet for the methyl group; integration shows a ratio of 1:3 for these protons.

Hydrolysis.—Hydrolysis in dilute sodium hydroxide of a weighed sample of dimer followed by the addition of excess 2,4-dinitrophenylhydrazine solution led to the formation and recovery of a 99% yield of the 2,4-dinitrophenylhydrazone of 1-cyclohexenecarboxaldehyde. Sulfuric acid hydrolysis, while slower, gave similar results.

Lithium Aluminum Hydride Reduction.—Reduction of a hemiacetal linkage with lithium aluminum hydride is known to result in the retention of configuration.[13,14] Such reduction of II led to a 95% yield of 2-(hydroxymethyl)cyclohexanol. This was converted to the silyl ether derivative by the published procedure,[15] and the ether was then chromatographed by v.p.c. Only one ether was present and it had the correct analysis and the expected infrared and n.m.r. spectra.

A sample of *cis*- and *trans*-methyl hexahydrosalicylate was purchased and the mixture separated by v.p.c. The pure isomers were identical with authentic samples of known configuration kindly furnished by Dr. R. F. Heck. Separate reduction of the two compounds with lithium aluminum hydride, followed by the formation of the silyl ether derivatives, gave the standards for comparison. In order to show that epimerization did not occur during the reduction,[14,16] a known mixture containing 95% *cis*- and 5% *trans*-methyl hexahydrosalicylate was reduced and the silyl ether derivatives were prepared. The same ratio of *cis* to *trans* isomer was obtained in the ether as was present in the starting ester.

Comparison of the infrared and n.m.r. spectra plus the v.p.c. retention times of the silyl ether derivatives showed unequivocally that the dimer had *trans* stereochemistry.

Equilibrium between Cyclic and Open Forms.—When the dimer II is melted and cooled, the melt does not crystallize on standing. An infrared spectrum of the melt showed the presence of a carbonyl band which was not present in the spectrum of II taken in a mull or in solutions of nonpolar solvents. The band at 3250 cm.$^{-1}$ (intermolecular hydrogen bonding) in the spectrum of II disappears and a strong band at 3400 cm.$^{-1}$ (intramolecular hydrogen bonding) appears in the melt; the remainder of the spectrum is

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[12] E. Fischer, *Chem. Ber.*, **44**, 1898 (1911).

[13] W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Am. Chem. Soc.*, **85**, 2283 (1963).

[14] D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950).

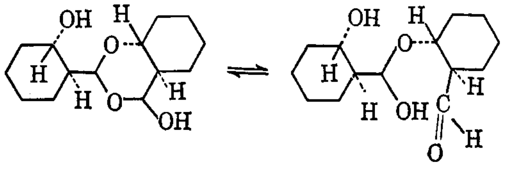
[15] C. C. Sweely, R. Bentley, M. Makita, and W. W. Wells, *ibid.*, **85**, 2497 (1963).

[16] E. L. Eliel, "The Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 188.

essentially the same. The n.m.r. spectrum of a warm chloroform solution of the dimer showed a weak doublet at 574 p.p.m., due to an aldehydic proton; this doublet disappeared on cooling. The infrared spectrum of the warm solution corroborated the presence of a carbonyl group.

That the dimer had not dissociated into its monomeric form was shown by a v.p.c. of the above solution; no trace of 1-cyclohexenecarboxaldehyde could be detected nor was any evidence for this compound found in the infrared spectrum.

This evidence suggested that the dimer (IIa) might be in equilibrium with the open-chain isomer III, analogous to similar equilibria in the sugar series.


IIa III

Further evidence for this equilibrium is the fact that the n.m.r. spectrum in nitrobenzene, diglyme, and acetophenone all showed that, as the temperature was increased and decreased, the relative intensity of the doublet, assigned to the carbonyl proton, increased and decreased correspondingly.

The infrared spectrum of II in nitrobenzene shows a strong carbonyl band, and this band is less intense in pyridine and in dimethyl sulfoxide.

Thin layer chromatography of II in acetone–methylene chloride solution showed the presence of two compounds.

The diacetate of the dimer which had been prepared earlier was now re-examined. The infrared spectrum was retaken using a slow-scan speed and an expanded wave length scale. In addition to the strong bands at 1780 and 1750 cm.$^{-1}$, which had also been previously observed, a shoulder at approximately 1760 cm.$^{-1}$ and a weaker band at 1740 cm.$^{-1}$ were now observed. The new bands may be assigned to the diacetate corresponding to structure III. Aldehyde bands at 2690, 2800, and 1370 cm.$^{-1}$ were also observed[17,18] in the slow-scan spectrum.

The presence of the aldehyde was confirmed by means of the 2,4-dinitrophenylhydrazone test. The infrared spectrum of the hydrazone was consistent with the presence of two acetate carbonyl groups.

The silyl ether of the equilibrium mixture was prepared, and two components were found on the v.p.c. The infrared spectra of the v.p.c. components were consistent with an open- and a closed-form structure, but it was difficult to separate sufficient pure material for analysis.

The stability of both IIa and III is enhanced by considerable intramolecular hydrogen bonding. Further collapse of the open-chain hemiacetal III to monomer is probably prevented by such interactions. In nitrobenzene solutions, where about one-half of the dimer exists as form III, the infrared spectrum shows considerable intramolecular hydrogen bonding (3410 cm.$^{-1}$) as well as free hydroxyl (3550 cm.$^{-1}$).[19]

Other Products of the Stoichiometric Hydroformylation.—The yield of products in a typical reaction starting with 13.0 mmoles of cyclohexene oxide and 12.0 mmoles of cobalt hydrocarbonyl was 86% recovered oxide, 0.8% cyclohexanone, 0.1% cyclohexanol, and 6.2% dimer. Some of the oxide is lost as a cobalt carbonyl complex, and about 5–6% is lost during purification of the dimer. These results are based on the assumption of 1 mole of oxide reacting with 2 moles of hydrocarbonyl; the formation of cyclohexanone is assumed to occur by rearrangement of the oxide.[4] The largest yield of pure dimer realized was 13%. Of the 12 mmoles of cobalt hydrocarbonyl used, 83% is recovered as dicobalt octacarbonyl; the rest is lost as chelated or otherwise complexed material which ends up principally as cobalt oxide. The recovery of so much cobalt as dicobalt octacarbonyl is difficult to explain, unless appreciable quantities are formed by the decomposition of cobalt hydrocarbonyl. However, little gas is evolved during the reaction, but perhaps carbon monoxide absorption and hydrogen liberation are somewhat balanced. This possibility was not investigated.

Results and Discussion of the Catalytic Hydroformylation

The results of a study of catalytic hydroformylation of cyclohexene oxide are summarized in Table I.

During the first 15 min. of reaction 2, where dimer yield is optimum, the gas absorption shows good first-order dependency. The rate constant evaluated from the slope is 0.8 min.$^{-1}$ at 115°, which is about 30 times the rate of hydroformylation of 1-pentene under somewhat comparable conditions.[20]

The reaction at lower temperature (expt. 3) took a totally different course. In the first place, the rate was much slower; the calculated rate constant was 0.04 min.$^{-1}$. Instead of dimer, a large amount of resinous polymer was formed. Difficulty was experienced in agitating the mixture before hydrogen addition because of increased viscosity. It therefore seems probable that in the presence of $Co_2(CO)_8$, the cyclohexene oxide first polymerizes or condenses and little conventional hydroformylation occurs.

In studying these reactions it was observed that, if the reaction exothermed, a good yield of dimer was realized. If no exotherm occurred, little or no dimer was found and only very viscous polymeric material was recovered. The infrared spectrum of the polymeric product shows strong ether bands in addition to the much smaller hydroxyl and carbonyl bands. The physical properties of the polymer are very much like those described by Conant,[21] Rothrock,[22] and Alvarado[23] for the polymers obtained from cyclohexene oxide.

Reaction 6 in ethylene glycol was performed in an attempt to trap the monomer as an acetal derivative. However, the glycol probably functions as a bidentate

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[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 9.

[18] M. St. C. Flett, "Characteristic Frequencies of Chemical Groups in the Infrared," Elsevier Publishing Co., New York, N. Y., 1963, p. 20.

[19] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 5.

[20] I. J. Goldfarb, M.S. Dissertation, University of Cincinnati, 1955.

[21] J. B. Conant and W. R. Peterson, *J. Am. Chem. Soc.*, **54**, 628 (1932).

[22] H. S. Rothrock, U. S. Patent 2,054,099 (1936).

[23] A. M. Alvarado and H. S. Holt, U. S. Patent 2,187,006 (1940).

TABLE I

RESULTS OF CATALYTIC HYDROFORMYLATION[a]

Expt.	Temp., °C.	Solvent	H_2:CO	Time, hr.	Major products
1	70–75	*n*-Hexane	1:1	7	40% dimer, 10% cyclohexanone, some high boiling materials
2[b]	110–115	*n*-Hexane	1:1	1.5	43% purified dimer, 10% cyclohexanone, small amount of high boiling material
3[b]	88–100	*n*-Hexane	1:1	12	White resinous polymer
4	118–129	*n*-Hexane	1:1	7	Highly viscous material only product
5	70–75	95% ethanol	1:1	5	60% 2-ethoxycyclohexanol, 20% cyclohexenecarboxaldehyde, many other compounds in trace quantities
6	100	Ethylene glycol	1:1	4	A cobalt–ethylene glycol complex, no other products

[a] Cyclohexene oxide (50 ml.), solvent (50 ml.). [b] The bomb was pressured with 2000 lb. of CO and heated to reaction temperature, and the calculated amount of hydrogen was added within 1 min.; otherwise the gases were added before heating.

ligand and complexes the cobalt tightly in a way that does not permit generation of cobalt hydrocarbonyl.

The implications of the above work for the mechanism of the hydroformylation reaction are under study.

Experimental

Infrared spectra were determined on a Perkin-Elmer 327 spectrophotometer, n.m.r. spectra on a Varian Associates Model A-60, and vapor phase chromatographs on a Beckman G.C.-2A. Melting points are uncorrected and were taken on a Fisher-Johns melting point apparatus.

All organic chemicals were obtained from Aldrich Chemical Co., Inc. and all analyses were performed by Galbraith Laboratories Inc.

The molecular weight of the dimer was obtained by freezing point depression in benzene and found to be 257 ± 25.

Preparation of $HCo(CO)_4$.—A 0.37 *M* hexane solution was prepared by disproportionation of $Co_2(CO)_8$ with N,N-dimethylformamide followed by acidification with concentrated HCl.[24,25] The solution was washed with water and dried by means of a Dry Ice–acetone bath. The exact concentration of $HCo(CO)_4$ was obtained by titrating an aliquot with 0.01 *N* NaOH to a phenolphthalein end point.

Stoichiometric Hydroformylation of Cyclohexene Oxide.—A 33-ml., dry solution of $HCo(CO)_4$ (12.5 mmoles) was injected into a 100-ml. flask connected to a 500-cc. gas buret. The flask was equipped with a serum-stoppered side arm and a magnetic stirring bar. The entire system was under 1 atm. of CO. Hexane was added and then 1.3 ml. of cyclohexene oxide (13 mmoles) to bring the total volume up to 40 ml. Smaller volumes decrease the yields accordingly. The solution turned dark with the absorption of a total of 90 cc. of gas (2.4 mmoles) over a period of 1 hr. After 20 min. a precipitate began to form. The reaction was halted after 2 hr. [all $HCo(CO)_4$ had disappeared] and the solution was filtered under a stream of nitrogen. The filtrate was stored at −20° under a CO atmosphere. The 0.2419 g. of the reddish precipitate was dissolved in a minimum of hot benzene and allowed to stand overnight. A fine gray precipitate (0.0355 g.) of cobalt salts was removed, and the dimer crystallized from solution upon the addition of hexane. A second recrystallization from benzene–hexane gave 0.0998 g. (13%) of white needlelike crystals, m.p. 136–137°.

Infrared analysis of a spectrum run in $CHCl_3$ shows the following characteristic absorptions: 3600 (m), 3450 (s), 3300 (s) (OH), 1120 (s), 1130 (s), and 1160 (s) cm.$^{-1}$ due to cyclic ether. N.m.r. (in parts per million from TMS) showed two broad bands at 278 and 307 p.p.m. due to hydroxyl protons. These disappeared upon addition of D_2O.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.43; O, 24.97. Found: C, 65.00; H, 9.28; O, 24.72.

The mother liquor contained 0.0921 g. of a yellow material which was partially composed of dimer, cyclohexenecarboxaldehyde, *trans*-hexahydrosalicylic acid, and polymeric material.

The mother liquor from the original reaction mixture was cooled to −80° and the orange precipitate of dicobalt octacarbonyl was collected (1.80 g. or 83%). The remaining solution was vapor phase chromatographed and compared with calibrated standards on a 7-ft. 20% Ucon 2000 on acid-washed Chromosorb P column at 150°, flow rate of He 35 cc./min. The analysis showed the presence of 11.1 mmoles of cyclohexene oxide, 0.1 mmole of cyclohexanone, and 0.01 mmole of cyclohexanol. Some traces of higher boiling material were present. A total of 93% of the initially used cyclohexene oxide was accounted for. The remaining solution was evaporated to dryness, and the red oil remaining behind was identified by infrared spectrum as a cobalt carbonyl complex containing both cyclohexanol and cyclohexanone.

Preparation of the Diacetate.—To a solution of 10 ml. of dry pyridine and 4 ml. of freshly distilled acetic anhydride there was added 0.64 g. of dimer (0.0025 moles) and the solution was stirred for 12 hr. This was added to 10 ml. of water and 10 g. of ice. The organic layer was extracted twice with 50-ml. portions of ligroin; the solution was washed with 1% $NaHCO_3$ and then dried and evaporated down to a 10-ml. volume. The white hexagonal crystals were collected, crude yield 0.72 g. (85%). Repeated recrystallization gave the pure compound, m.p. 102–103°.

Infrared analysis showed bands at 1750 (s) and 1780 (s) cm.$^{-1}$ (C=O); scale expansion showed a band at 1760 (sh) and 1740 (m) cm.$^{-1}$, due to acetate and aldehyde carbonyl, respectively. Bands at 1235 (s) and 1250 (s) cm.$^{-1}$ were due to ester, at 1125 (m), 1135 (m), and 1148 (s) cm.$^{-1}$ to cyclic ether. N.m.r. showed two bands at 123 and 117 p.p.m. due to methyl groups.

Anal. Calcd. for $C_{10}H_{28}O_6$: C, 63.52; H, 8.24; O, 28.20. Found: C, 63.81; H, 8.30; O, 27.89.

A repeat of the above reaction, with the dimer first being melted before adding the pyridine and acetic anhydride, gave the same compound, with the exception that the infrared spectrum showed an increase in intensity of the aldehydic carbonyl band.

Preparation of 2-Methoxycyclohexanecarboxaldehyde and 1-Cyclohexenecarboxaldehyde.—To a 500-ml. round-bottom two-necked flask, equipped with magnetic stirring bar, was added 1.3 g. of dimer (5.5 mmoles) in 40 ml. of cold anhydrous benzene. To this was added 0.5 ml. of freshly distilled boron trifluoride etherate. While the solution was kept between 0 and 10°, 28 ml. of 0.6 *M* diazomethane[26,27] was added dropwise until a yellow color persisted. The reaction mixture was heated gently for a short time and most of the solvent was removed. The mixture was separated on a 6-ft. preparative column packed

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[24] I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).

[25] L. Kirch and M. Orchin, *ibid.*, **80**, 4428 (1958).

[26] F. Arndt, "Organic Synthesis," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p.165.

[27] E. D. Amstutz and R. R. Meyers, ref. 26, p. 462.

with 30% by weight of Antara Igepal 880 on acid-washed Chromosorb P at 154°. Two compounds were collected. The first was 1-cyclohexenecarboxaldehyde, 2,4-dinitrophenylhydrazone (DNP) m.p. 217–218° (lit.[28] m.p. 215°). The ultraviolet spectrum had a λ_{max} of 231 mμ consistent with the calculated value[29] and that reported by Wheeler.[30] The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone (λ_{max} 377 mμ) when compared with that of the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde (λ_{max} 359 mμ) shows the expected[31] shift of approximately 20 mμ to longer wave length. The second compound collected was identified as 2-methoxycyclohexanecarboxaldehyde: infrared absorption at 2832 (OMe), 1730 (C=O), and 1105 cm.$^{-1}$ (C–O–C); n.m.r. showed a methyl group absorption at 195 p.p.m. and a doublet at 564 and 562 p.p.m. due to aldehydic proton; the 2,4-dinitrophenylhydrazone was recrystallized from methanol, m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{18}N_4O_5$: N, 18.31. Found: N, 18.19.

Hydrolysis of Dimer.—A 0.1778-g. sample of recrystallized and dried dimer was added to 10 ml. of a 0.1 *N* NaOH solution and gently refluxed for 2 hr. The reaction mixture was cooled to 0° and neutralized with a few drops of 2 *N* HCl. Then 51 ml. of a 0.047 *M* solution of 2,4-dinitrophenylhydrazine in methanol was added and the solution was refluxed for 2 hr.[32] The solution was cooled overnight at −20°. The precipitate was collected on a tared fritted-glass filter and washed with equal portions of water and 2 *N* HCl until constant weight was obtained. The filter and precipitate were dried at 3-mm. pressure at 100° for 12 hr. giving 0.4024 g. of the hydrazone (99.0% of theoretical). Substituting 2 *N* H_2SO_4 for NaOH led to similar results.

Reduction of Dimer.—A solution of 1.657 g. of dimer (0.0064 mole) in 100 ml. of anhydrous ether was added dropwise to a suspension of 1.5 g. of $LiAlH_4$ (0.03 mole) in 50 ml. of ether. After addition the mixture was gently heated, and then water was added until a flocculent white precipitate formed. The solution was filtered and the precipitate was carefully triturated with ether. The solvent was removed and the product diol was dried by azeotroping the water off with benzene. Upon removal of all solvent, 1.597 g. of the diol was recovered (96%). Comparison of the infrared spectrum with an authentic sample confirmed its structure as *trans*-2-(hydroxymethyl)cyclohexanol.

The diol was added to 8 ml. of hexamethyldisilazane, 2 ml. of anhydrous pyridine, and 0.5 ml. of trimethylchlorosilane.[17] The solution was stirred for 15 min. and washed four times with equal portions of water and *n*-pentane. The solution was dried and reduced in volume. V.p.c. showed that only one ether component was present; elemental analysis and comparison of the infrared and n.m.r. data with an authentic sample identified this compound as the *trans*-trimethylsilyl ether derivative of the diol.

Anal. Calcd. for $C_{13}H_{30}O_2Si_2$: C, 56.87; H, 11.01. Found: C, 57.05; H, 11.13.

cis- **and** *trans*-**Trimethylsilyl Ethers.**—A mixture of *cis* and *trans* methyl hexahydrosalicylate was separated by means of preparative v.p.c. (8 ft. × 0.75 in. column of diethylene glycol succinate on Chromosorb at 188°, flow rate 36 cc./min. of He). The mixture consisted of 94% *cis* and 6% *trans* ester. The infrared spectra of the compounds were compared with authentic standards: *cis*, 3490 (OH) and 1730 (C=O) cm.$^{-1}$; *trans*, 3420 (OH) and 1730 (C=O) cm.$^{-1}$. The separate esters were reduced as before with $LiAlH_4$.

The trimethylsilyl ethers of the *cis* and *trans* diols were prepared and infrared and n.m.r. spectra were obtained. Optimum separation of the *cis* and *trans* ethers occurred when a 7-ft. column of Igepal 880 at 120°, flow rate 40 cc./min. of He, was used.

Anal. Calcd. for *cis* and *trans* $C_{18}H_{30}O_2Si_2$: C, 56.87; H, 11.01. Found (*cis*): C, 56.64; H, 11.07. Found (*trans*): C, 56.72; H, 11.04.

Reduction of the Diacetate.—A solution of 0.2 g. of the diacetate (0.59 mmole) was dissolved in anhydrous ether and added dropwise to a suspension of 0.15 g. of $LiAlH_4$ (4 mmoles) in ether. After hydrolyzing and drying, the solution was chromatographed. The presence of ethyl alcohol was confirmed. Preparation of the trimethylsilyl ether derivative showed that the other alcohol present was the *trans*-2-(hydroxymethyl)cyclohexanol.

Temperature-Dependent Study of the N.m.r. Spectra.—The n.m.r. spectra of the dimer in nitrobenzene, diglyme, and acetophenone showed that, as the temperature was increased from 35 to 100°, the intensity of the doublet due to the aldehydic proton at 574 and 577 p.p.m. increased in intensity. Upon cooling, this band decreased. The infrared spectrum of the dimer in nitrobenzene shows the following characteristic bands: 3550 (s), 3430 (s) (hydroxyl), 2725 (m) (aldehydic proton), 1730 (s) (carbonyl), and 1130 (s) cm.$^{-1}$ (ether).

Preparation of the 2,4-Dinitrophenylhydrazone of the Diacetate of the "Open" Dimer.—To a solution of 0.5 g. of the diacetate in 1 ml. of methanol, an excess of 0.05 *M* 2,4-Dinitrophenylhydrazone solution was added. A small yellow precipitate formed quickly and was collected. An infrared spectrum of the compound showed bands at 3305 (s), 3110 (m) (N–H), 1730 (s), 1710 (s) (C=O), and 1245 (s) cm.$^{-1}$ (ester). Attempted purification by recrystallization and column chromatography on 60–100-mesh Florisil led only to decomposition products.

Catalytic Hydroformylation.—In a typical reaction, 50 ml. of cyclohexene oxide (0.48 mole), 50 ml. of hexane, and 0.3 g. of dicobalt octacarbonyl (0.8 mmole) were charged to a 150-ml. stainless steel Magnadash autoclave. The system was pressured with synthesis gas (1:1) to 400 p.s.i., heated to the desired temperature which was maintained until gas absorption ceased. The precipitate was filtered and recrystallized. The average yield of dimer based upon cyclohexene oxide was 40–45%. The filtrate was gas chromatographed and the following compounds were identified in approximate concentrations: cyclohexanone (10%), cyclohexanol (1%), and unreacted cyclohexene oxide. Evaporation of all these materials left behind about 10 g. of a yellow, sweet-smelling, viscous oil. The infrared spectrum of this material showed it to be highly oxygenated because strong hydroxyl, carbonyl, and ether absorption bands were present.

To study the kinetics, the bomb was charged with the reactants and pressured to 2000 p.s.i. of CO. It was heated and maintained at the reaction temperature, and 2000 p.s.i. of H_2 was added within 1 min. The pressure, as a function of time, was measured and the rate constants were calculated.[33]

Catalytic Hydroformylation in Ethanol.—When ethanol was substituted for hexane and a temperature between 70 and 75° was maintained, the reaction was over in 5 hr. A v.p.c. of the solution indicated the presence of two major components identified as 1-cyclohexenecarboxaldehyde (20%) and *trans*-2-ethoxycyclohexanol (60%). A large number of other unidentified compounds was present in trace quantities. The *trans*-2-ethoxycyclohexanol was identified by comparison of its 3,5-dinitrobenzoate derivative with an authentic sample,[34] m.p. 80–81°, lit.[35] m.p. 82–83°.

Acknowledgment.—We wish to thank Dr. F. Kaplan for his assistance in interpreting the n.m.r. spectra and Dr. R. F. Heck for his gift of pure samples of *cis* and *trans* methyl hexahydrosalicylate.

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