Summary

1. Four α-benzylindoles have been synthesized by a method based upon the reaction between α-arylamino ketones and arylamines.

2. In this connection a new type of ketone has been synthesized.

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Sterically Hindered Tertiary Carbinols. 2,4,6-Tribromotriphenylcarbinol[1]

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Only a little work[2] has been done on tertiary carbinols which have substituents in the 2,6 positions of one of the phenyl groups. Yet these compounds offer an interesting field, not only in the phenomenon of steric hindrance, but also in the chemistry of free radicals for which they are intermediates. We have determined the conditions for preparing 2,4,6-tribromotriphenylcarbinol. In so doing our study has developed two interesting points: namely, the addition of the Grignard reagent to the sterically hindered ester is far better if carried out in a mixture of chlorobenzene and ether as a solvent than in ether alone; and the yield of tertiary carbinol by the Grignard reaction is better through the addition of the Grignard reagent to the ester than to the ketone, although it would be possible to expect that the ketone is an intermediate phase of the reaction. Of further interest is the fact that a steric hindrance effect was not carried over into the behavior of the free radical, for a solution of 2,4,6-tribromotriphenylmethyl in benzene lost its color readily on exposure to air and changed its intensity of color on heating or cooling.

In view of the work of Boyd and Hatt,[3] reporting that the ketone was an intermediate step in the preparation of a tertiary carbinol from an ester, we had expected that better yields would be obtained if we started with the ketone, a compound obtained more easily than the ester. This expectation was not realized.[4] With 2,4,6-tribromobenzophenone only a trace of

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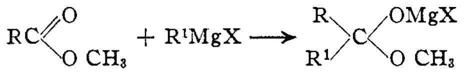
[1] From a portion of the thesis of Lawson V. Peakes, Jr., presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

[2] Lund, THIS JOURNAL, **49**, 1346 (1927), prepared several diorthomethoxy derivatives but could obtain no crystalline chloride from them. Reich, *Bull. soc. chim.*, [4] **21**, 219 (1917), prepared 2,6-dichlorotriphenylcarbinol in 6.3% yield from the diortho ester and phenylmagnesium bromide. We were unsuccessful in repeating Reich's experiment but believe that this may be due to using the methyl instead of the ethyl ester.

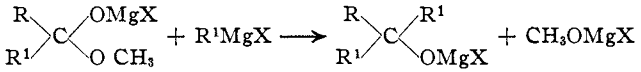
[3] Boyd and Hatt, *J. Chem. Soc.*, 898 (1927).

[4] Lund[2] found that the yield of carbinol from methylbenzoate and 2,4-dimethoxymagnesium iodide was better than that obtained by Kauffmann and Kieser, *Ber.*, **45**, 2335 (1912), who used the same Grignard reagent with the corresponding ketone. No other instance was found where a tertiary aromatic carbinol had been prepared by both methods in a yield sufficiently low to indicate that real difficulty with the reaction was encountered.

crystalline product could be found whereas with the methyl ester of tribromobenzoic acid a 28% yield of the carbinol was obtained. This result would appear to favor, in our particular reaction, at least, the general mechanism given in equations (1) and (2), which was first suggested by Grignard.[5]



$$\mathrm{RC}\begin{matrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O\,CH_3}\end{matrix} + \mathrm{R^1MgX} \longrightarrow \begin{matrix}\mathrm{R}\searrow\\ \mathrm{R^1}\nearrow\end{matrix}\mathrm{C}\begin{matrix}\nearrow \mathrm{OMgX}\\ \searrow \mathrm{O\,CH_3}\end{matrix} \qquad (1)$$



$$\begin{matrix}\mathrm{R}\searrow\\ \mathrm{R^1}\nearrow\end{matrix}\mathrm{C}\begin{matrix}\nearrow \mathrm{OMgX}\\ \searrow \mathrm{O\,CH_3}\end{matrix} + \mathrm{R^1MgX} \longrightarrow \begin{matrix}\mathrm{R}\searrow\\ \mathrm{R^1}\nearrow\end{matrix}\mathrm{C}\begin{matrix}\nearrow \mathrm{R^1}\\ \searrow \mathrm{OMgX}\end{matrix} + \mathrm{CH_3OMgX} \qquad (2)$$

The study of the preparation and properties of sterically hindered tertiary carbinols and carbyls will be continued in this Laboratory.

Experiments

Methyl 2,4,6-Tribromobenzoate.—2,4,6-Tribromoaniline was diazotized and treated with cuprous cyanide solution, using the same procedure which Olivier[6] employed in the preparation of the corresponding 2,6-dibromo compound. Hydrolysis of the nitrile was effected by the method of Montagne and van Charante[7] using sulfuric acid. The melting point of the resulting acid was 187–188°. The values for the same acid obtained by Montagne[8] and by Sudborough[9] are 194 and 187°, respectively. Conversion to the ester was accomplished by means of the silver salt and methyl iodide. When recrystallized from petroleum ether the ester melted at 67°, which is the same as the value obtained by Sudborough.[9]

2,4,6-Tribromotriphenylcarbinol.—Phenylmagnesium bromide was prepared[10] by the gradual addition, during thirty minutes, of 13 g. (0.082 mole) of bromobenzene in 10 cc. of ether to 2 g. of magnesium turnings in 30 cc. of the same solvent, the mixture being refluxed for thirty minutes after the addition had been completed. Four grams (0.011 mole) of the methyl ester dissolved in 20 cc. of chlorobenzene[11] was added during thirty minutes. The reaction flask was then set in an oil-bath maintained at 80–85° and the contents refluxed for four hours. After decomposing the reaction mixture and drying the ether–chlorobenzene solution over calcium chloride, the solvent was evaporated in a current of air. The crystalline residue was washed with petroleum ether, thereby yielding 1.8 g. of a solid melting at 105–110°. When recrystallized from ligroin, b. p. 58–70°, 1.5 g. (28%) melting from 115–116° was recovered. Further crystallization from the same solvent raised the melting point to 116.5–117.5°. An analysis of the halogen by the Parr bomb method showed 48.55% of bromide; calcd. for $C_{19}H_{13}OBr_3$, 48.24%. The carbinol caused a red color in concentrated sulfuric acid. When a drop of 60% perchloric acid was added to an acetic anhydride solution of the carbinol a bright red color formed.

Unsuccessful attempts to prepare the carbinol were made by refluxing the ester for five hours with the Grignard reagent, under the same conditions described above with the single exception that chlorobenzene was replaced by ether. The ester was re-

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(5) Grignard, *Compt. rend.*, **132**, 336 (1901); *Ann. chim.*, **24**, 473 (1901).

(6) Olivier, *Rec. trav. chim.*, **43**, 872 (1924).

(7) Montagne and van Charante, *ibid.*, **31**, 336 (1912).

(8) Montagne, *ibid.*, **27**, 351 (1908).

(9) Sudborough, *J. Chem. Soc.*, **67**, 596 (1895).

(10) Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923).

(11) The use of chlorobenzene was suggested by the observation of Gilman and St. John, *Rec. trav. chim.*, **49**, 222 (1930), that this solvent accelerated the addition of the Grignard reagent to benzonitrile.

covered unchanged. Upon repeating this experiment and refluxing for twenty hours no crystalline product was obtained.

2,4,6-Tribromotriphenylmethyl.—Boiling the carbinol with acetyl chloride failed to convert it to the chloride. When allowed to react in carbon tetrachloride with phosphorus pentachloride, a product was obtained which dissolved in anhydrous ether and gave a yellow-orange color when treated with silver. When warmed the color became red, and when cooled yellow. The solution was decolorized when exposed to air.

Reaction of 2,4,6-Tribromobenzophenone with Phenylmagnesium Bromide.—Tribromobenzophenone was prepared by the method of Montagne[12] from benzoyl chloride and 1,3,5-tribromobenzene. The product had a melting point of 146–147°. The value given by Montagne was 147°. The Grignard reagent was prepared as before from 6.5 g. (0.041 mole) of bromobenzene and 1 g. of magnesium in 15 cc. of anhydrous ether. A solution of 4.5 g. (0.011 mole) of 2,4,6-tribromobenzophenone in 10 cc. of chlorobenzene was added. Since only one mole of Grignard reagent could be added to the ketone instead of the two which were made to react with the ester, the quantity of bromobenzene was reduced in this experiment by a proportionate amount. The ketone was also less soluble and the last portion was, therefore, washed into the reaction flask with a mixture of 5 cc. of ether and 2 cc. of chlorobenzene. Otherwise the conditions were exactly the same as in the experiment with the ester. After refluxing in an oil-bath as before at 80–85° for four hours the solution was decomposed as usual and the ether layer dried over anhydrous potassium carbonate. The ether and chlorobenzene were removed as in the experiment with the ester. Only a tar remained which could not be crystallized. When the experiment was repeated, using half the amounts and refluxing for one hour, 0.1 g. of a crystalline material melting at 105–117° was obtained. A part of this material appeared to dissolve with a red color in sulfuric acid.

Attempted Preparation by Means of the Friedel–Crafts Synthesis.—Two grams of 1,3,5-tribromobenzene, 2 cc. of benzophenone chloride, and 2 g. of anhydrous aluminum chloride were refluxed in carbon disulfide solution in periods extending even to twenty-five hours without any reaction occurring.

Summary

The preparation of 2,4,6-tribromotriphenylcarbinol has been described.

Chlorobenzene has been found to favor the addition of the Grignard reagent to the ester of 2,4,6-tribromotriphenylbenzoic acid.

The yield of tertiary carbinol is better when the Grignard reagent is added to the ester than to the corresponding ketone. This fact is interpreted as favoring the idea that no ketone is present as an intermediate state.

The behavior of the free radical prepared from the sterically hindered carbinol was normal.

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[12] Montagne, *Rec. trav. chim.*, **27**, 353 (1908).