

giving yellow needles, m.p. 120 °C (dec.). Anal. $C_{15}H_{18}N_3$: C, H, N. 1H NMR ($CDCl_3$): δ 6.80–7.55 (15 H, m), 8.83 (1 H, s).

N^1 -Methyl- N^2 -phenyl- N^1 -p-tolyldiazoformamide 2b. This compound was prepared analogously to 2a, m.p. 90 °C, yield 63 %. Anal. $C_{15}H_{16}N_4$: C, H, N. 1H NMR ($CDCl_3$): δ 2.33 (3 H, s), 3.54 (3 H, s), 6.57–7.62 (9 H, m), 8.54 (1 H, s).

N^2 -Phenyl- N^1 -p-tolyl- N^1 -p-tolyldiazoformamide 2c. This compound was prepared analogously to 2a, m.p. 135 °C (dec.), yield 100 %. Anal. $C_{21}H_{20}N_4$: C, H, N. 1H NMR ($CDCl_3$): δ 2.32 (3 H, s), 2.41 (3 H, s), 6.67–7.38 (13 H, m), 8.70 (1 H, s).

N^1 -Benzyl- N^2 -phenyl- N^1 -phenyldiazoformamide 2d. The reaction did not take place in benzene solution analogously to 2a even at reflux temperature. Without solvent the reaction proceeded for 3 h with a yield of 79 % of a yellow mass which could be recrystallized from ethanol, m.p. 100 °C. Anal. $C_{20}H_{18}N_4$: C, H, N. 1H NMR ($CDCl_3$): δ 5.50 (2 H, s), 6.95–7.56 (15 H, m), 8.60 (1 H, s).

N^1 -Benzyl- N^2 -phenyl- N^1 -p-tolyldiazoformamide 2e. This compound was prepared analogously to 2a, m.p. 106 °C, yield 85 %. Anal. $C_{21}H_{20}N_4$: C, H, N. 1H NMR ($CDCl_3$): δ 2.35 (3 H, s), 5.53 (2 H, s), 7.00–7.63 (14 H, m), 8.75 (1 H, s).

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Preparation of *N*-Acylformimidates.

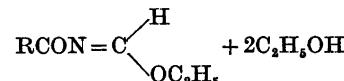
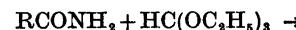
Reaction of Carboxamides with Triethyl Orthoformate

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Several reports on the synthesis of *N*-acylformimidates by reaction between triethyl orthoformate and amides have appeared in the literature.^{1–4} For the carboxamides^{1,2} more extensive work has shown the structural assignment to be wrong.^{5–7} The compounds formed were trisacylaminomethanes and not *N*-acylformimidates. For the reaction of sulfonylamides⁸ and phosphorylamides⁹ with triethyl orthoformate the corresponding formimidates were actually formed.

N-Acylimidates have previously been synthesized by alkylation of the silver salts of diacylamines⁸ and by acylation^{9,10} of the corresponding imidates; no formimidate has been reported. We have reinvestigated the reaction between carboxamides and triethyl orthoformate in order to prepare the hitherto unknown *N*-acylformimidates and report here the preparation of the formimidates listed in Scheme 1. Attempts to prepare ethyl *N*-benzoylformimidate 2d by benzoylation of *O*-ethyl formimidate^{11,12} were unsuccessful.



<i>1a–k</i>	<i>2a–k</i>	<i>R</i>
<i>a</i>	<i>f</i>	<i>o</i> -ClC ₆ H ₄
<i>b</i>	<i>g</i>	<i>m</i> -ClC ₆ H ₄
<i>c</i>	<i>h</i>	<i>p</i> -ClC ₆ H ₄
<i>d</i>	<i>i</i>	<i>o</i> -BrC ₆ H ₄
<i>e</i>	<i>j</i>	<i>o</i> -FC ₆ H ₄
	<i>k</i>	2,6-Cl ₂ C ₆ H ₃

Scheme 1.

Results. The reactions were carried out by refluxing the amide with excess orthoester and a few drops of concentrated sulfuric acid distilling off ethanol while it was formed. Evaporation of excess orthoester and subsequent distillation gave the acylformimidates in yields ranging from 11 to 90 %. It turned out that the electronegativity of the substituent in 1 strongly influenced the reaction pathway and the yield of formimidate. Thus benzamide gave a yield of 33 % and *o*-fluorobenzamide a yield of 73 %. The same was observed with

the chloro-substituted acetamides. Chloroacetamide gave a yield of 11 % while dichloro- and trichloroacetamide gave the imidates in yields of 48 % and 90 %, respectively, while unsubstituted acetamide only gave trisacetaminomethane. This observation is in accordance with the easy formation of imidates from phosphoryl- and sulfonylamides where the nitrogen atom is more electron-deficient compared to the nitrogen atom in carboxamides.

Experimental. Microanalyses were carried out in the Microanalysis Department of Chemical Laboratory II, the H. C. Ørsted Institute. ^1H NMR spectra were obtained on a JEOL MH 60/II instrument. IR spectra were recorded on a Perkin Elmer model 157 NaCl spectrophotometer, only the carbonyl and carbon-nitrogen double bond stretching frequencies being given.

General procedure for preparation of N-acylformimidates. The amide (0.1 mol) was refluxed with triethyl orthoformate (0.3 mol) and three drops of concentrated sulfuric acid in a distillation apparatus. Ethanol was distilled off while it was formed (2–9 h). Excess triethyl orthoformate was evaporated off and the residue distilled in vacuum.

Ethyl N-chloroacetylformimidate 2a. Yield 11 %, b.p. 47°C/1.0 mmHg, reaction time 4 h. Anal. $\text{C}_5\text{H}_8\text{ClNO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.32 (3 H, t), 4.10 (2 H, s), 4.25 (2 H, q), 8.08 (1 H, s). IR (CHCl_3 , cm^{-1}): 1510 s, 1700 s.

Ethyl N-dichloroacetylformimidate 2b. Yield 48 %, b.p. 56°C/0.2 mmHg, reaction time 2.5 h. Anal. $\text{C}_5\text{H}_6\text{Cl}_2\text{NO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.40 (3 H, t), 4.41 (2 H, q), 6.00 (1 H, s), 8.25 (1 H, s). IR (CHCl_3 , cm^{-1}): 1710 s, 1600 s.

Ethyl N-trichloroacetylformimidate 2c. Yield 90 %, b.p. 60°C/0.8 mmHg, reaction time 3.5 h. Anal. $\text{C}_5\text{H}_4\text{Cl}_3\text{NO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.44 (3 H, t), 4.46 (2 H, q), 8.33 (1 H, s). IR (CHCl_3 , cm^{-1}): 1730 s, 1600 s.

Ethyl N-benzoylformimidate 2d. Yield 33 %, b.p. 103°C/1.3 mmHg, reaction time 7.5 h with 60 drops of conc. H_2SO_4 . Anal. $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.38 (3 H, t), 4.37 (2 H, q), 7.10–8.20 (5 H, m), 8.26 (1 H, s). IR (CHCl_3 , cm^{-1}): 1670 s, 1600 s.

Ethyl N-o-fluorobenzoylformimidate 2e. Yield 73 %, b.p. 85°C/0.3 mmHg, reaction time 8.5 h. Anal. $\text{C}_{10}\text{H}_{10}\text{FNO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.37 (3 H, t), 4.43 (2 H, q), 6.78–8.07 (4 H, m), 8.13 (1 H, s). IR (CHCl_3 , cm^{-1}): 1680 s, 1620 s.

Ethyl N-o-chlorobenzoylformimidate 2f. Yield 65 %, b.p. 113°C/0.3 mmHg, reaction time 4.8 h. Anal. $\text{C}_{10}\text{H}_{10}\text{ClNO}_2$: C, H, N. ^1H NMR (CCl_4): 1.34 (3 H, t), 4.32 (2 H, q), 7.00–7.96 (4 H, m), 8.19 (1 H, s). IR (CHCl_3 , cm^{-1}): 1690 s, 1610 s.

Ethyl N-m-chlorobenzoylformimidate 2g. Yield 64 %, b.p. 102°C/0.2 mmHg, reaction time 5.5 h. Anal. $\text{C}_{10}\text{H}_{10}\text{ClNO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.33 (3 H, t), 4.40 (2 H, q), 7.27–8.07 (4 H, m), 8.32 (1 H, s). IR (CHCl_3 , cm^{-1}): 1680 s, 1610 s.

Ethyl N-p-chlorobenzoylformimidate 2h. Yield 45 %, b.p. 100°C/0.2 mmHg, reaction time 5 h. Anal. $\text{C}_{10}\text{H}_{10}\text{ClNO}_2$: C, H, N. ^1H NMR (CCl_4): 1.34 (3 H, t), 4.28 (2 H, q), 7.17–8.10 (4 H, m), 8.27 (1 H, s). IR (CHCl_3 , cm^{-1}): 1680 s, 1600 s.

Ethyl N-o-bromobenzoylformimidate 2i. Yield 56 %, b.p. 105°C/0.2 mmHg, reaction time 3.5 h. Anal. $\text{C}_{10}\text{H}_{10}\text{BrNO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.38 (3 H, t), 4.38 (2 H, q), 7.10–7.95 (4 H, m), 8.24 (1 H, s). IR (CHCl_3 , cm^{-1}): 1690 s, 1610 s.

Ethyl N-o-methylbenzoylformimidate 2j. Yield 18 %, b.p. 93°C/0.3 mmHg, reaction time 9 h with 30 drops of conc. H_2SO_4 . Anal. $\text{C}_{11}\text{H}_{13}\text{NO}_2$: C, H, N. ^1H NMR (CCl_4): δ 1.34 (3 H, t), 3.62 (3 H, s), 4.33 (2 H, q), 6.95–8.15 (4 H, m), 8.20 (1 H, s). IR (CHCl_3 , cm^{-1}): 1680 s, 1610 s.

Ethyl N-2,6-dichlorobenzoylformimidate 2k. Yield 20 %, b.p. 105°C/0.3 mmHg, reaction time 9 h. Anal. $\text{C}_{10}\text{H}_8\text{Cl}_2\text{NO}_2$: C, H, N. ^1H NMR (CCl_4): 1.33 (3 H, t), 4.32 (2 H, q), 7.13–7.40 (3 H, m), 8.27 (1 H, s). IR (CHCl_3 , cm^{-1}): 1690 s, 1600 s.

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