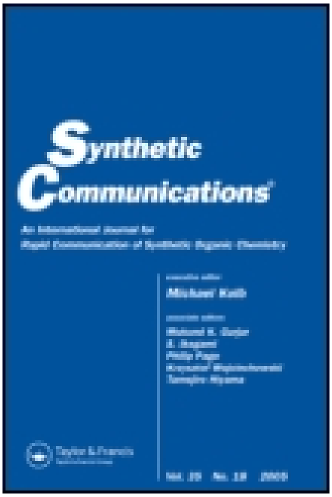

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Regioselective Synthesis of α-Iodoacetates from Alkenes/Ammonium Acetate/I_2 by Woodward's Reaction

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ABSTRACT

Regioselective synthesis of α-iodoacetates from alkenes, ammonium acetate, and iodine in acetic acid is reported. The reaction is facile, fast, environmentally, friendly, and cost effective. α-Iodoacetates are obtained from both acyclic and cyclic alkenes in high yields ranging from 80–95% within 10–20 min.

Key Words: α-Iodoacetates; Alkenes; Ammonium acetate; Molecular iodine; Acetic acid.

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α-Iodoacetates are important in organic synthesis as they can be transformed into other functional groups such as *cis*- and *trans*-diols, monohydroxy compounds, Grignard reagents, iodohydrins, diacetates, monoacetates, hydroxy acetates, and epoxides. They are also used in C—C bond formation reactions. There are only a few methods available in the literature for their preparation. The reported methods require the use of heavy metal acetates like those of silver,[1–3] thallium(I),[4] mercury(II),[5,6] bismuth(III),[7] or copper(II).[8–10] Silver acetate is more commonly used for the iodoacetoxylation of olefins with iodine in glacial acetic acid.

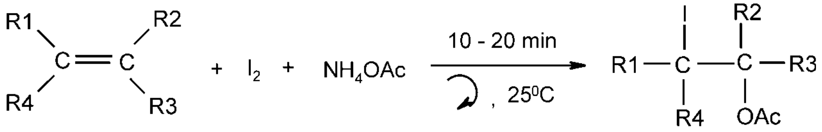
In this paper we report a novel and an extremely efficient addition reaction of alkenes in the presence of iodine and ammonium acetate to give the corresponding α-iodoacetates (Sch. 1). This reaction is environmentally benign with no toxic by-products.

From Table 1, it is clear that different α-iodoacetates are obtained from both acyclic and cyclic alkenes in excellent yields within very short reaction periods (10–20 min). A noteworthy feature of the reaction is that it is selective, and the major product is a less-substituted iodo product (entries 7–11). Cyclic alkenes furnish the *trans*-iodoacetates exclusively (entries 1–3).

In conclusion, a mild, highly efficient, convenient, selective, and environmentally benign method for the preparation of α-iodoacetates in a short time has been developed.

EXPERIMENTAL

Alkenes, ammonium acetate, and glacial acetic acid were obtained from Spectrochem or Rankem. Nicolet 400D FT-IR spectrometer was used for IR spectral analysis, ^{13}C and ^{1}HNMR spectra were recorded on a 100/400 MHz, respectively, using a Bruker instrument. Elemental analysis was performed on ThermoFinnigan FLASH EA 1112 CHNS analyser.



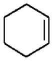
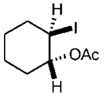
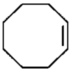
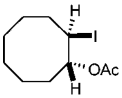
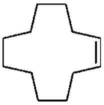
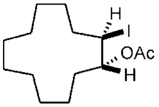
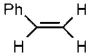
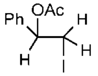
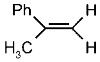
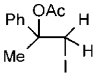
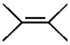
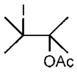
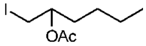
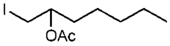
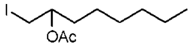
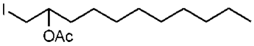
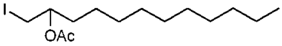
$R1 = R2 = H, CH_3$

$R3 = CH_3, C_4H_9, C_9H_{19}, C_{10}H_{21}, C_6H_5$, $R4 = H, CH_3$

$R3\text{-}R4 = -(CH_2)_4-, -(CH_2)_6-, -(CH_2)_{10}-$

Scheme 1.

Table 1. α-Iodoacetoxylation of olefins with ammonium acetate and iodine in acetic acid.

Entry	Alkene	Product	Time (min)	Yield[a] (%)
1			10	94
2			15	94
3			12	90
4			15	82
5			15	80
6			15	93
7			10	95
8			15	90
9			15	91
10			15	87
11			20	93

[a]Isolated by column chromatography.

The chemical shift values (δ ppm) are reported relative to TMS in $CDCl_3$ as solvent.

Preparation of *Trans*-1-Acetoxy-2-Iodocyclohexane: General Procedure

Ammonium acetate (0.89 g, 5 mmol), glacial acetic acid (5 mL), and cyclohexene (0.82 g, 10 mmol) were taken in a two-neck, 50-mL RB flask.

Iodine (2.54 g, 10 mmol) in glacial acetic acid (5 mL) was added slowly to the above mixture, which was stirred at 25°C. The reaction was monitored by TLC (5% EtOAc: pentane). The reaction mixture was extracted with ether (3 × 10 mL) and the combined ethereal extract was washed with saturated $NaHCO_3$ solution and water, and dried over anhydrous Na_2SO_4. The crude product was subjected to silica gel chromatography to give *trans*-1-acetoxy-2-iodocyclohexane (2.52 g, 94%).

***Trans*-1-acetoxy-2-iodocyclohexane**: 2.52 g, 94%. IR (cm^{-1}): 1740, 1243, 1036, 420. ^{1}HNMR: δ_H 2.06 (*s*, $-COCH_3$), 4.01–4.07 (*ddd*, $J_{1,2} = J_{2,3a} = 10$ Hz, $J_{2,3e} = 4$ Hz, –CHI–), 4.84–4.90 (*ddd*, 1H, $J_{1,2} = J_{1,6a} = 10$ Hz, $J_{1,6e} = 5$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 169.923, 76.745, 37.845, 31.757, 31.559, 27.048, 23.584, 21.215. Anal. Calcd. for $C_8H_{13}IO_2$: C, 35.82; H, 4.85; Found: C, 35.60; H, 4.85%.

***Trans*-1-acetoxy-2-iodocyclooctane**: 2.78 g, 94%. IR (cm^{-1}): 1734, 1243, 1047, 410. ^{1}HNMR: δ_H 2.07 (*s*, $-COCH_3$), 4.38–4.43 (*ddd*, $J_{1,2} = J_{2,3a} = 6$ Hz, $J_{2,3e} = 3$ Hz, –CHI–), 5.19–5.23 (*ddd*, 1H, $J_{1,2} = J_{1,6a} = 8$ Hz, $J_{1,6e} = 4$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 169.919, 80.446, 37.891, 33.167, 32.438, 26.801, 25.840, 25.589, 25.264, 21.227. Anal. Calcd. for $C_{10}H_{17}IO_2$: C, 40.54; H, 5.74; Found: C, 40.35; H, 5.58%.

***Trans*-1-acetoxy-2-iodocyclododecane**: 3.17 g, 90%. IR (cm^{-1}): 1745, 1238, 416, 721. ^{1}HNMR: δ_H 2.09 (*s*, $-COCH_3$), 4.33–4.40 (*ddd*, $J_{1,2} = J_{2,3a} = 6$ Hz, $J_{2,3e} = 12$ Hz, –CHI–), 4.83–4.87 (*dd*, 1H, $J_{1,2} = J_{1,6a} = 6$ Hz, $J_{1,6e} = 11$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.226, 72.653, 35.542, 34.994, 30.329, 28.548, 24.809, 24.401, 24.147, 23.628, 23.003, 21.948, 21.087, 20.660. Anal. Calcd. for $C_{14}H_{25}IO_2$: C, 47.73; H, 7.1; Found: C, 47.59; H, 7.3%.

$PhCH(OAc)CH_2I$: 2.38 g, 82%. IR (cm^{-1}): 1755, 1233, 1062, 545. ^{1}HNMR: δ_H 2.14 (*s*, $-COCH_3$), 3.46–3.49 (*dd*, $J = 4$ Hz, $J = 8$ Hz, $-CH_2I-$), 5.86–5.90 (*dd*, 1H, $J = 5$ Hz, $J = 8$ Hz, $-CHCOCH_3$), 7.36–7.37 (*m*, 5H, Ph). ^{13}CNMR: δ_C 169.768, 138.427, 128.746, 128.700, 126.411, 75.160, 21.051, 7.833. Anal. Calcd. for $C_{10}H_{11}IO_2$: C, 41.38; H, 3.79; Found: C, 41.12; H, 3.93%.

$PhC(Me)(OAc)CH_2I$: 2.43 g, 80%. IR (cm^{-1}): 1734, 1243, 1031, 545. ^{1}HNMR: δ_H 2.08 (*s*, CH_3), 2.09 (*s*, $-COCH_3$), 3.25–3.28 (*dd*, $J = 2.5$ Hz, $J = 5$ Hz, $-CH_2I-$), 7.26 (*s*, 5H, Ph). ^{13}CNMR: δ_C 169.387, 142.027, 128.519, 127.758, 124.709, 80.908, 26.217, 22.020, 17.159. Anal. Calcd. for $C_{11}H_{13}IO_2$: C, 43.42; H, 4.28; Found: C, 43.27; H, 4.25%.

2-Iodo-3-acetoxy-2, 3-dimethylbutane: 2.51 g, 93%. IR (cm^{-1}): 1719, 1279, 1166, 410. ^{1}HNMR: δ_H 1.29 [*s*, 6H, $(CH_3)_2C(COCH_3)-$], 1.54 [*s*, $(CH_3)_2CI-$], 2.20 (*s*, $-COCH_3$). ^{13}CNMR: δ_C 170.213, 82.731, 30.845, 28.156, 24.239, 18.352. Anal. Calcd. for $C_8H_{15}IO_2$: C, 35.56; H, 5.56; Found: C, 35.33; H, 5.52%.

1-Iodo-2-acetoxyhexane: 2.57 g, 95%. IR (cm^{-1}): 1719, 1259, 1031, 415. ^{1}HNMR: δ_H 2.08 (*s*, $-COCH_3$), 3.22–3.37 (*dd* H_A, *dd* H_B, $J = 5$ Hz, $J = 10$ Hz, $-CH_AH_BI-$), 4.66–4.72 (*quin*, 1H, $J = 6$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.170, 72.431, 38.004, 28.994, 21.218, 18.477, 13.157, 9.575. Anal. Calcd. for $C_8H_{15}IO_2$: C, 35.56; H, 5.56; Found: C, 35.24; H, 5.29%.

1-Iodo-2-acetoxyheptane: 2.56 g, 90%. IR (cm^{-1}): 1745, 1243, 1036, 498. ^{1}HNMR: δ_H 2.09 (*s*, $-COCH_3$), 3.22–3.38 (*dd* H_A, *dd* H_B, $J = 5$ Hz, $J = 10$ Hz $-CH_AH_BI-$), 4.67–4.74 (*quin*, 1H, $J = 7$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.453, 72.403, 31.677, 31.618, 29.087, 21.840, 18.462, 13.863, 9.651. Anal. Calcd. for $C_9H_{17}IO_2$: C, 38.03; H, 5.99; Found: C, 37.67; H, 5.64%.

1-Iodo-2-acetoxyoctane: 2.71 g, 91%. IR (cm^{-1}): 1740, 1243, 1036, 493. ^{1}HNMR: δ_H 2.07 (*s*, $-COCH_3$), 3.20–3.39 (*dd* H_A, *dd* H_B, $J = 5$ Hz, $J = 10$ Hz $-CH_AH_BI-$), 4.66–4.72 (*quin*, 1H, $J = 6$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.264, 72.437, 34.129, 31.610, 28.941, 28.429, 22.529, 20.799, 14.005, 8.216. Anal. Calcd. for $C_{10}H_{19}IO_2$: C, 40.27; H, 6.38; Found: C, 40.26; H, 6.63%.

1-Iodo-2-acetoxyundecane: 2.96 g, 87%. IR (cm^{-1}): 1745, 1243, 1000, 420. ^{1}HNMR: δ_H 2.08 (*s*, $-COCH_3$), 3.23–3.37 (*dd* H_A, *dd* H_B, $J = 5$ Hz, $J = 10$ Hz $-CH_AH_BI-$), 4.66–4.72 (*quin*, 1H, $J = 6$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.256, 72.461, 36.510, 34.132, 31.871, 31.043, 29.464, 29.271, 28.774, 25.056, 22.656, 14.062, 8.187. Anal. Calcd. for $C_{13}H_{25}IO_2$: C, 45.88; H, 7.35; Found: C, 46.20; H, 7.42%.

1- Iodo -2- acetoxydodecane: 3.29 g, 93%. IR (cm^{-1}): 1750, 1238, 1031, 416. ^{1}HNMR: δ_H 2.11 (*s*, $-COCH_3$), 3.23–3.38 (*dd* H_A, *dd* H_B, $J = 5$ Hz, $J = 10$ Hz $-CH_AH_BI-$), 4.66–4.74 (*quin*, 1H, $J = 5$ Hz, $-CHCOCH_3$). ^{13}CNMR: δ_C 170.268, 72.482, 36.522, 34.137, 31.898, 31.043, 29.555, 29.413, 29.297, 28.779, 25.056, 22.665, 14.065, 8.183. Anal. Calcd. for $C_{14}H_{27}IO_2$: C, 47.46; H, 7.92; Found: C, 47.7; H, 7.92%.

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