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Selective formylation of alcohols in the presence of phenols with chloral

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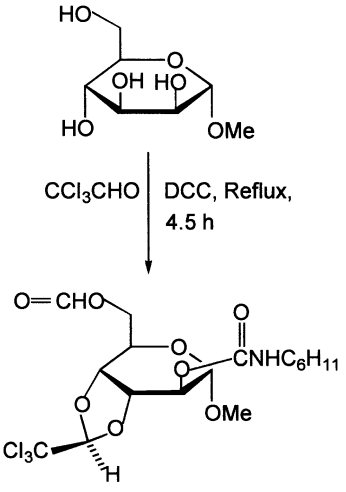
Abstract—Primary and secondary alcohols were formylated selectively in the presence of phenols by stirring with chloral in acetone over anhydrous K_2CO_3 at ambient temperatures in high yields.

O-Formylation could be the method of choice for protecting an alcoholic group in a complex synthetic sequence because deformylation can be effected selectively in the presence of acetate or other ester protecting groups.[1] Further, if the alcoholic group is planned to be oxidised later in the synthetic scheme, the formylated alcoholic group need not be deprotected and direct oxidation under Oppenauer conditions can be realised.[2,3] In some steroidal transformations, formylation has been found to be superior in detail to acetylation.[2] Formate esters also serve as useful synthetic reagents and intermediates.[4] Despite these uses and considerable potential, the formyl protecting group has been rather overlooked. This is partly due to the fact that efficient formylation procedures under mild conditions are not available. The acid halide or anhydride procedure is unsuitable for formylation because formyl halides and anhydride are unstable. The classical methods of formylation with formic acid with or without an acid catalyst ($HClO_4$,[5] BF_3[6]) employ rather drastic conditions. Therefore, several formylation procedures have been reported over the years. These are based on formylation with formic acid in the presence of a dehydrating agent (Ac_2O,[7] DCC,[8] 1,1′-oxalyldiimidazole[9]), transesterification with methyl/ethyl formate (catalysed by silica-gel supported metal sulphates,[10] $Ce(OTf)_4$,[11] $Cu(NO_3)_{2\cdot3}H_2O$,[12] PPh_3/CBr_4,[13] $K_5CoW_{12}O_{40}\cdot3H_2O$[14]) or with active formates (enol formates,[15] cyanomethyl formate,[16] β-oxopropyl formate[17] under imidazole or DBN catalysis) and formyl transfer from DMF (in conjunction with benzoyl chloride,[18] $SOCl_2$/LiI,[19] polymer-supported phosphine–halogen complex,[20] secondary bromide/Cs_2CO_3,[21]) or from other active *N*-formyl compounds such as *N*,*N*-diformylacetamide,[22] *N*-formyl formamide (generated in situ by ozonolysis of oxazole[23]) as well as *N*-formyl heterocycles (*N*-formylbenzotriazole, *N*-formylimidazole, *N*-formyl-4-pyridone, *N*-formyl-2-pyridone, 4-formyl-2-methyl-1,3,4-thiadiazolin-5-thione).[24] Most of these methods, however, use uncommon and in some cases moisture sensitive or thermally unstable reagents which need to be prepared before use, in some cases, by multistep procedures employing expensive catalysts. Many of these methods also suffer from some of the following limitations: elevated temperatures, long reaction times, inert atmosphere, separation of the spent or deformylated reagent, acidic reaction conditions or work up, side reactions, and moderate yields.

Chloral reacts with alcohols easily to form stable hemiacetals.[25] It is also known to formylate the primary hydroxy group of methyl mannopyranoside when heated in 1,2-dichloroethane at reflux in the presence of DCC.[26] However, the reaction was not found to be selective and other hydroxy groups reacted differently as shown in Scheme 1.



Scheme 1.

Keywords: formylation; chloral; primary and secondary alcohols; selective formylation; phenolic alcohols.

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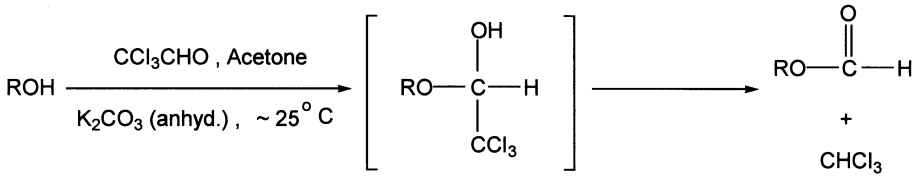

Scheme 2.

Table 1. Formylation of cinnamyl alcohol with chloral at room temperature

Entry	Solvent	Base	Time (h)	Yield (%) of cinnamyl formate
1	Acetone	K_2CO_3	4	93
2	THF	K_2CO_3	19	86
3	CH_2Cl_2	K_2CO_3	24	12
4	EtOAc	K_2CO_3	24	89
5	THF	Et_3N	24	Trace
6	C_6H_6	K_2CO_3	24	6
7	CH_3CN	K_2CO_3	3.5	91
8	CH_3CN	Et_3N	9	92

Our interest in the synthesis of chlorofurans using chloral hemiacetals[27] led us to observe that chloral cinnamyl hemiacetal was cleaved easily to give cinnamyl formate in high yield, apparently by elimination of $CHCl_3$, on stirring in acetone over anhydrous K_2CO_3 at ambient temperatures. Considering the potential of this reaction as a simple and mild formylation procedure, the reaction was investigated in detail and forms the subject of the present paper.

Thus, it was observed that the hemiacetal of chloral need not be prepared separately and the whole transformation could be done in a single step by mixing the alcohol, chloral and anhydrous K_2CO_3 together in acetone and stirring at ambient temperatures (~25°C) (Scheme 2). Taking cinnamyl alcohol as the test case, the reaction was examined in various other solvents. Et_3N was also used as the base in the place of K_2CO_3 (Table 1). The most effective solvent-base combinations were found to be acetone–K_2CO_3 and acetonitrile–K_2CO_3. Acetonitrile–Et_3N combination also gave the formate in comparable yields but required longer reaction time.

Next, a variety of primary and secondary alcohols was converted to their formates at ambient temperatures in high yields (Table 2) except benzylic alcohols where the yields of the products were curiously found to be lower (entries 3 and 10, Table 2). Cyclohexanol was also formylated but the formate could be isolated only in poor yields (17%) probably due to its volatility. The reaction seems to be unsuitable for tertiary alcohols, as the formylation of 2-phenyl-2-propanol was found not to be clean and gave a complex mixture of products along with the unreacted alcohol. Under these conditions, phenolic compounds, e.g. *p*-cresol and methyl *p*-hydroxybenzoate remained unreacted and were recovered unchanged, indicating that the reaction could be selective for the formylation of primary and secondary alcohols in the presence of phenols. The selectivity was demonstrated by competition experiments in which equimolar mixtures of an alcohol and a phenol were subjected to formylation whereby alcohols were completely formylated but phenols were mostly recovered unchanged (entries 16–18, Table 2). Formylation of some phenolic alcohols also displayed the same type of selectivity (entries 19–21, Table 2). Most of the existing reports on formylation of alcohols do not describe this type of selec-

Table 2. Selective formylation of alcohols with chloral/K_2CO_3/acetone

Entry	Alcohol[ref.]	Chloral (equiv.)	Time (h)	Alkyl formate[ref.]	Yield (%)
1	$CH_3(CH_2)_7CH_2OH$	1.14	3.5	$CH_3(CH_2)_7CH_2OCHO$[6]	93
2	$CH_3(CH_2)_{10}CH_2OH$	1.14	5	$CH_3(CH_2)_{10}CH_2OCHO$[6]	93
3	$PhCH_2OH$	1.14	4.5	$PhCH_2OCHO$[24]	62
4	$PhCH_2CH_2OH$	1.14	3	$PhCH_2CH_2OCHO$[29]	87
5	PhCH=$CHCH_2OH$	1.14	4	PhCH=$CHCH_2OCHO$[30]	93
6	2-(1-Naphthyl)ethanol	1.14	3	2-(1-Naphthyl)ethyl formate	95
7	$PhCH(Me)CH_2OH$	1.14	3	$PhCH(Me)CH_2OCHO$[31]	87
8	$PhCO_2CH_2CH_2OH$	1.14	5	$PhCO_2CH_2CH_2OCHO$[32]	88
9	*m*-MeO_2CPhCH_2OH	1.14	4	*m*-MeO_2CPhCH_2OCHO	91
10	PhCH(OH)Me	1.14	6	PhCH(OCHO)Me[33]	76
11	α-Tetralol	2	10	α-Tetralinyl formate[24]	88
12	Cyclododecanol	2	10	Cyclododecanyl formate[19]	85
13	Cholesterol	6	48	Cholesteryl formate[13]	93
14	9-Fluorenol	4.5	31	9-Fluorenyl formate	89
15	Ph_2CHOH	4.5	25	$Ph_2CHOCHO$[34]	91
16	{PhCH=$CHCH_2OH$+ *p*-MePhOH}	1.14	5	{PhCH=$CHCH_2OCHO$+ *p*-MePhOH}	{89+88}
17	{PhCH=$CHCH_2OH$+ *p*-MeO_2CPhOH}	1.14	6	{PhCH=$CHCH_2OCHO$+ *p*-MeO_2CPhOH}	{90+83}
18	{Cyclododecanol+*p*-cresol}	2	10	{Cyclododecanyl formate+*p*-cresol}	{89+92}
19	*p*-$HOPhCH_2CH_2OH$[35]	2	5	*p*-$HOPhCH_2CH_2OCHO$	91
20	*p*-$HOPhOCH_2CH_2OH$[36]	2	5	*p*-$HOPhOCH_2CH_2OCHO$	92
21	*m*-$HOPhOCH_2CH_2OH$[37]	2	5	*m*-$HOPhOCH_2CH_2OCHO$	79

tivity. The present method of selective formylation uses weakly basic conditions and is complimentary to the reported method for the formylation of some *ortho*-substituted phenolic alcohols with formic acid.[28] All the compounds have been characterised by IR and NMR spectroscopy.

Chloral is a stable inexpensive and commercially available reagent. The formylation procedure is very simple and the reaction conditions are mild enough not to seriously interfere, with many common functional and protecting groups.

1. Experimental

Melting points are uncorrected and recorded in a glass capillary with electrical heating. The IR spectra have been recorded on a Nicolet 5DX FTIR Spectrometer on samples taken as neat or as KBr discs. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Spectrospin DPX 300 MHz NMR Spectrometer in $CDCl_3$ with TMS as the internal standard. The mass spectra were recorded on Jeol SX-102 Spectrometer at RSIC, CDRI, Lucknow. The microanalysis was carried out using Perkin–Elmer 240 rapid elemental analyser.

2-Phenylethanol, 2-(1-naphthyl)ethanol and 4-hydroxyphenylethanol were prepared by reduction of the corresponding methyl ester with $LiAlH_4$. 2-Phenylpropanol, 1-phenylethanol, α-tetralol, cyclododecanol, 9-fluorenol and diphenylmethanol were prepared by the reduction of the corresponding carbonyl compounds with $NaBH_4$. 2-Hydroxyethyl benzoate[38] was prepared by the reaction of benzoyl chloride with excess of ethylene glycol in the presence of triethylamine followed by purification on silica gel column using 12% ethylacetate in hexane as the eluting solvent. Methyl 3-hydroxymethylbenzoate[39] was prepared by selective hydrolysis of the corresponding bromo compound in refluxing aqueous dioxane/$CaCO_3$.[40] 2-(4-Hydroxyphenoxy)ethanol[36] and 2-(3-hydroxyphenoxy)-ethanol[37] were prepared from hydroquinone and resorcinol, respectively, by reaction with ethylene chlorohydrin in 10% aqueous NaOH at room temperature followed by purification on silica gel column using 27% ethylacetate in hexane for elution. All the prepared alcohols showed satisfactory melting point, IR and NMR spectra. All the other alcohols were procured commercially and were used as received.

1.1. General procedure for formylation

A solution of anhydrous chloral (0.84 g, 5.7 mmol) in acetone (4 ml) was added rapidly to a stirred suspension of the alcohol (5 mmol) and anhydrous K_2CO_3 (0.69 g, 5 mmol) in acetone (6 ml) (16 ml in the case of cholesterol). The stirring was continued and the progress of the reaction was monitored by TLC. After the completion of the reaction (Table 2), the solid was filtered through a celite pad and washed with acetone. The solvent was removed under reduced pressure. The residue was taken up in ether, washed successively with water (2×15 ml) and brine (2×10 ml), dried (anhyd. Na_2SO_4) and evaporated. The crude formate thus obtained was purified by column chromatography on silica gel column. The pure formate was collected by eluting with 2–3% ethyl acetate in hexane (10–11% ethyl acetate in hexane in the case of phenolic formates, entries 19–21, Table 2).

1.2. Spectral data of some formates

The formates 1–5, 7, 8, 10–13 and 15 (compound number refers to the serial number in Table 2) are known in the literature. These have been prepared from the corresponding alcohols by formylation with formic acid or formic acid in the presence of Lewis or mineral acids (1, 2, 4, 7, 8, 10–12), or with *N*-formyl benzotriazole (3, 11), or by transesterification with ethyl formate using $Ce(OTf)_4$ or PPh_3/CBr_4 (5, 13). The formates 3, 10, 11 and 13 have been characterised by spectral analysis. The spectral data of new formates (6, 9, 14, 19–21) and of the formates 1, 2, 4, 5, 7, 8, 12 and 15 for which the spectral data are not reported are given below:

1.2.1. 1-Nonanyl formate (1).[6] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 2926, 2856, 1731, 1467, 1378, 1170. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.88 (t, 3H, *J*=6.5 Hz), 1.28 (bs, 12H), 1.66 (quintet, 2H, *J*=6.9 Hz), 4.16 (t, 2H, *J*=6.7 Hz), 8.06 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 13.91, 22.53, 25.71, 28.42, 29.09, 29.35, 31.74, 63.94, 161.03.

1.2.2. 1-Dodecanyl formate (2).[6] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 2925, 2854, 1731, 1467, 1377, 1179. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.88 (t, 3H, *J*=6.6 Hz), 1.26 (bs, 18H), 1.66 (quintet, 2H, *J*=6.6 Hz), 4.16 (t, 2H, *J*=6.7 Hz), 8.06 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 13.88, 22.55, 25.71, 28.41, 29.09, 29.24, 29.54, 29.52, 31.80, 63.84, 160.89.

1.2.3. 2-Phenylethyl formate (4).[29] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 3030, 2936, 1724, 1498, 1455, 1170. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.97 (t, 2H, *J*=7.0 Hz), 4.38 (t, 2H, *J*=7.0 Hz), 7.21–7.33 (m, 5H), 8.02 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 34.57, 63.93, 126.37, 128.23, 128.55, 137.14, 160.55.

1.2.4. Cinnamyl formate (5).[30] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 3027, 2934, 1724, 1449, 1494, 1165. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.82 (d, 2H, *J*=6.4 Hz), 6.23–6.33 (dt, 1H, *J*=6.4, 15.9 Hz), 6.68 (d, 1H, *J*=15.9 Hz), 7.25–7.40 (m, 5H), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 63.54, 122.08, 126.09, 127.52, 128.02, 133.62, 135.50, 160.11.

1.2.5. 2-(1-Naphthyl)ethyl formate (6). Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 3047, 2951, 1717, 1597, 1510, 1464, 1397, 1171. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.43 (t, 2H, *J*=7.3 Hz), 4.49 (t, 2H, *J*=7.3 Hz), 7.34–7.56 (m, 4H), 7.74–8.07 (m, 3H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 31.64, 63.48, 123.04, 125.12, 125.35, 125.92, 126.68, 127.25, 128.53, 131.60, 132.86, 133.53, 160.64. Analysis: Found C, 77.48; H, 5.81%, $C_{13}H_{12}O_2$ requires C, 77.98; H, 6.04%. MS (*m*/*z*): 200 (M^+, 18%), 154 ($M^+-HCOOH$, 100%), 141 (83%).

1.2.6. 2-Phenylpropyl formate (7).[31] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 2967, 1724, 1495, 1454, 1172. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.31 (d, 3H, *J*=7.0 Hz), 3.12 (sextet, 1H, *J*=6.9 Hz), 4.19–4.31 (m, 2H), 7.25–7.38 (m, 5H), 8.05 (s,

1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 17.96, 38.75, 68.67, 126.77, 127.17, 128.50, 142.68, 160.91.

1.2.7. 2-Benzoyloxyethyl formate (8).[32] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 2952, 1724, 1452, 1277, 1175, 1110. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.44 (d, 4H, J=4.8 Hz), 7.33–7.38 (m, 2H), 7.46–7.50 (m, 1H), 7.94–8.02 (m, 3H). ^{13}C NMR ($CDCl_3$): δ (ppm) 61.52, 62.32, 128.35, 129.62, 133.15, 160.57, 166.19.

1.2.8. 3-(Methoxycarbonyl)benzyl formate (9). Colourless crystals (pentane), mp 49−50°C. IR (KBr): ν_{max} (cm^{-1}) 2954, 1724, 1449, 1436, 1290, 1207,1159, 1109, 750. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.93 (s, 3H), 5.25 (s, 2H), 7.46 (t, 1H, J=7.6 Hz), 7.57 (d, 1H, J=7.6 Hz), 8.02 (d, 1H, J=7.8 Hz), 8.05 (s, 1H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 51.95, 64.70, 128.53, 129.03, 129.34, 130.40, 132.36, 135.52, 160.39, 166.33. Analysis: Found C, 62.14; H, 5.22%, $C_{10}H_{10}O_4$ requires C, 61.85; H, 5.19%. MS (m/z): 194 (M^+, 63%), 164 (M^+-HCHO), 163 (M^+-OCH_3, 59%), 149 (43%), 133 (60%), 107, 89 (100%), 77, 63, 51.

1.2.9. Cyclododecanyl formate (12).[19] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 2933, 2864, 1724, 1471, 1183. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.35–1.80 (m, 22H), 5.14 (m, 1H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 20.67, 23.02, 23.18, 23.63, 23.85, 28.91, 71.87, 160.55.

1.2.10. 9-Fluorenyl formate (14). Colourless crystals (pentane), mp 74–76°C. IR (KBr): ν_{max} (cm^{-1}) 3005, 2926, 1715, 1453, 1310, 1155, 926, 757, 735. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.89 (s, 1H), 7.30 (t, 2H, J=7.4 Hz), 7.42 (t, 2H, J=7.4 Hz), 7.55 (d, 2H, J=7.4 Hz), 7.67 (d, 2H, J=7.5 Hz), 8.39 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 74.45, 119.90, 125.72, 127.70, 129.45, 140.88, 141.21, 161.40. Analysis: Found C, 79.49; H, 4.17%, $C_{14}H_{10}O_2$ requires C, 79.98, H, 4.79%. MS (m/z): 210 (M^+, 64%), 182 (M^+-CO, 45%), 181 (M^+-CHO, 58%), 165 (M^+-OCHO, 100%).

1.2.11. Diphenylmethyl formate (15).[34] Colourless liquid. IR (neat): ν_{max} (cm^{-1}) 3032, 2929, 1727, 1495, 1454, 1163. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.00 (s, 1H), 7.29–7.35 (m, 10H), 8.22 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 77.72, 128.52, 129.43, 129.91, 141.07, 161.28.

1.2.12. 2-(4-Hydroxyphenyl)ethyl formate (19). Colourless crystals (pentane+ether), mp 46°C. IR (KBr): ν_{max} (cm^{-1}) 3344, 2958, 1686, 1517, 1219 IR (Neat): ν_{max} (cm^{-1}) 3403 (m, br), 1717, 1614, 1516, 1220, 1172. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.90 (t, 2H, J=6.9 Hz), 4.34 (t, 2H, J=6.9 Hz), 5.55 (bs, 1H, D_2O-exchangeable), 6.78 (d, 2H, J=8.1 Hz), 7.08 (d, 2H, J=8.1 Hz), 8.04 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 33.90, 64.86, 115.44, 129.01, 129.92, 154.54, 161.56. Analysis: Found C, 64.51; H, 5.97%, $C_9H_{10}O_3$ requires C, 65.05, H, 6.06%. MS (m/z): 166(M^+, 10%), 120($M^+-HCOOH$, 100%), 107, 77.

1.2.13. 2-(4-Hydroxyphenoxy)ethyl formate (20). Colourless crystals (pentane+ether), mp 71–72°C. IR (KBr): ν_{max} (cm^{-1}) 3400 (s, br) 2959, 2928, 1717, 1697, 1511, 1217, 1179, 1080. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.14 (t, 2H, J=4.7 Hz), 4.49 (t, 2H, J=4.7 Hz), 4.78 (s, 1H, D_2O-exchangeable), 6.75–6.82 (m, 4H), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 62.47, 66.42, 115.92, 116.11, 150.14, 152.19, 161.25. Analysis: Found C, 59.62; H, 5.69%, $C_9H_{10}O_4$ requires C, 59.34; H, 5.53%. MS (m/z): 182 (M^+, 12%), 110 (p-$HOC_6H_4OH^+$, 25%), 73 ($CH_2CH_2OCHO^+$, 100%).

1.2.14. 2-(3-Hydroxyphenoxy)ethyl formate (21). Colourless crystals (pentane+ether), mp 67–68°C. IR (KBr): ν_{max} (cm^{-1}) 3323 (m, br), 2961, 2941, 1686, 1594, 1493, 1451, 1223, 1179, 1151. ^{1}H NMR ($CDCl_3$): δ (ppm) 4.17 (t, 2H, J=4.6 Hz), 4.51 (t, 2H, J=4.6 Hz), 5.32 (s, 1H, D_2O-exchangeable), 6.42–6.50 (m, 3H), 7.13 (t, 1H, J=8.1 Hz), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 62.33, 65.44, 102.22, 106.68, 108.52, 130.18, 156.83, 159.39, 161.42. Analysis: Found C, 59.24; H, 5.67%, $C_9H_{10}O_4$ requires C, 59.34; H, 5.53%. MS (m/z): 182 (M^+, 16%), 110 (m-$HOC_6H_4OH^+$ 16%), 73 ($CH_2CH_2OCHO^+$, 100%).

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