known compounds (>25). 1,4-Cyclohexadiene, 4-vinylcyclohexene, benzene, 1,5-cyclooctadiene, and styrene were identified by comparison of glpc retention times with those of authentic samples and by combination glpc–mass spectral analysis. Tricyclo[2.2.2.0^{2,6}]oct-7-ene was identified by combination glpc–mass spectral analysis and by its known[1,2] formation from 5-vinylcyclohexa-1,3-diene at elevated temperatures. 5-Vinylcyclohexa-1,3-diene, 1,3,6-cyclooctatriene, and 1,3,5-cyclooctatriene were isolated by preparative glpc and were identified from their mass and nmr spectra. 5-Vinylcyclohexa-1,3-diene could also be isolated by distillation: bp 63–66° (90 mm) [lit.[2] bp 43–46° (42 mm)]; ir identical with that reported in the literature;[2] nmr (neat) τ 4.40 (m, 5, CH=CH$_2$ and CH=CHCH=CH), 5.15 (m, 2, CH=CH$_2$), 7.25 (m, 1, CHCH$_2$), and 8.00 ppm (m, 2, CHCH$_2$); mass spectrum (70 eV) *m/e* (rel intensity) 106 (49), 105 (31), 91 (100), 79 (51), 78 (80), 77 (41), 51 (26), 39 (25), and 29 (25). Identification of 1,3,6-cyclooctatriene is based upon the following: nmr (CCl$_4$) τ 3.8 (d, 2, J = 9 Hz, CH=CHCH=CH), 4.27 (m, 4, CH=CHCH=CH and CH$_2$-CH=CHCH$_2$), and 3.15 ppm (dd, 4, J = 7, 3.5 Hz, CH$_2$CH=CHCH$_2$); mass spectrum (70 eV) *m/e* (rel intensity) 106 (27), 91 (49), and 78 (100). Identification of 1,3,5-cyclooctatriene is based upon the following: nmr (CCl$_4$) τ 4.23 (broad d, 6, CH=CHCH=CHCH=CH) and 7.50 ppm (broad s, 4, CH$_2$-CH$_2$); mass spectrum (70 eV) *m/e* (rel intensity) 106 (24), 91 (52), and 78 (100).

B. By Ni(1,5-COD)$_2$ and P(n-Bu)$_3$.—A predried pressure bottle was charged with 0.10 g (0.36 mmol) of Ni(1,5-COD)$_2$ and capped in a drybox. After the bottle was partially evacuated and cooled to −78°, 0.80 mmol of P(n-Bu)$_3$ in 6 ml of cyclohexane was syringed into the bottle, and the ball stopcock was closed. Then 12.7 g (235 mmol) of butadiene and 1.5 g (58 mmol) of acetylene were added, the bottle was warmed to 25°, and the reaction was carried out and analyzed as in A. The yield of 5-vinylcyclohexa-1,3-diene was 52%.

C. By Nickel(II) Complexes at Elevated Temperatures.—A predried pressure bottle was charged with cyclohexane, the nickel(II) compound (if any), a *tert*-phosphine (if any), 1–2 ml of methanol (if any), butadiene, and acetylene as in A. As the mixture was stirred, its temperature was increased (the bottle was immersed in a heated oil bath) until the system pressure began to decrease. After no further reaction was apparent, the reaction solution was cooled and then analyzed as in A. Results are reported in Table I.

Treatment of a Cooligomerization Product Mixture with Tetrachloroethylene.—A cooligomerization reaction was carried out as in A except with 0.30 g (1.2 mmol) of Ni(acac)$_2$, 0.27 g (2.3 mmol) of PEt$_3$, and 2.4 ml of 25% AlEt$_3$ in cyclohexane. After 1 hr at 25°, the cooligomerization was complete, and a product distribution comparable to those shown in Table I for tri-*n*-alkylphosphines was obtained (by glpc analysis). This crude reaction mixture was treated with 3.2 g (19 mmol) of tetrachloroethylene, and the resulting solution was stirred overnight at 25° while unreacted gases were allowed to vent. Concentration of the solution under vacuum left a brown sludge which was chromatographed on acid-washed alumina. A viscous yellow oil was eluted with 50% ether in pentane and was rechromatographed. Elution with benzene afforded 0.12 g (23%) of *trans*-(Et$_3$P)$_2$Ni(CCl=CCl$_2$)Cl which, after recrystallization from MeOH, was found to be identical in all respects with an authentic sample.[7]

7-Vinylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Anhydride.—A solution of 1.49 g (14.1 mmol) of 5-vinylcyclohexa-1,3-diene and 1.50 g (15.3 mmol) of maleic anhydride in 2 ml of benzene was stirred at 25° for 48 hr. Pentane (10 ml) was added, and a mushy solid was collected by filtration. The solid was washed with ice water until the filtrate no longer gave a positive test with Congo red paper. Recrystallization of the solid from hot cyclohexane afforded 1.68 g (58%) of the product: mp 81–83°; ir (Nujol) 1840 (m) and 1765 (vs) (C=O), 1628 (m) (C=C), 1375 (m), 1350 (w), 1300 (w), 1258 (m), 1245 (m), 1225 (s), 1210 (w), 1175 (w), 1086 (s), 1063 (w), 1042 (w), 1018 (w), 990 (w), 958 (s), 938 (s), 924 (s), 908 (s), 902 (s), 866 (w), 833 (m), 823 (m), 778 (w), 754 (s), 697 (m), and 687 cm^{-1} (m); nmr (CDCl$_3$) τ 3.75 (m, 2, CH=CH), 4.60 (m, 1, CH=CH$_2$), 5.10 (m, 2, CH=CH$_2$), 6.85 (broad s, 4, bridgehead CH), 7.6, 8.05, and 8.8 ppm (broad multiplets, 3, CH$_2$CH); mass spectrum (70 eV) *m/e* (rel intensity) 204 (0.2), 96 (12), 78 (100), and 54 (70).

Anal. Calcd for C$_{12}$H$_{12}$O$_3$: C, 70.58; H, 5.92. Found: C, 70.7; H, 6.0.

Registry No.—5-Vinylcyclohexa-1,3-diene, 3725-32-4; acetylene, 74-86-2; butadiene, 106-99-0; Ni(1,5-COD)$_2$, 1295-35-8; P(Bu)$_3$, 998-40-3; *trans*-(Et$_3$P)$_2$Ni(*o*-tolyl)Br, 26521-33-5; *trans*-(Et$_3$P)$_2$NiCl$_2$, 15638-51-4; 7-vinylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride, 36749-22-1; nickel, 7440-02-0.

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Ozonolysis of the 7-Phenylnorcaranes

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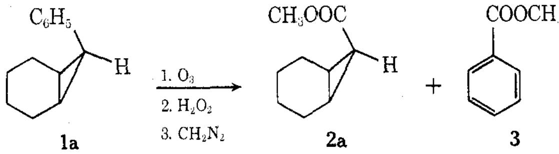
Conflicting reports of Hodgkins,[1] Closs,[2] Jensen,[3] and Ledlie[4] concerning the stereochemical assignments of the 7-phenylnorcaranes **1a** and **1b** have prompted us to reinvestigate the stereochemistry of these compounds. The structural assignments found in the literature have been based primarily on nmr data. In this paper we present the first conclusive chemical evidence supporting Closs', Jensen's, and Ledlie's assignments.

Reduction of a mixture of the 7-phenyl-7-chloronorcaranes[1] employing triphenyltin hydride yields 80% **1a**, ~1% **1b**, and 19% olefin. The olefin was removed with ozone.[1] Then work-up and distillation resulted in a sample of **1a** which was 99% pure. Subjecting **1a** to ozonization[5] furnishes a mixture of two acids which are converted to their corresponding methyl esters **2a** and **3** to facilitate their separation and identification. Preparative gas chromatography employing a 30% SE-30 column allowed separation of these materials. Compound **3** was produced in 20% yield and was identified as methyl benzoate by comparison of its ir spectrum with that of authentic material. **2a** was formed in 14% yield and was identified as *endo*-7-carbomethoxynorcarane, thereby identfying **1a** as the endo isomer of 7-phenylnorcarane. **2a** analyzed correctly for C$_9$H$_{14}$O$_2$ and exhibited an absorption band in its ir spectrum at 1734 cm^{-1} due to the C=O stretch of the ester function. Further evidence supporting the structure of compound **2a** was obtained



1a **2a** **3**

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[3] F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, 3837 (1966).

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by comparing its ir spectrum with that of an authentic sample.

Authentic **2a** was prepared by treating the known *endo*-norcarane-7-carboxylic acid[6,7] with diazomethane. The resulting ester analyzed correctly for $C_9H_{14}O_2$. Authentic 7-carbomethoxynorcarane displayed an absorption band in its ir spectrum at 1734 cm^{-1} as did **2a**. Its nmr spectrum exhibited absorptions at 3.58 ppm (3 protons, singlet) and 0.8–2.1 ppm (11 protons, multiplet).

When **1a** is treated with a 10% solution of potassium *tert*-butoxide in dimethyl sulfoxide,[2] *exo*-7-phenylnorcarane (**1b**) is obtained, which, after work-up and distillation, resulted in a sample of **1b** which was 97% pure. When **1b** was treated in turn with ozone, hydrogen peroxide,[5] and diazomethane, it furnished a 24% yield of *exo*-7-carbomethoxynorcarane (**2b**) and a 13% yield of methyl benzoate. The products were separated by preparative gas chromatography employing a 20% Carbowax 1500 column. Methyl benzoate was identified as before. Compound **2b** was identified as *exo*-7-carbomethoxynorcarane on the basis of a correct elemental analysis and by comparing its ir spectrum (1728 cm^{-1}, ester carbonyl) with that of an authentic sample.

Authentic *exo*-7-carbomethoxynorcarane was prepared in the same manner as its endo isomer. Authentic *exo*-7-carbomethoxynorcarane exhibits nmr absorptions at 3.57 ppm (3 protons, singlet) and 1.0–2.3 ppm (11 protons, multiplet). These data indicate that **1a** and **1b** are indeed the endo and exo isomers, respectively, of 7-phenylnorcarane, and are in complete agreement with the conclusions reached by Closs, Jensen, and Ledlie. We are presently investigating the ozonization of other bicyclo[*n*.1.0] systems as a function of structure and reaction temperature.

Experimental Section

An F & M gas chromatograph, Model 810, equipped with a 7 ft by 0.25 in. 20% Carbowax 1500 column operated at 125°, was employed for separation of methyl benzoate from *exo*-7-carbomethoxynorcarane. A 6 ft by 0.25 in. 30% SE-30 column was operated at 160° to achieve separation of methyl benzoate and *endo*-7-carbomethoxynorcarane. Ir spectra were obtained using a Beckman Model 10 grating ir spectrophotometer with potassium bromide cells. Nmr spectra were recorded in carbon tetrachloride with a Varian A-60 spectrometer employing tetramethylsilane as an internal reference. A Welsbach ozonator, Model T-816, generating a stream of 3% ozone at a flow of 1 l./min was used for all ozonolyses. The elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. All boiling points are uncorrected.

Ozonolysis[5] of *endo*-7-Phenylnorcarane (1a).—A stream of 3% ozone was bubbled through a 250-ml gas wash bottle containing a magnetically stirred mixture of 2.0 g of **1a** (99% pure) in 100 ml of 95% acetic acid until a test in water showed no turbidity. The time required for this reaction when carried out at 25° was 2.5 hr. After completion of the reaction, 10 ml of 30% hydrogen peroxide was added, and the solution was allowed to stir at room temperature overnight. The mixture was then heated in an oil bath at 95° for 4 hr, the acetic acid removed by vacuum distillation, and the residue extracted four times with 5-ml portions of hot hexane. Evaporation of the hexane furnished 0.92 g of a mixture of two acids. These acids were treated with diazomethane and the resulting esters were separated by preparative gas chromatography employing a 6 ft by 0.25 in. column containing 30% SE-30 on Chromosorb P operated at 160°. The faster eluting compound (**3**) was proven to be methyl benzoate by comparison of its ir and nmr spectra with reference spectra. The slower eluting compound, **2a**, was collected and found to have ir and nmr spectra identical with those of an authentic sample of *endo*-7-carbomethoxynorcarane (see below). The yield of esters **2a** and **3** based on **1a** was 14 and 20%, respectively. The yields were calculated by comparing the area found under the vpc curves with those obtained from standard samples.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.21; H, 9.20.

Ozonolysis of *exo*-7-Phenylnorcarane (1b).—Ozonolysis of **1b** was carried out in exactly the same manner described for **1a**. A yield of 0.72 g of a mixture of two acids was obtained. These acids were treated with diazomethane and the resulting esters were separated by preparative gas chromatography employing a 7 ft by 0.25 in. column containing 20% Carbowax 1500 on Chromosorb P operated at 125°. The faster eluting compound (**3**) was proven to be methyl benzoate by comparison of its ir and nmr spectra with reference spectra. The slower eluting compound, **2b**, was collected and found to have ir and nmr spectra identical with those of an authentic sample of *exo*-7-carbomethoxynorcarane (see below). The yield of esters **2b** and **3** based on **1b** was 24 and 13%, respectively. The yields were calculated by comparing the area found under the vpc curves with those obtained from standard samples.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.19.

***exo*-7-Carbomethoxynorcarane (2b).**—*exo*-Norcarane-7-carboxylic acid[6] was methylated by dissolving 5 g of the acid in 50 ml of ether and treating the solution with an excess of diazomethane.[8] The solution was allowed to stand in the dark for 30 min. The unreacted diazomethane was treated with a dilute solution of acetic acid in ether. The ether was evaporated and the residue distilled *in vacuo* to give 4.31 g (78%) of **2b**, bp 99° (15 mm), n^{28}_{D} 1.4700.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.30; H, 9.23.

***endo*-7-Carbomethoxynorcarane (2a).**—*endo*-Norcarane-7-carboxylic acid[6] was methylated in the same manner as its exo isomer except that only 0.4 g of the acid was used, and the reaction was allowed to stand in the dark for 2.5 hr after the diazomethane was added. A yield of 0.36 g (71%) of **2a**, bp 95° (15 mm), was isolated.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 9.12.

Registry No.—**1a**, 10503-37-4; **1b**, 10503-36-3; **2a**, 36744-58-8; **2b**, 36744-59-9; **3**, 93-58-3.

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Cycloaddition Reactions of Vinylketene Thioacetals

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The relative unavailability of vinylketenes from readily available precursors coupled with their tendency to ring close has precluded their use in synthesis. An obvious application would be in cyclohexenone synthesis by Diels–Alder addition of olefins to a vinylketene, but here an additional complication arises in that vinylcyclobutanones could arise by a ${}_{\pi}2_s + {}_{\pi}2_a$ process in competition with the desired ${}_{\pi}4_s + {}_{\pi}2_s$ process.[1]

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