Perhydroindanone Derivatives. II. Stability Relationships [a]

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The *cis* and *trans* isomers of perhydro-1-indanone (**6** and **7**), 7-methylperhydro-1-indanone (**12** and **13**), 3a,4,7,7a-tetrahydro-1-indanone (**4** and **5**) and 7-methyl-3a,4,7,7a-tetrahydro-1-indanone (**9** and **10**) have been prepared and the positions of *cis–trans* equilibrium determined.

Having found previously[3] that cyclohexenone could serve as a preparatively useful dieneophile with reactive dienes provided high temperatures (175–200°) and excess diene were employed, we elected to study the reaction of cyclopentenone (**1**) with butadiene (**2**)[4] and *trans*-1-methylbutadiene (**3**, piperylene), as possible preparative routes to perhydroindanone derivatives. The results of these studies are summarized in Chart I. At the temperatures employed for reaction of butadiene (**2**) with cyclopentenone (**1**), partial equilibration of the expected, kinetically favored isomer **4**[5] with its epimer **5** was observed, the equilibration being more nearly complete at higher temperatures. The corresponding reaction with piperylene could be effected at lower temperature; the expected[5] *cis* isomer **9** was the major product at 80–100° and diminished in amount as the reaction temperature was raised to 160°. Although the 7-methyltetrahydroindanones **9** and **10** were the major products of this reaction, at least two additional components were present as minor by-products. The formulation of these by-products as isomers of structure **11** was indicated by the spectral properties of these materials and by their dehydrogenation to 4-methylindanone (**15**). Each of the tetrahydroindanones **4**, **5**, **9**, and **10** could be hydrogenated to form the corresponding hexahydroindanone **6**, **7**, **12**, and **13** as the predominant product.

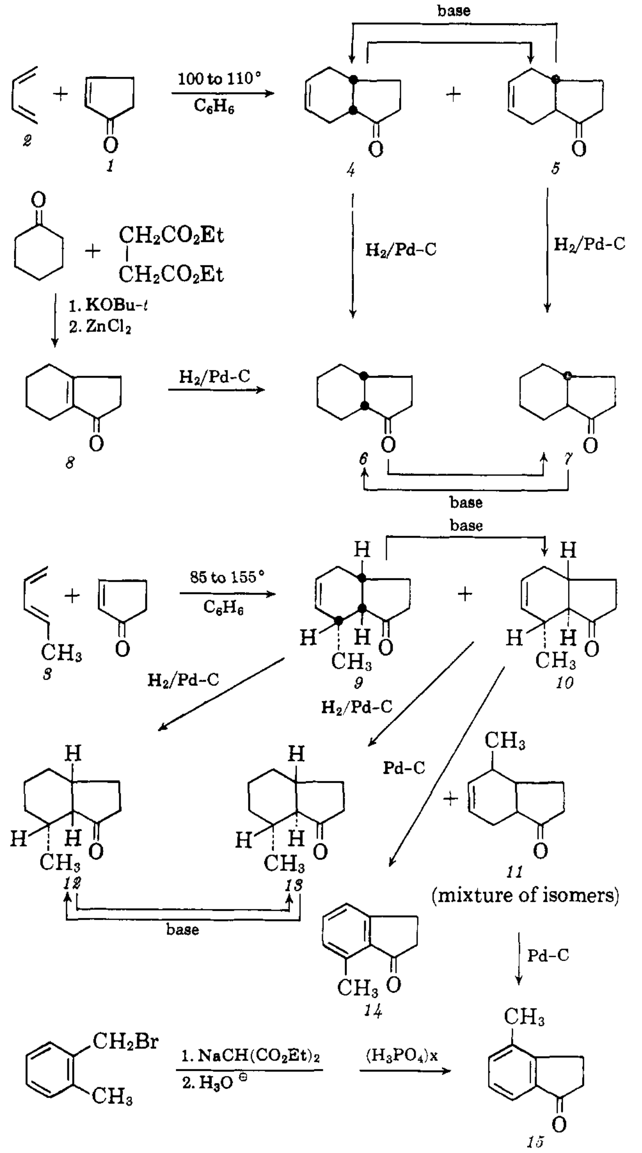

CHART I

Since we wished to obtain the tetrahydroindanone **16** as a possible precursor of 7-carboxy-7-methyl-1a,3a,4,5,6,7-hexahydroindanone, the transformations outlined in Chart II were explored. Although dehydrohalogenation of the crude bromo ketone **17** afforded small amounts of this desired ketone **16**, identified by comparison with a subsequently described sample,[6] the major product was the endocyclic isomer **18**. Since this product **18** was the only tetrahydroindanone obtained by isomerization of **9** and **10** under a variety of conditions, we are led to the conclusion that the endocyclic isomer **18** is appreciably more stable than the exocyclic isomer **16** in spite of the fact that both substances contain a tetrasubstituted carbon–carbon double bond. Although these observations could be construed as additional data concerning the relative stabilities of double bonds exocyclic and endocyclic to a

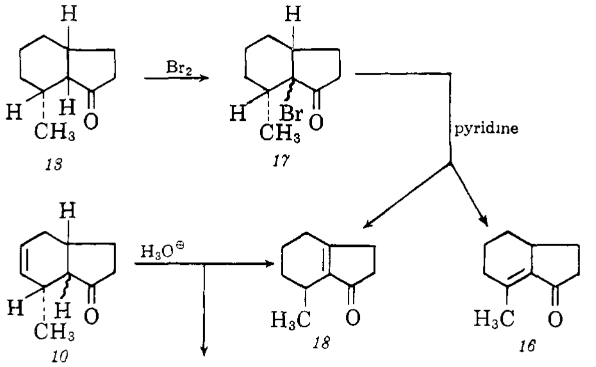

CHART II

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[1] (a) Supported in part by National Science Foundation Grant No. G-9486; (b) National Science Foundation Predoctoral Fellow, 1958–1962.

[2] Part I, *J. Org. Chem.*, **28**, 27 (1963).

[3] H. O. House, W. F. Gannon, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1463 (1960) and references cited therein.

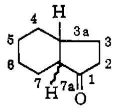
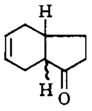
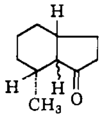
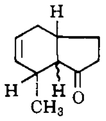
[4] Although the product characterization was rather fragmentary, this reaction has been reported by E. Dane and K. Eder, *Ann.*, **539**, 207 (1939).

[5] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[6] H. O. House and M. Schellenbaum, *J. Org. Chem.*, **28**, 34 (1963).

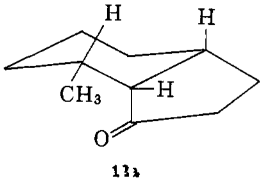
TABLE I

EQUILIBRATION OF THE TETRAHYDRO- AND HEXAHYDROINDANONES

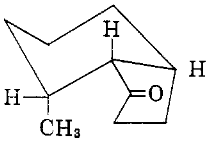
Structure		K_{equil} for *cis* ⇌ *trans*
	**6** and **7**	0.33
	**4** and **5**	0.90
	**12** and **13**	3.08
	**9** and **10**	>50

five-membered ring,[7] we believe that the primary source of destabilization in structure **16** derives from a serious eclipsing interaction between the methyl group and carbonyl oxygen atom which will exist if *pi* orbital overlap between the carbon–carbon double bond and the carbonyl function is to be maintained.

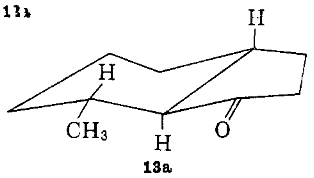
It was of interest to determine the positions of equilibrium for the various tetrahydro- and hexahydroindanone epimers which had been prepared. These data, listed in Table I, were conveniently obtained by equilibrating each of the various compounds in triethylamine solution at 100°. It is apparent that the presence of a methyl group at position 7 and *trans* to the hydrogen atom at position 3a reverses the usual stability order of perhydroindan-1-ones where the *cis* isomer is more stable.[8] The examples reported here represent an additional case[9] in which conformational effects can alter the usual order of stability. Apart from the obvious 1,3-diaxial interaction in conformation **12b** of the *cis* isomer **12**, the general tendency of a *cis*-fused five-membered ring in a perhydroindane to flatten the six-membered ring[10] tends to increase the interaction between the equatorial methyl group and axial carbonyl function in conformation **12a**. This interaction is greatly diminished in the *trans* isomer **13a** where the five-membered ring tends to increase the puckering of the six-membered ring.[10]



12b

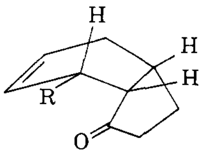


12a

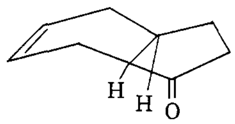


13a

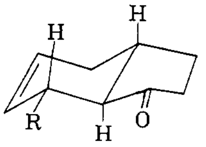
The effect of introducing a 5,6-double bond into these molecules was surprising since previous work[11] with octalin systems had suggested that introduction of a double bond in an analogous position tended to flatten the six-membered ring containing the double bond and, consequently, to favor a *cis* ring fusion (or at least to destabilize a *trans* ring fusion). As will be noted in Table I, exactly the reverse effect is found in the perhydroindanone system. We believe the most reasonable explanation for this effect to be that the *cis*-fused tetrahydroindanones **4** and **9** exist in suitably twisted modifications of the boat conformations **4a, 4b,** and **9a** to avoid serious bond angle deformations in spite of the resulting increase in steric interactions. In the *trans* isomers **5** and **10** the usual chair conformations **5a** and **10a** offer a satisfactory compromise between bond angle deformation and steric interactions. It is interesting to note that a combination of the effects of a 7-methyl substituent and a 5,6-double bond completely reverse to usual order of stability expected in the perhydroindan-1-one system.



4a. R = H
9a. R = CH₃



4b



5a. R = H
10a. RCH

Experimental[12]

3a,4,7,7a-Tetrahydro-1-indanones 4 and 5.—A solution of 85 g. (1.04 moles) of cyclopentenone,[13] 200 g. (3.7 moles) of butadiene and 10 g. of 2,5-di-*t*-butylhydroquinone in 250 ml. of benzene was heated to 110° for 12 days in an autoclave. The resulting mixture was concentrated under reduced pressure and then distilled to separate 128 g. of a liquid mixture, b.p. 36–100° (8 mm.), containing,[14] in addition to unchanged cyclopentenone and other low-boiling components, a mixture of 40% of the *trans* isomer **5** (the first eluted) and 60% of the *cis* isomer **4**. Fractional distillation with a 70-cm. spinning band column afforded 41.7 g. (29%) of fractions, b.p. 91–92° (5–7 mm.), containing[14] varying proportions of the two tetrahydroindenones **4** and **5**. Several of the higher-boiling fractions [b.p. 92° (5 mm.), $n^{25}D$ 1.5038] contained[14] the pure *cis* isomer **4** which exhibits infrared absorp-

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[7] For discussion and leading references see (a) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958); (b) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Zacura, *ibid.*, **82**, 1750 (1960).

[8] (a) W. Hückel, M. Sachs, J. Yantschulewitsch, and F. Nerdel, *Ann.*, **518**, 155 (1935); (b) G. Quinkert, *Experientia*, **13**, 381 (1957); (c) N. L. Allinger, R. B. Hermann, and C. Djerassi, *J. Org. Chem.*, **25**, 922 (1960).

[9] J. F. Biellmann, D. Francetic, and G. Ourisson, *Tetrahedron Letters*, No. **18**, 4 (1960).

[10] (a) E. L. Eliel and C. Pillar, *J. Am. Chem. Soc.*, **77**, 3600 (1955); (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, pp. 275–278.

[11] For references and discussion see S. K. Balasubramanian, *Tetrahedron*, **12**, 196 (1961).

[12] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, Model B, or a Perkin–Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. Unless otherwise stated magnesium sulfate was employed as a drying agent. The n.m.r. spectra were measured at 60 Mc. with a Varian, Model A-60, n.m.r. spectrometer.

[13] Prepared by the procedure of C. H. DePuy and K. L. Eilers, *J. Org. Chem.*, **24**, 1380 (1958).

[14] A gas chromatography column packed with Dow Corning silicone fluid no. 710 on 60–80-mesh firebrick was employed for this analysis.

tion[15] at 1735 cm.$^{-1}$ (cyclopentanone C═O) and at 1655 cm.$^{-1}$ (C═C) with weak end absorption (ε 400 at 210 mμ) in the ultraviolet[16] as well as a maximum at 284 mμ (ε 26). The n.m.r. spectrum[15] exhibits a peak (insufficient resolution to determine splitting pattern) at 4.42 τ (2*H*, vinyl C—H) and a complex series of peaks in the region 7.4 to 8.6 τ (10H, saturated C—H).

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88; mol. wt., 136. Found: C, 79.13; H, 8.86; mol. wt., 136 (mass spectrum.)

Refractionation of the lower boiling fractions separated the pure *trans* isomer, b.p. 99° (12 mm.), n^{25}D 1.4942, with infrared absorption[15] at 1740 cm.$^{-1}$ (cyclopentanone C═O) and at 1635 cm.$^{-1}$ (C═C) with an ultraviolet maximum[16] at 288 mμ (ε 34) and weak end absorption (ε 294 at 210 mμ). The n.m.r. spectrum[15] has two peaks (separated by 3 c.p.s.) centered at 4.37 τ (2H, vinyl C—H) as well as a series of peaks in the region 7.4 to 8.7 τ (10 H, saturated C—H).

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88; mol. wt., 136. Found: C, 79.15; H, 8.89; mol. wt., 136 (mass spectrum).

When the reaction was repeated with 10 g. (0.185 mole) of butadiene, 5 g. (0.061 mole) of cyclopentenone, 0.4 g. of 2,5-di-*t*-butylhydroquinone, and 10 ml. of benzene at 100° for 4 days, the mixture of tetrahydroindanones obtained [0.984 g. of 12%, b.p. 81–88° (10 mm.)] contained[14] 24% of the *trans* isomer **5** and 76% of the *cis* isomer **4**.

Reaction of either the *cis* (**4**) or *trans* (**5**) isomer with ethanolic 2,4-dinitrophenylhydrazone containing a few drops of hydrochloric acid produced the same **2,4-dinitrophenylhydrazone** (shown by a mixed melting point and comparison of infrared and ultraviolet spectra) as orange microplates from an ethanol–ethyl acetate mixture, m.p. 201–201.5° dec., yield 46.5% from the *cis* isomer **4** and 42.5% from the trans isomer **5**. The material has an ultraviolet maximum[17] at 364 mμ (ε 22,800). We have tentatively assigned the *trans* configuration (*cf.* **5**) to this derivative.

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 57.07; H, 5.15; N, 17.52.

7-Methyl-3a,4,7,7a-tetrahydro-1-indanones 9 and 10.—A solution of 16.02 g. (0.195 mole) of cyclopentenone,[13] 30 g. (0.44 mole) of *trans*-1-methyl-1,3-butadiene,[18] and 2.04 g. of 2,5-di-*t*-butylhydroquinone in 30 ml. of benzene was heated to 155° for 55 hr. Two consecutive distillations of the reaction mixture separated 20.63 g. (71%) of a mixture of adducts, b.p. 95–104° (13 mm.), which contained[14] 70% of the *trans* isomer **10** as well as several minor components. Fractional distillation with a 70-cm. spinning band column separated fractions, b.p. 97–98° (13 mm.), n^{25}D 1.4872 which contained[14] more than 95% of the *trans* isomer **10**. The **2,4-dinitrophenylhydrazone of the trans ketone 10** was obtained as a red microcrystalline solid from an ethanol–ethyl acetate mixture, m.p. 231–231.5°, yield 65%, with an ultraviolet maximum at 364 mμ (ε 23,500).

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.29; H, 5.42; N, 16.81.

A pure sample of the *trans* ketone **10**, collected by gas chromatography,[14] has infrared absorption[15] at 1740 cm.$^{-1}$ (cyclopentanone C═O) and at 1635 cm.$^{-1}$ (C═C) with an ultraviolet maximum[16] at 292 mμ (ε 31) and weak end absorption (ε 404 at 210 mμ). The n.m.r. spectrum[15] has broad, poorly resolved absorption centered at 4.51 τ (2 H, vinyl C—H) with a series of peaks in the region 7.4 to 8.6 τ (9 H, saturated C—H) and a doublet (*J* = 7 c.p.s.) centered at 8.83 τ (3 H, CH_3).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39; mol. wt., 150. Found: C, 80.15; H, 9.63; mol. wt., 150 (mass spectrum).

A mixture of 636 mg. (4.2 mmoles) of the ketone **10**, 6 ml. of *p*-cymene and 125 mg. of a 30% palladium-on-carbon catalyst was refluxed for 17 hr. and then filtered and chromatographed on neutral alumina. The crude product, **7-methyl-1-indanone** (**14**), eluted with benzene amounted to 249 mg. (40.5%), m.p. 40–50°. Recrystallization from petroleum ether afforded 130 mg. (21%) of the indanone as pale yellow needles, m.p. 52–53.3°, and addition recrystallization followed by sublimation raised the melting point to 54.7–55.2°. The product has infrared absorption[15] at 1705 cm.$^{-1}$ (cyclopentenone C═O), ultraviolet maxima[16] at 248 mμ (ε 13,600), and 297 mμ (ε 2630) and a series of n.m.r. peaks[19] in the region 2.4 to 3.1 τ (3 H, aromatic C—H) as well as a singlet at 7.39 τ (3*H*, CH_3) and series of peaks having the pattern of an A_2B_2 system in the region 6.7 to 7.6 τ (4*H*, CH_2).

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.20; H, 6.83.

The indanone **14** formed a **2,4-dinitrophenylhydrazone** as red prisms from a methanol–ethyl acetate mixture, m.p. 290–290.5° dec., yield 83%, with ultraviolet maxima[17] at 255 mμ (ε 16,300), 293 mμ (ε 10,800) and 386 mμ (ε 34,400).

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 58.58; H, 4.15; N, 16.97.

A 760-mg. sample (5.0 mmoles) of a fraction from this Diels–Alder reaction which was enriched in the minor components and contained less than 10% of the *trans* ketone **10** was mixed with 7.5 ml. of *p*-cymene and 225 mg. of a 30% palladium-on-carbon catalyst and refluxed for 24 hr. After filtration, the crude product was chromatographed on neutral alumina to separate 160 mg. (22%) of 7-methyl-1-indanone (**14**), m.p. 48–52° (eluted with benzene-petroleum ether mixtures) and 20 mg. (3%) of 4-methyl-1-indanone (**15**), m.p. 97–97.8° (eluted with benzene). Both products were identified by mixed melting-point determinations and comparison of infrared spectra.

An authentic sample of **4-methyl-1-indanone** (**15**), prepared from α-bromo-*o*-xylene as previously described,[20] was isolated as microprisms from petroleum ether, m.p. 97.5–98.2° (lit.,[20] 99–100°). The product has infrared absorption[15] at 1715 cm.$^{-1}$ (cyclopentenone C═O), ultraviolet maxima[16] at 250 mμ (ε 13,800) and 296 mμ (ε 3050), and a series of n.m.r. peaks[19] in the region 2.2 to 3.0 τ (3*H*, aromatic C—H) as well as a singlet at 7.68 τ (3*H*, CH_3) and a series of peaks having the pattern of an A_2B_2 system in the region 6.7 to 7.6 τ (4*H*, CH_2).

After a solution of 30.1 g. (0.366 mole) of cyclopentenone, 33 g. (0.486 mole) of *trans*-1-methyl-1,3-butadiene, and 1.5 g. of 2,5-di-*t*-butylhydroquinone in 50 ml. of benzene had been heated to 85° for 7 days, distillation of the mixture separated 22.52 g. (41%) of a mixture of adducts, b.p. 92–100° (10 mm.), containing[14] 68% of the *cis* ketone **9** and 15% of the *trans* ketone **10**. A sample of the pure *cis* ketone **9** collected from the gas chromatogram[14] has infrared absorption[15] at 1740 cm.$^{-1}$ (cyclopentanone C═O), an ultraviolet maximum[16] at 297 mμ (ε 31) with weak end absorption (ε 650 at 210 mμ) and an n.m.r. peak[15] at 4.42 τ (2 H, vinyl C—H) with a doublet (*J* = 7 c.p.s.) centered at 8.75 τ (3*H*, CH_3) and a series of peaks in the region 7.2 to 8.6 τ (9 *H*, saturated C—H).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39; mol. wt., 150. Found: C, 80.01; H, 9.40; mol. wt., 150 (mass spectrum).

After a solution of 120 mg. (0.80 mmole) of the *cis* ketone **9** in five times its volume of triethylamine had been heated to 120° overnight, only the *trans* ketone **10** could be detected[14] in the solution. An ether solution of the reaction mixture was washed with dilute, aqueous hydrochloric acid, dried, concentrated, and distilled to separate 93 mg. (77%) of the pure *trans* ketone **10** identified with the previously described sample by comparison of retention times and infrared spectra.

A solution of 1.00 g. (6.7 mmoles) of the mixture of Diels–Alder adducts containing 68% of the *cis* ketone **9** in ethyl acetate was hydrogenated over 15 mg. of a 5% palladium-on-carbon catalyst at room temperature and atmospheric pressure. After the hydrogen uptake (153 ml. or 1.03 equiv.) ceased, the solution was filtered and concentrated to leave a liquid exhibiting three gas chromatographic peaks[14,21] corresponding to the *cis*-perhydroindanone **12** (57%), the *trans*-perhydroindanone **13** (12%), and one of the 4-methylperhydro-1-indanones (31%). A sample of the pure **7-methyl-*cis*-perhydro-1-indanone** (**12**) collected[14] from the gas chromatograph has infrared absorption[15] at 1735 cm.$^{-1}$ (cyclopentanone C═O) with broad, partially resolved n.m.r. absorption[15] in the region 7.5 to 9.0 τ including a doublet (*J* = 7 c.p.s.) centered at 8.77 τ (CH_3).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59; mol. wt., 152. Found: C, 78.72; H, 10.59; mol. wt., 152 (mass spectrum).

A solution of 920 mg. (6.1 mmoles) of the mixture of Diels–Alder adducts containing more than 95% of the *trans* ketone **10** in 20 ml. of ethyl acetate was hydrogenated over 70 mg. of a 5% palladium-on-carbon catalyst at room temperature and atmospheric pressure. After the hydrogen uptake (154 ml. of 1.11 equiv.) had ceased, the mixture was filtered, concentrated, and distilled to separate 687 mg. (74%) of colorless liquid, b.p.

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(15) Determined in carbon tetrachloride solution.

(16) Determined in ethanol solution.

(17) Determined in chloroform solution.

(18) Prepared as described in ref. 2.

(19) Determined as a solution in perdeuteriochloroform.

(20) S. Dev, *J. Indian Chem. Soc.*, **32**, 403 (1955).

(21) A 100-ft. capillary column packed with Dow Corning silicone fluid no. 710 was employed for this analysis.

105° (20 mm.), which contained[14] more than 95% of the *trans* isomer **13**. A pure sample of the **7-methyl-*trans*-perhydro-1-indanone (13)**, collected from the gas chromatograph[14] had infrared absorption[15] at 1740 cm.$^{-1}$ with broad, partially resolved n.m.r. absorption in the region 7.5 to 9.0 τ including a doublet (J = 4 c.p.s.) centered at 8.86 τ (CH_3).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59; mol. wt., 152. Found: C, 78.64; H, 10.61; mol. wt., 152 (mass spectrum).

4,5,6,7-Tetrahydro-1-indanone (8).—3-Carbethoxy-3-(1-cyclohexenyl)propionic acid[22] was converted to the tetrahydroindanone **8** as previously described.[23] The product, obtained as a colorless liquid, b.p. 121–125° (15 mm.), n^{27}D 1.5200 [lit.[23] b.p. 83.5–85° (2 mm.), n^{18}D 1.5260], has infrared absorption[15] at 1700 cm.$^{-1}$ (cyclopentenone C═O) and at 1645 cm.$^{-1}$ (C═C), an ultraviolet maximum[16] at 237 mμ (ϵ 13,500) and complex n.m.r. absorption in the region 7.2 to 8.6 τ with no peak at lower field attributable to a vinyl proton.

A solution of 1.882 g. (13.8 mmoles) of the tetrahydroindanone **8** in 35 ml. of methanol was hydrogenated over 401 mg. of a 5% palladium-on-carbon catalyst at room temperature and atmospheric pressure. After the hydrogen uptake (330 ml. or 1.06 equiv.) ceased, the mixture was filtered, concentrated, and distilled to separate 1.6305 g. (85%) of *cis*-perhydro-1-indanone (**6**), b.p. 98° (16 mm.), which was identified with a subsequently described sample by comparison of retention times and infrared spectra.

7-Methyl-4,5,6,7-tetrahydro-1-indanone (18).—To a solution of 600 mg. (3.95 mmoles) of the *trans* ketone **13** in 10 ml. of ether, cooled to 0°, was added dropwise and with stirring, 650 mg. (4 mmoles) of bromine. The mixture was stirred for 10 min. and then concentrated and a solution of the residue in petroleum ether was washed with water and concentrated. A solution of the residual yellow oil (which darkened on standing) in 10 ml. of pyridine was refluxed under nitrogen for 8 hr. and then diluted with ether and filtered to separate the pyridine hydrobromide. The organic filtrate was washed successively with aqueous hydrochloric acid, water, aqueous sodium bicarbonate, and water and then dried and concentrated. Distillation of the residue in a short-path still afforded 348 mg. (59%) of a pale yellow oil which contained[14] the tetrahydroindanones **18** (85%) and **16** (15%). A sample of the tetrahydroindanone **16** was collected and identified with an authentic sample[6] by comparison of retention times and ultraviolet spectra. The pure tetrahydroindanone **18**, collected from the gas chromatograph, has infrared absorption[15] at 1700 cm.$^{-1}$ (cyclopentenone C═O) and at 1640 cm.$^{-1}$ (C═C), an ultraviolet maximum[16] at 238 mμ (ϵ 11,300) and complex n.m.r. absorption[15] in the region 7.3 to 8.7 τ (11 H, saturated C—H) as well as a doublet (J = 7 c.p.s.) centered at 8.95 τ (3 H, CH_3).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.65; H, 9.37.

Comparable mixtures of the tetrahydroindanones **16** and **18** were obtained by dehydrohalogenation of the crude bromo ketone thermally, with collidine or with lithium chloride and dimethylformamide. A solution of 424 mg. (2.82 mmoles) of the tetrahydroindanone **10** in 5 ml. of a 1 M solution of sulfuric acid in a benzene–acetic acid mixture (1:2 by volume) was heated to 125° in a sealed ampoule for 18 hr. After the mixture had been diluted with 50 ml. of petroleum ether and washed with aqueous sodium hydroxide, the organic layer was washed with water, dried, and concentrated. Distillation of the residue afforded 93 mg. (23%) of a liquid, b.p. 130–140° (20 mm.), which contained[14] 85% of the tetrahydroindanone **18**. A sample of the product was collected and identified with the previously described sample by comparison of retention times, infrared spectra, and ultraviolet spectra.

Perhydro-1-indanones 6 and 7.—A solution of 1.30 g. (9.56 mmoles) of the *trans* ketone **5** in 25 ml. of ether was hydrogenated over 150 mg. of a 30% palladium-on-carbon catalyst at room temperature and atmospheric pressure. After the hydrogen uptake ceased (260 ml. or 1.2 equiv.) the mixture was filtered, concentrated and distilled to separate 789.3 mg. (64%) of the *trans*-perhydroindanone **7**, b.p. 81.5–86.5° (10 mm.), n^{27}D 1.4764, containing[14] less than 9% of the *cis* isomer **6**. The product has infrared absorption[15] at 1740 cm.$^{-1}$ (cyclopentanone C═O), ultraviolet maxima[16] at 288 mμ (ϵ 29) and 237 mμ (ϵ 37, this latter peak is apparently attributable to contamination with a small amount of the unsaturated ketone **8**) and broad n.m.r. absorption[15] in the region 7.5 to 9.2 τ with no peaks attributable to vinyl hydrogen.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21; mol. wt., 138. Found: C, 78.30; H, 10.33; mol. wt., 138 (mass spectrum).

A solution of 400 mg. (2.95 mmoles) of the *cis* ketone **4** in 15 ml. of ether was hydrogenated over 40 mg. of a 30% palladium-on-carbon catalyst at room temperature and atmospheric pressure. After the absorption of hydrogen (59 ml. or 0.91 equiv.) ceased, the mixture was filtered and concentrated to leave 293 mg. (73%) of colorless liquid[24] containing 80% of the *cis* isomer **6** and 20% of the unsaturated ketone **8** (identified by comparison of the infrared spectra of a collected sample and the previously described material). The *cis* isomer **6**, collected from the gas chromatogram,[14] contained less than 11% of the *trans* isomer **7** and has infrared absorption[15] at 1740-cm.$^{-1}$ (cyclopentanone C═O), ultraviolet maxima[16] at 288 mμ (ϵ 22) and at 237 mμ (ϵ 71, apparently attributable to contamination with a small amount of the unsaturated ketone **8**), broad n.m.r. absorption[15] in the region 7.5 to 9.2 τ with no peaks attributable to vinyl hydrogen and a molecular weight (mass spectrum) of 138.

Equilibration Studies.—The positions of equilibrium listed in Table I were obtained by dissolving each of the *cis* and *trans* isomers in four times its volume of triethylamine. The solutions were sealed in ampoules and heated to 100°, samples being removed periodically for analysis.[14] For these analyses, the columns were calibrated by use of standard mixtures. The equilibrations were allowed to proceed until the values obtained with each *cis-trans* pair of isomers agreed to within 1%.

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[22] This diester, b.p. 148–153° (0.47 mm.), n^{25}D 1.4921, was prepared as described by W. S. Johnson, C. E. Davis, R. H. Hunt, and G. Stork [*J. Am. Chem. Soc.*, **70**, 3021 (1948)], who report n^{25}D 1.4830, b.p. 150–155° (0.5 mm.).

[23] D. W. Mathieson, *J. Chem. Soc.*, 3248 (1953).

[24] The *cis* isomer **6** is reported to boil at 72–73° (6 mm.) with n^{25}D 1.4813. See ref. 23.

Perhydroindanone Derivatives. III. Acid-catalyzed Ring Closure[1,2]

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The preparation (Chart II) and cyclization (Chart I) of the lactone **2** to form the tetrahydroindanones **1**, **3**, and **4** are described.

The successful use of acid-catalyzed ring closures for the production of tetrahydroindanone[3] prompted us to consider this synthetic method for the preparation of appropriately substituted tetrahydroindanones. In particular our failure to obtain a satisfactory yield of the 7-methyltetrahydroindanone (**1**) by use of the Diels–Alder reaction and subsequent transformations,[2] led us to reinvestigate the reported[3a] conversion of the lactone

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[2] Part II, *J. Org. Chem.*, **28**, 31 (1963).

[3] For examples see (a) R. L. Frank and R. C. Pierle, *J. Am. Chem. Soc.*, **73**, 724 (1951); (b) S. Dev, *J. Indian Chem. Soc.*, **34**, 169 (1957); (c) S. Dev and C. Rai, *ibid.*, **34**, 266 (1957).