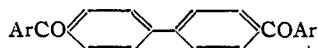


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

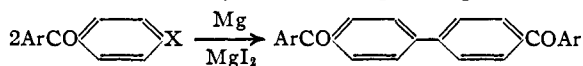
A New Method of Coupling Aryl Radicals: 4,4'-Diaroylbiphenyls

BY REYNOLD C. FUSON AND M. D. ARMSTRONG

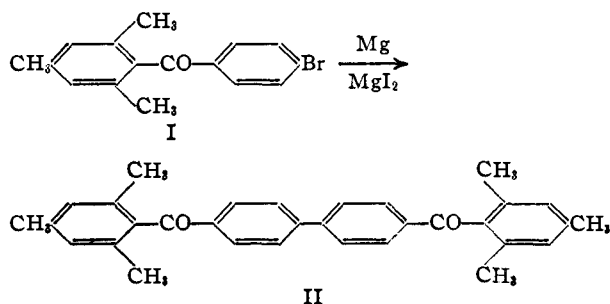
Diketones of the type



are vinylogs of the corresponding benzils, and for this reason were needed in a study of the production of enediols from benzils and related compounds. A somewhat unusual method of synthesis has been discovered. It consists in coupling two molecules of a *p*-halobenzophenone by the action of the binary mixture, Mg + MgI₂.¹



It had been shown earlier² that simple halobenzophenones were converted to pinacols by this reagent. In the present work, however, interest centered in sterically hindered benzophenones with which pinacol formation was hardly to be expected. *p*-Bromobenzoylmesitylene (I) is an example. When treated with the binary mixture it gave a 55% yield of 4,4'-dimesitylbiphenyl (II).



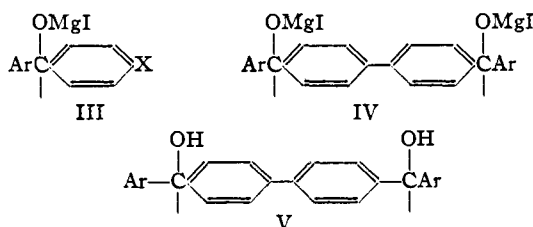
The structure of the biphenyl (II) was established by cleavage with phosphoric acid according to the general method of Klages and Lickroth³ to the known 4,4'-dicarboxybiphenyl.⁴ An unsuccessful effort was made to synthesize the diaroylbiphenyl from the acid chloride of 4,4'-dicarboxybiphenyl and mesitylene.

Since metallic magnesium alone did not produce coupling, it seems certain that the reaction involves the carbonyl group. This conclusion was supported by the observation that the reaction was independent of the halogen involved. *p*-Chlorobenzoylmesitylene behaved very much as did the bromo analog.

- (1) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 237 (1927).
- (2) Gomberg and Bailar, *ibid.*, **51**, 2229 (1929).
- (3) Klages and Lickroth, *Ber.*, **32**, 1549 (1899).
- (4) Doebner, *ibid.*, **9**, 272 (1876).

The reaction mixtures all gave indications of the presence of free radicals. They had intense red colors. Treatment of the reaction mixture with dilute hydrochloric acid produced a deep-red color that persisted indefinitely in the absence of oxygen but was discharged when the solution was exposed to the air.

This suggests that, in the ketyl (III) produced initially, the halogen atom has enhanced reactivity⁵ which facilitates coupling to a biketyl (IV). The red air-sensitive solution obtained by treatment with dilute hydrochloric acid would then be the corresponding biradical, V. By analogy with *p,p'*-biphenylene-*bis*-(diphenylmethyl),⁶ it seems probable that both IV and V may have the quinoid rather than the biradical structure. Attempts to demonstrate the existence of such a compound were fruitless. Treatment of the reaction mixture with acetic anhydride did, however, give a solid derivative which may serve as a clue to the structure of the product.



The idea that the para halogen atom is activated by the ketyl grouping finds support in the fact that no coupling was observed with *m*-bromobenzoylmesitylene. The ortho isomer also failed to undergo coupling; it was converted into benzoylmesitylene.

The reaction seems to be conditioned by the presence of ortho substituents. The results obtained with *p*-bromobenzoyl derivatives of 1,3,5-triethylbenzene and 1,3,5-triisopropylbenzene were similar to those described for the analogous mesitylene compound.

Experimental

The halobenzoyl derivatives of mesitylene, 2,4,6-triethylbenzene and 2,4,6-triisopropylbenzene⁷ were made by







- (5) This is similar to the activation of a para halogen atom in a triarylmethyl (Gomberg, *Ber.*, **40**, 1851 (1907); Gomberg and Blicke, *THIS JOURNAL*, **45**, 1765 (1923)).
- (6) Müller and Müller-Rodloff, *Ann.*, **517**, 134 (1935).
- (7) Alkazene 13 of the Dow Chemical Company was used.

condensation of the corresponding aroyl chlorides with the appropriate aromatic hydrocarbon by the Friedel-Crafts method. The method is illustrated by the following directions for making *p*-bromobenzoylmesitylene.

A solution of 160 g. of *p*-bromobenzoyl chloride in 500 cc. of carbon disulfide was added slowly to a well-stirred mixture of 106 g. of anhydrous aluminum chloride, 90 g. (105 cc.) of mesitylene and 350 cc. of carbon disulfide. The addition was made over a period of two hours and the reaction mixture was decomposed by pouring it into a mixture of ice and concentrated hydrochloric acid. The mixture was allowed to warm up to room temperature, and the crude product was extracted with ether. The ether layer was separated, washed with water, 10% sodium hydroxide solution and finally with water. The ether was evaporated and the ketone was crystallized from alcohol. It formed small yellowish needles, which were readily soluble in the common organic solvents.

The melting points, yields and analytical data for this and other similar ketones are given in the table.

TABLE I

Compound	Melting point, °C.	Yield, %	Analyses, % ^a			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
MesCO-  -Br ^b	70-71 ^c	75	63.37	63.36	4.95	4.39
MesCO-  -Cl	68-69.5	66	74.42	73.78	5.81	6.04
MesCO-  -Br	86-87	86	63.37	63.47	4.95	4.99
MesCO-  -Br	113-115	85	63.37	63.75	4.95	5.03
TepCO-  -Br ^d	...	61	66.09	66.74	6.09	6.39
TipCO-  -Br	99-99.5	97	68.22	67.83	6.98	6.98

^a Microanalyses by Mr. L. G. Fauble and Miss Mary S. Kreger. ^b Mes, Tep and Tip are used to represent mesityl, 2,4,6-triethylphenyl and 2,4,6-triisopropylphenyl, respectively. ^c The solid compounds listed in this table were purified by recrystallization from 95% ethanol. ^d This compound was a light yellow oil boiling at 170-185° (7 mm.); n_D^{20} 1.5840.

The Reaction of *p*-Bromobenzoylmesitylene with the Binary Mixture.—The binary mixture was prepared by gently refluxing a solution of 15 g. of iodine in a mixture of 120 cc. of dry benzene and 60 cc. of anhydrous ether with 7.0 g. of magnesium until the solution became colorless. A solution of 30 g. of *p*-bromobenzoylmesitylene in 100 cc. of dry ether was then added slowly to the reagent. The surface of the magnesium became red, and eventually a finely divided red precipitate formed. The reaction mixture was refluxed gently and stirred for three hours after the addition was completed. It was cooled and then decomposed by the addition of cold dilute hydrochloric acid. The resulting deep red ether solution was washed with water. As long as this solution was kept from contact with air, it remained deep red, but when exposed to the air, it was gradually decolorized and an almost colorless solid crystallized in very fine needles. The suspended solid was collected on a filter and purified by recrystallization from 95% ethanol. Twelve grams of a product, melting at 221-222°, was obtained.

Anal. Calcd. for C₃₂H₃₀O₂: C, 86.49; H, 6.72; mol. wt., 444. Found: C, 86.25, 87.04, 86.04; H, 7.18, 7.18, 6.85; mol. wt., 457, 437.

The absence of hydroxyl groups was indicated by the fact that benzoylation and acetylation could not be effected.

A quantitative reduction of the carbonyl groups according to the method of Gomberg and Bailar² indicated the presence of two carbonyl groups.

Hydrolysis with sirupy phosphoric acid yielded a hydrocarbon and a small amount of an organic acid. The melting points of the acid chloride, methyl ester and ethyl ester derived from the acid all agreed with the known values⁴ for the corresponding derivatives of 4,4'-dicarboxybi-phenyl.

The Reaction of *p*-Bromobenzoylmesitylene with Magnesium in the Presence of Phenylmagnesium Bromide.—A phenylmagnesium bromide solution prepared from 0.5 g. of bromobenzene and 1.0 g. of magnesium in 10 cc. of ether, was diluted with 40 cc. of ether, and 10 g. of *p*-bromobenzoylmesitylene in 30 cc. of ether was added. The solution was refluxed and stirred for five hours and the diketone was isolated in the manner described in the coupling with the binary mixture; yield, 2 g., m. p. 215-220°.

The Reaction of *p*-Chlorobenzoylmesitylene with the Binary Mixture.—The binary mixture was formed from 1 g. of magnesium and 5.3 g. of iodine dissolved in 40 cc. of benzene and 20 cc. of ether. Five grams of *p*-chlorobenzoylmesitylene, dissolved in 20 cc. of ether, was added to the reagent. The reaction started readily and proceeded exactly as did the corresponding reaction with *p*-bromobenzoylmesitylene; yield, 2.5 g., m. p. 215-222°.

An Attempted Coupling of *p*-Chlorobenzophenone.—Mesitylmagnesium bromide was prepared from 0.5 g. of bromomesitylene and 2 g. of magnesium in 10 cc. of ether. The solution of the reagent was then diluted with 20 cc. of ether, and 10 g. of *p*-chlorobenzophenone, dissolved in 20 cc. of ether was added slowly to the well-stirred and refluxing solution. After the addition was completed, the reaction mixture was refluxed and stirred overnight. At the end of this time, there were no signs that reaction had taken place; the solution was colorless and no magnesium had dissolved. Only starting material could be isolated from the mixture.

The Reaction of *p*-Bromobenzoylmesitylene with the Binary Mixture Followed by Treatment with Acetic Anhydride.—The metallo-organic complex formed by the action of the binary mixture upon *p*-bromobenzoylmesitylene was prepared in the usual manner from 0.4 g. of magnesium, 1.3 g. of iodine and 2 g. of *p*-bromobenzoylmesitylene. To this solution was added slowly 10 cc. of acetic anhydride with continuous heating and stirring. After the addition was completed, the reaction mixture was refluxed for one and a half hours and was then cooled and decomposed with dilute hydrochloric acid. The ether layer was separated, washed with water, dried with anhydrous sodium sulfate, and the solvent evaporated. A very dark viscous oil was obtained. After considerable manipulation a small amount of a white crystalline compound was obtained, m. p. 190-191°.

Anal. Calcd. for C₂₆H₂₈O₂: C, 83.50; H, 7.34. Found: C, 83.69; H, 7.28.

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'-Dimesityl-biphenyl has been prepared by the action of the binary mixture, Mg + MgI₂, 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

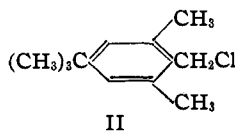
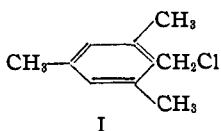
RECEIVED JULY 5, 1941

[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

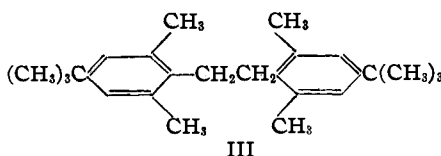
The equivalent conductance of 2,4,6-trimethylbenzyl chloride (I) in liquid sulfur dioxide is ten times that of benzyl chloride.² It seemed probable that the chemical reactivity of the former would show a corresponding augmentation. A wide difference already had been noted in the behavior of these two 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).



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).



(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 (1938).