NEW SYNTHESIS OF BICYCLO[1.1.0]BUTANE HYDROCARBONS

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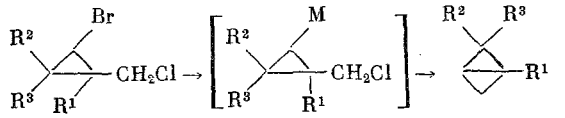
Until now the principal method for synthesizing bicyclo[1.1.0]butanes (BCB) has been the closing of a bridge bond in difficult-to-obtain cyclobutane functional derivatives. While the yield of BCB itself by this method is 75%, for other hydrocarbons of this series the yields do not exceed 18-40% [1, 2]. Intermolecular introduction of a substituted cyclopropylidene at the substituent C–H bond is of limited value for BCB synthesis because it gives good results only for tetraalkylcyclopropylidenes [3]. Electrochemical and photochemical methods have not been widely developed.

The present work presents a new synthesis of BCB hydrocarbons by 1,3-cyclization of 1-bromo-2-chloromethylcyclopropanes [4]; at the same time a simple two-step synthesis of the latter from available allyl halides has been developed.

Cyclization of 1,3-dihalides by the action of metals is one of the best known methods for synthesizing cyclopropanes [5]; however, the use of this reaction to close the second three-member ring to produce the BCB skeleton has escaped the attention of investigators and has never been studied.

We have shown that by reaction with Mg in THF or Na in dioxane both 1-bromo-2-chloromethylcyclopropane and its homologs with CH_3 groups in different positions can undergo cyclization to give BCB (Scheme 1). The experimental results are given in Table 1.

Scheme 1



(Ia–d) (IIIa–d) (IIa–d)

$R^1 = R^2 = R^3 = H$ (a); $R^1 = Me$, $R^2 = R^3 = H$ (b); $R^1 = R^2 = H$, $R^3 = Me$ (c); $R^1 = H$, $R^2 = R^3 = Me$ (d).

1,3-Cyclization of (Ia-d) to form BCB (IIa-d) is accompanied by the formation of unsaturated compounds (10-40% based on BCB). The PMR spectra of (IIa,b,d) agree with those published [1, 6, 7]. The structure of (IIc) was confirmed by its PMR spectrum (multiplet at 0.4-0.5 ppm, typical of endoprotons of BCB CH_2 groups), and its Raman spectrum (valence vibration frequencies in the 3038-2960 cm^{-1} region, specific for the bicyclobutane system [8]). The olefin structures were established by comparison of GLC and PMR data with those of authentic samples.

In our opinion, BCB and the dienes are formed by different mechanisms. From the data on the stereochemistry of dihalide 1,3-cyclization by the action of metals and the concepts of MO interaction, together with the principle of retention of orbital symmetry, we conclude that the reaction proceeds via a γ-halometalorganic compound that cyclizes by intramolecular nucleophilic substitution during the interaction of σ_{CM} and σ^*_{CX} orbitals [9]. Starting from these concepts the most likely scheme of 1,3-cyclization of Ia-d to BCB (IIa-d) is the intermediate formation of 1-metal-2-chloromethylcyclopropanes (IIIa-d), which cyclize to (IIa-d) with elimination of MX. According to [10], such cyclization can take place with either cis or trans approach of the interacting MO, so that cyclization is possible with either cis or trans orientation of M and the CH_2Cl group in (IIa-d). The proposed mechanism of (IIa-d) formation ac-

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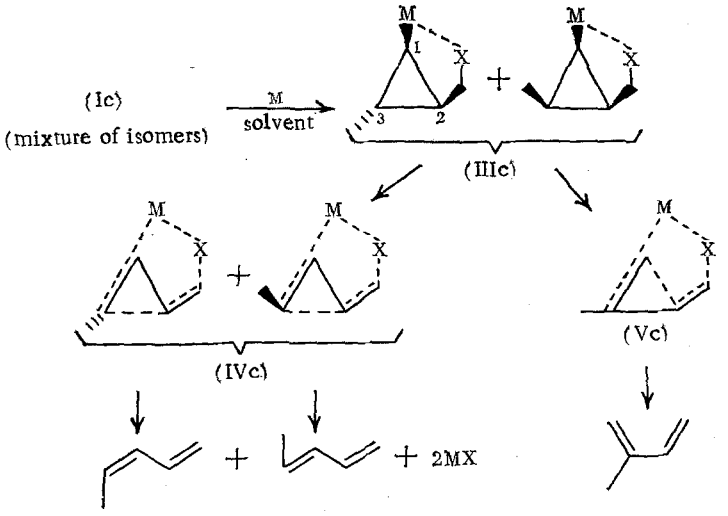
TABLE 1. 1,3-Cyclization of 1-Bromo-2-chloromethylcyclopropanes

Starting compound	Metal	Solvent	Overall hydrocarbon yield, %	Composition of hydrocarbon mixture, %	
				bicyclobutanes (II)	unsaturated compounds
(Ia)	Mg	THF	70	70	1,3-Butadiene, 30
(Ib)	Mg	THF	60	90	Diene mixture, 10
(Ic)	Mg	THF	50	63	cis-1,3-Pentadiene, 20 trans-1,3-Pentadiene, 10 2-Methyl-1,3-butadiene, 7
(Id)	Na	1,4-dioxane	72	40	4-Methyl-1,3-butadiene, 40 3,3-Dimethylbutene-1, 20

cording to [9] excludes the formation of an intramolecular M—Cl coordination bond. Formation of such a bond can explain diene formation in this reaction. Scheme 2, using (Ic) as an example, shows a probable mechanism of diene formation. Formation of the M—X coordination bond initiates cyclic electron transfer to the six-center transition states (IVc) or (Vc), which lead to scission of the C^2—C^3 or C^1—C^2 ring bonds, elimination of the metal salt, and diene formation.

Scheme 2



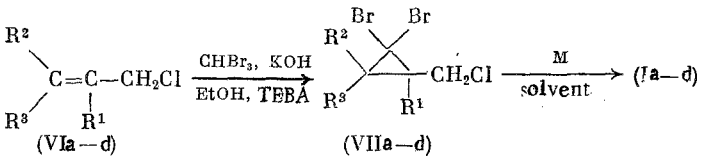
According to this mechanism, diene formation is possible, in contrast to the formation of (IIa-d), only with cis orientation of M and the CH_2X group, since only in this orientation can the coordination bond between metal and halogen be closed.

Formation of t-BuCH=CH_2 in the reaction of (Id) with Na in 1,4-dioxane is apparently related to the reduction of intermediate organosodium compounds and their allylic isomerization.

Our synthesis of BCB is limited by the availability of starting compounds (Ia-d). We therefore developed a synthesis of the latter by dibromocyclopropanation of available allyl chlorides followed by selective reduction of one Br (Scheme 3). The dibromocyclopropanation was carried out (by a method that we previously proposed) by generation of CBr_2 in nonaqueous medium by the action of solid KOH in the presence of triethylbenzylammonium chloride (TEBA) [11]. In the present work the method was modified somewhat. The reaction was carried out in CH_2Cl_2 with addition of a small amount of EtOH; this enabled us to use a nearly equimolar ratio of allyl halide and $CHBr_3$, and gave 50-70% yields, based on separated product. When applied to allyl halides, this procedure has definite advantages over the usual Makosza procedure, which uses aqueous alkali [12]. In control experiments by the procedure of [12] the yields were significantly lower. Thus (VIIa) was formed from (VIa) in 35-40% yield.

The selective reduction of one Br atom was carried out by two procedures: Zn activated with conc. HCl in MeOH medium [13] and Mg in THF—MeOH [14]. In both cases the yield of monobromide reached 70% and the allylic Cl was not touched.

Scheme 3



M = Zn, solvent MeOH (VIIa, b, d); M = Mg, solvent THF–MeOH (VIIa-c).

Thus our synthesis of bicyclobutanes can be considered not only as general for this class of hydrocarbons, but also as the most practical of present-day methods.

EXPERIMENTAL

PMR spectra were obtained on BS-467 (60 MHz) and BS-497 (100 MHz) instruments; chemical shifts are given in ppm on the σ-scale. Raman spectra were obtained on a PHO Coderg laser spectrometer. GLC analysis was carried out on a PYE-104 instrument; glass column 1.5 m, liquid phase 3% SE-30, solid support GAS CHROM 80-100 mesh, at 60-120°; glass column 2.0 m, liquid phase 25% β,β'-dihydroxypropionitrile, solid support C-22 Celite, 80-100 mesh, at 25-60°; and on a LKhM-8MD instrument, capillary column, liquid phase diethylene glycol dibutyrate.

GENERAL PROCEDURE FOR SYNTHESIS OF 1,1-DIBROMO-2-CHLOROMETHYL-CYCLOPROPANES

To a stirred mixture of 1 mole of VIa-d, 2.5 mole of KOH granules, 1.6 g TEBA, and 8 ml EtOH in 200 ml of CH_2Cl_2 was added 0.8 mole $CHBr_3$ slowly. After the addition the reaction mixture was stirred another 2-3 h. $CHBr_3$ consumption was monitored by GLC. The precipitate was filtered off, the organic layer was washed and dried, the solvent was evaporated, and the residue was vacuum-distilled. (VIIa-d) were obtained.

1,1-Dibromo-2-chloromethylcyclopropane (VIIa). Yield 50%, bp 95-99°C (22 mm). PMR spectrum (CCl_4, TMS): 1.1-1.57 m (1H), 1.73-2.24 m (2H), 3.42-3.82 m (2H).

1,1-Dibromo-2-methyl-2-chloromethylcyclopropane (VIIb). Yield 51%, bp 110-112°C (25 mm). PMR spectrum (CCl_4, C_6H_6): 1.47 s (3H), 1.51-1.55 m (2H), 3.61-3.64 (2H).

1,1-Dibromo-3-methyl-2-chloromethylcyclopropane (VIIc). Yield 53%, bp 106-108°C (21 mm).

1,1-Dibromo-3,3-dimethyl-2-chloromethylcyclopropane (VIId). Yield 70%, bp 115-118°C (25 mm). PMR spectrum (CCl_4, C_6H_6): 1.30 s (3H), 1.45 s (3H), 1.68 t (1H), 3.25-3.92 m (2H).

The Br atom was reduced by Zn in MeOH (method *a*) or by Mg in THF–MeOH (method b). *a*) To a stirred suspension of 2 moles of Zn dust in 200 ml MeOH was added for activation at 0°C a solution of 10 ml conc. HCl in 30 ml MeOH. The mixture was cooled to 0°C and a solution of 0.2 mole of (VIIa-c) in 40 ml MeOH was added dropwise at such a rate that the temperature did not rise above 10°. The mixture was stirred for 2-3 h and consumption of the starting material was monitored by GLC. The precipitate was filtered off and washed with methanol. The filtrate was diluted with water and extracted with pentane. The extract was washed and dried, the solvent was evaporated, and the residue was vacuum distilled to give (Ia-c).

b) To 0.5 mole of Mg turnings in 200 ml of boiling THF was added 0.3 g $HgCl_2$ and the mixture was boiled for 10 min. A solution of 0.3 mole of (VIIa,b,d) in 40 ml MeOH was added at such a rate that the mixture boiled very vigorously . The mixture was boiled another 2 h and filtered. The filtrate was diluted with water and extracted with pentane. The organic extract was washed and dried, the solvent was evaporated, and the residue was vacuum distilled to give Ia,b,d.

1-Bromo-2-chloromethylcyclopropane (Ia). Yield 70% (a), 65% (b), bp 82-83°C (50 mm). PMR spectrum (CCl_4, HMDS): 0.63-1.58 m (3H), 2.7 and 2.9 m (1H), 3.2-3.7 m (2H), mixture of isomers.

1-Bromo-2-methyl-2-chloromethylcyclopropane (Ib). Yield 70% (a) and 70% (b), bp 82-85°C (25 mm). PMR spectrum (CCl_4, C_6H_6): 0.89 m and 1.27 m (2H), 1.23 s and 1.36 s (3H), 2.6 m and 2.83 m (1H), 3.15-3.70 m (2H), mixture of cis and trans isomers.

1-Bromo-3-methyl-2-chloromethylcyclopropane (Ic). Yield 70% (b), bp 83-85°C (25 mm). PMR spectrum (C_6H_6, C_6H_6): 0.82-1.45 m (5H), 2.7-3.05 m (1H), 3.25-3.83 m (2H), mixture of cis and trans isomers.

1-Bromo-3,3-dimethyl-2-chloromethylcyclopropane (Id). Yield 70% (a), bp 83-85°C (20 mm). PMR spectrum (CCl_4, HMDS): 0.88-1.48 m (7H), 2.61 d and 2.71 d (1H), 3.03-3.91 m (2H), mixture of cis and trans isomers.

Bicyclo[1.1.0]butane (IIa). To 0.3 mole Mg turnings activated with 0.1 g I_2 stirred in 150 ml of boiling THF with an Ar stream was added 2 ml of 1,2-dibromoethane. After the start of the vigorous reaction 0.2 mole of (Ia) was added slowly, the mixture was heated another 2 h, and the volatile fraction was blown out by a slow Ar stream into a trap cooled to −78°C. When heating was finished the contents of the trap were passed at ~20°C through two wash bottles with 10% NaOH and a drying column containing K_2CO_3 and BaO. There was obtained 7.6 g (70%) of a gas mixture consisting of 70% of (IIa) and 30% of 1-3-butadiene (by GLC and PMR).

1-Methylbicyclo[1.1.0]butane (IIb). The procedure was the same as for the synthesis of (IIa), but as it accumulated the hydrocarbon mixture was periodically distilled into THF in a receiver cooled to −78°C. At the end of the reaction the distillate was washed free of THF with cold brine, and the hydrocarbon layer was dried and distilled. There was obtained a mixture (60%) consisting of 90% of (IIb) and 10% of unsaturated compounds (by PMR), bp 32-34°C. PMR spectrum (CCl_4, TMS): 0.44 m (endo-2H), 1.0 m (1H methine), 1.28 d (exo-2H), 1.55 br.s (3H).

2-Methylbicyclo[1.1.0]butane (IIc). The procedure was the same as for (IIb). There was obtained 50% of a hydrocarbon mixture consisting of 63% (IIc), 20% cis-piperylene, 10% trans-piperyline, and 7% isoprene (by GLC), bp 39-41°. PMR spectrum of (IIc) (CCl_4, TMS): 0.47 m (endo-1H), 0.84 m (exo-1H), 0.96 s (3H, endo-CH_3), 1.16 m (2H-methine), 1.37 m (exo-1H). Raman spectrum: 1250, 2925, 2960, and 3035 cm^{-1}.

2,2-Dimethylbicyclo[1.1.0]butane, (IId). To 0.4 mole Na in 50 ml boiling dioxane, stirred in a Ar stream, was added 39.4 g (0.2 mole) of (Id). The reaction mixture was boiled for 2 h and the hydrocarbons were blown with Ar into a trap cooled to −78°C. At the end of the reaction the distillate was washed free of dioxane with cold brine, dried, and distilled. There was obtained 11.8 g (72%) of a mixture of 40% of (IId), 40% 4-methylpenta-1,3-diene, and 20% tert-butylethylene, bp 64-65°. PMR spectrum of (IId) (CCl_4, HMDS): 0.8 s (3H, endo-CH_3), 1.05 s (3H, exo-CH_3), 1.20 m (3H), 1.60 m (exo-1H).

CONCLUSIONS

A new general synthesis is proposed for bicyclo[1.1.0]butanes, by 1,3-cyclization of 1-bromo-chloromethylcyclopropanes, and a two-step synthesis of the latter from available allyl chlorides has been developed.

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RADICAL REACTIONS OF 1,1-DIETHOXYMETHANE AND ETHYL FORMATE WITH TRIMETHYLVINYLSILANE

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Radical telomerization of ethylene with linear formals proceeds by cleavage of an α-C—H bond in an alkoxy group and leads to the formation of asymmetric formals [1]:

$$CH_2(OEt)_2 \xrightarrow{RO^\cdot} CH_2(OEt)\dot{O}CHMe \xrightarrow{nCH_2=CH_2} CH_2(OEt)OCH(Me)(CH_2CH_2)_nH \quad (1)$$

In the present work, the radical addition of diethoxymethane (DEM) and ethyl formate to trimethylvinylsilane (TVS) initiated by tert-butyl peroxide (TBP) is investigated (Table 1). The use of unsaturated heteroorganic compounds as monomers is of interest both from the point of view of the synthesis of various carbofunctional compounds containing a C—heteroatom bond as well as from theoretical standpoints, since the nature of the monomer has a vital influence on the course of radical addition reactions and telomerization [2].

It could be expected that the reaction of TVS with DEM would proceed according to scheme (1) with the formation of the asymmetric formal (F), $CH_2(OEt)OCH(Me)CH_2CH_2SiMe_3$. However, preparative NMR (see Experimental section) showed that in the reaction mixture there is present only the silicon-substituted formate (T_a), formation of which can be shown by the following scheme:

$$CH_2(OEt)_2 \xrightarrow{RO^\cdot} CH_2(OEt)\dot{O}CHMe \xrightarrow{CH_2=CHSiMe_3} \underset{(A)}{CH_2(OEt)OCH(Me)CH_2\dot{C}HSiMe_3}$$
$$(A) \xrightarrow{1,5\text{-}H} \underset{(B)}{\dot{C}H(OEt)OCH(Me)CH_2CH_2SiMe_3} \quad (2)$$
$$(B) \xrightarrow{-Et^\cdot} \underset{(T_a)}{HC(O)OCH(Me)CH_2CH_2SiMe_3}$$

Until now, rearrangement of the type A → B for dialkoxymethanes has not been observed. An analogous rearrangement was studied previously for the case of the telomerization of ethylene with dimethoxyethane, where H migrates from the tertiary C atom in the radical $MeCH(OMe)\cdot OCH_2(CH_2CH_2)_n\bullet$ [3].

Since ethyl formate is formed by radical conversions of the very same diethoxymethane, it is possible to present another pathway for formation of T_a:

$$HCO_2Et \xrightarrow{RO^\cdot} \begin{cases} \longrightarrow HCO_2\dot{C}HMe \\ \longrightarrow \dot{C}O_2Et \end{cases} \quad (3)$$
$$HCO_2\dot{C}HMe + CH_2=CHSiMe_3 \rightarrow \underset{(C)}{HCO_2CH(Me)CH_2\dot{C}HSiMe_3} \xrightarrow{HD^*} T_a$$

Moreover, the isomeric compound T_b can also be formed in this reaction:

$$\dot{C}O_2Et + CH_2=CHSiMe_3 \xrightarrow{HD} \underset{(T_b)}{Me_3SiCH_2CH_2CO_2Et} \quad (4)$$

*HD = hydrogen donor.

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