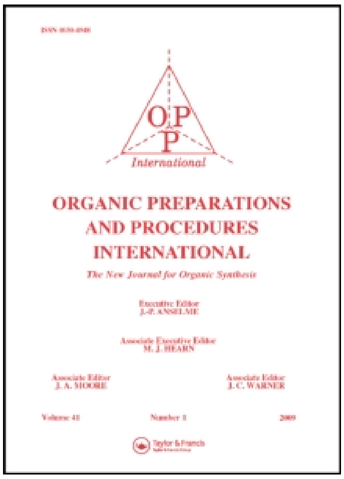

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A GENERAL METHOD FOR THE PREPARATION OF FORMATES

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A GENERAL METHOD FOR THE PREPARATION OF FORMATES

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Classical methods of syntheses of formates[1-4] are time consuming and inconvenient because HCl gas is toxic and corrosive. Industrial methods[5-10] are not suitable for small-scale laboratory preparations because these methods require special autoclaves and high pressures (200-700 atm) to force the reaction of carbon monoxide with alcohols. Thus, a very simple and convenient method has been developed by reacting equimolar amounts of formic acid and alcohols, in the presence of catalytic amounts of boron trifluoride methanol complex, in absence of any solvent. This method was used to prepare sec. butyl formate and seventeen n-alkyl formates (Table 1), including the heretofore unknown nonyl, tridecyl, heptadecyl, and stearyl formates. The yields ranged from 85-97% (Table 1). t-Butanol did not react.

$$\mathrm{HCOOH} \xrightarrow[\mathrm{BF_3 \cdot 2CH_3OH}]{\mathrm{ROH},\ \Delta} \mathrm{HCOOR}$$

A number of catalysts including H_2SO_4, $p\text{-}CH_3 \cdot C_6H_4 \cdot SO_3H$, $p\text{-}CH_3 \cdot C_6H_4 \cdot SO_2Cl$, and $BF_3 \cdot 2CH_3OH$, were evaluated with respect to time of esterification and yield. The most satisfactory results were obtained with boron trifluoride, using about 0.03 mole of the catalyst per mole of the acid.

esterification being complete in 45-60 min. The other catalysts required 2.5-4 hr to achieve the same results. Boron trifluoride methanol complex, in an excess of methanol, was known to be the catalyst of choice for preparation of methyl esters of aliphatic and aromatic acids.[11-13]

EXPERIMENTAL

Formic acid (98%) was obtained from Baker & Adamson General Chemical Co.[14] Boron trifluoride methanol complex, with 51.41% BF_3, and most of the alcohols were obtained from Aldrich Chemical Co. All the chemicals were used without further purification. The indices of refraction were determined on Bausch & Lomb refractometer (Abbe-3L), and the molecular refraction (Table 1) was calculated from the Lorenz & Lorentz relation.[15] IR spectra were determined on Perkin-Elmer 421 grating spectrophotometer.

Methyl Formate.- A mixture of 13.80 g (0.3 mole) of formic acid, 9.60 g (0.3 mole) of methanol, and 1 ml of boron trifluoride methanol complex (0.00758 mole BF_3) was placed into a 100 ml reaction flask equipped with a magnetic stirrer and a distillation set up, with a receiving flask cooled to about 5°. The reaction flask was immersed in a silicon bath at 55-60° and heated with stirring. The ester began to distill almost immediately at 31.5°. In about 15 min, 9.12 g ester was collected and the boiling point rose to 32°. The temperature of the bath was increased to 75° and within 30 min additional 7.91 g ester was obtained; the total yield was 17.03 g (94%).

Ethyl Formate.- A mixture of 13.80 g (0.3 mole) of formic acid, 13.82 g (0.3 mole) ethanol, and 1 ml boron trifluoride methanol complex was reacted for 45 min at 80°, as described above, whereupon 21.65 g (97.5%) of the ester, bp. 52-53°, was obtained.

n-Propyl Formate.- The same mole-ratio was used as given above. The reaction was conducted at 80-5°, whereupon 21.1 g of an azeotropic mixture, bp. 72-73°; was obtained. The distillate formed two layers, 1.45 g water and 19.65 g upper layer which was separated, dissolved in 100 ml anhydrous ether, dried over 20 g anhydrous Na_2CO_3 for about 15 min, and filtered with suction through a sintered glass funnel M. After removal of the solvent, 16.2 g (92%) of ester was collected at 80-81°.

n-Butyl Formate.- The same molar ratio was used (0.3 mole), as given above. The reaction mixture was heated to about 85°, then the temperature of the bath was increased to 125° and an azeotropic mixture distilled at 91-98°. After separation of the layers, the upper layer was dissolved in 100 ml n-hexane, dried over 20 g anhydrous Na_2CO_3, and filtered as above. After removal of the solvent, 27.88 g (91%) of the ester was collected at 105-105.5°.

The remaining esters (Table 1) were prepared in the same way as outlined for the preparation of n-butyl formate; however, for the preparation of amyl, hexyl, heptyl, and octyl formates, 0.2 mole of each of the reactants were used and for the preparation of all the higher esters 0.1 mole. One ml of the catalyst was used for each preparation, i.e., for the preparation of higher esters the molar ratio of the catalyst was increased.

Nonyl Formate: Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 5.80
Found: C, 69.48; H, 5.88

Tridecyl Formate: Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.62; H, 12.40
Found: C, 73.32; H, 12.24

Heptadecyl Formate: Anal. Calcd. for $C_{18}H_{36}O_2$: C, 75.99; H, 12.75
Found: C, 75.56; H, 12.86

Octadecyl Formate: Anal. Calcd. for $C_{19}H_{38}O_2$: C, 76.44; H, 12.83
Found: C, 76.19; H, 12.72

The IR spectra of the esters gave a strong, characteristic absorption at 2920, 2950 (sh), 1715-1725, 1460, and at 1165-1175 cm^{-1}.

TABLE 1. Alkyl Formates (HCOOR)

				Lit. bp.
R	Yield (%)	n_D^{25}	Bp. (°C)	Bp. (°C)
Methyl	94.6	1.3427	31.5-32	32-32.5[1]
Ethyl	97.5	1.3592	54-54.5	54[2]
Propyl	92	1.3770	80-81	80.5-81[2]
n-Butyl	91	1.3888	105-105.5	106.7[3]
sec. Butyl	89.5	1.3835	93-95	94-97[17]
n-Amyl	88.7	1.3995	130-131	130.4[3]
Hexyl	91.5	1.4067	151-153	153.6[3]
Heptyl	87.8	1.4116	176-177	176.7[3]
Octyl	90.5	1.4167	197-198	198.1[3]
Nonyl	91.2	1.4231	222-223	Ref. 18
Decyl	88.5	1.4262	57-58/0.05 mm 240-243/760 mm	240[16]
Undecyl	89.2	1.4290	76-77/0.1 mm 264-266/760 mm	265[16]
Dodecyl	87.2	1.4325	86-88/0.1 mm 144-146/15 mm	145-6/15[4]mm
Tridecyl	86.5	1.4371	87-88/0.3 mm	Unknown
Tetradecyl	87.7	1.4383	130/1.5 mm 164-167/17 mm	166/17[4]mm
Cetyl	86.0	1.4425	124/0.05 mm 188-189/17 mm	188/17[4]mm
Heptadecyl	85.5	1.4423	133-134/0.2 mm	Unknown
Octadecyl	-	-	136-138/0.05 mm mp. 34-34.5	Ref. 19

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