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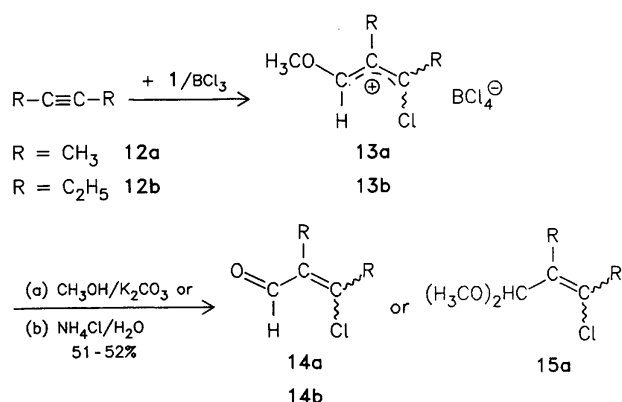
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A different situation arises, when the 1:1 products give resonance-stabilised carbenium ions. It has been reported that vinylsilanes can be formylated by **1** in the presence of equimolar amounts of  $\text{TiCl}_4$ <sup>6</sup>, while allylsilanes give only 2:1 products under these conditions<sup>6c</sup>.

We interpret this finding by the low intrinsic reactivity of the cations **10** which are initially formed from **1** and vinylsilanes. Since similar types of 1:1 products may be formed by the addition of **1** to CC triple bonds, we investigated the formylation of alkynes under similar reaction conditions.

When the dialkylacetylenes **12a, b** were added to solutions of **1** and 1.2 equivalents of boron trichloride, the reactions terminate at the 1:1 product stage. Workup of the product obtained from 2-butyne (**12a**) with methanol/potassium hydrogencarbonate gave a mixture of **14a** and **15a** which was converted into pure **15a** by treatment with methyl orthoformate. Hydrolysis of the formylation product of 3-hexyne (**12b**) was carried out with aqueous ammonium chloride solution to yield the stereoisomeric aldehydes (*E,Z*)-**14b**.



The ionic character of the intermediates **13** was proven by <sup>1</sup>H-NMR spectroscopy. The spectrum taken after addition of 2-butyne to a mixture of **1** and  $\text{BCl}_3$  in  $\text{CD}_2\text{Cl}_2$  showed methyl resonances at  $\delta = 2.04, 2.80,$  and  $4.97$  and a broad one-proton singlet at  $\delta = 9.67$ , as expected for 1-alkoxyallyl cations<sup>7</sup>. Additional signals at  $\delta = 1.34, 2.24,$  and  $2.30$  (1:1:2) are close to those reported for the tetramethylcyclobutadiene aluminium chloride complex (1.32, 2.29, 2.40)<sup>8</sup> and indicate that the  $\text{BCl}_3$ -initiated dimerisation of **12a** takes place as a side reaction. Lewis-acid-initiated oligomerisations of alkynes become dominant with terminal and aryl-substituted acetylenes, and attempts to formylate these types of compounds have not been successful.

**Conclusion.** Electrophilic formylations with dichloromethyl methyl ether (**1**) have previously been achieved with aromatic compounds and vinylsilanes and now with dialkylacetylenes. Since all these reactions require the use of at least 1 equivalent of strong Lewis acids and lead to the formation of intermediate delocalised carbenium ions of low intrinsic reactivity, it appears that these two conditions are needed for the use of **1** as formylating agent, in accordance with theoretical considerations<sup>4</sup>. Until now, appropriate conditions for the formylation of ordinary alkenes (very strong Lewis acids would be needed) have not yet been found, and **1** could only be used for the electrophilic formylation of alkenes, when the electrophilic centre of the formylation product was sterically shielded.

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## Experimental

**General:** NMR: XL 200 (Varian), chemical shifts are recorded with respect to internal TMS. — Mass spectra: 70–250 (VG-Instruments). — IR: IR-435 (Shimadzu).

**3-Chloro-2,2,3-trimethylbutanal (8):** A 1 M solution of  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  (36 ml) was added to a solution of **1** (3.45 g, 30.0 mmol) in 30 ml of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . A solution of 2,3-dimethyl-2-butene (**2c**) (5.40 g, 64.2 mmol) in 60 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise within 30 min and allowed to react for 3 h at  $-78^\circ\text{C}$ . The mixture was washed with 100 ml of 25% aqueous  $\text{NH}_4\text{Cl}$  solution, the aqueous layer extracted with two 20-ml portions of ether, and the combined organic layers were dried with  $\text{CaCl}_2$ . Evaporation of the solvents gave 4.01 g (90%) of spectroscopically pure **8**. — IR (neat):  $2974 \text{ cm}^{-1}$ , 1720, 1458, 1375, 1155, 1104, 829. — <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta = 1.21$  (s, 6H, 2- $\text{CH}_3$ ), 1.63 (s, 6H, 3- $\text{CH}_3$ ), 9.83 (s, 1H, 1-H). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta = 18.95$  (q, 2- $\text{CH}_3$ ), 28.90 (q, 3- $\text{CH}_3$ ), 52.87 (s, C-2), 73.68 (s, C-3), 204.41 (s, C-1). — 2,4-Dinitrophenylhydrazone of **8**: M.p.  $141-143^\circ\text{C}$  (methanol). — MS (70 eV):  $m/z$  (%) = 330 (3), 328 (10) [ $\text{M}^+$ ], 252 (39), 251 (100).

$\text{C}_{13}\text{H}_{17}\text{ClN}_4\text{O}_4$  (328.8) Calcd. C 47.50 H 5.21  
Found C 47.62 H 5.14

**Dichloromethyl Methyl Ether (1) and 2-Butyne (12a):** A 1 M solution of  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  (36 ml) was added to a solution of **1** (3.45 g, 30.0 mmol) in 30 ml of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . Compound **12a** (1.62 g, 30.0 mmol), dissolved in 60 ml of  $\text{CH}_2\text{Cl}_2$ , was added with stirring within 1 h to give a slightly yellow solution which became turbid 30 min after completion of the addition. After 2 h, 25.0 g of  $\text{K}_2\text{CO}_3$  and 10 ml of anhydrous methanol were added, and stirring at  $-78^\circ\text{C}$  was continued for another 15 min. The mixture was warmed at ambient temperature and washed with 30 ml of concentrated aqueous ammonia. The aqueous layer was extracted with two 20-ml portions of ether, the combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated to give a mixture of (*E,Z*)-**14a** and (*E,Z*)-**15a**. Complete acetalisation of **14a** was achieved by stirring this mixture with methanol (0.96 g, 30.0 mmol), methyl orthoformate (3.18 g, 30.0 mmol), and  $\text{NH}_4\text{NO}_3$  (0.2 g) for 14 h. After alkalisation with diisopropylamine, 30 ml of ether was added. The mixture was filtered and distilled (64–66°C/25 mbar) to give 2.58 g (52%) of **15a** (2:1 mixture of stereoisomers).

**(E,Z)-3-Chloro-1,1-dimethoxy-2-methyl-2-butene (15a):** <sup>1</sup>H NMR ( $\text{CDCl}_3$ ), major isomer:  $\delta = 1.71$  ( $m_c$ , 3H, 2- $\text{CH}_3$ ), 2.14 ( $m_c$ , 3H, 4-H), 3.39 (s, 6H,  $\text{OCH}_3$ ), 5.27 (s, 1H, 1-H); minor isomer:  $\delta = 1.80$  ( $m_c$ , 3H, 2- $\text{CH}_3$ ), 2.21 ( $m_c$ , 3H, 4-H), 3.34 (s, 6H,  $\text{OCH}_3$ ), 4.93 (s, 1H, 1-H). — <sup>13</sup>C NMR ( $\text{CDCl}_3$ ), major isomer:  $\delta = 12.19$  (q, 2- $\text{CH}_3$ ), 22.23 (q, C-4, possibly other isomer), 54.90 (q,  $\text{OCH}_3$ ), 103.91 (d, C-1), 128.76 (s, C-2), 130.96 (s, C-3); minor isomer:  $\delta = 14.01$  (q, 2- $\text{CH}_3$ ), 22.78 (q, C-4, possibly other isomer), 54.17 (q,  $\text{OCH}_3$ ), 102.8 (d, C-1), 128.1 (s, C-2), 129.7 (s, C-3). — MS (70 eV):  $m/z$  (%) = 166 (0.23), 164 (0.73) [ $\text{M}^+$ ], 135 (18), 133 (57), 129 (18), 97 (10), 75 (58), 31 (100).

$\text{C}_7\text{H}_{13}\text{ClO}_2$  (164.6) Calcd. C 51.07 H 7.96  
Found C 51.67 H 7.81

**Dichloromethyl Methyl Ether (1) and 3-Hexyne (12b):** A 1 M solution of  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  (36 ml) was added to a precooled solution ( $-78^\circ\text{C}$ ) of **1** (3.45 g, 30.0 mmol) in 30 ml of  $\text{CH}_2\text{Cl}_2$ . A solution of **12b** (2.46 g, 30.0 mmol) in 60 ml of  $\text{CH}_2\text{Cl}_2$  was added within 30 min and stirred for 2 h at  $-78^\circ\text{C}$ . The mixture was poured onto 200 ml of aqueous  $\text{NH}_4\text{Cl}$  solution (25%), the aqueous layer was washed with two 30-ml portions of  $\text{CH}_2\text{Cl}_2$ , and the combined organic layers were dried with  $\text{CaCl}_2$ . Distillation at 65–80°C (bath)/32 mbar gave 2.24 g (51%) of (*E,Z*)-3-chloro-2-ethyl-2-pen-

tenal (**14b**) ( $\approx 2:1$  mixture of stereoisomers) contaminated with small amounts ( $\approx 10\%$ ) of an unknown impurity. — Mixture of (*E,Z*)-**14b**: IR (neat): 1676  $\text{cm}^{-1}$ , 1609. —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 0.98$  (t,  $J = 7.5$  Hz,  $\text{CH}_3$ ), 1.26 and 1.29 (2 t,  $J = 7.4$  Hz,  $\text{CH}_3$ ), 2.34, 2.44, 2.64, 2.93 (4 q,  $J = 7.5$  Hz,  $\text{CH}_2$ ), 10.01, 10.21 (2 s, ratio 2:1,  $\text{CH}=\text{O}$ ). —  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 11.93$ , 11.98, 13.47 (3 q,  $\text{CH}_3$ ), 19.47, 20.48 (2 t), 28.24, 30.59 (2 t), 139.40 (s, C-2), 154.82, 159.20 (2 s, C-3, assignment uncertain), 186.94, 191.21 (2 d, CHO). — MS (70 eV):  $m/z$  (%) = 148 (32), 146 (100) [ $\text{M}^+$ ], 133 (3), 131 (8), 119 (9), 117 (24), 111 (37), 95 (36), 93 (17), 89 (20), 81 (36), 67 (76).

When the crude reaction product obtained from 30 mmol of **1** and **12b** was not distilled but treated with 2,4-dinitrophenylhydrazine<sup>9)</sup>, a mixture of stereoisomeric 2,4-dinitrophenylhydrazones (5.00 g, 51%) was obtained, which was separated by MPLC (30  $\times$  2.5 cm LiChroprep Si 60, 15–25  $\mu$ , hexane: $\text{CH}_2\text{Cl}_2 = 5:1$ , 12.5 ml/min) to give 2.47 g of an isomer I with  $R_t = 8.7$  min and 0.89 g of an isomer II with  $R_t = 9.7$  min. — 2,4-Dinitrophenylhydrazone of **14b** (isomer I): M.p. 147–148 °C (hexane/ $\text{CH}_2\text{Cl}_2$ ). —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.14$  (t,  $J = 7.5$  Hz, 3H,  $\text{CH}_3$ ), 1.24 (t,  $J = 7.4$  Hz, 3H,  $\text{CH}_3$ ), 2.60 (q,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 2.63 (q,  $J = 7.4$  Hz, 2H,  $\text{CH}_2$ ), 11.26 (br. s, 1H, NH), aryl H as usual. —  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 12.63$  (q), 13.90 (q), 21.51 (t), 29.91 (t), 116.6 (d), 123.5 (d), 129.4 (s), 130.0 (d), 132.3 (s), 138.2 (s), 144.3 (s), 144.8 (s), 147.2 (d).

$\text{C}_{13}\text{H}_{15}\text{ClN}_4\text{O}_4$  (326.7) Calcd. C 47.79 H 4.63  
Found C 47.91 H 4.68

2,4-Dinitrophenylhydrazone of **14b** (isomer II): M.p. 154–156 °C (hexane/ $\text{CH}_2\text{Cl}_2$ ). —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.13$  (t,  $J = 7.5$  Hz,

3H,  $\text{CH}_3$ ), 1.26 (t,  $J = 7.5$  Hz, 3H,  $\text{CH}_3$ ), 2.70 (q,  $J = 7.5$  Hz, 4H, 2  $\text{CH}_2$ ), 11.24 (br. s, 1H, NH), aryl H as usual. —  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): 12.41 (q), 13.47 (q), 22.65 (t), 29.03 (t), 116.7 (d), 123.5 (d), 129.3 (s), 130.1 (d), 133.8 (s), 138.2 (s), 144.5 (d), 144.8 (s), 146.1 (s).

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