JOC*Note*

Direct Reaction of Dibromoacetic Acid with Aldehydes Promoted by Samarium Diiodide: An Easy, Efficient, and Rapid Synthesis of (*E*)-α,*β*-Unsaturated Carboxylic Acids with Total Stereoselectivity†

José M. Concellón* and Carmen Concellón

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Julián Clavería, 8, 33071 Oviedo, Spain

jmcg@fq.uniovi.es

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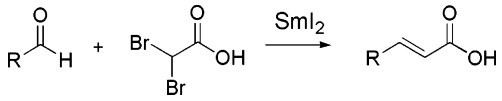

A promoted SmI_2 direct reaction of dibromoacetic acid with different aldehydes, followed by an elimination reaction also promoted by samarium diiodide, affords (*E*)-α,*β*-unsaturated carboxylic acids **2** with total stereoselectivity. A mechanism to explain this transformation is proposed.

The synthetic applications of dianions derived from carboxylic acids are limited, probably a result of the low solubility of these dianions in organic solvents.[1] In particular, no generation of bromo- or chloroacetic acid dianions (Li, Na, K, Mg, Zn) have been described to the best of our knowledge. Also, synthetic applications of acetic dianion[2] are very scarce.

Regarding the application of SmI_2 in organic synthesis, except pinacol coupling reactions,[3] no C−C bond formation from using carboxylic acids (without protection of the acid function) and, consequently, from the α-condensation of acetic acid has been described to date.[4]

In addition, (*E*)-α,*β*-unsaturated carboxylic acids are present in some natural products (i.e., the secretion juice of the honeybee queen[5] and caffeic acid[6]) and are also versatile building blocks in organic syntheses. For example, they have been used to prepare compounds of biological relevance such as tetrahydromyricoid[7] or the antibacterial reutericyclin.[8]

However, the methods to directly transform aldehydes into (*E*)-α,*β*-unsaturated carboxylic acids, through sequential addition and elimination reactions, are scarce[9] and present some drawbacks. So, the Knoevenagel reaction with malonic acid[10] gave low yields with enolizable aldehydes.[11] The use of (trimethylsilyl)acetic acid dianion (Peterson olefination)[12] and the cycloaddition of (trimethylsilyl)ketene[13] suffered from a lack of stereoselectivity. No application of the Wittig−Horner reaction[14] with highly enolizable aldehydes has been described, and, in general, this method required fairly stringent conditions to isolate the α,*β*-unsaturated acids.[14b] Finally, the synthesis of α,*β*-unsaturated carboxylic acids by the reaction of *C*,*O*,*O*-tris(trimethylsilyl)ketene acetal with enolizable aldehydes took place in low yield,[15] and to prepare the starting ketene acetal from (trimethylsilyl)acetic ester, three steps are necessary.

For these reasons, to obtain α,*β*-unsaturated carboxylic acids, sometimes it is preferable to carry out a condensation reaction of esters with aldehydes,[16] followed by hydrolysis (deprotection of acid function), instead of the direct synthesis of α,*β*-unsaturated carboxylic acids. Consequently, a direct synthesis of α,*β*-unsaturated carboxylic acids from commercially available compounds, obviating the protection−deprotection steps of the carboxylic function, would be very interesting.

Previously, we have described the highly diastereoselective preparation of (*E*)-α,*β*-unsaturated esters[17] or amides[18] by the treatment of 2-halo-3-hydroxyesters or amides with SmI_2. No generalization of this methodology to the synthesis of α,*β*-unsaturated carboxylic acids could be performed as a result of the difficulty in obtaining the starting 2-halo-3-hydroxyacids. Most recently, we have also reported the synthesis of α,*β*-unsaturated esters by a promoted SmI_2 reaction of aldehydes with ethyl dibromoacetate.[19]

† Dedicated to Professor Miguel Yus on the occasion of his 59th birthday.

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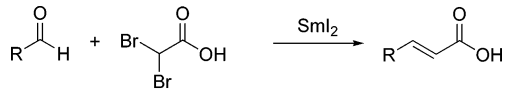
SCHEME 1. SmI_2-Mediated Synthesis of α,β-Unsaturated Carboxylic Acids



1 **2**

TABLE 1. Synthesis of α,β-Unsaturated Carboxylic Acids 2

entry	2	R^1	yield[b,c] (%)
1	**2a**	*n*-C_7H_{15}	70
2	**2b**	*n*-C_7H_{15}	83
3	**2c**	Cy	75
4	**2c**	Cy	76[d]
5[c]	**2d**	$(CH_3)_2CHCH_2$	78
6	**2d**	$(CH_3)_2CHCH_2$	75[d]
7	**2e**	$PhCH_2$	93
8	**2e**	$PhCH_2$	89[d]
9	**2f**	$PhCH(CH_3)$	71
10	**2g**	Ph_2CH	84

[a] All reactions were carried out using 5 equiv of SmI_2 and with a reaction time of 120 min. [b] Diastereoisomeric excess (de) in all reactions was >98% and was determined by CGL/MS and 300 MHz ^1H and ^{13}C NMR analysis of the crude products **2**. [c] Isolated yield after column chromatography on the basis of compound **1**. [d] These reactions were carried out using 5 equiv of SmI_2 generated in situ and with a reaction time of 120 min.

Now we describe the first SmI_2-mediated method to obtain (*E*)-α,β-unsaturated carboxylic acids with total stereoselectivity by using commercially available dibromoacetic acid and aldehydes. This transformation takes place through a sequential process: an aldol-type reaction (without the protection of the acid function) in the first step, followed by a β-elimination reaction in the second step. (Scheme 1). In addition, the reaction can be carried out with easily enolizable aldehydes.

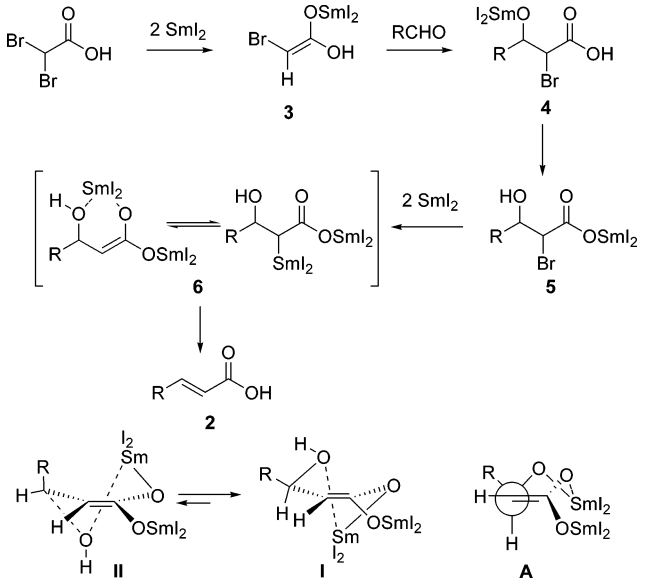
The reaction of different aldehydes (1 equiv) with dibromoacetic acid (1.5 equiv) in the presence of a solution of SmI_2 (5 equiv) in THF over a period of 2 h at room temperature afforded the corresponding (*E*)-α,β-unsaturated carboxylic acids **2** after hydrolysis, with total stereoselectivity and in good to excellent yields. Table 1 presents the results obtained.

The presence of a single diastereoisomer was determined on the crude reaction mixtures by GC-MS and ^1H NMR spectroscopy.

The *E* stereochemistry of the double C═C bond of the α,β-unsaturated acids **2** was assigned on the basis of the following: (a) the NOESY experiments of compounds **2b**, **2c**, and **2e**; (b) the value of the ^1H NMR coupling constant of the olefinic protons;[20] and (c) the comparison of the ^1H NMR data of compounds **2a**, **2b**, **2e**, and **2f** with those previously reported.[21]

The same transformation can be carried out by using SmI_2 generated in situ from a mixture of samarium and diiodomethane.[22] In the latter cases (Table 1, entries 4, 6, and 8), negligible effects on the reaction outcome were appreciable; the corresponding α,β-unsaturated carboxylic acids were obtained with similar yields and with total *E* selectivity.

SCHEME 2. Mechanism and Chair Transition State Model



Several comments are worth mentioning: (1) Aliphatic (linear, branched, or cyclic) (*E*)-α,β-unsaturated carboxylic acids **2** can be prepared; starting from aromatic or cinnamaldehyde aldehydes, the corresponding pinacol compounds were obtained instead of the α,β-unsaturated carboxylic acids. (2) In opposition to other previously described syntheses of α,β-unsaturated acid derivatives, this preparation of α,β-unsaturated carboxylic acids can be carried out by using easily enolizable aldehydes (Table 1, entries 7, 9, and 10). (3) To the best of our knowledge, this sequential C—C bond formation/elimination reaction constitutes the first example described in the literature in which a new C—C bond is performed by SmI_2 with a nonprotected carboxylic acid.[3,4] (4) This synthesis of α,β-unsaturated acids is very simple (especially when SmI_2 is generated in situ) and requires considerably less time, effort, and material than other classical methods. First, the synthesis is based on a sequential reaction, and second, no protection−deprotection of the carboxylic function is necessary. (5) The synthesis of α,β-unsaturated acids can be carried out on a bigger scale (**2e** was obtained starting from 4 mmol of **1e**).

The obtention of the compounds **2** might be explained assuming a sequential process (Scheme 2). Thus, the reaction of 2 equiv of SmI_2 with dibromoacetic acid generates a samarium enolate **3** rapidly. The reaction of this enolate with the aldehyde afforded the corresponding 2-bromoacid **4**, which could be hydrolyzed to afford the samarium-carboxylate **5**. Metalation of **5** with 2 equiv of samarium diiodide gives another enolate intermediate **6**, which suffers a spontaneous elimination reaction before it is hydrolyzed, yielding, after workup hydrolysis, the corresponding α,β-unsaturated carboxylic acid. Chelation of the Sm(III) center with the oxygen atom of the alcohol group leads to the formation of a six-membered ring.[23] Tentatively, we propose a chairlike transition state model **I** with the group R in the equatorial orientation (to avoid 1,3-diaxial interactions). Elimination from **I** affords (*E*)-α,β-unsaturated carboxylic acids **2**.

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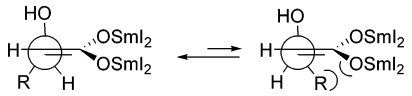
SCHEME 3. Mechanism and Nonchelated Transition State Model



The most questionable aspect of this mechanism is the proposition of a samarium enolate derived from the bromoacetic acid **3**. We do not have direct evidence for the existence of such an intermediate. However, a radical mechanism could be rejected, considering that no differences were observed in the course and result of the reaction when it was performed in the dark or in the presence of AIBN. Possibly, after enolate formation, the tautomeric form $I_2SmCHBrCO_2H$ might evolve to the most stable counterpart $BrCH{=}C(OH)OSmI_2$. This could be argued considering the high oxophilic character exhibited by the Sm(III) ions.[24] In this sense, the tautomer $BrCH{=}C(OH)OSmI_2$ is capable of coexisting in the presence of a hydroxyl group. To reinforce this argument, β-hydroxy samarium enolates were previously generated by the treatment of the corresponding 2-chloro-3-hydroxyesters[17] or amides[18] with samarium diiodide to afford, after a β-elimination reaction, the corresponding α,β-unsaturated ester or amide and byproducts such as those generated from the hydrolysis of the enolate by the alcohol function, which were not detected.

Another alternative nonchelated model to explain the *E* stereochemistry is shown in Scheme 3. In this model, recently proposed by Mioskowski and co-workers[25] to explain an elimination reaction promoted by Cr(II), the steric interactions between the samarium enolate and the R group are minimized in transition state **B** to give the observed *E* isomer.

In conclusion, in this paper we have presented an easy, simple, general, and efficient methodology for the preparation of α,β-unsaturated carboxylic acids starting from commercially available aldehydes and dibromoacetic acid and being promoted by samarium diiodide. The elimination reaction proceeds with total or high *E* diastereoselectivity. A mechanism to explain the total stereoselectivity has been proposed. This reaction constitutes the first example of a C−C bond formation promoted by SmI_2 with carboxylic acids. Different SmI_2-promoted reactions to form C−C bonds from carboxylic acids or other compounds with active hydrogens are currently under investigation within our laboratory.

Experimental Section

General Procedure for the Synthesis of α,β-Unsaturated Carboxylic Acids (2). SmI_2 (2.5 mmol) was added to a stirred suspension of dibromoacetic acid (0.75 mmol) and the corresponding aldehyde (0.5 mmol) in THF (2 mL). When the reaction was performed by using SmI_2 generated in situ, CH_2I_2 (2.5 mmol) was added to a suspension of Sm powder (2.5 mmol), dibromoacetic acid (0.75 mmol), and the aldehyde (0.5 mmol). After stirring the reaction at room temperature for 2 h, it was quenched with aqueous HCl (0.1 M) before the organic material was extracted with dichloromethane. The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (hexane/ethyl acetate, 5:1) afforded pure products **2**.

(*E*)-Hept-2-enoic Acid (2a). ^{1}H NMR (300 MHz, $CDCl_3$): 7.08 (dt, J = 6.8, 15.7 Hz, 1H), 5.83 (d, J = 15.7 Hz, 1H), 2.35−2.18 (m, 2H), 1.64−1.26 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5 (C), 152.2 (CH), 120.5 (CH), 31.9 (CH_2), 29.9 (CH_2), 22.1 (CH_2), 13.7 (CH_3). IR (neat): 2680, 1697, 1651 cm^{-1}. R_f = 0.3 (hexane/EtOAc, 3:1). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.10; H, 9.21.

(*E*)-Dec-2-enoic Acid (2b). Pale orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): 7.08 (dt, J = 7.0, 15.4 Hz, 1H), 5.82 (dt, J = 1.6, 15.4 Hz, 1H), 2.35−2.18 (m, 2H), 1.46−1.25 (m, 10H), 0.88 (t, J = 5.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1 (C), 152.4 (CH), 120.5 (CH), 32.2 (CH_2), 31.6 (CH_2), 29.6 (CH_2), 29.0 (CH_2), 27.8 (CH_2), 22.5 (CH_2), 13.9 (CH_3). MS (70 eV, EI, %) *m*/*z*: 170 (M^+, <1), 152 (13), 123 (25), 73 (100). HRMS (70 eV): [M^+] calcd for $C_{10}H_{18}O_2$, 170.1307; found, 170.1287. IR (neat): 2676, 1698, 1652 cm^{-1}. R_f = 0.3 (hexane/EtOAc, 3:1). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.34; H, 10.57.

(*E*)-Cyclohexylprop-2-enoic Acid (2c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (dd, J = 6.9, 15.7 Hz, 1H), 5.78 (dd, J = 1.60, 15.8 Hz, 1H), 2.2−1.2 (m, 11H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.4 (C), 156.9 (CH), 118.2 (CH), 40.4 (CH), 31.4 (2 × CH_2), 25.8 (CH_2), 25.5 (2 × CH_2), 14.0 (CH_3). MS (70 eV, EI, %) *m*/*z*: 154 (M^+, 3), 136 (21), 94 (40), 82 (100). HRMS (70 eV): [M^+] calcd for $C_9H_{14}O_2$, 154.0994; found, 154.0984. IR (neat): 2920, 1686 cm^{-1}. R_f = 0.2 (hexane/EtOAc, 3:1). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.21; H, 9.01.

(*E*)-5-Methylhex-2-enoic Acid (2d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12−7.02 (ddt, J = 1.5, 7.4, 15.7 Hz, 1H), 5.82 (dd, J = 1.4, 15.7 Hz, 1H), 2.13 (dd, J = 6.9, 7.4 Hz, 2H), 1.78 (sept, J = 6.8 Hz, 1H), 0.94 (d, J = 6.54 Hz, 3H), 0.92 (d, J = 6.54 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9 (C), 151.5 (CH), 121.4 (CH), 41.4 (CH_2), 27.67 (CH), 22.2 (2 × CH_3). R_f = 0.6 (hexane/EtOAc, 3:1). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.48; H, 9.50.

(*E*)-4-Phenylbut-2-enoic Acid (2e). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.17 (m, 6H), 5.86−5.79 (dt, J = 1.41, 15.6 Hz, 1H), 3.57−3.54 (dd, J = 1.41, 6.81 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6 (C), 150.0 (CH), 137.2 (C), 128.7 (2 × CH), 128.6 (2 × CH), 126.7 (CH), 121.5 (CH), 38.4 (CH_2). MS (70 eV, EI, %) *m*/*z*: 162 (M^+, 64), 144 (21), 117 (100), 115 (58). HRMS (70 eV): [M^+] calcd for $C_{10}H_{10}O_2$, 162.0681; found, 162.0683. IR (neat): 2921, 1697 cm^{-1}. R_f = 0.2 (hexane/EtOAc, 3:1). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.90; H, 6.90.

(*E*)-4-Phenylpentan-2-enoic Acid (2f). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.20 (m, 6H), 5.83 (dd, J = 1.6, 15.6 Hz, 1H), 3.71−3.62 (m, 1H), 1.46 (d, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9 (C), 155.1 (CH), 142.8 (C), 128.6 (2 × CH), 127.2 (2 × CH), 126.7 (CH), 119.4 (CH), 42.0 (CH), 20.0 (CH_3). MS (70 eV, EI, %) *m*/*z*: 176 (M^+, 32), 130 (100), 115 (38). HRMS (70 eV): [M^+] calcd for $C_{11}H_{12}O_2$, 176.0837; found, 176.0848. IR (neat): 2974, 1694, 1643 cm^{-1}. R_f = 0.2 (hexane/EtOAc, 3:1). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.69; H 6.74.

(*E*)-4,4-Diphenylbut-2-enoic Acid (2g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57−7.49 (m, 1H), 7.35−7.16 (m, 10H), 5.77−5.72 (m, 1H), 4.90 (d, J = 7.11 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7 (C), 152.6 (CH), 141.0 (2 × C), 128.6 (4 × CH), 128.5 (4 × CH), 126.9 (2 × CH), 122.1 (CH), 53.4 (CH). MS (70 eV, EI, %) *m*/*z*: 238 (M^+, 30), 220 (9), 192 (100), 178 (31), 114 (83).

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HRMS (70 eV): [M^+] calcd for $C_{16}H_{14}O_2$, 238.0994; found, 238.0966. IR (neat): 2923, 1693, 1648 cm^{-1}. $R_f = 0.2$ (hexane/EtOAc, 3:1). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 70.99; H, 5.71.

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Note Added after ASAP Publication. There was an error in the dedication line in the version published ASAP January 20, 2006; the corrected version was published ASAP February 1, 2006.

Supporting Information Available: General methods and spectroscopic data of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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