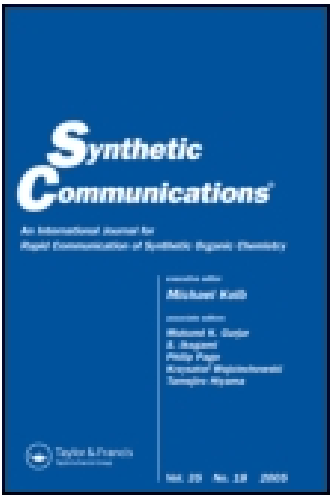

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ONE-POT OXIDATION AND WITTIG OLEFINATION OF ALCOHOLS USING O-IODOXYBENZOIC ACID AND STABLE WITTIG YLIDE*

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ONE-POT OXIDATION AND WITTIG OLEFINATION OF ALCOHOLS USING O-IODOXYBENZOIC ACID AND STABLE WITTIG YLIDE*

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ABSTRACT

Benylic, allylic, and propargylic alcohols, as well as diols, can be oxidized with o-iodoxybenzoic acid (IBX) in the presence of stabilized Wittig ylide to generate α,β-unsaturated ester in one pot. This is useful when the intermediate aldehydes are unstable and difficult to isolate.

The oxidation of primary alcohols to reactive aldehydes and their subsequent homologation using stabilized Wittig ylide[1] is a useful and common step in synthetic organic chemistry (Eq. 1). Problems arise when the intermediate aldehydes are inductively destabilized by strongly electronegative substituents, leading to hydration, decomposition,[2,3] polymerization[4] or difficulty in isolating due to volatility and toxicity. Such problems can be overcome by preparing the aldehydes and reacting them in situ with stabilized ylide to give α,β-unsaturated esters.

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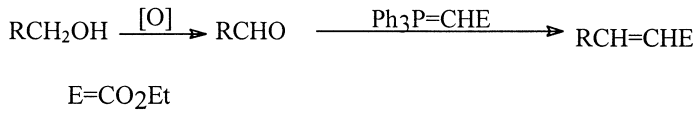


Equation 1.

Several recent publications have highlighted the advantage of one-pot oxidation-Wittig reaction under different conditions. These include Swern oxidation[5] active manganese dioxide oxidation,[6] barium permanganate oxidation,[7] in the presence of ylide in the reaction mixture. Another report by Barrett's group[8] used Dess-Martin periodinane (DMP) ([12-I-5] species)[9] for a similar process.

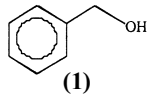
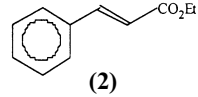
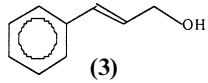
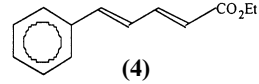
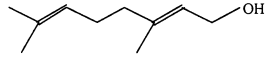
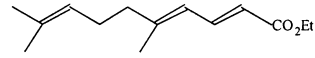
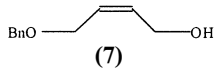
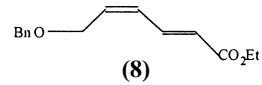
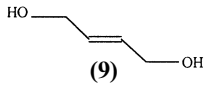
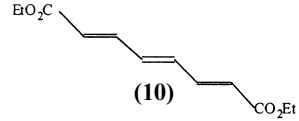
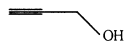
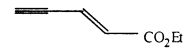
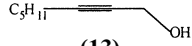
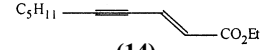
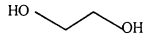
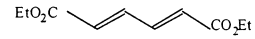
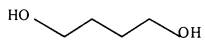
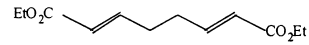
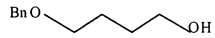
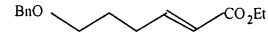
Inexpensive o-iodoxybenzoic acid (IBX) ([10-I-4] species)[11] which is used to prepare expensive DMP is itself a very efficient oxidizing agent.[12–18] A number of applications of this reagent have emphasized its generality as a mild oxidizing agent, as well as its ability to perform delicate transformations.[12–18] In particular, IBX oxidizes vic-diols without cleaving the glycol C-C bond[12] and is stable to moisture. The oxidation can be performed in an open flask without any particular precaution, such as inert atmosphere and dry solvent.[12]

To utilize this characteristic of IBX, we report the oxidation of primary alcohols by IBX in the presence of stabilized ylide to trap the unstable intermediate aldehydes, before they decompose or isomerize, to yield the corresponding α,β-unsaturated ester at room temperature.

To demonstrate its utility and functional group compatibility, we successfully carried out the oxidation, followed by olefination of aldehydes derived from a wide variety of substrates, such as benzylic, allylic, and propargylic alcohols and diols with (carboethoxymethylene)tripheylphosporane, to obtain the corresponding α,β-unsaturated ester in good yields, as shown in Table 1.

Propargyl alcohol **11** gave ynenote **12** in good yield. The intermediate aldehyde, propynal, is a lachrymator and has a tendency to polymerize easily in basic medium. Even 1,2-diols as in ethylene glycol **15** produced diester **16** in very high yield. The oxidation of 1,2-diols itself is very difficult to achieve by a method operable in the laboratory. In the case of the allyl alcohols **5** and **9**, the reaction proceeded with retention of E-alkene geometry and alcohol **7** retained its Z-alkene geometry. Only cinnamyl alcohol **3** underwent very slow oxidation-Wittig reaction. All the products obtained (as shown in Table 1) were major in E-alkene product (above 90%).

Table 1. IBX Oxidation of Alcohols in the Presence of Wittig Ylide at Room Temperature

Entry no.	Alcohols	Products	Time (h)	Yield (%)
1.	 **(1)**	 **(2)**	1.5	98
2.	 **(3)**	 **(4)**	48	65
3.	 **(5)**	 **(6)**	6	90
4.	 **(7)**	 **(8)**	10	95
5.	 **(9)**	 **(10)**	10	90
6.	 **(11)**	 **(12)**	10	85
7.	 **(13)**	 **(14)**	10	80
8.	 **(15)**	 **(16)**	8	70
9.	 **(17)**	 **(18)**	8	80
10.	 **(19)**	 **(20)**	8	80

In conclusion, the present procedure is a very efficient method for homologation of unstable aldehydes. The significiant advantages offered by this procedure are: a) inexpensive reagent; b) general application (effective for all types of primary alcohols); c) mild and neutral conditions (room temperature, no inert or dry atmosphere or solvent needed); d) easy work-up; e) high yield; and f) environmentally friendly reaction (no toxic reagent). Certainly this method offers a practical alternative to the existing procedures.

EXPERIMENTAL

Melting points were recorded on a Buchi R-535 apparatus. IR spectras were recorded on a Perkin-Elmer Infrared 683 spectrophotometer with NaCl optics. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200 MHz spectrometer. The samples were recorded in $CDCl_3$ using tetramethysilane as the internal standard and are given on the δ-scale. Mass measurements were carried out on either Fnnigan-MAT1020B or MicroMass VG70-70H mass spectrometer operating at 70 eV using direct inlet system and are given in the mass units (m/z). TLC was performed on 0.25-mm E.Merk precoated silicagel plate (60F-254). All products were purified by column chromatography on silicagel (100–200 mesh).

General Procedure

To a solution of alcohol (1.0 mmol) in dimethylsulfoxide (5 mL), a mixture of (carboethoxy-methylene)triphenylphosphorane (1.5 mmol) and iodoxybenzoic acid (1.5 mmol) was added and the reaction mixture stirred at room temperature. After a few minutes, IBX was dissolved and the solution turned orange-brown and hot. The resulting mixture was stirred until TLC indicated the completion of reaction. After that, 10 mL water was added and stirred for 5 m. Solid precipitate was filtered through a celite pad and filtrate was extracted with ether (2×25 mL). Ether solution was concentrated in vacuum. The residue was chromatographed on silica gel.

Ethyl cinnamate (Entry 1)[19]

Color1ess oil; TLC R_f 0.85 (hexane:Ethylacetate 4:1); IR (neat) ν 1714, 1638, 1450, 1366, 1312, 1270, 1204, 1178, 769 cm^{-1}. EI-MS m/z 176 (M+).

Ethyl 5-phenyl-2(E),4(E)-pentadienoate (Entry 2)

Colorless oil (lit.[20] m.p. 25°–26°C); TLC R_f 0.4 (hexane:Ethylacetate 9:1); IR (neat) ν 3026, 2981, 1707, 1626, 1341, 1314, 1297, 1239, 1133, 1037, 998, 775, 714, 689 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.30(3H, t, J = 7.0 Hz), 4.23(2H, q, J = 7.0 Hz), 5.99(1H, d, J = 18.0 Hz), 6.80–7.60 (7H, m), 7.55(1H, d, J = 18.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 167.3, 144.6, 140.5, 136.4, 129.3, 128.9, 127.4, 126.5, 121.5, 60.5, 14.5; EI-MS m/z 202(M+). Anal. calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found C, 76.96; H, 6.88.

Ethyl 5,9-dimethyl-2(E),4(E),8-decatrienoate (Entry 3)

Colorless oil (lit.[21] bp. 103°–105°C/0.5 mHg); TLC R_f 0.8 (hexane:Ethylacetate 4:1); IR (neat) ν 2911, 2890, 1727, 1640, 1610, 1420, 1355, 1232, 1102, 1065, 1024, 990, 764 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.29(3H, t, J = 7.0 Hz), 1.61(3H, br.s), 1.68(3H, br.s), 1.89(3H, br.s), 2.1–2.2(4H, m), 4.20(2H, q, J = 7.0 Hz), 4.80–5.20(1H, m), 5.78(1H, d, J = 18.0 Hz), 5.99(1H, br.d, J = 18.0 Hz), 7.58(1H, dd, J = 18.0, 12.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 167.8, 149.6, 140.9, 132.2, 123.4, 123.3, 118.9, 60.0, 40.2, 26.3, 25.6, 17.6, 17.3, 14.3; EI-MS m/z 222(M+). Anal. calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found C, 75.65; H, 9.86.

Ethyl 6-benzyloxy-2(E),4(Z)-hexadienoate (Entry 4)

Colorless oil. TLC R_f 0.82 (hexane:Ethylacetate 4:1); IR (neat) ν 1991, 1755, 1648, 1455, 1350, 1140, 1110, 982, 853, 765, 720 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.30(3H, t, J = 7.0 Hz), 4.20(4H, m), 4.51(2H, s J = 7.0 Hz), 5.99(2H, m), 6.20(1H, m), 7.31(5H, m), 7.49(1H, m); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.6, 141.4, 139.1, 133.5, 128.3, 127.8, 127.7, 127.6, 123.7, 69.6, 65.9, 60.7, 14.3; FABMS m/z 247$(M+H)^+$ Anal. calc. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.31. Found C, 73.18; H, 7.40.

Diethyl octa-2(E),4(E),6(E)-triene-dioate (Entry 5)

White crystals, m.p. 86°C (pentane-ether) (lit.[22] 88°–89°C); TLC R_f 0.55 (hexane:Ethylacetate 5:1); IR (KBr) ν 1711, 1627, 1370, 1340, 1300, 1236, 1134, 1026, 866 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (6H, t, J = 7.0 Hz). 4.20(2H, q, J = 7.0 Hz), 6.00(2H, d, J = 18.0 Hz),

6.60(2H, dd, J = 3.0, 7.0 Hz), 7.30(2H, ddd, J = 3.0, 7.0, 17.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.4, 142.7, 136.9, 124.7, 60.6, 14.3; FABMS m/z 225$(M+H)^+$. Anal. calc. for $C_{12}H_{16}O_4$: C, 64.28; H, 7.14. Found C, 64.29; H, 7.16.

Ethyl 2(E)-penten-4-ynoate (Entry 6)[23]

Colorless oil; TLC R_f 0.8 (hexane:Ethylacetate 4:1); IR (neat) ν 3293, 3262, 2101, 1725, 1259, 1170, 1039, 963 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31(3H, t, J = 7.0 Hz), 2.29(1H, d, J = 3.0 Hz), 4.21(2H, q, J = 7.0 Hz), 6.29(1H, d, J = 18.0 Hz), 6.69(1H, dd, J = 3.0, 17.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.5, 132.6, 123.9, 85.9, 80.4, 60.9, 14.2. EI-MS m/z 124 (M+). Anal. calc. for $C_7H_8O_2$: C, 67.77; H, 6.45. Found C, 67.78; H, 6.50.

Ethyl 2(E)-decane-4-ynoate (Entry 7)

Colorless oil; TLC R_f 0.8 (hexane:Ethylacetate 4:1); IR (neat) ν 3218, 2929, 2903, 2832, 2201, 2112, 1715, 1618, 1460, 1366, 1299, 1176, 1155, 1035, 961 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90(3H, t, J = 7.0 Hz), 11.2–1.6(8H, m), 2.35(2H, m), 4.20(2H, q, J = 7.0 Hz), 6.10(1H, d, J = 18.0 Hz), 6.72(1H, d, J = 18.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 129.2, 126.0, 100.6, 78.2, 60.2, 31.2, 77.9, 60.3, 30.9, 27.9, 22.1, 19.9, 14.1, 13.8; EI-MS m/z 194 (M+). Anal. calc. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found C, 74.18; H, 9.26.

Diethyl hexa-2(E),4(E)-diene-1,6-dioate (Entry 8)

White crystals, m.p. 60°C (pentane-ether) (lit.[24] 63°–64°C); TLC R_f 0.55 (hexane:Ethylacetate 5:1); IR (KBr) ν 1699, 1612, 1254, 1172, 1025, 866 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31(6H, t, J = 7.0 Hz), 4.20(2H, q, J = 7.0 Hz), 6.15–6.30(2H, m), 7.20–7.38(2H, m); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.9, 140.8, 128.4, 60.9, 14.3; FABMS m/z 199$(M+H)^+$. Anal. calc. for $C_{10}H_{14}O_4$: C,60.60; H, 7.07. Found C, 60.61; H, 7.07.

Diethly octa-2(E),6(E)-diene-1,6-dioate (Entry 9)[25]

Colorless oil; TLC R_f 0.43 (hexane:Ethylacetate 5:1); IR (neat) ν 2930, 2910, 2850, 1724, 1655, 1392, 1300, 1254, 1142, 1112, 1042, 993, 770 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30(6H, t, J = 7.0 Hz), 2.37(4H, d, J = 7.0 Hz), 4.17(4H, q, J = 7.0 Hz), 5.80(2H, d, J = 18.0 Hz), 6.91(2H, dt, J = 7.0, 17.5 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.3, 146.8, 122.3, 60.2, 30.4, 14.3: MS *m/z* 227$(M+H)^+$. HRMS for $C_{12}H_{19}O_4(M+H)^+$ 227.1287 calc. for 227.1283.

Ethyl 6-benzyloxy-2(E)-hexenoate (Entry 10)

Colorless oil; TLC R_f 0.43 (hexane:Ethylacetate 5:1); IR (neat) ν 2925, 2701, 2660, 1725, 1642, 1440, 1332, 1286, 1221, 1181, 1102, 1035, 977, 760 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29(3H, t, J = 7.0 Hz), 1.75 (2H, m), 2.30(2H, m), 3.45(2H, m), 4.17(4H, q, J = 7.0 Hz), 4.45(2H, s, J = 7.0 Hz), 5.79(1H, d, J = 18.0 Hz) 6.91(1H, dt, J = 7.0, 17.5 Hz), 7.25(5H, m); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.5, 149.4, 139.4, 129.3, 127.5, 121.7, 72.9, 69.7, 60.0, 53.1, 29.7, 29.1, 14.7; MS *m/z* 249 $(M+H)^+$. Anal. calc. for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06. Found C, 72.59; H, 8.01.

CAUTION

IBX has been reported to detonate[26] upon heavy impact and heating over 200°C. Dess and Martin reported[9,10] that heating and striking IBX with a hammer did not cause any detonation. In our hands, we observed no hazard using IBX at room temperature.

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