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Syntheses of Phenyl Formates and Naphthyl Formates with Acetic Formic Anhydride

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A new method for the syntheses of phenyl and naphthyl formates has been devised. The formates were obtained in good yields from phenols and naphthols with acetic formic anhydride, which had been prepared from formic acid and ketene. The formyl ester of *N*-hydroxysuccinimide was also prepared by the same method.

Phenyl formate has been prepared by several methods[1,2] in which phenol and formic acid were treated with phosphorus oxychloride, but the yield was generally low because of the difficulty of isolating and purifying the formate from the reaction mixture. Also, Petrov[3] obtained phenyl formate from phenol, and *m*-tolyl formate from *m*-cresol, with silicoformic anhydride, and Okawa[4] prepared *p*-nitrophenyl formate from *p*-nitrophenol and formic acid with *N*, *N'*-dicyclohexylcarbodiimide. Stevens and Van Es[5] discussed the difficulty of preparing phenyl formate and reported the successful esterification of phenols with a mixture of formic acid and acetic anhydride. Their synthetic method, however, seems to require a very long period for the reaction to be completed. We ourselves reported the formylation of amino acids with acetic formic anhydride (A. F. A.) in a previous paper.[6] In the present investigation, it was found that this anhydride is also very useful for the formylation of the hydroxy group of phenols, naphthols, and *N*-hydroxysuccinimide. Although our method for the syntheses of these formates has already been reported in a short communication,[7] we shall report the detailed results in this paper.

Results and Discussion

Phenyl formates and naphthyl formates were obtained in generally good yields by the following method. Two equivalents of pure A. F. A.[6] were added to a solution of one equivalent of a phenol or naphthol in dry ether with or without two equivalents of sodium bicarbonate. After the mixture had been stirred at room temperature for several hours and the insoluble salts had been removed by filtration if necessary, the solution was concentrated under reduced pressure. The pure ester was obtained by fractional distillation *in vacuo* or by recrystallization. The yields and physical properties of these phenyl and naphthyl formates are listed in Tables 1 and 2.

The formates were also successfully prepared by using an undistilled A. F. A. solution (experimental: Method C) instead of pure A. F. A. This method gave pure phenyl (80%), *o*-tolyl (61%), and *m*-tolyl (71%) formates, which had the same physical constants as those shown in Table 1.

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[4] K. Okawa and S. Hase, This Bulletin, **36**, 754 (1963).

[5] W. Stevens and A. Van Es, *Recuell*, **83**, 1294 (1964).

[6] I. Muramatsu, M. Murakami, T. Yoneda and A. Hagitani, This Bulletin, **38**, 244 (1965).

[7] I. Muramatsu, S. Sōfuku, M. Tsuji and A. Hagitani, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 113 (1965).

TABLE 1. RESULTS OF THE PREPARATION OF PHENYL FORMATES WITH ACETIC FORMIC ANHYDRIDE

Formate	Yield, %		Bp °C/mmHg	Mp* °C	n_D^{20}
	without $NaHCO_3$	with $NaHCO_3$			
Phenyl	69	80	79/20	—	1.509
o-Tolyl	82	—	53/2	—	1.507
m-Tolyl	79	—	95.5—98.5/20.5	—	1.508
p-Tolyl	73	87	62—63/3	—	1.509
o-Chlorophenyl	—	72	59—59.5/1.5	—	1.527
p-Chlorophenyl	—	79	82/4	—	1.531
o-Isopropylphenyl	65	70	99—100.5/17	—	1.506
p-*t*-Butylphenyl	—	93	68—71/1	—	1.500
2,6-Xylyl	—	68	58.5—60/1	—	1.506
p-Acetylphenyl**	87	—	120/2	36—38	—
m-Nitrophenyl	—	82	—	37.5—38.5	—
p-Nitrophenyl	82	—	—	72—73	—
m-Methoxycarbonylphenyl	—	87	—	48—50	—
p-Methoxycarbonylphenyl	—	70	—	76—78	—

* All melting points are uncorrected.

** 0.25 equivalent of water was added.

TABLE 2. RESULTS OF THE PREPARATION OF NAPHTHYL FORMATES WITH ACETIC FORMIC ANHYDRIDE ($NaHCO_3$ ADDED)

Formate	Yield %	Bp °C/mmHg	Mp °C	n_D^{20}
α-Naphthyl	89	120/1	—	1.608
β-Naphthyl	73	113/0.5	19.5—22	—

The method of the formylation of phenols and naphthols was useful for the *N*-hydroxy group. *N*-Hydroxysuccinimide was treated with pure or crude A. F. A. in the above way and then formylated in a good yield.

Although our method could be used for the formylation of numerous phenols and naphthols, *o*-*t*-butyl, 4-methyl-2, 6-di-*t*-butyl, *o*-nitro, *o*-acetyl, and *o*-methoxycarbonyl phenols were recovered unchanged. The first two phenols may not be formylated because of the steric hindrance of large ortho-substituted groups. The hydroxy group of the three others may form chelate rings with their respective ortho-substituted groups, therefore not reacting with A. F. A.

The question may arise of whether the product of our method is formate or acetate. The elementary analyses of the isolated products agreed with the values calculated for a formate, and their infrared spectra were also characteristic of formate. The absorption of the C=O stretching vibration in formates generally occurred near 1740—1750 cm^{-1}. In a comparison of this band of formate with that of the corresponding acetate (1770 cm^{-1}) in phenyl and *p*-nitrophenyl esters, it was found that the former occurred at a lower frequency than the latter, and that the relationship between aryl formate and acetate was the same as in alkyl esters.[8] In the region of the C–O stretching vibration, the absorption of phenyl formate (1090—1120 cm^{-1}) was also different from that of acetate (1190—1210 cm^{-1}).

The separation of free phenols from the products by distillation is usually very difficult because of the close proximity of the boiling points of phenols and their formates, but by our method the contamination of the product by free phenol was negligible as measured by infrared spectrophotometry; that is, the infrared absorption band of the free hydroxy group of phenols (about 3600 cm^{-1}) could not be detected.

Experimental[9]

Phenyl Formate. *Method A.* Into a solution of 9.4 g of phenol (0.1 mol) in 20 m*l* of dry ether, 17.6 g of distilled pure A. F. A. (0.2 mol) was added; the solution was then stirred at 25°C for 2.5 hr, after which time the solvent was evaporated *in vacuo*. The fractional distillation of the oily residue gave the pure ester (8.4 g). It was identified as the formate by its infrared spectrum (in carbon tetrachloride): 1750, 1190, 1110 cm^{-1}.

Found: C, 68.28; H, 5.06%. Calcd for $C_7H_6O_2$: C, 68.84; H, 4.95%.

Method B. Into a solution of phenol (9.4 g) in 20 m*l* of dry ether, 16.8 g of sodium bicarbonate (0.2 mol) and pure A. F. A. (17.6 g) were added. The mixture was then stirred at 25°C for 2.5 hr. The insoluble salts were filtered off, and the filtrate was concentrated *in vacuo* to an oily residue, the fractional distillation of which gave 9.8 g of phenyl formate.

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[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London (1958), p. 179.

[9] The infrared spectra were recorded on a Shimadzu model IR 27-B spectrophotometer.

Method C. A solution of 92 g of formic acid (2 mol) in 150 m*l* of dry ether was saturated with ketene in an ice salt bath. After the removal of the excess ketene by passing dry air through, a crude solution of A. F. A. was obtained. Into this solution 94 g of phenol (1 mol) and 168 g of sodium bicarbonate (2 mol) were added. The mixture was then stirred at room temperature. After 4 hr, the precipitate was removed and the filtrate was concentrated under reduced pressure to an oily residue. By fractional distillation the pure ester was obtained as a clear liquid in a yield of 80% (97.6 g).

***p*-Nitrophenyl Formate.** Into a solution of *p*-nitrophenol (27.8 g) in 50 m*l* of dry ether, pure A. F. A. (35.2 g) was added, after which the mixture was stirred at 28°C for 4 hr. The solution was then concentrated under reduced pressure to dryness below 60°C. The recrystallization of the residue from tetrahydrofuran gave the pure ester (27.3 g). It was identified as the formate by comparing its infrared spectrum with that of the ester prepared by the dicyclohexylcarbodiimide method (lit.[4] mp 73—74°C). The mixed-melting-point of the esters prepared by these two methods did not drop. IR spectrum (in carbon tetrachloride): 1755, 1200, 1090 cm^{-1}.

***m*-Nitrophenyl Formate.** To a mixture of *m*-nitrophenol (13.9 g) and sodium bicarbonate (16.8 g) in 20 m*l* of dry ether, pure A. F. A. (17.8 g) was added; this mixture was then stirred at room temperature (28—29°C) for 1 hr. After filtration, the reaction mixture was evaporated *in vacuo* to give a crystalline residue. It was recrystallized from ether and petroleum ether; yield, 13.6 g. IR spectrum (in carbon tetrachloride): 1745, 1200, 1110 cm^{-1}.

Found: C, 50.47; H, 3.13; N, 8.05%. Calcd for $C_7H_5O_4N$: C, 50.31; H, 3.02; N, 8.38%.

***p*-Methoxycarbonylphenyl Formate.** Into a solution of methyl *p*-hydroxybenzoate (6.8 g) in 20 m*l* of dry ether, sodium bicarbonate (6.7 g) and pure A. F. A. (7.0 g) were added. The mixture was then stirred at room temperature for 4 hr. The insoluble salts were filtered off, and the filtrate was concentrated *in vacuo*. The recrystallization of the residue from benzene (10 m*l*) gave the pure ester (5.6 g). IR spectrum (in chloroform): 1740, 1190, 1100 cm^{-1}.

Found: C, 60.11; H, 4.64%. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48%.

***m*-Methoxycarbonylphenyl Formate.** This formate was obtained from methyl *m*-hydroxybenzoate (3.0 g) and pure A. F. A. (3.52 g) in the presence of sodium bicarbonate (3.36 g) by the same procedure as was used for the para isomer; yield, 3.13 g. IR spectrum (in carbon tetrachloride): 1745, 1200, 1115 cm^{-1}.

Found: C, 59.87; H, 4.64%. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48%.

***p*-Tolyl Formate.** *Method A.* A solution of *p*-cresol (10.8 g) in 10 m*l* of dry ether was treated with pure A. F. A. (17.7 g) under the same conditions as were used to produce the *p*-nitrophenyl formate. The reaction mixture was then concentrated under reduced pressure to an oily residue. The fractional distillation of this gave a pure transparent liquid; yield, 9.9 g.

Method B. This was the same as Method A in all respects except one: sodium bicarbonate (16.8 g) was added. After the mixture had been filtered, the same product was obtained from the filtrate by fractional distillation; yield, 11.8 g. IR spectrum (in carbon tetrachloride): 1735, 1190, 1100 cm^{-1}.

Found: C, 70.11; H, 6.16%. Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92%.

***m*-Tolyl Formate.** By Method A above 10.8 g of this formate was obtained from 10.8 g of *m*-cresol. IR spectrum (in chloroform): 1745, 1190, 1110 cm^{-1}.

Found: C, 70.61; H, 6.18%. Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92%.

***o*-Tolyl Formate.** By using Method A as for the *p*-tolyl formate, 11.1 g of this formate was obtained from 10.8 g of *o*-cresol. IR spectrum (in carbon tetrachloride): 1740, 1170, 1120 cm^{-1}.

Found: C 70.48; H, 6.02%. Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92%.

***p*-Chlorophenyl Formate.** In a solution of *p*-chlorophenol (6.4 g), in 10 m*l* of dry ether, sodium bicarbonate (8.4 g) was suspended and to it pure A. F. A. (8.8 g) was added; the mixture was then stirred at room temperature for 4 hr. The insoluble salts were filtered off, and the filtrate was concentrated under reduced pressure to an oily residue. Fractional distillation gave the product; yield, 6.15 g. IR spectrum (in carbon tetrachloride): 1740, 1205, 1095 cm^{-1}.

Found: C, 53.57; H, 3.59%. Calcd for $C_7H_5O_2Cl$: C, 53.70; H, 3.21%.

***o*-Chlorophenyl Formate.** By the same method as was used to produce the *p*-chlorophenyl formate, this formate was obtained from *o*-chlorophenol (6.4 g); yield, 5.6 g. IR spectrum (in carbon tetrachloride): 1745, 1205, 1095 cm^{-1}.

Found: C, 53.64; H, 3.37%. Calcd for $C_7H_5O_2Cl$: C, 53.70; H, 3.21%.

***o*-Isopropylphenyl Formate.** *Method A.* To a solution of *o*-isopropylphenol (6.8 g) in 10 m*l* of dry ether, pure A. F. A. (8.8 g) was added; the mixture was then stirred at room temperature for 4 hr. After it had been concentrated to an oily residue under reduced pressure at a low temperature, the formate was obtained by fractional distillation; yield, 5.3 g.

Method B. Sodium bicarbonate (8.4 g) was added to the ether solution, and the reaction mixture was filtered. Otherwise Method B was the same as Method A; yield, 5.7 g. IR spectrum (in carbon tetrachloride): 1740, 1170, 1120 cm^{-1}.

Found: C, 73.02; H, 7.58%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36%.

***p*-Acetylphenyl Formate.** To a solution of *p*-acetylphenol (6.8 g) in 40 m*l* of dry ether, 0.24 m*l* of 10% water/tetrahydrofuran (0.25 eq. water to *p*-acetylphenol) and pure A. F. A. (13.1 g) were added. The solution was then allowed to stand at room temperature for one day. After it had been concentrated under reduced pressure, the formate was obtained by fractional distillation (under a nitrogen stream); yield, 7.16 g. IR spectrum (in chloroform): 1735, 1190, 1105 cm^{-1}.

Found: C, 65.91; H, 5.02%. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91%.

***p-t*-Butylphenyl Formate.** This formate was obtained, by the same procedure as was used to produce the *o*-isopropylphenyl formate (Method B), from *p-t*-butylphenol (3.75 g), sodium bicarbonate (6.8 g), and pure A. F. A. (6.6 g); yield, 4.15 g. IR spectrum (in carbon tetrachloride): 1740, 1200, 1095 cm^{-1}.

Found: C, 74.39; H, 7.95%. Calcd for $C_{11}H_{14}O_2$:

C, 74.13; H, 7.92%.

2, 6 - Dimethylphenyl Formate. From 2, 6-dimethylphenol (12.3 g) and pure A. F. A. (17.5 g) this formate was obtained by the same procedure as has been described above; yield, 10.4 g. IR spectrum (in carbon tetrachloride): 1735, 1165, 1125 cm^{-1}.

Found: C, 72.35; H, 7.26%. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71%.

α-Naphthyl Formate. To a solution of α-naphthol (7.2 g) in 10 m*l* of dry ether, sodium bicarbonate (8.4 g) and pure A. F. A. (8.8 g) were added; the mixture was then stirred at 27—28°C for 4 hr and concentrated under reduced pressure to an oily residue. The formate was obtained by fractional distillation; yield, 7.67 g. IR spectrum (in carbon tetrachloride): 1740, 1155, 1125 cm^{-1}.

Found: C, 76.57; H, 4.83%. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68%.

β-Naphthyl Formate. By the same method as was used to produce the α-naphthyl formate, this formate was obtained from β-naphthol (7.2 g). It was a colorless liquid which crystallized on cooling; yield, 6.3 g. IR spectrum (in carbon tetrachloride): 1735, 1210, 1090 cm^{-1}.

Found: C, 76.84; H, 4.59%. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68%.

Succinimide Formate. A solution of 4.6 g of formic acid (100 mmol) in 30 m*l* of dry ether was saturated with ketene in an ice bath. After the removal of the excess ketene by passing dry air through, 20 m*l* of ether and 5.75 g of *N*-hydroxysuccinimide (50 mmol) were added. The suspension was stirred at room temperature for 3 hr and then allowed to stand overnight. The precipitate was filtered and washed with ether. White, needle-like crystals of succinimide formate were thus obtained; yield, 6.12 g (85.6%). Mp 120—121°C.

Found: C, 41.77; H, 3.58; N, 10.13%. Calcd for $C_5H_5O_4N$: C, 41.97; H, 3.57; N, 9.79%.

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