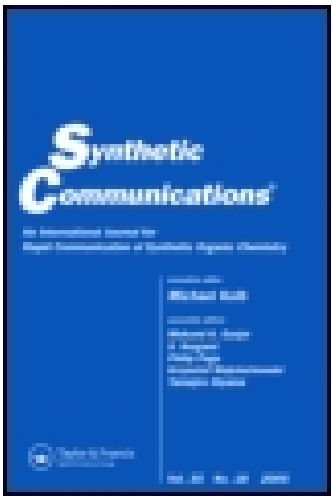


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A New Convenient Bromination with $KBrO_3$/KBr/Dowex®

J. Košmrlj [a], M. Kočevar [a] & S. Polanc [a]
[a] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SLO-61000, Ljubljana, Slovenia
Published online: 21 Aug 2006.

To cite this article: J. Košmrlj, M. Kočevar & S. Polanc (1996) A New Convenient Bromination with $KBrO_3$/KBr/Dowex®, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:19, 3583-3592, DOI: 10.1080/00397919608003769

To link to this article: http://dx.doi.org/10.1080/00397919608003769

SYNTHETIC COMMUNICATIONS, 26(19), 3583-3592 (1996)

A NEW CONVENIENT BROMINATION WITH $KBrO_3$/KBr/ Dowex®

Janez Košmrlj, Marijan Kočevar and Slovenko Polanc*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SLO-61000 Ljubljana, Slovenia

Abstract: Bromination of various 1,3-dicarbonyl compounds was achieved by using the mixture of potassium bromate and potassium bromide in the presence of Dowex® 50X2-200 ion-exchange resin. Reactions were carried out under mild conditions and gave good yields of the corresponding brominated products.

Potassium bromate was described as a convenient source of strongly electrophilic bromine.[1] It was employed in bromination of benzene,[2] as well as deactivated aromatics, such as benzoic acid,[3] nitrobenzene,[4] *p*-chloronitrobenzene[5] and benzophenone.[6] Its reaction with benzaldehyde resulted in bromination of the ring and oxidation of the aldehyde function leading to *m*-bromobenzoic acid.[7] Those experiments were carried out at room temperature or at higher temperatures, under strongly acidic conditions, where HOBr was postulated as the key intermediate.[4] More recently, primary alcohols or simple ethers were transformed with sodium bromate in the presence of catalytic

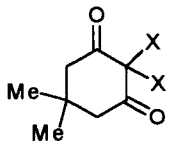
* To whom correspondence should be addressed.

amounts of HBr to esters, α,ω-diols or cyclic ethers gave lactones, and a treatment of secondary alcohols led to the formation of ketones.[8] Sodium bromate was also applied for the preparation of *N*-bromo imides and *N*-bromo amides.[9]

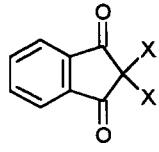
We now report on bromination of various 1,3-dicarbonyl substrates (Scheme) with the mixture of potassium bromate and potassium bromide in the presence of Dowex® 50X2-200 ion-exchange resin, leading to α-bromo derivatives. Reaction takes place in methanol, under mild reaction conditions with cheap reagents, which are easy to handle. The ion-exchange resin can be regenerated and reused. Yields of the products are good to excellent and are higher than those reported in the literature (Table).

Several reagents were used in the past for such transformations,[10] including bromine[11, 12] or bromine in the presence of $AlCl_3$,[13] pyrrolidone hydrotribromide,[14] 2,4-diamino-1,3-thiazole hydroperbromide,[15] phenyltrimethylammonium perbromide,[16] 4-(dimethylamino)pyridinium perbromide or pyridinium perbromide,[17] 5,5-dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxane,[18] hexabromocyclopentadiene,[19] selenium bromide,[12] *tert*-butyl bromide - dimethyl sulfoxide,[20] *N*-bromosuccinimide,[21] *N*-bromosaccharin,[22] polymer-supported reagents,[23, 24] and others.[25]

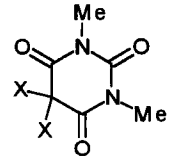
Thus, dimedone (**1a**), 1,3-indandione (**2a**) and 1,3-dimethylbarbituric acid (**3a**) were transformed into dibromo derivatives **1b**, **2b** and **3b**. 1,3-Diphenyl-1,3-propanedione (**4a**) was brominated under similar conditions, leading to 2-bromo-1,3-diphenyl-1,3-propanedione (**4b**). We also employed 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (**5a**), which was transformed into its monobromo derivative **5b**. The isolated compound represented the hydrate of 1,3-dione and was found to be perfectly stable. It was also obvious from its mass spectrum, obtained under EI conditions, which showed the corresponding molecular ion (M^+). One



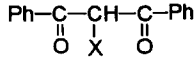
1a X=H
1b X=Br



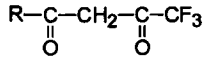
2a X=H
2b X=Br



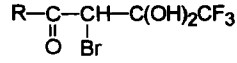
3a X=H
3b X=Br



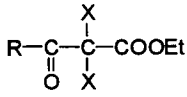
4a X=H
4b X=Br



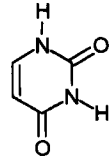
5a R=2-thienyl



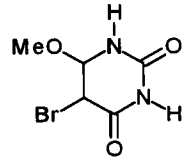
5b R=2-thienyl



6a R=Me, X=H
6b R=Me, X=Br
7a R=Ph, X=H
7b R=Ph, X=Br



8a



8b

Scheme

could explain the stability of **5b** by the influence of the adjacent trifluoromethyl group.

Our approach was also found to be successful in the case of β-keto esters. For example, bromination of ethyl acetoacetate (**6a**) and ethyl benzoylacetate (**7a**) led to the appropriate dibromo esters **6b** and **7b**. Further application of our new bromination procedure involved uracil (**8a**). It was transformed into 5-bromo-5,6-dihydro-6-methoxyuracil (**8b**). The latter was described to eliminate methanol in aqueous solutions, which did not contain $NaHSO_3$, to give 5-

Table. Products **1b** - **8b** Prepared[a]

Substrate	Product	Reaction Time (h)	Yield[b,c] (%)	mp (°C) or bp/mm	
				found	reported
1a	**1b**	1	91 (82[27])	147-149	148-150[27]
2a	**2b**	1[d]	86 (81[27])	182-182.5	172-174[27]
3a	**3b**	0.25	94 (60[28])	172-174	172-173[29]
					148-149[30]
4a	**4b**	0.5[d]	94 (86[31])	90.5-91.5	92[31]
5a	**5b**	0.5[d] + 0.5	95	97-100	
6a	**6b**	2	79 (72[32])	61/0.45	83-84/1.6[32]
7a	**7b**	4	84 (67[32])	120-121/0.38	121-124/0.3[32]
8a	**8b**	1	78 (--[e])	315-318 dec.	310 dec.[26]

[a] Reactions were carried out at room temperature unless noted otherwise.
[b] Isolated yields are given.
[c] The highest yields, reported in the literature, are in the brackets.
[d] At 0 °C.
[e] No yield is given in ref. 26. Following their procedure, compound **8b** was prepared in 69% yield.

bromouracil.[26] In contrast to their report we found that product **8b**, prepared by either of methods, was enough stable in water to be crystallised from it.

In conclusion, we have demonstrated a new efficient bromination of various 1,3-dicarbonyl substrates and uracil, employing the mixture of potassium bromate and potassium bromide in the presence of Dowex® 50X2-200 ion-exchange resin. This practical route offers new procedure for the introduction of the bromine under mild reaction conditions by using convenient reagents.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage and are uncorrected. IR spectra were obtained on a Perkin-Elmer 1310 spectrometer. NMR spectra were recorded on a Bruker Avance DPX 300 instrument (^{1}H NMR

at 300.13 MHz and ^{13}C NMR at 75.5 MHz, respectively). Mass spectra were obtained on a VG-Analytical AutospecQ instrument; M^+ indicates molecular ion of the molecule, containing bromine atom(s) ^{79}Br. Elemental analyses (C, H) were performed on a Perkin-Elmer 2400 CHN Analyser. Fluka silica gel plates (F_{254}) were used for TLC. Ion-exchange resin Dowex® 50X2-200 was obtained from Aldrich (Cat. No. 21,746-8). Starting materials and solvents were used as received from commercial sources (Aldrich, Fluka, Merck).

2,2-Dibromo-5,5-dimethyl-1,3-cyclohexanedione (1b)

A mixture of dimedone (**1a**, 140 mg, 1 mmol), KBr (119 mg, 1 mmol) and Dowex® (2 g) was stirred in MeOH (5 mL) at 0 °C for 10 min. $KBrO_3$ (167 mg, 1 mmol) was then added in one portion and the reaction mixture was stirred at r.t. for 1 h. Inorganic salts and Dowex were separated by filtration and washed with MeOH (5 mL) and CH_2Cl_2 (5 mL). Solvents were distilled off under reduced pressure and the residue was treated with H_2O (10 mL). Product **1b** (270 mg, 91% yield) was separated by filtration and crystallised from benzene-hexane. IR (KBr): ν = 2960, 2940, 2920, 2860, 1730, 1710, 1455, 1420, 1410, 1385, 1365, 1315, 1290, 1240, 1195, 1155, 1108, 1055, 985, 915, 880, 805, 710, 610 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (s, 6H, 2 x Me), 3.01 (s, 4H, 2 x CH_2); lit.[27] ^1H NMR ($CDCl_3$): δ = 1.10 (s, 6H, 2 x Me), 2.57 (s, 4H, 2 x CH_2). ^{13}C NMR ($CDCl_3$): δ = 27.75, 30.56, 48.22, 66.43, 192.78. MS (EI): m/z (%) = 296 (4, M^+), 298 (7, $M^+ + 2$), 300 (4, $M^+ + 4$), 83 (100).

2,2-Dibromo-1,3-indandione (2b)

Prepared from **2a** as described for **1b**. After the addition of $KBrO_3$, the reaction mixture was stirred at 0 °C for 1 h. Product **2b** (260 mg, 86%) was crystallised from AcOH. IR (KBr): ν = 3060, 1745, 1710, 1575, 1460, 1345, 1320, 1280, 1240, 1150, 1075, 990, 970, 845, 825, 770, 755, 635 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.98-8.05 (m, 2H, Ar); 8.08-8.15 (m, 2H, Ar); lit.[27] ^1H NMR ($CDCl_3$): δ = 8.02 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ = 51.28, 125.74, 135.78, 137.81, 187.22. MS (EI): m/z (%) = 302 (53, M^+), 304 (100, $M^+ + 2$), 306 (52, $M^+ + 4$).

5,5-Dibromo-1,3-dimethylbarbituric Acid (3b)

A mixture of 1,3-dimethylbarbituric acid (**3a**, 156 mg, 1 mmol), KBr (119 mg, 1 mmol) and Dowex® (2 g) was stirred in MeOH (5 mL) at r.t. for 10 min. After addition of $KBrO_3$ (167 mg, 1 mmol) the reaction mixture was stirred for additional 15 min. Solid material was filtered off, washed with MeOH (5 mL) and CH_2Cl_2 (5 mL). Solution was concentrated *in vacuo* to give **3b** (294 mg,

94%), which was then crystallised from water. IR (KBr): ν = 2945, 1650-1730, 1485, 1430, 1410, 1360, 1290, 1280, 1240, 1115, 1100, 1030, 985, 805, 775, 765, 740, 660 cm^{-1}; lit.[30] IR: ν = 1720, 1705, 1685 cm^{-1}. ^1H NMR (CD_3COCD_3): δ = 3.34 (s, 6H, 2 x Me); lit.[30] ^1H NMR (DMSO-d_6): δ = 3.23 (s, 6H, 2 x Me). ^{13}C NMR (CD_3COCD_3): δ = 30.55, 47.73, 150.40, 163.52. MS (EI): m/z (%) = 312 (28, M^+), 314 (49, $M^+ + 2$), 316 (27, $M^+ + 4$), 200 (100).

2-Bromo-1,3-diphenyl-1,3-propanedione (4b)

A mixture of 1,3-diphenyl-1,3-propanedione (**4a**, 224 mg, 1 mmol), KBr (119 mg, 1 mmol) and Dowex® (2 g) was stirred in MeOH (5 mL) at 0 °C for 10 min. Then $KBrO_3$ (167 mg, 1 mmol) was added in one portion and the reaction mixture was stirred at 0 °C for 30 min. Insoluble material was filtered off and washed with MeOH (5 mL) and CH_2Cl_2 (5 mL). Solvents were distilled off under reduced pressure and the residue was treated with H_2O (5 mL). Product **4b** (284 mg, 94%) was crystallised from MeOH. IR (KBr): ν = 3070, 3045, 3010, 2940, 1685, 1665, 1585, 1570, 1440, 1315, 1300, 1275, 1245, 1180, 1150, 1070, 1025, 990, 980, 935, 860, 800, 780, 755, 735, 680, 645, 610 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.56 (s, 1H, CH); 7.43-7.50 (m, 4H, Ar); 7.56-7.63 (m, 2H, Ar); 7.96-8.02 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ = 52.67, 129.02, 129.25, 133.85, 134.24, 188.99. MS (EI): m/z (%) = 301 (0.34 , M^+ - H), 302 (0.24, M^+), 303 (0.38, M^+ - H + 2), 304 (0.23, $M^+ + 2$), 105 (100).

2-Bromo-3,3-dihydroxy-1-(2-thienyl)-4,4,4-trifluoro-1-butanone (5b)

A mixture of 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (**5a**, 222 mg, 1 mmol), KBr (119 mg, 1 mmol) and Dowex® (2 g) was stirred in MeOH (5 mL) at 0 °C for 10 min. Then $KBrO_3$ (167 mg, 1 mmol) was added. The reaction mixture was stirred at 0 °C for 30 min and then at r.t. for 30 min. Solid material was filtered off and washed with MeOH (5 mL) and CH_2Cl_2 (5 mL). Solvents were removed under reduced pressure and the residue was treated with H_2O (10 mL), $Na_2S_2O_3$ (5 mg) and extracted with CH_2Cl_2 (3 x 10 mL). The solution was dried over Na_2SO_4 and evaporated *in vacuo* to yield **5b** (304 mg, 95%). Crude product was crystallised from CH_2Cl_2; mp 97-100 °C. IR (KBr): ν = 3340, 3200-3300, 1640, 1505, 1430, 1405, 1365, 1305, 1265, 1245, 1200, 1170, 1120, 1080, 1045, 1000, 970, 935, 860, 790, 735, 665, 650, 630 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.05 (s, 1H, OH), 5.07 (s, 1H, OH), 5.24 (s, 1H, H_2), 7.24 (dd, J_1 = 4.80 Hz, J_2 = 4.08 Hz, 1H, H_4 of the thiophene ring), 7.87-7.90 (m, 2H, H_3 and H_5 of the thiophene ring). ^{13}C NMR ($CDCl_3$): δ = 41.75, 93.74 (q, $J_{C\text{-}F}$ = 32.70

Hz), 121.46 (q, J_{C-F} = 288.46 Hz), 129.10, 134.99, 138.11, 140.10, 187.45. MS (EI): m/z (%) = 318 (4, M^+), 320 (4, $M^+ + 2$), 300 (2, $M^+ - H_2O$), 302 (2, $M^+ + 2 - H_2O$), 111 (100). HRMS (EI) calc. for $C_8H_6{}^{79}BrF_3O_3S$: 317.9181. Found: 317.9173. Anal. calc. for $C_8H_6BrF_3O_3S$ (319.09): C 30.11; H 1.90. Found: C 30.18; H 1.42.

Ethyl α,α-Dibromoacetoacetate (6b)

Ethyl acetoacetate (**6a**, 130 mg, 1 mmol), KBr (119 mg, 1 mmol) and Dowex® (2 g) were stirred in MeOH (5 mL) at r.t. for 10 min, $KBrO_3$ (100 mg, 0.6 mmol) was added and stirring continued for 1 hr. The second portion of $KBrO_3$ (100 mg, 0.6 mmol) was introduced into reaction mixture and stirring prolonged for 1 hr. Unsoluble material was filtered off and washed with MeOH (5 mL), followed by CH_2Cl_2 (5 mL). The filtrate was concentrated under reduced pressure, treated with water (10 mL), extracted with CH_2Cl_2 (3 x 10 mL), dried over Na_2SO_4, and evaporated *in vacuo* to yield **6b** (227 mg, 79%). IR (neat): ν = 2975, 2930, 2900, 1710-1750, 1460, 1440, 1420, 1390, 1355, 1290, 1210-1260, 1180, 1155, 1110, 1090, 1030, 1010, 885, 865, 845, 810, 775, 760, 740, 675 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.35 (t, J = 7.16 Hz, 3H, CH_3-CH_2); 2.59 (s, 3H, CH_3); 4.37 (q, J = 7.16 Hz, 2H, CH_3-CH_2). ^{13}C NMR ($CDCl_3$): δ = 13.73, 23.50, 59.88, 64.74, 163.69, 190.86. MS (CI/NH_3): m/z (%) = 287 (65, MH^+), 289 (100, $MH^+ + 2$), 291 (66, $MH^+ + 4$).

Ethyl α,α-Dibromobenzoylacetate (7b)

Prepared from **7a** as described above for **6b**, using 2 x 1 mmol of $KBrO_3$. Reaction mixture was stirred at r.t. for 2 hrs after each addition of $KBrO_3$. Compound **7b** was obtained as an oily product (293 mg, 84%). IR (neat): ν = 3050, 2975, 2930, 2900, 1745, 1720, 1695, 1680, 1590, 1570, 1460, 1440, 1385, 1360, 1320, 1290, 1220-1250, 1205, 1180, 1160, 1090, 1000-1035, 935, 875, 820, 795, 775, 735, 715, 685, 645, 605 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.15 (t, J = 7.12 Hz, 3H, CH_3-CH_2); 4.29 (q, J = 7.12 Hz, 2H, CH_3-CH_2); 7.42-7.48 (m, 2H, H_m); 7.59 (tt, $J(H_p, H_m)$ = 7.42 Hz, $J(H_p, H_o)$ = 1.29 Hz, 1H, H_p); 7.99-8.04 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ = 13.47, 59.50, 64.74, 128.59, 130.20, 130.74, 133.93. 164.49, 183.02. MS (CI/NH_3): m/z (%) = 349 (1, MH^+), 351 (2, $MH^+ + 2$), 353 (1, $MH^+ + 4$), 105 (100).

5-Bromo-5,6-dihydro-6-methoxyuracil (8b)

A mixture of uracil (**8a**, 560 mg, 5 mmol), KBr (59.5 mg, 0.5 mmol) and Dowex® (10 g) in MeOH (25 mL) was stirred at r.t. for 10 min. Then $KBrO_3$ (835 mg, 5 mmol) was added and stirring continued for 1 hr. The solid material

was filtered off and washed with MeOH (2 x 10 mL). The filtrate was evaporated to dryness and the residue was treated with H_2O (5 mL) to yield the compound **8b**, which was recovered by filtration and washed with H_2O (2 mL). The product (865 mg, 78%), was crystallised from H_2O and was found to be identical (mp, IR, ^1H and ^{13}C NMR) with that, obtained according to known prucedure.[26] IR (KBr): ν = 3200-3250, 3000-3100, 2880-2950, 2820, 1660-1730, 1470-1490, 1420, 1365, 1335, 1265, 1245, 1190, 1160, 1130, 1070-1090, 1020, 965, 920, 850, 790, 770, 640 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 3.30 (s, 3H, CH_3); 4.48 (ddd, $J(H_5, H_6)$ = 2.2 Hz, $J(H_1, H_5)$ = 1.1 Hz, $J(H_3, H_5)$ = 1.1 Hz, 1H, H_5); 4.57 (dd, $J(H_1, H_6)$ = 4.6 Hz, $J(H_5, H_6)$ = 2.2 Hz, 1H, H_6); 8.84 (br. d, $J(H_1, H_6)$ = 4.6 Hz, 1H, H_1); 10.65 (br. s, 1H, H_3); lit.[26] ^1H NMR (DMSO-d_6): δ = 3.3 (s, 3H, CH_3); 4.5 (d, J = 2 Hz, 1H, H_5); 4.6 (t, 1H, H_6); 7.9 (br. d, J = 6 Hz, 1H, H_1); 8.8 (br. s, 1H, H_3). ^{13}C NMR (DMSO-d_6): δ = 38.56, 54.96, 82.77, 151.30, 166.62. MS (EI): m/z (%) = 222 (9, M^+), 224 (9, $M^+ + 2$), 60 (100).

Acknowledgement: Financial support from The Ministry of Science and Technology of Slovenia is gratefully acknowledged. We would like to thank Dr. Bogdan Kralj and Dr. Dušan Žigon (Mass Spectrometry Center, Jožef Stefan Institute, Ljubljana, Slovenia) for mass measurements.

REFERENCES

1. Sasson, Y. In "The Chemistry of Functional Groups. Supplement D2: The Chemistry of Halides, Pseudo-Halides and Azides", Part 1, Patai, S. and Rappoport, Z., Eds., Wiley, Chichester, **1995**, p 582.
2. Banerjee, A.; Banerjee, G. C.; Banerjee, S. and Samaddar, H. *J. Indian Chem. Soc.* **1979**, *56*, 518.
3. (a) Banerjee, A.; Banerjee, S. and Samaddar, H. *J. Indian Chem. Soc.* **1979**, *56*, 985. (b) Banerjee, A.; Banerjee, G. C.; Dutt, S.; Banerjee, S. and Samaddar, H. *J. Indian Chem. Soc.* **1980**, *57*, 640.
4. Harrison, J. J.; Pellegrini, P. J. and Selwitz, C. M. *J. Org. Chem.* **1981**, *46*, 2169.
5. Kosandal, K.; Rao. A. K. S. B.; Rao, C. G. and Singh, B. B. *Org. Prep. Proced. Int.* **1991**, *23*, 395.
6. Banerjee, A.; Banerjee, G. C.; Adak, M. M.; Banerjee, S. and Samaddar, H. *J. Indian Chem. Soc.* **1981**, *58*, 985.

7. Banerjee, A.; Banerjee, S. and Samaddar, H. *J. Indian Chem. Soc.* **1979**, *56*, 988.
8. Kajigaeshi, S.; Nakagawa, T.; Nagasaki, N.; Yamasaki, H. and Fujisaki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 747.
9. Fujisaki, S.; Hamura, S.; Eguchi, H. and Nishida, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2426.
10. (a) De Kimpe, N. and Verhé, R. In "The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines". Updates from The Chemistry of Functional Groups, Patai, S. and Rappoport, Z., Eds., Wiley, Chichester, **1988**, p 25 and p 121; and references cited therein. (b) Larock, R. C. In "Comprehensive Organic Transformations", VCH Publishers, New York, **1989**, pp 369-380.
11. (a) Seeger, D. E.; Lahti, P. M.; Angelo, R. R. and Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251. (b) Hales, N. J.; Heaney, H.; Hollinshead, J. H. and Ley, S. V. *Tetrahedron* **1995**, *51*, 7741.
12. Abdul-Hajj, Y. J. *J. Org. Chem.* **1986**, *51*, 3380.
13. Pirkle, W. H. and Simmons, K. A. *J. Org. Chem.* **1983**, *48*, 2520.
14. Tu, C.-Y. J. and Lednicer, D. *J. Org. Chem.* **1987**, *52*, 5624.
15. Forlani, L. *Synthesis* **1980**, 487.
16. Ando, M.; Wada, T.; Kusaka, H.; Takase, K.; Hirata, N. and Yanagi, Y. *J. Org. Chem.* **1987**, *52*, 4792.
17. (a) Arrieta, A.; Ganboa, I. and Palomo, C. *Synth. Commun.* **1984**, *14*, 939. (b) Kelly-Rowley, A. M.; Lynch, V. M. and Anslyn, E. V. *J. Am. Chem. Soc.* **1995**, *117*, 3438.
18. Baasov, T. and Sheves, M. *J. Am. Chem. Soc.* **1985**, *107*, 7524.
19. Magen, S.; Oren, J. and Fuchs, B. *Tetrahedron Lett.* **1984**, *25*, 3369.
20. Armani, E.; Dossena, A.; Marchelli, R. and Casnati, G. *Tetrahedron* **1984**, *40*, 2035.
21. (a) Mehta, G. and Padma, S. *J. Am. Chem. Soc.* **1987**, *109*, 7230. (b) Boyd, R. E.; Rasmussen, C. R. and Press, J. B. *Synth. Commun.* **1995**, *25*, 1045.
22. Sánchez, E. I. and Fumarola, M. J. *J. Org. Chem.* **1982**, *47*, 1588.
23. Bongini, A.; Cainelli, G.; Contento, M. and Manescalchi, F. *Synthesis* **1980**, 143.
24. (a) Johar, Y.; Zupan, M. and Šket, B. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2059. (b) Babadjamian, A. and Kessat, A. *Synth. Commun.* **1995**, *25*, 2203.

25. Bolton, R. In "Bromine Compounds: Chemistry and Applications", Price, D.; Iddon, B. and Wakefield, B. J., Eds., Elsevier, Amsterdam, **1988**, p 151.
26. Rork, S. G. and Pitman, H. I. *J. Am. Chem. Soc.* **1975**, *97*, 5566.
27. Šket, B. and Zupan, M. *Synth. Commun.* **1989**, *19*, 2481.
28. Kölle, U.; Kolb, B. and Mannschreck, A. *Chem. Ber.* **1980**, *113*, 2545.
29. Biltz, H. and Hamburger, T. *Ber Dtsch. Chem. Ges.* **1916**, *49*, 635.
30. Szilágyi, G. and Wanhoff, H. *Synthesis* **1981**, 701.
31. Regitz, M. and Schäfer, A. *Liebigs Ann. Chem.* **1981**, 1172.
32. Ogilvie, W. and Rank, W. *Can. J. Chem.* **1987**, *65*, 166.

(Received in The Netherlands 15 April 1996)