Exploring the reaction of iodine with α-diazo esters

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In this paper we describe the unprecedented reaction between α-diazo esters 1 and iodine. The reaction, carried out in the presence of aqueous NaHCO₃, afforded the *Z*-isomer of the corresponding unsaturated-2-iodo ester 8. The configuration of compounds 8 was determined using the $^3J_{C-H}$ coupling between carbonyl carbon atom and alkene proton. Mechanistic considerations accounting for the observed phenomena and including quantum chemical calculations are proposed. Copyright © 2008 John Wiley & Sons, Ltd.

INTRODUCTION

A few years ago, we have studied the reaction of some diazo compounds[1,2] in the presence of a ruthenium(II) organometallic catalyst. As an extension of our interest in this field, we have now investigated in detail the reaction of iodine with α-diazo esters[3–5] yielding the *Z*-isomer of the corresponding 2-iodo-2-unsaturated esters. These derivatives, usually prepared via the condensation reaction of aldehydes with arsonium salts[6] or (ethoxycarboxyiodomethyl)triphenylphosphonium iodide,[7–9] are useful building blocks in the Sonogashira coupling reaction.[10]

It is well documented that the reaction of halogens with diazoalkanes or α-diazo ketones produces *gem*-dihalides.[11–21] In the particular case of phenylselenyl halides, subsequent oxidation of the selenium atom allowed the formation of 2-halo-2-unsubstituted carbonyl compounds.[22–24]

In contrast, the reaction of halogens, and in particular iodine, with α-diazo esters has no precedent so far. In fact, only two reports described the use of α-diazo esters in the formation of the corresponding (*Z*)-2-fluoro-, (*E*)- and/or (*Z*)-2-bromo- and (*Z*)-2-iodo-2-unsaturated esters, but these reactions were carried out in the presence of phenylselenyl fluoride[23] and the hexafluorophosphate of bis(*sym*-collidine)bromine(I) or iodine(I),[25] respectively. In particular, the reaction leading to the iodo esters was tested only with a substrate and the main reaction product was the (*Z*)-2-unsubstituted ester due to the decomposition by collidine of the diazo group.

The aim of this contribution is to describe and rationalize, including quantum chemical calculations, the experimental results observed exploring the reaction of iodine with some α-diazo esters prepared according to Takamura[4] but using *tert*-butyl nitrite as diazotizing agent and CH₂Cl₂ as solvent.

RESULTS AND DISCUSSION

Our first approach to this reaction was the slow addition of a mixture of iodine in CH₂Cl₂ to a vigorously stirred solution of methyl 2-diazo-4-methylpentanoate (**1a**) in CH₂Cl₂ at 0 °C under argon and in the dark. After stirring at room temperature for 4 h,

the reaction mixture was treated with a saturated sodium metabisulphite solution and analysed by GC–MS. The GC–MS profile showed the presence of eight reaction products, identified as methyl (*Z*)-4-methyl-2-pentenoate (**2a**), methyl (*E*)-4-methyl-2-pentenoate (**3a**), methyl 4-methyl-2-oxopentanoate (**4a**), methyl 2-hydroxy-4-methylpentanoate (**5a**), methyl 2-iodo-4-methylpentanoate (**6a**), methyl (*E*)-2-iodo-4-methyl-2-pentenoate (**7a**), methyl (*Z*)-2-iodo-4-methyl-2-pentenoate (**8a**) and methyl 2,2-diiodo-4-methylpentanoate (**9a**). It is interesting to notice that compounds **4a**, **5a** and **8a** made up some 94% of the total amount (Scheme 1), as determined from the integrated gas chromatographic peaks, and the main product was the unsaturated iodo ester **8a** (68%, GC yield) and not the saturated geminal diiodo derivative **9a** (1%, GC yield) as described for α-diazo ketones.

We proposed the mechanistic pathway depicted in Scheme 3 for the formation of compounds **2a**–**9a** taking into consideration that (i) the CH₂Cl₂ solution of α-diazo ester **1a**,[4] was utilized in the subsequent reaction with iodine without purification and therefore excess *tert*-butyl nitrite, acetic acid and water were present (Scheme 2), and (ii) the *tert*-butyl nitrite-iodine system was found to oxidize secondary alcohols to ketones.[26]

The reaction of iodine with the α-diazo ester **1a** yields the α-iodo-α-diazonium ion **10** (Scheme 3, path a) which, in the presence of iodide ion or water, losses a proton and N₂ to give the unsaturated iodo ester **8a**, the main reaction product, and its isomer **7a** (Scheme 3, path b). The reaction of **10** leading to the saturated diiodo ester **9a** is disfavoured probably because of steric hindrance. The α-diazo ester **1a** may also react with a proton (acetic acid and HI present) to give the diazonium ion **11** (Scheme 3, path c) which produces the methyl 2-hydroxy-4-methylpentanoate (**5a**) and the methyl 2-iodo-4-methylpentanoate (**6a**) by the reaction with water or iodide

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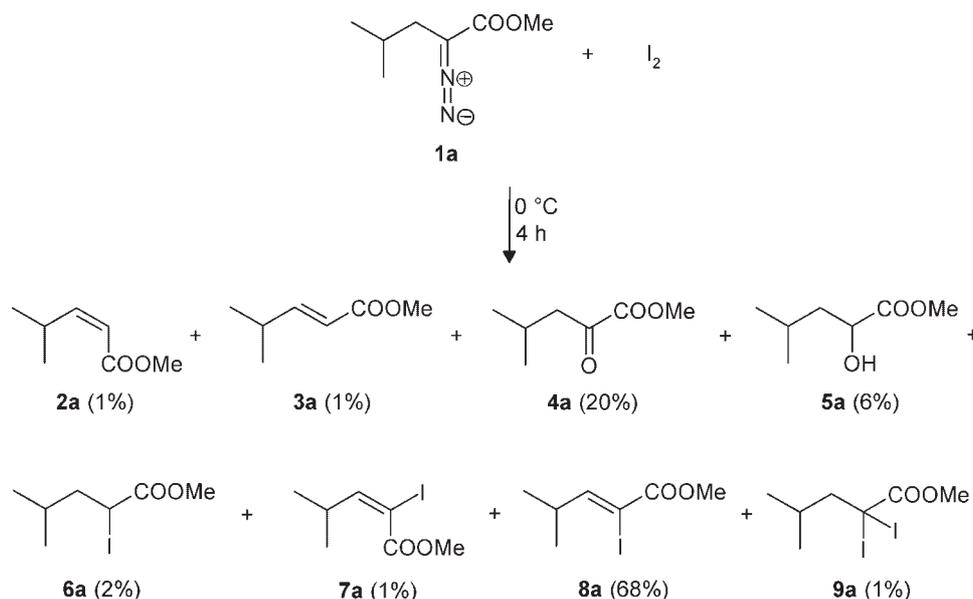
Scheme 1. Reaction of methyl 2-diazo-4-methylpentanoate (**1a**) and iodine. The numbers in parentheses represent the percentages calculated from the integrated gas chromatographic peaks

ion, respectively. Finally, compound **5a** may be oxidized[26] to methyl 4-methyl-2-oxopentanoate (**4a**) and, in the presence of HI, it forms **6a** by a substitution reaction or the two isomeric unsaturated esters **2a** and **3a** by dehydration.

When the reaction was carried out with the α-diazo ester **1a** obtained after purification (refer to Experimental Section) from acetic acid and excess *tert*-butyl nitrite (Scheme 2), the GC–MS profile showed that, also in this case, the main reaction product was **8a** (66%, GC yield) but the second most abundant one was the saturated iodo ester **6a** (20%, GC yield). Furthermore, as expected under these reaction conditions, we did not observe the presence of methyl 4-methyl-2-oxopentanoate (**4a**) because excess *tert*-butyl nitrite was previously eliminated under reduced pressure.

At this point, as the precursor of the main side products was the diazonium ion **11** (Scheme 3, path c), the neutralization of the acidity produced in path b (Scheme 3) should favour path a and then the formation of **8a** (Scheme 3, path b).

Indeed, when iodine was slowly added to a vigorously stirred mixture of **1a** in CH_2Cl_2 and saturated aqueous $NaHCO_3$ at 0 °C in the dark, the GC–MS analysis of the reaction mixture, obtained after stirring for 4 h at room temperature, showed that the yield of **8a** was increased to 89%. Column chromatography (silica gel; hexane/Et_2O, 97:3) of the residue obtained after work-up gave **8a** in 66% yield. The same result was obtained when the reaction was carried out with **1a** obtained from the racemic mixture of leucine methyl ester.

Following our efforts to investigate theoretically the reactions of iodine with α-diazo esters, we performed electronic structure calculations to characterize the relevant regions of the ground state potential energy surface (PES) associated with the proposed reactions.

Density functional theory (DFT) calculations were carried out to model the ground state PES for the reactions starting from Scheme 2, where the α-amino ester (leucine methyl ester, **LeuMe**), gives **1a**, and all the other pathways described in Scheme 3.

These DFT calculations were run using the Gaussian 03 program package[27] and performed with the B3LYP method which combines Becke's three-parameter nonlocal hybrid exchange potential[28,29] with the nonlocal correlation functional of Lee et al.,[30] and the 6–31+G(d,p) standard basis set. The MidiX basis set,[31] as implemented in the Gaussian package, was used for the iodine atom.

For all the molecules involved in the reactions described in Schemes 2 and 3, the structures were optimized to determine the nature of any stationary points. PES has therefore been generated for molecules with the overall stoichiometry $C_{11}H_{24}O_4N_2I_2$. For the intermediate compounds **10** and **11**, the iodide salts labelled as **10a** and **11a**, respectively, were taken into account during the calculations.

Additional self-consistent reaction field (SCRF) calculations were performed to take into account the solvent effect for all the molecules in CH_2Cl_2 ($\varepsilon = 8.93$) at 0 °C. Analytic frequency calculations were performed using the same SCRF method and model chemistry. From the output of these computations the zero-point energy (ZPE) corrections to the total electronic energy are available together with the thermal enthalpies and Gibbs free
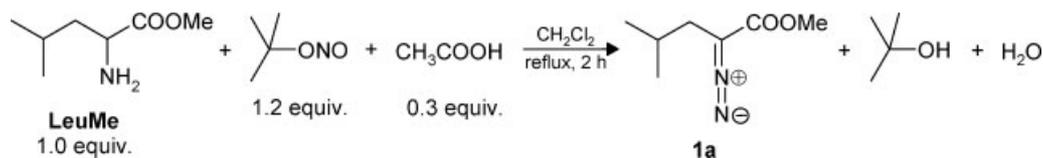
Scheme 2.
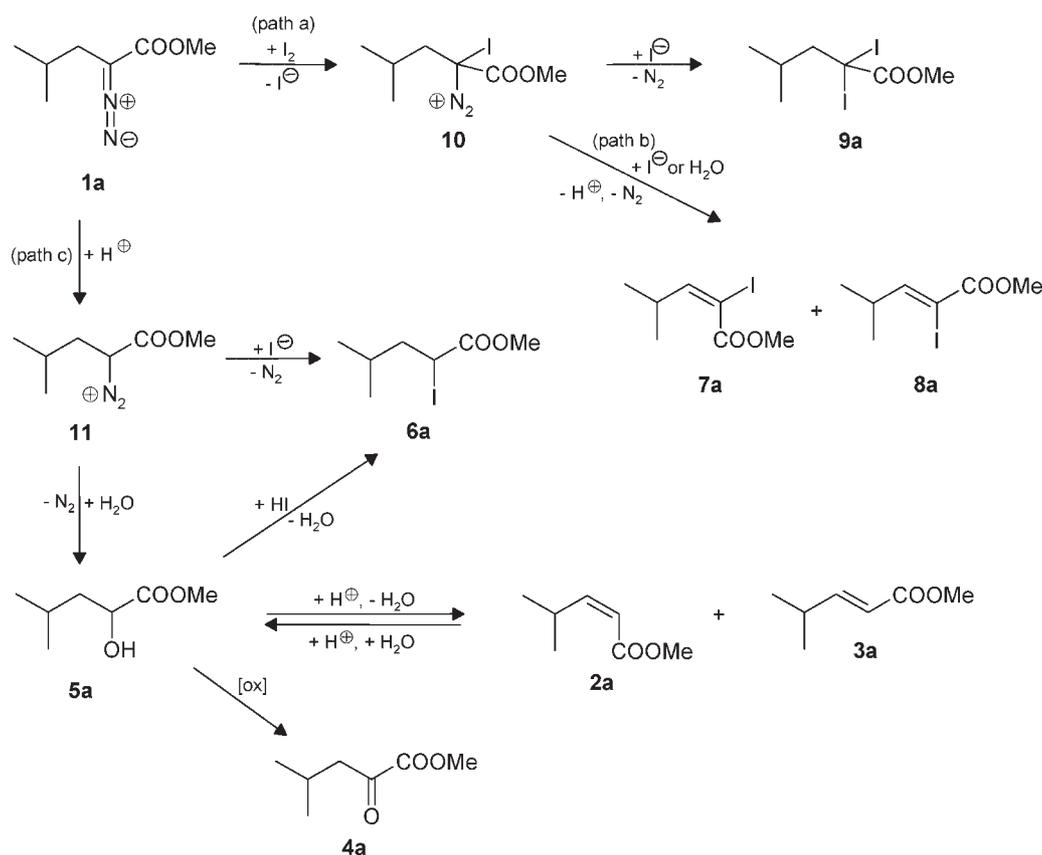
Scheme 3. Proposed mechanism pathway for the formation of compounds **2a**–**9a**

energies. For all surfaces, the molecules must fulfil the stoichiometric requirements of that surface. The total energy of the chosen initial step, labelled with START and corresponding to the preparation of the α-diazo ester **1a** (Scheme 2), was taken as the global zero, that is the reference point for all the other species formed. These energy data are collected in Table 1 whereas in Fig. 1 are depicted the reaction pathways leading to the formation of the observed species.

Table 1. Relative energies, enthalpies and Gibbs free energies (in unit of kJ/mol) of the stationary points, all having the overall stoichiometry $C_{11}H_{24}O_4N_2I_2$, located in this study

		Gas, 0 K	CH$_2$Cl$_2$, 273.15 K		
		ΔE	ΔE	ΔH	ΔG
START	**LeuMe** + *t*-BuONO + I$_2$	0.00	0.0	0.0	0.0
A	**1a** + *t*-BuOH + I$_2$ + H$_2$O	−91.43	−107.55	−123.17	−154.33
B	**10a** + *t*-BuOH + H$_2$O	−55.59	−65.41	−73.97	−71.95
C	**7a** + N$_2$ + H$_2$O + HI + *t*-BuOH	−208.85	−222.66	−252.78	−330.91
D	**8a** + N$_2$ + H$_2$O + HI + *t*-BuOH	−220.69	−235.54	−266.21	−346.41
E	**9a** + N$_2$ + H$_2$O + *t*-BuOH	−271.69	−276.69	−291.40	−324.94
AA	**1a** + *t*-BuOI + HI + H$_2$O	24.67	16.26	−12.25	−37.28
F	**11a** + H$_2$O + *t*-BuOI	−5.93	−13.67	−21.94	−18.48
G	**6a** + N$_2$ + H$_2$O + *t*-BuOI	−214.88	−219.75	−231.86	−266.59
H	**5a** + N$_2$ + HI + *t*-BuOI	−172.47	−174.19	−195.58	−224.99
I	**2a** + N$_2$ + HI + H$_2$O + *t*-BuOI	−150.20	−167.65	−197.79	−272.38
J	**3a** + N$_2$ + HI + H$_2$O + *t*-BuOI	−147.04	−164.76	−198.20	−269.11
K	**4a** + N$_2$ + 2HI + *t*-BuOH	−219.82	−222.83	−256.77	−343.93

In the first column total energies for the gas phase at 0 K are reported. The last three columns report, respectively, the total energies, enthalpies and Gibbs free energies for the molecules in CH$_2$Cl$_2$ solvent at 273.15 K.
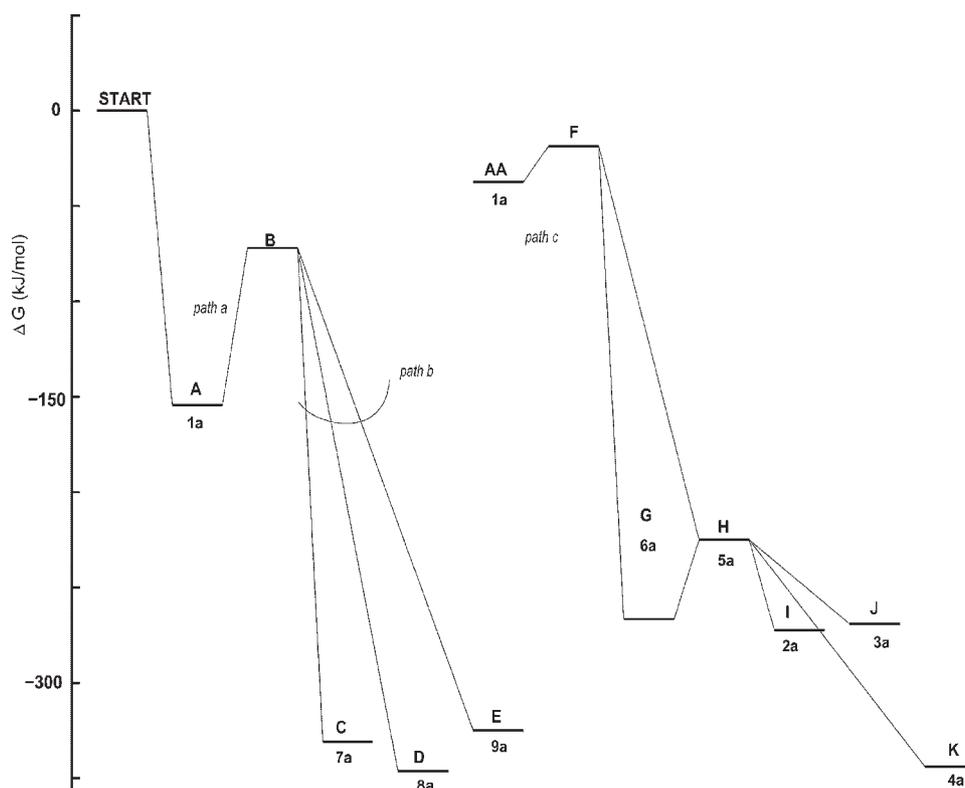
Figure 1. Schematic potential energy diagram for the reactions described in Schemes 2 and 3. The values are the relative Gibbs free energies (in kJ/mol) reported in Table 1

The first column of Table 1 reports the total energies for the molecules taken in the gas phase at 0 K and in the last three columns are reported the total energies, the enthalpies and Gibbs free energies for the solution in CH_2Cl_2 at 0 °C, respectively.

The comparison of the energies involved in the reactants and products is based on the Gibbs free energies in order to take into account the entropic factor which becomes significant when the number of molecular species change. In Fig. 1 'path c', which is related to the release of H^+ during the formation of **8a** (refer to text above), is also reported.

As can be seen from Table 1 and Fig. 1, the most energetically favourable pathways direct to the production of **8a** and **4a**. The differences in energies among the several stable compounds are consistent with the relative yields assessed experimentally. The focus of this study was on the thermodynamics of the reactions investigated. The transition states and kinetics were not

considered because of their complexity for this kind of reactions and therefore, there can be large energy barriers between reactants and products. However, the thermodynamics of the reactions enable the identification of the energetically most favourable reaction paths.

Barton et al.[32] reported that 3β-hydroxy-5α-pregnan-20-one hydrazone in the presence of iodine and Et_3N gave, under the influence of the base, 20-iodo-5α-pregn-20-en-3β-ol according to the mechanism reported in Scheme 4.

In our case, we have proposed (Scheme 3) that compound **8a** arises from the diazonium ion **10** and not from the geminal diiodo derivative **9a** because (i) the reaction proceeds also in the absence of a base, (ii) the reaction of iodide with **10** leading to **9a** is affected by steric hindrance and, finally, (iii) when the reaction was carried out in the presence of $NaHCO_3$, the GC–MS analysis of the reaction mixture showed that **8a** and **9a** were present in the

Scheme 4.

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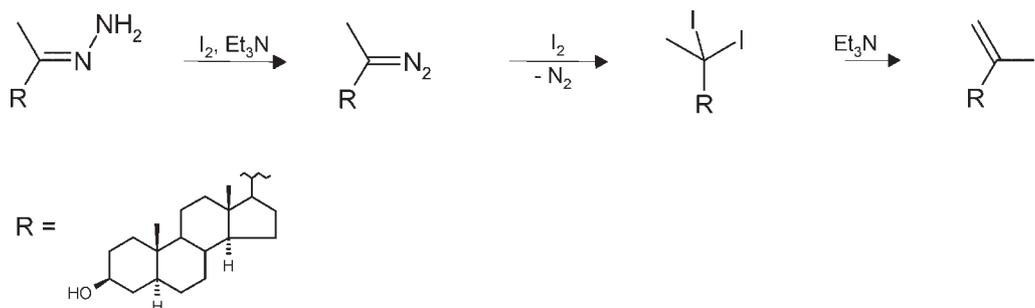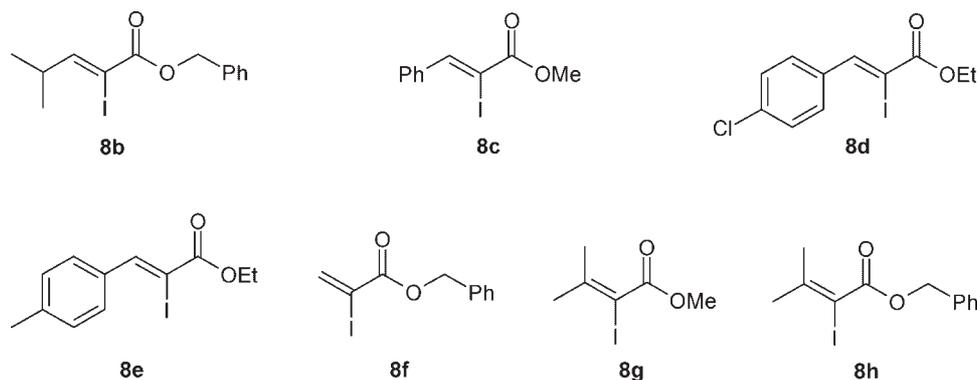
Chart 1.

ratio 89:1 which remained the same after 4 days with a pH of the final reaction mixture of *ca.* 9. This is a clear indication that the unsaturated halo ester **8a** did not come from the saturated dihalo ester **9a**.

We extended the reaction to the α-diazo derivatives of leucine benzyl ester (**1b**), phenylalanine methyl ester (**1c**), 4-chlorophenylalanine (**1d**) and 4-methylphenylalanine (**1e**) ethyl ester. The GC–MS analysis evidenced that also in these cases the main reaction product was the *Z*-isomer of the unsaturated iodo ester **8**. After silica gel chromatography benzyl (*Z*)-2-iodo-4-methyl-2-pentenoate (**8b**), methyl (*Z*)-2-iodo-3-phenyl-2-propenoate (**8c**), ethyl (*Z*)-3-(4-chlorophenyl)-2-iodo-2-propenoate (**8d**)[9] and ethyl (*Z*)-2-iodo-3-(4-methylphenyl)-2-propenoate (**8e**)[9] could be isolated in 75, 66, 70 and 71% yields, respectively (Chart 1). The reaction of the α-diazo derivatives of alanine benzyl ester (**1f**), valine methyl (**1g**) and benzyl (**1h**) ester with iodine gave the corresponding 2-iodo-2-unsaturated esters **8f**–**8h** in 52, 58 and 55% yields, respectively (Chart 1).

The configuration of the unsaturated iodo esters **8a**–**8e** was unambiguously determined using the $^3J_{C-H}$ coupling between carbonyl carbon atom and alkene proton. The selective decoupling of the α-protons of the alcoholic-ester moiety revealed a $^3J_{C-H}$ coupling constant value ranging from 5.6 and 6.5 Hz in agreement with the *Z* configuration.[33,34]

Compounds **8** are thermally and photochemically unstable.

CONCLUSIONS

In this report we have described the reaction of α-diazo esters **1** with iodine. This unprecedented reaction afforded the *Z*-isomer of the corresponding unsaturated-2-iodo ester **8** as the main product contrary to what is reported with α-diazo ketones.

EXPERIMENTAL

General remarks

All reagents and solvents were used as purchased from commercial suppliers (Aldrich, Fluka, CSPS Pharmaceuticals) without further purification. *tert*-Butyl nitrite was prepared according to described method.[35] GC–MS analyses were performed with a Fisons TRIO 2000 gas chromatograph–quadrupole mass spectrometer, working in the positive ion 70 eV electron impact mode, equipped with a MDN-5S capillary column (Supelco, 30 m × 0.25 mm i.d.; flow rate, 0.8 ml/min; He as

carrier gas). After preliminary compound identification with the help of the available mass spectral libraries (Wiley and NIST mass spectral database), each recorded spectrum was carefully examined to securely establish the nature of the eluted component. IR spectra were obtained with a Nicolet FT-IR Magna 550 spectrophotometer from a thin film supported on KBr disks and recorded in the range 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-F 200 spectrometer at 200 and 50 MHz, respectively, using CDCl$_3$ at room temperature as solvent. NMR peak locations are reported as δ-values from TMS. Some ^{1}H multiplets are characterized by the term *app* (apparent): this refers only to their appearance and may be an over-simplification. Routine monitoring of reactions was performed using Merck silica gel 60 F$_{254}$ coated on aluminium-supported TLC plates. Column chromatography was performed with silica gel 60 (230–400 mesh) and hexane/Et$_2$O (97:3, v/v) as eluent. Elemental analyses were performed with a Carlo Erba Mod. 1106 elemental analyser.

General procedure for the synthesis of α-diazo esters 1a–1h[4]

A mixture of α-amino ester (6.0 mmol), acetic acid (0.10 ml, 1.8 mmol) and *tert*-butyl nitrite (0.86 ml, 7.2 mmol) in CH$_2$Cl$_2$ (30 ml) was gently refluxed for 2 h under argon. The reaction mixture was allowed to cool to room temperature and used in the subsequent reaction with iodine.

Reaction of methyl 2-diazo-4-methylpentanoate (1a) with iodine

A mixture of iodine (0.28 g, 1.1 mmol) in CH$_2$Cl$_2$ (5 ml) was slowly added to the CH$_2$Cl$_2$ (5 ml) solution of **1a** prepared as described above using leucine methyl ester (0.145 g, 1.0 mmol) at 0 °C under argon and in the dark. After stirring at room temperature for 4 h, the reaction mixture was treated with a saturated sodium metabisulphite solution to eliminate excess iodine and analysed by GC–MS. The GC–MS[36] profile showed the presence of methyl (*Z*)-4-methyl-2-pentenoate (**2a**), methyl (*E*)-4-methyl-2-pentenoate (**3a**), methyl 4-methyl-2-oxopentanoate (**4a**), methyl 2-hydroxy-4-methylpentanoate (**5a**), methyl 2-iodo-4-methylpentanoate (**6a**), methyl (*E*)-2-iodo-4-methyl-2-pentenoate (**7a**), methyl (*Z*)-2-iodo-4-methylpentenoate (**8a**) and methyl 2,2-diiodo-4-methyl-pentanoate (**9a**) in 1, 1, 20, 6, 2, 1, 68 and 1% yields, respectively, calculated from the integrated gas chromatographic peaks.

Purification of α-diazo esters 1a–1h prepared

The CH$_2$Cl$_2$ solution of the α-diazo ester **1** (30 ml), obtained as described above, was successively washed with a saturated NaHCO$_3$ solution (2 × 15 ml) to eliminate acetic acid and saturated brine (15 ml), and dried over Na$_2$SO$_4$. After filtration, CH$_2$Cl$_2$ and excess *tert*-butyl nitrite were distilled off under reduced pressure affording the α-diazo ester **1** in pure form.

Reaction of purified methyl 2-diazo-4-methylpentanoate (1a) with iodine

The reaction was carried out as described above but using a solution of the purified α-diazo ester **1a** (0.156 g, 1.0 mmol) in CH$_2$Cl$_2$ (5 ml). After treatment, the GC–MS[36] profile showed the presence of methyl (Z)-4-methyl-2-pentenoate (**2a**), methyl (E)-4-methyl-2-pentenoate (**3a**), methyl 2-hydroxy-4-methylpentanoate (**5a**), methyl 2-iodo-4-methylpentanoate (**6a**), methyl (E)-2-iodo-4-methyl-2-pentenoate (**7a**), methyl (Z)-2-iodo-4-methylpentenoate (**8a**) and methyl 2,2-diiodo-4-methylpentanoate (**9a**) in 2, 2, 8, 20, 1, 66 and 1% yields, respectively, calculated from the integrated gas chromatographic peaks.

General procedure for the synthesis of Z-unsaturated-2-iodo esters 8a–8h

A mixture of iodine (1.67 g, 6.6 mmol) in CH$_2$Cl$_2$ (30 ml) was slowly added to a mixture of the appropriate purified α-diazo ester **1** (6.0 mmol) in CH$_2$Cl$_2$ (30 ml) and 5% aqueous NaHCO$_3$ (35 ml) at 0 °C under argon and in the dark. After stirring at room temperature for 4 h, the organic phase was separated and successively washed with a saturated aqueous sodium metabisulphite solution (2 × 15 ml) to eliminate excess iodine and saturated brine (15 ml), and dried over anhydrous Na$_2$SO$_4$. After filtration, CH$_2$Cl$_2$ was distilled off under reduced pressure and the residue was purified by silica gel column chromatography using hexane/Et$_2$O (97:3, v/v) to furnish the unsaturated-2-iodo esters **8a**–**8h** as pale yellow oils (purity >95% by ^{1}H NMR spectroscopy).

Methyl (Z)-2-iodo-4-methyl-2-pentenoate (8a)

1.0 g, (66% yield). IR (film): ν = 2963, 2930, 2871, 1724, 1648, 1612, 1466, 1435, 1328, 1248, 1142, 1030, 892, 751 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.09 [d, 6 H, J = 6.6 Hz, CH(CH$_3$)$_2$], 2.60–2.85 (m, 1 H, CH), 3.81 (s, 3 H, OCH$_3$), 6.99 (d, 1 H, J = 9.2 Hz, =CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.6, 36.4, 53.4, 91.5, 158.9, 163.5 ppm. EI-MS (70 eV): m/z (%) = 254 [M$^+$] (75), 222 (8), 181 (15), 179 (26), 127 (21), 112 (33), 95 (100), 73 (41), 67 (31), 41 (31), 39 (31). Anal. calcd. for C$_7$H$_{11}$IO$_2$ (254.07): C 33.09, H 4.36; found: C 33.14, H 4.30.

Benzyl (Z)-2-iodo-4-methyl-2-pentenoate (8b)

1.48 g, 75% yield). IR (film): ν = 2963, 2931, 2870, 1718, 1652, 1610, 1458, 1235, 1142, 1010, 748, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.07 (d, 6 H, J = 6.6 Hz, CH(CH$_3$)$_2$], 2.60–2.85 (m, 1 H, CH), 5.24 (s, 2 H, PhCH$_2$), 7.01 (d, 1 H, J = 9.2 Hz, =CH), 7.28–7.47 (m, 5 H, H$_{arom}$) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.6, 36.6, 68.2, 91.0, 128.2, 128.3, 128.6, 135.5, 159.2, 162.8 ppm. EI-MS (70 eV): m/z (%) = 330 [M$^+$] (4), 288 (7), 203 (28), 185 (8), 157 (8), 91 (100). Anal. calcd. for C$_{13}$H$_{15}$IO$_2$ (330.17): C 47.29, H 4.58; found: C 47.36, H 4.63.

Methyl (Z)-2-iodo-3-phenyl-2-propenoate (8c)

1.1 g, (66% yield). IR (film): ν = 2951, 1718, 1637, 1598, 1493, 1446, 1443, 1254, 1237, 1201, 1076, 1032, 765, 692 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 3.87 (s, 3 H, CH$_3$), 7.35–7.45 (m, 3 H, H$_{arom}$), 7.70–7.79 (m, 2 H, H$_{arom}$), 8.25 (s, 1 H, =CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 53.7, 89.9, 128.2, 129.4, 130.0, 135.3, 148.2, 164.2 ppm. EI-MS (70 eV): m/z (%) = 288 [M$^+$] (26), 257 (9), 161 (100), 129 (34), 121 (18), 115 (13), 102 (27). Anal. calcd. for C$_{10}$H$_9$IO$_2$ (288.08): C 41.69, H 3.15; found: C 41.58, H 3.22.

Ethyl (Z)-3-(4-chlorophenyl)-2-iodo-2-propenoate (8d)[9]

1.41 g (70% yield). IR (film): ν = 2980, 1715, 1595, 1491, 1260, 1071, 780, 636 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.35 (t, 3 H, J = 7.0 Hz, CH$_3$), 4.28 (q, 2 H, J = 7.0 Hz, CH$_2$), 7.45 (*app* d, 2 H, J = 8.1 Hz, H$_{arom}$), 7.68 (*app* d, 2 H, J = 8.1 Hz, H$_{arom}$), 8.43 (s, 1 H, =CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.6, 59.3, 91.1, 128.7, 129.3, 132.3, 134.1, 149.0, 165.0 ppm. EI-MS (70 eV): m/z (%) = 338 [M$^+$, ^{37}Cl] (18), 336 [M$^+$, ^{35}Cl] (55), 211 (16), 209 (50), 183 (32), 181 (100), 138 (25), 136 (80). Anal. calcd. for C$_{11}$H$_{10}$ClIO$_2$ (336.56): C 39.26, H 2.99; found: C 39.33, H 2.82.

Ethyl (Z)-2-iodo-3-(4-methylphenyl)-2-propenoate (8e)[9]

1.33 g (71% yield). IR (film): ν = 2980, 1715, 1596, 1503, 1443, 1240, 1183, 765, 635 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.28 (t, 3 H, J = 7.0 Hz, CH$_2$CH$_3$), 2.35 (s, 3 H, CH$_3$), 4.25 (q, 2 H, J = 7.0, OCH$_2$), 7.20 (*app* d, 2 H, J = 7.7 Hz, H$_{arom}$), 7.65 (*app* d, 2 H, J = 7.7 Hz, H$_{arom}$), 8.25 (s, 1 H, =CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 14.8, 20.5, 60.0, 89.8, 128.0, 128.9, 134.7, 138.1, 149.5, 165.1 ppm. EI-MS (70 eV): m/z (%) = 316 [M$^+$] (60), 189 (50), 161 (100), 115 (83). Anal. calcd. for C$_{12}$H$_{13}$IO$_2$ (316.14): C 45.59, H 4.14; found: C 45.43, H 4.22.

Benzyl 2-iodoacrylate (8f)

0.90 g (52% yield). IR (film): ν = 3042, 2955, 1720, 1592, 1461, 1372, 1253, 1157, 1092, 1030, 1002, 945, 795, 753, 738, 702, 639 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 5.24 (s, 2 H, PhCH$_2$), 6.59 (d, 1 H, J = 1.4 Hz, CHH), 7.30–7.43 (m, 5 H, H$_{arom}$), 7.46 (d, 1 H, J = 1.4 Hz, CHH) ppm. ^{13}C NMR (CDCl$_3$): δ = 68.5, 96.3, 128.1, 128.5, 128.6, 135.2, 140.0, 162.2 ppm. EI-MS (70 eV): m/z (%) = 288 [M$^+$] (10), 217 (15), 181 (38), 153 (15), 143 (10), 133 (30), 127 (10), 117 (21), 91 (100). Anal. calcd. for C$_{10}$H$_9$IO$_2$ (254.07): C 41.69, H 3.15; found: C 41.77, H 3.20.

Methyl 2-iodo-3-methyl-2-butenoate (8g)

0.84 g (58% yield). IR (film): ν = 2982, 2956, 1718, 1628, 1438, 1245, 1216, 1014, 857 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.94 (s, 3 H, CH$_3$CCH$_3$), 2.00 (s, 3 H, CH$_3$CCH$_3$), 3.77 (s, 3 H, OCH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.5, 28.6, 52.0, 89.3, 154.6, 163.5 ppm. EI-MS (70 eV): m/z (%) = 240 [M$^+$] (100), 209 (46), 208 (67), 181 (24), 127 (10), 73 (27), 59 (24), 54 (33), 53 (58), 41 (51). Anal. calcd. for C$_6$H$_9$IO$_2$ (240.09): C 30.02, H 3.78; found: C 30.15, H 3.60.

Benzyl 2-iodo-3-methyl-2-butenoate (8h)

1.04 g (55% yield). IR (film): ν = 3030, 2978, 2934, 1720, 1630, 1440, 1263, 1120, 1035, 760, 685 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.08 (s, 3 H, CH$_3$CCH$_3$), 2.10 (s, 3 H, CH$_3$CCH$_3$), 5.27 (s, 2 H, PhCH$_2$), 7.23–7.48 (m, 5 H, H$_{arom}$) ppm. ^{13}C NMR (CDCl$_3$): δ = 22.8, 31.8, 67.5, 84.0, 127.9, 128.2, 128.5, 135.4, 152.4, 165.1 ppm. EI-MS (70 eV): m/z (%) = 316 [M$^+$] (3), 189 (15), 171 (58), 91 (100). Anal.

calcd. for $C_{12}H_{13}IO_2$ (316.14): C 45.59, H 4.14; found: C 45.48, H 4.23.

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[36] Mass spectra of compounds **2a**–**7a** and **9a**; **2a**: EI-MS (70 eV), m/z (%) = 128 [M^+] (100), 113 (62), 97 (58), 95 (14), 81 (18), 73 (15), 69 (18), 41 (33). **3a**: EI-MS (70 eV), m/z (%) = 128 [M^+] (100), 113 (36), 97 (56), 96 (20), 95 (8), 81 (12), 73 (17), 69 (25), 41 (52). **4a**: EI-MS (70 eV), m/z (%) = 144 [M^+] (26), 114 (5), 99 (77), 85 (76), 57 (41), 43 (100), 42 (37), 41 (94), 39 (59). **5a**: EI-MS (70 eV), m/z (%) = 90 (27), 87 (75), 69 (55), 45 (44), 43 (100), 41 (64), 39 (29). **6a**: EI-MS (70 eV), m/z (%) = 256 [M^+] (3), 225 (2), 200 (2), 129 (100), 114 (14), 97 (52), 87 (37), 69 (25), 55 (16), 43 (27), 41 (39), 39 (17). **7a**: EI-MS (70 eV), m/z (%) = 254 [M^+] (97), 239 (10), 223 (16), 222 (15), 128 (5), 127 (23), 112 (50), 95 (100), 73 (37), 67 (42), 59 (15), 53 (19), 43 (24), 41 (73), 39 (55). **9a**: EI-MS (70 eV), m/z (%) = 255 (8), 199 (51), 128 (100), 140 (37), 59 (26), 43 (31), 41 (72), 39 (39).

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