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Thermolysis of 1-(1-Aryl-1-bromomethyl)cyclopropyl Bromides: A Reinvestigation

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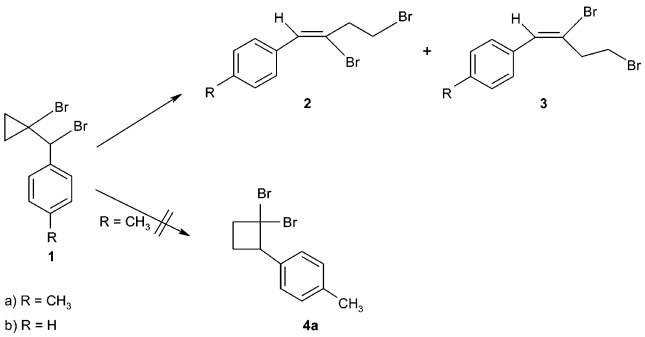
Abstract: Two compounds, the (*Z*)- and (*E*)-isomers of 2,4-dibromo-1-*p*-tolyl-1-butene **2a** and **3a**, respectively, were isolated in 65% total yield when 1-(1-bromo-1-*p*-tolylmethyl)-cyclopropyl bromide (**1a**) was heated at 150 °C for 1 h. 1,1-Dibromo-2-*p*-tolylcyclobutane (**4a**), previously reported to be the only product in this reaction, was not detected. The phenyl analogue of **1a** reacted similarly and gave the (*Z*)- and (*E*)-isomers of 2,4-dibromo-1-phenyl-1-butene **2b** and **3b**, respectively, in 60% yield. A rationale for the reaction is presented.

Geminal dibromocyclobutanes are a convenient source for the generation of cyclobutyliden(oid)es.[1,2] The divalent carbon of the four-membered ring can easily be generated when geminal dibromocyclobutanes are reacted with alkyllithium (preferentially methyllithium) in diethyl ether at temperatures below −35 °C. Historically, parent 1,1-dibromocyclobutane has been synthesized either by HBr addition to 1-bromocyclobutene[2a,3] or more conveniently through a double Hunsdiecker−Borodin degradation of the commercially available 1,1-cyclobutanedicarboxylic acid.[4] In another synthesis published in 1975 the formation of 1,1-dibromo-2-*p*-tolylcyclobutane **(4a)** was reported, when 1-(1-bromo-1-*p*-tolylmethyl)cyclopropyl bromide **(1a)** was heated for 1 h at 150 °C (Scheme 1).[5]

Because of our studies of the reactive behavior of cyclobutylidenes,[2] we became interested in exploring the scope and limitations of this apparently new approach to geminal dibromocyclobutanes. Therefore, we reinvestigated the reaction of **1a**, but also of **1b** where at C-1 instead of the tolyl a phenyl group is present. These two compounds are easily available through bromination of the double bond in (1-*p*-tolylmethylene)cyclopropane and (1-phenylmethylene)cyclopropane, respectively.[5] These compounds were synthesized by a Wittig reaction of cyclopropyltriphenylphosphonium bromide and *p*-tolylaldehyde and benzaldehyde, respectively.[5]

While according to the literature the reaction of **1a** led only to the formation of one product, i.e., **4a**[5] we isolated two compounds in a ratio of 78:22. Comparison of the spectroscopical data (^{1}H NMR and MS) reported for **4a** proved them to be identical with those observed by us. Moreover, with the phenyl analogue **1b** the reaction proceeded in the same fashion. Again, two products were formed in a 75:25 ratio. GC and GC-MS analyses were performed during the experiments. During the course of the reactions no product other than the two mentioned could be detected. With use of flash chromatography, from each experiment two compounds were isolated.

SCHEME 1: Thermal Ring Opening of 1-(1-Bromo-1-*p*-tolylmethyl)cyclopropyl Bromide (1a) and 1-(1-Bromo-1-phenylmethyl)cyclopropyl Bromide (1b)



In the proton spectra of **4a** a singlet at 6.8 ppm obviously had been assigned to the tertiary hydrogen in the α position to the geminal dibromo moiety.[5] However, in stark contrast the corresponding proton of, for example, 1,1-dibromo-2-hexylcyclobutane resonates at a much higher field at 3.40 ppm.[6] Moreover, HETCOR experiments with the major compound showed that the proton at 6.84 ppm had a cross-peak to a carbon at 132.5 ppm. In the minor compound, due to the presence of the bromine atom at the same side of the double bond, the proton at C-1 was shifted further downfield to 7.11 ppm. In the literature, the chemical shifts for the double bond proton in 2-bromo-1-phenyl-1-propenes have been reported. These protons appear at 6.74 and 6.75 ppm for the (*Z*)- and (*E*)-isomer, respectively.[7] COSY experiments finally confirmed that the compounds formed were (*Z*)- and (*E*)-isomers of 2,4-dibromo-1-*p*-tolyl-1-butene (**2a** and **3a**) and (*Z*)- and (*E*)-isomers of 2,4-dibromo-1-phenyl-1-butene (**2b** and **3b**), respectively. NOE measurements of the major product from the reactions of **1a** and **1b**, respectively, confirmed them to be the (*Z*)-isomers **2a** and **2b** (Scheme 1). In the overall reaction the three-membered ring in **1** was converted into a 1-aryl-1-butene system.

Since the reported structure **4a** does not agree with our ^{1}H and ^{13}C NMR data, we looked for other reaction pathways than the proposed ring enlargement **1a** → **4a**. The first step of a mechanism for the conversion **1** → **2** + **3** could consist of the loss of the benzylic bromine atom

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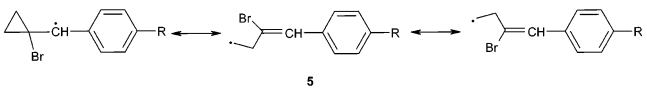

5

FIGURE 1. Representation of resonance forms of radical **5**.

and the formation of an arylcyclopropylcarbinyl radical **5**. It is well-documented that cyclopropylcarbinyl radicals undergo rapid ring opening to give exclusively butenyl radicals.[8] Radical **5** (Figure 1), however, is stabilized by the presence of the neighboring benzene ring.[8a,b]

If **5** is represented as shown in Figure 1, recombination with a bromine atom leads directly to the observed (*Z*)- and (*E*)-isomers **2** and **3**, respectively. Loss of strain of the three-membered ring in **1** and formation of a styrene substructure are the driving forces to bring about this transformation.

Experimental Section

Synthesis of (1-*p*-Tolylmethylene)cyclopropane and (1-Phenylmethylene)cyclopropane: General Procedure. NaH (5.20 g, 55−65% suspension in oil, 0.12−0.14 mol) was slowly added to a solution of cyclopropyltriphenylphosphonium bromide (25.00 g, 0.065 mol) in dry THF (100 mL) and stirred at room temperature for 12 h. Then, a THF solution of *p*-tolylaldehyde or benzaldehyde, respectively (0.070 mol in 5 mL of THF), was added dropwise and the mixture was refluxed for 6 h. After cooling, the suspension was filtered and the filtrate was washed with 10% HCl (3 × 50 mL) and brine (1 × 50 mL) and dried ($MgSO_4$). After the solvents were removed in vacuo, the products were purified by bulb-to-bulb distillation.

(1-*p*-Tolylmethylene)cyclopropane. Yield 59%; bp 75 °C/0.35 Torr; ^{1}H NMR ($CDCl_3$) δ 1.16−1.23 (m, 2H), 1.40−1.47 (m, 2H), 2.37 (s, 3H), 6.75 (t, 1H, J = 1.8 Hz), 7.17 ("d", 2H, J = 7.8 Hz), 7.46 ("d", 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 0.5, 4.1, 21.2, 118.1, 123.0, 126.5, 129.1, 135.5, 136.3; IR (neat) ν 3048, 3022, 2976, 2953, 2864, 2829, 1611, 1513, 1466, 1259, 1156, 1122, 1042, 909, 833, 734 cm^{-1}; MS (*m*/*z*) 144 (30, M$^+$), 143 (14), 130 (10), 129 (100), 128 (49), 127 (14), 115 (12).

(1-Phenylmethylene)cyclopropane. Yield 60%; bp 60 °C/0.3 Torr; ^{1}H NMR ($CDCl_3$) δ 1.16−1.22 (m, 2H), 1.41−1.47 (m, 2H), 6.77 (t, 1H, J = 2 Hz), 7.20−7.25 (m, 1H), 7.31−7.37 (m, 2H), 7.53−7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.5, 4.2, 118.2, 124.3, 126.6, 126.7, 128.4, 138.2; IR (neat) ν 3027, 2977, 2926, 2854, 1599, 1497, 1452, 1082, 1027, 934, 909, 807, 734, 694 cm^{-1}; MS (*m*/*z*) 130 (67, M$^+$), 129 (100), 128 (53), 127 (21), 115 (53), 91 (7), 64 (13), 51 (13).

Synthesis of 1-(1-Bromo-1-*p*-tolylmethyl)cyclopropyl Bromide (1a) and 1-(1-Bromo-1-phenylmethyl)cyclopropyl Bromide (1b): General Procedure. Br_2 (3.60 g, 0.023 mol) was slowly added to a solution of (1-tolylmethylene)cyclopropane and (1-phenylmethylene)cyclopropane, respectively, in CCl_4 (50 mL) at 0 °C. After being stirred for 1 h, the mixture was quenched with 10% Na_2SO_3 (10 mL) and washed with brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The products were purified by bulb-to-bulb distillation.

1-(1-Bromo-1-*p*-tolylmethyl)cyclopropyl Bromide (1a). Yield 88%; bp 100 °C/0.5 Torr; R_t = 26.65 min; ^{1}H NMR ($CDCl_3$) δ 1.27−1.33 (m, 1H), 1.35−1.45 (m, 3H), 2.37 (s, 3H), 5.11 (s, 1H), 7.18 ("d", 2H, J = 7.8 Hz), 7.42 ("d", 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 17.4, 17.5, 21.2, 37.3, 61.0, 128.3, 129.0, 136.4, 138.6; IR (neat) ν 3008, 2922, 1612, 1512, 1416, 1265, 1150, 1130, 1031, 824, 807, 754, 739, 580, 568 cm^{-1}; MS (*m*/*z*) 306 (28), 304 (53, M$^+$), 302 (25), 225 (32), 223 (32), 211 (13), 209 (13), 144 (31), 143 (47), 142 (13), 141 (11), 131 (11), 130 (80), 129 (100), 128 (66), 127 (17), 117 (10), 115 (36), 80 (11), 71 (21).

1-(1-Bromo-1-phenylmethyl)cyclopropyl Bromide (1b). Yield 61%; bp 90 °C/0.5 Torr; R_t = 25.70 min; ^{1}H NMR ($CDCl_3$) δ 1.28−1.33 (m, 1H), 1.36−1.47 (m, 3H), 5.11 (s, 1H), 7.31−7.41 (m, 3H), 7.51−7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 17.47, 17.54, 37.2, 60.9, 128.3, 128.4, 128.7, 139.3; IR (neat) ν 3088, 3061, 3029, 3007, 1494, 1451, 1418, 1203, 1151, 1133, 1077, 1030, 906, 824, 750, 696, 609, 542 cm^{-1}; MS (*m*/*z*) 292 (8), 290 (18, M$^+$), 288 (10), 211 (46), 209 (45), 130 (34), 129 (100), 128 (32), 127 (14), 116 (23), 115 (32), 104 (14), 103 (13), 102 (11), 86 (24), 85 (52), 84 (36), 83 (83), 64 (31) 63 (11), 51 (22), 50 (10), 49 (17).

Thermal Ring Opening of 1-(1-Bromo-1-*p*-tolylmethyl)-cyclopropyl Bromide (1a) and 1-(1-Bromo-1-phenylmethyl)cyclopropyl Bromide (1b): General Procedure. The cyclopropyl bromides (**1a,** 1.00 g, 3.29 mmol; or **1b**, 1.92 g, 6.62 mmol) were placed in a 5-mL flask and heated at 150 °C for 1 h. After cooling, the products were separated by flash chromatography as colorless oils, (0.51 g of **2a** and 0.14 g of **3a**, total yield 65%; and 0.86 g of **2b** and 0.29 g of **3b**, total yield 60%).

(*Z*)-2,4-Dibromo-1-*p*-tolyl-1-butene (2a). R_t = 27.45 min; R_f 0.18 (pentane);^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 3.13 (t, 2H, J = 6.8 Hz), 3.66 (t, 2H, J = 6.8 Hz), 6.84 (s, 1H), 7.20 ("d", 2H, J = 8.1 Hz), 7.52 ("d", 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.3, 30.5, 46.0, 122.0, 128.82, 128.83, 130.5, 132.5, 138.0; IR (neat) ν 3023, 2955, 2923, 2855, 1642, 1611, 1510, 1441, 1413, 1286, 1258, 1213, 1185, 1143, 1057, 1009, 913, 865, 803, 759, 682 cm^{-1}; MS (*m*/*z*) 306 (54), 304 (97, M$^+$), 302 (52), 211 (25), 209 (23), 144 (12), 143 (24), 131 (12), 130 (100), 129 (64), 128 (40), 115 (24), 58 (14), 57 (17), 56 (20); HRMS calcd for $C_{11}H_{12}{}^{79}Br_2$ 301.9306, found 301.9311. Anal. Calcd for $C_{11}H_{12}Br_2$: C, 43.45, H, 3.97. Found: C, 43.64, H, 3.88.

(*E*)-2,4-Dibromo-1-*p*-tolyl-1-butene (3a). R_t = 27.10 min; R_f 0.29 (pentane); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 3.15 (t, 2H, J = 7.1 Hz), 3.61 (t, 2H, J = 7.1 Hz), 7.11 (s, 1H), 7.12−7.19 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.2, 30.0, 38.9, 125.0, 128.0, 129.3, 133.0, 135.1, 137.6; IR (neat) ν 3025, 2922, 2854, 1630, 1610, 1510, 1444, 1380, 1272, 1212, 1144, 1010, 870, 809, 752, 698 cm^{-1}; MS (*m*/*z*) 306 (43), 304 (89, M$^+$), 302 (42), 211 (24), 209 (23), 143 (27), 131 (13), 130 (100), 129 (76), 128 (48), 127 (13), 116 (10), 115 (38), 51 (12); HRMS calcd for $C_{11}H_{12}{}^{81}Br_2$ 303.9286, found 303.9291.

(*Z*)-2,4-Dibromo-1-phenyl-1-butene (2b). R_t = 26.56 min; R_f 0.27 (pentane); ^{1}H NMR ($CDCl_3$) δ 3.13 (t, 2H, J = 6.8 Hz), 3.67 (t, 2H, J = 6.8 Hz), 6.88 (s, 1H), 7.30−7.42 (m, 3H), 7.58−7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 30.5, 46.0, 122.8, 128.0, 128.1, 128.9, 130.7, 135.4; IR (neat) ν 3056, 3025, 2966, 2926, 1642, 1599, 1492, 1446, 1430, 1417, 1345, 1288, 1258, 1212, 1143, 1080, 1056, 1030, 1009, 919, 849, 749, 693, 618, 555 cm^{-1}; MS (*m*/*z*) 292 (43), 290 (90, M$^+$), 288 (45), 197 (21), 195 (23), 130 (26), 129 (97), 128 (48), 127 (18), 117 (15), 116 (100), 115 (96), 102 (14), 85 (53), 83 (83), 77 (15), 64 (23), 63 (16), 51 (26), 50 (14), 47 (19); HRMS calcd for $C_{10}H_{10}{}^{79}Br_2$ 287.9149, found 287.9152. Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.42, H, 3.48. Found: C, 41.64, H, 3.49.

(*E*)-2,4-Dibromo-1-phenyl-1-butene (3b). R_t = 26.25 min (20%); R_f 0.38 (pentane); ^{1}H NMR ($CDCl_3$) δ 3.14 (t, 2H, J = 7.1 Hz), 3.61 (t, 2H, J = 7.0 Hz), 7.15 (s, 1H), 7.22−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 30.0, 38.8, 125.7, 127.7, 128.1, 128.6, 135.1, 135.8; IR (neat) ν 3057, 3025, 2967, 1632, 1600, 1493, 1444, 1430, 1272, 1212, 1147, 1075, 1031, 1010, 919, 863, 753, 700 cm^{-1}; MS (*m*/*z*) 292 (22), 290 (46, M$^+$), 288 (24), 195 (10), 172 (10), 170 (10), 154 (11), 131 (10), 130 (12), 129 (33), 128 (15), 116 (32), 115 (27), 91 (100), 65 (13), 64 (11), 51 (11); HRMS calcd for $C_{10}H_{10}{}^{81}Br_2$ 289.9130, found 289.9137.

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Supporting Information Available: General experimental information; ^{1}H and ^{13}C NMR spectra of **2a**, **2b**, **3a**, and **3b**; COSY of **2a**, **2b**, and **3a**; NOESY of **2a**, **2b**, and **3b**; and HETCOR of **2a**, **2b**, and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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