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Ring-Opening Products of 1-Phenyltricyclo[4.1.0.0^{2,7}]-heptane and 2-Phenyltricyclo[4.1.0.0^{2,7}]heptane in SiO_2

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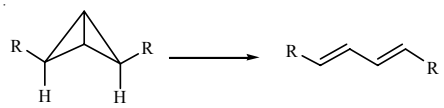
Treatment of the mixture of 1-phenyltricyclo[4.1.0.0^{2,7}]-heptane (**8**) and 2-phenyltricyclo[4.1.0.0^{2,7}]heptane (**15**) with SiO_2 gave the ring-opening products *i.e.*, 2-phenylbicyclo-[4.1.0]hept-2-ene (**19**), 1-phenylbicyclo[4.1.0]hept-2-ene (**20**), (1E,4Z)-2-phenylcyclohepta-1,4-diene (**21**), (E)-3-phenylcyclohept-3-en-1-ol (**22**) and 1-phenylbicyclo[4.1.0]-heptan-2-ol (**23**). In addition to these products, phenyl (1-phenylbicyclo[4.1.0]heptan-2-yl)sulfane (**18**) and (Z)-phenyl(2-phenylcyclohept-3-enyl)sulfane (**17**) were obtained by the addition of PhSH to the mixture of **8** and **15**. The addition of bromine to the mixture of **8** and **15** gave 2-bromomethylbiphenyl as the main product.

Key Words: Ring-opening reaction, 1-Phenyltricyclo-[4.1.0.0^{2,7}]heptane, 2-Phenyltricycle[4.1.0.0^{2,7}]heptane, SiO_2.

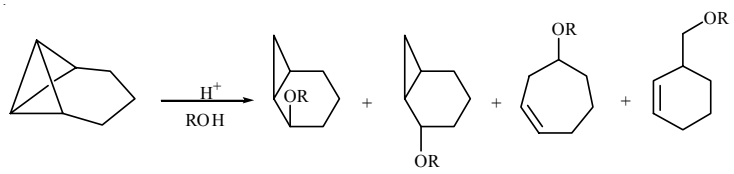
INTRODUCTION

The bicyclo[1.1.0]butane ring system, with its strain energy of over 60 kcal/mol[1,2], has been the subject of theoretical and experimental investigations. Mechanistic aspects of thermal[3], cationic[4] or metal-promoted[5] isomerization of bicyclobutane ring are well established. Of particular interest have been studies of the ring opening to 1,3-butadienes. When the ring opening of bicyclo[1.1.0]butane **1** to 1,3-butadiene **2** is carried out thermally, the central bond remains intact while two opposite peripheral C-C bonds are broken in formation of the product[6-8].



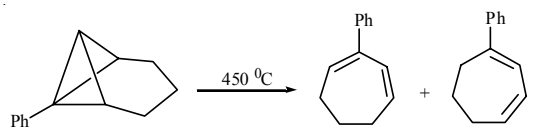
1 **2** (1)

Similarly, acid-catalyzed ring-opening reactions of tricyclo[4.1.0.0^{2,7}]-heptane (**3**) system has been investigated by Wiberg and Szeimies[9]. They reported that the norcarane (**4, 5**) and homoallylstructures (**6, 7**) were occured from the reaction of tricyclo[4.1.0.0^{2,7}]heptane (**3**) with H^+ in ROH.



3 4 5 6 7 (2)

Fujita *et al.*[10] obtained the ring-opening products (1,3-dienes) **9** and **10** from the rearrangement of 1-phenyltricyclo[4.1.0.0^{2,7}]heptane (**8**) at 450 ºC.



8 9 10 (3)

In this paper, we report the ring-opening products of 1-phenyltricyclo-[4.1.0.0^{2,7}]heptane (**8**) and 2- phenyltricycle[4.1.0.0^{2,7}]heptane (**15**) in SiO_2. In addition of these reactions, the addition of PhSH and Br_2 to 1-phenyltricyclo[4.1.0.0^{2,7}]heptane (**8**) and 2-phenyltricycle[4.1.0.0^{2,7}]heptane (**15**) were also investigated.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded with Varian 200 and Varian Mercury 400 instruments. As internal standards served TMS (δ 0.00) for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR spectroscopy, *J* values are given in Hz. IR spectra were recorded on a Jasco FT/IR-430 spectrometer. Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer. All column chromatographies were performed on silica gel (60-230 mesh, Merck).

Reaction of 7,7-dibromo-1-phenylbicyclo[4.1.0]heptane (14) with *n*-BuLi: To a stirred solution of **14** (4 g, 12,1 mmol) in 50 mL of *n*-hexane was added *n*-BuLi (9 mL, 12.2 mmol) and stirred at room temparature for 3 h. The mixture was washed with water (100 mL) and dried (Na_2SO_4). The solvent was evaporated and the residue (1.76 g) was chromatographed on silica gel with *n*-hexane/$CHCl_3$ (8:2) as the eluent. The first fraction was unidentified product (350 mg). Second fraction was 1-phenylbicyclo-[4.1.0]hept-2-ene (**19**)[11] (85 mg, 5 %). Third fraction was 2-phenylbicyclo-[4.1.0]hept-2-ene (**20**)[12] (250 mg, 14 %). The fourth fraction was (1E,4Z)-2-phenylcyclohepta-1,4-diene (**21**) (145 mg, 8 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37-7.27 (m, 5H, ArH), 6.09 (t, *J* = 6.8 Hz, 1H, olefinic H1), 5.73-5.69 (m, 2H, olefinic H4, H5), 3.29-3.28 (m, 2H), 2.51-2.46 (m, 2H), 2.28-2.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.98, 131.29, 128.98,

128.59, 127.40, 127.04, 126.69, 126.00, 30.98, 29.94, 26.44. IR (CCl_4) 3054, 2923, 2852, 1652, 1635, 1558, 1488, 1459, 755, 698 cm^{-1}. Anal. calcd. (%) for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found (%): C, 91.58; H, 8.48. The fifth fraction was (E)-3-phenylcyclohept-3-en-1-ol (**22**) (250 mg, 13 %), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.29 (m, 2H, ArH), 7.27-7.24 (m, 2H, ArH), 7.21-7.15 (m, 1H, ArH), 6.17 (t, *J* = 6.9 Hz, 1H, olefinic), 3.81 (ddt as "t", *J* = 8.9, 3.3, 2.2 Hz, 1H, H1), 2.87 (dd, *J* = 14.5, 9.2 Hz, A part of AB system, 1H, H2), 2.78 (dt, *J* = 14.5, 1.8 Hz, B part of AB system, 1H, H2), 2.25-2.19 (m, 2H) 2.12-2.06 (m, 1H), 1.84-1.77 (m, 1H), 1.76 -1.64 (m, 1H), 1.60 (broad s, 1H, -OH), 1.48-1.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.34, 138.84, 131.98, 128.25, 126.62, 125.87, 68.44, 41.31, 41.15, 28.17, 23.34. IR ($CHCl_3$) 3380, 3073, 3027, 2921, 2836, 1596, 1457, 1440, 1307, 1029, 852, 755, 698 cm^{-1}. Anal. calcd. (%) for $C_{13}H_{15}O$: C, 82.94; H, 8.57. Found (%): C, 82.96; H, 8.48. Sixth fraction was 1-phenyl-bicyclo[4.1.0]heptan-2-ol (**23**) (350 mg, 18 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.35 (m, 2H, ArH), 7.33-7.29 (m, 2H, ArH), 7.25-7.19 (m, 1H, ArH), 4.24-4.20 (dd, *J* = 9.7, 5.7 Hz, 1H, CHOH), 2.18-2.05 (m, 1H), 1.62-1.55 (m, 2H), 1.54-1.49 (m, 2H), 1.39 (br s, 1H, -OH),1.32-1.06 (m, 2H), 0.76-0.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.44, 129.61, 128.61, 128.45, 72.96, 30.08, 23.72, 22.88, 21.61, 18.96, 15.36. IR ($CHCl_3$) 3370, 3054, 3018, 2927, 2852, 1490, 1444, 1307, 1068, 927, 790, 750 cm^{-1}. Anal. calcd. (%) for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found (%): C, 82.92; H, 8.68.

Reaction of the mixture 8 and 15 with PhSH: To the mixture of **8** and **15** (1 g, 6 mmol) was added thiophenol (0.6 mL, 6 mmol) and stirred at room temperature for 2 h. The reaction mixture was washed with a solution of $NaHCO_3$ and water and dried on Na_2SO_4. The solvent was removed in vacuum. The crude product was submitted on a silica gel column and eluted with *n*-hexane/$CHCl_3$ (7:3). The first fraction was phenyl(1-phenyl-bicyclo[4.1.0]heptan-2-yl)sulfane (**18**) (430 mg, 27 %). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.41-7.19 (m, 10H, ArH), 4.03-3.94 (dd, *J* = 6.2, 2.4 Hz, 1H), 2.28-2.16 (m, 2H), 1.96-1.83 (m, 3H), 1.62-1.59. (m, 2H), 1.33-1.31 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 145.44, 135.24, 133.63,130.61, 129.65, 129.06, 128.48, 126.04 52.66, 42.44, 30.08, 23.72, 20.41, 16.76, 14.38. IR (CCl_4) 3033, 3018, 2933, 2862, 1540, 1506, 1444, 1263, 1178, 1083, 1022, 786, 761, 696 cm^{-1}. Anal. calcd. (%) for $C_{19}H_{20}S$: C, 81.38; H, 7.99; S, 11.43. Found (%): C, 81.58; H, 7.74; S, 11.58.

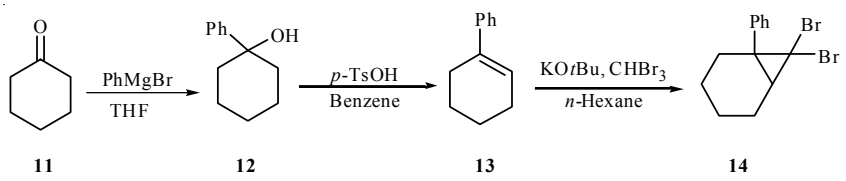
The second fraction was (Z)-phenyl(2-phenylcyclohept-3-enyl)sulfane (**17**) (300 mg, 19 %). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.06-8.01 (m, 2H, ArH), 7.67-7.49 (m, 8H, ArH), 6.06-5.96 (m, 1H, olefinic), 5.84-5.76 (m, 1H, olefinic), 4.16-4.13 (m, 1H), 2.18-2.06 (m, 1H), 2.04-1.61 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.44, 134.24, 132.63, 129.61, 128.61, 128.56, 128.45, 127.04, 49.96, 41.38, 33.72, 32.88, 28.61, 26.66, 23.36. IR

(CCl_4) 3079, 3054, 3023, 2938, 2857, 1581, 1475, 1440, 1087, 1022, 786, 755, 700 cm^{-1}. Anal. calcd. (%) for $C_{19}H_{20}S$: C, 81.38; H, 7.99; S, 11.43. Found (%): C, 81.08; H, 7.69; S, 11.63.

Reaction of the mixture 8 and 15 with PhSH with Br_2: To the mixture of **8** and **15** (1 g, 6 mmol) was added bromine (0.3 mL) and stirred at room temperature for 0.5 h. The reaction mixture was washed with a solution of $NaHCO_3$ and water and dried on Na_2SO_4. The solvent was removed in vacuum. The crude product was submitted on a silica gel column and eluted with *n*-hexane. The 2-bromomethylbiphenyl was isolated as the main product in yield of 22 %. (0.32 g, colourless crystal, m.p. 45-46 ºC). ^1H NMR (200 MHz, $CDCl_3$) δ = 7.69-7.64 (m, 2H, ArH), 7.58-7.36 (m, 7H, ArH), 4.63 (s, 2H, CH_2Br); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 142.64, 141.92, 139.72, 136.32, 131.23, 130.45, 129.10, 128.38, 127.54, 124.68, 51.19. IR ($CHCl_3$) 3358, 3029, 2948, 2917, 2848 1594, 1479, 1440, 1213, 755, 696 cm^{-1}. Anal. calcd. (%) for $C_{13}H_{11}Br$: C, 63.18; H, 4.49. Found (%): C, 63.38; H, 4.29.

RESULTS AND DISCUSSION

The known starting material **14** was synthesized according to previous reported procedure[13]. Bromobenzene was coverted to the Grignard reagent, which was condensed with cyclohexanone (**11**). Dehydration of the alcohol **17** with *p*-TsOH in benzene gave 1-phenylcyclohexene (**13**) in 86 % overal yield. Dibromocarbene addition to alkene **13** gave the 7,7-dibromo-1-phenylbicyclo[4.1.0]heptane (**14**) (**Scheme-I**). In this reaction, when less than 2 equiv. of $CHBr_3$ and KOtBu were employed, alkene was not consumed completely.

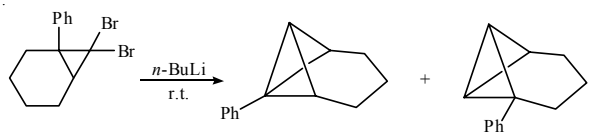


11 **12** **13** **14**

Scheme-I

The treatment of dibromocyclopropane **14** with *n*-BuLi in *n*-hexane at room temperature afforded the two insertion products *i.e.*, 1-phenyltricyclo-[4.1.0.$0^{2,7}$]heptane (**8**) and 2-phenyltricyclo[4.1.0.$0^{2,7}$]heptane (**15**) in total yield of 85 % (**Scheme-II**). The same products were obtained by Stangl *et al.*[11] using the similar method in ratio of 13:1, respectively.

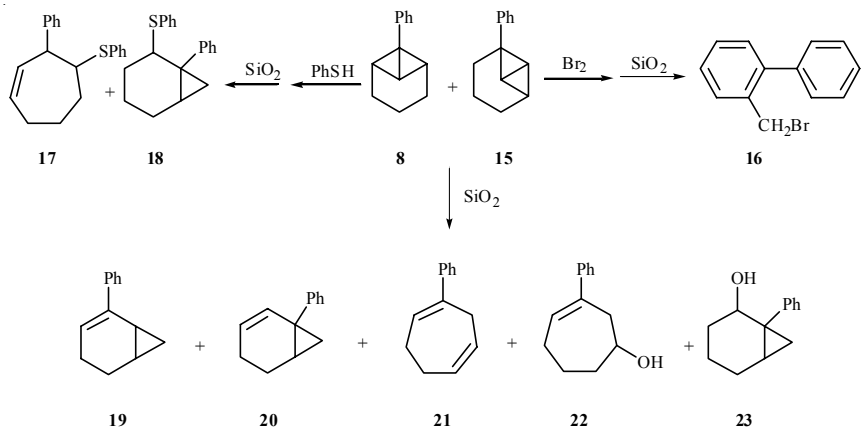
The structures of **8** and **15** were determined on the basis of ^1H and ^{13}C NMR spectra and compared with their published data[11].



14 **8** **15**

Scheme-II

After the successful synthesis and characterization of **8** and **15**, the mixture was submitted to on a silica gel column and eluted *n*-hexane then *n*-hexane/$CHCl_3$. After the column repeated chromatographed, five products **19-23** could be isolated (**Scheme-III**).

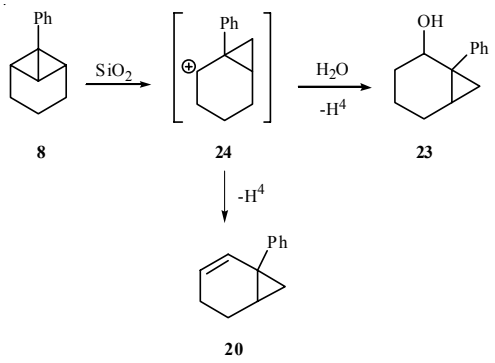


Scheme-III

The structures of norcarane derivatives **19** and **20** were determined on the basis of spectral data and comparison with their published data. The norcarene derivative **20** was previously synthesized in quantitative yield by the reaction of a trace amount of $BF_3(Et_2O)$ with of 1-phenyltricyclo-[4.1.0.$0^{2,7}$]heptane[10] and the reaction of 6-phenylbicyclo[3.2.0]hept-6-ol with *p*-TsOH[12]. Additon, the norcarene derivative **19** was already obtained by Stangl *et al.*[11] from the rearrangement of 1-phenyltricyclo[4.1.0.$0^{2,7}$]-heptane (**8**) in SiO_2.

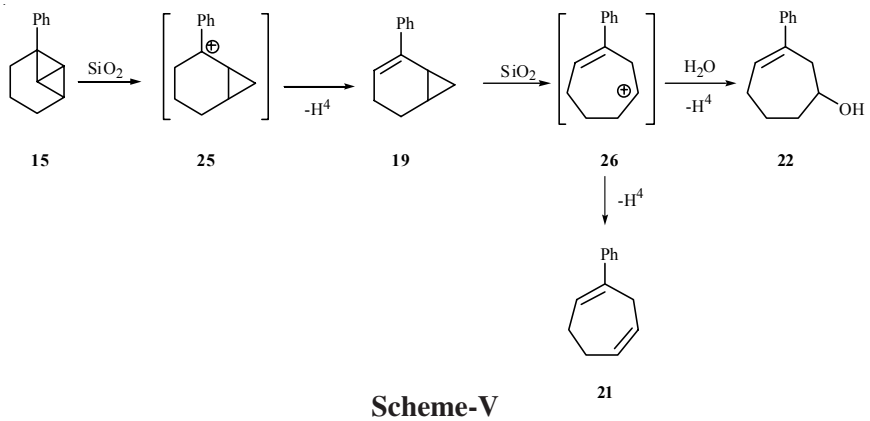
Formation of the compounds **20** and **23** can be explained as shown in **Scheme-IV**. We assume that the cation **24** is formed by the action of SiO_2 to1-phenyltricyclo[4.1.0.$0^{2,7}$]heptane (**8**). Elimination of H^+ ion from **24** gives alkene norcarene **20** and extracted of **24** by H_2O yields alcohol **23** (**Scheme-IV**).

The structures of compounds **21-23** were determined on basis of spectral data. All spectral findings are in good agreement with purposed structures.



Scheme-IV

The formation of compounds **21** and **22** can be explained as shown in **Scheme-V**. The norcarene cation **25** is formed by the action of SiO_2 to 2-phenyltricyclo[4.1.0.$0^{2,7}$]heptane (**15**). The cation **25** converts to norcarene derivative **19** by the elimination of H^+ ion. Then, compound **19** converts to cationic intermediate **26** with ring-opening rearrangement. While the addition of H_2O to **26** gives alcohol **22**, elimination of H^+ ion from **26** yields 1,4-diene **21** (**Scheme-V**).

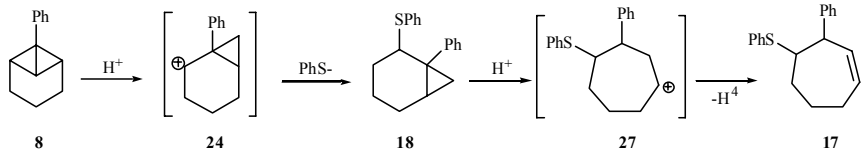


Scheme-V

Addition, to mixture of **8** and **15** was added thiophenol (PhSH) and the reaction mixtutre was submitted on a silica gel column. After the column chromatographed, two PhSH addition products **17** and **18** could be isolated (**Scheme-III**).

The structural assignment of **18** was carried out by the comparison of its NMR spectra with that of the parent compound **23**.

The formation mechanism of **17** and **18** were account for as shown in **Scheme-VI**. The norcarene **18** is formed by the similar mechanism that of **23**.



Scheme-VI

In last, in mixture of **8** and **15**, molecular bromine was added in CCl_4 at 0 ºC. The mixture of brominated products was submitted on a silica gel column and 2-bromomethylbiphenyl **16** was isolated as the main product (**Scheme-III**). The others products were not isolated.

Conclusion

Treatment of the mixture of 1-phenyltricyclo[4.1.0.$0^{2,7}$]heptane (**8**) and 2- phenyltricyclo-[4.1.0.$0^{2,7}$]heptane (**15**) with SiO_2 gave the ring-opening products *i.e.*, 1-phenylbicyclo[4.1.0]-hept-2-ene (**19**), 2-phenylbicyclo-[4.1.0]hept-2-ene (**20**), (1E,4Z)-2-phenylcyclo-hepta-1,4-diene (**21**), (E)-3-phenylcyclohept-3-en-1-ol (**22**) and 1-phenylbicyclo[4.1.0]heptan-2-ol (**23**). Addition, phenyl(1-phenylbicyclo[4.1.0]heptan-2-yl)sulfane (**18**) and (Z)-phenyl(2-phenyl-cyclohept-3-enyl)sulfane (**17**) were obtained by the addition of PhSH to the mixture of **8** and **15**. Addition of Br_2 to the mixture of **8** and **15** gave 2-bromomethylbiphenyl as the main product.

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