residual solid was recrystallized from 80% ethanol affording 12.3 g (80%) of the *exo,exo* quaternary salt **4d** as white needles, mp 243–245° dec. The ir spectrum was identical with that of the product obtained from the reaction of the *exo,exo*-diiodide **4c** with aqueous trimethylamine. A mixture melting point determination showed no depression.

Treatment of the Dibromide 4a with Methylmagnesium Iodide. Formation of 1,1′-Biindenyl (8).—Excess magnesium was quickly removed from a freshly prepared solution of methylmagnesium iodide generated from magnesium turnings (0.73 g, 0.03 g-atom) and methyl iodide (1.25 ml) in 15 ml of dry ether. A solution of the dibromotruxane **4a** (3.0 g, 7.7 mmol) in dry benzene (30 ml) was then added dropwise over a 15-min period with manual agitation. The temperature of the reaction mixture rose to 37° during the addition. The reaction mixture was then heated under gentle reflux for 19 hr. After being cooled to room temperature, the light yellow solution was shaken in turn with 30 ml of cold 10% hydrochloric acid and 100 ml of water, and finally dried over sodium sulfate. Removal of the volatile solvents under reduced pressure afforded a light yellow-orange amorphous solid which was boiled in 95% ethanol. The hot ethanolic solution was decanted from insoluble oils and then diluted with water until the solution became cloudy. On standing overnight at room temperature the alcoholic solution deposited 95 mg (5.3%) of 1,1′-biindenyl, mp 93–99°. A pure sample (mp 97–99°, lit.[13] mp 98°) was prepared by recrystallization from 95% ethanol: ir 1465, 803, 770, 760, 733, and 718 cm^{-1}; nmr ($CDCl_3$) τ 2.35–2.98 (m), 3.33 (d), 4.17 (d), and 5.85 (s) in the respective area ratio of 4:1:1:1.

Isomerization of 1,1′-Biindenyl (8) to 3,3′-Biindenyl (9).—To a solution of 1,1′-biindenyl (85 mg) in 2 ml of dry methanol was added 5 drops of a 5% potassium methoxide solution. The resulting reddish brown solution was boiled gently for 5 min and subsequently refrigerated at −10° for 1 hr. The precipitated yellow-brown solid was collected on a filter and recrystallized from petroleum ether (bp 60–90°) to afford 3,3′-biindenyl (55 mg, 65%) melting at 129–131° (lit.[14] mp 130–131°). The ir spectrum was identical in all respects with that of an authentic sample of **9** prepared by reductive dehalogenation of 1,1′-dibromo-3,3′-diindenylene.[14]

Registry No.—**4b,** 20286-93-5; **4c,** 10425-94-2; **4d,** 20286-95-7; **4g,** 20286-96-8; **4h,** 20286-97-9; **5a,** 20286-98-0; **5b,** 20286-99-1; **5c,** 20287-00-7; **5c,** dipicrate, 20287-01-8; **5d,** 20287-02-9; **5f,** dipicrate, 20287-03-0; **6a,** 20287-04-1; **6b,** 20287-05-2; **6c,** 20287-06-3.

Acknowledgment.—We are indebted to the National Science Foundation (Grants G-12759, G.P. 3764, and G.P. 2543) for financial support of this work.

Chemistry of Allene. IV. Catalyzed Cyclodimerization of Allene and a New Allene Pentamer

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Received February 19, 1969

Allene undergoes cyclodimerization to 1,3- and 1,2-dimethylenecyclobutane in the vapor phase over phosphine-modified nickel carbonyls. A polymeric complex of composition $[p\text{-}(C_6H_5)_2PC_6H_4P(C_6H_5)_2\cdot Ni(CO)_2]_x$ is a particularly effective catalyst. This same complex catalyzes the cyclomerization of allene in the liquid phase to a tetramer, a pentamer, and higher oligomers.

Catalyzed 1,2 cycloadditions involving carbon–carbon double bonds have previously been observed only with norbornadiene,[1] benzonorbornadiene,[2] a tetracyclononene,[2] and butadiene,[3] all in the liquid phase.

We now report the first example of such a metal-catalyzed cyclodimerization in the vapor phase and a novel type of catalyst for this reaction. Thus, 1,3- and 1,2-dimethylenecyclobutane, along with higher oligomers, are obtained when allene is passed over certain phosphine-modified nickel carbonyls at elevated temperatures.

Our most effective catalyst (catalyst I) is a complex of empirical composition $[(C_6H_5)_2PC_6H_4P(C_6H_5)_2\cdot Ni(CO)_2]$, prepared by reaction of an equimolar mixture of 1,4-bis(diphenylphosphino)benzene and nickel tetracarbonyl. During the reaction, 2 mol of carbon monoxide are evolved/mol of the bisphosphine and the complex precipitates as a white powder of surprising thermal stability. The complex is presumed to be polymeric (linear or macrocyclic) from consideration of its stoichiometry and ligand geometry. The phosphorus–phosphorus distance in the ligand, which is of the order of 6 Å, is too large to permit chelate formation.

The closely related monomeric complex, $[(C_6H_5)_3P]_2$–$Ni(CO)_2$, also catalyzes the cyclodimerization of allene in the vapor phase but is less effective, possibly because of lower thermal stability. It was previously reported[4] to catalyze the cyclomerization of allene in the liquid phase to trimers and higher oligomers, but not dimers.

Oligomerizations were conducted by passing allene diluted with helium over a mixture of catalyst and 20-mesh quartz in a tube attached directly to a gas chromatography column. With catalyst I at 200°, 61% of the allene was converted into volatile products containing 60% 1,3-dimethylenecyclobutane, 13% 1,2-dimethylenecyclobutane, and 27% trimers, mainly 1,2,4-trimethylenecyclohexane. With $[(C_6H_5)_3P]_2Ni(CO)_2$ as catalyst at 175°, 43% of the allene was converted into volatile products consisting of 11% 1,3-dimethylenecyclobutane, 4% 1,2 isomer, and 74% trimer. The dimers were positively identified by means of their retention times, infrared spectra, and proton magnetic resonance spectra. The trimer was identified by comparison with an authentic sample.

It is of interest that the predominant dimer in the catalyzed process is 1,3-dimethylenecyclobutane. In contrast, thermal dimerizations either in the liquid phase at about 140° or in the gas phase at 400–

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[1] For a review, see G. N. Schrauzer, *Advan. Catal.*, **18**, 377 (1968).

[2] T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967).

[3] P. Heimbach and W. Brenner, *Angew. Chem. Intern. Ed. Engl.*, **6**, 800 (1967).

[4] R. E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4247 (1959).

600° give 1,2-dimethylenecyclobutane as the principal isomer.[5]

The dimers are quite stable and are essentially unchanged when passed over catalyst I at 225°. However, little trimer is recovered under these conditions. No oligomerization was observed when allene was passed over quartz at 200° in the absence of catalyst.

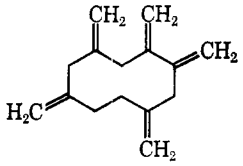
On a preparative scale, the catalyzed oligomerization is highly exothermic and difficult to control. It is advantageous to use very low ratios of nickel complex to inert support and either to dilute the allene with nitrogen or to operate under reduced pressure. Even with these precautions, the relative amounts of products, particularly the ratio of dimers to trimers, varied considerably and conversions into volatile products were generally lower than those reported above. In a typical run at 200° with a nitrogen/allene ratio of 5:1 about 10 g of volatile product/g of catalyst I was formed before activity was lost, presumably because of buildup of nonvolatile products.

The addition of carbon monoxide to the allene inhibits the reaction. However, reaction resumes when the addition is stopped. This indicates that allene cannot compete favorably with carbon monoxide for coordination sites on nickel.

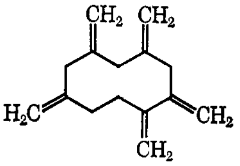
We have also examined the reaction of allene with catalyst I in the liquid phase to complete the comparison with $[(C_6H_5)_3P]_2Ni(CO)_2$. The products obtained were a tetramer, a pentamer, and higher boiling oligomers. No dimers were observed.

The tetramer is identical with the tetramethylenecyclooctane obtained previously with $[(C_6H_5)_3P]_2Ni(CO)_2$ catalyst.[4]

The pentamer, which is different from the one of undetermined structure obtained with $[(C_6H_5)_3P]_3RhCl$ catalyst,[6] has been assigned structure **8a** or **8b** on the basis of the following spectral evidence.[7] Mass spectroscopy gave the parent peak of 200 required for the pentamer. The ultraviolet spectrum showed λ_{max}^{EtOH} 235 mμ (ε 5140), consistent with one conjugated diene group. Both the near-ir and nmr spectra indicated an equal number of hydrogens on saturated and unsaturated carbon atoms. The nmr spectrum determined in $CDCl_3$ showed peaks at δ 2.28 (4 H), 2.80 (2 H), 3.00 (4 H), 4.82 (4 H), 4.91 (4 H, broad), and 5.19 (2 H, triplet *J* = 2 Hz). This spectrum clearly established the presence of ten vinylic and ten allylic protons, consistent only with a pentamethylenecyclodecane structure. On the basis of established[5] chemical-shift correlations, the peaks at δ 2.28 can be related to the four singly allylic protons in **8a** or **8b** and the peaks at 2.80 and 3.00 to six doubly allylic protons. The ir spectrum showed strongest absorptions at 3100, 2990, 2920, 2860, 1650, 1600, and 890 cm^{-1}. Neither the ir nor the nmr spectrum suggests the presence of $CH_2{=}CH{-}$ or $-CH{=}CH-$ groups.



8a



8b

Experimental Section[8]

Reaction of 1,4-Bis(diphenylphosphino)benzene with Nickel Tetracarbonyl. Preparation of Catalyst I.—To a solution of 22.3 g (0.05 mol) of 1,4-bis(diphenylphosphino)benzene[9] and 600 ml of tetrahydrofuran was added 8.5 g (0.05 mol) of $Ni(CO)_4$ in 100 ml of tetrahydrofuran at 25°. After the initial rapid carbon monoxide evolution had subsided, the reaction was completed by heating the mixture for 1 hr at 65°. A total of 0.10 mol of CO was liberated. The product separated as a white, powdery solid and was collected by filtration: yield 25.4 g (91%). *Anal.* Calcd for $C_{32}H_{24}NiO_2P_2$: C, 68.4; H, 4.3; Ni, 10.4. Found: C, 68.1; H, 4.8; Ni, 10.0.

On thermogravimetric analysis, catalyst I showed a weight loss of only 5% when heated slowly to 200°. Differential thermal analysis under N_2 showed a shallow exotherm near 165° with the degradation endotherm at 265–290°.

Vapor Phase Cyclization of Allene.—Vapor phase cyclization of allene was conducted in a 290 × 13 mm i.d. Inconel tube attached to a gas chromatography column packed with 1,2,3-tris(2-cyanoethoxy)propane on firebrick. The tube was packed with an intimate mixture of catalyst (3 g) and 20-mesh quartz (30 ml). Allene (1–4 ml) contained in glass loops fitted with a four-way 2V-bore stopcock was carried into the reactor with helium. The dimers and trimers were identified by their retention times and by comparison of their ir spectra and/or nmr spectra with those of authentic samples.

On a preparative scale, an allene–nitrogen mixture (1:5) was passed over a mixture of 1 g of catalyst I and 40 ml of 30-mesh quartz in a 450 × 25 mm o.d. Pyrex tube fitted with a central thermocouple well. The catalyst bed was heated to 195° and the rate of flow was then adjusted to keep the temperature inside the catalyst bed below 225°. During about 2.5 hr, 11 g of allene oligomers and about 14 g of unreacted allene were collected. An undetermined amount of tar remained on the catalyst, which gradually became deactivated. Gas chromatographic analysis of the oligomers using a column packed with dimethyl sulfolene on firebrick showed the presence of 30% 1,3 dimer, 8% 1,2 dimer, and 42% trimers, mainly 1,2,4-trimethylenecyclohexane. These were separated by preparative gas chromatography and characterized as follows.

1,3-Dimethylenecyclobutane: ir (gas phase) 3040 (=CH), 2920 (CH), 1660 (C=C), and 880 ($=CH_2$) cm^{-1}; nmr (neat) δ 3.27 (m, 4, *J* = 2.5 Hz, CH_2) and 4.85 (m, 4, *J* = 2.5 Hz, $=CH_2$).

1,2-Dimethylenecyclobutane: ir (gas phase) 3120 (C=CH), 3280 (CH), 1670 (C=C), and 880 ($=CH_2$) cm^{-1}.

1,2,4-Trimethylenecyclohexane: ir (neat) 3120 (C=CH), 3280 (CH), 1640 (C=C), and 880 ($=CH_2$) cm^{-1}

Liquid Phase Cyclization of Allene with Catalyst I.—A mixture of 40 g of allene, 50 ml of tetrahydrofuran, and 0.5 g of catalyst I was heated in a 400-ml Hasteloy C bomb for 8.5 hr at 100–124°. The reaction mixture was filtered and the filtrate was distilled to obtain 13 g of product, bp 80–100° (0.1 mm), and 15.9 g of higher boiling residue. Redistillation gave 3 g of tetramethylenecyclooctane,[4] bp 52° (2 mm), and 10 g of pentamer, bp 90° (2 mm): mass spectrum, *m/e* (rel intensity), 200 (7), 185 (35), 172 (67), 157 (87), 143 (97), and 129 (100); ir (cm^{-1}) 3100, 2990, 2920, 2860, 1650, 1600, 890; uv max (C_2H_5OH) 235 mμ (ε 5140); near-ir (CCl_4) 6120 cm^{-1} (intensity indicates one $=CH_2$ per 37–44 mol wt).

Registry No.—Allene, 463-49-0; 1,3-dimethylenecyclobutane, 2045-78-5; 1,2-dimethylenecyclobutane, 14296-80-1; 1,2,4-trimethylenecyclohexane, 14296-81-2; **8a**, 20628-85-7; **8b**, 20628-86-8.

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[5] For recent reviews of allene oligomerizations, see (a) B. Weinstein and A. H. Fenselau, *J. Chem. Soc.*, *C*, 368 (1967), and (b) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **32**, 2278 (1967).

[6] F. N. Jones and R. V. Lindsey, Jr., *ibid.*, **33**, 3838 (1968).

[7] While our manuscript was in preparation, S. Otsuka, A. Nakamura, K. Tani, and S. Ueda [*Tetrahedron Lett.*, 297 (1969)] reported two new allene pentamers. One of these, which was obtained with a nickel catalyst, was assigned structure **8a** (1,2,4,6,9-pentamethylenecyclodecane). The properties of our pentamer are in quite close agreement with those reported.

[8] Infrared spectra (linear in wavelength) were recorded using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride prism. Nmr spectra were determined with tetramethylsilane as internal standard using a Varian A-60 instrument.

[9] D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).