Some Novel Reactions of 1, 1-Diphenyl-3, 3-dibromoprop-1-ene

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In previous papers,[1] the synthesis of 1, 1-diphenyl-3, 3-dibromoprop-1-ene (I) from 1, 1-diphenylprop-2-yn-1-ol and phosphorus tribromide in acetic acid has been reported.

During the course of the studies of the reactions of the *gem*-dibromide (I), some novel reactions were found. The present paper deals with these reactions and will discuss the reaction mechanism.

The treatment of the *gem*-dibromide (I) with sodium ethoxide in ethanol resulted in *trans*-1, 1-diphenyl-1-ethoxy-3-bromoprop-2-ene (IIIa) in a 33% yield. The structure of the compound IIIa was determined by infrared and ultraviolet spectral determination. The ultraviolet spectrum of IIIa is almost identical with that of benzene, indicating the absence of conjugation between benzene nuclei and the double bond. The infrared spectrum of IIIa shows the presence of a non-conjugated trans double bond, an ethoxy group and ether linkage (Fig. 2).

As is shown in the Scheme, this reaction may be attributable to the S_N2' mechanism. At the transition state, the less hindered intermediate (II) most reasonably produces the trans-compound (IIIa).

Although the crystals of IIIa were fairly stable for several days in the absence of air, IIIa was converted into an oily material in about one hour in the presence of air. Some parts of the oil gradually solidified, and the solid was identified as the *gem*-dibromide (I) by mixed melting point determination with an authentic specimen. The unsolidified oil was determined to be 3, 3-diphenylprop-3-en-1-al (IV) by infrared spectroscopy. It may be most reasonable to consider the mechanism of this reaction to be the disproportionation of IIIa. The aldehyde IV was also obtained by the hydrolysis of I.[1]

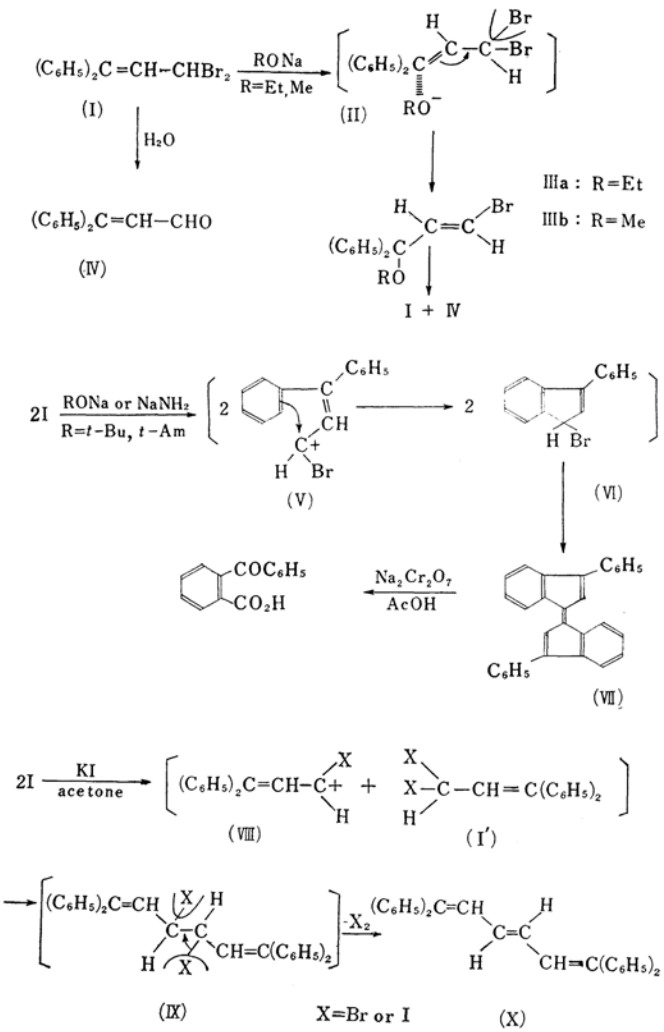
A lower homologue of IIIa, IIIb, obtained by the similar treatment of I with sodium methoxide in methanol, behaved in the same way as IIIa. The less hindered methoxy compound IIIb was less stable than IIIa.

In contrast with the reactions with sodium methoxide or sodium ethoxide, the reaction of I with sodium amide in liquid ammonia resulted in the formation of 3, 3'-diphenyl-bis-(1-indenylidene) (VII) in a 50% yield. The compound VII was also obtained, by the treatment of I with sodium *t*-butoxide or sodium *t*-amyloxide, in a 40% yield in both cases. The electronic spectrum (Fig. 1) of the bis(1-indenylidene) (VII) is typical of fulvene derivatives and is similar to that of 3, 3'-dibromo-bis(1-indenylidene).[2] The oxidation of VII with potassium bichromate in acetic acid gave *o*-benzoylbenzoic acid. Satisfactory analysis and consistent infrared (Fig. 2) and NMR spectra were also obtained for the compound VII.

As is shown in the Scheme, the formation of VII can be interpreted as the result of the ionic dimerization of the cyclic compound VI produced by the intramolecular cyclization of

1) H. Tani and F. Toda, *Chem. & Ind.*, **1963**, 1083; This Bullein, **37**, 470 (1964).

2) F. Straus, R. Kuhnel and R. Haensel, *Ber. dtsch. Chem. Ges.*, **66**, 1847 (1933).



the cationic intermediate V initially formed from I.

The heating of the *gem*-dibromide (I) with potassium iodide in acetone for two hours led to *trans*-1, 1, 6, 6-tetraphenylhexa-1, 3, 5-triene (X) in a 74% yield. The ultraviolet (Fig. 1) and infrared (Fig. 2) spectra of X are identical with that recorded by Kuhn and Fischer[3] for X prepared by the partial hydrogenation of 1, 1, 6, 6-tetraphenylhexapentaene. The triene melted at 204°C with or without the addition of an authentic sample, kindly supplied by Professor Richard Kuhn.

On the basis of the experimental finding that the *trans*-triene was obtained exclusively, the following mechanism may be put forward. As is shown in the Scheme, an S_N2 attack of a cationic intermediate VIII on a *gem*-dihalide (I') leads to a dihalogeno compound IX, in which two halogens are located in meso-form fashion, and the intermediate IX finally gives *trans*-triene (X) by the trans-elimination of halogens.

During the reaction of I with potassium iodide, an ionic salt containing an iodide anion formulated as $[C_{30}H_{24}\cdot H_2O]^+I^-$ was isolated as purple black needles; m. p. 155°C. The salt was easily converted into the triene (X) by treatment with ethanol. The structure of this salt is being investigated.

Experimental*

1, 1-Diphenyl-1-ethoxy-3-bromoprop-2-ene (IIIa). —I (1.0 g.) was dissolved in 30 ml. of a 1% solution of sodium ethoxide in ethanol. The mixture was refluxed for 30 min., thus causing sodium bromide

3) R. Kuhn and H. Fischer, *Chem. Ber.*, **93**, 2285 (1960).

* All melting points are uncorrected. Molecular weights were determined in a benzene solution using a Mechrolab Vapor Pressure Osmometer, model 301 A.

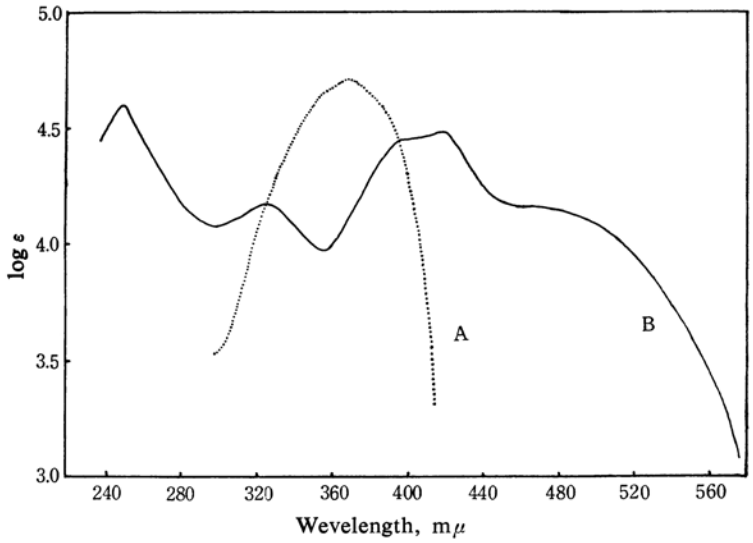


Fig. 1. Electronic absorption spectra.

A *trans*-1,1,6,6-Tetraphenylhexa-1,3,5-triene (X)
B 3,3'-Diphenyl-bis(1-indenylidene) (VII), in dioxane

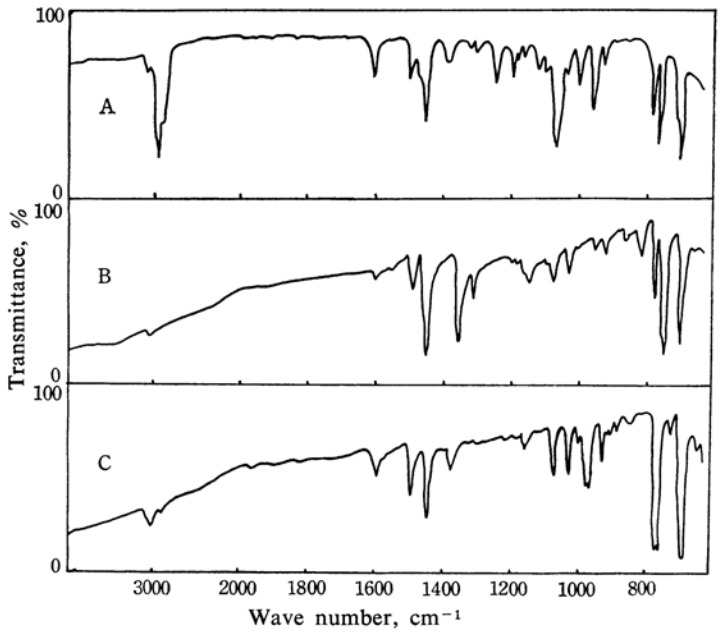


Fig. 2. Infrared absorption spectra.

A *trans*-1,1-Diphenyl-1-ethoxy-3-bromoprop-2-ene (IIIa)
B 3,3'-Diphenyl-bis(1-indenylidene) (VII)
C. *trans*-1,1,6,6-Tetraphenylhexa-1,3,5-triene (X)
A: Nujol mull; B, C: KBr disk

to be deposited. The reaction mixture was poured into water, and the oily material was extracted with ether. The ether layer was washed with water and dried over sodium sulfate. The oily substance obtained by the evaporation of the ether gradually solidified. Recrystallization of the solid from aqueous ethanol yielded IIIa as colorless needles (0.3 g. (33%), m. p. 60°C). IR: KBr disk, 2980 (ethoxy), 1620 (double bond), 1060 (ether) and 952 cm^{-1} (trans). UV: $\lambda_{max}^{Dioxane}$, 253 (470) and 259 mμ (ε, 530).

Found: C, 64.28; H, 5.30; Br, 25.96. Calcd. for $C_{17}H_{17}BrO$: C, 64.35; H, 5.36; Br, 25.24%.

When treated with 2,4-dinitrophenylhydrazine,

IIIa gave directly 2,4-dinitrophenylhydrazone of 3,3-diphenylprop-3-en-1-al quantitatively (m. p. 200 °C (lit.[4] 196°C)).

On being kept standing for an hour, IIIa was degraded into an oily material, some of which was converted into rhombic plates. The crystals melted at 75~78°C and were identified as the *gem*-dibromide (I) by mixed melting point determination.

1,1-Diphenyl-1-methoxy-3-bromoprop-2-ene (IIIb).—By the same treatment employed for the preparation of IIIa, IIIb was obtained from I and sodium methoxide as colorless needles (30%); m. p. 58°C. IR: KBr disk, 1615 (double bond), 1075 (ether) and 970 cm^{-1} (trans).

Found: C, 63.21; H, 5.01. Calcd. for $C_{16}H_{15}BrO$: C, 63.70; H, 5.01%.

IIIb behaved similarly to IIIa but was less stable.

3,3'-Diphenyl-bis(1-indenylidene) (VII), Sodium Amide Method.—To a stirred suspension of sodium amide (3.9 g., 0.1 mol.) in liquid ammonia (100 ml.), a solution of I (8.5 g., 0.024 mol.) in tetrahydrofuran (20 ml.) was added drop by drop over a period of 10 min. After the stirring had then been continued for a further hour, the reaction mixture was decomposed with ammonium chloride (7.0 g.). The solid which remained after the evaporation of the ammonia was extracted with benzene (200 ml.). The benzene solution was washed with water and dried over sodium sulfate. The recrystallization from ethyl acetate of the crude crystals obtained by the evaporation of the solvent from the benzene solution afforded VII as purple red needles (2.3 g. (50%); m. p. 208°C). UV: $\lambda_{max}^{Dioxane}$, 249 (39400), 325 (14800), 400 (27800), 418 (30700) and 500 mμ (shoulder) (ε, 12000).

Found: C, 94.31; H, 5.35. Mol. wt., 380. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30%. Mol. wt., 380.

3,3'-Diphenyl-bis(1-indenylidene) (VII), Sodium *t*-Butoxide Method.—The *gem*-dibromide (I) (0.5 g.) was added to 30 ml. of a 5% solution of sodium *t*-butoxide in *t*-butyl alcohol. The mixture was heated at 90°C. for 10 min. After the reaction mixture had been decomposed by the addition of water, the crude solid which remained was collected by filtration and washed with water and methanol. Two successive recrystallizations of this dried solid from ethyl acetate yielded VII as purple red needles (0.1 g. (40%); m. p. 208°C); these did not show any depression of melting point when mixed with the authentic sample obtained above.

The same treatment of I with sodium *t*-amyloxide in *t*-amyl alcohol also gave VII in a 40% yield.

The Potassium Bichromate Oxidation of VII.—A mixture of VII (0.2 g.), potassium bichromate (1.0 g.) and acetic acid (20 ml.) was heated at 90°C for 30 min. and then refluxed for a further hour. After cooling, the reaction mixture was poured into dilute hydrochloric acid. The crude crystals which separated were collected by filtration and dissolved in ether. The ether solution was extracted with aqueous sodium bicarbonate. Crystals obtained from the acidified alkaline layer were recrystallized from petroleum ether (b. p. 60~70°C) to give *o*-benzoylbenzoic acid as colorless needles (0.1 g. (43%); m. p. 127°C (lit.[5] 127°C)). The substance showed no depression of its melting point on admixture with an authentic specimen.

***trans*-1,1,6,6-Tetraphenylhexa-1,3,5-triene (XI).**—A mixture of I (0.50 g.), finely powdered potassium iodide (0.75 g.) and acetone (20 ml.) was heated under reflux for 2 hr. After the acetone had been removed, the residue was decomposed with water and extracted with ether. The ether layer was washed with aqueous sodium thiosulfate and water, and dried over sodium sulfate. The crude crystals obtained by the evaporation of the solvent were suspended in ethanol and heated for 10 min. The yellow solid collected by filtration was recrystallized from ethyl acetate to yield XI as bright yellow needles (0.2 g. (74%); m. p. 204°C). A mixed melting point determination with an authentic sample, kindly supplied by Professor Richard Kuhn, showed no depression. IR: KBr disk, 977, 968 cm^{-1} (trans) UV: $\lambda_{max}^{Dioxane}$, 355 (shoulder) (42100), 370 (51200) and 390 mμ (shoulder) (ε, 37100).

Found: C, 93.34; H, 6.35. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

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