NMR δ 3.04 (t, J = 7 Hz, 2 H), 4.13 (t, J = 7 Hz, 2 H), 6.98 (m, 2 H), 7.22–7.55 (m, 13 H); IR ($CDCl_3$) 1805, 1740, 1490, 1230, 1185 cm^{-1}; MS (DCI-NH_3) m/e 395 $(M + NH_4)^+$, 378 $(M + H)^+$, 259, 232. Anal. Calcd for $C_{24}H_{19}NO_5$: C, 70.02; H, 5.07, N, 3.71. Found: C, 70.00; H, 4.87; N, 3.62.

N-(2-Phenylethyl)-N-hydroxyurea (11c). Compound **11c** was prepared as described for **11a** from **8c** (0.65 g, 1.72 mmol) in 2-methyl-2-propanol (5 mL) and NH_3 (5 mL). Purification by flash column (silica gel, eluting with 5% MeOH/CH_2Cl_2) gave 0.23 g (75%) of a white solid: mp 135–136 °C (EtOAc/hexanes); ^1H NMR δ 2.80 (t, J = 7 Hz, 2 H), 3.53 (t, J = 7 Hz, 2 H), 6.31 (bs, 2 H), 7.33–7.55 (m, 5 H), 9.35 (s, 1 H); IR (KBr) 3455, 3190, 1655, 1625, 1575, 1480 cm^{-1}; MS (DCI-NH_3) m/e 198 $(M + NH_4)^+$, 181 $(M + H)^+$, 165. Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.55. Found: C, 60.14; H, 6.70; N, 15.44.

N,O-Bis(phenoxycarbonyl)-N-(1-benzo[b]thien-2-ylethyl)hydroxylamine (8d). Compound **8d** was prepared as described for **8a** from 2-(hydroxyethyl)benzo[b]thiophene (**3d**) (0.5 g, 2.81 mmol), **1a** (0.843 g, 3.09 mmol), triphenylphosphine (0.85 g, 3.24 mmol), and diisopropyl azodicarboxylate (0.65 g, 3.21 mmol) in THF (20 mL). Purification by flash column chromatography (silica gel, eluting with 10% EtOAc/hexanes) gave 1.04 g (85%) of a thick oil that contained N-alkylated **8d** and a E/Z mixture of O-alkylated hydroximates **12d** (an approximately 3:1 **8d** to **12d** ratio by ^1H NMR). A second chromatography gave a small amount of pure **12d**, which was prone to decomposition after isolation. A combustion analysis could not be obtained, and the compound would even rapidly transform in DMSO-d_6. A ^1H NMR of the E/Z mixture could be obtained in $CDCl_3$: ^1H NMR ($CDCl_3$) δ 1.86 (d, J = 7 Hz, 1.5 H), 1.87 (d, J = 7 Hz, 1.5 H), 6.21 (m, 1 H), 6.65 (bs, 1 H); 6.97 (bm, 1 H), 7.13–7.57 (m, 13 H). The second chromatography also gave some mixed fractions and 0.58 g (48%) of **8d** as a thick oil: ^1H NMR ($CDCl_3$) δ 1.89 (d, J = 7 Hz, 3 H), 5.92 (q, J = 6 Hz, 1 H), 6.85–7.54 (m, 13 H), 7.73–7.88 (m, 2 H); MS (DCI-NH_3) m/e 451 $(M + NH_4)^+$, 296, 202, 161. Anal. Calcd for $C_{24}H_{19}NO_5S$: C, 66.5; H, 4.42; N, 3.23. Found: C, 66.78; H, 4.37; N, 2.95.

O-(tert-Butyloxycarbonyl)-N-(phenoxycarbonyl)-N-(1-benzo[b]thien-2-ylethyl)hydroxylamine (9d). Compound **9d** was prepared as described for **8a** from 2-(hydroxyethyl)benzo[b]thiophene (**3d**) (0.25 g, 1.4 mmol), **1b** (0.37 g, 1.47 mmol), triphenylphosphine (0.41 g, 1.55 mmol), and diisopropyl azodicarboxylate (0.31 g, 1.53 mmol) in THF (25 mL). Purification by flash column chromatography (silica gel, eluting with 10% EtOAc/hexanes) gave 0.48 g (82%) of a thick oil that contained N-alkylated **9d** and a E/Z mixture of O-alkylated hydroximates **13d** (>7:1, **9d** to **13d** ratio by ^1H NMR). A second chromatography gave 0.042 g of pure **13d**. This material was prone to decomposition after isolation, and a combustion analysis could not be obtained: ^1H NMR ($CDCl_3$) δ 1.35 (bm, 9 H), 1.82 (d, J = 7 Hz, 1.5 H), 1.83 (d, J = 7 Hz, 1.5 H), 6.15 (m, 1 H), 6.57 (bs, 1 H), 7.08–7.53 (m, 9 H); MS m/e 431 $(M + NH_4)^+$, 202, 161. The second chromatography also gave some mixed fractions and 0.29 g (50%) of **9d** as a thick oil: ^1H NMR ($CDCl_3$) δ 1.25–1.65 (bm, 9 H), 1.81 (bm, 3 H), 5.84 (q, J = 7 Hz, 1 H), 7.10–7.54 (m, 8 H), 7.70–7.84 (m, 2 H); MS (DCI-NH_3) m/e 431 $(M + NH_4)^+$, 331, 202, 161. Anal. Calcd for $C_{22}H_{23}NO_5S$: C, 63.91; H, 5.61; N, 3.39. Found: C, 64.01; H, 5.60; N, 3.20.

N-(1-Benzo[b]thien-2-ylethyl)-N-hyroxyurea (11d). Compound **11d** was prepared as described for **11a** from **8d** (0.43 g, 0.99 mmol) in 2-methyl-2-propanol (2 mL) and NH_3 (2 mL). Purification by flash column (silica gel, eluting with 5% MeOH/CH_2Cl_2) gave 0.131 g (56%) of a white solid: mp 158–160 °C (EtOAc/hexanes); ^1H NMR δ 1.51 (d, J = 7 Hz, 3 H), 5.57 (q, J = 7 Hz, 1 H), 6.44 (bs, 2 H), 7.24–7.37 (m, 3 H), 7.76 (m, 1 H), 7.89 (m, 1 H), 9.23 (s, 1 H); IR (KBr) 3460, 3180, 1655, 1520, 1470 cm^{-1}; MS (DCI-NH_3) m/e 254 $(M + NH_4)^+$, 237 $(M + H)^+$, 219, 161. Anal. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.92; H, 5.12; N, 11.86. Found: C, 55.93; H, 4.96; N, 11.74. Treatment of **9d** (0.21 g, 0.51 mmol) in 2-methyl-2-propanol (4 mL) and NH_3 (1 mL) for 24 h, followed by workup as described for **8d**, gave 0.09 g (75%) of **11d**.

N,O-Bis(phenoxycarbonyl)-N-(3,3-dimethyl-1-butyl)-hydroxylamine (8e). Compound **8e** was prepared as described for **8a** from 3,3-dimethyl-1-butanol (**3e**) (0.5 g, 4.89 mmol), **1a** (1.40 g, 5.13 mmol), triphenylphosphine (1.41 g, 5.38 mmol), and diisopropyl azodicarboxylate (1.08 g, 5.34 mmol) in THF (60 mL). Purification by flash column chromatography (silica gel, eluting with 10% EtOAc/hexanes) gave 1.65 g of a thick oil that after high vacuum solidified on standing to give 1.60 g (92%) of a white solid: mp 73–75 °C; ^1H NMR δ 0.97 (s, 9 H), 1.65 (m, 2 H), 3.86 (m, 2 H), 7.14–7.54 (m, 10 H); IR ($CDCl_3$) 1800, 1735, 1490, 1230, 1175 cm^{-1}; MS (DCI-NH_3) m/e 375 $(M + NH_4)^+$, 358 $(M + H)^+$, 239, 222. Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.13; H, 6.44; N, 3.97.

N-(3,3-Dimethyl-1-1-butyl)-N-hydroxyurea (11e). Compound **11e** was prepared as described for **11a** from **8e** (0.52 g, 1.46 mmol) in 2-methyl-2-propanol (2 mL) and NH_3 (2 mL). Purification by flash column (silica gel, eluting with 5% MeOH/CH_2Cl_2) gave 0.16 g (68%) of a white solid: mp 87–89 °C (EtOAc/hexanes); ^1H NMR δ 0.88 (s, 9 H), 1.41 (m, 2 H), 3.32 (m, 2 H), 6.17 (bs, 2 H), 9.11 (s, 1 H); IR (KBr) 3490, 3270, 3200, 2875, 1635, 1580, 1480 cm^{-1}; MS (DCI-NH_3) m/e 195 $(M + NH_4)^+$, 178 $(M + 1)^+$, 162. Anal. Calcd for $C_7H_{16}N_2O_2$: C, 52.48; H, 10.07; N, 17.48. Found: C, 52.41; H, 10.05; N, 17.51.

N,O-Bis(phenoxycarbonyl)-N-[(2-pyridyl)methyl]-hydroxylamine (8f). Compound **8f** was prepared as described for **8a** from 2-pyridylcarbinol (**3f**) (0.5 g, 4.58 mmol), **1a** (1.31 g, 4.80 mmol), triphenylphosphine (1.32 g, 5.03 mmol), and diisopropyl azodicarboxylate (1.02 g, 5.04 mmol) in THF (60 mL). Purification by flash column chromatography (silica gel, eluting with 4% acetone/hexanes) gave 1.69 g of a thick oil that after high vacuum solidified to give 1.50 g (90%) of a white solid: mp 103–107 °C dec; ^1H NMR δ 5.24 (s, 2 H), 7.12–7.55 (m, 12 H), 7.88 (m, 1 H), 8.65 (m, 1 H); IR ($CDCl_3$) 1810, 1750, 1590, 1490, 1190 cm^{-1}; MS (DCI-NH_3) m/e 365 $(M + H)^+$, 232, 135. Anal. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found: C, 66.03; H, 4.65; N, 7.79.

N-[(2-Pyridyl)methyl]-N-hydroxyurea (11f). Compound **11f** (0.55 g, 1.51 mmol) was dissolved in 3% NH_3 in MeOH (15 mL) and allowed to stir overnight at rt. The reaction was then concentrated, and purification by flash column (silica gel, eluting with 7% MeOH/CH_2Cl_2) gave 0.135 g (54%) of a white solid: mp 158–159 °C dec (EtOAc); ^1H NMR δ 4.65 (s, 2 H), 6.46 (bs, 2 H), 7.22–7.36 (m, 2 H), 7.76 (m, 1 H), 8.49 (m, 1 H), 9.48 (s, 1 H); IR (KBr) 3405, 3330, 2670, 1695, 1645, 1415 cm^{-1}; MS (DCI-NH_3) m/e 168 $(M + H)^+$, 152. Anal. Calcd for $C_7H_9N_3O_2$: C, 50.30; H, 5.43; N, 25.14. Found: C, 50.40; 5.43; N, 24.86.

Electrohalogenation of Propargyl Acetates and Amides To Form the 1,1-Dibromo-2-oxo Functionality and a Facile Synthesis of Furaneol

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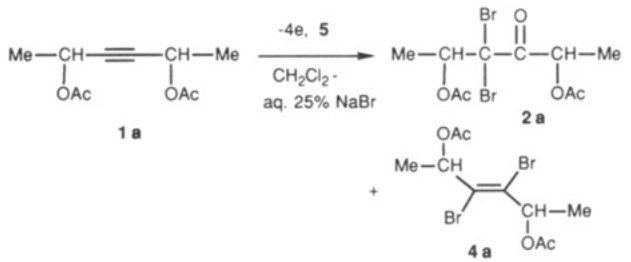
Oxidation of acetylenic bonds with metallic peroxides offers a practical access to 1,2-diketones.[1] Alternative promising approaches to this functionality reported in the literature involve π-complexation of alkynes with mercury(II) ion followed by oxidation with Mo(VI) or W(VI) peroxo complexes.[2] However, the undesired carbon–carbon bond cleavage of the 1,2-dicarbonyl framework is a drawback to this method which occurs as a result of overoxidation.[3] In addition, hazardous mercury(II) acetate

(1) Reviews: (a) Warig, A. J. *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 1. (b) Plesnicar, B. *The Chemistry of Peroxide*; Patai, S., Ed.; Wiley-Interscience: New York, 1983; pp 536–539.

(2) (a) Ballistreri, F. P.; Failla, S.; Tomaselli, G. A.; Curci, R. *Tetrahedron Lett.* **1986**, *27*, 5139. (b) Ballistreri, F. P.; Failla, S.; Tomaselli, G. A. *J. Org. Chem.* **1988**, *53*, 830. (c) Ballistreri, F. P.; Failla, S.; Spina, E.; Tomaselli, G. A. *Ibid.* **1989**, *54*, 947.

0022-3263/92/1957-5023$03.00/0

Scheme I



is inevitably required to facilitate the reaction. Consequently, finding a nonmercuric method of providing either 1,2-diketones or synthetic equivalents is a desirable goal in current organic synthesis. Our attention was focused on halogenative hydroxylation processes involving acetylenic bonds, because α,α-dihalo ketones or their analogues are synthons of 1,2-diketones which are versatile, highly functionalized intermediates.[4] To this end, hypohalorites[5,6] were employed as a source of positively charged halogen species, and their reactions with terminal alkynes or phenylacetylenes were studied. Although the regiochemical control of halogen addition to internal acetylenes has remained unexplored,[5e] we report in this paper that acetylenes **1**, bearing 1-acetoxyalkyl(s) at one or both sites, can be converted into the corresponding α,α-dibromo ketones **2** or **3** by electrochemical bromination in media containing *N*-oxyl compound **5**. Furthermore, this *N*-oxo-mediated brominative hydroxylation is of great interest not only from a mechanistic point of view, but also as a means of obtaining compounds bearing an array of different substituents at 1,2,3-positions. One of these compounds was shown to be useful for the synthesis of furaneol, a key flavoring ingredient used in foods.[7]

Results and Discussion

Conversion of the propargyl acetate **1a** into the corresponding α,α-dibromo ketone **2a** was readily achieved by electrolysis in the presence of a catalytic amount of *N*-oxyl compound **5** in a two-phase mixture consisting of CH_2Cl_2 and aqueous 25% NaBr (1:2 v/v). Passage of about 7.6 F/mol of electricity under a constant current of 20 mA/cm^2 gave the desired **2a** in 88% yield; no 1,2-dibromination was detected at all (Scheme I).

Presence of the *N*-oxyl compound **5** was found to be essential to the formation of the 1,1-dibromo-2-oxo functionality. Correlations between the halogenation yields of **2a** and **4a** and the amount of *N*-oxyl **5** used are shown in

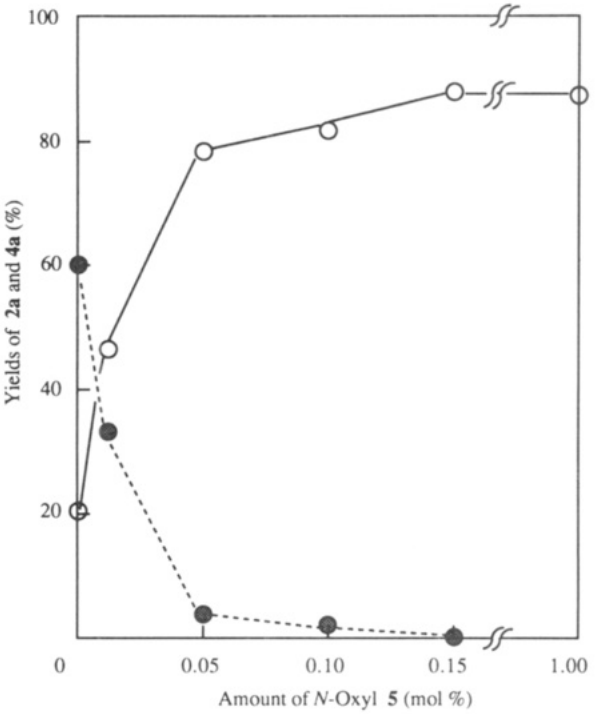
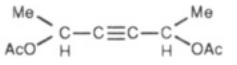
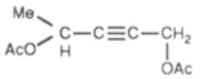
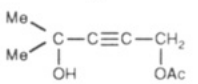
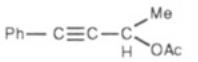
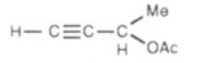
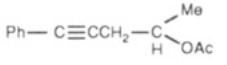


Figure 1. Profiles between the amount of *N*-oxyl **5** and yields of **2a** and **4a**. The electrolyses were carried out at 10 mA/cm^2 for 7.0 F/mol in CH_2Cl_2–aqueous 25% NaBr. Yield of **2a**: (○), yield of **4a** (●).

Table I. *N*-Oxoammonium Salt-Assisted Electrobromination of Propargyl Acetates 1 and Their Related Compounds[a]

entry	substrate, 1	electricity[b] (F/mol)	product (yield,[c] %) 2	3	4
1	 **1a**	7.6	88	–	–
2	 **1b**	8.8	85	–	–
3	 **1c**	9.2	67	–	–
4	 **1d**	6.2	–	68	12
5	 **1e**	8.2	72	–	–
6		10.0	–	45	31
7	$C_8H_{17}C{\equiv}CH$	11.4	–	–	84

[a] Carried out by using **1** (1 mmol) and *N*-oxyl **5** (0.02 mmol) in CH_2Cl_2 (3 mL)–aqueous 25% NaBr (6 mL) at 10 mA/cm^2. [b] Electricity passed (based on **1**). [c] Based on isolated products.

Figure 1. Electrochemical bromination of **1a** in the absence of **5** gives 1,2-dibromide **4a** as the major product (60%) along with the α,α-dibromo ketone **2a** in only 20% yield. By contrast, formation of **2a** is dramatically improved by the addition of a small amount of *N*-oxyl **5**. Formation of **4a** is suppressed to a negligible level when

(3) Permanganate: (a) Srinivasan, N. S.; Lee, D. G. *J. Org. Chem.* **1979**, *44*, 1574. RuO_4: Müller, P.; Godoy, A. J. *Helv. Chim. Acta* **1981**, *64*, 2531. OsO_4: (b) Schroder, M.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1599. $Tl(NO_3)_3$: (c) McKilklop, A.; Oldenziel, O. H.; Swann, B. P.; Taylor, E. C.; Robey, R. L. *J. Am. Chem. Soc.* **1973**, *95*, 1296. Peracid: (d) McDonald, R. N.; Schwab, P. A. *Ibid.* **1964**, *86*, 4866. Peroxotungsten–H_2O_2: (e) Ishii, Y.; Sakata, Y. *J. Org. Chem.* **1990**, *55*, 5545. Electrooxidation: (f) Cariou, M.; Simonet, J. *J. Chem. Soc., Chem. Commun.* **1990**, 445.

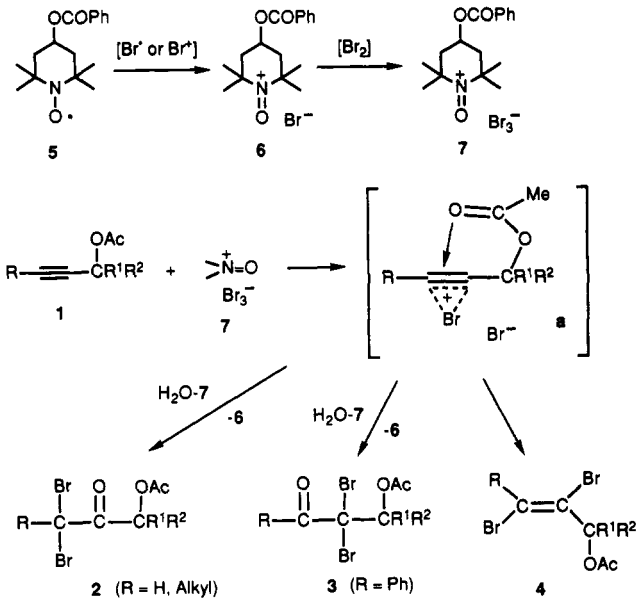
(4) (a) Verhe, R.; Courtheyn, D.; De Kimpe, N.; De Buyck, L. *Synthesis* **1982**, 667. (b) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D. *J. Org. Chem.* **1990**, *55*, 4523.

(5) EtOCl: (a) Goldschmidt, S.; Endres, R.; Dirsch, R. *Ber.* **1925**, *58*, 572. Cl_2–MeOH: (b) Jackson, E. L. *J. Am. Chem. Soc.* **1934**, *56*, 977. Cl_2–MeOH: (c) Verbanc, J. J.; Hennion, G. F. *Ibid.* **1938**, *60*, 1711. Cl_2–*t*-BuOH, AcOH, or Ac_2O: (d) Norris, R. O.; Vogt, R. R.; Hennion, G. F. *Ibid.* **1939**, *61*, 1460. NCS–MeOH: (e) Reed, S. F. *J. Org. Chem.* **1965**, *30*, 2195.

(6) NBA–AcOH/*t*-BuOH: (a) Salamon, I.; Reichstein, T. *Helv. Chim. Acta* **1947**, *30*, 1616. Br_2–AcOH: (b) Pincock, J. A.; Yates, K. *Ibid.* **1968**, *90*, 5643. Br_2–AcOH/H_2O: (c) Ehrlich, S. J.; Berliner, E. *Ibid.* **1978**, *100*, 1525.

(7) Rodin, J. O.; Himel, C. M.; Silverstein, R. M.; Leeper, R. W.; Gortner, W. A. *J. Food. Sci.* **1965**, *30*, 280. (b) Wild, H. *Chem. Ind.* **1988**, 580.

Scheme II



the concentration of **5** reaches 0.15 mol % in the electrolysis medium.

Chlorinative hydroxylation of **1a** by similar electrolysis in an aqueous saturated NaCl–CH_2Cl_2 solution, using a catalytic amount of **5**, gave the corresponding α,α-dichloro ketone in low yield (18%) along with the corresponding 1,2-dichloride in 47% yield. These unfavorable results may be ascribed to destruction of the *N*-oxyl compound **5** by the action of active chlorine species, such as molecular chlorine, during the electrolysis and before the reaction is completed.[8] The iodination of **1a** by electrolysis in a CH_2Cl_2/H_2O–NaI binary system was unsuccessful; starting material was recovered unchanged.[9]

The α,α-dibromo ketones obtained from a variety of propargyl acetates **1** are collected in Table I, which reveals the diverse applicability of the present synthetic methodology. For instance, acetylenes directly connected to 1-acetoxyalkyl and/or 1-hydroxyalkyl groups at the two sp-carbons provide the corresponding α,α-dibromo ketones **2** in excellent yields (entries 1–3). On the other hand, the dibrominative hydroxylation of compound **1d**, which has an aryl group instead of a 1-acetoxyalkyl group as in **1a** (entry 1), is accompanied by a small amount of the 1,2-dibromide (entry 4). The amount of 1,2-dibromide obtained increases considerably when the acetoxy group is two carbons removed from the sp-carbon (entry 6). Furthermore, the alkyne bearing no acetoxyalkyl substituent yields almost exclusively the corresponding 1,2-dibromide (entry 7). These clear trends observed in entries 6 and 7 may reflect whether participation of the acetoxy group is operative or not and provide a starting point for discussion concerning the mechanistic aspects of the present halogenation processes.

In order to better understand the successful formation of the 1,1-dibromo-2-oxo functionality from various propargyl acetates **1**, one may consider several elementary reactions involved in this transformation. First of all, sodium bromide would be electrochemically oxidized to generate either bromine radicals or positively charged

Scheme III

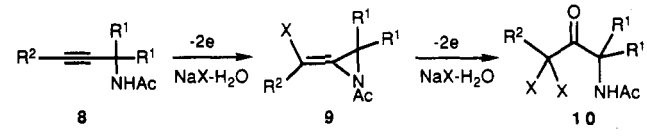
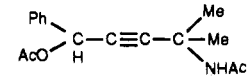
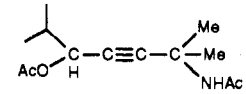


Table II. Electrohalogenations of Propargyl Amides 8[a]

entry	alkynes, 8	NaX	F/mol[b]	products (yield,[c] %) 9	10	8
1	 **8a**	NaBr	2	76	–	23
2		NaBr	5	2	90	–
3		NaCl	6	–	87	–
4		NaI	7	60	–	–
5	 **8b**	NaBr	5	–	70	–

[a] Carried out by using **8** (0.3–0.5 mmol) in a CH_2Cl_2 (5 mL)–aqueous 25% NaX–H_2O (10 mL)–Pt system (buffered at pH = 7) under 20 mA/cm^2 at 20–25 °C. [b] Electricity passed (based on **8**). [c] Based on isolated products.

bromine species. These reactive species would immediately react with the *N*-oxyl compound **5** via an electron-transfer process in the organic phase to generate *N*-oxoammonium bromide **6**. Subsequently, the bromide salt **6** may be transformed into the *N*-oxoammonium tribromide **7**, a plausible electrophilic brominating reagent, by the action of active bromine species such as molecular bromine (Scheme II).[10]

Brominative hydroxylation of propargyl acetate **1** with the *N*-oxoammonium tribromide **7** is proposed to proceed through the bromonium intermediate **a** stabilized by participation of the neighboring acetoxy group.[11,12] Selection of the reaction pathways leading either to **2** or to **3** is highly dependent on the nature of the substituent R. In general, alkyl groups including 1-oxyalkyls and hydrogen favor the formation of **2**; regioisomers **3** become the exclusive products when R = phenyl, and they are accompanied by a considerable amount of 1,2-dibromides. Thus, the regiochemistry of the present reaction seems to depend on the stability of the bromonium ion intermediate, which in turn relies on the cation-stabilizing ability of the substituents (Scheme II).[13]

On the basis of the proposed reaction mechanism, we expected that propargyl amide **8** might lead to products arising from the reaction of a halonium ion intermediate with the neighboring *N* nucleophile (Scheme III).

In fact, halogenation of propargyl amide **8a** (R^1 = Me, R^2 = PhCH(OAc))[14] gave γ,γ-dihalo-β-oxo amide **10a** without the use of a catalyst [4-BzO-TEMPO (**5**)]. In addition, the (1-bromoalkylidene)aziridine **9a** (X = Br) was

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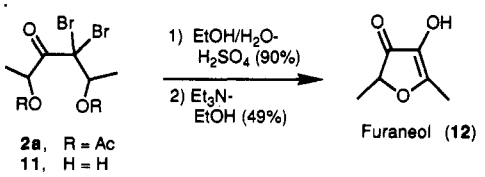
successfully isolated from a reaction mixture of **8a**, after consumption of about 3 F/mol (aqueous 25% NaBr–CH_2Cl_2 (2:1 v/v)). The time course of this reaction shows that **9a** (X = Br) is the only isolable intermediate and is converted solely to **10a** (X = Br).[15] Thus, the isolation of aziridine intermediate **9a** (X = Br) supports the proposed general concept of intramolecular cation trapping (cf. Scheme II), and the pathway leading to **10a** (X = Br).

Table II summarizes the reaction conditions and yields related to propargyl amide conversion. The reaction is somewhat sensitive to the pH of the aqueous phase, and best results were obtained at pH 7 (buffered with 3% Na_2HPO_4–3% KH_2PO_4). Significantly, dichloro ketone **10a** (X = Cl) is obtained from propargyl amide **8a** (aqueous NaCl–CH_2Cl_2) in good yield (entry 3), while iodination of **8a** (aqueous NaI–CH_2Cl_2) gave aziridine **9a** (X = I) exclusively, even though the electrolysis was prolonged to 7 F/mol of electricity (entry 4).[9]

Electrosynthesized 2,5-diacetoxy-4,4-dibromo-3-hexanone (**2a**) is nicely functionalized and ready for transformation to heterocyclic compounds. We have succeeded in synthesizing furaneol (**12**), a key flavoring ingredient of foods, from **2a**.[7,16] Thus, dibromo ketone **2a** was hydrolyzed with sulfuric acid in a mixed solution of ethanol and water to give the corresponding diol **11**. Upon exposure to triethylamine in ethanol, **11**, in turn, cyclized to furaneol **12**, in 39% overall yield from **1a**.



2a, R = Ac
11, H = H

Furaneol (**12**)

In conclusion, the results described in this paper indicate that electrochemical oxybromination in the presence of a catalytic amount of *N*-oxyl compound **5** is effective for the selective formation of α,α-dihalo ketone derivatives from propargyl acetates, in which the 1-acetoxyalkyl groups dictate the regioselectivity of the reactions. Some of the dibrominated products have considerable synthetic potential as intermediates in the preparation of heterocycles such as furanone and pyrrole derivatives.

Experimental Section[17]

Electrolysis Apparatus. Unless otherwise noted, an undivided cell (2.5-cm diameter and 10-cm height, 30-mL volume or 8.0-cm diameter and 12-cm height, 300-mL volume) fitted with a gas inlet pipe, a stirring bar, and a thermometer was used. Two platinum foil electrodes (3 cm^2) or glassy carbon electrodes (3 cm^2) were placed parallel to each other 10 mm apart. The vessel was immersed in a water bath maintained at 15–25 °C by external cooling.

Electrochemical Bromohydroxylation of 1a to 2,5-Diacetoxy-4,4-dibromo-3-hexanone (2a). A Typical Procedure. A solution of propargyl acetate (**1a**, 198 mg, 1.0 mmol) in CH_2Cl_2 (15 mL) was added to aqueous 25% NaBr (10 mL, buffered at pH 4 with 6% NaH_2PO_4). Into the upper phase of the binary mixture were immersed two platinum foil electrodes (3 cm^2). The mixture was electrolyzed under a constant current of 20 mA/cm^2 (applied voltage: 2 V) until 7.6 F/mol of electricity had been charged. The aqueous phase was extracted with CH_2Cl_2 (5 mL × 3) and the combined organic layers were dried (Na_2SO_4) and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2, hexane–AcOEt (5:1)) to give the dibromo ketone **2a** (329 mg, 88%) as a mixture of *dl*- and meso-isomers: bp 82–84 °C (0.2 mm); IR (neat) 2998, 2946, 1750 (CO), 1450, 1375, 1232, 1139, 1083, 1013, 959, 907, 775 cm^{-1}; (major component) ^1H NMR (500 MHz) δ 1.49 (d, J = 6.0 Hz, 3, CH_3), 1.67 (d, J = 6.8 Hz, 3, CH_3), 2.09, 2.13 (s, 6, CH_3CO), 5.58 (q, J = 6.0 Hz, 1, CHOAc), 6.03 (q, J = 6.8 Hz, 1, CHOAc); ^{13}C NMR (126 MHz) δ 17.3, 18.5, 20.6, 20.8, 66.5, 70.6, 73.6, 168.9, 169.7, 194.7; (minor component) ^1H NMR (500 MHz) δ 1.54 (d, J = 6.0 Hz, 3, CH_3), 1.71 (d, J = 6.8 Hz, 3, CH_3), 2.07, 2.12 (s, 6, CH_3CO), 5.60 (q, J = 6.0 Hz, 1, CHOAc), 6.05 (q, J = 6.8 Hz, 1, CHOAc); ^{13}C NMR (126 MHz) δ 16.9, 18.5, 20.6, 20.7, 66.2, 71.1, 73.1, 169.1, 169.5, 194.5. Anal. Calcd for $C_{10}H_{14}Br_2O_5$: C, 32.11; H, 3.77. Found: C, 32.48; H, 3.80.

Spectral data of the compounds listed in Table I are as follows.

A ca. 86:14 mixture of 1,4-diacetoxy-2,2-dibromo-3-pentanone and 1,4-diacetoxy-3,3-dibromo-2-pentanone (2b): bp 65–67 °C (0.2 mm); IR (neat) 2996, 2946, 1738 (CO), 1448, 1375, 1230, 1050, 944, 919, 866, 775 cm^{-1}; (major component) ^1H NMR (500 MHz) δ 1.66 (d, J = 6.5 Hz, 3, CH_3) 2.13, 2.14 (s, 6, CH_3CO), 4.81 (ABq, J = 17.2 Hz, 2, CH_2OAc), 6.02 (q, J = 6.5 Hz, 1, CHOAc); ^{13}C NMR (126 MHz) δ 18.5, 20.6, 20.7, 69.4, 70.2, 73.0, 169.4, 169.6, 193.9; (minor component) ^1H NMR (500 MHz) δ 1.56 (d, J = 6.5 Hz, 3, CH_3), 2.08, 2.19 (s, 6, CH_3CO), 5.42 (ABq, J = 12 Hz, 2, CH_2OAc), 5.54 (q, J = 6.5 Hz, 1, CHOAc). Anal. Calcd for $C_9H_{12}Br_2O_5$: C, 30.03; H, 3.36. Found: C, 30.18; H, 3.40.

1-Acetoxy-3,3-dibromo-4-hydroxy-4-methyl-2-pentanone (2c): bp 101–104 °C (0.2 mm); IR (neat) 3426, 2990, 2946, 1738 (CO), 1410, 1377, 1230, 1139, 1056, 977, 853, 808, 741 cm^{-1}; ^1H NMR (500 MHz) δ 1.63 (s, 6, CH_3), 2.20 (s, 3, CH_3CO), 3.46 (brs, 1, OH), 5.46 (s, 2, CH_2OAc); ^{13}C NMR (126 MHz) δ 20.4, 25.8, 62.4, 65.5, 77.4, 170.5, 194.3.

3-Acetoxy-2,2-dibromobutyrophenone (3d): bp 97–99 °C (0.2 mm); IR (neat) 3066, 1750 (CO), 1684, 1599, 1578, 1448, 1373, 1230, 1139, 1071, 812, 690 cm^{-1}; ^1H NMR (500 MHz) δ 1.58 (d, J = 6.0 Hz, 3, CH_3), 2.09 (s, 3, CH_3CO), 5.72 (q, J = 6.0 Hz, 1, CHOAc), 7.46–7.48 (m, 2, ArH), 7.56–7.59 (m, 1, ArH), 8.26–8.28 (m, 2, ArH); ^{13}C NMR (126 MHz) δ 17.8, 21.0, 67.4, 73.9, 128.0, 130.8, 132.8, 133.4, 169.2, 187.6. Anal. Calcd for $C_{12}H_{12}Br_2O_3$: C, 39.59; H, 3.32. Found: C, 39.54; H, 3.31.

3-Acetoxy-1,1-dibromo-2-butanone (2e): IR (neat) 2998, 2944, 1744 (CO), 1450, 1375, 1236, 1143, 1085, 1044, 942, 868, 766 cm^{-1}; ^1H NMR (500 MHz) δ 1.59 (d, J = 6.5 Hz, 3, CH_3), 2.14 (s, 3, CH_3CO), 5.50 (q, J = 6.5 Hz, 1, CHOAc), 6.30 (s, 1, $CHBr_2$); ^{13}C NMR (126 MHz) δ 17.8, 20.7, 39.5, 70.8, 170.1, 193.4.

4-Acetoxy-2,2-dibromopentanophenone: bp 124–127 °C (0.2 mm); IR (neat) 3066, 1742 (CO), 1682, 1599, 1578, 1448, 1375, 1241, 1137, 1065, 801, 690 cm^{-1}; ^1H NMR (500 MHz) δ 1.36 (d, J = 6.5 Hz, 3, CH_3), 1.98 (s, 3, CH_3CO), 2.96 (dd, J = 15.5, 2.9 Hz, 1, CH_2), 3.24 (dd, J = 15.5, 7.4 Hz, 1, CH_2), 5.27–5.33 (m, 1, CHOAc), 7.44–7.47 (m, 2, ArH), 7.55–7.60 (m, 1, ArH), 8.29–8.31 (m, 2, ArH); ^{13}C NMR (126 MHz) δ 21.1, 21.3, 51.8, 62.1, 69.5, 128.0, 131.0, 132.2, 133.3, 170.1, 188.1. Anal. Calcd for $C_{13}H_{14}Br_2O_3$: C, 41.30; H, 3.73. Found: C, 41.60; H, 3.79.

4-Acetoxy-1,2-dibromo-1-phenyl-1-pentene: IR (neat) 3062, 1742 (CO), 1491, 1446, 1373, 1241, 1133, 1064, 1017, 957, 862, 762, 696 cm^{-1}; ^1H NMR (500 MHz) δ 1.39 (d, J = 6.4 Hz, 3, CH_3), 2.09 (s, 3, CH_3CO), 3.00 (dd, J = 14.3, 5.4 Hz, 1, CH_2), 3.26 (dd, J = 14.3, 7.9 Hz, 1, CH_2), 5.38–5.45 (m, 1, CHOAc), 7.31–7.39 (m, 5, ArH); ^{13}C NMR (126 MHz) δ 19.6, 21.3, 46.9, 68.9, 118.4, 119.1, 128.3, 128.7, 128.8, 140.7, 170.4.

1,2-Dibromodecene: bp 55–57 °C (0.2 mm); IR (neat) 3090, 2928, 2858, 1466, 1379, 1122, 779 cm^{-1}; ^1H NMR (500 MHz) δ 0.89 (t, J = 7.0 Hz, 3, CH_3), 1.25–1.35 (m, 10, CH_2), 1.55–1.59 (m, 2, CH_2), 2.59 (t, J = 7.4 Hz, 2, CH_2), 6.40 (s, 1, CBrH); ^{13}C NMR (126 MHz) δ 14.1, 22.6, 27.0, 28.4, 29.2, 29.3, 31.8, 36.9, 102.1, 127.0. Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.30; H, 6.09. Found: C, 40.06; H, 6.15.

4-Acetamido-1-acetoxy-4-methyl-1-phenyl-2-pentyne (8a). To a solution of *i*-Pr_2NH (5.7 mL, 40.6 mmol) in THF (40 mL) was added dropwise a 1.5 M solution of *n*-BuLi in hexane (27.1

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(17) Melting points and boiling points indicated by an air-bath temperature are uncorrected. IR spectra were recorded on a JASCO FT-5000 spectrometer. ^1H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ (Me_4Si as an internal standard). Column chromatography was carried out with a Merck Kieselgel 60 Art. 7734 (silica gel) with hexane–AcOEt as an eluent. The purity of all electrolyzed products, isolated, was judged to be >95% by ^1H NMR and ^{13}C NMR spectral determination. Elemental analyses were performed in our laboratory.

mL, 40.7 mmol) with cooling at −78 °C in a liquid N_2–EtOH bath. The mixture was stirred at −78 to −60 °C for 30 min, and to the resulting solution was added a solution of *N*-(1,1-dimethylpropargyl)acetamide (1.27 g, 10.1 mmol) in THF (10 mL) at −78 °C. Stirring was continued for 30 min at −78 to −60 °C, and to the mixture was added dropwise a solution of benzaldehyde (2.0 mL, 20 mmol) in THF (10 mL) at −78 °C. The mixture was stirred at −78 to −60 °C for 1 h and at −60 to −20 °C for 4 h. To the mixture was added dropwise acetic anhydride (3.8 mL, 40.3 mmol), and the resulting mixture was stirred at −20 °C for 5 h and then allowed to warm to room temperature. The mixture was poured into aqueous cold 10% tartaric acid (100 mL), the organic layer separated, and the aqueous layer extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine (100 mL), aqueous $NaHCO_3$ (100 mL × 2), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane:AcOEt = 5:1) to give 1.50 g (55%) of **8a** as colorless crystals: mp 85–87 °C (from ether–CH_2Cl_2); IR (KBr) 1738, 1651 cm^{-1}; ^1H NMR (200 MHz) δ 1.67 (s, 6, CH_3), 1.94 (s, 3, CH_3CO), 2.09 (s, 3, CH_3CO), 5.70 (brs, 1, NH), 6.49 (s, 1, CH-O), 7.31–7.43 (m, 3, ArH), 7.48–7.57 (m, 2, ArH); ^{13}C NMR (50 MHz) δ 21.1, 24.1, 28.7 (2 C), 48.0, 65.5, 77.4, 90.6, 127.8 (2 C), 128.6 (2 C), 128.8, 137.0, 169.0, 169.8. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.01; H, 7.35; N, 5.12.

4-Acetamido-1-acetoxy-2,2-dibromo-4-methyl-1-phenyl-3-pentanone (10a, X = Br) from 8a by Electrobromination. A side-armed cylindrical vessel (2.5-cm diameter and 10.0-cm height) equipped with a magnetic stirring bar was used for the electrolysis. Into this vessel was placed a solution of propargyl amide **8a** (R^1 = Me, R^2 = Ph, 82.2 mg, 0.30 mmol) in CH_2Cl_2 (5.0 mL), which was covered with aqueous 25% NaBr (10 mL, buffer solution at pH 7 with 3% Na_2HPO_4 and 3% KH_2PO_4). The mixture was electrolyzed with two platinum foil electrodes (3 cm^2) under a constant current density of 20 mA/cm^2 (applied voltage, 2.0 V), and 5 F/mol of electricity was charged. Two layers were separated, and the aqueous phase was extracted with ethyl acetate (20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, hexane–AcOEt (5:1)) to give 2.1 mg (2.2%) of **9a** (X = Br) and 122.0 mg (90%) of **10a** (R^1 = Me, R^2 = Ph, X = Br). **1-Acetyl-2,2-dimethyl-3-(2-acetoxy-1-bromo-2-phenethylidene)aziridine (9a, X = Br)**: mp 140–141 °C; IR (KBr) 2936, 1744 (CO), 1705 (CO), 1667, 1450, 1383, 1238, 1067, 1025, 969, 698 cm^{-1}; ^1H NMR (200 MHz) δ 1.52 (s, 3, CH_3), 1.58 (s, 3, CH_3), 2.13 (s, 3, CH_3CO), 2.21 (s, 3, CH_3CO), 6.92 (s, 1, CH), 7.36 (m, 5, ArH); ^{13}C (50 MHz) δ 13.9, 21.1, 25.0, 25.2, 71.4, 72.0, 99.6, 126.0 (2 C), 128.0, 128.4 (2 C), 137.7, 159.0, 159.2, 169.5. Anal. Calcd for $C_{16}H_{17}BrNO_3$: C, 54.72; H, 4.88; N, 3.99. Found: C, 54.45; H, 4.29; N, 4.30. **10a** (X = Br): mp 142–143 °C (ethyl acetate); IR (KBr) 3266, 3074, 1760 (CO), 1717 (CO), 1659, 1562, 1373, 1224, 1073, 1025, 787, 706 cm^{-1}; ^1H NMR (200 MHz) δ 1.74 (s, 3, CH_3), 1.78 (s, 3, CH_3), 1.99 (s, 3, CH_3CO), 2.12 (s, 3, CH_3CO), 6.06 (brs, 1, NH), 6.65 (s, 1, CH), 7.35–7.38 (m, 3, ArH), 7.56–7.59 (m, 2, ArH); ^{13}C (50 MHz) δ 20.9, 23.9, 25.8, 26.3, 62.9, 63.0, 78.2, 127.6 (2 C), 129.2, 130.1 (2 C), 134.2, 168.3, 169.1, 196.3. Anal. Calcd for $C_{16}H_{19}Br_2NO$: C, 42.79; H, 4.26; N, 3.12. Found: C, 42.99; H, 4.31; N, 3.05.

Spectral data of the compounds listed in Table II are as follows.

1-Acetyl-2,2-dimethyl-3-(2-acetoxy-1-iodo-2-phenylethylidene)aziridine (9a, X = I): IR (KBr) 3290, 1682, 1636, 1593, 1539, 1450, 1363, 1102, 690 cm^{-1}; ^1H NMR (200 MHz) δ 1.54 (s, 3, CH_3), 1.60 (s, 3, CH_3), 2.13 (s, 3, CH_3CO), 2.21 (s, 3, CH_3CO), 6.62 (s, 1, CH), 7.34 (s, 5, ArH); ^{13}C (50 MHz) δ 13.7, 21.3, 25.6, 27.1, 71.4, 72.6, 74.9, 125.8 (2 C), 127.9, 127.3 (2 C), 138.4, 159.0, 160.5, 169.4.

4-Acetamido-1-acetoxy-2,2-dichloro-4-methyl-1-phenyl-3-pentanone (10a, X = Cl): mp 47–48 °C (from ethyl acetate); IR (KBr) 3390, 1765 (CO), 1731 (CO), 1659, 1537, 1373, 1220 cm^{-1}; ^1H NMR (200 MHz) δ 1.64, 1.70 (s, 6, CH_3), 1.98 (s, 3, CH_3CO), 2.11 (s, 3, CH_3CO), 6.18 (brs, 1, NH), 6.62 (s, 1, CH), 7.34–7.39 (m, 3, ArH), 7.50–7.55 (m, 2, ArH); ^{13}C (50 MHz) δ 20.8, 23.5, 25.3, 25.6, 62.1, 78.0, 85.1, 127.7 (2 C), 129.2, 129.7 (2 C), 133.4, 168.4, 169.2, 197.0.

2-Acetamido-5-acetoxy-4,4-dibromo-2,6-dimethyl-3-heptanone (10b, X = Br): mp 138–140 °C (from hexane); IR (KBr) 3290, 1744 (CO), 1611, 1539, 1468, 1375, 1230, 1044 cm^{-1}; ^1H NMR (200 MHz) δ 0.96, 1.10 (d, J = 6.9 Hz, 6, CH_3), 1.84, 1.86 (s, 6, CH_3), 1.97 (s, 3, CH_3CO), 2.10 (s, 3, CH_3CO), 2.16–3.32 (m, 1, CH), 5.54 (d, J = 3.6 Hz, 3, CHOAc), 6.22 (brs, 1, NH); ^{13}C (50 MHz) δ 18.4, 20.6, 21.0, 22.9, 23.7, 26.6, 27.1, 31.5, 62.8, 64.6, 80.4, 169.2, 169.6, 196.2.

2,5-Dihydroxy-4,4-dibromo-3-hexanone (11). A solution of **2a** (3.74 g, 10 mmol) and concd sulfuric acid (five drops) in aqueous 50% ethanol (100 mL) was heated at reflux for 2 h under Ar. The mixture was concentrated under vacuum and taken up in ethyl acetate (100 mL). The organic layer was washed with 5% sodium hydrogen carbonate and brine, dried (Na_2SO_4), and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2, hexane–AcOEt (1:1)) to give 2.61 g (90%) of **11** as an oil: (nonpolar component) IR (neat) 3322 (OH), 1729 (CO), 1456, 1429, 1373, 1321, 1116, 1077, 936, 870, 785 cm^{-1}; ^1H NMR (500 MHz) δ 1.52 (d, J = 6.2 Hz, 3, CH_3), 1.61 (d, J = 6.5 Hz, 3, CH_3), 2.65 (brs, 1, OH), 2.98 (brs, 1, OH), 4.38 (q, J = 6.2 Hz, 1, CH), 5.11 (q, J = 6.5 Hz, 1, CH); ^{13}C (126 MHz) δ 18.9, 22.6, 69.0, 72.4, 72.6, 201.8; (polar component) IR (neat) 3306 (OH), 1723 (CO), 1454, 1375, 1270, 1110, 1081, 1038, 934, 874, 822 cm^{-1}; ^1H NMR (500 MHz) δ 1.52 (d, J = 6.2 Hz, 3, CH_3), 1.64 (d, J = 6.8 Hz, 3, CH_3), 2.58 (br, 2, OH), 4.36 (q, J = 6.2 Hz, 1 CH), 5.12 (q, J = 6.8 Hz, 1, CH); ^{13}C (126 MHz) δ 18.9, 22.5, 69.6, 72.0, 72.6, 202.3.

4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (Furaneol, 12). A solution of diol (**11**, 1.02 g, 3.5 mmol) and triethylamine (1.06 g, 10.5 mmol) in ethanol (167 mL) was heated at reflux under Ar for 2 h. The mixture was concentrated under vacuum and dissolved in ethyl acetate (100 mL). The organic layer was washed with brine (10 mL × 2), dried (Na_2SO_4), and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2, hexane–AcOEt (1:1)) to give the furaneol **12** as solid: mp 77–78 °C (lit.[16a] mp 77–79 °C).

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Supplementary Material Available: ^1H or ^{13}C NMR spectrum of **2c**, **2e**, **4f**, **9a** (X = I), **10a** (X = Cl), and **10b** (X = Br) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

2,2-Dichloro[1.1.1]propellane

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The synthesis and study of strained hydrocarbons has been an active area of organic chemistry for many years.[1] Recently, much attention has been devoted to small-ring propellanes, compounds in which the two bridgehead carbons of a bicyclo[*p.q.r*]alkane ring system are connected by a transanular bond. These compounds have attracted interest both for their unusual structural properties and for their synthetic utility in the generation of a number of novel compounds and materials.[2]

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