Saponification of this compound was attempted, using a solution of potassium hydroxide in diethylene glycol. Starting material was recovered quantitatively.

The Reaction of *p*-Bromobenzoyltriethylbenzene with the Binary Mixture.—The binary mixture was prepared from 0.6 g. of magnesium and 2.55 g. of iodine in a mixture of 12 cc. of ether and 24 cc. of benzene. A solution of 3.5 g. of *p*-bromobenzoyltriethylbenzene in 20 cc. of ether was added slowly to the reagent. The reaction was completed in the manner described for *p*-bromobenzoylmesitylene. The 4,4'-di-(2,4,6-triethylbenzoyl)-biphenyl was recrystallized from absolute ethanol; yield, 0.35 g., m. p. 148–149°.

Anal. Calcd. for $C_{38}H_{42}O_2$: C, 85.34; H, 8.30. Found: C, 84.86; H, 8.01.

Reaction of *p*-Bromobenzoyltriisopropylbenzene with the Binary Mixture.—This reaction was carried out using 3.9 g. of *p*-bromobenzoyltriisopropylbenzene and the same quantities of other reagents as used in the preceding experiment. The same procedure was also used; yield of 4,4'-di-(2,4,6-triisopropylbenzoyl)-biphenyl, 0.55 g., m. p. 190–191°.

Anal. Calcd. for $C_{44}H_{54}O_2$: C, 85.99; H, 8.79. Found: C, 86.09; H, 8.80.

Reaction of *o*-Bromobenzoylmesitylene with the Binary Mixture.—*o*-Bromobenzoylmesitylene was treated with the binary mixture in the usual way. Heating and stirring of the solution was continued for two hours after the reaction appeared to be complete. The crude benzoylmesitylene, a deep yellow oil, was distilled *in vacuo* at 135–140° (4 mm.).

Treatment of this oil with fuming nitric acid for five minutes at 0° converted it into a trinitro derivative. It separated from alcohol in short needles melting at 202–204°.

Anal. Calcd. for $C_{16}H_{13}O_7N_3$: N, 11.69. Found: N, 11.78, 11.58.

The same derivative was obtained by nitration of a known sample of benzoylmesitylene.

Summary

4,4'-Dimesitoylbiphenyl has been prepared by the action of the binary mixture, Mg + MgI_2, on *p*-halobenzoylmesitylenes. *p*-Bromobenzoyl derivatives of 1,3,5-triethyl- and 1,3,5-triisopropylbenzene have been shown to undergo the coupling in a similar manner.

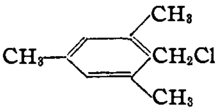
URBANA, ILLINOIS RECEIVED JULY 5, 1941

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

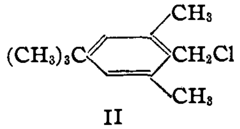
The Coupling Action of the Grignard Reagent. VII.[1] Di-*o*-methyl Benzyl Chlorides

BY REYNOLD C. FUSON, J. J. DENTON AND J. W. KNEISLEY

The equivalent conductance of 2,4,6-trimethylbenzyl chloride (I) in liquid sulfur dioxide is ten times that of benzyl chloride.[2] It seemed probable that the chemical reactivity of the former would show a corresponding augmentation. A wide difference already had been noted in the behavior of these two chlorides in the Sommelet aldehyde synthesis.[3] The present work was undertaken to determine the influence of the two ortho methyl groups on the tendency of the benzyl chloride to undergo coupling under the influence of the Grignard reagent. A study has therefore been made of the action of methylmagnesium iodide on α^2-chloroisodurene (I) and 2,6-dimethyl-4-*t*-butylbenzyl chloride (II).



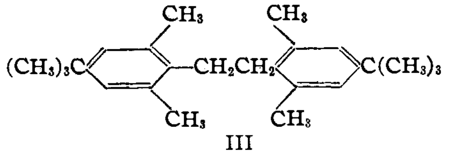
I



II

The conditions employed were those used earlier for benzal chloride and benzotrichloride.[4] α^2-Chloroisodurene gave an 86% yield of 1,2-dimesitylethane and a small amount of ethylmesitylene. 2,6-Dimethyl-4-*t*-butylbenzyl chloride underwent coupling similarly to give an 85% yield of 1,2-di-(2,6-dimethyl-4-*t*-butylphenyl)-ethane (III). Since benzyl chloride is coupled to a less extent (75%), it is clear that the ortho methyl groups not only offer no opposition to the condensation but actually favor it.

The 2,6-dimethyl-4-*t*-butylbenzyl chloride, a new compound, was prepared by chloromethylation of 1,3-dimethyl-5-*t*-butylbenzene. Since no isomeric chloro compound was detected, it was concluded that the chloromethyl group had gone exclusively into the position between the two methyl groups. The only by-product isolated was halogen-free and had the composition of the expected di-(2,6-dimethyl-4-*t*-butylphenyl)-methane. Reduction of the chloromethyl compound gave 1,2,3-trimethyl-5-*t*-butylbenzene (IV).



III

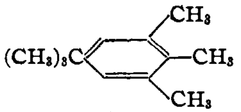
---

[1] For the sixth communication in this series see Fuson and Corse, THIS JOURNAL, **60**, 2063 (1938).

[2] Nauta and Dienske, *Rec. trav. chim.*, **55**, 1000 (1936).

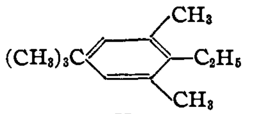
[3] Fuson and Denton, THIS JOURNAL, **63**, 654 (1941).

[4] Fuson and Ross, *ibid.*, **55**, 720 (1933).



IV

The ethane (III) yielded a dibromo and a tetranitro derivative. The ethyl derivative (V) yielded a dinitro derivative.



V

The latter had a marked odor of musk.

Experimental

The Action of Methylmagnesium Iodide on α^2-Chloroisodurene.—α^2-Chloroisodurene, prepared by the method of Nauta and Dienske,[2] was treated with methylmagnesium iodide under the conditions used by Fuson and Ross[4] for similar substances. The ethane was isolated as a white solid melting at 117–117.5°;[5] yield 86%.

The liquids from several runs were combined and distilled to obtain ethylmesitylene. It boiled at 212–214°; n^{20}D 1.5078.[6] The dinitro derivative melted at 109–111°.[7]

The Action of Methylmagnesium Iodide on 2,6-Dimethyl-4-*t*-butylbenzyl Chloride.—This experiment was conducted in the manner indicated for the coupling of α^2-chloroisodurene. The ethane was separated by use of a mixture of benzene and ether and the solution was evaporated to a small volume. Alcohol was then added and the ethane allowed to crystallize. It melted at 216–217°; yield 85%.

Anal. Calcd. for $C_{26}H_{38}$: C, 89.06; H, 10.94. Found: C, 89.22; H, 10.85.

Bromination of the ethane in chloroform solution gave the dibromo derivative. It crystallized from alcohol in the form of white needles melting at 190–191°.

Anal. Calcd. for $C_{26}H_{36}Br_2$: C, 61.41; H, 7.14. Found: C, 61.60; H, 6.94.

The mother liquor from the coupling was poured into water and the solution extracted with ether. The ether solution was washed with water to remove any alcohol and then dried over magnesium sulfate. The ether was concentrated by evaporation and the residue distilled. The 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene boiled at 125° (20 mm.); n^{20}D 1.5044.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.37; H, 11.63. Found: C, 88.30; H, 11.62.

One gram of the hydrocarbon was added dropwise to 40 cc. of yellow fuming nitric acid which was kept below 5°. After the mixture had stood at this temperature for one hour, it was poured on ice. The yellow dinitro derivative was recrystallized repeatedly from methanol; m. p. 128.5–129°.

Anal. Calcd. for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 10.00. Found: C, 59.59; H, 7.06; N, 10.18.

Chloromethylation of 1,3-Dimethyl-5-*t*-butylbenzene.—This condensation was carried out in the manner indicated for the preparation of α^2-chloroisodurene. The reaction time, however, was twelve hours instead of six and the temperature was 35° instead of 65°. From 162 g. of the hydrocarbon there was obtained 116.5 g. of the chloromethylation product, 1,3-dimethyl-2-chloromethyl-5-*t*-butylbenze. It boiled at 124–125° (6 mm.).

Anal. Calcd. for $C_{13}H_{19}Cl$: C, 74.08; H, 9.09. Found: C, 73.95; H, 8.84.

Considerable amounts were always obtained of the hydrocarbon, di-(2,6-dimethyl-4-*t*-butylphenyl)-methane. The yield of this compound was increased by higher temperatures. The compound crystallized from ethanol; m. p. 135°.

Anal. Calcd. for $C_{25}H_{36}$: C, 89.22; H, 10.78. Found: C, 89.02; H, 10.72.

1,2,3-Trimethyl-5-*t*-butylbenzene.—A solution of 10.5 g. of 1,3-dimethyl-2-chloromethyl-5-*t*-butylbenzene in 20 cc. of benzene was added, with stirring, over a period of one and a half hours to a mixture of 80 cc. of 10% sodium hydroxide and 12.5 g. of zinc dust. The stirring was continued for twenty-four hours. The hydrocarbon was isolated in the usual manner; b. p. 114–115° (17 mm.); n^{20}D 1.5049.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.12, 88.86; H, 11.51, 11.11.

1,2,3-Trimethyl-5-*t*-butylbenzene was converted to the dinitro derivative in the manner described for 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene. It melted at 136–136.5°.

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.62; H, 6.82. Found: C, 58.75; H, 6.81.

Summary

α^2-Chloroisodurene and 2,6-dimethyl-4-*t*-butylbenzyl chloride have been coupled by methylmagnesium iodide to give the corresponding ethanes in yields of 86 and 85%, respectively. The ortho methyl groups not only offer no opposition to the condensation, but actually favor it.

URBANA, ILLINOIS RECEIVED JULY 11, 1941

---

[5] Wenzel, *Monatsh.*, **35**, 954 (1914).

[6] Smith and Kiess, THIS JOURNAL, **61**, 284 (1939).

[7] Smith and Kiess. *ibid.*, **61** 989 (1939).