SYNTHESIS OF BRIDGEHEAD CHLORO-, BROMO- AND IODOBICYCLO[2.2.2]OCTANES

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The paper describes transformations of hydroxy-, acetoxy- or methoxy-bridgehead bicyclo-[2.2.2]octanes into bridgehead chloro, bromo or iodo derivatives by action of inorganic halides in the medium of orthophosphoric or polyphosphoric acids.

Due to relative availability of bridgehead hydroxybicyclo[2.2.2]octanes or their acetates or methyl ethers[1-5] these compounds became potential starting materials for preparation of other bridgehead derivatives of bicyclo[2.2.2]octanes. The present communication deals with preparation of bridgehead halogenobicyclo[2.2.2]-octanes (except for the fluoro derivatives[6,7]) from mentioned compounds. At the same time we were interested in partial transformation of hydroxy groups in 1,4-dihydroxybicyclo[2.2.2]octane, in the reaction conditions of formation of mixed 1,4-dihalo derivatives, in reductive dehalogenations of bridgehead bromobicyclo-[2.2.2]octanes, as well as in the reaction of 1-hydroxy-4-methyl- and 1-hydroxy--4-phenylbicyclo[2.2.2]octanes with 1,1-dichloroethylene in orthophosphoric acid medium.

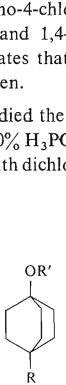
The first transformation of bridgehead hydroxyl group in the bicyclo[2.2.2]octane series was carried by Sayigh[8] who used the Lucas reagent, and this method was used later by other authors, too[9-11]. Suzuki and Morita[4,12] used acyl halogenides as halogenation agents for substitution of 1-methoxy group, the reaction being catalyzed by tin tetrachloride. This approach has the drawback that the prepared fluoro, bromo and iodo derivatives can be contaminated by the 1-chloro derivatives due to the presence of tin tetrachloride[12]. Kauer[13] and other authors[14] use aqueous hydrohaloic acids at higher temperatures in pressure vessels for transformations of hydroxyl group into halogen group (except for fluoro group) at the bridgehead positions of the bicyclo[2.2.2]octane skeleton. Recently Kraus and Graef[15] described a mild method for transformation of bicyclo[2.2.2]oct-1-yl *p*-toluenesulphonates into the corresponding halogeno derivatives by action of titanium, iron or magnesium halides.

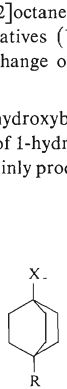
We have found that the bridgehead hydroxybicyclo[2.2.2]octanes, their acetates or methyl ethers *I*–*IV* can easily be transformed into the corresponding halogeno

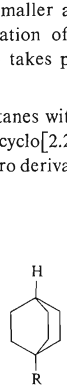
derivatives *V–IX* by heating with halides of inorganic acids in 100% H_3PO_4 or polyphosphoric acid media. In the absence of phosphoric acids the substitution of hydroxyl by halogen does not take place. Thus *e.g. IIa* only gave the ester-dichloride *X* of phosphoric acid on boiling with freshly distilled $POCl_3$, whereas in the presence of phosphoric acids 1-chloro-4-methylbicyclo[2.2.2]octane (*VIa*) was formed in high yield. The procedure can be simplified fundamentally by application of alkali halides. In this case the respective hydrogen halide liberated *in situ* acts as the proper halogenation agent. Substitution of the hydroxyl group by fluorine by action of alkali fluorides under the given reaction conditions does not take place. In the case of reactions of 1,4-dihydroxybicyclo[2.2.2]octane with alkali halides in 100% H_3PO_4 we could also trap the products of partial halogenation, *i.e.* 1-halogeno-4-hydroxybicyclo[2.2.2]octanes *IXa–IXc* besides the respective 1,4-dihalogeno derivatives *VIIIa–VIIIc*.

Using gas chromatography we have found that the given procedure also produces the "mixed" 1,4-dihalogenobicyclo[2.2.2]octanes. Thus *e.g.* heating of 1-hydroxy-4-bromobicyclo[2.2.2]octane (*IXb*) with sodium chloride in 100% H_3PO_4 produces mainly 1-bromo-4-chlorobicyclo[2.2.2]octane (*XI*) besides smaller amounts of the 1,4-dibromo- and 1,4-dichloro derivatives (*VIIIa,b*). Formation of *VIIIa* in this reaction indicates that mutual interchange of halogens also takes place under the conditions given.

We also studied the reaction of 1-hydroxybicyclo[2.2.2]octanes with 1,1-dichloroethylene in 100% H_3PO_4. In the case of 1-hydroxy-4-methylbicyclo[2.2.2]octane (*IIa*) the reaction with dichloro ethylene mainly produces the 1-chloro derivative *VIa* (23%).







I, R = R' = H
IIa, R = CH_3, R' = H
IIb, R = R' = CH_3
IIc, R = CH_3, R' = $COCH_3$
III, R = C_6H_5, R' = H
IVa, R = OH, R' = H
IVb, R = OH, R' = $COCH_3$
IVc, R = $OCOCH_3$, R' = $COCH_3$

Va–c, R = H, X = Cl, Br or I
VIa–c, R = CH_3, X = Cl, Br or I
VIIa–c, R = C_6H_5, X = Cl, Br or I
VIIIa–c, R = X = Cl, Br or I
IXa–c, R = OH, X = Cl, Br or I
X, R = CH_3, X = $OPOCl_2$
XI, R = Br, X = Cl
XII, R = CH_3, X = CH_2COOH
XIII, R = CH_3, X = $CH_2\overset{+}{C}Cl_2$

XIV, R = CH_3
XV, R = H

This reaction gave 13% 4-methylbicyclo[2.2.2]oct-1-ylacetic acid (*XII*) as a side product. Whereas formation of *VIa* in this reaction can be explained by participation of hydrogen chloride (which, under the given conditions, is produced by acid hydrolysis from 1,1-dichloroethylene), the compound *XII* is most probably formed *via* the intermediate *XIII*. Reaction of 1-hydroxy-4-phenylbicyclo[2.2.2]octane (*III*) with 1,1-dichloroethylene produces in this way the chloro derivative *VIIa* only.

The 1-halogenobicyclo[2.2.2]octanes can also be used for preparation of other bridgehead derivatives (see[9,13,2]). In this work we have dealt with substitution of halogen by hydrogen, catalytic reductive dehalogenation of the bridgehead bromo-derivatives *VIb*, *VIIIb* and *IXb*, in alkaline medium under normal pressure and with the use of the Raney catalyst.

EXPERIMENTAL

The temperature data were not corrected. The IR spectra were measured with a UR-10 apparatus (Zeiss, Jena). The ^{1}H-NMR spectra were measured with a Varian 60 apparatus (tetramethylsilane). The mass spectra were measured with a MCH-1303 apparatus (USSR) and were published elsewhere[16] (except for the compounds *IXa—IXc*). Purity of the compounds was checked by gas chromatography using a Chrom 3 apparatus (Laboratorní přístroje, Prague). 100% H_3PO_4 was prepared from 85% H_3PO_4 by addition of calculated amount of P_2O_5; polyphosphoric acid was prepared according to ref.[17]. For the reductive dehalogenation the Raney nickel according to Urushibara[18] was used.

Halogenation of Bicyclo[2.2.2]octan-1-ols, Their Acetates or Methyl Ethers

The starting compounds *I—IV* were mixed with 100% H_3PO_4 or polyphosphoric acid and with the halogenation agent and were heated at 80—150°C with stirring for 1/2 to 2 h. For 5 mmol of the starting bicyclo[2.2.2]octan-1-ol (or its acetate or methyl ether) 3 g orthophosphoric or polyphosphoric acid and 1 g alkali halogenide (NaCl, KBr, KI) were used (method *A*); according to method *B*, 10 to 15 g inorganic acid halides ($SOCl_2$, $POCl_3$, PBr_3) were used. After cooling the mixture was decomposed with ice water and extracted with ether or chloroform. The extracts were washed with 5% aqueous $KHCO_3$, and water (in the case of the iododerivatives the extracts were washed also with cold 5% aqueous $Na_2S_2O_3$) until neutral. After drying ($MgSO_4$) and evaporation of the solvent the raw halogenobicyclo[2.2.2]octane was purified by sublimation, crystallization or column chromatography (Al_2O_3). In the case of the halogenations of 1,4-dihydroxy derivative *IVa* by the method *A* the column chromatography (cyclohexane as eluent) gave first the respective 1,4-dihalogeno derivatives *VIIIa—VIIIc*; then the column was eluated with mixture ether–acetone (1 : 1) to give the respective 1-halogeno-4-hydroxybicyclo[2.2.2]octane (*IXa—IXc*). In the following text we give the individual halogenobicyclo[2.2.2]octanes prepared according to the abovementioned procedures *A* and *B* along with brief description of the reaction conditions (reaction time in min, reaction temperature in °C, yield in %) and spectra characteristics.

1-*Chlorobicyclo*[2.2.2]*octane* (Va): Method *A* (orthophosphoric acid, 90 min, 120°C, 71%), method *B* (polyphosphoric acid–$POCl_3$, 60 min, 105°C, 65·5%). M.p. 103—104°C (ref.[19–21] m.p. 99—100°C; ref.[4] m.p. 101·5—102·5°C; ref.[22] m.p. 103·5—104·5°C). IR spectrum (CS_2, cm^{-1}): 2945, 2915, 2865, 2850, 1375, 1320, 1100, 940, 840.

1-*Bromobicyclo*[2.2.2]*octane* (Vb): Method *B* (polyphosphoric acid, 60 min, 130°C, 67%). M.p. 66—67°C (ref.[22] m.p. 58·5—59·5°C; ref.[4] m.p. 63·5—64·5°C; ref.[8,20] m.p. 64—65°C). IR spectrum (CCl_4, cm^{-1}): 2945, 2915, 2865, 2850, 1455, 1375, 1320, 1135, 1005, 920, 830.

1-*Iodobicyclo*[2.2.2]*octane* (Vc): Method *A* (polyphosphoric acid, 60 min, 80°C, 59%). M.p. 29—29·5°C (ref.[4] m.p. 29—29·5°C). IR spectrum (CCl_4, cm^{-1}): 2950, 2915, 2865, 2850, 1455, 1375, 1320, 1135, 1000, 920.

1-*Chloro*-4-*methylbicyclo*[2.2.2]*octane* (VIa): Method *A* (polyphosphoric acid, 60 min, 100°C, 79%); method *B* (polyphosphoric acid–$POCl_3$, 45 min, 105°C, 75%; polyphosphoric acid–$SOCl_2$, 120 min, 80°C, 73%). M.p. 76—77°C (ref.[4] m.p. 75·5—76°C). IR spectrum (CS_2, cm^{-1}): 2945, 2915, 2865, 2850, 1380, 1330, 940, 838. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 0·77 (s, 3 H, CH_3); 1·4—1·7 (m, 6 H, CH_2); 1·85—2·2 (m, 6 H, CH_2).

1-*Bromo*-4-*methylbicyclo*[2.2.2]*octane* (VIb): Method *A* (polyphosphoric acid, 60 min, 100°C, 74%); method *B* (polyphosphoric acid, 60 min, 130°C, 77%). M.p. 92—93°C (ref.[10] m.p. 90 to 93°C; ref.[9] m.p. 92—94°C. IR spectrum (CS_2, cm^{-1}): 2945, 2915, 2865, 2850, 1375, 1320, 925, 830. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 0·75 (s, 3 H, CH_3); 1·4—1·7 (m, 6 H, CH_2); 2·1—2·4 (m, 6 H, CH_2).

1-*Iodo*-4-*methylbicyclo*[2.2.2]*octane* (VIc): Method *A* (polyphosphoric acid, 90 min, 90°C, 80%). M.p. 74—75°C. IR spectrum (CCl_4, cm^{-1}): 2950, 2915, 2865, 2850, 1455, 1378, 1320, 1135, 1000, 920. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 0·7 (s, 3 H, CH_3); 1·44—1·7 (m, 6 H, CH_2); 2·31—2·63 (m, 6 H, CH_2). For $C_9H_{15}I$ (250·1) calculated: 43·21% C, 6·05% H, 50·74% I; found: 43·01% C, 5·94% H, 50·05% I.

1-*Chloro*-4-*phenylbicyclo*[2.2.2]*octane* (VIIa): Method *A* (orthophosphoric acid, 60 min, 100°C, 73·5%). M.p. 86—88°C (ref.[23] m.p. 88·5—89·5°C). IR spectrum (CS_2, cm^{-1}): 3080, 3055, 3020, 2948, 2910, 2860, 985, 885, 758.

1-*Bromo*-4-*phenylbicyclo*[2.2.2]*octane* (VIIb): Method *A* (orthophosphoric acid, 60 min, 100°C, 70%); method *B* (orthophosphoric acid, 30 min, 120°C, 49%). M.p. 108—109°C (ref.[10] m.p. 107—108°C; ref.[9] m.p. 109—110°C). IR spectrum (CS_2, cm^{-1}): 3080, 3050, 3020, 2948, 2910, 2860, 978, 870, 825.

1-*Iodo*-4-*phenylbicyclo*[2.2.2]*octane* (*VIIc*): Method *A* (orthophosphoric acid, 60 min, 100°C, 71%). M.p. 123—125°C. IR spectrum (CS_2, cm^{-1}): 3075, 3050, 3020, 2945, 2908, 2860, 972. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 1·88—2·12 (m, 6 H, CH_2); 2·50—2·75 (m, 6 H, CH_2); 7·22 (s, 5 H, C_6H_5). For $C_{14}H_{17}I$ (312·2) calculated: 53·86% C, 5·49% H, 40·65% I; found: 54·14% C, 5·56% H, 39·95% I.

1,4-*Dichlorobicyclo*[2.2.2]*octane* (VIIIa): Method *A* (orthophosphoric acid, 90 min, 150°C, 46%); method B (polyphosphoric acid–$POCl_3$, 45 min, 105°C, 70%). M.p. 234—235°C (ref.[2] m.p. 233·5—234·5°C; ref.[9] m.p. 239—240°C). IR spectrum ($CHCl_3$, cm^{-1}): 2970, 2950, 2925, 2872, 1460, 1345, 990. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 2·18 (s).

1,4-*Dibromobicyclo*[2.2.2]*octane* (VIIIb): Method *A* (orthophosphoric acid, 60 min, 140°C, 37%); method *B* (polyphosphoric acid, 45 min, 130°C, 66%). M.p. 256—258°C (ref.[14] m.p. 251°C; ref.[2] m.p. 256·6—258°C. IR spectrum ($CHCl_3$, cm^{-1}): 3030, 2970, 2925, 2875, 1605, 1460, 1345, 975. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 2·36 (s).

1,4-*Diiodobicyclo*[2.2.2]*octane* (VIIIc): Method *A* (polyphosphoric acid, 45 min, 100°C, 74%; orthophosphoric acid, 60 min, 100°C, 20%). M.p. 245—246°C (ref.[14] m.p. 240°C; ref.[2] m.p. 245—246°C). IR spectrum ($CHCl_3$, cm^{-1}): 3020, 3015, 2960, 2920, 2870, 1455, 965, 945. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 2·57 (s).

1-*Chloro*-4-*hydroxybicyclo*[2.2.2]*octane* (IXa): Method *A* (orthophosphoric acid, 90 min, 150°C, 9%). M.p. 172—173°C (ref.[9] m.p. 173—175°C). IR spectrum ($CHCl_3$, cm^{-1}): 3600, 3030, 2960, 2920, 2870, 1460, 1350, 1110, 1095, 960, 840.

1-*Bromo*-4-*hydroxybicyclo*[2.2.2]*octane* (IXb): Method *A* (orthophosphoric acid, 60 min, 140°C, 28%). M.p. 163—165°C. IR spectrum ($CHCl_3$, cm^{-1}): 3600, 3015, 2960, 2920, 2870, 1460, 1345, 1110, 1095, 805. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 1·57 (s, 1 H, OH); 1·7—1·98 (m, 6 H, CH_2); 2·25—2·5 (m, 6 H, CH_2). For $C_8H_{13}BrO$ (205·1) calculated: 46·84% C, 6·39% H, 38·97% Br; found: 46·86% C, 6·43% H, 38·65% Br.

1-*Iodo*-4-*hydroxybicyclo*[2.2.2]*octane* (IXc): Method *A* (orthophosphoric acid, 60 min, 100°C, 6%), M.p. 159·5—160·5°C. IR spectrum ($CHCl_3$, cm^{-1}): 3600, 3020, 2960, 2870, 1460, 1345, 1100, 1090, 940. For $C_8H_{13}IO$ (252·1) calculated: 38·11% C, 5·20% H, 50·34% I; found: 38·61% C, 5·22% H, 50·41% I.

1-*Bromo*-4-*chlorobicyclo*[2.2.2]*octane* (XI): By heating of *IXb* with NaCl in 100% H_3PO_4 at 120—130°C for 1 h. Gas chromatography (Carbowax 2000, t_{column} 160°C) showed the main reaction product 80% *XI* (retention time 9 min 30 s) besides 12·5% dichloro derivative *VIIIa* (retention time 5 min 45 s) and 7·5% dibromo derivative *VIIIb* (retention time 15 min 15 s.)

Phosphoric Acid 4-Methylbicyclo[2.2.2]oct-1-yl Ester Dichloride (*X*)

Mixture of 0·97 g *IIa* and 13 ml freshly distilled $POCl_3$ was refluxed with a drop of hexamethylphosphoramide for 7 h. The excess $POCl_3$ was distilled off, the residue was diluted with chloroform (10 ml) and decomposed with ice. The chloroform solution was shaken with ice-cold 5% $KHCO_3$ solution, with water, and dried with $CaCl_2$. After evaporation of chloroform the residue was sublimed at $1·3 . 10^3$ Pa. Yield of *X* was 1·42 g (80%), m.p. 39—40°C. For $C_9H_{15}Cl_2O_2P$ (257·1) calculated: 42·04% C, 5·88% H, 27·58% Cl; found: 41·98% C, 5·98% H, 27·36% Cl. IR spectrum (CS_2, cm^{-1}): 2945, 2916, 2858, 1308, 1295, 1025, 1005, 992. ^{1}H-NMR spectrum (CCl_4), chemical shift (ppm): 0·82 (s, 3 H, CH_3); 1·5—1·8 (m, 6 H, CH_2); 2·0—2·3 (m, 6 H, CH_2).

Reactions of Bicyclo[2.2.2]octan-1-ols with 1,1-Dichloroethylene

a) Mixture of 3·5 g *IIa*, 50 ml 1,1-dichloroethylene and 24 g 100% H_3PO_4 was heated in a sealed ampoule at 70°C for 7 h with intermittent shaking. After cooling the mixture was decomposed with ice and extracted with 3·30 ml $CHCl_3$. The chloroform extracts were shaken with 50 ml *c.* 20% sodium hydroxide and water, dried, the solvent was evaporated, and the residue was sublimed at 70°C at $1·6 . 10^3$ Pa. Yield 0·9 g (23%) *VIa*, m.p. 76—77°C. The alkaline extract was acidified with concentrated hydrochloric acid, and the separated solid (raw 4-methylbicyclo-[2.2.2]oct-1-ylacetic acid (*XII*)) was purified by repeated precipitation. Yield 0·6 g (13·2%): m.p. 83—84°C. For $C_{11}H_{18}O_2$ (182·3) calculated: 72·49% C, 9·95% H; found: 72·55% C, 9·87% H. IR spectrum ($CHCl_3$, cm^{-1}): 3510, 2940, 2860, 1710, 1300, 1140, 1115. ^{1}H-NMR spectrum ($CDCl_3$), chemical shift (ppm): 0·76 (s, 3 H, CH_3); 1·44 (m, 12 H, CH_2); 2·1 (s, 2 H, CH_2); 11·1 (s, 1 H, COOH).

b) Mixture of 0·4 g *III*, 8 ml 1,1-dichloroethylene and 10 ml 100% H_3PO_4 was heated in an autoclave at 100°C for 1 h. The treatment analogous to that of *IIa* only gave 68% yield of *VIIa*, m.p. 83—85°C.

Dehalogenation of Bromobicyclo[2.2.2]octanes *VIb*, *VIIIb* and *IXb*

a) Solution of 0·9 g *VIb* and 0·45 g solid KOH in 20 ml ethanol was treated with 1·5 g Raney nickel and hydrogen under normal pressure at 20—25°C. After usual treatment the residue was distilled in vacuum. The fraction boiling within 46 to 48°C at 2 . 10^3 Pa was taken; n_D^{24} = = 1·4604. Yield of 1-methylbicyclo[2.2.2]octane (*XIV*) was 0·3 g (55%). For C_9H_{16} (124·2) calculated: 87·02% C, 12·98% H; found: 86·93% C, 13·27% H. Ref.[11] gives b.p. 145°C at 1 . 10^5 Pa; n_D^{26} 1·4572.

b) Solution of 1·2 g *VIIIb* and 0·9 g KOH in 20 ml ethanol was treated with 2 g Raney nickel and hydrogenated and worked up in similar way as in the preceding case. Sublimation of the residue at 60°C at 1·3 . 10^3 Pa gave 0·25 g (50·5%) bicyclo[2.2.2]octane (*XV*), m.p. 170·5—173°C (ref.[19–21] m.p. 164·3 to 173°C).

c) Hydrogenation of mixture of 0·4 g *IXb*, 0·2 g KOH, 0·8 g Raney nickel and 10 ml ethanol and subsequent sublimation (120°C and 1·3 . 10^3 Pa) gave 73% yield of 1-hydroxybicyclo[2.2.2]-octane (*I*), m.p. 214—216°C (sealed capillary) which was proved identical with the standard prepared by independent way[5].

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