1497, 1455, 1426, 1372, 1329, 1298, 1248, 1142, 1028, 876 cm^{-1}; MS m/e calcd for $C_{13}H_{15}N$ 185.1205, found 185.1194.

Electrolysis of *N*-(2-Bromophenyl)-*N*-methyl-2-propenamide [14 (X = Br)].[49] From the electrolysis of 8 in the presence of 120 mg of 14 were isolated 63 mg of 15, 16, and 17 in a 1.6:0.5:1 ratio.

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Supplementary Material Available: ^{13}C NMR spectra of 9 (X = Cl, R = COPh), 9 (X = Br, R = COPh), 10 (X = Cl), 10 (X = Br), 12, and 13 (7 pages). Ordering information is given on any current masthead page.

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Electrochemical Cyclopropanation of Alkenes Using Dibromomethane and Zinc in CH_2Cl_2/DMF Mixture

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An efficient electrosynthesis of cyclopropanes from *gem*-dibromoalkanes and alkenes is achieved in a one-compartment cell fitted with a sacrificial zinc anode. The part played by the anodically generated Zn(II) in the coupling reaction is pointed out, and evidence for the existence of an organozinc species as intermediate is presented.

Introduction

The occurrence of the cyclopropane ring in many natural products and the utility of cyclopropanes as intermediates for ring expansions and chain elaborations[1] makes the cyclopropanation of a carbon–carbon double bond a highly useful operation in organic synthesis.

The Simmons–Smith reaction[2] is the most convenient method for the synthesis of these derivatives. An organozinc reagent is prepared from diiodomethane and zinc metal activated by preparation of zinc/copper or zinc/silver couples.[3] However, the reaction mixture is heterogeneous and long reaction time is required.

Some useful modifications of the reaction conditions have subsequently appeared. Diethylzinc, in Furukawa's method,[4] or triethylaluminum, in Yamamoto's one,[5] can be used as reductant instead of zinc metal. But the pyrophoric character of these compounds restricts the usefulness of these methods. Recently, Molander[6] reported the convenience of samarium–mercury amalgam to generate samarium carbenoids from diiodomethane for the efficient cyclopropanation of allylic alcohols.

Although dibromomethane is considerably less expensive, and more easy to store than diiodomethane, only few works have been reported about its use in the Simmons–Smith reaction. In fact, the Zn/Cu couple needs a special activation to react with CH_2Br_2, such as ultrasound irradiation[7] or $TiCl_4$ catalysis.[8] The metal powder can also be prepared by Rieke's method.[9]

Electrosynthesis with sacrificial anodes has been successfully used as a substitute for many organometallic reactions,[10] and the applicability of this method in the field of cyclopropanation had to be investigated. The already described electrocatalytic process using nickel catalyst and zinc anode in DMF as solvent[11] was applied to dibromomethane with the aim of generating the desired organozinc reagent. This procedure enabled the cyclopropanation of cyclooctene, but with 1-octene rapid isomerization of the starting olefin occurred. Consequently, the nickel catalyst was excluded and direct reduction of CH_2Br_2 was attempted; cyclopropanes were obtained in high yield from a variety of alkenes, using a sacrificial zinc anode in a one-compartment cell supplied with constant current.

The scope of this electrochemical cyclopropanation reaction using various alkenes and dihalo compounds was examined and the role played by electrogenerated zinc(II) salts in the eventual formation of an organozinc species discussed.

Results and Discussion

The effects of the solvent and electrolysis conditions on the product cyclopropane yield were determined. Cyclopropanation of either cyclooctene or crotyl alcohol (eq 1) has served as a model to optimize the coupling reaction. The criteria were not only the chemical yield of isolated cyclopropane but also the amount of CH_2Br_2 used for total

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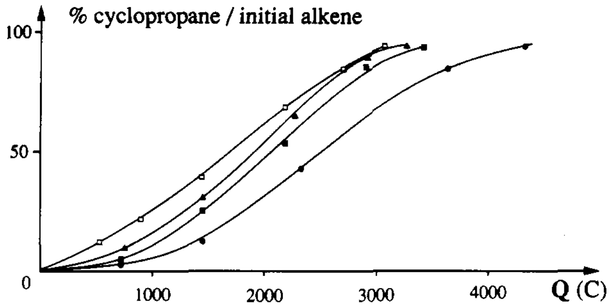
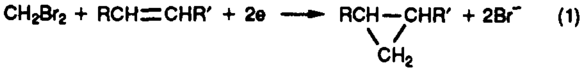


Figure 1. Variation of the cyclopropane/initial alkene ratio during the electrolysis: crotyl alcohol (7.5 mmol), dibromomethane (17–25 mmol); (●) without $ZnBr_2$ added, (■) with $ZnBr_2$, 2 DMF (5 mmol), (▲) with $ZnBr_2$, 2 DMF (10 mmol), (□) with preelectrolysis of $BrCH_2CH_2Br$ (20 mmol).

conversion of the alkene and the amount of electricity needed.



$$CH_2Br_2 + RCH{=}CHR' + 2e \longrightarrow \underset{CH_2}{RCH{-}CHR'} + 2Br^- \quad (1)$$

The cyclopropanation could be achieved in DMF, CH_3CN, or CH_2Cl_2/DMF mixtures with slight modifications in the chemical yield. CH_2Cl_2/DMF mixtures were the most efficient concerning the amount of CH_2Br_2 needed. A 90/10 mixture led to the best results, zinc electrodeposition being observed only at the end of the electrolyses.[12]

A cathodic material, carbon fiber gave slightly better results than steel.

The use of a zinc anode was imperative; an aluminum anode, although organoaluminum compounds suit in chemical systems,[5] did not enable the cyclopropanation, and a fast polymerization of the alkene occurred.

An induction period was always observed at the beginning of the electrolyses (Figure 1); it could be reduced or suppressed by addition of a zinc salt to the initial solution. A preelectrolysis of 1,2-dibromoethane, affording $ZnBr_2$ and ethylene, followed by an argon flush was found to be a convenient way to obtain anhydrous zinc salt. Alternatively, commercial zinc bromide, once recrystallized in DMF, could be used.

The results of the electrochemical cyclopropanation of various alkenes with CH_2Br_2 in these optimized conditions are presented in Table I. Some results obtained with CH_2I_2 or CH_2BrCl are included for comparison.

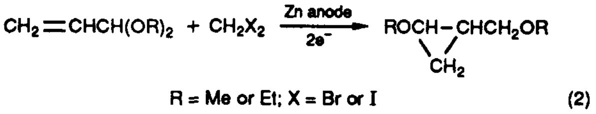
The best chemical yields were obtained with allylic alcohols and unfunctionalized alkenes. Concerning the amount of consumed dihalomethane, the most efficient cyclopropanation was observed with allylic alcohols (entries 1–8). An example of this particular reactivity is the case of geraniol, which was selectively cyclopropanated at the allylic double bond. The mechanism was clearly a syn addition (entries 1, 6, 8). Unfunctionalized olefins (entries 9–12) needed more dibromomethane and therefore extended electrolysis duration. As expected, selective monocyclopropanation of a diene like 1,3-cyclooctadiene could not be obtained.

For several functionalized alkenes, competition between cyclopropanation and Lewis acid-promoted polymerization was observed. Interesting yields were still obtained with vinyl and allyl ethers (entries 13, 14); cyclopropanation of styrene, enamines, α,β-unsaturated ketones, and ketals (entries 15–19) was only partially achieved, although the substrate was entirely consumed. For acrolein acetals, the only isolated products were rearranged cyclopropanes (eq 2).[13] Finally, with vinyl chloride (entry 21), no cyclopropanation was observed and the alkene was recovered.

Table I. Electrochemical Cyclopropanation of Alkenes by Dihalomethanes

entry	alkene	method[a]	CH_2XY (equiv)	cyclopropane isolated yield[b] (%)
1	$CH_3CH{=}CHCH_2OH$- (*trans*)	A	CH_2Br_2 (3.4)	56 (94[c])
2	$CH_3CH{=}CHCH_2OH$- (*trans*)	B	CH_2Br_2 (2.2)	52
3	$CH_3CH{=}CHCH_2OH$- (*trans*)	B	CH_2BrCl (2.6)	54
4	$CH_3CH{=}CHCH_2OH$- (*trans*)	A	CH_2I_2 (2.5)	47[d]
5	$CH_2{=}CHCH_2OH$	A	CH_2Br_2 (2.5)	42[e]
6	$PhCH{=}CHCH_2OH$- (*trans*)	B	CH_2BrCl (4)	59
7	2-cyclohexen-1-ol	B	CH_2BrCl (2.2)	75
8	geraniol	B	CH_2Br_2 (2.6)	70
9	cyclooctene	A	CH_2Br_2 (5)	64
10	cyclooctene	A	CH_2I_2 (4)	75
11	n-$C_6H_{13}CH{=}CH_2$	A	CH_2Br_2 (5)	66
12	1,3-cyclooctadiene	B	CH_2Br_2 (7)	66[f]
13	3,4-dihydro-2*H*-pyran	B	CH_2Br_2 (4)	54
14	$CH_2{=}CHCH_2OPh$	B	CH_2Br_2 (7)	50
15	$PhCH{=}CH_2$	B	CH_2Br_2 (4.5)	26
16	$PhCH{=}CH_2$	A	CH_2I_2 (4)	33
17	pyrrolidino-1-cyclohexene	B	CH_2Br_2 (3)	8
18	2-cyclohexen-1-one	B	CH_2Br_2 (6)	trace
19	2-cyclohexen-1-one	A	CH_2I_2 (4)	20
20	$CH_2{=}CHCH(OEt)_2$	B	CH_2Br_2 (3.5)	15[g]
21	$(CH_3)_2C{=}CHCl$	B	CH_2Br_2 (3.5)	no reaction[h]

[a] Key: method A, no Zn(II) at the beginning of the electrolysis; method B, $ZnBr_2$ ($8\ 10^{-1}$ M), from a preelectrolysis of dibromoethane. [b] Yields are relative to initial olefin. [c] Chromatographic yield in parentheses. [d] CH_2I_2 progressively added; 26% cyclopropane recovered as methanal acetal. [e] (Acetoxymethyl)cyclopropane; acetylation is carried out in situ with acetic anhydride and pyridine. [f] Tricyclo[$7.1.0.0^{2,4}$]decane; the product of monocyclopropanation is formed at the beginning of reaction but cannot be obtained alone. [g] 1-Ethoxy-2-(ethoxymethyl)cyclopropane. [h] Alkene is recovered.



$$CH_2{=}CHCH(OR)_2 + CH_2X_2 \xrightarrow[2e^-]{Zn\ anode} \underset{CH_2}{ROCH{-}CHCH_2OR}$$

R = Me or Et; X = Br or I (2)

When the more reactive CH_2I_2 was used instead of CH_2Br_2, slightly better yields were obtained with polymerizable olefins (entries 10, 16, 19); cyclopropanation may have occurred before the zinc(II) concentration reached

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(12) The reduction potential of $ZnBr_2$ in CH_2Cl_2/DMF mixtures is closely related to the DMF content of the solvent: it shifts from −0.9 V vs SCE in neat CH_2Cl_2 to −1.4 V vs SCE in the 90/10 mixture or in neat DMF. The reduction potential of CH_2Br_2 could not be determined, but is probably ranging between these two values. The presence of a minimum amount (7%) of DMF in CH_2Cl_2 is necessary not only to ensure a sufficient conductance of the medium but also to avoid exclusive deposition of zinc and enable the coupling reaction.

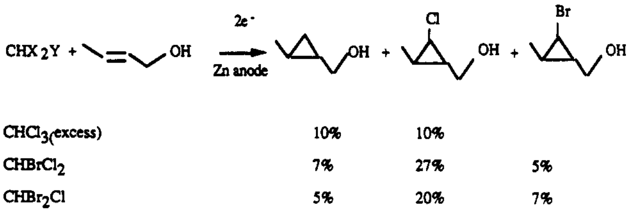
(13) This rearrangement is proposed on the bases of ^1H NMR spectra of the product, which corresponds to a disubstituted cyclopropane ring (4 H) and does not exhibit the acetal H. Mass spectra also agree with the formula. The product is not stable within a few days.

Table II. Electrochemical Cyclopropanation of Alkenes by 2,2-Dibromopropane or α,α-Dihalotoluenes[a]

alkene	dihalo compound (equiv)	isolated yield[b] (%)
$CH_3CH{=}CHCH_2OH$(*trans*)	$(CH_3)_2CBr_2$ (4.3)	51
$(CH_3)_2C{=}CHCH_2OH$	$(CH_3)_2CBr_2$ (3.6)	53
cyclooctene	$(CH_3)_2CBr_2$ (10)	46
cyclooctene	$PhCHCl_2$ (10)	20
cyclooctene	$PhCHBr_2$ (7)	27

[a] Method B. [b] Yields are relative to initial olefin.

Scheme I



$CHCl_3$(excess)	10%	10%	
$CHBrCl_2$	7%	27%	5%
$CHBr_2Cl$	5%	20%	7%

a level allowing polymerization. However, with allylic alcohols, nucleophilic substitution on the iodide happened and the (hydroxymethyl)cyclopropane was recovered mainly as a methanal acetal[14] even if CH_2I_2 was progressively added, its concentration, monitored by GC, being kept at a low level during the electrolysis (entry 4). Such a side reaction was not observed with dibromomethane. With these particularly reactive substrates, CH_2Br_2 could be replaced by CH_2BrCl without any change in the yield (entries 3, 6, 7).

Other dihalo compounds were tested for cyclopropane formation. The results are summarized in Table II. From 2,2-dibromopropane, good yields were obtained, as in the case of dibromomethane, but a large excess of dibromopropane was needed to consume all the substrate, especially cyclooctene. With dihalotoluenes, only partial cyclopropanation was achieved, the alkene being however fully consumed; large amounts of stilbene were obtained. Methyl dichloroacetate or dibromoacetate did not condense with the alkene, which was recovered.

Tri- and tetrahalomethanes gave poor yields of cyclopropane. The reaction of crotyl alcohol with CHX_2Y (X, Y = Br or Cl) afforded the expected halocyclopropanes in low yield together with nonhalogenated cyclopropanes (Scheme I). Significant amounts of dimers (CHXY–CHXY) were formed (20–30%). In the case of CX_3Y, only traces of dihalocyclopropane were detected.

Many similarities may be observed between the electrochemical Zn-based system and the classical Zn-promoted Simmons–Smith reaction: firstly, for both methods, allylic alcohols were more reactive sustrates than unfunctionalized alkenes, probably related to the presence of zinc species. Secondly, no cyclopropanation was observed with dihalo esters, which are claimed to be efficient only when copper is used instead of zinc.[15] Thirdly, the formation of halocyclopropane could not be achieved with the electrochemical process; these compounds are not generally prepared by the Simmons–Smith methodology but by generation of carbene intermediates.[16-18]

It may then be inferred that the electrolytic process involved as intermediate a zinc carbenoid as proposed for the classical chemical reaction. In fact, the final hydrolysis of the reaction mixture was vigorous and evolved gas, suggesting that a stable organometallic species was accumulated during electrolysis, especially when the reaction with alkene was slow.

This was further confirmed by two-step experiments: electrolysis of a CH_2Br_2 solution and subsequent addition of crotyl alcohol gave the expected cyclopropane in significant amounts (22% vs alkene, 7% vs CH_2Br_2). Reaction with iodine also indicated that the electrolyzed solution contained an organometallic species; depending on the electrolysis conditions, either diodomethane or a mixture of diodomethane and bromoiodomethane were obtained.

Electrochemical studies are in progress to complete these preliminary results and elucidate the mechanism of formation of the reactive species responsible for the observed cyclopropanation.

Conclusion

The electrochemical procedure using a sacrificial zinc anode allowed the formation from *gem*-dihalo compounds of organozinc species, intermediates in the cyclopropanation of olefins. We described an efficient process to synthesize cyclopropanes from dibromomethane and various alkenes, except for the most polymerizable ones. This process could be extended to other *gem*-dihalo compounds with good (2,2-dibromopropane) or poor results ($PhCHX_2$, CHX_2Y). Tetrahalomethanes and dihaloacetates could not be used.

This method compares favorably with the chemical procedure involving zinc metal: the starting reagent is the less expensive dibromomethane instead of diiodomethane, and acetalization, in the case of allylic alcohols, is avoided. The solvent CH_2Cl_2 is more attractive than benzene or ethers. An ordinary solid metal is used and does not need any other activation than the electrolysis itself. The simplicity of the electrolysis procedure makes it an attractive alternative for cyclopropane synthesis.

Experimental Section

The anodes were zinc and aluminum rods; they were obtained from Alfa. The cathode was carbon fiber. Tetrabutylammonium iodide (Fluka), tetrabutylammonium bromide, 1,2-dibromoethane, 2,2-dibromopropane, dibromomethane, diiodomethane, bromochloromethane, methyl dichloroacetate, α,α-dibromotoluene, and α,α-dichlorotoluene (Janssen) were commercially available. Methyl dibromoacetate was prepared from dibromoacetic acid (Janssen). Zinc bromide (Alfa) was dried by heating overnight at 70 °C in a vacuum oven and recrystallized in DMF.

Other reagents were obtained from Aldrich and generally used as received. *N,N*-Dimethylformamide (Prolabo) was dried over calcium hydride and then distilled from copper sulfate under reduced pressure. Acetonitrile (Merck) and dichloromethane (Prolabo for synthesis) were dried over molecular sieves (4 Å).

The reaction products were identified by the usual techniques: ^1H NMR spectra were recorded with a Brücker instrument operating at 200 MHz, locked on $CDCl_3$). Mass spectra were recorded with an ITD Finnigan spectrometer coupled to a gas chromatograph (column 25 m, CPS15, capillary). Microanalyses and high-resolution mass spectra were performed by the Service Central d'Analyses (CNRS, Lyon).

General Procedure. Reactions were carried out in a one-compartment cell containing a magnetic stirring bar, a carbon fiber cathode (20 cm^2 area) and a zinc rod anode (1.6-cm diameter,

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immersed to 2 cm) and fitted with a reflux condenser. The cell was immersed into a water bath.

Method A. To a 90/10 CH_2Cl_2/DMF mixture (30 mL) containing 1.3 mmol of NBu_4Br and 0.5 mmol of NBu_4I were added the alkene (5–25 mmol) and the dihalo compound (1.5 equiv). The electrolysis (I = 200 mA) was performed at 40 °C under an argon stream. The composition of the solution was followed by GC. Further dihalo compound was progressively added, ad the electrolysis was pursued until the alkene was totally consumed (3–8 h). Then, the reaction mixture was hydrolyzed by a NH_4Cl solution (75 mL) and extracted three times with ether or pentane (3 × 50 mL). The combined organic phases were washed with 50 mL of a $NaHCO_3$ solution and with 2 × 50 mL of saturated NaCl aqueous solution. The organic phases were dried over anhydrous $MgSO_4$, and solvent was removed under vacuum or by distillation for low-boiling products. The crude product was purified by column chromatography on 60–200 μm silica gel (pentane/ether).

Method B. To a 90/10 CH_2Cl_2/DMF mixture (30 mL) containing 1.3 mmol of NBu_4Br and 0.5 mmol of NBu_4I was added 1,2-dibromoethane (20 mmol). The electrolysis (I = 70–300 mA) monitored by GC was continued until complete. Then, the reaction mixture was flushed with argon to eliminate ethylene, and the alkene and the dihalo compound were added. The subsequent procedure was the same as in method A.

Two-Step Procedure. A $ZnBr_2$ solution was prepared according to method B, and dibromomethane (15 mmol) was added. Electrolysis, at constant intensity (I = 200 mA), was performed until dibromomethane was totally consumed. The anode and the cathode were drawn out of the solution, and crotyl alcohol (4.5 mmol) or iodine (10 mmol) were added. The solution was stirred, and, in the case of crotyl alcohol, heated at 40 °C until the product cyclopropane concentration remained constant. The following workup was the same as described previously.

After reaction with iodine, the reaction mixture was neutralized by a saturated aqueous $Na_2S_2O_4$ solution (50 mL) and extracted with pentane (3 × 50 mL). The combined organic phases were washed with water, NH_4Cl solution, and water. The amount of products (bromoiodomethane and diiodomethane) was determined by GC assays with an internal reference: 2.5 mmol CH_2I_2 was obtained after exhaustive electrolysis; 1.3 mmol CH_2I_2 and 0.7mmol CH_2BrI were obtained when the electrolysis of CH_2Br_2 was stopped at 1F/mol.

Characterization of Products. A. Reactions with Dibromomethane. The identities of the following products were confirmed by comparison of their spectra with spectra data from the literature: *trans*-1-(hydroxymethyl)-2-methylcyclopropane,[8] (acetoxymethyl)cyclopropane,[19] *trans*-1-(hydroxymethyl)-2-phenylcyclopropane,[20] *cis*-bicyclo[4.1.0]heptan-2-ol,[6] *trans*-1-(hydroxymethyl)-2-methyl-2-(4-methyl-3-pentenyl)cyclopropane,[6] bicyclo[6.1.0]nonane,[8] hexylcyclopropane,[8] *trans*-tricyclo-[7.1.0.0^{2,4}]decane,[21] 2-oxabicyclo[4,1,0]heptane,[8] phenylcyclopropane,[19] and bicyclo[4.1.0]heptan-2-one.[2e]

(Phenoxymethyl)cyclopropane: ^{1}H NMR ($CDCl_3$) δ 0.27–0.36 (m, 2 H), 0.52–0.66 (m, 2 H), 1.2–1.3 (m, 1 H), 3.375 (d, J = 6.9 Hz, 2 H), 6.75–7.3 (m, 5 H); MS 148 (M^+), 133, 120 (base peak), 107, 94; exact mass calcd for $C_{10}H_{12}O$ 148.0888, found 148.0874.

1-Pyrrolidinobicyclo[4.1.0]heptane:[22] ^{1}H NMR ($CDCl_3$) 0.03 (dd, J = 6, 4.5 Hz, 1 H), 0.54 (dd, J = 9.9, 4.5 Hz, 1 H), 0.8–1 (m, 5 H), 1.2–1.8 (m, 8 H), 2.4–2.55 (m, 4 H); MS 165 (M^+), 150 (base peak), 136, 122, 108, 94, 80, 70, 55.

1-Ethoxy-2-(ethoxymethyl)cyclopropane: ^{1}H NMR ($CDCl_3$) 0.49 (m (4 lines), J = 6 Hz, 1 H), 0.82 (m (8 lines), J = 3.2, 5.8, 9.9 Hz, 1 H), 1.19 (t, J = 7 Hz, 3 H), 1.2 (t, J = 7 Hz, 3 H), 1.15–1.32 (m, 1 H), 3.11 (m (5 lines), J = 2.9, 3.2, 6 Hz, 1 H), 3.2 (dd, J = 7, 10.6 Hz, 1 H), 3.3 (dd, J = 7.1, 10.6 Hz, 1 H), 3.4–3.6 (m, 4 H); MS 144 (M^+), 129, 98, 85, 72, 57 (base peak); exact mass calcd for $C_8H_{16}O_2$ 144.1150, found 144.1165.

B. Reactions with 2,2-Dibromopropane. The identity of 1-(hydroxymethyl)-2,2,3,3-tetramethylcyclopropane was confirmed by comparison of its spectra with spectral data from literature.[23]

***trans*-1-(Hydroxymethyl)-2,2,3-trimethylcyclopropane:**[24] ^{1}H NMR ($CDCl_3$) 0.28–0.46 (m, 2 H), 0.965 (d, J = 6 Hz, 3 H), 0.969 (s, 3 H), 0.997 (s, 3 H), 2.86 (s, OH), 3.4 (dd, J = 8.1, 11.3 Hz, 1 H), 3.6 (dd, J = 6.5, 11.3 Hz, 1 H); MS 99 ($M-CH_3$), 97 (M–OH), 95, 83, 81, 55 (base peak).

9,9-Dimethylbicyclo[6.1.0]nonane: ^{1}H NMR ($CDCl_3$) 0.75–1.2 (m, 4 H), 1.02 (s, 3 H), 1.06 (s, 3 H), 1.3–1.8 (m, 8 H), 2–2.1 (m, 2 H); MS 152 (M^+), 137, 124, 109, 95, 81, 67 (base peak), 55; exact mass calcd for $C_{11}H_{20}$ 152.1565, found 152.1575.

C. Reactions with α,α-Dihalotoluenes. The structure of 9-phenylbicyclo[6.1.0]nonane (mixture of endo and exo) was confirmed by comparison of its spectra with spectral data from literature.[25]

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Supplementary Material Available: ^{1}H NMR spectra for all new compounds (5 pages). Ordering information is given on any current masthead page.

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