giving yellow needles, m.p. 120 °C (dec.). Anal. $C_{19}H_{16}N_8$: C, H, N. ^{1}H 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-*tolyldiazoformamidine* 2b. This compound was prepared analogously to *2a*, m.p. 90 °C, yield 63 %. Anal. $C_{15}H_{10}N_4$: C, H, N. ^{1}H 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-*tolyldiazoformamidine* 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. ^{1}H 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}-*phenyldiazoformamidine* 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. ^{1}H NMR ($CDCl_3$): δ 5.50 (2H, s), 6.95–7.56 (15 H, m), 8.60 (1 H, s).

N^1-*Benzyl*-*N*^{2}-*phenyl*-*N*^{1}-*p-tolyldiazoformamidine* 2e. This compound was prepared analogously to *2a*, m.p. 106 °C, yield 85 %. Anal. $C_{21}H_{20}N_4$: C, H, N. ^{1}H 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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Preparaton 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.[1–6] 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 sulfonylamides [3] and phosphorylamides [4] with triethyl orthoformate the corresponding formimidates were actually formed.

N-Acylimidates have previously been synthesized by alkylation of the silver salts of diacylamines [8] 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.

$$RCONH_2 + HC(OC_2H_5)_3 \rightarrow RCON{=}C(H)(OC_2H_5) + 2C_2H_5OH$$

1a–k	R	*2a–k*	R
a	$ClCH_2$	*f*	*o*-ClC_6H_4
b	Cl_2CH	*g*	*m*-ClC_6H_4
c	Cl_3C	*h*	*p*-ClC_6H_4
d	C_6H_5	*i*	*o*-BrC_6H_4
e	*o*-FC_6H_4	*j*	*o*-$CH_3C_6H_4$
		k	2,6-$Cl_2C_6H_3$

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. ^{1}H 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 – 9h). 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. $C_5H_8ClNO_2$: C, H, N. ^{1}H 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. $C_5H_7Cl_2NO_2$: C, H, N. ^{1}H 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. $C_5H_6Cl_3NO_2$: C, H, N. ^{1}H 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. $C_{10}H_{11}NO_2$: C, H, N. ^{1}H 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. $C_{10}H_{10}FNO_2$: C, H, N. ^{1}H 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. $C_{10}H_{10}ClNO_2$: C, H, N. ^{1}H 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. $C_{10}H_{10}ClNO_2$: C, H, N. ^{1}H 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. $C_{10}H_{10}ClNO_2$: C, H, N. ^{1}H 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. $C_{10}H_{10}BrNO_2$: C, H, N. ^{1}H 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. $C_{11}H_{13}NO_2$: C, H, N. ^{1}H 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. $C_{10}H_9Cl_2NO_2$: C, H, N. ^{1}H 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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