BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1245—1248 (1967)

Dimerization and Rearrangement of Diphenylcyclopropenone

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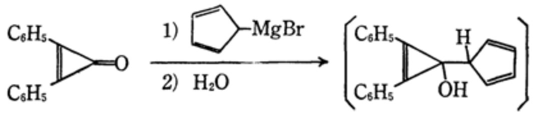
(Received November 22, 1966)

The reaction of diphenylcyclopropenone with cyclopentadienylmagnesium bromide did not give the expected tertiary carbinol, but resulted in the formation of tetraphenylcyclopentadienone, tetraphenyl-*p*-benzoquinone, and tetraphenylpyrocatechol in 1%, 2%, and 8% yields respectively. When diphenylcyclopropenone was treated with a mixture of metallic magnesium and iodine, the same products were obtained in increased yields. Similarly, the treatment of diphenylcyclopropenone with sodium amalgam in isopropyl alcohol - acetic acid gave tetraphenyl-*p*-benzoquinone and tetraphenylpyrocatechol in 4% and 20% yields respectively. These results suggest that diphenylcyclopropenone gives pinacol, 1, 1′-dihydroxy-2, 2′, 3, 3′-tetraphenyl-1, 1′-bicyclopropenyl, under the reaction conditions, but the pinacol is too unstable to be isolated and rearranges to the benzene derivatives.

It is well known that cyclopropenone undergoes facile rearrangements under the various reaction conditions,[1-3] and the labile nature of this particular ketone has been understood by means of its highly strained ring system. On the other hand, there are several reactions in which the cyclopropene skeleton survives the reaction.[4-11] The reaction of diphenylcyclopropenone (I) with phenylmagnesium bromide has been reported by Breslow.[2] It gives the triphenylcyclopropenyl cation after an appropriate work-up, but the same procedure does not work well with some aliphatic Grignard reagents.[2] In the present paper, the reaction of I with cyclopentadienylmagnesium bromide will be investigated; interest will be focused on the stability of the cyclopropenyl cation and the facile rearranging nature of the unsaturated three-membered ring system.

Results and Discussion

We had expected that 1-(2′, 4′-cyclopentadien-1′-yl)-2, 3-diphenyl-2-cyclopropen-1-ol (II) would be given when I was reacted with cyclopentadienylmagnesium bromide. When the reaction was carried out in dry tetrahydrofuran at room temperature, however, the only reaction product was a tar; there was no sign of the presence of II in it.



I II

From the tar, however, three crystalline materials, III (1%), IV (2%), and V(8%), were isolated with an aid of column chromatography. By comparison with authentic samples, the compounds III (mp 217—218°C) and IV (mp 317—320°C) are identified as tetraphenylcyclopentadienone and tetraphenyl-*p*-benzoquinone respectively. The molecular formula for V, mp 252.6—253.7°C, is found to be $C_{30}H_{22}O_2$ on the basis of the analytical results and the molecular weight determination. Examinations of the infrared and NMR spectra show that the compound V consists of benzene ring(s) and hydroxy group(s). Accordingly, V must be one of the isomeric tetraphenyldihydroxybenzenes. Since V is not identical with authentic tetraphenyl-*p*-hydroquinone, it must be either tetraphenylpyrocatechol or tetraphenylresorcinol. When V was oxidized by potassium bromate-vanadium pentoxide,[12] tetraphenylcyclopentadienone (III) was formed, and there was a loss of carbon monoxide. This suggests that the two hydroxyl groups in V occupy 1, 2-positions. A similar oxidation of 9, 10-phenanthraquinone to fluorenone has been achieved with hot lead monoxide.[13] Moreover,

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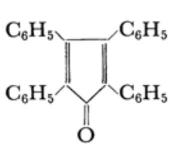
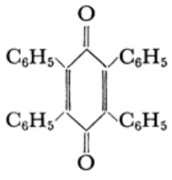
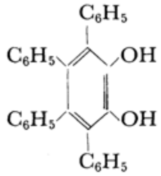
[12] J. Cason, "Organic Reactions," Vol. IV, p. 305 (1948).

the characteristic pyrocatechol tests, including the phosphomolybdic acid test[14] and lead acetate test,[15] were positive in the compound V. Thus, it may be concluded that V is tetraphenylpyrocatechol.


(III)


(IV)

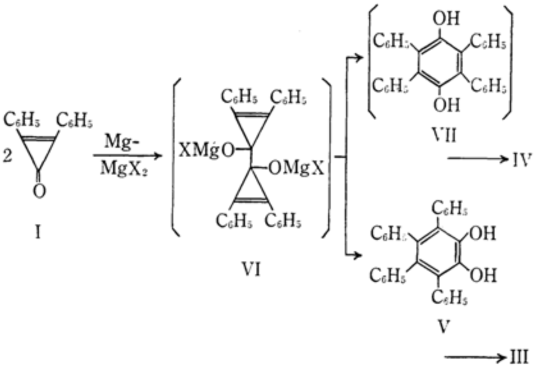

(V)

Some other attempts to establish the pyrocatechol structure for V have failed. These include oxidative condensation with *o*-phenylenediamine[16] and dioxymethylene ring formation with methylene bromide.[17] These results indicate that a severe steric hindrance is present around the hydroxyl groups of V. The steric hindrance is also evident in the following observations. The treatment of V with *p*-toluenesulfonyl chloride in dry pyridine at room temperature[18] resulted in the recovery of the starting pyrocatechol V. When V was treated with an excess of *p*-toluenesulfonyl chloride in dry pyridine under a reflux for 4 hr, the monosulfonate was formed. When the refluxing was continued for one week, di-*p*-toluenesulfonate was obtained. In an attempt to convert the pyrocatechol V to the known 1, 2, 3, 4-tetraphenylbenzene, the disulfonate was treated with an active catalyst under a hydrogen atmosphere.[19] However, under ordinary conditions,[19] the starting disulfonate was recovered quantitatively. When the reaction was carried out under drastic conditions, the O-S bond rather than the C-O bond was cleaved and pyrocatechol V was obtained.

Now it is clear that the reaction products identified so far are derived from the ketone I alone. A cyclopentadienyl skeleton is not included in any of the products. Consequently, the ketone I was treated with a mixture of magnesium and magnesium iodide in an ether-benzene mixture to see whether or not a similar reaction could then occur. When a tarry reaction product was treated in the same way, the same compounds, III, IV, and V, were obtained in 2%, 3%, and 10% yields respectively.

Actually, the reaction is a dimerization of I, followed by a rearrangement to six-membered-ring derivatives. A possible course of the dimerization under these conditions is the pinacol formation.[20] Consequently, I was treated under the conditions typically used for pinacol formation.[21] When I was treated with sodium amalgam in 1-propanol - acetic acid, the same compounds, IV and V, were obtained in 4% and 20% yields respectively. The possibility that the pinacol, 1, 1′-dihydroxy-2, 2′, 3, 3′-tetraphenyl-1, 1′-bicyclopropenyl (VI), rearranges to IV and V in the course of column chromatography can be removed by the following observation. An effort to isolate the expected pinacol VI prior to the chromatography had failed, but the pyrocatechol V was crystallized out. No cyclopropenyl derivative could be detected in the crude reaction product.

Accordingly, it may be concluded that, under the conditions investigated, the ketone I first dimerizes to the pinacol VI, but this pinacol is unstable and rearranges to the benzene derivatives, tetraphenylpyrocatechol (V) and tetraphenyl-*p*-hydroquinone (VII). The latter compound can be oxidized by oxygen in air to tetraphenyl-*p*-benzoquinone (IV).[22] Tetraphenylcyclopentadienone (III) might be formed upon the oxidation of V during the course of the reaction, although no evidence to support this theory is available.[23]



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[22] During the recrystallization of VII from cyclohexane-benzene it was found hydroquinone VII was gradually oxidized to benzoquinone IV. See experimental section.

[23] It was shown as described before that V was oxidized by potassium bromate - vanadium pentaoxide to result III. However, III was not obtained from V under the same condition in which III was obtained from I.

An interesting feature of the present results is formation of both pyrocatechol and *p*-benzoquinone. In other words, the C-1 in the ketone I comes to 1, 2- and 1, 4-positions in the rearranged benzene derivatives. Dimerization at the double bond of cyclopropene[24,25] leads only to the 1, 4-derivative, *p*-benzoquinone; it can not account for the formation of pyrocatechol in an appreciable amount. A very similar rearrangement of bicyclopropenyl to isomeric 1, 2- and 1, 4-benzene derivatives has been reported by Breslow;[26] it supports the idea of the mechanism that the first step of the present dimerization is the formation of the pinacol VI, although the rearrangement has been achieved under much milder conditions in the present case and although the proportions of isomeric benzene derivatives differ significantly in the two cases.

Since another well known condition for pinacol formation is a photochemical procedure, a solution of ketone I in isopropyl alcohol was irradiated with visible light. The results were the same as those obtained under irradiation with ultraviolet light.[27] No dimeric material was detected in the product, and diphenylacetylene was obtained quantitatively.

Experimental[28]

Diphenylcyclopropenone (I). Diphenylcyclopropenone (I) was prepared from dibenzyl ketone according to the route established by Breslow *et al.*[2,29] Ketone I melted at 118—119°C (lit. mp 119—120°C), and it showed all of the characteristic properties reported in the literature.

Reaction of I with Cyclopentadienylmagnesium Bromide. To a solution of ethylmagnesium bromide, prepared from 1.2 g of ethyl bromide (11 mmol) and 0.5 g of magnesium (21 mmol) in 50 m*l* of dry tetrahydrofuran, 0.8 g of cyclopentadiene (12.1 mmol) was added; the mixture was then heated under refluxing for 12 hr in order to replace the ethyl group by cyclopentadienyl.[30] Two grams of I (10 mmol) in 15 m*l* of dry tetrahydrofuran were added, drop by drop, at room temperature to the solution of cyclopentadienylmagnesium bromide, and the mixture was stirred at room temperature for an additional hour. The reaction mixture was then decomposed by aqueous ammonium chloride, and the organic materials were extracted three times with ether. A combined ether solution was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether was then removed under reduced pressure at room temperature. The brownish residue was dissolved in a minimum amount of benzene and chromatographed on 130 g of activated alumina. Elution with 200 m*l* of benzene gave 24 mg of a violet, crystalline material. The recrystallization of this material from benzene gave violet, crystalline tetraphenylcyclopentadienone (III) melting at 217—218°C (lit.[31] mp 215.2—216.2°C). The present sample was identical in all respects with authentic III prepared from dibenzyl ketone and benzil.[31]

Further elution with 100 m*l* of benzene gave 40 mg of orange material, which was found to be 2, 3, 5, 6-tetraphenyl-*p*-benzoquinone (IV), mp 317—320°C (from benzene) (lit.[32] mp 311—314°C). The present sample was found to be identical with authentic IV prepared from 1 mol of *p*-benzoquinone and 4 mol of benzene diazonium chloride.[32] The reduction of this quinone with lithium aluminum hydride produced 2, 3, 5, 6-tetraphenyl-*p*-hydroquinone, mp 300—315°C (lit.[33] mp 322—325°C); however, the hydroquinone was oxidized easily by oxygen in the air, and *p*-benzoquinone was obtained after several recrystallizations.

Finally, elution with 5 *l* of ether yielded 0.45 g of white crystals. This substance melted at 252.6—253.7°C after recrystallization from benzene.

Found: C, 86.90; H, 5.31%; mol wt, 415 (by osmotic pressure in chloroform). Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%; mol wt, 414.5.

The infrared spectrum (in CS_2) showed a strong absorption at 3515 cm^{-1}. The NMR spectrum (in chloroform-*d*) exhibited a multiplet at τ 2.4—3.2 (20 hydrogens) and a singlet at τ 4.87 (2 hydrogens) which disappeared upon the addition of D_2O. In the ultraviolet region (in CH_3CN) V showed peaks at 243.5 mμ (log ε 4.3), at 297 mμ (sh) (log ε 3.6), and at 378 mμ (log ε 2.5). Consequently, it is apparent that V is composed of phenolic hydroxyl groups and benzene rings. The compound V exhibited a positive ferric chloride test in the presence of a drop of pyridine. Moreover, the addition of lead acetate to a solution of V in a large amount of ethanol caused the solution to change from colorless to yellow after 24 hr at room temperature.[15] The addition of phosphomolybdic acid in glacial acetic acid to the solution of V in the same solvent caused the solution to change from yellow to green.[14] The last two tests are characteristic of pyrocatechol. Accordingly, the compound V may be identifed as 1, 2, 3, 4-tetraphenylpyrocatechol.

Reaction of I with Mg-MgI$_2$.[34] A mixture of 1.5 g of metallic magnesium (62 mmol), 6 g of iodine (24 mmol), and 1.0 g of I (5 mmol) in 10 m*l* of dry ether and 28 m*l* of dry benzene was refluxed for 19 hr. The reaction mixture was then poured into a large amount of water. The organic materials were extracted with

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three 50-ml portions of ether; the combined ether extract was then washed successively with a saturated ammonium chloride solution, with a sodium thiosulfate solution, and with a saturated sodium chloride solution. After the solution had been dried over anhydrous magnesium sulfate, the ether was removed. The resulting residue was chromatographed on activated alumina. We thus obtained 20 mg of tetraphenylcyclopentadienone (III, 2%), 30 mg of tetraphenyl-*p*-benzoquinone (IV, 3%), and 105 mg of tetraphenylpyrocatechol (V, 10%).

Reaction of I with Sodium Amalgam.[21] To a solution of I (4.0 g, 20 mmol) in 300 m*l* of a 1 : 1 mixture of 1-propanol and glacial acetic acid, 417 g of 3% sodium amalgam was added over a period of an hour; during the last 10 min of addition, the solution boiled gently. After stirring for an additional hour at room temperature, the reaction mixture was poured into a large amount of water, and the organic material was extracted three times with ether. The combined ether solution was then washed with dilute aqueous sodium hydroxide, followed by water. After the solution had then been dried over anhydrous magnesium sulfate, the ether was removed. A semicrystalline, dark red residue was thus obtained. Several recrystallizations from methylene chloride and from benzene gave 0.17 g of pure crystalline V. The mother liquid was concentrated, and the residue was chromatographed on activated alumina. Finally there were obtained 0.18 g of tetraphenyl-*p*-benzoquinone (IV, 5%) and 0.81 g of tetraphenylpyrocatechol (V, 20%).

Oxidation of V with Potassium Bromate.[12] To a refluxing solution of tetraphenylpyrocatechol (V, 52.3 mg, 0.125 mmol) in glacial acetic acid (1.0 m*l*) - tetrahydrofuran (1.5 m*l*), there was added, at once, a mixture of potassium bromate (7.7 mg) and vanadium pentaoxide (1.0 mg) in a few drops of water. The mixture was then heated with magnetic stirring for 15 min. After work-up as usual, the residue was chromatographed on activated alumina. Elution with benzene gave 4.0 mg (8%) of tetraphenylcyclopentadienone (III), mp 217—218°C.

Preparation of Di-*p*-toluenesulfonate of V. The treatment of V with *p*-toluenesulfonyl chloride in dry pyridine at room temperature resulted in the recovery of the starting pyrocatechol. When V was treated with an excess of *p*-toluenesulfonyl chloride in dry pyridine under refluxing for 4 hr, the monosulfonate of V, mp 198—200°C, was obtained.

Found: C, 78.21; H, 5.10%. Calcd for $C_{37}H_{28}O_4S$: C, 78.15; H, 4.96%.

A solution of V (212.3 mg, 0.5 mmol) and *p*-toluenesulfonyl chloride (519.6 mg, 2.7 mmol) in 2 m*l* of dry pyridine was refluxed for one week. After work-up as usual, we obtained 240 mg (66%) of the white crystalline di-*p*-toluenesulfonate of V, mp 248—249°C (from ethanol-benzene).

Found: C, 73.16; H, 4.70%; mol wt, 685 (by osmotic pressure in chloroform). Calcd for $C_{44}H_{34}O_6S_2$: C, 73.11; H, 4.74%; mol wt, 723.

In the IR region this material showed the absorptions characteristic of the $-OSO_2-$ group at 1370 and 1175 cm^{-1}.

Catalytic Cleavage of Ditosylate of V.[19] In an attempt to obtain 1, 2, 3, 4-tetraphenylbenzene, the ditosylate of V was refluxed with a large excess of Raney nickel in an ethanol-tetrahydrofuran-benzene mixture under atmospheric pressure of hydrogen. However, this resulted in the recovery of the starting ditosylate. On the other hand, the treatment of ditosylate (450 mg, 0.623 mmol), dissolved in a mixture of ethanol (150 m*l*) and benzene (100 m*l*), with 40 g of Raney nickel in an autoclave at 50°C under an atmospheric pressure of hydrogen of 60 for 40 hr gave 111 mg (43%) of a white, crystalline material, mp 249.0—250.5°C. This material was found to be tetraphenylpyrocatechol (V), and no hydrocarbon was detected in the product.

Other attempts, including the treatment of ditosylate with $Pt\text{-}PtCl_6\cdot 6H_2O$ in tetrahydrofuran, ethanol, or acetic acid under an atmospheric pressure of hydrogen of 87 at 100°C, resulted in the recovery of the starting ditosylate. At 300°C under an 84 atm, an oxygen-sulfur cleavage occurred as has been described in the reaction with Raney nickel.

Photochemical Reaction of Diphenylcyclopropenone (I).[35] A solution of I (1.0 g, 5.0 mmol) in isopropyl alcohol (50 m*l*), agitated by the bubbling in of nitrogen gas, was irradiated with a 300-watt tungsten lamp for 55 hr. The reaction was followed by an examination of the characteristic peaks of I in the ultraviolet region. The evaporation of the solvent gave diphenylacetylene (0.79 g, 91%), mp 57.0—58.2°C (lit.[36] mp 60—61°C). A mixed melting point determination with an authentic sample showed no depression. Similarly, the irradiation of I in carbon tetrachloride or methyl iodide resulted in the formation of diphenylacetylene in quantitative yields.

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