

the use of decolorizing carbon, gave white, fluffy needles of 2-propylretenoxazole; yield 23%; m. p. 100–100.5°.

Reaction of Retenequinonimine with *n*-Butylidene-aniline in the Presence of One Equivalent of Piperidine.—No oxazole could be isolated from this reaction mixture after refluxing for fourteen hours.

Reaction of Phenanthraquinonimine with Benzal-*n*-butylamine.—The solution was refluxed for forty-five minutes and the crude 2-phenylphenanthroxazole recrystallized from 80% dioxane–water using decolorizing carbon and finally alcohol; yield 79%; m. p. 205–205.8°. *Anal.* Calcd. for C₂₁H₁₈NO: N, 4.74. Found: N, 4.57.

Reaction of Phenanthraquinonimine with Benzalaniline.—The 2-phenylphenanthroxazole obtained after refluxing the solution for four hours was recrystallized from 80% dioxane–water with the use of decolorizing carbon; yield 21.7%; m. p. 206–207°. *Anal.* Calcd. for C₂₁H₁₈NO: N, 4.74. Found: N, 4.72.

Reaction of Phenanthraquinonimine with Benzalaniline in the Presence of One Equivalent of Piperidine.—In the presence of piperidine, the yield of 2-phenylphenanthroxazole increased from the 21.7% noted above to 85%, after only two hours of refluxing.

Reaction of Phenanthraquinonimine with *n*-Butylidene-*n*-butylamine.—The solution was refluxed for four hours. After three weeks of standing in the cold, a small amount of yellowish-brown solid separated and was removed. Evaporation of the filtrate yielded only an intractable gum. The crude 2-propylphenanthroxazole was recrystallized from 80% alcohol and finally from 50% alcohol and obtained as colorless needles; yield 0.8%; m. p. 84.3–86.2°. Several runs were necessary to obtain sufficient material for

the analyses. *Anal.* Calcd. for C₁₈H₁₈NO: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.56; H, 5.71; N, 5.30.

Reaction of Phenanthraquinonimine with *n*-Butylidene-*n*-butylamine in the Presence of One Equivalent of Piperidine.—After refluxing for four hours, the solution was evaporated and the viscous residue stirred with 50% methyl alcohol and a few pellets of sodium hydroxide until it had solidified. The 2-propylphenanthroxazole was then recrystallized from 80% alcohol, with the aid of decolorizing carbon; yield 30%; m. p. 85–86°. *Anal.* Calcd. for C₁₈H₁₈NO: N, 5.36. Found: N, 5.27.

Reaction of Phenanthraquinonimine with *n*-Butylidene-aniline.—No 2-propylphenanthroxazole could be isolated in the absence or the presence of piperidine, after four hours of refluxing.

Summary

1. Retenequinonimine and phenanthraquinonimine have been shown to react with most types of Schiff bases to form 2-substituted retenoxazoles or phenanthroxazoles.

2. The first step in the reaction has been shown to consist of an aldol-type of condensation, with the quinonimine supplying the labile hydrogen. Some Schiff bases are sufficiently basic to catalyze the condensation.

3. This base-catalyzed reaction is a new and useful method for the synthesis of 2-substituted retenoxazoles and phenanthroxazoles.

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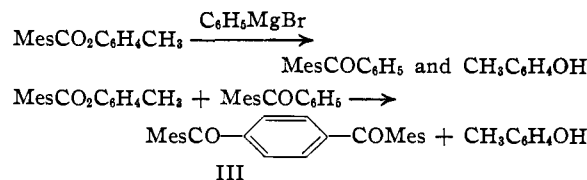
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Para Acylation of Polyalkylbenzophenones by Aryl 2,4,6-Trialkylbenzoates

BY REYNOLD C. FUSON, E. M. BOTTORFF, R. E. FOSTER AND S. B. SPECK

Alkylmagnesium halides and arylmagnesium halides that carry a substituent in the para position have been shown to condense with aryl mesitoates to produce ketones.¹ A much more remarkable result was obtained with arylmagnesium halides that had no substituent in the para position. *p*-Tolyl mesitoate and phenylmagnesium bromide, for example, yielded *p*-cresol and a substance that proved to be *p*-dimesitylbenzene (III). The structure of this compound was proved by synthesizing it from terephthalyl chloride and mesitylene by the Friedel–Crafts method.

The first step in this transformation appeared to be the formation of benzoylmesitylene, which then condensed with unchanged mesitoic ester to produce the diketone (III). In confirmation of this hypothesis, it was discovered that the dike-



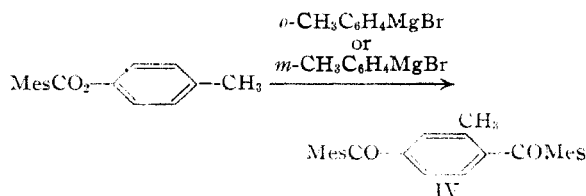
tone could be made also by condensing benzoylmesitylene with *p*-tolyl mesitoate.

This condensation is without parallel. The net result is the acylation, under the influence of the Grignard reagent, of a benzene ring in the position which is *para* to the *meta*-directing carbonyl group. The condensation can be formulated as a Claisen reaction in which a nuclear hydrogen atom is replaced by an acyl group. This point of view is supported by the fact that the condensation between the ketone and the ester can be effected with the aid of a number of alkaline cata-

(1) Fuson, Bottorff and Speck, *THIS JOURNAL*, **64**, 1450 (1942).

lysts. Among these are sodium, ethylmagnesium bromide, mesitylmagnesium bromide and the binary mixture, Mg-MgI₂.² The binary mixture afforded the best yields, but usually gave less than 50% of the theoretical amount.

Under the influence of this reagent *p*-tolyl mesitoate condensed with *m*-toluylmesitylene, *m*-methoxybenzoylmesitylene, dibromomesityl phenyl ketone and α -naphthoylmesitylene to yield the expected diketones. It is interesting that *o*- and *m*-tolylmagnesium bromide reacted with *p*-tolyl mesitoate to yield the same diketone—1,4-dimesityl-2-methylbenzene (IV).



The formation of 1,4-diaroylbenzenes appears to be general for highly hindered ketones. Aryl esters of 2,4,6-triethylbenzoic, 2,4,6-triisopropylbenzoic and 2,3,5,6-tetramethylbenzoic acids were found to condense with the corresponding aryl phenyl ketones to yield, respectively, 1,4-di-(2,4,6-triethylbenzoyl)-benzene, 1,4-di-(2,4,6-triisopropylbenzoyl)-benzene and 1,4-di-(2,3,5,6-tetramethylbenzoyl)-benzene.

Experimental

Synthesis of Ketones.—The ketones prepared in this work are listed in Table I, which indicates also melting points, yields, solvents and analytical data. All except the last four in the table were prepared by the condensation of the corresponding acid chloride with the appropriate hydrocarbon by the Friedel-Crafts method. A description of the preparation of *p*-dimesitylbenzene will illustrate the procedure.

***p*-Dimesitylbenzene.**³—A solution of 15 g. of terephthalyl chloride,⁴ 40 cc. of carbon disulfide and 10 cc. of mesitylene was added dropwise, with stirring, at room temperature to a mixture of 26 g. of mesitylene, 28 g. of aluminum chloride and 50 cc. of carbon disulfide. The solution was refluxed gently and stirred for six hours. The dark-red reaction mixture was poured into an ice-hydrochloric acid mixture. The carbon disulfide was evaporated and the solution extracted with three portions of hot benzene. The benzene extracts were washed with hot water, hot 5% sodium hydroxide solution and again with water. A portion of the benzene was removed by distillation, and the remaining solution was allowed to cool; 12 g. of *p*-dimesitylbenzene crystallized. The melting

point after two recrystallizations from benzene was 244–246°.

Dibromomesityl Phenyl Ketone.—This compound was prepared by direct bromination of benzoylmesitylene in carbon tetrachloride.

2,4,6-Tribromophenyl Mesitoate.—This compound was prepared in 84% yield by condensing 2,4,6-tribromophenol with mesityl chloride. It crystallized from alcohol in colorless needles melting at 86°.

*Anal.*⁵ Calcd. for C₁₆H₁₃O₂Br₂: C, 40.26; H, 2.74. Found: C, 40.56; H, 2.89.

Condensation of Hindered Esters with Aryl Grignard Reagents.—The reactions of a few hindered esters with certain aryl Grignard reagents have been studied. The arylmagnesium halides selected were those having no substituents in the para position. The results of this work are shown in Table II. Since the experimental details were very similar for all of these reactions, the procedure will be described only for one, *viz.*, that between *p*-tolyl mesitoate and phenylmagnesium bromide.

***p*-Tolyl Mesitoate and Phenylmagnesium Bromide.**—The reagent was prepared from 5 g. of magnesium and 28.2 g. of bromobenzene in 50 cc. of *n*-butyl ether. A solution of 20.4 g. of *p*-tolyl mesitoate in 60 cc. of *n*-butyl ether was added, with stirring. The clear solution slowly became a deep wine color. The mixture was heated at 100° for two hours in an atmosphere of nitrogen.

The reaction mixture was decomposed with cold dilute hydrochloric acid and the aqueous layer extracted twice with ether. The ether solution was washed once with water, then with three 100-cc. portions of 10% sodium hydroxide. The sodium hydroxide solution was washed twice with ether, acidified with hydrochloric acid and extracted with ether. The ether solution was washed with water, dried over magnesium sulfate, and freed of solvent by evaporation. The residual *p*-cresol weighed 6.4 g.

The solvent was removed from the ether solution and the oil treated with alcohol. The *p*-dimesitylbenzene which separated was collected on a filter and washed with alcohol; yield 5 g. The filtrate was distilled under reduced pressure and small amounts of biphenyl and *p*-tolyl mesitoate were obtained.

Many of the products shown in Table II could be isolated only by distillation of the neutral portion of the reaction mixture under reduced pressure. The fractions obtained were then taken up in ethanol, and crystallization was induced.

Condensation of Hindered Esters with Diaryl Ketones.—The condensation reactions are listed in Table III. The starting materials, reaction temperatures, reagent, products and yields are given. Since the procedures used for these reactions are very similar, only two will be described in detail.

Benzoylmesitylene and *p*-Tolyl Mesitoate.—A solution of 11.2 g. of benzoylmesitylene and 12.7 g. of *p*-tolyl mesitoate in 60 cc. of 1:1 toluene-*n*-butyl ether mixture was added slowly to a solution of the binary mixture, Mg-MgI₂, prepared from 2.5 g. of magnesium and 12.7 g. of iodine in 60 cc. of 1:1 ethyl ether-*n*-butyl ether mixture. The reaction mixture was stirred in an atmosphere of nitrogen at

(2) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

(3) This experiment was carried out by Dr. C. H. McKeever.

(4) Beund and Herms, *J. prakt. Chem.*, [2] **74**, 123 (1906).

(5) The analyses reported in this paper are microanalyses. They were performed by Miss Mary S. Kreger and Mr. L. G. Fauble.

TABLE I
KETONES^a

Ketone	Yield, %	Melting point, °C.	Solvent	Analyses, %			
				Calcd. C	H	Found C	H
MesCOTol(<i>m</i>)	91	67	Ethanol	85.64	7.64	85.97	7.97
MesCO α -C ₁₀ H ₇ ^b	60	159	Ethanol	87.59	6.57	87.65	6.67
DurCOC ₆ H ₅ ^c	40	119					
TipCOC ₆ H ₅	81	97-99	Methanol	85.66	9.15	86.01	9.39
TepCOC ₆ H ₅ ^d	81	85.70	8.28	85.41	8.40
<i>m</i> -MesCOC ₆ H ₄ COMes	94	149-151	Benzene-ethanol	84.30	7.08	84.33	7.00
<i>p</i> -MesCOC ₆ H ₄ COMes	44	244-246	Benzene	84.30	7.08	84.28	6.83
<i>p</i> -MesCOC ₁₀ H ₆ COMes	45	171	Ethanol-benzene	85.61	6.66	86.04	6.88
		193.5		85.61	6.66	85.52	6.77
<i>p</i> -TipCOC ₆ H ₄ COTip	50	223-225	Ethanol-chloroform	84.71	9.35	84.49	8.98
<i>p</i> -TepCOC ₆ H ₄ COTep ^f	67	119-120	Ethanol	84.54	8.42	84.64	8.51
<i>p</i> -DurCOC ₆ H ₄ CODur	67	246	Chloroform-pet. ether	84.35	7.61	84.41	7.87
MesCOC ₆ H ₃ (CH ₃)COMes(1,3,4)	29	189	Ethanol-benzene	84.31	7.34	84.07	7.36
Br ₂ MesCOC ₆ H ₅	23	113	Ethanol	50.26	3.66	50.46	3.61
<i>p</i> -Br ₂ MesCOC ₆ H ₄ COMes	27	274-277	Ethane-pet. ether	59.09	4.58	59.68	4.97
MesCOC ₆ H ₃ (OCH ₃)COMes(1,3,4)	35	210	Ethanol-benzene	80.96	7.05	81.12	7.09

^a The radicals tolyl, mesityl, 2,4,6-triisopropylphenyl, 2,4,6-triethylphenyl and 2,3,5,6-tetramethylphenyl are represented by Tol, Mes, Tip, Tep and Dur, respectively. ^b This compound was prepared by Dr. M. D. Armstrong from α -naphthoyl chloride and mesitylene by the Friedel-Crafts method. ^c This compound was prepared by B. C. McKusick by the Friedel-Crafts method. ^d B. p. 144-145° (3 mm.); d_{20}^{20} 1.022; n_D^{20} 1.5648. ^e This compound was prepared by Dr. C. H. McKeever by the method described for *p*-dimesitylbenzene.

TABLE II
REACTIONS OF HINDERED ARYL ESTERS WITH GRIGNARD REAGENTS

Ester	Grignard reagent	Product (% yield)	Product (% yield)
MesCO ₂ Tol(<i>p</i>)	C ₆ H ₅ MgBr	<i>p</i> -Cresol (74)	<i>p</i> -MesCOC ₆ H ₄ COMes ^a (34)
MesCO ₂ Tol(<i>m</i>) ^b	C ₆ H ₅ MgBr	<i>m</i> -Cresol (80)	<i>p</i> -MesCOC ₆ H ₄ COMes (small amounts)
MesCO ₂ Tol(<i>p</i>)	<i>o</i> -CH ₃ C ₆ H ₄ MgBr	<i>p</i> -Cresol	<i>o</i> -MesCOC ₆ H ₄ C ₆ H ₅ ^c
MesCO ₂ Tol(<i>p</i>)	<i>m</i> -CH ₃ C ₆ H ₄ MgBr	<i>p</i> -Cresol	(1,3,4)MesCOC ₆ H ₃ (CH ₃)COMes (29)
MesCO ₂ Tol(<i>p</i>)	<i>m</i> -CH ₃ OC ₆ H ₄ MgBr	<i>p</i> -Cresol	(1,3,4)MesCOC ₆ H ₃ (CH ₃)COMes (11)
TipCO ₂ Tol(<i>p</i>)	C ₆ H ₅ MgBr	<i>p</i> -Cresol	(1,3,4)MesCOC ₆ H ₃ (OCH ₃)COMes (3.5)
TepCO ₂ Tol(<i>p</i>) ^d	C ₆ H ₅ MgBr	<i>p</i> -Cresol	<i>p</i> -TipCOC ₆ H ₄ COTip ^e
			<i>p</i> -TepCOC ₆ H ₄ COTep ^e

^a A mixed melting point with an authentic specimen prepared by the Friedel-Crafts method gave no depression. ^b This ester was made by the method¹ described earlier for the para isomer; m. p. 38-39°. *Anal.* Calcd. for C₁₇H₁₃O₂: C, 80.30; H, 7.10. Found: C, 80.22; H, 7.37. ^c Identified by a mixed melting point with an authentic specimen.⁶ ^d This ester was made by the method¹ described earlier for *p*-tolyl mesitoate; b. p. 170-171° (3 mm.); d_{20}^{20} 1.0355; n_D^{20} 1.5435. *Anal.* Calcd. for C₂₀H₂₄O₂: C, 81.04; H, 8.10. Found: C, 81.14; H, 7.85.

115° for five hours. The color gradually became a very deep red.

The reaction mixture was decomposed with cold dilute hydrochloric acid and the aqueous layer extracted twice with ether. The ether solution was washed once with water, then with three 100-cc. portions of 10% sodium hydroxide. The sodium hydroxide solution was washed twice with ether, acidified with hydrochloric acid and extracted with ether. The ether solution was washed with water, dried over magnesium sulfate, and freed from ether by evaporation. The residual *p*-cresol weighed 4.3 g.

The solvent was removed from the original ether solution and the oil taken up in alcohol. *p*-Dimesitylbenzene separated and was collected on a filter and washed with alcohol; yield 7.4 g. A small amount (0.45 g.) of a bright yellow compound, m. p. 189°, was isolated. It was not identified.

The filtrate was distilled under reduced pressure; 2 g. of

benzoylmesitylene and 3.4 g. of *p*-tolyl mesitoate were recovered.

α -Naphthoylmesitylene and *p*-Tolyl Mesitoate.—A solution of the binary mixture, Mg-MgI₂, was prepared from 2.5 g. of magnesium and 12.7 g. of iodine in 50 cc. of 1:1 toluene-*n*-butyl ether. A solution of 13.7 g. of α -naphthoylmesitylene and 12.7 g. of *p*-tolyl mesitoate in 40 cc. of the solvent was added slowly. The mixture was stirred at 115° for three hours under an atmosphere of nitrogen. It was then treated with dilute hydrochloric acid and washed as described in the preceding experiment. *p*-Cresol was obtained from the alkaline extract.

After the solvent was removed from the neutral portion, a solid separated. The mixture was treated with alcohol, and the solid material collected on a filter and washed with alcohol. The yield was 5.7 g. of 1,4-dimesitylnaphthalene, which melted at 171°, after many recrystallizations from an alcohol-benzene mixture, and was yellow in color.

The alcohol filtrate was distilled under reduced pressure,

(6) Fuson, Armstrong and Speck, *J. Org. Chem.*, **7**, 297 (1942).

TABLE III
 CONDENSATION OF HINDERED ESTERS WITH DIARYL KETONES

Starting materials	Reagent	Temp. of reaction, °C.	Diketone	Yield, %
MesCO ₂ Tol(<i>p</i>) ^a and MesCOC ₆ H ₅	C ₂ H ₅ MgBr	115	<i>p</i> -MesCOC ₆ H ₄ COMes ^b	14
MesCO ₂ Tol(<i>p</i>) and MesCOC ₆ H ₅	C ₆ H ₅ MgBr	115	<i>p</i> -MesCOC ₆ H ₄ COMes ^c	13
MesCO ₂ Tol(<i>p</i>) and MesCOC ₆ H ₅	MesMgBr	115	<i>p</i> -MesCOC ₆ H ₄ COMes	17
MesCO ₂ Tol(<i>p</i>) and MesCOC ₆ H ₅	Na	100	<i>p</i> -MesCOC ₆ H ₄ COMes ^d	8
MesCO ₂ Tol(<i>p</i>) ^a and MesCOC ₆ H ₅ ^e	ZnCl ₂	115		
MesCO ₂ Tol(<i>p</i>) and MesCOC ₆ H ₅	Mg-MgI ₂	115	<i>p</i> -MesCOC ₆ H ₄ COMes	40
MesCO ₂ Tol(<i>p</i>) and MesCOC ₆ H ₅	Mg-MgI ₂	60	<i>p</i> -MesCOC ₆ H ₄ COMes	36
MesCO ₂ Tol(<i>p</i>) and Br ₂ MesCOC ₆ H ₅	Mg-MgI ₂	60	<i>p</i> -Br ₂ MesCOC ₆ H ₄ COMes	27
MesCO ₂ Tol(<i>p</i>) and MesCOTol(<i>m</i>)	Mg-MgI ₂	115	(1,3,4)MesCOC ₆ H ₃ (CH ₃)COMes	32
MesCO ₂ Tol(<i>p</i>) and <i>m</i> -MesCOC ₆ H ₄ OCH ₃	Mg-MgI ₂	70	(1,3,4)MesCOC ₆ H ₃ (OCH ₃)COMes	35
MesCO ₂ Tol(<i>p</i>) and <i>m</i> -MesCOC ₆ H ₄ COMes	Mg-MgI ₂	115	(1,3,4)(MesCO) ₃ C ₆ H ₃	13
MesCO ₂ CH ₃ ^f and MesCOC ₆ H ₅	Mg-MgI ₂	115		
MesCO ₂ C ₆ H ₂ Br ₃ (2,4,6) and MesCOC ₆ H ₅	Mg-MgI ₂	100	<i>p</i> -MesCOC ₆ H ₄ COMes ^g	
MesCO ₂ Tol(<i>p</i>) and MesCOC ₁₀ H ₇ (α)	Mg-MgI ₂	115	<i>p</i> -MesCOC ₁₀ H ₆ COMes	30
DurCO ₂ Tol(<i>p</i>) ^h and DurCOC ₆ H ₅	Mg-MgI ₂	60	<i>p</i> -DurCOC ₆ H ₄ CODur	54
TipCO ₂ Tol(<i>p</i>) and TipCOC ₆ H ₅	C ₂ H ₅ MgBr	140	<i>p</i> -TipCOC ₆ H ₄ COTip	trace
TepCO ₂ Tol(<i>p</i>) and TepCOC ₆ H ₅	Mg-MgI ₂	115	<i>p</i> -TepCOC ₆ H ₄ COTep	16

^a All reactions involving esters of *p*-cresol yielded *p*-cresol as one of the products. ^b Propiomesitylene was also produced. ^c A trace of 2-mesitylphenyl was formed also. ^d Mesitoic acid was formed in 13% yield. ^e *p*-Cresol and mesitoic acid were the only products isolated. The yields were very low. ^f A 58% yield of mesitoic acid was obtained. ^g 2,4,6-Tribromophenol was also a product. ^h This compound was prepared by B. C. McKusick from the acid chloride and *p*-cresol; m. p. 138°, from alcohol. Anal. Calcd. for C₁₈H₂₀O₂: C, 80.55; H, 7.47. Found: C, 80.02; H, 7.41.

and the following substances were isolated from the distillate; 3.2 g. of *p*-tolyl mesitoate, 2.0 g. of α -naphthoilmesitylene and 0.75 g. of 1,4-dimesitylnaphthalene.

The 1,4-dimesitylnaphthalene was found to have two crystalline forms. When the yellow compound was heated above its melting point (171°) for a few minutes or was treated with chromic acid in glacial acetic acid and then recrystallized from alcohol, colorless needles were obtained. This colorless form showed a definite softening point at 171° and melted sharply at 193.5° to a bright yellow liquid, which when cooled rapidly gave the yellow solid.

This compound was synthesized from 1,4-dicyanonaphthalene⁷ by way of the dicarboxylic acid and the acid chloride. Hydrolysis of the dinitrile by the method of Scholl and Neumann,⁸ gave a 76% yield of the crude acid. The acid was converted to the acid chloride by the method of Beund and Herms.⁴ The condensation of the impure acid chloride with mesitylene produced a mixture from which the diketone melting at 193.5° could be isolated.

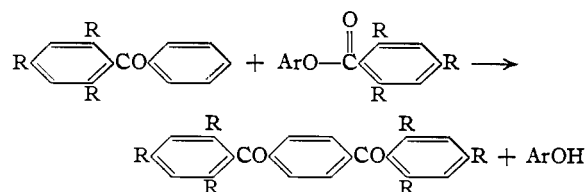
A by-product, melting at 134° (cor.), was found to contain nitrogen and is believed to be 1-mesityl-4-cyanonaphthalene. Its origin may be traced to incomplete hydrolysis of the dinitrile giving rise to 4-cyanonaphthoic

acid and eventually to the cyano ketone. It was purified by recrystallization from methanol and petroleum ether. It had a bright yellow color.

Anal. Calcd. for C₂₁H₁₇ON: C, 84.22; H, 5.75. Found: C, 84.36; H, 5.85.

Summary

It has been shown that certain highly hindered benzophenones undergo acylation in an unsubstituted para position when treated with aryl 2,4,6-trialkylbenzoates. The generalized equation for the reaction is



The reaction takes place under the influence of Grignard reagents, the binary mixture (Mg-MgI₂) and certain other alkaline catalysts.

(7) Newman, *THIS JOURNAL*, **59**, 2472 (1937).

(8) Scholl and Neumann, *Ber.*, **55B**, 118 (1922).