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Hunsdiecker-Type Bromodecarboxylation of Carboxylic Acids with Iodosobenzene Diacetate–Bromine

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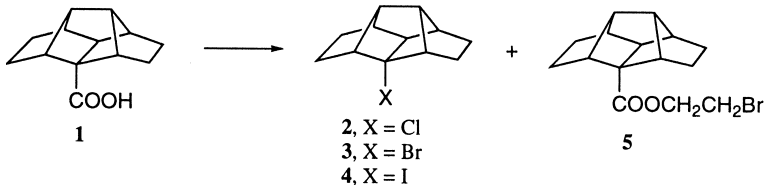
Abstract—Carboxylic acids are bromodecarboxylated in moderate to good yields on reaction with iodosobenzene diacetate and bromine under irradiation with a tungsten lamp. The reaction works very well with carboxylic acids having a primary, secondary or tertiary α-carbon atom, although diphenylacetic acid gives benzophenone. Benzoic acid derivatives are bromodecarboxylated in moderate yields if electron-withdrawing substituents are present in the benzene ring, while they are recovered mostly unchanged if the substituents are electron-donating. Partially iodinated products have been isolated in low yield from the bis-bromodecarboxylation of dicarboxylic acids having two bridgehead α-carbon atoms.

Recently, we published[1] the synthesis of 8-chloro-, 8-bromo- and 8-iodo-pentacyclo[6.4.0.0^{2,8}.0^{3,7}.0^{4,9}]dodecane, (**2**), (**3**) and (**4**), respectively, by halodecarboxylation of acid **1** (Scheme 1). The synthesis of **2** was straightforward through the Barton procedure[2–4] as was the preparation of **4** by using the Suárez procedure.[5,6] However, the preparation of **3** by using the Cristol–Firth[7] modification of the Hunsdiecker reaction was not an easy task. When 1,2-dibromoethane was used as the solvent and the water, formed by reaction of the carboxylic acid with mercury (II) oxide, was completely removed prior to the bromine addition,[8,9] the yield of **3** was only 44% and a significant amount of the 2-bromoethyl ester **5** (14%) was formed. Under similar conditions, the yield of **3** was slightly improved (54%) by using dibromomethane as the solvent. Chlorinated solvents were not tested to avoid competitive formation of **2**.

The Barton bromodecarboxylation procedure[2,3] of carboxylic acids via the corresponding thiohydroxamic esters using bromotrichloromethane as the bromine source and solvent works very well with various aliphatic and electron-rich or electron-deficient aromatic carboxylic acids. However, the simplicity and good yield of the Suárez iododecarboxylation procedure led us to try a similar procedure to carry out the bromodecarboxylation of acid **1**.

Results and Discussion

Reaction of **1** with iodosobenzene diacetate (IBDA) (2 equiv.) and bromine (2 equiv.) in CH_2Br_2 as solvent under irradiation with 2×100 W tunsgten lamps for 4 h, followed by addition of more IBDA (2 equiv.) and more Br_2 (2 equiv.) and continuing irradiation for 18 h more, gave **3** in 78% yield. This result prompted us to study the scope of this new bromodecarboxylation procedure. The optimum reaction conditions were studied with myristic acid (**6**). Benzene, the usual solvent in the Suárez iododecarboxylation reaction, was replaced by dibromomethane since formation of bromobenzene was observed. The best results were obtained by using an excess of reagents, IBDA (3 equiv.) and bromine (3 equiv.), which were added in two portions. After addition of the first half of the reagents, the



Scheme 1. (a) (i) 2,2′-Dithiobis(pyridine-1-oxide), tributyl phosphine; (ii) CCl_4, Δ, **2**: 51%; (b) HgO, Br_2, $BrCH_2CH_2Br$, Δ, **3**: 44%, **5**: 14%; (c) HgO, Br_2, $BrCH_2Br$, Δ, **3**: 54%; (d) Iodosobenzene diacetate, Br_2, CH_2Br_2, hν, Δ, **3**: 78% (e) Iodosobenzene diacetate, I_2, benzene, hν, Δ, **4**: 82%.

Keywords: decarboxylation; halogenation; bridgehead chemistry.

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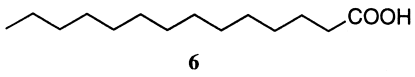
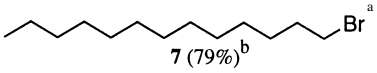
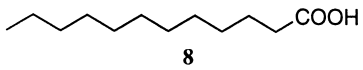
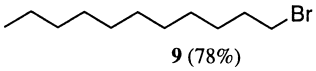
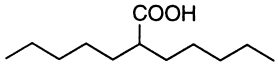
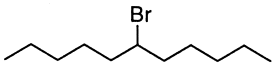
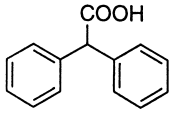
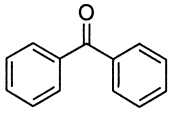
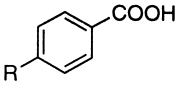
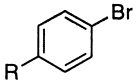
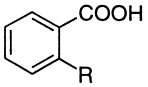
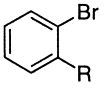
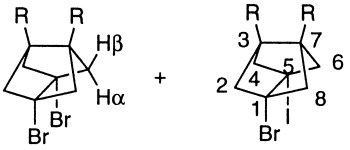
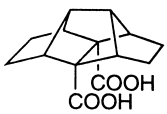
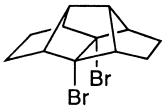
mixture was irradiated for 3.5–4 h, then the second half of the reagents was added and the mixture was irradiated for 18 h more. Under these reaction conditions, 1-bromotridecane (**7**) was obtained in 79% yield. Lower amounts of reagents gave lower yields of **7**, part of the starting acid being recovered (Table 1).

The standard bromodecarboxylation conditions were then applied to different aliphatic carboxylic acids having primary, secondary or tertiary α-carbon atoms, as shown in Table 1. Lauric acid (**8**) gave 1-bromoundecane (**9**) in 78% yield. Similarly, α-*n*-pentylheptanoic acid (**10**), prepared as described[10] gave 6-bromoundecane[11] (**11**) in 66% yield, some starting product (6%) being recovered. Diphenylacetic acid (**12**) did not give the expected benzhydryl bromide, benzophenone (**13**) being formed instead in 84% yield. The formation of this compound may be explained by bromination of the initially formed benzhidryl bromide followed by hydrolysis during the working-up. When this reaction was carried out by using a lower excess of reagents (1.2 equiv. IBDA and 1.2 equiv. Br_2), benzophenone was obtained in lower yield (48%) while much starting acid was recovered (49%).

The same reaction conditions were also applied to different substituted benzoic acid derivatives. The reaction gave reasonable yields with benzoic acids having electron-withdrawing substituents as it is usual in related

Table 1. Starting acids, products, yields and references to other procedures in the bromodecarboxylation of carboxylic acids using iodosobenzene diacetate and bromine in dibromomethane under irradiation (two portions of iodosobenzene diacetate (1.5 equiv. each) and bromine (1.5 equiv. each) were used)

Substrates	Products (yields)	Lit. Method and yield (%)
 **6**	 **7** (79%)[b] [a]	Tl (l) salt, 92[16] Hg (II) salt, 92[17]
 **8**	 **9** (78%)	Tl (l) salt, 85[16] Ag (I) salt, 91[18]
 **10**	 **11** (66%)	
 **12**	 **13** (84% yield)[b]	
 **14**, R = NO_2 **16**, R = OCH_3 **18**, R = C_6H_5	 **15**, R = NO_2 (59%) (8% recovered **14**) **17**, R = OCH_3 (0%) (68% recovered **16**) **19**, R = C_6H_5 (42%) (40% recovered **18**)	Barton proc., 69[3] Barton proc., 87[3]
 **20**, R = NO_2 **22**, R = $COOCH_3$ **24**, R = OCH_3	 **21**, R = NO_2 (51%) (8% recovered **20**) **23**, R = $COOCH_3$ (57%) (1% recovered **22**) **25**, R = OCH_3 (0%) (84% recovered **24**)	Ag (I) salt, 95[19]
 **26**, R = H **29**, R = CH_3	 **27**, R = H (50%) **28**, R = H (10%) **30**, R = CH_3 (55%) **31**, R = CH_3 (6%)	**27**: Ag (I) salt, 28[20] **30**: Ag(I) salt, 30[20]
 **32**	 **33** (50%)	Ag (I) salt, 50[14]

[a] 58% yield of **7** and 13% yield of recovered **6**, when using a total amount of 2 equiv. IBDA and 2 equiv. bromine; 33% yield of **7** and 48% yield of recovered **6**, when using a total amount of 1.2 equiv. IBDA and 1.2 equiv. bromine.

[b] 49% yield of **13** and 48% yield of recovered **12**, when using a total amount of 1.2 equiv. of IBDA and 1.2 equiv. bromine.

Hunsdiecker-type reactions. Thus, *p*-nitrobenzoic acid (**14**) gave *p*-bromonitrobenzene (**15**) in 59% yield, *o*-nitrobenzoic acid (**20**) gave *o*-bromonitrobenzene (**21**) in 51% yield, and *o*-methoxycarbonylbenzoic acid (**22**) gave methyl *o*-bromobenzoate (**23**) in 57% yield. In all cases, small amounts of the starting acids (1–8%) were recovered. In the case of benzoic acids having electron-releasing substituents, such as *p*-methoxybenzoic acid (**16**) or *o*-methoxybenzoic acid (**24**), no bromodecarboxylation products were obtained, and the starting acids were mainly recovered (68 and 84%, respectively) while the formation of brominated by-products was observed by GC/MS. Under the standard conditions, 4-biphenylcarboxylic acid (**18**) gave 4-bromobiphenyl (**19**) in 42% yield, 40% of **18** being recovered unchanged. Most of these compounds had been obtained previously through the Hunsdiecker reaction via Ag (I), Tl (I) or Hg (II) salts or through the Barton procedure (see Table 1).

The new bromodecarboxylation reaction was also applied to several bridgehead 1,2-dicarboxylic acids, such as **26**,[12] **29**,[13] and **32**[14] (Table 1). In these cases, 6 mol IBDA and 6 mol Br_2 were used per mole diacid, thus keeping the ratio of 3 equiv. IBDA and 3 equiv. Br_2 per equiv. of carboxylic acid. The yields of the isolated dibromo-derivatives were acceptable taking into account the double bromodecarboxylation: dibromide **27** (50%), dibromide **30** (55%) and dibromide **33** (50%). Worthy of note, from two of these reaction mixtures, small amounts of partially iodinated derivatives, **28** and **31**, were also isolated. Formation of these by-products may be explained by iodine abstraction from the iodobenzene, formed in these reactions, by a radical intermediate. Such a reaction must be more probable in the bromodecarboxylation of bridgehead carboxylic acids, which give more reactive intermediate radicals,[15] especially in the case of double bridgehead dicarboxylic acids. In these reactions, traces of $CHBr_3$ and bromobenzene were also observed by GC/MS.

Compounds **27** and **30** had been obtained previously[20] although in much lower yields (28 and 30%, respectively) through the classical Hunsdiecker reaction, via the corresponding disilver salts, working in dibromomethane as solvent. Similarly, compound **33** had been prepared in about 50% yield.[14] In this case, the reaction was carried out, in carbon tetrachloride and the product was contaminated with the corresponding bromochloro-derivative (about 10%).

The new compounds (**27**, **28**, **30** and **31**) were fully characterized through their spectroscopic data and elemental analysis (**27** and **30**) or high resolution mass spectra (HRMS) (**28** and **31**). The HRMS spectrum of **31** showed a very low intensity molecular ion, but the (M^+-Br) and (M^+-I) ions were clearly observed. Moreover, all of the spectroscopic data of **31** parallel those of **28**. Assignment of the ^1H and ^{13}C NMR spectra was carried out in a standard way with the aid of DEPT, $^1H/^1H$ and $^1H/^{13}C$ COSY experiments. Differentiation between the H_α/H_β protons in compounds **28** and **31** could be easily carried out taking into account the presence of cross signals in their COSY $^1H/^1H$ spectra corresponding to W-couplings between 2(6)-H_β/4(8)-H_β. In the cases of dibromides **27** and **30**, assignment of the H_α/H_β protons was carried out by comparison with **28** and **31** and the corresponding diiodides.[12,13]

In conclusion, a new bromodecarboxylation procedure has been developed, which may be applied to a wide range of aliphatic carboxylic acids having primary, secondary or tertiary α-carbon atoms and to electron-deficient benzoic acids. Diphenylacetic acid gave benzophenone, while electron-rich benzoic acids failed to give the bromodecarboxylation products.[15] The new procedure is easier to carry out, does not require the use of toxic metal ions, and, in some cases, gives higher yields than the classical Hunsdiecker reaction via the Ag (I) salt and the Cristol–Firth modification via the Hg (II) salt and the only drawbacks seem to be the separation of the iodobenzene, formed as a by-product in this reaction, from volatile products, and the formation of minor amounts of partially iodinated compounds in the bromodecarboxylation of double bridgehead dicarboxylic acids. Compared with the Barton bromodecarboxylation reaction, the new procedure can not be applied to benzoic acids substituted with electron-releasing substituents, as is the case for other kinds of Hunsdiecker bromodecarboxylation reactions. However, it works well in the case of double bridgehead 1,2-dicarboxylic acids which easily form cyclic anhydrides, where the Barton procedure usually fails due to difficulties in preparing the dicarboxylic acid dichloride or to dehydration of the diacid to the corresponding anhydride.

Experimental

General

Melting points were determined with a MFB 595010 M Gallenkamp melting point apparatus. 500 MHz ^1H NMR spectra, $^1H/^1H$ and $^1H/^{13}C$ COSY experiments (HMQC sequence) were performed on a Varian VXR 500 spectrometer while 75.4 MHz ^{13}C NMR spectra were taken on a Varian Gemini 300 spectrometer. ^1H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra at 75.4 MHz, in $CDCl_3$. Chemical shifts (δ) are reported in ppm related to internal tetramethylsilane. IR spectra were recorded on a FT/IR Perkin–Elmer spectrometer, model 1600. Routine MS spectra were taken on a Hewlett Packard 5988A spectrometer, introducing the sample through a gas chromatograph, Hewlett Packard model 5890 Series II, equipped with a 30-metre HP-5 (5% diphenyl-95% dimethyl-polysiloxane) column [conditions: 10 psi, initial temperature: 30°C (1 min), then heating at a rate of 15°C/min till 250°C, then isothermic] and the electron impact technique (70 eV). Significant ions given have a relative abundance of 50% or more except for the ions with higher *m/z* values. High resolution mass spectra were recorded on an Autospec-Q mass spectrometer from Micromass using the electron impact technique (70 eV) and direct sample introduction. Silica gel SDS 60 (70–200 μm) or (35–70 μm) was utilized for the standard and flash column chromatography, respectively. Elemental analyses and high resolution mass spectra were carried out, respectively, at the Microanalysis Service and the Mass Spectrometry Laboratory of the Centro de

Investigación y Desarrollo (C.I.D.), C.S.I.C., Barcelona, Spain.

General procedure for the bromodecarboxylation of carboxylic acids

A mixture of the carboxylic acid (500 mg), iodosobenzene diacetate (1.5 equiv.) and bromine (1.5 equiv.) in CH_2Br_2 (20 mL) was irradiated under reflux with magnetic stirring in an argon atmosphere with two 100 W-tungsten lamps for 4 h. The solution thus obtained was allowed to cool to room temperature, more iodosobenzene diacetate (1.5 equiv.) and bromine (1.5 equiv.) were added and irradiation under the same conditions was continued for 18 h more. The solution was allowed to cool to room temperature, washed with a 10% aqueous solution of $Na_2S_2O_3$ (3×20 mL), saturated aqueous solution of $NaHCO_3$ (3×20 mL) and brine (2×20 mL) and dried with anhydrous Na_2SO_4.

*Work-up A (for the products **7**, **9**, **11**, **15**, **19**, **21** and **23**):* The dried organic phase was concentrated in vacuo to give a residue which was submitted to column chromatography [silica gel (70–230 mesh, 40 g)/hexane].

*Work-up B (for the products **27**, **30** and **33**):* Most of the solvent from the dried organic phase was distilled at atmospheric pressure using a 10 cm-Vigreux column. Iodobenzene and remaining solvent were distilled from the residue at room temperature and reduced pressure (0.5–0.7 Torr) in a rotary microdistillation apparatus. The residue was submitted to flash column chromatography [1 m×1 cm column, silica gel (80 g)/hexane] eliminating the solvent from the fractions by careful distillation at atmospheric pressure using a 10 cm-Vigreux column. Iodobromo derivatives **28** and **31** were eluted prior to the corresponding dibromo derivatives **27** and **30**.

Notes:

1. For dicarboxylic acids, 3 equiv. of iodosobenzene diacetate and 3 equiv. bromine were used each time.
2. For the preparation of compound **3**, 2 equiv. of iodosobenzene diacetate and 2 equiv. of bromine were used each time.
3. The yields for the compounds obtained by this procedure are given in Table 1, and correspond to pure isolated products.

1,5-Dibromotricyclo[3.3.0.0^{3,7}]octane 27. White solid, mp 101–102°C (sublimed at 50°C/1 Torr). IR (KBr) ν 2997, 2942, 2894, 1477, 1284, 1264, 1140, 1099, 1004, 969, 933, 916, 817 cm^{-1}. ^{1}H NMR δ 2.00 [broad d, J=7.5 Hz, 4 H, 2(4,6,8)-H$_\alpha$], 2.08 [broad d, J=7.5 Hz, 4 H, 2(4,6,8)-H$_\beta$], 2.39 [broad s, 2 H, 3(7)-H]. ^{13}C NMR δ 36.3 [CH, C3(7)], 56.2 [CH_2, C2(4,6,8)], 63.3 [C, C1(5)]. MS (EI), *m/z* (%): 226 (2), 224 (4), 222 ($M^+-C_3H_6$, 2), 187 (17), 185 (M^+-Br, 18), 159 (11), 157 ($M^+-C_2H_4$-Br, 12), 106 (27), 105 (M^+-HBr$-$Br, 100). Anal. Calcd for $C_8H_{10}Br_2$: C, 36.12; H, 3.78; Br 60.08. Found: C, 36.07; H, 3.84; Br 59.65.

1-Bromo-5-iodotricyclo[3.3.0.0^{3,7}]octane 28. White solid, mp 92–93°C (sublimed at 50°C/1 Torr). IR (KBr) ν 2993, 2939, 2893, 1475, 1283, 1264, 1172, 1135, 1096, 1002, 961, 931, 907, 809, 739 cm^{-1}. ^{1}H NMR δ 1.98 [m, 2 H, 4(6)-H$_\alpha$], 2.01 [m, 2 H, 4(6)-H$_\beta$], 2.08 [m, 2 H, 2(8)-H$_\beta$], 2.15 [m, 2 H, 2(8)-H$_\alpha$], 2.24 [t, J=1.5 Hz, 2 H, 3(7)-H]. ^{13}C NMR δ 37.6 [CH, C3(7)], 42.0 (C, C5), 56.1 [CH_2, C4(6)], 59.4 [CH_2, C2(8)], 64.7 (C, C1). MS (EI), *m/z* (%): 233 (M^+-Br, 8), 187 (7), 185 (M^+-I, 8), 106 (56), 105 (M^+-HBr$-$I, 100), 79 (56). Exact mass calcd for $C_8H_{10}BrI$ 311.9011, obsd 311.9007.

1,5-Dibromo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane 30. White solid, mp 78–79°C (sublimed at 50°C/1 Torr). IR (KBr) ν 2976, 2937, 2889, 2866, 1474, 1457, 1445, 1381, 1295, 1238, 1218, 1181, 1142, 998, 965, 902 cm^{-1}. ^{1}H NMR δ 1.15 [s, 6 H, 3(7)-CH_3], 1.95 [d, J=7.5 Hz, 4 H, 2(4,6,8)-H$_\beta$], 2.04 [d, J=7.5 Hz, 4 H, 2(4,6,8)-H$_\alpha$]. ^{13}C NMR δ 15.7 [CH_3, 3(7)-CH_3], 46.7 [C, C3(7)], 62.4 [CH_2, C2(4,6,8)], 63.5 [C, C1(5)]. MS (EI), *m/z* (%): 215 (31), 213 (M^+-Br, 33), 173 (9), 171 ($M^+-C_3H_6-$Br, 9), 134 (47), 133 (M^+-HBr-Br, 100), 105 (50), 91 (69). Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.84; H, 4.79; Br 54.35. Found: C, 40.77; H, 4.84; Br 54.23.

1-Bromo-5-iodo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane 31. White solid, mp 76–78°C (sublimed at 50°C/1 Torr). IR (KBr) ν 2974, 2955, 2927, 2862, 1480, 1446, 1377, 1295, 1237, 1218, 1180, 1142, 1001, 964, 888, 816 cm^{-1}. ^{1}H NMR δ 1.18 [s, 6 H, 3(7)-CH_3], 1.91 [m, 2 H, 4(6)-H$_\beta$], 1.99 [m, 2 H, 2(8)-H$_\beta$], 2.04 [m, 2 H, 4(6)-H$_\alpha$], 2.20 [m, 2 H, 2(8)-H$_\alpha$]. ^{13}C NMR δ 15.4 [CH_3, 3(7)-CH_3], 42.9 (C, C5), 48.0 [C, C3(7)], 62.3 [CH_2, C4(6)], 64.9 (C, C1), 65.5 [CH_2, C2(8)]. MS (EI), *m/z* (%): 261 (M^+-Br, 17), 215 (18), 213 (M^+-I, 19), 173 (5), 171 (M^+-I$-C_3H_6$, 6), 134 (M^+-Br$-$I, 99), 133 (76), 119 (51), 105 (60), 91 (100), 77 (63). Exact mass: calcd for $C_{10}H_{14}Br$ (M^+-I) 213.0279, obsd 213.0272; calcd for $C_{10}H_{14}I$ (M^+-Br) 261.0140, obsd 261.0139.

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