equilibrium values determined at 100°.[11] On the other hand, the amounts of 2- and 3-methylpentane and 2,3-dimethylbutane are in the proper sequence. The data indicate that insufficient time was allowed for equilibration to occur, since the concentration of neohexane is too low relative to that of 2-methylpentane.

NORWOOD, PENNSYLVANIA RECEIVED NOVEMBER 1, 1951

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

Acylations of Phenol Ethers with Diphenoyl Chloride[1]

BY DOROTHY V. NIGHTINGALE, ROBERT L. SUBLETT AND ROBERT H. WISE

RECEIVED NOVEMBER 29, 1951

Diphenoyl chloride reacted with phenol ethers in the presence of aluminum chloride at room temperature or at temperatures of −10 to +5° in carbon disulfide, nitrobenzene or *sym*-tetrachloroethane to form the corresponding 2,2′-diaroylbiphenyls. When the solution of diphenoyl chloride was stirred with aluminum chloride for about two hours at room temperature prior to the addition of the phenol ether, the product was a 4-aroylfluorenone and/or a 9,9-diaryl-4-aroylfluorene. Without solvent, the products were the 2,2′-diaroylbiphenyls.

In a previous publication[2] it was established that 2,2′-diphenoyl chloride reacted with some alkylbenzenes in the presence of aluminum chloride to form 2,2′-diaroylbiphenyls. When the isomerization of the diphenoyl chloride was attempted in nitrobenzene solution prior to the addition of the hydrocarbon, 4-aroylfluorenones were formed.

The study has been extended to the reaction of diphenoyl chloride with phenol ethers in the presence of aluminum chloride under similar conditions, both without solvent and in nitrobenzene, carbon disulfide and *sym*-tetrachloroethane. The types of products formed from the ethers in these solvents were largely determined by the reaction temperature and by the rate at which the reactants were mixed.

If the phenol ethers and the diphenoyl chloride were first dissolved in these solvents and cooled to −10° prior to the slow addition of the aluminum chloride, or if the phenol ether was added immediately to the cooled solution of diphenoyl chloride and aluminum chloride at such a rate that the temperature did not exceed 5°, the 2,2′-diaroylbiphenyls were obtained in good yields.

When the solution of diphenoyl chloride was cooled to 0° followed by the addition of the aluminum chloride at such a rate that the temperature did not exceed 15° and then stirred for an hour or more at room temperature prior to the addition of the phenol ether, different products were obtained. *o*-Cresol methyl ether and veratrole yielded 4-aroylfluorenones II and/or 4-aroyl-9,9-diarylfluorenes III (54–70%) while *m*- and *p*-cresol methyl ethers yielded only 4-aroylfluorenones (40–73%). Anisole yielded 4-anisoylfluorenone (47%) and 4-anisoyl-9,9-dianisilfluorene (31%) in nitrobenzene, but only 4-anisoylfluorenone (50%) in carbon disulfide.

TABLE I

PRODUCTS OBTAINED FROM DIPHENOYL CHLORIDE AND PHENOLIC ETHERS

	M.p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2,2′-Bis-(3-methyl-4-methoxybenzoyl)-biphenyl	145.5–146	$C_{30}H_{26}O_4$	79.99	79.90	5.82	6.05
2,2′-Bis-(4-methyl-6-methoxybenzoyl)-biphenyl	147–148	$C_{30}H_{26}O_4$	79.99	79.92	5.82	5.98
2,2′-Bis-(5-methyl-2-methoxybenzoyl)-biphenyl	166–167	$C_{30}H_{26}O_4$	79.99	79.85	5.82	6.03
2,2′-Bis-(3,4-dimethoxybenzoyl)-biphenyl	186–186.5	$C_{30}H_{26}O_6$	74.67	74.45	5.43	5.46
2,2′-Bis-(2,4-dimethoxybenzoyl)-biphenyl	191.5–192	$C_{30}H_{26}O_6$	74.67	74.55	5.43	5.26
	141.5–142					
4-(3-Methyl-4-methoxybenzoyl)-fluorenone	125–126	$C_{22}H_{16}O_3$	80.47	80.38	4.91	5.07
	139.5–140					
4-(4-Methyl-6-methoxybenzoyl)-fluorenone	126–126.5	$C_{22}H_{16}O_3$	80.47	80.37	4.91	4.91
	114–114.5					
4-(2-Methoxy-5-methylbenzoyl)-fluorenone	167.5–168	$C_{22}H_{16}O_3$	80.47	80.36	4.91	4.92
4-(3,4-Dimethoxybenzoyl)-fluorenone	167–168	$C_{22}H_{16}O_4$	76.73	76.72	4.68	4.80
	155–156					
4-(2,4-Dimethoxybenzoyl)-fluorenone	141.5–142	$C_{22}H_{16}O_4$	76.73	76.52	4.68	4.73
4-(3-Methyl-4-methoxybenzoyl)-9,9-bis-(3-methyl-4-methoxyphenyl)-fluorene	193.5–194	$C_{38}H_{34}O_4$	82.39	82.21	6.27	6.26
4-(3,4-Dimethoxybenzoyl)-9,9-bis-(3,4-dimethoxyphenyl)-fluorene	225.5–226	$C_{38}H_{34}O_4$	75.73	75.65	5.67	5.80
4-(4-Methoxybenzoyl)-9,9-bis-(4-methoxyphenyl)-fluorene	177.5–178	$C_{35}H_{28}O_4$	82.01	82.22	5.51	5.81

When the phenol ether was used in excess as solvent for the reaction and the aluminum chloride was added last at room temperature, the corresponding 2,2′-diaroylbiphenyls were formed in yields of 59–77%.

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(1) Abstracted from the Ph.D. dissertation of Robert L. Sublett, 1950, and the Master's dissertation of Robert H. Wise, 1951.

(2) D. V. Nightingale, H. E. Heiner and H. E. French, THIS JOURNAL, **72**, 1875 (1950).

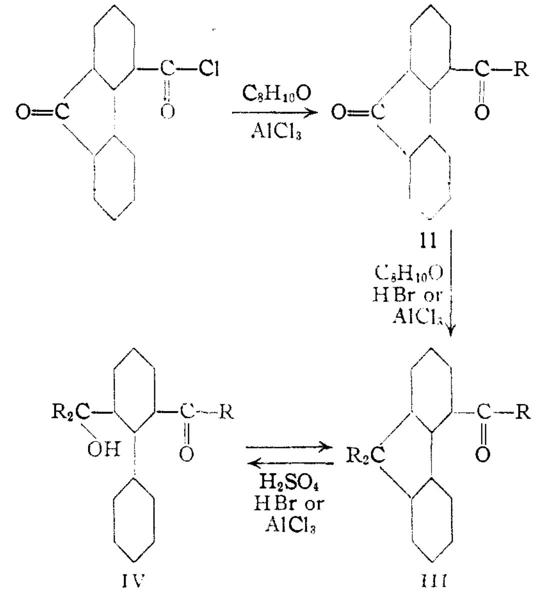
Hydroquinone dimethyl ether did not react with diphenoyl chloride in any of the solvents or without solvent.

One sample of 2,2′-bis-(2,4-dimethoxybenzoyl)-biphenyl melted at 191–192° rather than 140–142°, the recorded value.[3] Carbon and hydrogen analyses and a molecular weight determination substantiated the identity of the compound as a 2,2′-diaroylbiphenyl. After this compound had stood for nearly a year, it was found that the melting point had dropped to 141.5–142°, and it could not be changed by recrystallization. Subsequent preparations of this ketone melted at 141–142°. It is possible that the compound crystallized originally in an unstable polymorphic form. 2,2′-Bis-(3,4-dimethylbenzoyl)-biphenyl, m.p. 143–143.5°, behaved similarly.[2]

Three of the 4-aroylfluorenones (Table I) crystallized in two forms. The higher melting form crystallized from ether and the lower melting form crystallized from alcohol.

o-Cresol methyl ether reacted with the methyl ester of fluorenone-4-carboxylic acid to form the corresponding methyl ester of 9,9-diarylfluorene-4-carboxylic acid. This phenol ether would not react with fluorenone, but veratrole did react to yield the 9,9-diarylfluorene. *o*-Xylene would not react with any of these fluorenone compounds.

The identity of the 4-aroyl-9,9-diarylfluorene obtained from *o*-cresol methyl ether was established as



R = 3-Methyl-4-methoxy-phenyl

There does not appear to be any convenient way to determine whether the diarylhydroxymethyl group in IV is in the 6- or 6′-position.[4]

The three types of ketones gave characteristic color reactions with concd. sulfuric acid. The 2,2′-diaroylbiphenyls gave a yellow color, the fluorene ketones gave a wine-red color, and the fluorene compounds gave a deep purple color.

It is assumed that the phenol ethers acylate in the same position with diphenoyl chloride as with acyl or aroyl chlorides.[5]

Experimental[6]

The 2,2′-diphenoyl chloride was prepared by previously published procedures.[2] When very pure diphenic acid was used, it was desirable to add a trace of anhydrous zinc chloride to the reactants to obtain a maximum yield of acid chloride.

Fluorenone-4-carboxylic acid was prepared according to the method of Grabe and Aubin.[7]

Fluorenone-4-carboxylic acid chloride was prepared from the acid and thionyl chloride.[8]

The methyl ester of fluorenone-4-carboxylic acid was prepared from the acid and absolute methanol in the presence of dry hydrogen chloride. It melted at 131.5–132°, the recorded value.[7]

Each acylation described in detail is representative of its type. Table I lists the acylation products, their physical constants and analyses.

The Preparation of 2,2′-Diaroylbiphenyls (a) Without Solvent.—In a three-necked flask equipped with a mechanical stirrer, a gas trap and an addition tube, 6.6 g. of diphenoyl chloride was dissolved in 10 ml. of *o*-cresol methyl ether at room temperature. The solution was stirred rapidly while aluminum chloride (8.5 g.) was added during 30 minutes. The mixture was stirred an additional two hours. The complex was decomposed in the usual manner, and the reaction products extracted with ether. The ether solution was washed first with 5% sodium hydroxide, then with water and finally dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the excess *o*-cresol methyl ether was removed by distillation at 2 mm. The yellowish solid which remained was recrystallized from ethanol to yield 7.1 g. (66%) of the diketone I, m.p. 147–148°.

(b) **With Solvent.**—Diphenoyl chloride (4.2 g.), 7 ml. of *o*-cresol methyl ether and 30 ml. of carbon disulfide were placed in the reaction flask and the solution cooled to −10°. Gradually and with stirring, 4.6 g. of aluminum chloride was added at such a rate that the temperature did not rise above 0°. The stirring was continued while the solution came to room temperature and then stirred an additional four hours. The diketone I was isolated as described above; yield 5.1 g. (75%), m.p. 147–148°.

Similar yields were obtained when nitrobenzene or *sym*-tetrachloroethane were used as solvents.

The Preparation of the 4-Aroylfluorenones (a) From Diphenoyl Chloride.—A solution of 7 g. of diphenoyl chloride in 15 ml. of nitrobenzene was placed in the reaction flask, cooled to 0°, and 9.8 g. of aluminum chloride was added slowly with stirring. During the addition the temperature rose to 12°. The stirring was continued for 1.5 hours or until the temperature was 0° again, then 10 ml. of *m*-cresol methyl ether was added slowly and the temperature rose to 19°. The mixture was stirred four hours, then decomposed with iced hydrochloric acid. The nitrobenzene was removed by steam distillation and the solid residue recrystallized from ethanol to yield 6 g. of 4-(4-methyl-6-methoxybenzoyl)-fluorenone, IIa, m.p. 113–114° (alcohol) or 126–126.5° (ether).

(b) **From Fluorenone-4-carboxylic Acid Chloride.**—The reaction of 1.5 g. of *o*-cresol methyl ether with 2.3 g. of fluorenone-4-carboxylic acid chloride and 1.6 g. of aluminum chloride in 20 ml. of carbon disulfide at 0–5° yielded 2 g. of II, m.p. 139–140° (ether) or 125–126° (alcohol).

The Preparation of a 4-Aroyl-9,9-diarylfluorene III (a).—*o*-Cresol methyl ether (10 ml.) was treated with 7 g. of diphenoyl chloride and 9.8 g. of aluminum chloride in 15 ml. of nitrobenzene as described for IIa. The reaction product was recrystallized from ethanol to yield a white solid, m.p. 193–194°, which was identified as III. Calculated molecular weight, for $C_{38}H_{34}O_4$, 556; found: 560, 542.

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(3) F. Bell and F. Briggs, *J. Chem. Soc.*, 1661 (1938).

(4) F. Ullmann and R. Von Wurstenburger, *Ber.*, **38**, 4105 (1905), prepared 9,9-diphenylfluorene from 2-(diphenylhydroxymethyl)-diphenyl by heating it on a water-bath with concd. sulfuric acid.

(5) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 308, 315.

(6) The carbon and hydrogen analyses were done by R. L. Sublett, J. S. Finney and P. D. Strickler.

(7) C. Grabe and C. Aubin, *Ann.*, **247**, 261 (1888).

(8) R. Gotz, *Monatsh.*, **23**, 27 (1902); H. Pick, *ibid.*, **25**, 979 (1904).

(b).—When 15 ml. of *o*-cresol methyl ether was added to 5.5 g. of diphenoyl chloride and 6.6 g. of aluminum chloride in 150 ml. of carbon disulfide as described in the preparation of IIa, the products were 2.6 g. of III, m.p. 193.5–194° and 4.6 g. of II, m.p. 125.5–126° (alcohol) and 139.5–140° (ether). The melting point and mixed melting point of the oximes obtained from these two forms of II was 141.5–142°.

Anal. Calcd. for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.98. Found: C, 77.22; H, 4.81.

Reactions of Fluorenone Derivatives with Phenol Ethers.—The reaction of *o*-cresol methyl ether (1 ml.), 0.24 g. of aluminum chloride and 0.2 g. of II in nitrobenzene yielded III, m.p. 193.5–194°.

4-(2,4-Dimethylbenzoyl)-fluorenone reacted with *o*-cresol methyl ether in nitrobenzene solution to form the corresponding 9,9-diaryl-4-aroylfluorene, m.p. 174.5–175°.

Anal. Calcd. for $C_{38}H_{34}O_3$: C, 84.73; H, 6.36. Found: C, 84.69; H, 6.54.

The reaction of veratrole and fluorenone under the same conditions yielded 9,9-bis-(3,4-dimethoxyphenyl)-fluorene, m.p. 224–225°.

Anal. Calcd. for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98; mol. wt., 438. Found: C, 79.39; H, 5.94; mol. wt., 439, 429.

The methyl ester of fluorenone-4-carboxylic acid (1.5 g.), 2 ml. of *o*-cresol methyl ether and 1.8 g. of aluminum chloride in 10 cc. of tetrachloroethane yielded 1.5 g. of the methyl ester of 9,9-bis-(3-methyl-4-methoxyphenyl)-fluorene-4-carboxylic acid, m.p. 170–171°.

Anal. Calcd. for $C_{31}H_{28}O_4$: C, 80.14; H, 6.07. Found: C, 79.89; H, 6.26.

Reaction of the 9,9-Diaryl-4-aroylfluorenes with Sulfuric Acid.—Three grams of III was dissolved in 30 ml. of concd. sulfuric acid. The deep purple solution was allowed to stand at room temperature for six hours and then poured onto 30 g. of crushed ice. The light blue solid which separated melted with decomposition and contained sulfur even after several washings. This solid was boiled for several hours with concd. sodium carbonate solution to yield a white solid IV, m.p. 186–187° (61%).

Anal. Calcd. for $C_{38}H_{36}O_5$: C, 79.70; H, 6.34. Found: C, 79.43; H, 6.54.

The yield of IVa (R = 3,4-dimethoxyphenyl) was 35%, m.p. 212–213°.

Anal. Calcd. for $C_{38}H_{36}O_8$: C, 73.53; H, 5.85. Found: C, 73.83; H, 5.65.

The yield of IVb (R = 2,4-dimethylphenyl, R_2 = 3-methyl-4-methoxyphenyl) was 35%, m.p. 164–165°.

Anal. Calcd. for $C_{38}H_{36}O_4$: C, 82.99; H, 6.52. Found: C, 82.35; H, 6.80.

Recyclization of IV (a) With Aluminum Chloride.—Aluminum chloride (0.4 g.) was added slowly and with stirring to 0.37 g. of IV dissolved in 10 ml. of nitrobenzene. The stirring was continued for 24 hours at room temperature and the product was isolated in the usual manner. A small amount of III, m.p. and mixed m.p. 192–193°, was isolated.

(b) **With 38% Hydrobromic Acid.**—Two-tenths of a gram of IV was dissolved in 20 ml. of glacial acetic acid and 5 ml. of 38% hydrobromic acid was added. The solution turned a deep red color and was warmed until it became colorless. The same amount of hydrobromic acid was added and the solution warmed until it remained colorless. Water was added to precipitate III, m.p. and mixed m.p. 191–192°.

COLUMBIA, MISSOURI

[CONTRIBUTION NO. 834 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Chemistry of Allenic Acids. I. The Reaction of 1,2-Heptadiene-3-carboxylic Acid with Ethylmagnesium Bromide

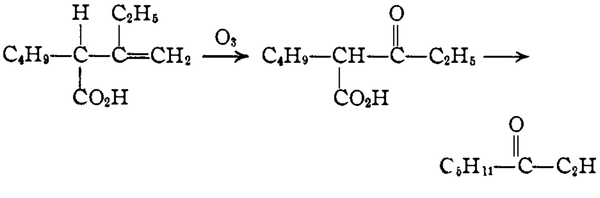
BY JOHN H. WOTIZ AND JOSEPH S. MATTHEWS[1]

The reaction of 1,2-heptadiene-3-carboxylic acid with ethylmagnesium bromide produced 2-butyl-3-ethyl-3-butenoic acid in 85% yield. The mechanism of this reaction was studied and the structure of the product established.

Unpublished observations from this Laboratory dealing with the origin of the dimeric acid, $R_2C_7H_5O_2CO_2H$, found in the carbonation products of Grignard reagents from primary propargylic bromides, R—C≡C—CH_2Br,[2] showed it to be formed by the action of these Grignard reagents with the bromomagnesium salt of the allenic acid, $\underset{\displaystyle CO_2H}{\text{R—C}}\text{=C=CH}_2$ followed by carbonation and hydrolysis. These findings suggested a novel reaction of Grignard reagents. In this paper we are reporting the reaction of ethylmagnesium bromide (I) with the allenic acid 1,2-heptadiene-3-carboxylic acid, $C_4H_9\text{—}\underset{\displaystyle CO_2H}{C}\text{=C=CH}_2$ (II).

The Yield of Product.—A solution of a one molar quantity of II in ether was added to 2.5 molar quantity of I and the solution poured on Dry Ice. On hydrolysis and distillation a monocarboxylic acid, III, identified as $C_4H_9\text{—}\underset{\displaystyle CO_2H}{CH}\text{—}\overset{\displaystyle C_2H_5}{C}\text{=CH}_2$, was isolated in 85% yield. When a molar quantity of I was added to a molar ether solution of II, the yield depended upon the rate of addition and agitation. Since the first reaction is the formation of the bromomagnesium salt of the allenic acid, $C_4H_9\text{—}\underset{\displaystyle CO_2MgBr}{C}\text{=C=CH}_2$ (IIMgBr), a slow addition with agitation did not yield any III, whereas a rapid addition produced III in 26% yield, owing to the formation of local high concentration of IIMgBr with which I reacted.

The Proof of Structure of III.—The acid III, $C_9H_{17}CO_2H$, on low pressure catalytic hydrogenation using Adams catalyst absorbed one mole of hydrogen. Its infrared spectrum (Fig. 1) indicates the presence of a terminal double bond by the strong absorption near 900 cm.$^{-1}$ and the absence of any starting allenic compound. When acid III was ozonized, ethyl *n*-amyl ketone was isolated.



$$C_4H_9\text{—}\underset{\displaystyle CO_2H}{\overset{\displaystyle H}{C}}\text{—}\overset{\displaystyle C_2H_5}{C}\text{=CH}_2 \xrightarrow{O_3} C_4H_9\text{—}\underset{\displaystyle CO_2H}{CH}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_2H_5 \longrightarrow C_5H_{11}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_2H$$

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[1] Abstracted from the thesis of J. S. M. presented in partial fulfillment for the requirement for the degree of Master of Science.

[2] J. H. Wotiz, THIS JOURNAL, **72**, 1639 (1950).