[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

The Reactions of Some Polynuclear Aroyl Acid Chlorides with Organocadmium Reagents[1,2]

BY DOROTHY V. NIGHTINGALE, WILLIAM S. WAGNER AND ROBERT H. WISE

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8-Benzoyl-1-naphthoyl chloride reacted with diphenylcadmium to form a mixture of 3,3-diphenylnaphthalide and 1,8-dibenzoylnaphthalene. It reacted with diethylcadmium and di-*n*-butylcadmium to form the corresponding 3-phenyl-3-alkylnaphthalide. The product from 8-*p*-toluyl-1-naphthoyl chloride was an oil from which some 3,3-di-*p*-toluylnaphthalide was isolated. 2-(3,4-Dimethylbenzoyl)-2'-biphenylcarboxylic acid chloride reacted with diethylcadmium and di-*n*-butylcadmium to form the corresponding 7-alkyl-7-(3,4-dimethylphenyl)-diphenide. With di-*p*-tolylcadmium, the reaction product was the 2,2'-diaroylbiphenyl. 2-Mesitoyl-2'-biphenylcarboxylic acid chloride reacted with diethylcadmium and di-*n*-butylcadmium to form the corresponding 2-aroyl-2'-acylbiphenyls.

French and Kircher[3] have reported chemical and spectroscopic evidence which proved that 8-benzoyl-1-naphthoyl chloride I, m.p. 125–127°, is the cyclic form. In the present investigation, I has been treated with organocadmium reagents in a further study of the reactions of this acid chloride.

Diphenylcadmium and I reacted to form a mixture of 3,3-diphenylnaphthalide and 1,8-dibenzoylnaphthalene. The product from 8-*p*-toluoyl-1-napthoyl chloride and di-*p*-tolylcadmium was the 3,3-diarylnaphthalide along with an unidentified oil.

Diethylcadmium or di-*n*-butylcadmium and I formed only the 3-alkyl-3-phenylnaphthalides. The 3-*n*-butyl-3-phenylnaphthalide reacted by addition with one mole of methylmagnesium iodide in the Grignard machine, establishing the presence of one carbonyl group. The 1,8-diaroylnaphthalenes add two moles of methylmagnesium iodide under these conditions. The ultraviolet absorption spectra of these compounds (Table I) were very similar to the absorption spectrum of 3,3-di-*p*-tolylnaphthalide.[3]

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF THE NAPHTHALIDES

	Maxima and minima in mμ									
Compound	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Max.	Min.	Max.
3,3-Di-*p*-tolylnaphthalide		236	243	271	274	277		315	326	329
3-Methyl-3-phenylnaphthalide		234	241	271				314	326	328
3-Ethyl-3-phenylnaphthalide		233	241	268				314	326	328
3-*n*-Butyl-3-phenylnaphthalide		233	242	268				314	326	328
3-*n*-Heptyl-3-phenylnaphthalide		236	240	271				314	326	328
Diethyl naphthalate	225			268			296			

Dimethylcadmium and di-*n*-heptylcadmium reacted with I to form oils which could not be crystallized or completely purified by chromatographic adsorption, but their absorption spectra (Table I) indicated that they were chiefly the naphthalides. These oils and the solid naphthalides were unaffected by hot concentrated potassium hydroxide and would not form derivatives with carbonyl reagents.

Di-*p*-tolylcadmium reacted with 2-(3,4-dimethylbenzoyl)-2'-biphenylcarboxylic acid chloride(II) to form 2-(3,4-dimethylbenzoyl)-2'-*p*-toluylbiphenyl. Diethylcadmium and di-*n*-butylcadmium reacted with II to form only the corresponding 7-alkyl-7-(3,4-dimethylphenyl)-diphenide. These reactions indicate that the normal form of II can be isomerized to the cyclic form. The two diphenides were hydrolyzed slowly by sodium carbonate solution and rapidly by solutions of strong bases. In this respect they differ from the stable naphthalides, which are not hydrolyzed by strong bases. They showed a light blue fluorescence under ultraviolet light similar to that of diphenic anhydride, whereas the aroylcarboxylic acids and the diketones in this series were not fluorescent.

2-Mesitoyl-2'-biphenylcarboxylic acid chloride reacted with diethylcadmium and di-*n*-butylcadmium to form the corresponding 2-mesitoyl-2'-acylbiphenyls. These compounds could not be hydrolyzed by alkali under any conditions.

Diphenoyl chloride reacted as the symmetrical dichloride with diphenylcadmium to form only 2,2'-dibenzoylbiphenyl in 83% yield. With diethylcadmium, the product was an oil which could not be completely purified. This oil was not soluble in sodium carbonate solution but dissolved in hot concentrated potassium hydroxide solution. It was not fluorescent in ultraviolet light.

Naphthalic anhydride reacted readily with diphenylcadmium to form 8-benzoyl-1-naphthoic acid in 85% yield. Knapp[4] obtained this acid in 25% yield by adding a solution of phenylmagnesium bromide to a suspension of naphthalic anhydride in boiling toluene. In the present investigation, the yield of the acid was raised to 95% by adding the ether solution of the Grignard reagent to a suspension of the anhydride in toluene at room temperature. The preparation from the diphenylcadmium reagent has the slight advantage that the crude product is suitable for most uses without further purification. The synthesis of this acid by either of these procedures is preferable to Mason's

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[1] Presented before the Organic Division of the American Chemical Society at the Los Angeles Meeting, March, 1953.

[2] Abstracted from the Master's thesis of Robert H. Wise, August, 1951, and the Ph.D. thesis of William S. Wagner, August, 1952.

[3] H. E. French and J. E. Kircher, THIS JOURNAL, **66**, 298 (1944).

[4] W. Knapp, *Monatsh.*, **67**, 332 (1936).

synthesis[5] from naphthalyl dichloride, benzene and aluminum chloride. The naphthalyl dichloride is difficult to prepare and yields of the keto acid are 50–60%.[3]

Naphthalic anhydride reacted with diethylcadmium to form 8-propionyl-1-naphthoic acid in 57% yield. This acylnaphthoic acid is not available by other means.

Diphenic anhydride reacted with diphenylcadmium to form 2-benzoyl-2′-biphenylcarboxylic acid in 87% yield. This compound has not been previously reported in the literature. Sergeev[6] reports the isolation of 2-(diphenylhydroxymethyl)-2′-biphenylcarboxylic acid and 2-(diphenylhydroxymethyl)-2-benzoyl-biphenyl (or the isomeric diphenide structure) from the reaction of diphenic anhydride and phenylmagnesium bromide.

Experimental[7]

Preparation of 8-Benzoyl-1-naphthoic Acid from Naphthalic Anhydride and Diphenylcadmium.—The procedure is an adaptation of that of de Benneville.[8] Phenylmagnesium bromide was prepared in the usual apparatus from 99 g. (0.62 mole) of bromobenzene in 150 ml. of dry ether. To this solution, cooled in ice, 51 g. of cadmium chloride was added with rapid stirring. The mixture was heated and stirred for an additional 80 minutes, when the ether was removed by distillation and replaced with 500 ml. of dry toluene. The solution of diphenylcadmium was cooled in an ice-bath and 50 g. (0.25 mole) of naphthalic anhydride[9] was added during 15 minutes. The mixture was heated for 2.25 hours at 60–70° with stirring. The complex was hydrolyzed with 1:1 hydrochloric acid, the unchanged naphthalic anhydride was removed by filtration, and the separated toluene layer was extracted with 10% sodium carbonate solution. When the carbonate extracts were acidified, 60 g. (85%) of 8-benzoyl-1-naphthoic acid was obtained, m.p. 128–129°, literature value 129–130°,[5] without further purification.

8-Propionyl-1-naphthoic acid was obtained similarly from diethylcadmium and naphthalic anhydride. The melting point was 147.5–148.5° after recrystallization from toluene; yield 57%.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.68; H, 5.30. Found: C, 73.52; H, 5.53.

Preparation of 8-*p*-Toluoyl-1-naphthoic Acid from Naphthalic Anhydride and *p*-Tolylmagnesium Bromide.—The procedure is an improvement of the method of Knapp.[4] *p*-Tolylmagnesium bromide was prepared in the usual apparatus from 48 g. of *p*-bromotoluene in 100 ml. of ether. The Grignard reagent was siphoned into a well-stirred suspension of 50 g. (0.25 mole) of naphthalic anhydride in 500 ml. of dry toluene at room temperature. The ether was removed by distillation and the complex was decomposed with hydrochloric acid. The acid was isolated as described above and recrystallized from alcohol; yield 44.5 g. (61%), m.p. 134–136°, literature value[5] 136°.

8-Benzoyl-1-naphthoic acid was obtained by this procedure in 95% yield.

8-Benzoyl-1-naphthoyl chloride, m.p. 127–128°, and 8-*p*-toluoyl-1-naphthoyl chloride, m.p. 144–145°, were prepared by the method of Mason[5] from the acids and thionyl chloride.

Reaction of 8-Benzoyl-1-naphthoyl Chloride with Diethylcadmium.—This procedure is typical and is described in detail. Ethylmagnesium bromide was prepared in the usual apparatus from 5.6 g. of ethyl bromide in 100 ml. of ether. Cadmium chloride (22.9 g.) was added to this cooled solution. After heating and stirring the solution of diethylcadmium, the ether was removed by distillation and replaced with 150 ml. of dry toluene. The toluene solution of the cadmium reagent was heated to 50–70° and 11 g. (0.037 mole) of 8-benzoyl-1-naphthoyl chloride in 50 ml. of toluene was added with vigorous stirring during 20 minutes. The mixture was heated for two hours with continuous stirring, then hydrolyzed with 1:1 hydrochloric acid. The water layer was separated and extracted with toluene. The toluene extract was combined with the original toluene layer and extracted with sodium carbonate solution. The toluene solution was washed and dried, the solvent removed at reduced pressure and the sirupy residue (10.3 g., 95%) was recrystallized from ethyl acetate to yield white needles of 3-ethyl-3-phenylnaphthalide, m.p. 128–129°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.32; H, 5.59. Found: C, 83.65; H, 5.12.

8-Benzoyl-1-naphthoyl Chloride and Di-*n*-butylcadmium.—The product, 3-*n*-butyl-3-phenylnaphthalide, m.p. 148–149°, was obtained in 99% yield.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.37. Found: C, 83.59; H, 6.91.

Reaction of 8-Benzoyl-1-naphthoyl Chloride with Diphenylcadmium.—A toluene solution (50 ml.) of diphenylcadmium was prepared from 0.12 mole of phenylmagnesium bromide. To this cooled solution was added 12 g. (0.04 mole) of 8-benzoyl-1-naphthoyl chloride in 50 ml. of toluene, as described above. A total of 9.5 g. (60%) of crystalline product, m.p. 160–167°, was obtained. Repeated recrystallizations of this mixture failed to change the melting point, and the carbon and hydrogen values agreed with those calculated for the isomeric diketone or diphenide.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.71; H, 4.76. Found: C, 85.77; H, 5.05.

Reaction of 8-*p*-Toluoyl-1-naphthoyl Chloride with Di-*p*-tolylcadmium.—A toluene solution (125 ml.) of di-*p*-tolylcadmium was prepared from 0.16 mole of *p*-tolylmagnesium bromide. To this cooled solution was added 18 g. of 8-*p*-toluoyl-1-naphthoyl chloride in 125 ml. of toluene as described above. After the complex was decomposed and the toluene extracts were concentrated, a brown oil (25.3 g.) was obtained. All efforts to obtain crystals from the oil with a variety of solvents and solvent pairs were fruitless. Distillation of the oil at 1 mm. gave a semi-crystalline product which, when dissolved in alcohol, gave pale yellow crystals, m.p. and mixed m.p. with an authentic sample of 3,3-di-*p*-tolylnaphthalide, 234–236°, the literature value.[3] The oily by-product could not be purified or identified.

Preparation of 2-(3,4-Dimethylbenzoyl)-2′-biphenylcarboxylic Acid.—The procedure is an improvement of the method of Bell and Briggs.[10] In a 500-ml. three-necked flask equipped with a mechanical stirrer and a T-tube gas outlet through which passed a thermometer were placed 250 ml. of *sym*-tetrachloroethane and 100 g. (0.75 mole) of aluminum chloride. The contents of the flask were cooled to −5° with an ice–salt-bath, then 76 g. (0.34 mole) of diphenic anhydride[11] was gradually added at such a rate that the temperature remained below 0° within the flask. This low temperature was maintained while 40 g. (0.37 mole) of *o*-xylene was added dropwise with stirring. The ice–salt-bath was left in place and allowed to come to room temperature during four hours. After seven additional hours of stirring at room temperature, the complex was decomposed with iced hydrochloric acid.

The solvent and unchanged *o*-xylene were removed by steam distillation. The solid reaction product was separated, washed with water, then extracted with 500 ml. of 5% sodium carbonate solution which was agitated with steam. The solution was cooled slightly and filtered. The warm filtrate was made acid to congo paper with 6 *N* hydrochloric acid. The separated solid was collected on a filter, washed with water and dried. Recrystallization from toluene yielded 70 g. (62.5%) of the keto acid, m.p. 113–116°, literature value 114–117°. A sample purified *via* the sodium salt to remove a small amount of diphenic acid melted at 119–120°.

Preparation of 2-(Mesitoyl)-2′-biphenylcarboxylic Acid.—This acid was prepared similarly except that the aluminum chloride and the mesitylene (44 g.) were dissolved in the *sym*-tetrachloroethane (200 ml.) and the diphenic anhydride (75 g.) was added at such a rate that the temperature of the

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[5] F. Mason, *J. Chem. Soc.*, 2116 (1924).

[6] Sergeev, *J. Russ. Phys.-Chem. Soc.*, **61**, 1421 (1929); *C. A.*, **24**, 1365 (1930).

[7] The carbon and hydrogen analyses were performed by P. D. Strickler and Y. C. Lee.

[8] P. de Benneville, *J. Org. Chem.*, **6**, 462 (1941).

[9] C. Graebe and E. Gfeller, *Ann.*, **276**, 1 (1893).

[10] F. Bell and F. Briggs, *J. Chem. Soc.*, 1661 (1938).

[11] R. C. Roberts and T. B. Johnson, THIS JOURNAL, **47**, 1399 (1925).

reactants was maintained at 0–5°. The yield of keto acid was 91.8 g. (80%), m.p. 225–226°, literature value 213°.[10]

Preparation of 2-Naphthoyl-2′-biphenylcarboxylic Acid.—This acid was obtained in the same way. The crude reaction product contained tarry material and was more troublesome to purify. The yield was 21.3 g. (18%), m.p. 180–182°. Bell and Briggs[10] report 180° for the melting point of this compound but did not report an analysis.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 81.50; H, 4.90.

Preparation of 2-(3,4-Dimethylbenzoyl)-2′-biphenylcarboxylic Acid Chloride.—The preparation of this acid chloride is typical. In a 100-ml. round-bottom flask, to which was attached a gas trap, was placed 12 g. of 2-(3,4-dimethylbenzoyl)-2′-biphenylcarboxylic acid. To this was added gradually, with swirling of the flask, 25 ml. of thionyl chloride. The reaction mixture stood at room temperature for three hours with occasional swirling of the solution. Then the flask was heated at 40° on a water-bath for an additional hour. The excess thionyl chloride was removed *in vacuo* at 35°, after which 8 ml. of benzene was added to the viscous residue and then also removed *in vacuo*. The now crystalline residue was dissolved in 13 ml. of boiling dry benzene, quickly filtered by suction, 90 ml. of dry petroleum ether (60–70°) added and the solution cooled with ice to precipitate the acid chloride. The white solid was collected on a filter, washed rapidly with petroleum ether and dried in a vacuum desiccator; yield 10.8 g. (85%), m.p. 101.5–102.5°.

Anal. Calcd. for $C_{22}H_{17}O_2Cl$: C, 75.75; H, 4.91. Found: C, 75.98; H, 5.08.

The amide prepared from this acid chloride was crystallized from acetone and sublimed *in vacuo* to give a white solid, m.p. 184–186°.

Anal. Calcd. for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81. Found: C, 80.00; H, 5.95.

2-(Mesitoyl)-2′-biphenylcarboxylic Acid Chloride.—This acid chloride was obtained in 87% yield, m.p. 117–118°.

Anal. Calcd. for $C_{23}H_{19}O_2Cl$: C, 76.13; H, 5.28. Found: C, 75.85; H, 5.29.

The amide obtained from this acid chloride melted at 209–213°.

Anal. Calcd. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16. Found: C, 80.14; H, 6.45.

Reaction of 2-(3,4-Dimethylbenzoyl)-2′-biphenylcarboxylic Acid Chloride with Di-*p*-tolylcadmium.—*p*-Tolylmagnesium bromide was prepared from 15.4 g. (0.09 mole) of *p*-bromotoluene. Cadmium chloride (8.5 g., 0.04 mole) was added and the solution warmed till it gave a negative test for the Grignard reagent. The ether was removed and replaced with 80 ml. of dry benzene. To this benzene solution of di-*p*-tolylcadmium cooled in ice was added 60.8 g. (0.03 mole) of acid chloride in 25 ml. of dry benzene during ten minutes. The solution was stirred at room temperature for 30 minutes, then at 35–40° for three hours.

The complex was decomposed with ice hydrochloric acid, the benzene layer was separated and the aqueous layer extracted twice with 50-ml. portions of benzene. The benzene solutions were combined, washed with water and extracted with 20% sodium carbonate solution. The benzene was separated, dried over Drierite, and the solvent removed by distillation. The residue was steam distilled to remove any di-*p*-tolyl, then crystallized first from acetone and finally from alcohol. The yield was 4.7 g. (38%) of 2-(3,4-dimethylbenzoyl-2′-(*p*-toluoyl)-biphenyl, m.p. 161–163°.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.30; H, 6.15.

Reaction of 2-(3,4-Dimethylbenzoyl)-2′-biphenylcarboxylic Acid Chloride with Diethylcadmium.—The diethylcadmium was prepared from 48 g. (0.43 mole) of ethyl bromide. The ether was replaced with 310 ml. of dry benzene, the solution was warmed to 75–80°, and 25 g. of acid chloride in 75 ml. of dry benzene was added. The reaction mixture was stirred and heated at 60–70° for two more hours. The complex was decomposed with iced hydrochloric acid and the benzene solution extracted with sodium carbonate solution. Evaporation of the benzene left only a small neutral residue.

The carbonate extract was acidified and yielded a rather gummy tan product which could not be purified by recrystallization from the usual solvents. It dissolved slowly in 5% sodium bicarbonate solution and more readily in 5% sodium hydroxide solution. It had a light blue fluorescence under ultraviolet light similar to that of diphenic anhydride. A sample purified by chromatographic adsorption on silicic acid also would not crystallize. The analytical sample of the diphenide was obtained by vacuum sublimation, partly as a white powder of indefinite melting point and partly as a glass.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47; neut. equiv., 342.4. Found: C, 84.32; H, 6.75; neut. equiv., 341.7.

Reaction of 2-(3,4-Dimethylbenzoyl)-2′-biphenylcarboxylic Acid Chloride with Di-*n*-butylcadmium.—This reaction was carried out in the manner described above but in toluene solution rather than in benzene solution. The 7-*n*-butyl-7-(3,4-dimethylphenyl)-diphenide from 20 g. of acid chloride was 17.5 g. (82.5%) in the form of a glass. The glass dissolved very slowly in 5% sodium bicarbonate solution and rapidly in hot concentrated potassium hydroxide. It could not be crystallized from any of the usual solvents or solvent pairs. A portion of the glass was distilled in a molecular still to obtain an analytical sample.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07; neut. equiv., 370.5. Found: C, 84.01; H, 7.35; neut. equiv., 371.8.

Reaction of 2-Mesitoyl-2′-biphenylcarboxylic Acid Chloride with Diethylcadmium.—The reaction was carried out in benzene solution. The product from 24 g. of acid chloride was 12.1 g. (51%) of 2-mesitoyl-2′-propionylbiphenyl, m.p. 149.5–151.5°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.27; H, 7.09.

Reaction of 2-Mesitoyl-2′-biphenylcarboxylic Acid Chloride with Di-*n*-butylcadmium.—The reaction was carried out in toluene solution. The product from 30 g. of acid chloride was 27 g. (85%) of 2-mesitoyl-2′-*n*-valeroylbiphenyl, m.p. 90–91°.

Anal. Calcd. for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found: C, 84.27; H, 7.29.

Reaction of Diphenoyl Chloride with Diphenylcadmium.—The reaction was carried out in toluene solution. The product was 23 g. (83%) of 2,2′-dibenzoylbiphenyl, m.p. and mixed m.p. with an authentic sample of the diketone, 165–166°.

Reaction of Diphenic Anhydride with Diphenylcadmium.—The reaction was carried out in toluene solution. The product from 22.6 g. of anhydride was 26.5 g. (87%) of 2-benzoyl-2′-biphenylcarboxylic acid, m.p. 168–172°. The analytical sample, m.p. 179–180°, was obtained by crystallizing the sodium salt from water, acidifying to obtain the acid, and recrystallizing the acid from toluene.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67; neut. equiv., 302.3. Found: C, 79.80; H, 4.94; neut. equiv., 305.1.

Absorption Spectra.—The ultraviolet absorption spectra were measured with a Beckman model DU spectrophotometer. Values were obtained at intervals of 10 mμ or less.

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