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Some Derivatives of Pentaphenylcyclopentadiene

by

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Some Derivatives of Pentaphenyleyclopentadiene

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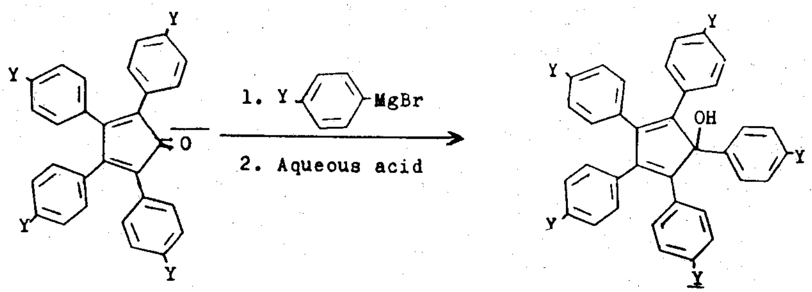
In this work, pentaphenylcyclopentadienols and pentaphenylcyclopentadienylbromides having methoxyl and chloride on the benzene rings, have been synthesized. Reaction between pentaphenylcyclopentadienylbromides and silver dust gave pentaphenylcycpentadienyl free radicals in solution.,

INTRODUCTION

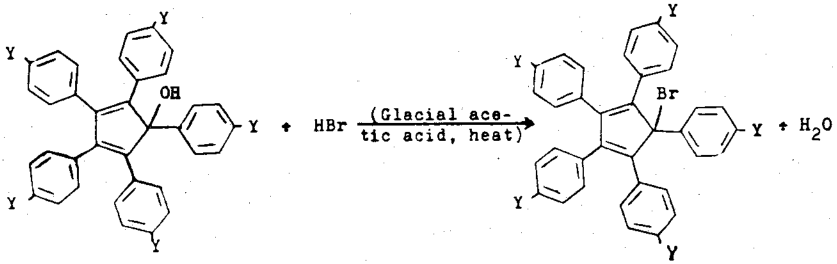
Pentaphenylcyclopentadienol, pentaphenylcyclopentadienylbromide and pentaphenylcyclopentadienyl free radical have been synthesized by Ziegler and Schnell [1]. Usuing the same methods but different starting materials, substituted pentaphenylcyclopentadienols, pentaphenylcyclopenradienyl bromides and pentaphenylcyclopentadienyl free radicals have been synthesized. Reaciton between substituted tetracysclones (tetraphenylcyclopentadienones) and substituted phenylmagnesium bromide (Grignard reagent) gave substituted pentaphenylcyclopentadienols (substituents are at the para- position of the benzen rings and for one compound all substituents are the same):



$Y = OCH_3(I);\ CH_3\ (II);\ Cl\ (III)$

Necessary tetracyclones for these reations, have been made by Becker and his coworkers [2], [3], [4], using Dilthey and Quint's method [5].

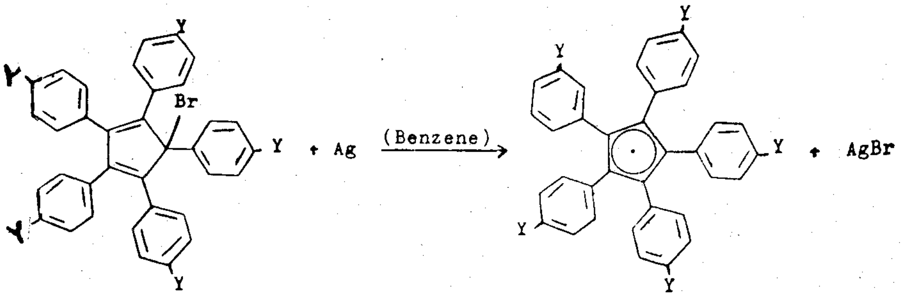
Bromine substitutions of OH in pentaphenylcyclopentadienols, have been accomplished by means of dry hydrobromic acid in glacial acetic acid as solvent:



Y = OCH_3 (IV); CH_3 (V); CI (VI)

Accordingto Dilthey and Quint's method, starting compound of tetracyclones are benzils and dibenzylketones. In order to make benzils, Staudinger's method [6], or, benzoin condensation of proper aldehyde then oxidation of benzoin to benzil; to make dibenzylketones Conant and Blatt's method have been used [7].

Reaction between cyclopentadienylbromides and silvder dust in benzene gave pentaphenylcyclopentadienyl free radicals:



Y = OCH_3 (VII); CH_3 (VIII); CI (IX)

EXPERIMENTAL

Penta (p-anisyl)cyclopentadienol (I). In a 1 100 ml threee neck round bottom flask, equipped with reflux condenser which was protected with a $CaCl_2$ bulb at the top, mechanical stirrer and dropping funnel, were introduced 2 .4 g (0 .10 atomgram) of magnesium turnures* and 20 ml of absolute ether. Into dropping funnel was put a solution of 18 .7 g (0 .10 moles) of p-bromoanisole in 60 ml of absolute ether. Inside of the apparatus was swept out with dry nitrogen, mechanical stirrer was started and a "Grignard reagent" was prepared as known manner. Into this Griggnard reagent, a suspension of 15 g(30 mmoles) of tetra (p-anisyl) cyclopentatadienone in 100 ml of absolute ether was poured immediately. Dark reaction mixture was stirred at room temperature to change pale yellow (about one hour). Flask was cooled in an ice bath, into the flask first ice, then 2 N HCI was added for decomposing complex which is formed. Yellow reaction mixture was filtered, washed several times with water and 13 .3 g crude product was obtained m.p. 190–5 °C. Recrystallization of this from benzene-hexane mixture (1:1, v:v) gave rise 12 .2 g (20 mmoles, 66 %) of yellow crystalline (I), m.p. 223–4 °C. This compound shows a yellow-green fluorescence under UV.

Anal. calcld. for $C_{40}H_{36}O_6$: C, 78 .40; H, 5 .93,
Found: C, 78 .73, 77 .95; H, 6 .23, 6 .01.

Penta (p-tolyl)cyclopentadienol (II). In a 100 ml three neck round bottom flask fitted with reflux condenser which was proctected with a $CaCl_2$ bulb at the top, mechanical stirrer and dropping funnel, were introduced 0 .70 g (29 X 10^{-3} atomgram) of magnesium turnures* and 25 ml of absolute ether. Into dropping funnel was put a solution of 5 .0 g (29 mmoles) of p-bromotoluene in 25 ml of absolute ether. Inside of the apparatus was swept out with dry nitrogen. mechanical stirrer was started and a "Grignard reagent" was prepared as known manner. Into this solution a suspension of 4 .0 g (9 .0 mmoles) of tetra (p-tolyl)cyclopentadienone in 30 ml of absolute ether was poured immediately and was stirred at room temperature about one hour. At the end of the reaction,

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* Purified magnesium by sublimation was used.

dark color was discharged and turned to gray. Flask was cooled in an ice bath, into the flask first ice, then 2N HCI was added to decompose complex which was formed. Ether layer was separated, aqueous layer extracted once with 50 ml of ether, ether solutions were combined, washed with dilute aqueous sodium carbonate, and was dried with anhydrous sodium sulfate. Removal of ether was left an oil which was triturated with methanol to solidify as a gray material. This was filtered, washed with methanol. Recrystallization of this from methanol afforded 3 .3 g (6 .1 mmoles, 68 %) of colourless microcrystalline (II), m.p. 206-8 °C. This compound has a blue fluorescence under UV.

Anal. calcld. for $C_{40}H_{36}O$: C, 90.19; H, 6 .81,

Found: C, 89 .76; H, 6 .73.

Penta (p-chlorophenyl)cyclopentadienol (III). In a 100 ml three neck round bottom flask, equipped with reflux condenser which was pratected with a $CaCl_2$ tube at the top, mechanical stirrer, and dropping funnel, were introduced 2 .7 g (0 .11 atom gram) of magnesium turnures* and 40 ml of absolute ether; into dropping funnel was put a solution of 19 .2 g (0 .10 moles) of p-bromochlorobenzene in 40 ml of absolute ether. Inside of the apparatus was swept out with dry nitrogen, mechanical stirrer was started and a "Grignard reagent" was prepared as known manner. Flask was cooled in an ice bath and a suspension of 12 .7 g (24 mmoles) of tetra (p-chlorophenyl)cyclopentadienone in 100 ml of absolute ether was added immediately. Ice bath was removed under the flask and was stirred at room temperature for three hours, dark color of the mixture was discharged at the end of the reation. Flask was cooled in an ice bath, first ice. then 2N HCI was added to decompose the complex which is formed. Ether layer which was brown in color, was separated, aqueous layer extracted once with 50 ml of ether, ether solutions were combined, washed with dilute aqueous sodium carbonate solution, dried over anhydrous sodium sulfate, ether was removed to leave a brown oil. In this oil 100 ml of methanol was added stirred well and was put in a refrigerator to stand overnight Separated brown crystals were filtered and washed with cold methanol to give 11 .9 g of crude product which was melted at 229 .232 °C.

Recrystallization of this from methanol gave rise 10 .8 g (17 mmoles, 70 %) of light gray, microcrystalline (III), m.p. 231–3 °C. This compound has a pale blue fluorescence under UV.

Analytical sample was prepared by several recrystallization from methanol and had melting point 233.5–234 .5 °C.

Anal. calcld. for $C_{35}H_{21}OC_5$: C, 66 .22; 3 .34; Cl, 27 .92,
Found: C, 66 .37; H, 3 .42; Cl, 27 .90.

Penta (p-anisyl)cyclopentadieny bromide (IV). In a 100 ml two neck round bottom flask equipped with reflux condenser and gas inlet tubing, were introduced 8 g (13 mmoles) of penta (p-anisyl) cyclopentadienol and 50 ml of benzene. In order to divide solid material finely, flask was heated to dissolve all material, then cooled rapidly in an ice bath while brisk shaking. Dry HBr gas was bubled in the mixture to saturation (about half hours), then was allowed to stand at room temperature for two hours (HBr gas was not bubled while standing) Excess of HBr and half of benzene was removed under reduced pressure (15–20 mm Hg). Remaining material was transferred in an evaporating dish, all of benzene was removed on a water bath to leave a brown oil which was triturated with heptane and was cooled to transform a brown solid. This was filtered and washed with heptane to give 7 .2 g of crude product, m.p. 200–206 °C. Recrystalization of this from hepatane afforded 6 .8 g (10 mmoles, 77 %) of (IV) which was melted at 214–7 °C (decomposed). This substance has not fluorescent property.

Anal. calcld. for $C_{40}H_{35}O_5Br$: C, 71 .11; H, 5 .22; Br, 11 .83,
Found: C, 71 .58; H, 5 .50; Br, 12 .80.

Penta (p-tolyl)cyclopentadenyl bromide (V). In a 100 ml two neck round bottom flask fitted with reflux condenser and gas inlet tubing, were introduced 9 .5 g (17 .5 mmoles) of penta (p-tolyl)cyclopentadienol and 50 ml of benzene. Flask was heated to dissolve all material. Dry HBr gas was bubled in the solution at room temperture for two hours for saturation, then was allowed to stand one hour more. Reaction mixture was transferred in an evaporating dish. Excess of HBr and benzene were removed on a water bath to leave a dark brown oil. Heptane was added in this oil, stirred well and was put in a refringerator to stand overnight. Separated orange solid material was filtered and washed with cold heptane to give 8 .2 g of crude material, m.p. 213 –6 °C. Recrystallization of this from benzene-heptane mixture (1:1, v:v), gave rise 7 .2 g (12 mmoles, 67 %) of orange crystalline (V), m.p. 217–9 °C, which showed no fluorescence under UV.

Anal. cacld. for $C_{40}H_{35}Br$: C, 80 .66; H, 5 .92; Br, 13 .42.

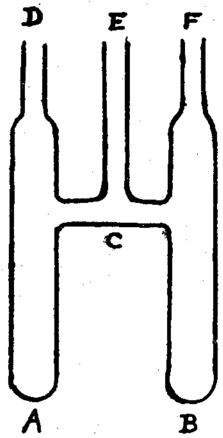
Found: C, 81 .00; H, 5 .96; Br, 13 .22.

Penta (p-chlorophenyl)cyclopentadienyl bromide (VI). In a 100 ml two neck round bottom flask fitted with reflux condenser and gas inlet tubing, were introduced 6.4 g (12 mmoles) of penta (p-chlorophenyl) cyclopentadienol and 40 ml of benzene. Flask was heated to dissolve all solid material and dry HBr gas was bubled in the solution in a moderate rate while heating for two hours. Brown reaction mixture was tranferred in an evaporating dish and excess of HBr and benzene was removed on a water bath to leave a viscous and dark brown oil which was cooled in an ice bath was triturated with hexane to transform a yellow-brown solid. This was filtered and washed with cold hexane then recrystallized from benzene-cyclohexane mixture ((1:1, v:v), to give 5.5 g (7 .8 mmoles, 78 %) of yellow crystalline (IV) which was melted at 225–6 °C. (In order to get better yield, solution shold be leaved to stand overnight in a refrigerator). This compound has no fluorescent property.

Anal. calcld. for $C_{35}H_{20}BrCl_5$: C, 60 .25; H, 2 .89; Br, 11 .46; Cl, 25 .40.

Found: C, 60 .43; H, 3 .06; Br, 11 .94; Cl, 25 .15.

Formation of p-methtyl and p-chlorophenyl pentapheıylcyclopentadienyl free radicals (VII), (VIII) and (IX). These compounds were made in a H shaped reaction vessel according to Ziegler and Schnell [1], (Figure). In (A) part of the vessel was put benzene as solvent; in (B), were put a mixture of p-methoxyl or p-methyl or p-substituted pentaphenylcyclopentadienyl bromide (namely, (IV) or (V) or (IV) and 4 or 5 folded equivalent amount of silver dust. A piece of cotton wad which used as a filtre was set in (C) part of the vessel. Inside of the apparatus was cleaned



out from oxygen and water vapour by means of several times evacuating then filling it with oxygen free dry nitrogen. (In order to remove trace amount of oxygen from commercial nitrogen, this was passed first over copper filings heated at 450-500 °C, then passed in benzophenoneketyl which has free radical character and ambitious to oxygen and water). 15–20 mm Hg vacuum was applied to the system then (D), (E) and (F) side tubings were sealed by melting. Solvent was distilled from (A) to (B) heating up (A) on a water bath while cooling down (B) in an ice bath. Coloration of solvent shows commencement of reaction. Whole apparatus was plunged in a water bath, having temperature 50 °C. for 15 hours. Mixture was filtered through the cotton wad tilting the apparatus properly and heating up (B) while cooling down (A). Solution containing free radical in (A), was condensed by evaporating solvent as above, to leave an uncrystallizable dark and viscous oil. Color of free radical solutions which were obtained: (VII) dark green, (VII) dark blue, (IX) violet.

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ÖZET

Bu çalışmada, benzen halkasının para– yerlerinde metoksil–, metil– ve klor– bulunan pentafenil– siklopentadienoller ve pentafenil– siklopentadienil–bromürler elde edilmiş ve özellikleri incelenmiştir. Ayrıca, pentafenil–siklopentadienil bromürlerin gümüş tozuyla etkileşmesinden, pentafenil siklopentadienil serbest radikalleri çözeltiler halinde elde edilmiştir.

AVIS IMPORTANT

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" sera publiée dorénavant sous forme de fascicules à l'arrivée de chaque article. Le tome 13 de la série B, continuant par ce fascicule, sera complété par le dernier fascicule à paraître avant le 31 décembre 1966.

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