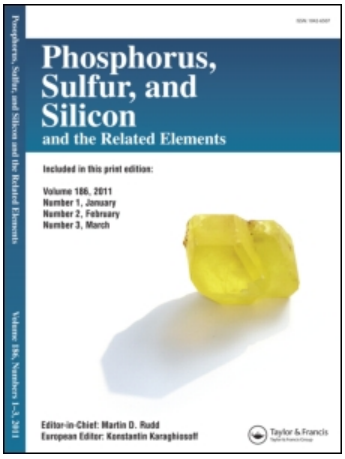

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FORMATION OF ACYL BROMIDES FROM CARBOXYLIC ACIDS AND N-BROMOSUCCINIMIDE; SOME REACTIONS O FBROMOCYANOTRIPHENYLPHOSPHORANE

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FORMATION OF ACYL BROMIDES FROM CARBOXYLIC ACIDS AND N-BROMOSUCCINIMIDE; SOME REACTIONS OF BROMOCYANOTRIPHENYLPHOSPHORANE

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Acyl halides, i.e., acyl bromides and acyl chlorides can be generated in high yields under mild conditions from the corresponding carboxylic acid in the presence of equivalent amounts of NBS/NCS and triphenylphosphine. The reaction between carboxylic acids, bromocyane and triphenylphosphine (Ph_3PBrCN), affords under similar conditions acyl bromides. Bromocyanotriphenylphosphorane reacts also smoothly with epoxides, e.g., phenyloxirane. It appears, however, that the expected bromocyanides are not obtainable by this reaction, vicinal dibromides being formed instead.

Key words: Acyl bromides, synthesis of from carboxylic acids and NBS, bromocyanotriphenylphosphorane, synthesis of alkylhalides.

Continuing our interest in the applicability of organophosphorus reagents in organic synthesis,[1-3] we have studied the formation of acyl halides, especially acyl bromides and acyl iodides from carboxylic acids via the corresponding acyloxyphosphonium salts.

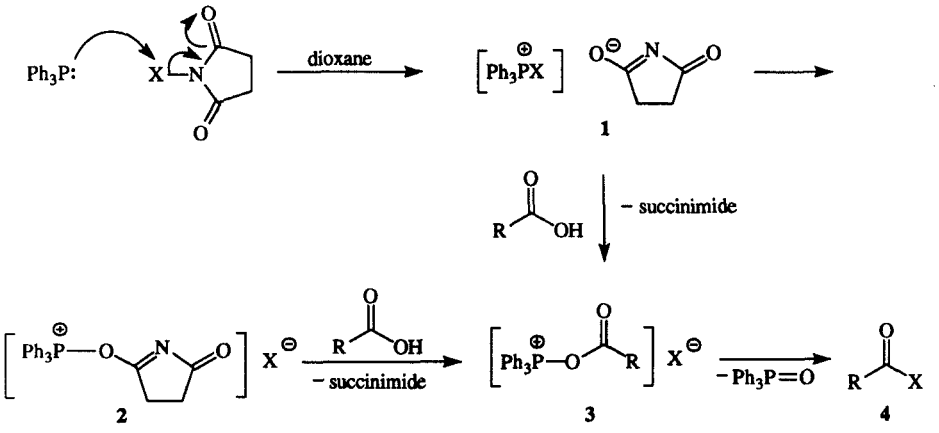
Although highly reactive and versatile, acyl bromides and the related iodides are of very limited use in organic synthesis. One reason for the lack of interest in these compounds is presumably that quite few useful methods are available for their preparation, especially so in the case of acyl iodides, and those at hand require reactants that are either expensive, not easily available,[4-6] or involve the formation of hydrogen halides. The latter side products always constitute an inconvenience, particularly so in the case of acid sensitive substrates.

We here report a simple and convenient one-flask synthesis of acyl bromides (**4**, Scheme I) from the corresponding carboxylic acids, triphenylphosphine, and NBS/bromocyane, respectively.

We have observed[1] that carboxylic acids react with a mixture of N-chlorosuccinimide, triphenylphosphine and sodium azide in acetone, at very mild conditions, to form acyl azides in good yields via acyloxyphosphonium salts **3** (Scheme I).

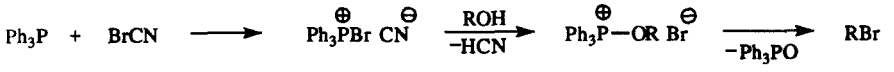
Furthermore, carboxylic acids in combination with Ph_3P/NBS react smoothly with alcohols[2] in dichloromethane solution forming esters and likewise with primary and secondary amines,[3] at or below room temperature, affording excellent yields of the corresponding amides. We believe the reactions proceed via the activated species **3** (Scheme I) which is subsequently attacked by the nucleophile (N_3^-, ROH, HNR_2), to yield the various products, presumably via an intermediate phosphorane.

Phosphonium salts generated as outlined in Schemes I and II constitute potentially valuable intermediates for the preparation of a large number of compounds,



X = Cl, Br, I

SCHEME I



SCHEME II

e.g., acyl halides, alkyl halides,[7] lactams and lactones. Under the abovementioned reaction conditions (CH_2Cl_2/room temperature) reaction of carboxylic acids with NCS, NBS or NIS did not afford the corresponding acyl halide, however. Neither did prolonged heating of the intermediate **3** (X = Br, I) in dichloromethane lead to noticeable quantities of acyl halides. Only NCS (X = Cl) leads to appreciable product formation under these conditions (refluxing dichloromethane). We argued therefore[1-3] that product formation in the abovementioned cases proceeds via a direct reaction of **3** with the various nucleophiles (N_3^-, ROH, HNR_2) and that acyl halides are not involved as intermediates in these reactions. We had hopes, however, that at more forcing conditions, i.e. heating above 40°C, displacement of the oxyphosphonium group of **3** by the halide ion, should lead to the corresponding acyl halides.

We now report the realization of these expectations together with the first positive results from related experiments with the BrCN/Ph_3P system.

The new methods[1-3] present several advantages: The transformations occur under extremely simple experimental conditions, afford good yields of products and require easily available, inexpensive starting materials. Nearly quantitative conversion of carboxylic acids into acyl halides is generally achieved within 5–10 min at 90–100°C in dioxane. The method can be used for a wide variety of substrates, including aromatic and aliphatic (saturated an unsaturated) carboxylic acids, and one set of reaction conditions is suitable for the synthesis of an assortment of acyl halides. The results are summarized in Table I.

The reaction of carboxylic acids with NIS (N-iodosuccinimide)/Ph_3P, or with

TABLE I
Conversion of carboxylic acids into acyl bromides

Entry	Substrate	Product	(%) Yield[a]
1	benzoic acid	benzoyl bromide	76
2	2-naphthoic acid	2-naphthoyl bromide	95
3	cinnamic acid	cinnamoyl bromide	72
4	nonanoic acid	nonanoyl bromide	82
5	hexanoic acid	hexanoyl bromide	71
6	heptanoic acid	heptanoyl bromide	75[b]
7	cyclohexanecarboxylic acid	cyclohexanoyl bromide	79
8	diphenylacetic acid	diphenylacetyl bromide	94
9	hexadecanoic acid	hexadecanoyl bromide	68
10	benzoic acid	benzoyl bromide	78[b]
11	acetic acid	acetyl bromide	74[c]

[a] The transformations were carried out with NBS/Ph_3P in dioxane.
[b] Ph_3P/BrCN/dioxane.
[c] The reaction was performed without solvent by gradually adding BrCN (5 mmol) to a stirred mixture of acetic acid (5 mmol) and triphenylphosphine (5 mmol). The product was thereafter distilled by means of a Kugelrohr apparatus.

Ph_3P/ICN, proceeds much more slowly than the corresponding reactions with NCS and NBS. In fact, after heating for several hours with a slight excess of Ph_3P/NIS or Ph_3P/ICN, heptanoic acid gave only 35 to 40% yield of heptanoyl iodide, and the method is considered unsuitable for the preparation of acyl iodides. Apparently the "softer" iodide ion is a much poorer nucleophile than chloride or bromide ions towards the relatively "hard" carbonyl site of **3** (Scheme I), making **3** (X = I) a relatively stable compound.

Formation of Alkyl Halides

The abovementioned results suggested that under appropriate conditions the intermediate **2**, or more probably **1** (Scheme I), might react also with alkohols in an analogous way (*vide supra*), yielding alkoxytriphenylphosphonium halides which are known to decompose under mild conditions in a rapid Michaelis-Arbuzov rearrangement to the corresponding alkyl halides and triphenylphosphine oxide.

We found that alkyl halides are obtained under mild condition and in high yields from the corresponding alkohols when they are treated with triphenylphosphine/N-bromosuccinimide in dichloromethane, dioxane or other inert solvents.

A search of the literature revealed, however, a paper directed at the preparation of acetylenes where Trippett,[8] reporting a series of interesting reactions, e.g., the formation of dehalogenated carbonyl compounds from triphenylphosphine and α-halogenated carbonyl compounds, is mentioning "an abnormal reaction" between triphenylphosphine and NBS, leading to a product which reacted vigorously with ethanol to give ethyl bromide.

It appears that no investigation of the generality of the reaction was made. Indeed, Trippett's interesting observation seems to have gone largely unnoticed.[9]

The intermediate product is doubtlessly **2** (Scheme I), which reacts not only with ethanol, but as we have found with almost any alcohol added to the reaction mixture.

The reaction conditions employed in the present work are considerably different from those applied by Trippett,[8] however, and yields are consistently higher. Considering the high yields and mild reaction conditions required, the method represents a valuable addition to the limited number of methods available for the transformation of alcohols into the corresponding bromo and iodo derivatives.

Reactions with Bromocyanotriphenylphosphorane

In analogy with the Ph_3P/NBS system, bromocyane reacts with a mixture of triphenylphosphine and an alcohol under mild conditions forming alkyl bromides in fair to high yields (Scheme II). The latter method have certain advantages since the formation of volatile HCN as a side product constitutes less of an inconvenience during workup than the voluminous mass of solid succinimide produced by the Ph_3P/NBS system.

A sample of the results are summarized in Table II.

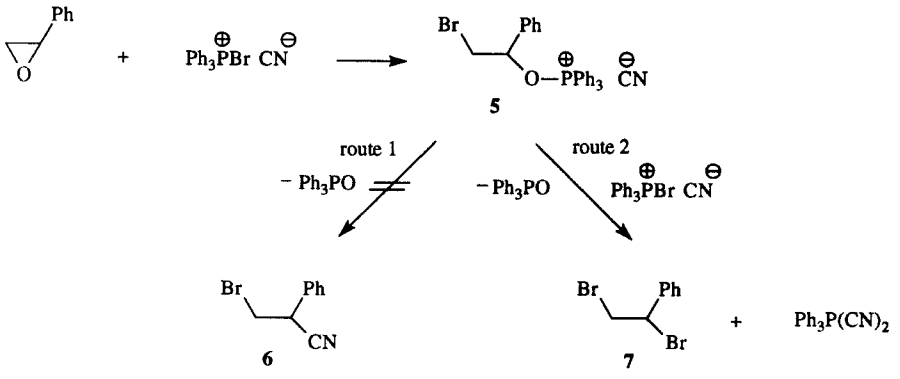
Furthermore, in an attempt to prepare 2-bromocyanides **6** (Scheme III), phenyloxirane was allowed to react with bromocyanotriphenylphosphorane **4**. The re-

TABLE II

Conversion of alcohols into alkyl halides

Entry	Substrate	Product	(%) Yield
12	benzyl alcohol	benzyl bromide	81[a]
13	propanol	1-bromopropane	75[b]
14	propanol	1-iodopropane	70[c]

[a] Prepared from the alcohol with triphenylphosphine/NBS in dioxane.
[b] The compound was prepared from the alcohol and BrCN/Ph_3P without any solvent.
[c] Prepared by mixing the alcohol with equivalent amounts of Ph_3P and NIS.



SCHEME III

action probably involves ring opening by the nucleophilic bromide in a first step, forming the intermediate **5** (Scheme III). The intermediate would then presumably undergo nucleophilic attack by the cyanide ion, leading to **6** and triphenylphosphine oxide. Treatment of phenyloxirane with equivalent amounts of **4** in various solvents gave not the expected bromocyanides (route 1), however. On the contrary, in accord with the proposed route 2 (Scheme III), the bromocyanotriphenylphosphorane reacts with the epoxide to give exclusively the corresponding vicinal dibromide **7**, demonstrating that the bromide ion is a better nucleophile than cyanide towards the carbon of the C—O—P bond in the intermediate **5**.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken at operating frequencies of 200 and 50.3 MHz on a Varian Gemini-200 spectrometer using TMS as internal standard. The mass spectra were obtained on a JEOL JMS-DX 303 mass spectrometer. IR spectra were measured as films with a Perkin Elmer 1310 infrared spectrophotometer. Column chromatography was carried out using Merck No. 9385 silica gel 60. Melting points, determined with a Reichert Thermopan melting point microscope, are uncorrected.

General Procedure for the Preparation of Acyl Bromides **1–11**

The reactants, triphenylphosphine and carboxylic acid (5 mmol of each) were dissolved in dioxane (5 ml). The mixture was vigorously stirred and NBS (0.91 g, 5.1 mmol) added in small portions. The reaction mixture was heated for 5–10 min. and allowed to cool to room temperature. Pentane (50 ml) was thereafter added. Stirring was continued for about 10 min until the by-products, triphenylphosphine oxide and succinimide, crystallized. The reaction mixture was filtered under nitrogen, the solids washed with pentane and the combined pentane extracts concentrated under reduced pressure. The remaining acyl bromide was distilled and stored under nitrogen.

Preparation of alkyl halides (**12–15**)

Benzyl bromide **12** was prepared by mixing benzyl alcohol (0.54 g, 5 mmol) and triphenylphosphine (1.32 g, 5 mmol) in dioxane (5 ml). NBS (0.90 g, 5 mmol) was added, and the reaction mixture heated for 2–3 min with continuous stirring. The reaction mixture was thereafter slightly cooled, pentane (50 ml) was added, and the suspension set aside at ambient temperature for a couple of hours. Filtration gave, in addition to succinimide, a nearly quantitative yield of triphenylphosphine oxide. The filtrate was evaporated *in vacuo*, and the residue distilled in a Kugelrohr apparatus, yielding 0.69 g (81%) of benzyl bromide, b.p. about 90°C/15 mm, lit.[10] 198°C/760 mm Hg.

1-Bromopropane **13** was made from propanol by mixing the alcohol (0.31 g, 5 mmol) with triphenylphosphine (1.32 g, 5 mmol), whereafter BrCN (5 mmol) was added to the slightly cooled reaction mixture. The resulting yellow oil was distilled in a Kugelrohr apparatus to give 1-bromopropane (0.63 g, 75%), b.p. 75–80°C. Lit.[11] 71.2°C/763 mm.

1-Iodopropane **14** was made in a similar way from propanol by mixing the alcohol with equivalent amounts of triphenylphosphine and N-iodosuccinimide. Distillation afforded 1-iodopropane 0.60 g (71%), b.p. 100–105°C, lit.[12] 102.5°C.

Attempted Preparation of 2-bromo-1-cyano-1-phenylethane

To a stirred mixture of triphenylphosphine (1.32 g, 5 mmol) and phenyloxirane (0.6 g, 5 mmol) in dioxane (5 ml) was added bromocyane (0.53 g, 5 mmol) in two portions. After the initially exothermic reaction was completed, the mixture was stirred at 90–100°C for 2 h and thereafter allowed to cool. Gas chromatography showed the presence of a new compound, besides triphenylphosphine, triphenylphosphine oxide, and some unreacted phenyloxirane. The reaction mixture was concentrated a little, and the residue added to a column of silica gel and eluted with a mixture of ether and petroleum ether (1:8). The unknown product was further purified by Kugelrohr distillation followed by crystallization (ethanol), which afforded 0.60 g the of a pure compound, melting at 74°C and shown by mass spectrometry and NMR analysis to be 1,2-dibromo-1-phenylethane (see below). Yield: 90% (on the basis of bromocyanotriphenylphosphorane).

Benzoyl bromide **1**. Filtration followed by evaporation of the solvent (pentane) and distillation (Kugelrohr) at about 120°C/15 mm Hg (lit.[13] 109–110°C/20), gave virtually pure **1**, which hydrolyzed very rapidly in the air; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.57 (m, 2H, H_m), 7.60–7.75 (m, 1H, H_p), 8.02–8.15 (m, 2H, H_o), ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 128.83, 130.02, 131.84, 134.66, 135.47, 165.50 (CO); MS (70 eV): m/z (%) 105 (100, M^+-Br), 77 (66, Ph); IR (film) 1820 cm^{-1} (C=O).

2-Naphthoyl bromide **2**. Distilled (Kugelrohr) at about 150°C/0.1 mm Hg; $C_{11}H_7BrO$ calc. (%): C 56.20, H 3.00. Found: C 56.35, H 3.12. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55–7.78 (m, 2H, $H_{aromatic}$), 7.85–8.10 (m, 4H, $H_{aromatic}$), 8.72 (d, 1H, $H_{aromatic}$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 125.22, 127.41, 127.69, 128.65, 129.96, 131.73, 132.05, 135.87, 136.38, 165.46 (CO); MS (70 eV); m/z (%) 236 (5.3, M^+), 234 (5.4), 155 (100, M^+-Br), 127 (73, 155-CO); IR (film) 1770 cm^{-1} (C=O).

Cinnamoyl bromide **3**. Distilled (Kugelrohr) at about 115°C/0.1 mm Hg, lit.[13] 110°C/0.1 mm; ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.47 (d, 1H, J = 16 Hz, CH), 7.30–7.50 (m, 5H, $H_{aromatic}$), 7.81 (d, 1H, J = 16 Hz, CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 117.01, 128.02, 128.57, 130.37, 133.62, 146.70, 172.14 (CO); MS (70 eV): m/z (%) 131 (53, M^+-Br), 104 (18), 103 (69), 102 (34), 91 (22), 80 (21), 77 (50), 51 (46); IR (film) 1770 cm^{-1} (C=O).

Nonanoyl bromide **4**. Distilled (Kugelrohr) at about 75°C/0.1 mm Hg, lit.[14] 74–76°C/0.5 mm; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.6 Hz, CH_3), 1.18–1.45 (m, 10H, CH_2), 1.60–1.80 (m, 2H, CH_2), 3.00 (t, 2H, J = 7.2 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.01, 22.59, 25.37, 28.24, 28.97, 31.69, 52.48, 169.62 (CO); MS (70 eV): m/z (%) 141 (100, M^+-Br), 98 (26), 97 (11), 84 (14), 83 (14), 81 (10), 71 (31), 69 (17), 60 (38), 57 (62); IR (film) 1810 cm^{-1} (C=O).

Hexanoyl bromide **5**. Distilled (Kugelrohr) at abut 80°C/10 mm Hg, Lit.[15] 175–176°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.89 (t, 3H, CH_3), 1.22–1.45 (m, 4H, CH_2), 1.60–1.82 (m, 2H, CH_2), 3.04 (t, 2H, J = 7.2 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.69, 22.08, 25.03, 30.34, 52.34, 169.64 (CO); MS (70 eV): m/z (%) 99 (100, M^+-Br); IR (film) 1800 cm^{-1} (C=O).

Heptanoyl bromide **6**. Distilled (Kugelrohr) at about 75°C/5 mm Hg, lit.[16] 80°C/12 mm; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.89 (t, 3H, J = 5.7 Hz, CH_3), 1.20–1.45 (m, 6H, CH_2), 1.55–1.80 (m, 2H, CH_2), 3.00 (t, 2H, J = 7.2 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.04, 22.42, 25.42, 27.99, 31.25, 52.54, 169.60 (CO); MS (70 eV): m/z (%) 113 (100, M^+-Br), 85 (29), 57 (18), 55 (22); IR (film) 1800 cm^{-1} (C=O).

Cyclohexanoyl bromide **7**. Distilled (Kugelrohr) at about 70°C/10 mm Hg; lit.[13] 86°C/26 mm; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20–2.20 (m, 10H, CH_2), 2.72–2.89 (m, 1H, CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 24.93, 25.50, 29.30, 172.42; MS (70 eV): m/z (%) 111 (47, M^+-Br), 83 (100, 111-CO), 73 (46), 55 (98); IR (film) 1800 cm^{-1} (C=O).

Diphenylacetyl bromide **8**. Oil; distilled (Kugelrohr) at about 80°C/0.01 mm Hg; $C_{14}H_{11}BrO$ calc. (%): C 61.11, H 4.03. Found: C 61.29, H 4.22. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.58 (s, 1H, CH), 7.20–7.45 (m, 10H, $H_{aromatic}$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 73.56, 128.17, 128.69, 128.97, 135.70, 169.21 (CO); MS (70 eV): m/z (%) 194 (14, M^+-HBr), 167 (100, Ph_2CH) 165 (66), 152 (20), 115 (10), 77 (12), 63 (15), 51 (27); IR (film) 1800 cm^{-1} (C=O).

Hexadecanoyl bromide **9**. Distilled (Kugelrohr) at about 165°C/0.01 mm Hg; $C_{11}H_7BrO$ calc (%): C 60.18, H 9.78. Found: C 60.25, H 9.92. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.86 (t, 3H, CH_3), 1.15–1.50 (m, 24H, CH_2), 71.60–1.75 (m, 2H, H_2), 2.98 (t, 2H, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.99, 22.51, 25.19, 28.04, 28.61, 28.83, 28.96, 29.10, 29.17, 29.31, 29.47, 31.71, 52.25, 169.12; MS (70 eV): m/z (%) 239 (61, M^+-HBr), 185 (18), 184 (25), 183 (87), 152 (19).; IR (film) 1800 cm^{-1} (C=O).

Benzoyl bromide **10**. Distilled (Kugelrohr) at about 120°C/15 mm Hg, lit.[13] 109–110°C/20 mm, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.57 (m, 2H, H_m), 7.60–7.75 (m, 1H, H_p), 8.02-8.15 (m, 2H, H_o), ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 128.83, 130.02, 131.84, 134.66, 135.47, 165.50 (CO); MS (70 eV): m/z (%) 105 (100, M^+-Br), 77 (66, Ph); IR (film) 1820 cm^{-1} (C=O).

Acetyl bromide **11**. Distilled (Kugelrohr) at about 80°C/760 mm Hg; lit.[13] 78°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.81 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 39.07, 165.10 (CO); MS (70 e V): m/z (%) 43 (62, M^+-Br), 42 (100, C_2H_2O); IR (film) 1820 cm^{-1} (C=O).

Benzyl bromide **12**. Distilled (Kugelrohr) at about 90°C/15 mm Hg, lit.[10] 198°C/760 mm; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.51 (s, 2H, CH_2), 7.28–7.46 (m, 5H, $H_{aromatic}$); ^{13}C NMR (50.3 MHz, $CDCl_3$):

δ 33.48, 128.29, 128.68, 128.93, 137.7; MS (70 eV): m/z (%) 172 (4.3, M^+), 170 (4.3), 91 (100, M^+-Br), 65 (13), 63 (10).

1-Bromopropane **13**. Distilled (Kugelrohr) at about 75–80°C/760 mm Hg, lit.[11] 71.2°C/763 mm.; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.02 (t, 3H, J = 7.2 Hz, CH_3), 1.78–1.96 (m, 2H, CH_2), 3.42 (t, 2H, J = 6.7 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 12.99, 26.26, 35.87; MS (70 eV): m/z (%) 124 (4.9, M^+), 122 (4.8), 43 (41, M^+-Br), 41 (18), 32 (100).

1-Iodopropane **14**. Distilled (Kugelrohr) at about 100–105°C/760 mm Hg, lit.[12] 102.5°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.05 (t, 3H, J = 7.2 Hz, CH_3), 1.75–1.96 (m, 2H, CH_2), 3.19 (t, 2H, J = 6.7 Hz, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 9.75, 15.58, 27.11; MS (70 eV): m/z (%) 170 (43, M^+), 127 (14), 43 (100, $M^+ - I$), 41 (33).

1,2-Dibromo-1-phenylethane **15**. Distilled (Kugelrohr) at about 140°C/0.1 mm Hg, m.p. 74°C, lit.[16] 74–74.5°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.05–4.10 (m, 2H, CH_2), 5.11–5.18 (q, 1H, CH), 7.35–7.43 (m, 5H, $H_{aromatic}$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 35.49, 51.14, 127.00, 128.20, 128.52, 137.81; MS (70 eV): m/z (%) 266 (2.6, M^+), 264 (5.9), 185 (97.7, M^+-Br), 183 (100, M^+-Br), 103 (12.3), 78 (32.9), 77 (35.3).

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