SYNTHESIS OF DIENES IN WHICH THE DOUBLE BONDS ARE IN FIXED POSITIONS

COMMUNICATION 3. CISOID DIENES*

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In continuation of our investigations on the synthesis of dienes in which the double bonds are in fixed positions, we attempted to prepare some dienes of the dimethylenecycloalkane type. Such dienes were recently prepared by various workers [1-4] and found to be extremely reactive and to undergo the diene condensation with ease. It was considered to be particularly interesting to develop methods of synthesizing dimethylenecycloalkanes having substituents at the ends of the diene bonds [[1] and [II]].



It is known that aliphatic dienes of this type (2, 5-dimethyl-2, 4-hexadiene, 1,1,4, 4-tetraphenyl-1,3-butadiene) either do not undergo diene condensation [5], or undergo preliminary isomerization with displacement of the double bonds [6]. It was therefore of interest to study the reactivities of dienes of types (I) and (II), which may have a greater tendency to undergo diene condensation than their aliphatic analogs because their double bonds are fixed in the cis position. We succeeded in improving the method of synthesizing 3-methyl-1,2-butadiene [7, 8], and we studied its thermal dimerization. The resulting dimers (III) and (IV) had similar constants to those of the substances isolated by Lebedev [9], and their structures were proved by permanganate oxidation. Neither of these dimers (III) and (IV) gave a crystalline product with maleic anhydride below 100°, and at higher temperatures, reaction was accompanied by opening of the cyclobutane ring [3].

Similar cisoid dienes having terminal phenyl groups (V) and (VI) were prepared recently [10, 11], and they also were found to be unable to undergo diene condensations with maleic anhydride and benzoquinone [12]. Another object of our investigation was the synthesis of 1,2-diisopropylidenecyclohexane (VII), for the preparation of which we followed the following scheme:

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It was found that, unlike the corresponding reaction with a cis-cyclobutanedicarboxylic ester [10], reaction of methylmagnesium iodide with diethyl cis-1,2-cyclohexanedicarboxylate [13] gives not the diol, but the tetrahydrofuran (VIII) (see [14]). In this reaction a small amount of the lactone (IX) was also isolated. With the object of synthesizing 1,2-diisopropylidenecyclohexane (VII), we studied the catalytic dehydration of the cistetrahydrofuran (VIII) over various catalysts (alumina, aluminum phosphate, magnesium sulfate, etc.). It is known from the literature [15-17] that the dehydration of tetrahydrofurans does not go readily, though the preparation of dienes in this way has been described in patents. After several unsuccessful attempts, we succeeded in developing a relatively convenient method for the dehydration of the cis-tetrahydrofuran (VIII): treatment over alumina in a stream of hydrogen sulfide [18]. The yield of diene fraction was then 50%. On ozonization, the diene (VII) gave acetone and adipic acid. It was found that, like 1,2-diisopropylidenecyclobutane (III), the diene (VII) does not undergo diene condensation with maleic anhydride and with benzoquinone at temperatures up to 100-120°.

We studied also the cleavage of the cis-tetrahydrofuran (VIII) with acetic anhydride in presence of zinc chloride [19]. It was found that the diacetic ester (X) then formed was fairly readily converted into 1,2-diiso-propenylcyclohexane (XI) by passage through a glass tube heated to 450°; in the ozonization of (XI) formalde-hyde and adipic acid were isolated.

When a Grignard reagent was caused to react with a trans-1,2-cyclohexanedicarboxylic ester, instead of with the corresponding cis-ester, the expected diol was obtained; reaction with methylmagnesium bromide gave the trans-diol, which we did not succeed in obtaining in a crystalline state; in attempts to purify it by distillation it was readily converted into the trans-tetrahydrofuran (XII) [20, 21], and this transformation went most readily in presence of potassium hydrogen sulfate or p-toluenesulfonic acid.

Reaction of phenylmagnesium bromide with cis-1,2-cyclohexanedicarboxylic ester gave a mixture of products, from which only the lactone (XIIIa) was isolated (yield 25%) [12].

Reaction of phenylmagnesium bromide with trans-1,2-cyclohexanedicarboxylic ester led to the trans-diol (XIII), which was previously prepared by Wittig by reaction of the trans-ester with phenyllithium [22]. The resulting diol (XIII) is always contaminated with a small amount of dehydration products, which are very difficult to remove: In our experiments the crude diol was taken for dehydration. Depending on the duration of the reaction, the dehydration of the trans-diol (XIII) with a mixture of acetic and hydrochloric acids leads either to the diene (XIV) or to the unsaturated alcohol (XV) which is readily converted into the diene (XIV). The structures of the products isolated were proved by ozonization. Like its cyclobutane analog [12], the diene (XV) did not undergo diene condensation.



We studied also the Reformatsky reaction with unsaturated cyclic ketones, and after several unsuccessful attempts, we succeeded in bringing about the condensations of 3,5-dimethyl-2-cyclopenten-1-one(XVI) with ethyl bromoacetate and with methyl 2-bromo-2-methylpropionate in presence of mercuric chloride. Under these conditions, the dienic esters (XVII) and (XVIII) were formed immediately:



The resulting dienes gave liquid products with maleic anhydride when heated in benzene to 90°, and hydrolysis of these gave high-melting acids which did not melt sharply but were characterized as their crystalline trimethyl esters. The structures of the dienic esters (XVII) and (XVIII) were proved by ozonization, which gave 2,4-pentanedione and the corresponding malonic acids. Reaction of ethyl bromoacetate with 3,6-dimethyl-2--cyclohexen-1-one[•] gave a mixture of the normal reaction product and the substance formed by the dehydration of this product. Vacuum distillation of the mixture over potassium hydrogen sulfate gave pure ethyl 2,5-dimethyl--1,5-cyclohexadiene-1-acetate, which also gave a liquid adduct with maleic anhydride.

EXPERIMENTAL

<u>Preparation of 3-Methyl-1,2-butadiene.</u> 2-Methyl-3-butyn-2-ol (200 g) was added over a period of 30 minutes to a stirred mixture of 50 g of cuprous chloride, 23 g of ammonium chloride, and 500 ml of concentrated hydrochloric acid, after which stirring was continued further for three hours. The chlorine compounds formed were separated, dried with potassium carbonate, and added with stirring to a hot suspension of 200 g of zinc dust and 60 g of copper powder in 200 ml of butyl alcohol. When the addition was complete, the reaction mixture was refluxed with stirring; stirring was continued while the reaction product was distilled off through a small column. After being dried with calcium chloride and with potassium carbonate, the allene fraction was redistilled through a column. We obtained 95 g of the allene (3-methyl-1,2-butadiene), b.p. 39.2-39.5° (734 mm); n_{20}^{20} 1.4150.

Dimerization of 3-Methyl-1,2-butadiene. 3-Methyl-1,2-butadiene (70 g) was heated in a metal ampoule at 130° for 48 hours. Fractionation of the reaction products through a product gave: Dimer (IV) (7 g); b.p. 72° (57 mm); n_D^{20} 1.4700; λ_{max} 243.5 m μ ; ϵ 7.77 ·10³ (heptane); infrared spectrum: 12.7; 11.4; 10.8; 6.9 μ ; Raman spectrum: 1681.1 (very intense); 1645.8 (average intensity); 1479.1; 1380.0; 1283.0 cm⁻¹. Diisopropylidenecyclobutane (III) (18 g); b.p. 99° (80 mm); n_D^{20} 1.5032; λ_{max} 253.5 m μ ; ϵ 1.02 · 10⁴ (heptane); infrared spectrum: 12.1; 7.4; 6.9 μ ; Raman spectrum: 1676.7 (very intense) 1579; 1443.9; 1380.5; 1257.4; 1145.7; 1086.3;

• The Russian text states that the reactant was methylcyclohexenone, but to obtain the product stated by a Reformatsky reaction followed by dehydration the ketone used must have been that stated here. -Publisher.

1065.0; 630.4; 552.9; 350.4; 147.2 cm⁻¹. Also trimer (38 g), b.p. 145-150° (40 mm), which was not investigated further. The dimers (III) and (IV) did not give crystalline adducts with maleic anhydride in the temperature range 25-100°.

Oxidation of the Dimers (III) and (IV). a) Dimer (III) (3.8 g; b.p. $90^{\circ}/50$ mm) was oxidized with K MnO₄ solution (24 g in 500 ml of water) with stirring and ice cooling. Stirring was continued while excess of permanganate was removed by addition of a little sodium sulfite; 100 ml of aqueous distillate was then distilled off. To 10 ml of the aqueous distillate 25 ml of a solution of 2,4-dinitrophenylhydrazine and phosphoric acid was added. The 1.4 g of dinitrophenylhydrazone isolated was crystallized from alcohol, and this gave 1.2 g (75%) of acetone 2,4-dinitrophenylhydrazone, m.p. 192-193°, undepressed by admixture of a known sample. After removal of acetone the reaction product was filtered from the precipitate of manganese dioxide, which was washed with 100 ml of hot water. The filtrate and wash waters were acidified with the calculated amount of sulfuric acid and vacuum-evaporated to dryness.

The residue was extracted with acetone, and solvent was vacuum-distilled off; crystallization of the new residue from hot water gave 2 g of succinic acid, m.p. 172-173°, undepressed by admixture of a known sample.

Synthesis of the cis-Tetrahydrofuran (VIII). With stirring and ice cooling, a solution of 30 g of diethyl cis-, 2-cyclohexanedicarboxylate in 200 ml of dry ether was added to a Grignard reagent prepared from 22.5 g of magnesium and 130 g of methyl iodide in 150 ml of dry ether. When the addition of the ester was complete, the mixture was heated under reflux and was then poured into cold dilute sulfuric acid. The reaction product was extracted with 500 ml of ether, the extract was dried with potassium carbonate, the solvent was distilled off. Vacuum distillation of the residue through a column gave 17 g (67%) of the cis-tetrahydrofuran (VIII), b.p. 72-75° (6 mm) and n_D^{25} 1.4683. The literature [13] gives b.p. 80-83° (15 mm) and n_D^{20} 1.4700. From the residue we isolated 2 g of the lactone (IX), m.p. 75-77° (from alcohol). The literature [13] gives m.p. 80°.

Synthesis of the trans-tetrahydrofuran (XII). A solution of 26 g of diethyl trans-1,2-cyclohexanedicarboxylate in 30 ml of ether was added to a Grignard reagent prepared from 12.7 g of magnesium and 76 g of methyl iodide in 75 ml of dry ether. On the next day, the reaction product was decomposed with a mixture of ice and ammonium chloride. Extraction with chloroform gave 18 g of a liquid reaction product, n_{D}^{20} 1.4835, and this corresponded in analysis to the trans-diol. Found: C 72.56; 72.64; H 12.5; 12.7%. C₁₂H₂₄O₂. Calculated: C 72.0; H 12.0%. After vacuum distillation, the trans-diol gave 8.2 g of the trans-tetrahydrofuran (XII), b.p. 110-112° (30 mm) and n_{D}^{20} 1.4740. Found %: C 79.2; 79.01; H 11.8; H 11.92. C₁₂H₂₂O. Calculated %: C 79.0; H 12.1.

Tserevitinov estimations showed that both the cis- and the trans-tetrahydrofuran contained only traces (less than 5%) of active hydrogen.

Dehydration of the cis-Tetrahydrofuran (VIII). In the course of eight hours 40 g of the cis-tetrahydrofuran (VIII) was passed in a stream of hydrogen sulfide at $335-350^{\circ}$ through a glass tube (diameter 10 mm, length of heated part 25 cm) filled with active alumina. The hydrocarbon part of the catalyzate was washed with water and with 20% potassium hydroxide solution; it was dried with potassium carbonate. Vacuum distillation through a column of 25-plate efficiency gave 10 g of diisopropylidenecyclohexane (VII); b.p. 81.6-81.7° (8 mm); n_D^{21} 1.4912; λ_{max} 259.5 m μ ; lg \in 2.877. Found: C 87.50; 87.37; H 11.80; 11.64%. C₁₂H₂₀. Calculated : C 87.80; H 12.20%. Diisopropylidenecyclohexane does not give crystalline adducts with maleic anhydride and with benzoquinone in the temperature range 20-120°.

Ozonization of Diisopropylidenecyclohexane (VII). Diisopropylidenecyclohexane (VII) (1.7 g) was ozonized in 59 ml of 95% acetic acid with a stream of ozonized oxygen (0.01 mole/ hour) for one hour. One-half of the resulting solution of ozonides was kept at 35° with 5 ml of 30% hydrogen peroxide for 40 hours. The solution was evaporated to dryness, and crystallization from water gave 0.42 g (65%) of adipic acid, m.p. 150-151°, undepressed by admixture of a known sample. The ozonization products in the remainder of the solution were hydrogenated in presence of 0.1 g of platinum dioxide. Catalyst was removed, and distillation gave 10 ml of distillate, in which acetone (28%) was detected and isolated as its 2,4-dinitrophenylhydrazone, m.p. 192-194°. The liquid remaining in the still was evaporated to dryness, and from the residue we isolated 1,2-cyclohexanedione as its dioxime (41%); m.p. 186-188° (from methanol). The literature [23] gives m.p. 189-190°. <u>Preparation of the Diacetic Ester (X).</u> A mixture of 10 g of the cis-tetrahydrofuran (VIII), 10 g of acetic anhydride, and 0.2 g of zinc chloride was heated for three hours at 120°. The reaction product was poured into water and extracted with benzene. The extract was washed with sodium bicarbonate solution and with water and was dried with magnesium sulfate. Benzene was removed under reduced pressure, and we obtained 5.2 g (42%) of the diacetic ester (X), b.p. 145-150° (7 mm) and n_D^{27} 1.4776. Found: C 51.10; 51.20; H 7.95; 8.01%. C₁₂H₂₂O₄. Calculated: C 50.70; H 7.74%.

<u>Pyrolysis of the Diacetic Ester (X)</u>. The pyrolysis was carried out at 450° in a glass tube filled with Pyrex glass rings; 5 g of the diacetic ester (X) was fed in dropwise. Distillation of the reaction products gave 1 g of disopropenylcyclohexane, b.p. 70-75° (10 mm) and n_D^{27} 1.4845. Found: C 87.60; 87.50; H 11.95; 12.10%. C₁₂H₂₀. Calculated: C 87.80; H 12.20%.

In the ozonolysis of 0.5 g of this diene in acetic acid we isolated formal dehyde as its dimedon derivative (60%), and also adipic acid (30%), m.p. $150-151^{\circ}$.

<u>Reaction of Phenylmagnesium Bromide with trans-1,2-Cyclohexanedicarboxylate</u>. A solution of 10 g of the trans-ester in 30 ml of dry ether was added over a period of one hour to a Grignard reagent prepared from 6.2 g of magnesium and 26 ml of bromobenzene in 150 ml of ether. The reaction product was left overnight, and on the next day it was decomposed with a mixture of ice and ammonium chloride. This gave 14 g of the trans-diol, (XIII), m.p. 170-175°; it contained a small amount of its dehydration products as impurity; it was sparing-ly soluble in ether. For the trans-diol the literature [22] gives m.p. 185°. As the purification of the crude diol is very difficult and results in great losses, for the dehydration we used the crude diol, the content of (XIII) in which was found by analysis to be 92-95%.

Reaction of phenylmagnesium bromide with the cis-1,2-cyclohexanedicarboxylic ester gave only the lactone (XIIa), which was obtained in 25% yield; m.p. 175-176° (from ethanol). Found: C 81.86; 81.88; H 7.11; 7.11%, C₂₀H₂₀O₂. Calculated: C 82.19; H 6.83%.

Dehydration of the Diol (XIII). A mixture of 1 g of the diol (XIII), 12 ml of acetic acid, and 1.5 ml of concentrated hydrochloric acid was boiled for three hours. When the mixture was cool, the crystals that separated were washed with water and recrystallized from aqueous acetic acid. We obtained 0.5 g of the tetraphenyl diene (XIV); m.p. 247-248°; λ_{max} 234.5 m μ ; ϵ 64200; λ_{max} 296 m μ ; ϵ 11600 (ethanol). Found: C 93.30; 93.13; H 6.78; 6.72% C₃₂H₂₈. Calculated: C 93.4; H 6.8%.

This diene was ozonized in acetic acid, and the ozonide was decomposed by heating it with 30% hydrogen peroxide for 40 hours at 30°. We then isolated benzophenone (75%), m.p. 32° (oxime, m.p. 141-142°), and adipic acid, m.p. 150-152°, undepressed by admixture of known samples. When (XIII) was boiled with a mixture of hydrochloric and acetic adids for 30 minutes, only the unsaturated alcohol (XV), m.p. 112-113°, was isolated. Found: C 89.61; 89.59; H 7.08; 7.21%, C₃₂H₃₀O. Calculated: C 89.4; H 7.02%. This alcohol (XV) was converted into the tetraphenyl diene (XIV), m.p. 245-247° and identical with the substance described above, when boiled further with the same mixture.

Ethyl 2,4-Dimethyl-1,4-cyclopentadiene-1-acetate (XVII). To a stirred mixture of 24 g of zinc filings activated with iodine, 60 ml of benzene, and 0.2 g of mercuric chloride we added 5 ml of a solution of 22 g of 3,5-dimethyl-2-cyclopenten-1-one and 42 g of ethyl bromoacetate in 100 ml of benzene. The contents of the flask were heated until a vigorous reaction set in, and with stirring the remainder of the solution was gradually added. Stirring was then continued further for 30 minutes at 80°, and the reaction product was poured into a mixture of ice and 10% sulfuric acid; the extract was carefully washed free from traces of zinc salts and acid, dried with magnesium sulfate, and distilled. We obtained 18 g of ethyl 2,4-dimethyl-1,4-cyclopentadiene-1--acetate (XVII); b.p. 120-125° (16 mm); n_D^{17} 1.4500; λ_{max} 268.5 m μ ; 1g ϵ 4.116 (heptane). Found: C 73.5; 73.4; H 8.25; 8.20%. C₁₁H₁₆O₂. Calculated: C 73.8; H 8.89%.

With maleic anhydride in benzene at 100° the ester (XVII) gave a liquid adduct, the hydrolysis of which gave a tricarboxylic acid which did not melt sharply but gave a trimethyl ester of m.p. 92-93° (benzene-petroleum ether mixture). The dienic ester (XVII) (1.8 g) was ozonized in 50 ml of 90% acetic acid at 0° with a stream of ozonized ozygen (0.01 mole/hour) until the double bonds had disappeared, as determined by a test for unsaturation with bromine. a) To 25 ml of the resulting ozonide solution, 8 ml of 30% hydrogen peroxide was added. The mixture was kept at room temperature for 40 hours, after which acetic acid was vacuum-distilled off with a water bath. The residue was hydrolyzed by heating it in a water bath with 2 ml of 10% aqueous sodium hydroxide, the product was acidified with the calculated amount of sulfuric acid, and the aqueous layer was extracted with ether. We isolated 0.1 g of malonic acid, m.p. 118-121°, undepressed by admixture of a known sample.

b) Platinum dioxide (0.2 g) was added to the remainder of the ozonide solution, and hydrogenation was carried out until hydrogen ceased to be absorbed. A solution of 1 g of 2,4-dinitrophenylhydrazine in 10 ml of acetic acid and 0.5 ml of concentrated hydrochloric acid was added to the solution of reaction products. The solution was heated in a water bath for one hour and filtered, after which acetic acid was vacuum-distilled off. The resulting pyrazolinone (0.2 g) was recrystallized from methanol; m.p. 120-122°. The literature [24] gives m.p. 122°.

<u>Preparation of Methyl α , α , 2, 4-Tetramethyl-1, 4-cyclopentadiene-1-1-acetate (XVIII).</u> The Reformatsky reaction was carried out with methyl 2-bromo-2-methylpropionate; the procedure was as in the preceding experiment. However, in this case the reaction was less vigorous, and for its completion it was necessary to apply further heating for two hours in a water bath. After analogous treatment, from 22 g of 3,5-dimethyl-2-cyclopenten-1-one we obtained 16.9 g of the ester (XVIII); b.p. 119-124° (17 mm); n_D^{17} 1.4740; λ_{max} 264 mµ; ϵ 1960 (in heptane). Found: C 72.05; 72.05; H 9.32; 9.31%. C₁₂H₁₈O₂. Calculated: C 72.22; H 9.44%.

In the ozonolysis, which was carried out as in the preceding experiment, we isolated dimethylmalonic acid (35%) and 2,4-pentanedione in the form of a pyrazolinone, m.p. 120.3°, undepressed by the sample obtained previously. As in the preceding experiment, the adduct of the diene (XVIII) with maleic anhydride was a liquid; after hydrolysis and methylation with diazomethane we obtained a trimethyl ester, m.p. 95°.

The Reformatsky reaction was carried out also with 3,6-dimethyl-2-cyclohexen-1-one*. In this case, however, a mixture of products was formed. Vacuum distillation of these with potassium hydrogen sulfate gave ethyl 2,5-dimethyl-1,5-cyclohexadiene-1-acetate (XXIII); b.p. 126-128° (20 mm); n_D^{20} 1.4985; λ_{max} 264 m μ ; ϵ 7510 (in heptane). Found: C 73.25; 73.22; H 8.35; 8.47%. Calculated: C 73.8; H 8.89%.

In the ozonolysis of the product by the above-described method, we isolated malonic acid (20%), m.p. 120°, and succinic acid (40%), m.p. 177-178°; in both cases, there was no depression of melting point in mixtures with known samples. The ester (XXIII) again did not give crystalline adducts with maleic anhydride; the trimethyl ester prepared from the liquid adduct had m.p. 85° (from a mixture of benzene and petroleum ether).

SUMMARY

1. A detailed study was made of the Grignard reaction with esters of cis- and trans-1,2-cyclohexanedicarboxylic acids.

2., 1,2-Bis(diphenylmethylene cyclohexane and diisopropylidenecyclohexane, and also their cyclobutane analogs, do not undergo diene condensation with maleic anhydride and with benzoquinone.

3. The Reformatsky reaction with 3,5-dimethyl-2-cyclopenten-1-one leads to 2,4-dimethyl-1,4-cyclopentadiene-1-acetic acids.

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^{*}Original Russian pagination. See C. B. translation.