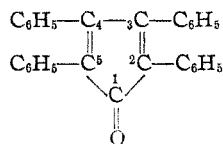


[CONTRIBUTION FROM MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

Reactions with Tetraphenylcyclopentadienone. Condensation with Cyclic 1,3-Diene Systems

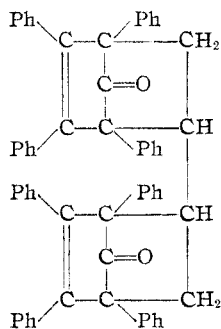
BY OLIVER GRUMMITT, R. S. KLOPPER¹ AND C. W. BLENKHORN²

Recent investigations by W. Dilthey and co-workers³ have made available several substituted cyclopentadienone compounds of which the tetraphenyl derivative⁴ is the simplest and most accessible



These compounds are of interest in diene reactions because of their ability to react with α,β -unsaturated carbonyl compounds and conjugated dienes, *i. e.*, with the two types of reactants usually employed in Diels-Alder syntheses.

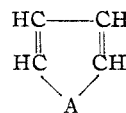
The condensation of tetraphenylcyclopentadienone with such typical α,β -unsaturated carbonyl compounds as maleic anhydride⁵ and vinyl ketones⁶ has already been reported. With butadiene-1,3 Dilthey⁷ found that two molecules of tetraphenylcyclopentadienone were added to one molecule of butadiene:



The 2,5-addition to tetraphenylcyclopentadienone indicates that it is functioning as a conjugated diene system, although an α,β -unsaturated car-

bonyl system is available for a normal Diels-Alder type of condensation. Furthermore, the normal Diels-Alder reaction would require 1,4-addition to butadiene, whereas only 1,2 and 3,4 additions occur.

The unusual course of the reaction with butadiene suggested the desirability of studying the condensation of tetraphenylcyclopentadienone with other 1,3-diene systems. The present report covers the reactions of tetraphenylcyclopentadienone with cyclopentadiene, furan, pyrrole, N-methylpyrrole, and thiophene, *i. e.*, cyclic 1,3-diene systems where A is CH₂, O, N-H, N-CH₃, and S, respectively



It has now been found that cyclopentadiene is the only one of this group of compounds which will condense with tetraphenylcyclopentadienone. The product is a colorless, crystalline, addition compound⁸ made up of one molecule of each reactant. There was no evidence of a product involving two molecules of tetraphenylcyclopentadienone as Dilthey found in the case of butadiene.⁷ The structure of the addition compound was inferred to be 4,5,6,7-tetraphenyl-4,7-endo-carbonyl-8,9-dihydroindene (I) from the sequence of reactions shown.

Attempts were made to eliminate carbon monoxide from I by thermal decomposition in the usual way,⁹ but this reaction was complicated by a reversal of the addition reaction which yielded cyclopentadiene and tetraphenylcyclopentadienone.¹⁰ Therefore the addition compound (I) was subjected to quantitative hydrogenation and, on the absorption of one mole of hydrogen, II was obtained. The addition of hydrogen was inter-

(8) This fact eliminates the possibility that the product was a fulvene.

(9) Many tetraphenylcyclopentadienone addition compounds obtained by Dilthey readily split out carbon monoxide on heating.

(10) Apparently the condensation involves an equilibrium: tetraphenylcyclopentadienone + cyclopentadiene \rightleftharpoons I, which is shifted in the reverse direction by elevated temperatures. This resembles the equilibria observed by Bachmann, *et al.*, in Diels-Alder reactions with maleic anhydride and polycyclic aromatic hydrocarbons. Bachmann and Kloetzel, *THIS JOURNAL*, **60**, 481 (1933).

(1) From the M.A. thesis of R. S. Kloppe. Present address: Ohio State University.

(2) From the M.A. thesis of C. W. Blenkhorn. Present address: Dow Chemical Co., Midland, Michigan.

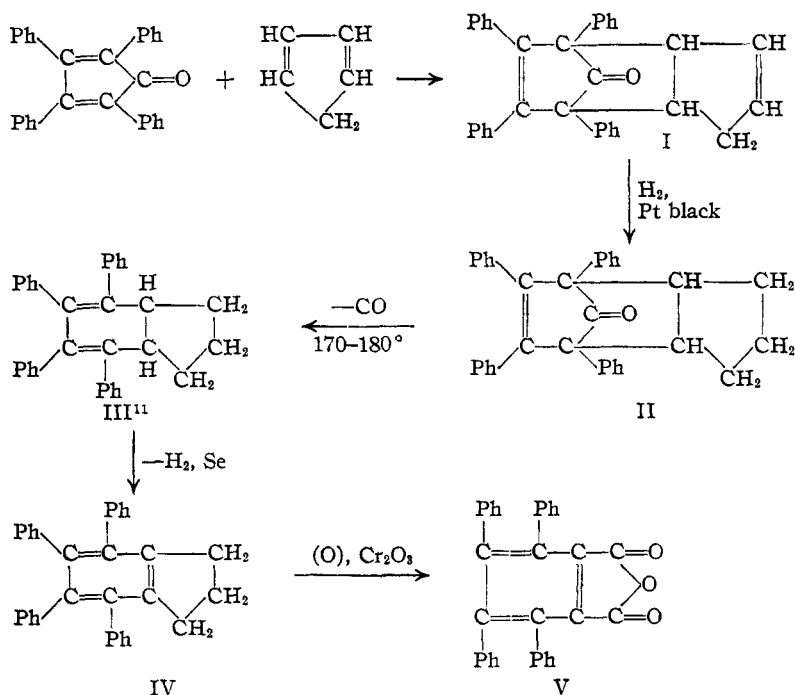
(3) Dilthey, *et al.*, *J. prakt. Chem. and Ber.* (1930-1940).

(4) Referred to as "tetracyclone" by Dilthey.

(5) Dilthey, Schommer, and Trosken, *Ber.*, **66B**, 1627 (1933); Allen and Sheps, *Can. J. Res.*, **11**, 171 (1934). The reaction with maleic anhydride proceeds through a 2,5-addition to the tetraphenylcyclopentadienone of the ethylenic bond of maleic anhydride. Subsequent elimination of carbon monoxide and hydrogen yields tetraphenylphthalic anhydride.

(6) Allen, Bell, Bell and Van Allen, *THIS JOURNAL*, **62**, 656 (1940).

(7) Dilthey, Schommer, Hoschen and Dierichs, *Ber.*, **68B**, 1159 (1935).



pretended as occurring at an ethylenic bond rather than at the carbonyl group because quantitative bromination also showed the presence of one reactive double bond. Furthermore, **II** on heating yielded carbon monoxide. The ethylenic bond in the tetraphenylcyclopentadienone nucleus of **I** is probably not hydrogenated since Dilthey has shown that tetraphenylcyclopentadienone is stable toward hydrogenation under the conditions employed here.¹²

The hydrogenated addition compound, being unable to decompose to the original reactants, eliminated carbon monoxide smoothly to yield the hydrocarbon **III**. Dehydrogenation of this with selenium gave **IV**, a tetraphenylhydrindene, which was oxidized to tetraphenylphthalic anhydride. The identity of the latter was established by comparison with an authentic sample prepared from tetraphenylcyclopentadienone and maleic anhydride according to Dilthey.⁵ The last reaction is especially significant because it eliminates the possibility that the original addition reaction could have followed any course other than that shown in the above reactions.¹³

Dicyclopentadiene does not react with tetra-

phenylcyclopentadienone at temperatures below 200° . At 250° reaction occurs but the product is resinous in nature.

The absence of any evidence of reaction of tetraphenylcyclopentadienone with furan, pyrrole, N-methylpyrrole, and thiophene is in accord with the fact that the olefinic bonds of these compounds are less reactive than those of cyclopentadiene. The greater stability of these compounds as compared with cyclopentadiene is due in part to large differences in resonance energies: the calculated value for butadiene-1,3 is 8.0 kcal. per mole and the value for cyclopentadiene is probably of this order whereas the values for furan,

pyrrole, and thiophene are 21.4, 22.6 and 31.1 kcal. per mole, respectively.^{14,15}

Experimental

Formation of Tetraphenylcyclopentadienone-Cyclopentadiene Addition Compound (I).—Tetraphenylcyclopentadienone was prepared by condensing benzil with dibenzyl ketone.¹² Cyclopentadiene was prepared by thermal depolymerization of redistilled dicyclopentadiene¹⁶ by refluxing the dimer in an apparatus fitted with an unpacked fractionating column 7 mm. in diameter and 75 cm. long. The monomer, distilling at $41-42^\circ$, was collected in an ice-cooled receiver and used immediately. Twenty-three grams (0.060 mole) of tetraphenylcyclopentadienone and 10 cc. (0.12 mole) of cyclopentadiene were dissolved in 70 cc. of benzene and the mixture refluxed for four hours. It was then diluted with 140 cc. of petroleum ether ($60-70^\circ$) and allowed to stand overnight at $0-10^\circ$. The pink crystalline mass was suction filtered, washed with petroleum ether, and dried in air. The yield was 17.0 g., 60% of the theoretical, m. p. $188-190^\circ$ with decomposition. Because of decomposition, the melting point varied somewhat with the rate at which the melting point bath was heated. Crystallization from hot solvents proved undesirable because of some decomposition to the original reactants, but by dissolving 15 g. of crude product in 110 cc. of chloroform at room temperature and cooling to about -60° overnight 7-8 g. of colorless crystals, m. p. $197-198^\circ$ with decomposition, could be obtained; molecular weight calculated for $\text{C}_{24}\text{H}_{20}\text{O}$, 451; found by cryoscopic determination in benzene, 445, 454.

(14) Pauling and Sherman, *J. Chem. Phys.*, **1**, 606, 679 (1933).

(15) Kistiakowsky, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **58**, 146 (1936).

(16) Furnished us through the courtesy of Dr. N. K. Chaney, United Gas Improvement Company, Philadelphia, Penna.

(11) The position of the double bonds in this compound was not proved.

(12) Dilthey and Quint, *J. prakt. Chem.*, [2] **128**, 143 (1930).

(13) This fact is evident from an examination of the structures of various other addition compounds formed through tetraphenylcyclopentadienone-cyclopentadiene reactions involving 2,5-1,4, 2,3-1,2, and 2,3-1,4 additions, respectively.

Anal. Calcd. for $C_{34}H_{28}O$: C, 90.63; H, 5.82. Found: C, 90.78; H, 5.25.

Tetraphenylcyclopentadienone with Dicyclopentadiene.—To determine if dicyclopentadiene and tetraphenylcyclopentadienone would react, either directly or through depolymerization of the dimeric hydrocarbon to the monomeric form with subsequent condensation with tetraphenylcyclopentadienone, the following experiments were run:

(1) Tetraphenylcyclopentadienone and excess dicyclopentadiene in a mole ratio of 1/50 were allowed to stand at room temperature for a week. Removal of the dicyclopentadiene by vacuum distillation yielded pure tetraphenylcyclopentadienone, identified by a mixed melting point.

(2) A similar experiment in which the reactants were heated in refluxing benzene also yielded unreacted tetraphenylcyclopentadienone.

(3) The reactants were heated in a sealed tube for seventeen hours at 200° with no evidence of reaction.

(4) A similar experiment at 275–300° for twelve hours yielded an amber-colored resinous product, melting over a wide range above 250°. It was insoluble in hot benzene, petroleum ether, alcohol, chloroform, and glacial acetic acid; it softened somewhat in boiling acetone but did not dissolve. Numerous attempts to crystallize this substance were unsuccessful.

Hydrogenation of the Addition Compound (I).—In an effort to split out the endo carbonyl group as carbon monoxide portions of the addition compound were heated in refluxing acetic acid (118°) and chlorobenzene (132°). Carbon monoxide was evolved slowly in both cases but the simultaneous formation of cyclopentadiene and tetra-cyclopentadienone made it impossible to purify the decarbonylated product. To prevent dissociation of the addition compound it was subjected to quantitative hydrogenation: 4.9 g. of the adduct in 10 cc. of absolute alcohol and 90 cc. of thiophene-free benzene and 0.5 g. of Adams platinum black catalyst¹⁷ was reduced at about 30 lb. of hydrogen pressure. The hydrogen consumed was about 95% of the theoretical amount for one double bond. Filtering the reaction mixture and evaporating the solvent yielded 7.0 g. of colorless crystals, m. p. 209–211° (compound II in the chart).

Anal. Calcd. for $C_{34}H_{28}O$: C, 90.23; H, 6.24. Found: C, 90.29; H, 6.50.

Addition of Bromine to Compound I.—Three grams of the addition compound (I) (0.007 mole) and 5 cc. (0.195 mole) of bromine in 40 cc. of carbon disulfide were refluxed one and one-half hours. Practically no hydrogen bromide was evolved showing that substitution was not taking place. The mixture was cooled, suction filtered, the solid washed with petroleum ether, and dried in air. The crude product was crystallized from 60 cc. of benzene; m. p. 222–223°; yield, 1.5 g.; 60% of the theoretical.

Anal. Calcd. for $C_{34}H_{28}Br_2O$: Br, 26.1. Found: Br, 25.9.

Thermal Decomposition of the Hydrogenated Addition Compound (II).—After trying various reaction temperatures to determine conditions that would split out the

endo carbonyl group, 170–180° was selected. Five grams of the hydrogenated addition compound (II) was refluxed in 60 cc. of *p*-cymene for fifteen hours. At the end of this time the evolution of carbon monoxide had practically ceased. Steam distillation of the reaction mixture to remove the *p*-cymene left 4.0 g. of light-colored, fluffy solid; m. p. 173–177°. Crystallization from *p*-cymene gave 3.0 g., 65% of the theoretical; m. p. 174–175°.

Anal. Calcd. for $C_{33}H_{28}$: C, 93.35; H, 6.65. Found: C, 93.40; H, 6.81.

Dehydrogenation of III to 4,5,6,7-Tetraphenylhydrindene (IV).—Dehydrogenation experiments were tried with lead tetraacetate, bromine, and selenium. With lead tetraacetate there was evidence that oxidation occurred but the crude product resisted purification. Bromine dehydrogenation in bromobenzene at steam-bath temperature was effective in two small-scale experiments but in other experiments under the same conditions some bromine substitution occurred. The cause of these uncertain results could not be found, so the method was discarded.¹⁸

Selenium effected the dehydrogenation satisfactorily although the removal of residual selenium from the product was troublesome. Two and one-half grams (0.006 mole) of the hydrocarbon III and 1.0 g. (0.126 atom) of selenium were refluxed in *p*-cymene for twenty-five hours. The mixture was filtered and the filtrate steam distilled. The residue was a bright yellow solid; m. p. 196–215°. This crude product was sublimed at 100° under reduced pressure to remove most of the selenium and the residue was crystallized from a 1–1 mixture of petroleum ether (60–70°) and cyclohexane. This purified 4,5,6,7-tetraphenylhydrindene (IV) melted at 225–226°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.90; H, 6.05.

Oxidation of 4,5,6,7-Tetraphenylhydrindene (IV) to Tetraphenylphthalic Anhydride (V).—The hydrocarbon (IV) resisted oxidation by chromic acid in dilute sulfuric acid at 100° and by alkaline potassium permanganate at 100°; in each case the original substance could be recovered. However, in glacial acetic acid solution the oxidation proceeded readily: 1.0 g. of the hydrocarbon (IV) and 2.0 g. of chromic anhydride in 35 cc. of glacial acetic acid were heated on the steam-bath forty-five minutes. The mixture was cooled, suction filtered, and the precipitate washed with water, several times with hot dilute (5%) sulfuric acid, and again with water. The solid was transferred to a small beaker and extracted with 20 cc. of 5% sodium hydroxide solution while heating on the steam-bath. This mixture was filtered and the insoluble portion washed several times with water. Acidifying the filtrate yielded some benzoic acid, identified by a mixed melting point with an authentic sample. Apparently the tetraphenylhydrindene and/or the tetraphenylphthalic anhydride can be oxidized to some extent under these conditions so as to degrade the phenyl-substituted benzene ring. The portion insoluble in sodium hydroxide is crude tetraphenylphthalic anhydride; this substance does not dissolve as a sodium salt because of its extreme inertness.⁵ Crystallization from benzene–petroleum ether gave a small

(17) "Organic Syntheses," Coll. Vol. I, p. 452.

(18) We are indebted to J. C. Baker for these experiments.

amount of crystals melting 277–281°; a mixed melting point with an authentic sample of tetraphenylphthalic anhydride (m. p. 284–286°) gave 279–283°. Because of the melting point ranges observed here additional proof of the identity of the product of oxidation was obtained by ultimate analysis.

Anal. Calcd. for $C_{32}H_{20}O_4$: C, 84.94; H, 4.46. Found: C, 85.05; H, 4.51.

Tetraphenylcyclopentadienone with Furan, Pyrrole, N-Methylpyrrole and Thiophene.—Six and eight-tenths grams of furan¹⁹ (0.1 mole) and 1.15 g. (0.003 mole) tetraphenylcyclopentadienone were heated in a closed tube at 100° for nine hours. In a second experiment the same quantities were heated at 200° for seventeen hours. In both cases the tetraphenylcyclopentadienone was recovered quantitatively and identified by a mixed melting point.

Of several experiments with pyrrole²⁰ the most vigorous conditions employed were as follows: 3.3 g. (0.05 mole) of pyrrole and 1.15 g. (0.003 mole) of tetraphenylcyclopentadienone were heated in a closed tube at 150–160° for twelve hours. The reaction mixture was warmed under reduced pressure to remove unreacted pyrrole. The residue melted 208–210° and a qualitative test for nitrogen was negative, showing that no addition compound had formed. Crystallization of this material from benzene and a mixed

melting point showed that the residue was tetraphenylcyclopentadienone. Other experiments likewise showed no reaction.

Several experiments with N-methylpyrrole²¹ and tetraphenylcyclopentadienone similar to that described above were tried but no evidence of reaction could be found even after heating at 185° for fourteen hours.

Likewise experiments with thiophene (Eastman Kodak Co.) and tetraphenylcyclopentadienone even at 150–160° for twelve hours gave negative results. The presence of 5% trichloroacetic acid²² in one experiment had no effect.

Summary

A study of the condensation of tetraphenylcyclopentadienone with certain cyclic 1,3-diene systems has shown that tetraphenylcyclopentadienone reacts with cyclopentadiene to form an addition compound which, by hydrogenation, decarbonylation, and dehydrogenation, can be converted to 4,5,6,7-tetraphenylhydrindene. Tetraphenylcyclopentadienone does not react with furan, pyrrole, N-methylpyrrole, or thiophene even under very vigorous conditions.

(21) Prepared from N-methylammonium mucate; Pictet, *Ber.*, **37**, 2792 (1904).

(22) Proposed as a catalyst for Diels-Alder reactions: Wasserman, French Patent 838,454 (1939); C. A., **33**, 7819 (1939).

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RECEIVED DECEMBER 16, 1941

(19) Prepared from furoic acid: "Organic Syntheses," Coll. Vol. I, p. 269.

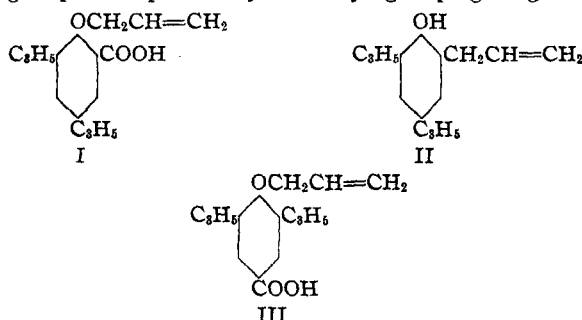
(20) Prepared from ammonium mucate: "Organic Syntheses," Coll. Vol. I, p. 461.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Rearrangement of O-Crotyl-3,5-dichlorosalicylic Acid and Related Compounds

BY D. S. TARBELL AND J. W. WILSON¹

In studying the behavior of allyl ethers of various substituted phenols, Claisen found² that allyl ethers of substituted salicylic acids, such as O-allyl-3,5-diallylsalicylic acid (I), undergo a smooth rearrangement during which the carboxyl group is displaced by the allyl group, giving II.



Carbon dioxide is evolved in the theoretical amount, and the reaction commences at about 100°—a lower temperature than is necessary for the ordinary Claisen rearrangement. Claisen also observed that carbon dioxide can be displaced smoothly from the para position, illustrated by 4-allyloxy-3,5-diallylbenzoic acid (III), which forms 2,4,6-triallylphenol quantitatively.

O-Allylsalicylic acid and similar compounds with a free ortho position were reported by Claisen to rearrange exclusively to the free ortho position without loss of carbon dioxide. O-Allyl-o-cresotic acid, which has a free para position, gave the displacement product, 2-allyl-6-methylphenol, and the para product, 3-methyl-5-allylsalicylic acid, in a ratio of three to one. This latter result would indicate that when the normal rearrangement is possible, it and the displacement reaction go at similar rates. Claisen's observa-

(1) Sherman Clarke Fellow, 1941–1942.

(2) Claisen and Eisleb, *Ann.*, **401**, 21 (1913); Claisen, *ibid.*, **418**, 69 (1918). For summary of the Claisen rearrangement, cf. Tarbell, *Chem. Rev.*, **27**, 495 (1940).