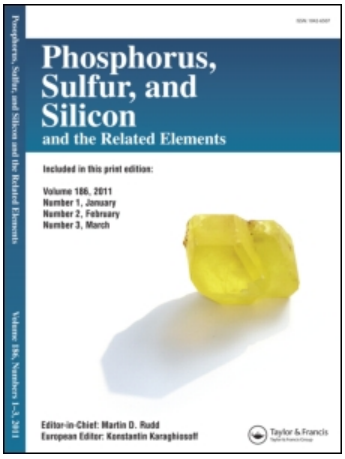

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A NEW METHOD FOR MIXED HALOGENATION. N-CHLOROAMINE-PHOSPHORUS BROMIDE SYSTEM AS A SYNTHETIC EQUIVALENT OF THE MIXED HALOGEN Cl^+Br^-

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A NEW METHOD FOR MIXED HALOGENATION. N-CHLOROAMINE - PHOSPHORUS BROMIDE SYSTEM AS A SYNTHETIC EQUIVALENT OF THE MIXED HALOGEN Cl^+Br^-

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A new method for the mixed halogenation of alkenes has been proposed based on the reaction of olefins with N-chloroamines in the presence of phosphorus bromide or oxybromide. The plausible reaction mechanism and the results of reactions with a number of model unsaturated compounds such as cyclohexene, 1-heptene, ethyl cinnamate, norbornene and those from the bicyclo[2.2.1]heptane series are discussed. In the reactions with reactive olefins this reagent acts as a synthetic equivalent of the unknown mixed halogen [Cl^+Br^-] with «abnormal» polarity of halogen atoms. The same reactions activated by PCl_3 or $POCl_3$ result in dichlorides in yields near to quantitative.

Keywords: bromochlorination; halogenation; N-chloroamines; phosphorus bromides

INTRODUCTION

Halogenation of olefins is one of the «classical» organic reaction, which had great importance for the development of organic chemistry. Ten thousands of the research works deal with the investigation of the chlorination and bromination processes. However, up to the present time only a few number of the papers on the mixed halogenation subject can be found in literature. At the same time, the importance of the selective insertion of

* Corresponding Author.

different halogen atoms to the carbon skeleton of molecule is not less than the significance of the simpler problem of the symmetrical halogenation.

There is the difficulty for the realization of a mixed process. Not numerous bromochlorinating agents, as a rule, are a selective, although they can give good results for limited number of substrates.

Thus, bromine chloride, which can be generated by direct interaction of bromine and chlorine [1-3], reacts with olefins giving dichlorides and dibromides as by-products, because of the presence of Br_2 and Cl_2 in the equilibrium with BrCl[2]. BrCl obtained *in situ* in the N-bromoacetanilide – HCl[3] or the N-chloroacetamide – HBr mixture gives these by-products too [4]. Although the BrCl/pyridine complex [3b,4] as well as the Br_2-$SbCl_5$ (or $SbBr_3$) mixture [6] are effective bromochlorinating reagents, they are not very convenient in practical work and, therefore, have not found wide use. Tetraalkylammonium dichlorobromide, $R_4N\ BrCl_2^-$[7], is the most convenient bromochlorinating reagent at this moment. Only a the relatively low effective electrophylicity [7]may be considered its disadvantages.

The catalysis by Lewis acids is the well-known method for increasing of electrophilicity of weak electrophiles. But in spite of the availability of a number of reagents and works in which this process was examined, the intensity of research in this area has not decreased Both activation and modification of the electrophilic reagents is attracting the investigators' attention now.

Traditionally, hard Lewis acids such as metal halides or sulfur trioxide are used to activate electrophilic processes. Phosphorus halides and oxyhalides, which are considerably softer Lewis acids, have not been examined in sufficient detail for this purpose, although the Vilsmeier reaction is the long known example of their use.

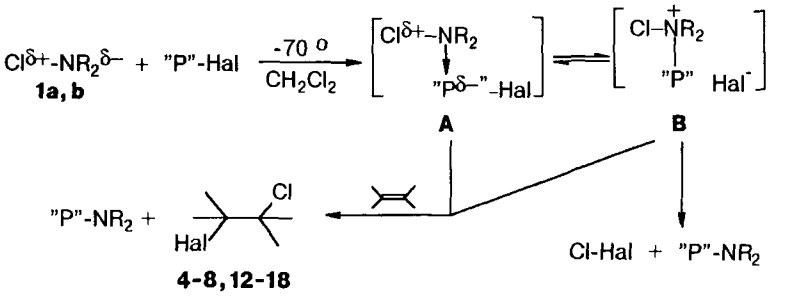
N-haloamides and N-haloamines were previously used for the mixed halogenation, but good results were obtained only for boron trifluoride-activated fluorohalogenation [8]. We have examined N-chloroethylamine (1a) and N-chloromorpholine (1b) in the reaction with olefins in the presence of $POBr_3$, PBr_5, PBr_3, and $POCl_3$ and PCl_3.

Results and Discussion

We have found that N-chloroamines can react with phosphorus halides to form the 1:1 complexes which are capable of electrophilic addition to alkene double bonds. After the phosphorus-containing products were

removed on a silica gel column, the residue was identified as a mixture of dihalogenation products, based on the ^1H NMR spectra.

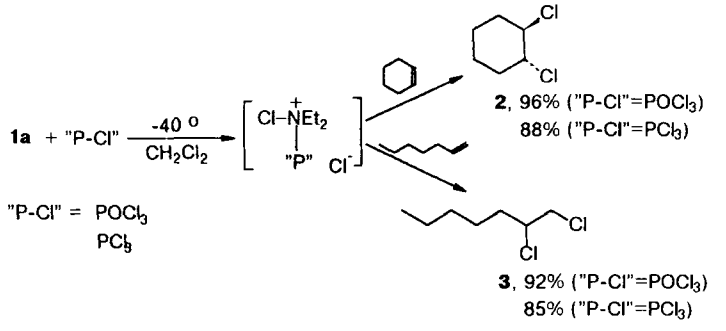
We assume that, first, the reaction proceeds as acid-base interaction between phosphorus halide as a Lewis acid and the nitrogen atom of the chloroamine causing the Cl-N bond of chloroamine polarization giving complex **A** (see Scheme 1). Halide anion can leave complex **A** then, forming **B**, the product of nucleophilic substitution at the phosphorus atom. Using AM-1 method the same probability as the complex **A** formation as well as the complete substitution for halogen giving the complex **B** was shown in the limits of the semi-empirical calculations. These data are in good agreement with the known investigation of the nucleophilic substitution at phosphorus atom 9. We assume that one of the forms **A** or **B**, in which the halogen atom is bound to the cationoic nitrogen atom, further reacts with olefins. The products of Cl-Hal addition (Hal = Cl or Br, depending on used phosphorus halide) are obtained as a result. Nucleophilic substitution of halogen for nitrogen in chloroamine forming the Cl-Hal takes place in the absence of olefins.



The structure of the complex formed was examined by ^{31}P NMR technique. In the spectrum of N-chloroamine 1a and $POBr_3$ mixture, the signals at −50.2 and −28.0 ppm were found besides the $POBr_3$ signal at −101.3 ppm. By an independe synthesis with $POBr_3$ and diethylamine it has been proved that the peak at −28.0 ppm is the signal due to $O{=}P(NEt_2)Br_2$. The signal at −50.2 disappeared after olefin addition to the reaction mixture, thus being attributed to the chlorinating complex.

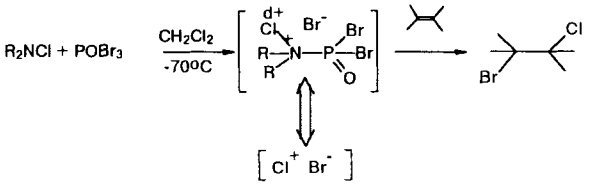
Only one of the halogen atoms from a phosphorus halide can be substituted by an amino group in these conditions. The attempts to substitute two or more atoms of Cl or Br by using N-chloroamine and «P-Hal» in the 2:1 or a greater ratio result in the formation the same products but in lower yields.

N-Chloroamine reactions with olefins in the presence of PCl_3 or $POCl_3$ at –40 ° C result in formation of the dichlorides. Yields in these reactions are near to quantitative. The *trans*stereoselectivity of the addition was shown by the example of cyclohexene: *trans-1,2*-dichlorocyclohexane **2** alone was isolated with 96% yield. 1,2-Dichloroheptane **3** was obtained in 92% yield from 1-heptene. The substitution of one chlorine atom in the phosphorus chloride by the ethylamino group accompanied this process.



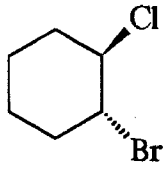
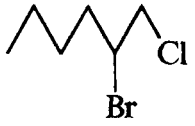
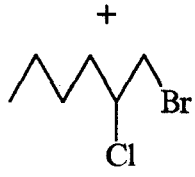
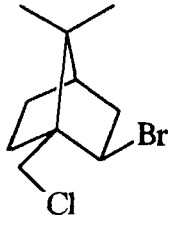
Thus, N-chloroamines in the presence of PCl_3 or $POCl_3$ are the soft and effective chlorinating reagents. Its high electrophilicity, the low temperature, of the reaction, preventing degradation of unstable substrates, and good yields are the advantages of the proposed method for the chlorination.

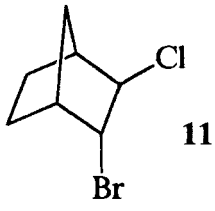
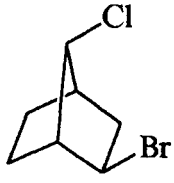
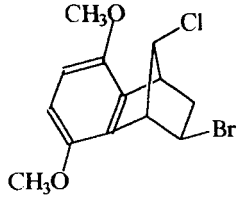
We have also found a promising method for the mixed halogenation, namely the reaction of olefins with complexes of N-chloroamines with phosphorus bromides or oxybromide: PBr_3, PBr_5 and $POBr_3$. These reactions take place in CH_2Cl_2 at –70 °C. After olefin addition to N-chloroamine – phosphorus halide mixture the formation of the products of bromochlorination was observed immediately.

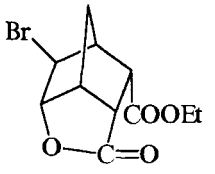
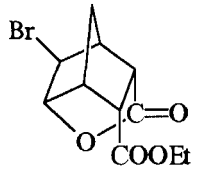


The structure and yields of products obtained are presented in table I. Dibromides were isolated as by-products in all of the reactions. Dichlorides were absent. Insignificant amounts of the elimination products (not more than 5%, as a rule) were also detected in the reaction mixtures.

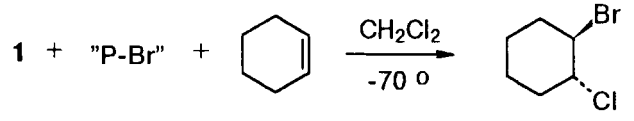
TABLE I The products of bromochlorination of olefins by N-chloroamine - phosphorus bromide complexes

Olefin	*Products of bromochlorination*	*N-μ chloro amine*	*Yields of bromochlorides*		
			$POBr_3$	PBr_3	PBr_5
Cyclo-hexene		**1a** **1b**	92% 90 %	85%	65%
1 -Hexene	 **5** +  **6** **5 : 6 = 1:1**	**1a**	86%	75%	70%
Camphene	 **7**	**1a**		43%	65%

Olefin	*Products of bromochlorination*	*N-μ chloro amine*	*Yields of bromochlorides*		
			$POBr_3$	PBr_3	PBr_5
Norbornene	 **11**	**1a** **1b**	40% 44%	22%	13%
	 **12**	**1a** **1b**	48 45%	59%	62%
5-methylene-norbornene	 **13**	**1a** **1b**	59%		62%
3',6'-dimethoxy-bensonor-borna-diene	 **1**	**1a**	59%	37%	

Olefin	*Products of bromochlorination*	*N-μ chloro amine*	*Yields of bromochlorides*		
			$POBr_3$	PBr_3	PBr_5
Diethyl5,6-di-*endo*norbornyldi-carboxilate	 **15** +  **16**	**1a**	78%	82%	95%
			trace	trace	trace
Ethylcinnamate	Ph-CHCl-CHBr-COOEt **17**	**1a**			71%

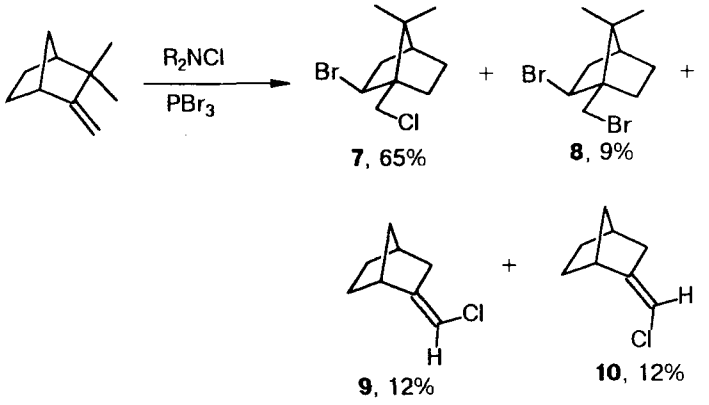
Cyclohexene is a convenient model for studying the stereochemistry of addition reactions. The addition of **1a,b** to this olefin in the presence of phosphorus bromides has been found to occur stereoselectively and to result in *trans*-1,2-adduct **4**, in agreement with the electrophilic addition mechanism.



4

Reaction with 1 -heptene lacks regioselectivity, and proceeds with the formation of both likely products **5** and **6.** The addition to 2-methyl-ene-3,3-dimethylbicyclo[2.2.1]heptene (camphene) is accompanied by the Wagner-Meerwein rearrangement, which is a prove of high electrophilicity of the reagent. Bromochlorocamphane **7** was isolated with 60% yield. Dibromide **8** and the stereoisomeric chlorocamphenes **9** and **10** are

by-products in this reaction, and, moreover, the yield of the products of elimination is significantly greater in this reaction than in the others.

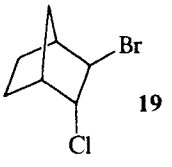
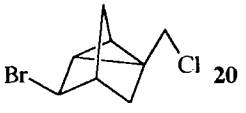


7, 65% **8**, 9% **9**, 12% **10**, 12%

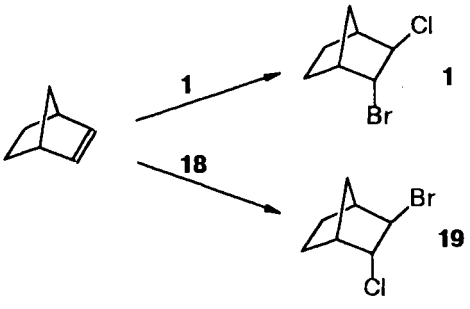
The determination of the halogen atoms position in the products of bromochlorination is of interest since the behavior of bromine or chlorine atom as an electrophilic species is responsible for this position.

We compared bromochlorides, which were obtained in reactions of olefins with known reagent Bu_4NBrCl_2 **18** (the synthetic equivalent of «normal polarized» Br^+Cl^-) [7], with those formed in the reactions investigated. The products synthesized using **18** are shown in table II.

TABLE II The products of bromochlorination of olefins by Bu4NBrCl$_2$

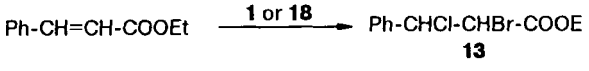
Olefin	*Products of bromochlorination*	*Yields of bromochlorides*
Norbornene	 **19**	53%
5-Methylenenorbornene	 **20**	85%
Ethyl cinnamate	**17**	47%

The detailed NMR investigation of the bromochlorination products of the olefins from the bicyclo[2.2.1]heptane series using COSY and HETCOR methods showed that the compounds formed in their reactions with reagents **1** and **18** are different substances. The elemental composition of these substances was identical and it corresponded to bromochlorides. The ^1H NMR spectra of substances obtained in the reactions of reactive olefins with Bu_4NBrCl_2 and N-chloroamine – phosphorus bromide complexes are practically identical, thus indicating the same character of substitution in the carbon skeleton of molecule. However, the ^{13}C NMR spectra strongly differ, which is the evidence that Cl and Br atoms have interchanged positions in these compounds. For example, for norbornene:

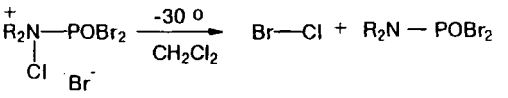


This result means, that in the reactions with the reactive olefins the supposed reagents, N-chloroamine/phosphorus bromide complexes, act as the synthetic equivalent of the previously unknown mixed halogen [Cl+Br-] with "abnormal" polarity of halogen atoms.

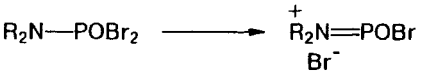
However, in the case of ethyl cinnamate and diethyl 5,6-di-*endo*-norbornenedicarboxylate, the electron-deficient substrates, the bromochlorides obtained by halogenation with tetrabuthylammonium bromochloride are identical to those, formed in the N-chloroamine - phosphorus halide-activated reaction. For example, for ethyl cinnamate:



It is quite likely that the removal of BrCl from complex **A** or **B** takes place with increasing of temperature. This process is accompanied by the re-polarization resulting in energetically favorable charge distribution:



The formation of dibromides as by-products can be explained by the yield of bromide anions from aminobromide under carbocation action. The bromide-anion acts then as a nucleophile.



The yield of dibromides is the highest in the case of PBr_5 but the lowest for $POBr_3$ activation. These facts are in good agreement with the brominating ability of PBr_5, whereas PBr_3 and $POBr_3$ do not possess this property. On the other hand, the reactions rates and the overall yields are higher in the case of PBr_5, in accordance with the order of Lewis acid strength: $PBr_3 \sim POBr_3 < PBr_5$ [10]. Thus, $POBr_3$ is the best of phosphorus bromides for this reaction.

In summary, a new method for alkene bromochlorination via generating of high by reactive N-chloroamine/phosphorus halide complexes was proposed. These reactions take place under mild conditions and proceed with good yields. The most interesting fact, in our opinion, is the behavior of the proposed reagent as an analogue of the unusual synthone [Cl^+Br^-] in the reactions with active olefins.

EXPERIMENTAL

General

The purity of the reaction products was monitored by TLC. The preparative separation of the reaction product was carried out by TLC on Silufol plates using ethyl acetate - petroleum ether (1:10) as the eluent. All solvents were dried by conventional techniques. NMR spectra were recorded in $CDCl_3$. IR spectra were obtained in nujol.

The starting compounds were synthesized using the known procedures : N-chlorodiethylamine **1a** [11], N-chloromorpholine **1b**[12], tetrabutylammonium bromochloride [7a]. The independent synthesis of $O{=}PBr_2NEt_2$ was made from $POPr_3$ and Et_2NH analogous to that in [13].

Reactions between N-chloroamines and alkenes in the presence of phosphorus halide or oxyhalide (general procedure)

The solution of phosphorus halide in absolute CH_2Cl_2 was placed to a flask supplied with a stirrer, a thermometer and a dropping funnel. The flask was cooled to –40 or –70 °C (in the case of phosphorus chloride or bromide, respectively) and an equivalent amount of N-chloroamine in CH_2Cl_2 was added. After 1 h stirring under this temperature the mixture was heated to 0 °C, passed through a column-filter with silica gel (h = 5 cm). After evaporation of the solvent the residue was chromatographed or distilled in vacuum.

The products isolated the particular reactions are listed below.

CHLORINATION

trans-1,2-dichloro-cyclohexane (2)

B.p. 65 °C/ 12 ppm; $n_D^{18} = 1.4915$ (lit. b.p. 78 °C/ 20 ppm, $nD^{20} = 1.4903$[14]), ^1H NMR δ 4.51 (bs, 2H , Δν/2 = 10 Hz), 2.45 (m, 2H), 1.89 (m, 2H), 1.80 (m, 2H), 1.52 (m, 2H).

1,2-Dichloro-heptane (3)

B.p. 52 °C/ 12 ppm; (lit. b.p. 172–174 °C [14]). ^{1}H NMR δ 4.25 (m, 1H), 3.83 (dd, 1H, J = 4.6, 10.4 Hz), 3.62 (dd, 1H, $J_1 = J_2 = 10.9$ Hz), 2.13 (m, 1H), 1.83 (m, 1H), 1.3–1.6 (m, 4H), 0.95 (t, 3H).

BROMOCHLORINATION

A. Bromochlorides

trans-1-Bromo-2-chloro-cyclohexane (4)

B.p. 92–93 °C/ 17 ppm; n_D^{20}= 1.5237 (lit. b.p. 80–83 °C/ 11 pp_m, n_D^{20}= 1.5232 [14]). ^{1}H NMR δ 4.48 (bs, 2H, Δν/2 = 10 Hz), 2.44 (m, 2H), 1.88 (m, 2H), 1.82 (m, 2H), 1.53 (m, 2H).

2-Bromo-1-chlorohexane (5) and 1-Bromo-2-chlorohexane (6)

R_f 0.61, ^{1}H NMR for 5 δ 4.17 (m, 1H), 3.85 (dd, 1H, J = 4.6, 10.4 Hz), 3.63 (dd, 1H, $J_1 = J_2 = 10.9$ Гu), 2.15 (m, 1H), 1.8 (m, 1H), 1.3–1.6 (m, 4H), 0.95 (t 3H). ^{13}C NMR for **5** δ 36.3, 53.1, 35.7, 28.9, 21.9, 13.9. ^{1}H NMR for **6** δ 4.25 (m, 1H), 3.94 (dd, 1H, J = 4.4, 10.6 Hz), 3.75 (dd, 1H, $J_1 = J_2 = 11.1$ Hz), 2.20 (m, 1H), 1.85 (m, 1H), 1.3–1.6 (m, 4H), 0.98 (t, 3H). ^{13}C NMR for **6** δ 57.5, 52.4, 36.5, 29.8, 22.7, 14.4. NMR spectra are identical to reported [6].

exo-2-Bromo-1-chloromethyl-7,7-dimethylbicyclo[2.2.1]heptane (7)

R_f 0.53. ^{1}H NMR δ 4.24 (dd, 1H, J = 4.6, 8.3 Hz), 3.75 (d, 1H, J = 9.7 Hz), 3.45 (d, 1H, J = 9.7 Hz), 2.42 (ddd, 1H, J = 4.5, 8.3, 14.2 Hz), 2.15 (dd, 1H, J = 8.3, 14.2 Hz), 1.97 (dd, 1H, $J_1 = J_2$= 4.5 Hz), 1.92 (dd, 1H, J = 4.5, 13.2 Hz), 1.78 (m, 2H), 1.56 (m, 1H), 1.20 (s, 3H), 0.93 (s, 3H). ^{13}C NMR δ 56.6, 53.0, 48.3, 42.0, 36.8, 34.4, 26.4, 21.0, 20.3. Anal. Calcd. for $C_{10}H_{16}BrCl$: C 47.74, H 6.41. Found: C 48.05, H 6.72.

endo-2-Bromo-exo-3-chlorobicyclo[2.2.1]heptane (11)

R_f 0.52, ^{1}H NMR 6 4.47 (m, 1H, J = 1.5, 3.0, 3.0 Hz), 3.90 (m, 1H, J = 3.0 Hz), 2.50 (m, 1H), 2.49 (m, 1H), 2.02 (d, 1H, J = 14.0 Hz), 1.89 (m, 1H), 1.54 (m, 1H), 1.53 (d, 1H, J = 14.0 Hz), 1.50 (m, 1H), 1.46 (m, 1H). ^{13}C

NMR δ 62.45, 61.90, 47.78, 45.56, 36.13, 28.75, 23.98. Anal. Calcd. for $C_7H_{10}BrCl$: C 40.13, H 4.81. Found:C 39.87, H 5.14.

exo-2-Bromo-sin-7-chlorobicyclo[2.2.1]heptane (12)

R_f 0.50. ^1H NMR δ 3.96(bs, 1H), 3.92 (m, 1H), 2.72 (d, 1H, J = 4 Hz), 2.70 (m, 1H), 2.25 (ddd, 1H, J = 1.5, 8.0, 14.0 Hz), 2.47 (t, 1H, $J_1 = J_2 = 3$ Hz), 1.75–1.68 (m, 2H), 1.39–1.32 (m, 2H). ^{13}C NMR δ 52.76, 49.93, 46.99, 44.13, 41.69; 28.23, 24.99 (C^5). Anal. Calcd. for $C_7H_{10}BrCl$: C 40.13, H 4.81. Found: C 39.88, H 5.05.

1-Bromomethyl-exo-3-chlorotricyclo[2.2.1.0^{2,6}]heptane (13)

R_f 0.59. ^1H NMR δ 4.01 (bs, 1H) 3.62 (bs, 2H), 2.24 (bs, 1H), 2,10 (d, 1H, J = 11.1 Hz,), 1.67 (d, 1H, J = 5.1 Hz), 1.2–1.6 (m, 4H). ^{13}C NMR δ 55.76, 39.43, 35.78, 34.32, 32.73, 27.68, 21.84, 14.12. Anal. Calcd. for $C_8H_{10}BrCl$: C 43.38, H 4.55. Found: C 43.87, H 4.80.

9-Bromo-sin-11-chloro-3,6-dimethoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (14)

R_f0.57. ^1H NMR δ 6.62 (d, 1H, J = 9.0 Hz), 6.58 (d, lH, J = 9.0 Hz), 4.09 (m, 1H), 3.93 (bs, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.71 (m, 1H), 3.69 (m, 1H), 2.82 (dt, 1H, J = 4.5, 4.5, 13.3), 2.19 (dd, 1H, J = 8.0, 13.3 Hz).^{13}C NMR δ 147.51, 147.29, 132.88, 131.31, 110.89, 110.11, 56.52, 55.79, 55.72, 55.34, 53.05, 47.33, 35.89. Anal. Calcd. for $C_{13}H_{14}O_2ClBr$: C 49.16, H 4.44. Found: C 49.52, H 4.94.

Methyl 2-bromo-5-oxo-4-oxatricyclo[4.2.1.0^{3,7}]nonane-9-carboxilate (15) and Methyl 2-bromo-5-oxo-4-oxatricyclo [4.3.0.0^{3,8}]nonane-7-carboxilate (16)

R_f 0.09. M.p. 85–87 °C (lit. m.p. = 83–85 °C [13]). ^1H NMR δ 4.9 (d, 1H, J = 5.0 Hz), 4.6 (d, 1H, J = 1.5 Hz), 3.7 (s, 3H), 3.3 (m, 1H), 3.0 (d, 1H, J = 2.0 Hz), 2.8 (m, 2H), 2.3 (d, 1H, J = 12.0 Hz), 1.7 (d, 1H, J = 12.0 Hz). IR 1800 (C=O, γ-lactone), 1750 (COOMe). In the IR spectra of reaction mixture the peak 1700 (C=O, 6-lactone) takes place.

Ethyl 2-bromo-3-chloro-3-phenyl-propanoate (17)

R_f 0.10. ^1H NMR δ 7.2 (bs., 5H). 5.2 (d, 1H, J = 10.0 Hz), 4.7 (d, 1H, J = 10.0 Hz), 4.1 (q, 2H, J = 7.0 Hz), 1.2 (t, 3H, J = 7.0 Hz). ^{13}C NMR 6

166.5, 130.0, 128.7, 128.0, 127.9, 62.3, 60.2, 50.6, 14.3. Anal. Calcd. for $C_{11}H_{12}O_2BrCl$: C 45.31; H 4.15. Found: C 45.80; H 4.18.

Bromochlorination of olefins by Bu4NBrCl$_2$ (general procedure)

The procedure is analogous to that in [7a,b]. An equivalent amount of Bu_4NBrCl_2 in absolute CH_2Cl_2 was slowly added to a solution of olefin in CH_2Cl_2 at 0 °C. After 1-h stirring, the mixture was passed through a column-filter with silica gel (h = 5 cm). After evaporation of the solvent the residue was chromatographed if more than one product were detected by TLC.

exo-2-Bromo-endo-3-chlorobicyclo[2.2.1]heptane (19)

R_f = 0.55. ^{1}H NMR δ 4.46 (m, 1H, J = 1.5, 3.0, 3.0 Hz), 3.74 (m, 1H, J = 3.0,3.0 Hz), 2.51 (m, 1H), 2.48 (m, 1H), 2.06 (d. 1H, J = 14.0 Hz), 1.97 (m, lH), 1.75 (m, 1H), 1.58 (d, 1H, J = 14.0 Hz), 1.48 (m, 1H), 1.42 (m, 1H). ^{13}C NMR δ 70.48, 59.86, 47.52, 44.89, 36.96, 28.22, 21.39. Anal. Calcd. for $C_7H_{10}BrCl$: C 40.13, H 4.81. Found: C 40.15, H 5.02.

exo-3-Bromo-1-chloromethyltricyclo[2.2.1.0^{2,6}]heptane (20)

R_f 0,58. ^{1}H NMR δ 4.00 (bs, 1H), 3.73 (d, 1H, J = 11.6 Hz), 3.69 (d, 1 H, J = 11.6 Hz), 2.22 (bs, 1H), 2.09 (d, 1H, J = 10.7 Hz), 1.64 (d, 1H, J = 5.3 Hz), 1.2–1.6 (m, 4H). ^{13}C NMR δ 55.2, 39.4, 34.9, 34.0, 32.2, 29.3, 26.0, 20.1. Anal. Calcd. for $C_8H_{10}BrCl$: C 43.38, H 4.55. Found: C 42.96, H 4.22.

B. Dibromides

1,2-Dibromo-hexane (21)

Yield 12; 15; 25 % (for using $POBr_3$, $PBr_3$and PBr_5, respectively). Rf 039. ^{1}H NMR δ 4.15 (m, 1H, 3.82 (dd, 1H, J = 3.9, 11.0 Hz), 3.61 (dd, 1H, $J_1 = J_2$= 10.2 Hz), 2.12 (m, 1H), 1.77 (m, 1H), 1.25–1.6 (m, 4H), 0.90 (t, 3H). ^{13}C NMR δ 41.15, 48.56, 33.21, 26.37, 20.53, 12.70.

exo-2-Bromo-1-bromomethyl-7,7-dimethylbicyclo[2.2.1]heptane (8)

Yield 9; 20 % (for using PBr_3 and PBr_5, respectively). Rf 0,52. ^{1}H NMR δ 4.23 (dd, 1H, J = 4.6, 8.3 Hz), 3.71 (d, 1H, J = 9.7 Hz), 3.42 (d, 1H, J = 9.7 Hz), 2.42 (ddd, 1H, J = 4.5, 8.3, 14.2 Hz), 2.15 (dd, 1H, J = 8.3, 14.2 Hz),

1.97 (dd, 1H, $J_1 = J_2 = 4.5$ Hz), 1.92 (dd, 1H, J = 4.5, 13.2 HzГu,), 1.78 (m, 2H), 1.56 (m, 1H), 1.20 (s, 3H), 0.93 (s. 3H). ^{13}C NMR δ 49.17, 45.1, 44.3, 36.9, 29.0, 27.0, 23.9, 23.6, 21.0, 20.3. Anal. Calcd. For $C_{10}H_{16}Br_2$: C 40.57, H 5.45. Found: C 40.03. H 5.47.

Cis- and trans- chlorocamphenes (9) and (10) in mixture with 1:1 ratio. Yield 24; 17% (for using $PBr_3$and PBr_5, respectively). Rf = 0.22. ^{1}H NMR δ 5.7 and 5.5 (s, 1H), 1.1–2.0 (m, 8H), 1.08 (s, 6H).

exo-2-sin-7-Dibromobicyclo[2.2.1]heptane (22)

Yield 5; 8; 10 % (for using $POBr_3$, PBr_3 and PBr_5, respectively). Rf 0–54. ^{1}H NMR 6 4.50 (bs, 1H), 4.01 (m, 1H, J = 3.0, 8.0 Hz), 2.72 (m, 1H), 2.58 (d, 1H, J = 4.0 Hz), 2.39 (t, 1H, J = 3.0 Hz), 2.25 (dd, 1H, J = 8.0, 14.0 Hz), 2.12–2.02 (m, 2H), 1.35–1.25 (m, 2H. ^{13}C NMR δ 55.64, 49.52, 43.48, 42.20, 42.30, 26.06, 25.84. Anal. Calcd. For $C_7H_{10}Br_2$: C 33.11, H 3.97. Found: C 32.83, H 4.01.

1-Bromomethyl-exo-3-bromotricyclo[2.2.1.0^{2,6}]heptane (23)

Yield 5; 15 % (for using $POBr_3$ and PBr_5, respectively). Rf = 0.56. ^{1}H NMR δ 3.92 (bs, 1H), 3.71 (bs, 2H), 2.14 (bs, 1H), 2.10 (d, 1H, J = 10.0 Hz), 1.65 (d, 1H, J = 4.9 Hz), 1.2–1.6 (m, 4H). ^{13}C NMR δ 58.51, 52.59, 45.38, 40.82, 34.63, 29.48, 21.79, 14.83. Anal. Calcd. For $C_8H_{10}Br_2$: C 36.13, H 3.79. Found: C 36.63, H 3.61.

9,sin-11-dibromoro-3,6-dimethoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (24)

Yield 32; 50 % (for using $POBr_3$ and PBr_3, respectively). Rf = 0.55. ^{1}H NMR δ 6.55 (d, 1H, J = 8.9 Hz), 6.53 (d, 1H, J = 8.9 Hz), 4.01 (m, 1H), 3.76 (bs, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.74 (m, 1H), 3.71 (m, 1H), 2.80 (dt1H,, J = 4.3, 4.3, 12.9 Hz), 2.14 (dd, 1H, J = 8.0, 13.3 Hz). ^{13}C NMR δ 147.64, 147.10, 132.56, 131.71, 111.01, 110.20, 55.77, 55.91, 55.56, 52.67, 47.57, 44.82, 36.03. Anal. Calcd. For $C_{13}H_{14}O_2Br_2$: C 43.13, H 3.90. Found: C 42.86, H 4.10.

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