SYNTHESIS OF CERTAIN SUBSTITUTED TRIPHENYLCARBINOLS

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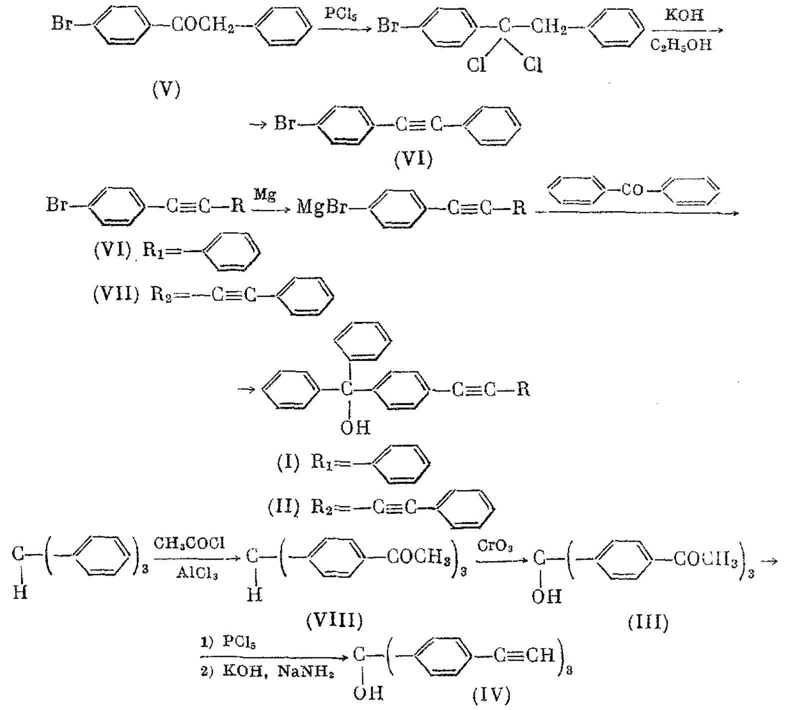
The purpose of this work was to develop methods of synthesizing substituted triphenylcarbinols, starting materials for the production of highly unsaturated hexaphenylethanes, the ability of which to dissociate into free radicals will be studied later:



The scheme presents the synthesis of diphenyl-p-(phenylethynyl)-phenylcarbinol (I), diphenyl-p-(phenylbutadiynyl)-phenylcarbinol (II), tris-(p-acetylphenyl)-carbinol (III), and tris-(p-ethynylphenyl)-carbinol (IV). The synthesis of all the carbinols presented substantial difficulties. The p-bromotolane (VI), starting material for the synthesis of (I), is produced from p-bromodeoxybenzoin (V) by replacement of the carbonyl oxygen by chlorine under the action of phosphorus pentachloride, followed by dehydrochlorination of the crude chlorides with an alcohol solution of potassium hydroxide. Yield of (VI) ~60%. The ketone (V) was produced by condensation of phenylacetyl chloride with bromobenzene according to Friedel-Crafts. A sufficiently high yield of (V) is achieved only when an excess of bromobenzene is used as the solvent.

In the synthesis of the carbinol (I) we attempted to use the method used in [1], consisting of the condensation of benzophenone with the dilithium derivative formed in the interaction of butyllithium with p,p-dibromotolane. However, as a result of the lower mobility of the bromine in (VI), this method proved unsuitable.

We decided to use the Grignard reaction to achieve the appointed goal. It should be mentioned that in contrast to bromobenzene, (VI) does not react at all with magnesium, either in abs ether or in tetrahydrofuran. An organomagnesium compound could be produced only by using a method of prolonged activation, in which (VI) and ethylene bromide [5 moles ethylene bromide per mole of (VI)] react simultaneously with magnesium. The yield of the Grignard reagent in this case is ~ 60% (according to the data of gas-liquid chromatography).

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The interaction of p-magnesiumbromotolane with benzophenone also proceeds with great difficulty and only when the reaction time is increased to six days (at 20-40°) does the yield of the carbinol increase to 71%, calculated on the basis of the Grignard reagent formed. An additional and extremely important condition for the formation of the carbinol (I) in a form sufficiently convenient for purification is the use of magnesium in amounts strictly corresponding to the stoichiometry. In the presence of excess magnesium, simultaneously with the carbinol (I), substantial amounts of benzpinacone are formed; it could not be entirely removed from the product needed either by recrystallization or by chromatography. The carbinol (I) was freed of tolane, p-bromotolane (VI), and benzophenone by chromatography on Al_2O_3 (activity II). The interaction of p-bromodiphenyldiacetylene (VII) with magnesium and then with benzophenone proceeds analogously. The use of prolonged activation made it possible to obtain the carbinol (II) in 52% yield. (VII) was produced according to the method of [2] by condensation of p-bromophenylacetylene with γ-bromophenylacetylene in the presence of cuprous chloride and ethylamine.

On account of the difficulties encountered in the synthesis of (I) and (II), we decided to introduce substituents into the compound with an already prepared triphenylmethane skeleton. In the oxidation of tri-(p-acetylphenyl)methane (VIII) with chromic anhydride in glacial acetic acid, the carbinol (III) was obtained in good yield. The introduction of electron-acceptor acetyl groups into triphenylmethane facilitates the nucleophilic reaction of oxidation. (VII) was produced according to the procedure of [3], somewhat modified. Under the action of phosphorus pentachloride on the carbinol (III), with dehydrochlorination of the mixture of chlorides thereby formed, the carbinol (IV) can be obtained, although in low yield. Dehydrochlorination is conducted in two steps – first with powdered potassium hydroxide in ether, then with sodium amide in liquid ammonia.

EXPERIMENTAL

p-Bromodeoxybenzoin (V). A mixture of 20 g phenylacetic acid and 160 g PCl_3 was heated for 1 h on a boiling water bath. The acid chloride was decanted from the residue of phosphoric acid, redistilled under water jet-pump vacuum, diluted with 150 ml abs. bromobenzene, and gradually added with cooling to a mixture of 100 ml bromobenzene and 91 ml aluminum chloride. The resultant mixture was heated for 1 h at 60° and decomposed with a mixture of ice and conc. HCl. The aqueous layer was extracted with a mixture of ether and benzene. The organic solution was washed with water, soda, dried over $MgSO_4$, evaporated, and the residue redistilled under vacuum. Yield of (V) 70%; b.p. 185-188° (3 mm); m.p. 112-112.5° (methanol). Found %: C 61.36; H 3.99; Br 29.20. $C_{14}H_{11}OBr$. Calculated %: C 61.11; H 4,03; Br 29.03. The redistilled product can be used immediately for the production of (VI).

p-Bromotolane (VI). A mixture of 100 g (V), 150 g PCl_3, and 420 ml abs. benzene was heated to 70° and exposed for 1.5 h. The mixture was then decomposed with 220 ml of a 30% KOH solution with intensive mixing and cooling with a mixture of ice and salt. The organic layer was removed. After the usual treatment, the benzene solution of the chloride was added to 125 g KOH in alcohol and boiled for 2 h. The KCl residue was filtered off, the solution evaporated to a minimum volume, and the residue diluted with water. (VI) was extracted with a mixture of ether and benzene, washed, dried over $CaCl_2$, evaporated, and redistilled under vacuum. The fraction with b.p. 170-185° (3 mm) – (71.09 g) was dissolved in the minimum amount of a benzene-heptane mixture (1:1) and purified on Al_2O_3 (activity II). We obtained 66.8 g (VI), yield 61%; m.p. 81° (methanol). Found %: C 66.04; H 3.65; Br 31.84. $C_{14}H_9Br$. Calculated %: C 65.39; H 3.53; Br 31.08. IR spectrum (cm^{-1}): $-C{\equiv}C-$ 2212 (w).

p-Bromodiphenyldiacetylene (VII). Produced according to [2].

Diphenyl-p-(phenylethynyl)-phenylcarbinol (I). To 5.7 g magnesium shavings, dried at 90-100°, we added one to two crystals of iodine. After sublimation of the iodine and cooling, we added 50 ml abs. ether and 2-3 ml of a mixture of 10 g (VI) and 17.2 ml ethylene bromide in 60 ml abs. ether. After the beginning of the reaction, the remaining solution was added over a period of an hour at a rate such that the ether boiled weakly. The mixture was boiled for 30 min for completion of the reaction, and 7.3 g benzophenone in 30 ml abs. ether was added to the solution of Grignard reagent obtained (of the color of strong tea) over a period of an hour with ice water cooling. After mixing for six days at 20-40°, the mixture was decomposed with 10% HCl, the ether solution treated as usual, evaporated, and chromatographed on Al_2O_3 (activity II). Fraction I, eluent benzene — tolane, (VI), benzophenone; from fraction II, eluent ether:benzene (1:1) we obtained 5.37 g (I) with m.p. 117,5-118° (alcohol); yield 71%. Found %: C 89.96; H 5.65. $C_{27}H_{20}O$. Calculated %: C 89.97; H 5.59. IR spectrum (cm^{-1}): $-C{\equiv}C-$ 2226 (w); O—H 3626 (s).

Diphenyl-p-(phenylbutadiynyl)-phenylcarbinol (II). Produced analogously to (I) from (VII) in 52.0% yield, m.p. 142.5-144° (alcohol). Found %: C 90.70; H 5.18. $C_{29}H_{20}O$. Calculated %: C 90.59; H 5.24. IR spectrum (cm^{-1}): $-C \equiv C-$doublet 2142 and 2202; O – H 3603 (s).

Tris-(p-acetylphenyl)-carbinol (III). Into a solution of 50 g (VIII) in 300 ml glacial acetic acid we gradually introduced 45 g CrO_3, heated for 8 h at 80°, poured out into two liters of water, and neutralized with soda. The precipitate of (III) was removed, washed with water, and dried over KOH in a vacuum desiccator. The solid product was dissolved in 1 liter of hot $CHCl_3$, freed of chromium salts on Al_2O_3 (activity I), and evaporated to dryness. We obtained 21.6 g (III), yield 40.5%; m.p. 180-182° (alcohol). Found %: C 77.71; H 5.75. $C_{25}H_{25}O_4$. Calculated %: C 77.70; H 5.74. IR spectrum (cm^{-1}): $-C=O$ 1702 (s), O – H 3617 (m).

Tris-(p-ethynylphenyl)-carbinol (IV). A mixture of 20 g (III), 86.2 g PCl_5, and 300 ml abs. benzene was heated to 50° and exposed for 35 min. The mixture was decomposed with 430 ml of a 30% KOH solution with intensive mixing and cooling with a mixture of ice and salt. The upper organic layer was removed and dried, passing through a column with Al_2O_3 (activity II). The column was washed with ether. To the ether-benzene solution of the chlorides was added 30 g KOH (powder), then the reaction mass was mixed for 5 h at room temperature, 2 h at 40°, and filtered through a thin layer of Al_2O_3 (activity II). The solution of chlorides was gradually poured into a solution of sodium amide in liquid NH_3 (7 g Na per liter of NH_3). After 3 h it was decomposed with 12 g of NH_4Cl. After evaporation of the NH_3, water was added, the organic layer was removed, combined with the ether extracts from the aqueous layer, washed with water, dried by passing through Al_2O_3 (activity II), evaporated, and chromatographed on Al_2O_3 (activity I). Successive elution was conducted: fraction I – ether:benzene (1:1), fraction II – ether:benzene (1:1), fraction III – ether:benzene (2:1), ether. After evaporation and treatment with petroleum ether, 2.4 g of crude (IV) was obtained from fraction III, yield 14.2%; m.p. 128° (purified chromatographically on Al_2O_3, activity II, eluent – ether). Found %: 90.20; H 5.19. $C_{25}H_{19}O$. Calculated %: 90.33; H 4.85. IR spectrum (cm^{-1}): $C \equiv C$ 2112 (m); $\equiv C-H$ 3307 (s); O–H 3603 (m).

CONCLUSION

Methods were developed for synthesizing triphenylcarbinol derivatives, possessing acetyl groups or fragments with a triple bond as substituents.

LITERATURE CITED

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