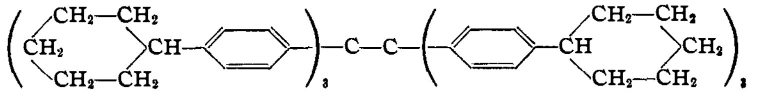
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Hexaalkylphenylethanes. III. Hexa-*p*-cyclohexylphenylethane and Hexa-*m*-tolylethane[1]

BY J. H. BROWN AND C. S. MARVEL

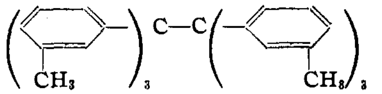
The work described in this communication was undertaken to extend the series of alkyl substituted hexaphenylethanes, in order that the effects of the size and position of the alkyl group on the dissociation of the ethanes could be determined. Previously, the para substituted compounds through the butyl series have been described,[2] but no *m*-substituted derivatives have been available for comparison.

Hexa-*p*-cyclohexylphenylethane (I) has been prepared in order to compare it with the closely related hexabiphenylethane[3] which is completely dissociated at room temperature. In a recent article, Neunhoffer[4] has described tri-*p*-cyclohexylphenylcarbinol, but he was apparently unable to obtain the corresponding chloride, and hence did not obtain the ethane. We have prepared the carbinol by treating *p*-cyclohexylphenylmagnesium bromide with diethyl carbonate. Our carbinol did not crystallize as did the product of Neunhoffer,[4] but we were able to obtain a crystalline tri-*p*-cyclohexylphenylchloromethane. Treatment of this compound in toluene with molecular silver by the method of Gomberg[5] gave a solution of the coupled product. The solution was a very deep red, and cooling the solution in a solid carbon dioxide–acetone mixture did not appreciably diminish the color. When air was admitted to the reaction mixture, the color was discharged instantly, and pure hexa-*p*-cyclohexylphenylmethyl peroxide was isolated from the reaction mixture.



I

Tri-*m*-tolylcarbinol was prepared in a similar manner from *m*-bromotoluene. It was an oily material which showed no tendency to crystallize. However, treatment with hydrogen chloride converted it into crystalline tri-*m*-tolylchloromethane. This was converted to hexa-*m*-tolylethane (II) in the usual manner. This ethane solution in toluene was orange in color. When this solution was cooled in a solid carbon dioxide–acetone bath, the color faded to a very light yellow. Exposure of the solution to air caused the orange color to be discharged, and the tri-*m*-tolylmethyl peroxide was isolated.



Experimental Part

p-Bromocyclohexylbenzene.—The method of Mayes and Turner[6] was used to prepare this compound, and the yield was about 30%, based on the cyclohexyl chloride. Considerable difficulty was encountered in getting a product free from *p*-dibromobenzene, which was formed from monobromobenzene under the influence of the aluminum chloride.

Tri-*p*-cyclohexylphenylchloromethane.—The Grignard reagent was prepared from 120 g. of *p*-bromocyclohexylbenzene and 12.15 g. of magnesium in about 325 cc. of dry ether. The yield was about 92%, as shown by titration.[7] To this solution was added 14.75 g. of diethyl carbonate in 100 cc. of ether. The reaction mixture was stirred for several hours, and then decomposed with a cold, saturated aqueous solution of ammonium chloride. The ether layer was separated, and this solvent evaporated. The residue was subjected to steam distillation until no more water-insoluble material was noted in a sample of the distillate. The carbinol was then taken up in ether and dried over anhydrous magnesium sulfate. Evaporation of this solvent left a straw-colored oil which would solidify in an ice-bath, but which did not really crystallize. About 50 g. of the crude carbinol was dissolved in 200 cc. of dry ether, 10 g. of anhydrous calcium chloride was added, and the solution was saturated with dry hydrogen chloride. Crystals began to separate from the ice-cold solution in about two hours. After allowing the mixture to stand at about 0° for approximately forty hours, the crystals were collected on a suction filter and washed with a little cold, low-boiling petroleum ether. Some additional material was obtained by concentration of the mother liquor. After three recrystallizations from dry ethyl acetate, the chloride was obtained as hard white crystals melting at 146–147°. The yield of crystalline compound was about 10%.

Anal. Calcd. for $C_{37}H_{45}Cl$: Cl, 6.76. Found: Cl, 6.56.

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[1] For the second communication in this series, see Schniepp and Marvel, THIS JOURNAL, **57**, 1635 (1935).

[2] Copenhaver, Roy and Marvel, *ibid.*, **57**, 1311 (1935).

[3] Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910).

[4] Neunhoffer, *ibid.*, **526**, 62 (1936).

[5] Gomberg, *Ber.*, **33**, 3150 (1900).

[6] Mayes and Turner, *J. Chem. Soc.*, 500 (1929).

[7] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

Hexa-*p*-cyclohexylphenylethane and Tri-*p*-cyclohexylphenylmethyl Peroxide.—A solution of 0.5244 g. (0.001 mole) of tri-*p*-cyclohexylphenylchloromethane in 10 cc. of dry toluene was shaken for about forty-eight hours with 0.04 g. of molecular silver in an atmosphere free from oxygen. Light was excluded by wrapping the tube in dark paper. When the silver chloride was allowed to settle after the shaking period, the solution was a deep red. Cooling this mixture in a solid carbon dioxide–acetone bath did not diminish appreciably the depth of the color, thus indicating a high degree of dissociation of the ethane.

When the tube was opened to the air, the color was discharged almost instantly. The solution was filtered, and most of the toluene was evaporated. The residue was crystallized from an ether–alcohol mixture. The pure peroxide melted at 151–152°.

Anal. Calcd. for $C_{74}H_{90}O_2$: C, 87.85; H, 8.98. Found: C, 87.62; H, 9.20.

Tri-*m*-tolylchloromethane.—This product was prepared by the same general procedure described above for tri-*p*-cyclohexylphenylchloromethane. From 86.5 g. of *m*-bromotoluene, 28 g. of crude tri-*m*-tolylcarbinol was obtained. This was a viscous, light yellow oil. Treatment with hydrogen chloride in ether solution gave the chloromethane. After recrystallization from low-boiling petroleum ether saturated with hydrogen chloride, the yield of product was 10 g.; m. p. 84–85°.

Anal. Calcd. for $C_{22}H_{21}Cl$: Cl, 11.05. Found: Cl, 11.18.

Hexa-*m*-tolylethane and Tri-*m*-tolylmethyl Peroxide.—The ethane was prepared as above from 0.3206 g. (0.001 mole) of the chloromethane in 10 cc. of toluene. This hydrocarbon solution was distinctly orange in color. Cooling the solution in a solid carbon dioxide–acetone bath caused the color to fade to a light yellow.

The tube was opened, and the contents filtered. The color was soon discharged. The toluene was evaporated, and the product was crystallized from a mixture of benzene and alcohol. The peroxide melted at 158–159°.

Anal. Calcd. for $C_{44}H_{42}O_2$: C, 87.66; H, 7.03. Found: C, 87.73; H, 6.90.

Summary

1. Hexa-*p*-cyclohexylphenylethane and hexa-*m*-tolylethane have been obtained in solution, and the corresponding peroxides have been characterized.

2. Comparisons of the colors of toluene solutions of equivalent concentrations indicate that hexa-*p*-cyclohexylphenylethane is less highly dissociated than is hexabiphenylethane, and that hexa-*m*-tolylethane is dissociated to about the same extent as hexa-*p*-tolylethane.

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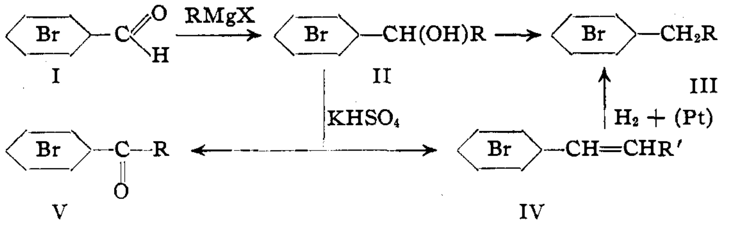
[Contribution from the Chemical Laboratory of the University of Illinois]

Hexaalkylphenylethanes. IV. Preparation of Some Alkylbromobenzenes[1]

By J. H. Brown and C. S. Marvel

In connection with the study of the effect of alkyl groups on the dissociation of hexaarylethanes, considerable work has been expended on a study of the preparation of a series of alkylbromobenzenes. Since it will likely be some time before the corresponding hexaalkylphenylethanes can be prepared from these intermediates, it seems wise to describe these synthetic experiments at the present time.

The general reaction which has been used in this work has been to treat *m*- or *p*-bromobenzaldehyde (I) with a Grignard reagent to yield the corresponding alkylbromophenylcarbinol (II), which was then reduced or dehydrated and reduced to yield the alkylbromobenzene (III). One interesting fact which was uncovered is that attempts to dehydrate the *p*-alkylbromophenylcarbinols (II) by heating them with potassium bisulfite leads to their oxidation to ketones (V), as well as to their dehydration to olefin derivatives (IV).



m-Bromoethylbenzene was prepared by the above general method, and also in 12% yields from ethylbenzene by nitration, reduction, acylation, bromination, hydrolysis and diazotization, followed by replacement of the diazonium group with hydrogen.

Experimental Part

***p*-Alkylbromophenylcarbinols.**—Using the usual technique for the Grignard reaction, *p*-bromobenzaldehyde was treated with various alkylmagnesium halides, and the carbinols purified by distillation under reduced pressure or, in the case of *p*-laurylbromophenylcarbinol, by re-

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[1] For the third communication in this series, see Brown and Marvel, This Journal, **59**, 1175 (1937).