Truxanes. II.[1a] Stereoisomerism in the 1,1'-Disubstituted *syn,trans*-Truxane System[1b]

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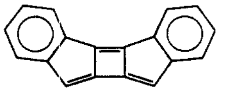
A number of potential precursors for the novel 18-π-electron system dibenzo[*a,g*]tricyclo[5.3.0.0^{2,6}]decapentaene have been prepared. Several stereoisomeric modifications of these precursors (1,1'-disubstituted *syn,trans*-truxanes) and their reaction products have been isolated. A general method for determining stereochemistry at the 1 and 1' positions in this series of compounds is also presented.

In continuing our efforts to generate diene **2**, a direct progenitor of the potentially aromatic dibenzo[*a,g*]tricyclo[5.3.0.0^{2,6}]decapentaene **1**, we have prepared several 1,1'-disubstituted *syn,trans*-truxanes in a variety of stereochemical modifications. At this time we wish to describe the formation of these truxane derivatives and to demonstrate how nmr spectroscopy may be utilized to differentiate the various possible stereoisomeric forms of these compounds.



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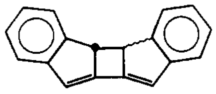

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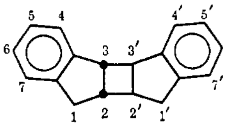

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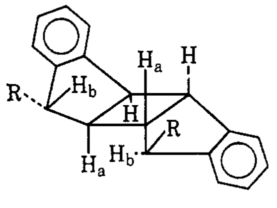
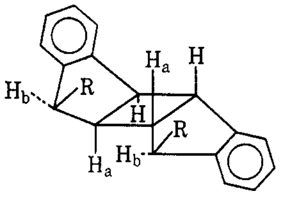
A potentially useful precursor for **1**, namely *syn,trans*-truxane (**3**), is readily accessible through photosensitized dimerization of indene.[1a] In principle, 1,1'-disubstituted truxanes may assume one of the three stereoisomeric modifications depicted in **4**, **5**, and **6**, to which we will henceforth refer as *exo,exo*, *exo,endo*, and *endo,endo*, respectively.

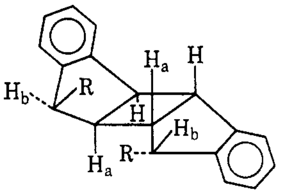
We have found that nmr spectroscopy serves as a valuable tool in distinguishing among these 1,1'-disubstituted *syn,trans*-truxanes. Inspection of simple molecular models indicates that in the *exo,exo*-substituent orientation the dihedral angle between the benzylic proton H_b and the adjacent cyclobutane proton H_a is on the order of 100°, while the corresponding angle for these protons in the *endo,endo*-disubstituted arrangement is nearly 0°. The coupling constants associated with these dihedral angles should be less than 2 Hz for the *exo,exo* orientation and approximately 8 Hz for the *endo,endo* disposition.[2] One would therefore expect that the nmr spectra of **4**, **5**, and **6** should display H_b as a 2 H singlet, 1 H singlet and 1 H doublet, and a 2 H doublet, respectively. This expectation is borne out by the observed spectral properties of the three dimethoxytruxanes **4b**, **5b**, and **6b** (Table I).



exo,exo **4a**, R = Br
b, R = OCH_3
c, R = I
d, R = $N^+(CH_3)_3I^-$
e, R = $N^+(CH_3)_3OH^-$
f, R = OTs
g, R = OH
h, R = Cl



exo,endo **5a**, R = OCH_2CH_3
b, R = OCH_3
c, R = $N(CH_3)_2$
d, R = $N^+(CH_3)_3I^-$
e, R = $N^+(CH_3)_3\text{-}OH^-$
f, R = $N(CH_3)_2 \rightarrow O$



endo,endo **6a**, R = OCH_2CH_3
b, R = OCH_3
c, R = Cl

Treatment of the *exo,exo*-dibromide **4a**[1a] (H_b, 2 H singlet at τ 4.45[3]) with various bases commonly employed to bring about dehydrohalogenation failed to afford the desired diene **2**.[4] In some cases low yields of substitution products were obtained. For example, ethyl ethers **5a** and **6a** and methyl ethers **5b** and **6b** were isolated when the dibromide was treated with ethanolic and methanolic potassium hydroxide, respectively.

The production of the *endo,endo*-diethers **6a** and **6b** from the *exo,exo*-dibromide **4a** is not unexpected in view of the strongly nucleophilic, nonpolar medium employed which should favor backside displacement. The observed formation of *exo,endo* products **5a** and **5b** is mechanistically less obvious, especially since it was demonstrated by separate experiment that epimerization of the corresponding *endo,endo*-ethers under the conditions of the reaction does not occur.

The remaining isomeric 1,1'-dimethoxytruxane **4b** was prepared by methanolysis of **4a** in a more polar medium (aqueous methanol containing sodium car-

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[1] (a) For the first paper in this series, see A. G. Anastassiou and G. W. Griffin, *J. Org. Chem.*, **33**, 3441 (1968). (b) Abstracted from the Ph.D. dissertations of F. L. S. (Tulane University, 1966) and A. G. A. (Yale University, 1963). (c) To whom inquiries and reprint requests should be addressed at the Department of Chemistry, Louisiana State University in New Orleans, Lakefront, New Orleans, La. 70122.

[2] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[3] The H_a and the methine benzylic (3,3') cyclobutane protons in **4a** appear as 2 H doublets at τ 7.00 and τ 6.25, respectively. That all aliphatic proton peak assignments are correct is supported by the spectrum of *exo,exo*-1,1'-dibromo-3,3'-dichloro-*syn,trans*-truxane in which both H_b (τ 4.55) and H_a (τ 7.16) appear as clean singlets: U. Heep and G. W. Griffin, unpublished results.

[4] Treatment of **4a** with potassium amide in liquid ammonia or **4c** with potassium *t*-butoxide resulted in opening of the cyclobutane ring to yield *sym*-dibenzfulvalene; see A. G. Anastassiou, F. L. Setliff, and G. W. Griffin, *J. Org. Chem.*, **31**, 2705 (1966).

TABLE I

CHEMICAL SHIFTS (τ) FOR THE BENZYLIC (H_b) AND METHOXY PROTONS OF THE THREE 1,1′-DIMETHOXY-*syn,trans*-TRUXANES

Compd	H_b	OCH_3
exo,exo **4b**	5.52 (2 H singlet)	6.76 (6 H singlet)
exo,endo **5b**	5.30 (1 H singlet)	6.45 (3 H singlet)
	4.95 (1 H doublet), $J = 8$ Hz	6.70 (3 H singlet)
endo,endo **6b**	5.10 (2 H doublet), $J = 8$ Hz	6.38 (6 H singlet)

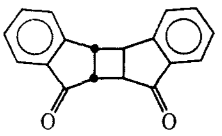
bonate). Reaction under these conditions probably proceeds through initial heterolysis of the C—Br bonds followed by entry of the nucleophilic solvent from the least hindered *exo* side.

Treatment of the dibromide **4a** with sodium iodide in acetone produced the *exo,exo*-diiodide **4c** (H_b, 2 H singlet at τ 4.25). The over-all retention of stereochemistry observed in this transformation suggests that a double displacement[5] has occurred at the 1 and 1′ positions, which is not unexpected in view of the relatively low polarity of the reaction medium. It thus appears that any *endo*-iodides introduced initially are readily displaced to give ultimately the thermodynamically most favorable *exo,exo* modification.

Treatment of **4c** with alcoholic hydroxide, as in the case of **4a**, led to ethers **5b**, **6b**, and **5a**, **6a** rather than **2**.[4] Treatment of **4c** with aqueous trimethylamine produced the *exo,exo* bisquaternary iodide **4d**, which in turn was converted into the *exo,exo* Hofmann base **4e**. Pyrolysis of **4e** under a variety of conditions yielded only intractable materials.

The failure to obtain **2** under strongly basic conditions is perhaps better ascribed to its inability to withstand the reaction conditions rather than to its resistance to form.[6] Indeed, from a stereochemical standpoint the *exo,exo* derivatives are potentially the most promising precursors for **2**, since the leaving groups (H_a and R) can assume the favorable coplanar transition state required for smooth bimolecular elimination, even though a *cis* elimination is required.

Since the ease with which tosylates undergo *cis* bimolecular elimination had been demonstrated previously,[7] we next undertook the synthesis of the *exo,exo*-ditosylate **4f**, in the hope that this compound would respond favorably to mild elimination conditions. The dibromotruxane **4a** was first converted into the *exo,exo*-diol **4g** by treatment with sodium carbonate in aqueous acetone. An S_N1 displacement similar to that proposed for the formation of **4b** is undoubtedly operative in the present case as well. Oxidation of **4g** to the known[1a] *syn,trans*-truxone **7** confirmed that the gross structure had been retained.



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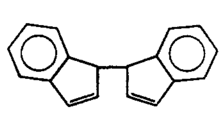
Attempts to prepare the ditosylate from this diol in pyridine solution at 0° resulted in the unexpected formation of the *endo,endo*-dichloride **6c** (H_b, 2 H doublet, $J = 8$ Hz, centered at τ 4.37). The dichloride is presumably formed *via* S_N2 displacement of the evanescent ditosylate by chloride present as pyridinium hydrochloride. The facile conversion of **6c** into *exo,exo*-diiodide **4c** on treatment with sodium iodide in acetone provided a useful cross check of gross structure.

To validate further the applicability of nmr spectroscopy to the characterization of these systems, the *exo,exo*-dichloride **4h** was prepared from the diol **4g** with thionyl chloride in pyridine. The dichloride, which was anticipated to have *exo,exo* stereochemistry,[8] exhibited the expected singlet for H_b (τ 4.62), and was converted into the *exo,exo*-diodide **4c** by sodium iodide in acetone. Double displacement by iodide to produce the most thermodynamically favorable *exo,exo* modification is apparently also operative here.

Our observations on the 1,1′-bisquaternary salt **5d** further substantiates our contention that the *exo,exo* configuration is favored thermodynamically in these *syn,trans*-truxane systems. The *exo,endo* bisquaternary iodide **5d**,[9] prepared by exhaustive methylation of the amine **5c**, which was in turn obtained by aminolysis of the dibromide **4a**,[10] was epimerized (80%) to the *exo,exo* modification **4d** on treatment with boiling aqueous potassium hydroxide. It is not surprising that equilibration under such conditions should favor the less sterically crowded *exo,exo* isomer. The quaternary iodide **4d**, which had been previously prepared from the diiodide **4c** and aqueous trimethylamine, exhibited the characteristic singlet for H_b (τ 4.85).

An interesting transformation was observed in one experiment designed to yield **2** *via* halogen-metal interchange. Dibromide **4a** reacted smoothly with methylmagnesium iodide[11,12] to yield 1,1′-biindenyl (**8**), which was identified by its spectral properties and the consistency of its melting point with the reported value.[13]



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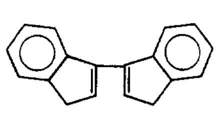

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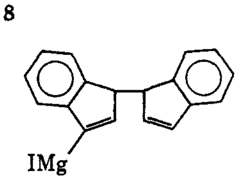

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Furthermore, **8** underwent facile isomerization to the conjugated 3,3′-biindenyl (**9**) on treatment with meth-

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(5) Multiple displacements involving iodide are not uncommon; *cf.* E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959, p 262.

(6) Although **2** would appear to suffer from considerable strain, we had hoped that elimination would be accompanied by epimerization at a methine benzylic (3,3′) center to offer some relief of strain.

(7) C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Amer. Chem. Soc.*, **84**, 1314 (1962).

(8) Although inversion of configuration might have been expected to occur in this instance owing to the presence of pyridine, internal displacement of the intermediate chlorosulfite ester resulting in ultimate retention of configuration, as was apparently the case here, is commonly observed if phenyl groups are attached to the carbon atom undergoing reaction; *cf.* W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

(9) Neither treatment of this quaternary iodide with a variety of bases nor pyrolysis of the derived quaternary hydroxide **5e**, or amine oxide **5f**, gave any evidence of the generation of diene **2**.

(10) The course of this transformation remains to be established.

(11) Methyllithium and phenyllithium led to intractable materials.

(12) The successful use of methylmagnesium iodide as a base in elimination reactions has been demonstrated previously: M. S. Kharasch, F. Englemann, and W. H. Urry, *J. Amer. Chem. Soc.*, **66**, 365 (1944).

(13) C. Courtct, *Ann. Chim.*, **10** (4), 79 (1915).

oxide, a conversion which had been observed previously by other workers.[14]

Two reasonable mechanistic alternatives for the formation of **8** from **4a** include either 1,4 elimination of HBr by methide followed by Grignard exchange yielding **10**, then hydrolysis of the Grignard derivative in work-up or 1,4 elimination initiated by nucleophilic attack of methide upon a bromine atom.

Experimental Section[15,16]

Reaction of the *exo,exo*-Dibromide 4a[1a] with Ethanolic Potassium Hydroxide. Formation of the *endo,endo*- and *exo,endo*-Ethers 6a and 5a.[17]—To a solution of potassium hydroxide (10.0 g) in absolute ethanol (50 ml) maintained at room temperature was added 2.0 g (6.8 mmol) of the dibromide **4a**. The resulting suspension was stirred at 75° for 20 hr. Removal of the volatile solvent under reduced pressure afforded a dark residue which was suspended in water (50 ml) and extracted with ether (two 75-ml portions). The ether extracts were combined and washed in turn with 5% hydrochloric acid (100 ml) and water (200 ml). The ether solution was dried over sodium sulfate and evaporated. The residual dark orange oil was dissolved in the minimum amount of benzene, and the benzene solution was applied to a 2 × 30 cm chromatographic column packed with neutral aluminum oxide. Elution was performed with 1:4 benzene–cyclohexane (200 ml), 1:2 benzene–cyclohexane (150 ml), and benzene (250 ml). Evaporation of the first 300 ml of eluted solvent (collected in 50-ml fractions) afforded the crude *endo,endo* isomer **6a** as a yellow-orange solid. Recrystallization from methanol (Norit) provided pure material (140 mg, 11%) as fluffy white needles: mp 136–138°; ir 1345, 1120, and 750 cm^{-1}; nmr ($CDCl_3$) τ 2.68 (s), 4.91 (d), 6.2 (q), 6.47 (m), and 8.7 (t) in the respective area ratio of 4:1:2:2:3.

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.40; H, 7.50.

Evaporation of the later-eluted solvents (300 ml) yielded yellow oils which were combined, dissolved in hot methanol, and filtered free of insoluble material. The filtrate was evaporated to leave a slightly colored solid, which upon recrystallization from a small amount of methanol provided the pure *exo,endo* isomer **5a** (70 mg, 6%) as a white solid: mp 94–96°; ir 1345, 1128, 1110, 1090, 760, and 748 cm^{-1}; nmr ($CDCl_3$) τ 2.65 (m), 4.91 (d), 5.20 (s), 6.2–6.9 (m), 7.2 (t), and 8.5–9.0 (two overlapping triplets) in the area ratio of 8:1:1:7:1:6.

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.25; H, 7.36.

Treatment of the *exo,exo*-Dibromide 4a with Methanolic Potassium Hydroxide. Formation of *endo,endo*- and *exo,endo*-Ethers 6b and 5b.[17]—The dibromide **4a** (1.5 g, 3.85 mmol) was added at room temperature to a solution of 10.0 g of potassium hydroxide in dry methanol (distilled from magnesium turnings). The resulting mixture was stirred at the reflux temperature for 20 hr. A small amount of inorganic material was removed by filtration and the filtrate taken to near dryness on a rotary evaporator. The residual material was suspended in water (30 ml) and extracted with two 50-ml portions of ether. The ether extracts were combined, washed successively with 5% hydrochloric acid and water (100 ml each), and dried over sodium sulfate; the volatile solvent was evaporated. The residual yellow-orange oil was dissolved in a minimum amount of benzene and the resulting solution applied to a 2 × 30 cm column packed with neutral aluminum oxide. Elution was performed with 1:4 benzene–cyclohexane (100 ml), 1:2 benzene–cyclohexane (100 ml), 1:1 benzene–cyclohexane (100 ml), and pure benzene (300 ml). Evaporation of the first 300 ml of eluted solvent afforded the crude *endo,endo*-diether **6b** as a white solid. Recrystallization from a small amount of 95% ethanol provided pure material (145 mg, 12%) as white needles: mp 115–116°; ir 1365, 1110, 1100, 755, and 740 cm^{-1}; nmr ($CDCl_3$) τ 2.65 (s), 5.10 (d), 6.38 (s), and 6.55 (m) in the area ratio of 4:1:3:2.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.22; H, 6.98.

Evaporation of the subsequently eluted fractions afforded the *exo,endo* isomer **5b** as a clear, viscous oil which solidified on standing. Recrystallization from a small quantity of 95% ethanol provided pure material (105 mg, 8%) as small needles: mp 86–87°; ir 1360, 1110, 1080, 765, 750, and 730 cm^{-1}; nmr ($CDCl_3$) τ 2.6 (m), 4.95 (d), 5.3 (s), 6.2–6.8 (m), 6.45 (s), 6.70 (s), and 7.15 (t) in the respective area ratio of 8:1:1:3:3:3:1.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.13; H, 7.00.

Methanolysis of the Dibromide 4a. Formation of the *exo,exo*-Dimethoxytruxane 4b.—To a stirred solution of the dibromide **4a** (1.5 g, 3.87 mmol) in 60 ml of methanol maintained at the reflux temperature was added dropwise a solution of sodium carbonate (1.5 g) in 20 ml of water. The resulting suspension was stirred under reflux for 24 hr. After concentration of the reaction mixture to a volume of approximately 15 ml, water (50 ml) was added and the resulting aqueous suspension extracted with ether (75 ml). The ether extract was dried over sodium sulfate and evaporated affording the crude diether. Recrystallization from aqueous ethanol provided white needles (850 mg, 75%): mp 76–78°; ir 1350, 1085, 760, and 750 cm^{-1}; nmr ($CDCl_3$) τ 2.55 (m), 5.22 (s), 6.40 (d), 6.76 (s), and 7.38 (d) in the respective area ratio of 4:1:1:3:1.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.09; H, 6.99.

Reaction of the Dibromide 4a with Sodium Iodide. Preparation of the *exo,exo*-Diiodide 4c.—A mixture of **4a** (6.0 g, 15.4 mmol), sodium iodide (6.3 g, 42 mmol), and 100 ml of dry acetone (distilled from potassium carbonate) was heated under reflux with stirring for 1.5 hr. The reddish brown reaction mixture was cooled to room temperature, the precipitated sodium bromide was collected on a filter, and the filtrate was subjected to slow evaporation in an air stream. The solid material remaining was washed in turn with water (50 ml) and cold, absolute ethanol (100 ml). The light yellow solid decomposes[18] at 83–85°, but remains unmelted up to 300°. Two recrystallizations from cyclohexane afforded an analytical sample that decomposed at 83–85°: ir 760, 745, 615, and 495 cm^{-1}; nmr ($CDCl_3$) τ 2.7 (s), 4.25 (s), 6.35 (d), and 6.95 (d) in the respective area ratio of 4:1:1:1.

Anal. Calcd for $C_{18}H_{14}I_2$: C, 44.60; H, 2.89; I, 52.48. Found: C, 44.82; H, 3.01; I, 52.70.

Treatment of the *exo,exo*-Diodide 4c with Trimethylamine. Formation of the *exo,exo* Bisquaternary Iodide 4d.—A mixture of the diiodide **4c** (1.0 g, 2.1 mmol) and 90% aqueous trimethylamine was maintained at 75° for 6 hr in an aerosol compatibility tube[19] equipped with coupling and needle valve. The reaction vessel was then cooled to 0° and opened; the solvent was allowed to evaporate at room temperature. The white solid remaining (0.6 g, 50%) melted at 240–244° dec. Two recrystallizations from 95% ethanol produced an analytical sample (mp 243–245° dec): ir 3475, 1475, 960, 885, 848, 788, 778, and 763 cm^{-1}; nmr [D_2O at 70°, $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ as internal standard] τ 2.22 (m), 4.85 (s), 6.16 (broad), 7.69 (broad), and 7.01 (s) in the respective area ratio of 4:1:1:1:9.

Anal. Calcd for $C_{24}H_{32}N_2I_2$: C, 47.84; H, 5.31; N, 4.65. Found: C, 47.65; H, 5.49; N, 4.54.

The Hofmann base **4e** was generated by treatment of **4d** with silver oxide in the usual manner. The nmr spectrum of a 35% aqueous solution of **4e**, with $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ as internal standard, exhibited signals at τ 2.09 (m), 4.61 (s), 6.02 (d), 6.60 (d), and 6.88 (s) in the respective area ratio of 4:1:1:1:9.

Pyrolysis of **4e** under vacuum in a preheated glass column led only to intractable materials.

Hydrolysis of the Dibromide 4a with Aqueous Sodium Carbonate. Formation of the *exo,exo*-1,1′-Dihydroxytruxane 4g.—To a stirred solution of the dibromide (3.0 g, 7.7 mmol) in 100 ml of acetone maintained at the reflux temperature was added dropwise over a 20-min period a solution of sodium carbonate (3.5 g) in 50 ml of water. The resulting mixture was stirred at the reflux

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[14] F. Straus, R. Kuhnel, and R. Haensel, *Chem. Ber.*, **66**, 1847 (1933).

[15] All melting points are uncorrected. Infrared spectra were recorded in potassium bromide on either a Perkin-Elmer Model 337 or a Beckman IR-8 spectrophotometer. Ultraviolet spectra were obtained using a Perkin-Elmer model 202 ultraviolet-visible spectrophotometer. All nmr spectra were obtained on a Varian A-60 instrument at room temperature with tetramethylsilane as internal standard unless otherwise specified. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[16] In the description of nmr data the abbreviations s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet are employed.

[17] This same procedure also yields the two ethers from the diiodide **4c**.

[18] This iodide is extremely sensitive to light and turns brown on prolonged exposure; however, it may be stored indefinitely without decomposition in an opaque container at 0°.

[19] Fischer Porter Co., Lab Crest Scientific Division, Warminster, Penn.

temperature for 24 hr. The reaction mixture was then concentrated to a volume of approximately 15 ml (rotary evaporator), and the remaining suspension diluted with 50 ml of water. The water-insoluble material was collected on a filter, and the filtrate was extracted with two 100-ml portions of ether. The solid residue obtained on evaporation of the ether was combined with the solid material originally filtered, and the entire crude product was recrystallized from aqueous acetone to afford 1.55 g (77.5%) of pure truxanediol **4g**: mp 159–161°; ir 3225 (broad), 1030, 755, 748, and 740 cm^{-1}; nmr (acetone D$_6$) τ 2.55 (m), 4.98 (s), 5.90 (broad), 6.45 (d), and 7.55 (d) in the respective area ratio of 4:1:1:1:1.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.67; H, 6.26.

Oxidation of the *exo,exo*-Diol 4g with Chromic Anhydride. Formation of *syn,trans*-Truxone 7.—A solution of the truxanediol (175 mg, 0.66 mmol) in pyridine (3 ml) was added over a 15-min period to a stirred suspension of the pyridine–chromic anhydride complex generated by adding 1.0 g of chromic anhydride to 10 ml of pyridine at 15°. The temperature of the reaction mixture was maintained at 20° during the course of the addition. After being stirred at room temperature for 18 hr, the dark solution was poured into water (150 ml), and the aqueous suspension extracted with 100 ml of ether. The ether extract was washed successively with 10% hydrochloric acid (50 ml) and water (100 ml), and dried over sodium sulfate. Removal of the volatile solvent provided the crude truxone **7** (80 mg, 46%) as a white solid, mp 218–222°. Pure material was obtained by recrystallization from methanol (mp 220–222°, lit.[1a] mp 221–223°). The infrared spectrum was superimposable on that of authentic material,[1a] and a mixture melting point determination showed no depression.

Treatment of the *exo,exo*-Diol 4g with *p*-Toluenesulfonyl Chloride. Formation of the *endo,endo*-Dichlorotruxane 6c.—To a stirred solution of the diol (1.5 g, 5.6 mmol) in 15 ml of dry pyridine (commercial Karl Fischer reagent redistilled from potassium hydroxide) maintained at 0° was added a precooled solution of 2.5 g of acid-free *p*-toluenesulfonyl chloride in 15 ml of dry pyridine in 1–2-ml portions over a period of 30 min. The resulting reaction mixture was stirred for 4 hr at 0–5° and subsequently allowed to warm gradually to room temperature where stirring was continued for an additional 4 hr. The orange solution was then poured into a mixture of 20 ml of concentrated hydrochloric acid, 20 ml of water, and 50 g of crushed ice, and the precipitated white solid was extracted with 150 ml of ether. The ether extract was washed successively with a saturated sodium bicarbonate solution (two 75 ml-portions) and water (100 ml), and dried over sodium sulfate. Removal of the ether (rotary evaporator) yielded the crude dichloride as a crystalline solid, which was washed free of a small amount of adhering oil with cold methanol. The solid material (75 mg, 4.5%) on recrystallization from methylcyclohexane melted at 219–221°: ir 1485, 1235, 845, 752, 746, and 660 cm^{-1}; nmr (CDCl$_3$) τ 2.62 (m), 4.38 (d), and 6.38 (m) in the respective area ratio of 4:1:2.

Anal. Calcd for $C_{18}H_{14}Cl_2$: C, 71.42; H, 4.65. Found: C, 71.60; H, 4.91.

Reaction of the Diol 4g with Thionyl Chloride. Formation of the *exo,exo*-Dichlorotruxane 4h.—Freshly distilled thionyl chloride (2 ml, 27.7 mmol) was added in small portions over a period of 30 min to a stirred solution of the diol (1.5 g, 5.7 mmol) in dry pyridine (Karl Fischer Reagent) maintained at 0–5°. The reaction mixture was allowed to warm gradually to room temperature, and stirring was continued for 6 hr. The dark reddish brown solution was then poured with stirring into 300 ml of ice water and the precipitated yellow solid extracted with 150 ml of ether. The ether extracts were washed in turn with 10% hydrochloric acid (two 75-ml portions) and water (100 ml) and subsequently dried over sodium sulfate. Removal of the ether (rotary evaporator) yielded the crude dichloride as a white solid. After being washed free of adhering oils with cold 95% ethanol the crude material (450 mg, 26.5%) was recrystallized from methylcyclohexane affording white crystals: mp 183–185°; ir 1480, 1240, 845, 769, 740, 700, 663, and 510 cm^{-1}; nmr (CDCl$_3$) τ 2.62 (s), 4.62 (s), 6.28 (d) and 7.10 (d), in the respective area ratio of 4:1:1:1.

Anal. Calcd for $C_{18}H_{14}Cl_2$: C, 71.42; H, 4.65. Found: C, 71.54; H, 4.70.

Formation of 4c from 4h upon Treatment with Sodium Iodide.—A mixture of the dichloride (270 mg, 0.9 mmol) and sodium iodide (400 mg, 2.6 mmol) in 20 ml of dry acetone was heated under reflux for 18 hr. The precipitated sodium chloride was collected on a filter, and the filtrate evaporated in an air stream. The residue was washed with cold, absolute alcohol and recrystallized from cyclohexane yielding 200 mg (46%) of *exo,exo*-1,1′-diiodo-*syn,trans*-truxane (**4c**) (dec pt 80–85°). The infrared spectrum was identical with that of authentic **4c**.

Preparation of 4c from 6c with Sodium Iodide in Acetone.—By a procedure analogous to that described in the preceding experiment, the *endo,endo*-dichloride **6c** (60 mg, 0.2 mmol) on stirring under reflux 8 hr with sodium iodide (150 mg, 1.0 mmol) in 15 ml of boiling acetone afforded 55 mg (57%) of the *exo,exo*-diiodide **4c**.

Reaction of the Dibromide 4c with Excess Dimethylamine. Formation of the *exo,endo*-Bisdimethylaminotruxane 5c.—A mixture of the dibromotruxane **4a** (6.0 g, 0.015 mol) and anhydrous dimethylamine (50 ml) was heated at 75° for 24 hr. An aerosol compatibility tube[19] equipped with coupling and needle valve served as the reaction vessel. The reaction mixture was cooled to 0°, the aerosol tube opened, and the excess dimethylamine was allowed to evaporate in an air stream. The residual dark brown viscous oil was dissolved in 20% aqueous hydrochloric acid (75 ml). The resulting acid solution was filtered and subsequently extracted with benzene (60 ml). The aqueous acid solution was then made basic with 10% potassium hydroxide solution. After being warmed to 50° to remove any residual dimethylamine, the oily, aqueous solution was extracted with ether (200 ml). The ether solution was dried over sodium sulfate, the volatile solvents were removed under reduced pressure, and 4.1 g (83%) of the crude amine **5c** remained as a dark brown oil. Further purification was achieved by molecular distillation (95–100°, 0.2 mm): ir (neat, salt plates) 1480, 1455, 1025, and 740 cm^{-1}; nmr (CDCl$_3$) τ 2.7 (m), 5.6–6.0 (m), 6.3–6.9 (m), 7.45 (unsymmetrical doublet), and 8.0 (s) in the respective area ratio of 8:2:3:7:6. A picrate generated in the normal manner melted at 209–210° dec after recrystallization from methanol.

Anal. Calcd for $C_{34}H_{32}N_8O_{14}$ (dipicrate): C, 52.57; H, 4.12; N, 14.43. Found: C, 52.30; H, 4.21; N, 14.31.

Oxidation of 5c with 30% Hydrogen Peroxide. Formation of the Bisamine Oxide 5f.—A solution of 30% hydrogen peroxide (65 ml), which had been precooled to −15°, was added in one portion to a stirred solution of the crude amine **5c** (3.5 g) in 70 ml of 95% ethanol maintained at 0–5°. The resulting mixture was stirred at 5° for 30 min and allowed to warm to room temperature where stirring was continued for 90 hr. At this point the reaction mixture was neutral to phenolphthalein, indicating that oxidation was complete. The excess peroxide was decomposed by adding 10–20 mg of platinum black catalyst to the reaction mixture with subsequent stirring for 16 hr. The catalyst was removed by filtration and the light yellow filtrate was evaporated to dryness (rotary evaporator), affording the amine oxide as a yellow-orange glass (3.62 g, 94%). This material is extremely hygroscopic and turns to liquid on exposure to the atmosphere. A picrate generated in the normal manner melted at 173–173.5°.

Anal. Calcd for $C_{34}H_{32}N_8O_{16}$ (dipicrate): C, 50.49; H, 3.96; N, 13.86. Found: C, 50.64; H, 4.20; N, 13.78.

Pyrolysis of **5f** under reduced pressure in a preheated glass column led only to intractable materials.

Quaternization of the Amine 5c. Formation of the *exo,endo* Bisquaternary Iodide 5d.—A solution of 8.0 g (0.025 mol) of the crude amine **5c** and excess methyl iodide (10 ml) in absolute ethanol (100 ml) was heated under gentle reflux for 3 hr. The reaction mixture was then cooled to room temperature, and the crude quaternary salt which deposited was collected by filtration. Subsequent recrystallization from 95% ethanol (Norit) afforded 11.1 g (74%) of white crystalline material: mp 226–228°; ir 3450 (broad), 1475, 960, 880, 853, 785, 760, 750, and 722 cm^{-1}; nmr [D$_2$O at 70° $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ as an internal standard] τ 2.3 (m), 4.62 (d), 4.84 (s), 6.49 (s), and 7.00 (s) in the respective area ratio of 8:1:1:9:9.[20]

Anal. Calcd for $C_{24}H_{32}N_2I_2$: C, 47.84; H, 5.31; N, 4.65. Found: C, 47.64; H, 5.26; N, 4.53.

Isomerization of the *exo,endo* Bisquaternary Iodide 5d to the *exo,exo* Configuration 4d.—The *exo,endo* quaternary salt **5d** (15.5 g, 0.026 mol) was suspended in a solution of potassium hydroxide (12.5 g) in water (250 ml) and the resulting mixture heated under reflux for 24 hr. The gray solution was decolorized (Norit) and taken to dryness on a rotary evaporator. The

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(20) The cyclobutane protons were not visible in the spectrum.

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.

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

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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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