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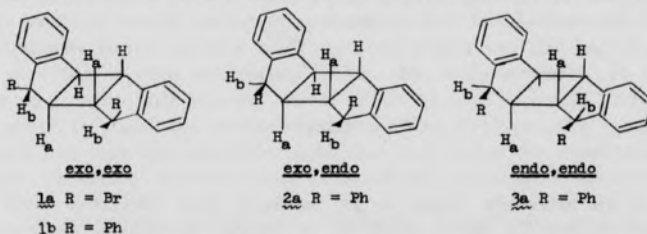
# ON THE PREPARATION AND PROPERTIES OF SOME 1,1'-DIPHENYL-*syn,trans*-TRUXANE DERIVATIVES

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## INTRODUCTION

In a previous report (1) we described the unique stereochemistry of several 1,1'-disubstituted *syn,trans*-truxanes as well as the utility of nmr spectroscopy in distinguishing the *exo,exo*, *exo,endo*, and *endo,endo* stereochemical modifications of these derivatives. To briefly summarize these nmr spectral considerations, an *exo,exo*-

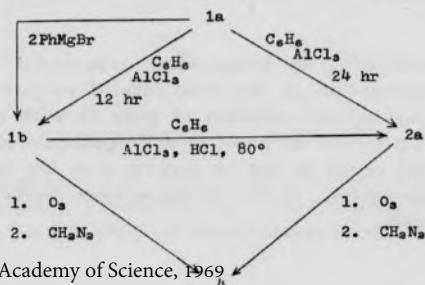


1,1'-*syn,trans*-truxane exhibits the two benzylic ( $H_b$ ) protons as a sharp singlet, while the non-equivalent  $H_b$  protons in the *exo,endo* derivative appear as two separate signals, a 1-H singlet and a 1-H doublet ( $J = 8\text{ Hz}$ ), and the spectrum of *endo,endo* disubstituted compounds displays the equivalent  $H_b$  protons as a 2-H doublet ( $J = 8\text{ Hz}$ ).

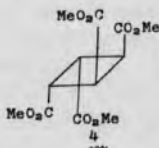
## RESULTS AND DISCUSSION

During the course of our work it became necessary to prepare a 1,1'-diphenyl-*syn,trans*-truxane as a synthetic intermediate. We now wish to describe some of the chemistry relative to these preparations, which is summarized in Scheme I.

Scheme I



The *exo-exo* dibromide 1a (1) coupled smoothly with two equivalents of phenylmagnesium bromide in ether-benzene to yield the *exo,exo*-diphenyltruxane 1b (mp 205-206°) in 50% yield. The appearance of the *exo,exo* product is not surprising, for it is almost certain that reactions of this type proceed homolytically, (2) and the coupling of a truxane and phenyl radical would be expected to occur preferably from the less hindered *exo* direction. The structure of 1b was assigned on the basis of its elemental analysis, infrared spectrum (monosubstituted phenyl, 698  $\text{cm}^{-1}$ ), and nmr spectrum (two-proton  $\text{H}_b$  singlet at  $\tau$  5.68). Furthermore, degradative ozonolysis of 1b in acetic acid at room temperature followed by esterification of the crude acid product afforded *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane 4 (3), thus demonstrating the preservation of both the cyclobutane ring and the *trans* nature of the molecule.

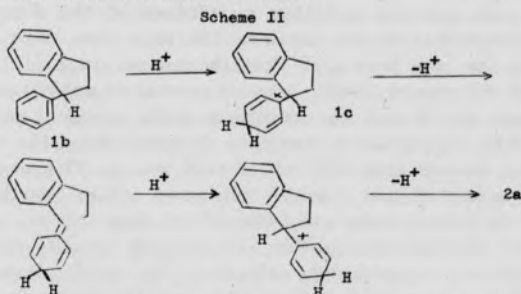


In an alternate route to 1b, benzene was alkylated with the dibromotruaxane 1a. Slow addition of excess aluminum chloride to a well-stirred benzene solution of 1a affords exclusively 1b in 20% yield when the reaction time is limited to 12 hr at room temperature followed by 1 hr at 50°. Allowing the reaction to proceed for longer periods together with raising the reaction temperature results in gradual disappearance of 1b with the formation of a new hydrocarbon (mp 147-149°). A reaction time of 24 hr culminating by heating 2 hr at gentle reflux affords exclusively the latter compound in 30% yield. The structure of this compound was established as *exo,endo*-1,1'-diphenyl-*syn,trans*-truxane (2a) on the basis of its elemental analysis, infrared spectrum (monosubstituted-phenyl, 695  $\text{cm}^{-1}$ ) and nmr spectrum (one-proton doublet at  $\tau$  4.67 and one-proton singlet at  $\tau$  6.28). Degradative ozonolysis followed by esterification of the crude product yielded *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane (4), thus demonstrating that the cyclobutane ring had survived the rather drastic treatment with aluminum chloride.

It was established by independent experiment that 2a may be formed by isomerization of the first-formed *exo,exo* isomer. Treatment of a boiling benzene solution of pure 1b with excess aluminum chloride in the presence of gaseous hydrogen chloride affords 2a in 37% yield. This result is not in accord with the expected thermodynamics of the system, in which the *exo,exo* isomer is assumed to be the most stable.

*Derivatives of 1,1'-Diphenyl-syn,trans-Truxane*

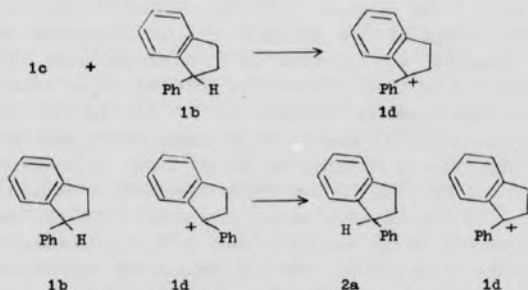
The sequence shown in Scheme II is offered as a possible account for the observed isomerization.



Initial protonation of one of the 1,1' phenyl groups in either the *o* or *p* position would generate carbonium ion 1c. Subsequent loss of the truxane benzyl proton and reprotonation from the less hindered *exo* direction would ultimately yield the *endo* product. It is not clear as to why this process would occur at only one site and not at the other to yield the *endo,endo* isomer 3a. Perhaps the latter was formed but was too unstable to be isolated under the conditions employed, resulting in conversion to observed intractable materials.

An alternate explanation (Scheme III) might involve intermolecular hydride transfer to an initially formed carbonium ion (possibly 1c). A resulting chain process would then involve subsequent generation of the benzylic carbonium ion 1d which would in turn abstract hydride from another truxane molecule with the phenyl group of 1d tucked in the *endo* position. An *endo,endo* isomer formed by this process could have escaped detection.

Scheme III



### EXPERIMENTAL SECTION

*Coupling of exo,exo-1,1'-Dibromo-syn,trans-truxane with Phenylmagnesium Bromide; Formation of exo,exo-1,1'-Diphenyl-syn,trans-truxane (1b)* — To a solution of phenylmagnesium bromide generated

from magnesium turnings (0.73 g; 0.03 gatom) and freshly distilled bromobenzene (2.1 ml; 0.02 mole) in dry ether (10 ml) was added dropwise with manual agitation a solution of the dibromotruxane (3.0 g; 7.7 mmoles) in dry benzene (30 ml). The addition required 20 min and the rate was such that the temperature of the reaction mixture did not exceed 35-40°. A small crystal of anhydrous cobaltous chloride was added and the resulting dark solution gently heated (65°) for 5 hr. The solution was then decanted from the excess magnesium and poured into 300 ml of cold water. The organic phase was then separated and washed with two 100-ml portions of 5% potassium hydroxide solution followed by two 100-ml portions of water. After drying over calcium chloride the volatile solvents were removed (rotary evaporator) affording the crude diphenyltruxane 1b as a yellow-white solid (1.5 g; 51% mp 195-205°). In some cases the crude product was obtained as a viscous oil which could be crystallized by digestion with hot 95% ethanol. Three recrystallizations from methylcyclohexane afforded pure material (mp 205-206°). The infrared spectrum exhibits strong absorption at 760, 739, and 698  $\text{cm}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) is characterized by absorption at  $\tau$  2.2-3.1 (18 H-multiplet), 5.68 (2 H-doubled), 7.11 (2 H-doublet), and 6.06 (2 H-doublet).

*Anal.* Calcd for  $\text{C}_{30}\text{H}_{24}$ : C, 93.75; H, 6.25. Found: C, 93.57; H, 6.45.

*The Reaction of exo,exo-1,1'-Dibromo-syn,trans-truxane with Benzene in the Presence of Aluminum Chloride; Formation of exo, endo- and exo,exo-1,1'-Diphenyl-syn,trans-truxane (2a) and (1b) —*

A. *exo,endo-1,1'-Diphenyl-syn,trans-truxane (2a)* — Finely pulverized anhydrous aluminum chloride (2.0 g; 0.015 mole) was added in small portions over a 1 hr period to a stirred solution of the dibromide (3.0 g; 7.7 mmoles) in 50 ml dry benzene (distilled from sodium metal). The original colorless solution became reddish-brown during the course of the addition of the aluminum chloride, and hydrogen bromide was evolved at a moderate rate. The resulting dark solution was then allowed to stir at room temperature for 23 hr and subsequently warmed to 70° for 2.5 hr. This reaction mixture was allowed to cool to room temperature and finally poured with stirring onto a mixture of 25 ml 10% hydrochloric acid and 100 g crushed ice. The yellow-green fluorescent organic phase was separated, and the aqueous phase extracted with 150 ml ether. The organic layers were combined, washed with 5% potassium hydroxide solution followed by water (100 ml), and dried over calcium chloride. Removal of the volatile solvents (rotary evaporator) afforded 2.8 g of a heavy oil which was dissolved in the minimum amount of benzene. The concentrated benzene solution was then chromatographed in two equal portions on two separate 2 x 30 cm chromatographic columns packed with acid-washed aluminum oxide. Each column was

*Derivatives of 1,1'-Diphenyl-syn,trans-Truxane*

eluted as follows: 1:4 benzene-cyclohexane (200 ml), 1:2 benzene-cyclohexane (100 ml), 1:1 benzene-cyclohexane (100 ml), and pure benzene (100 ml). Evaporation of the first eluted fractions (150 ml total) in an air stream afforded a clear viscous oil which solidified on drying overnight in a vacuum desiccator. Later eluates provided only polymeric materials which were not characterized further. The combined crude material from both columns (900 mg; 30.5%) was purified by recrystallization from 95% ethanol yielding white crystals of the *exo,endo* product (mp 147-149°). The infrared spectrum exhibits strong absorption at 760, 747, and 695  $\text{cm}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) shows absorption at  $\tau$  2.35-3.15 (multiplet), 5.67 (doublet), 6.32 (unsymmetrical doublet), 6.55 (singlet) and 7.31 (quartet) in the respective area ratio of 6:33:1:33:33.

*Anal.* Calcd for  $\text{C}_{30}\text{H}_{24}$ : C, 93.75; H, 6.25. Found: C, 93.69; H, 6.34.

B. *exo,exo*-1,1'-Diphenyl-*syn,trans*-truxane (1b) — When the above reaction was repeated with stirring at room temperature for 12 hr followed by 1 hr at 50°, there was obtained on evaporation of the first total 100 ml of eluted fractions from each chromatographic column a total of 580 mg (20%) of the *exo,exo* isomer (mp 198-202°). The infrared spectrum was superimposable on that of the hydrocarbon 1b derived from the Grignard coupling reaction, and a mixture melting point determination showed no depression.

*Ozonolysis of exo,exo*-1,1'-Diphenyl-*syn,trans*-truxane (1b) — A well-stirred suspension of the diphenyltruxane (350 mg; 0.91 mmole) in 90% aqueous acetic acid (100 ml) was treated with a stream of ozone at a flow rate of approximately 3.66 g of ozone per hour for 21 hr at room temperature. The resulting homogeneous reaction mixture was then allowed to stand in the presence of 30% hydrogen peroxide (20 ml) for 48 hr. The excess peroxide was subsequently destroyed by stirring the resulting reaction mixture with 10-20 mg of 10% palladium-on-charcoal catalyst at room temperature for 8 hr. The catalyst was removed by filtration and the filtrate evaporated on a rotary evaporator. The residual viscous oil was heated to 125° in an oil bath for 10 min prior to dissolution in anhydrous ether (20 ml). Excess diazomethane (approximately 2.0 g) in ether (70 ml) was then added and the reaction mixture was stirred at room temperature for 12 hr. After evaporation of the volatile solvents, a light yellow oil (25 mg) remained which crystallized on trituration with cold 95% ethanol. Recrystallization from methanol provided pure *cis,trans,cis*-1,2,3,4-tetracarboxymethoxycyclobutane (4) (15 mg; 6%; mp 139-144°; lit (3) mp 144-145°). The infrared spectrum of this material was identical to that of an authentic sample, and a mixture melting point determination showed no depression.

*Ozonolysis of exo,endo*-1,1'-Diphenyl-*syn,trans*-truxane (2a) —

When subjected to ozonolysis under conditions identical to those previously described for the *exo,exo* isomer in the preceding experiment, the *exo,endo* diphenyl derivative 2a (700 mg; 1.85 mmoles) yielded, after esterification of the crude ozonolysis product, a light yellow oil which partially crystallized on standing several days at room temperature. Further crystallization was achieved by trituration with cold 95% ethanol, and subsequent recrystallization from methanol afforded the *cis,trans,cis*-1,2,3,4-tetracarboxymethoxycyclobutane (4) (22 mg; 4.3%; mp 140-144°).

*Isomerization of exo-exo-1,1'-Diphenyl-syn,trans-truxane (1b) to exo,endo-1,1'-Diphenyl-syn,trans-truxane (2a)* — Finely pulverized anhydrous aluminum chloride (200 mg; 1.5 mmoles) was added in small portions over a 30 min period to a stirred solution of the hydrocarbon 1b (250 mg; 0.65 mmole) in 15 ml dry benzene. A slow stream of hydrogen chloride gas was bubbled through the solution during the course of the addition. The dark solution was stirred under reflux for 1.5 hr as treatment with hydrogen chloride gas was continued. The gas inlet tube was then removed and reflux was continued for an additional 40 min. The reaction mixture was poured with stirring onto a mixture of ice and hydrochloric acid, the organic phase was separated, and washed in turn with a saturated sodium bicarbonate solution (two 25 ml-portions) and water (50 ml) prior to drying over sodium sulfate. Removal of the volatile solvent afforded a yellow-brown oil which was dissolved in the minimum amount of benzene and applied to a 1 x 20 cm column packed with acid-washed aluminum oxide. Elution was performed with 1:4 benzene-cyclohexane (50 ml), 1:1 benzene-cyclohexane, and pure benzene (50 ml). Evaporation of the first 100 ml of eluted solvent afforded a clear viscous oil which solidified on drying overnight (vacuum desiccator). Recrystallization from 95% ethanol yielded 92 mg (37%) of the *exo,endo* isomer 2a (mp 142-147°).

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