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Synthesis of Strained Bi- and Tricyclic Systems by Rearrangements of Some Bromosubstituted Camphor Derivatives

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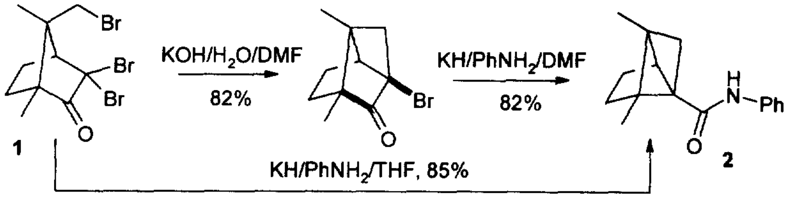
Abstract. Bromosubstituted camphor derivatives can be conveniently used to create some sterically congested bi- and tricyclic compounds by rearrangement reactions with nucleophilic reagents. The ease of these thermo-dynamically unfavorable reactions is explained by alignment of the migrating and breaking bonds within the rigid framework of camphor-derived skeleton.

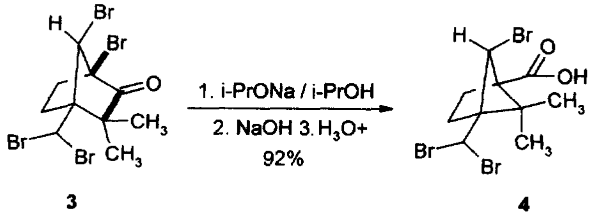
Recently,[1] a facile intramolecular cyclization - Favorski rearrangement reaction sequence of 3,3,8-dibromocamphor **1** was described, which led to formation of a novel tricyclic system **2** containing a small bridge (scheme 1). The ease of this process was suggested to be facilitated by the favorable *anti*-periplanar alignment of the migrating and breaking bonds (shown in bold):



Scheme 1.

Here we wish to report further examples of similar rearrangements of the camphor skeleton. Camphor proved to be a convenient starting point for the formation of strained bi- and tricyclic compounds due to the ease of its functionalization and favorable stereoelectronic factors which facilitate reactions leading to ring contraction.

A rearrangement analogous to that shown in the scheme 1, proceeds in high yield with a tetrabromo derivative of camphor, compound **3** (scheme 2). Again, a rather strained molecule **4** is formed; this is presumably a result of the *anti*-periplanar alignment of the C-C and C-Br bonds (highlighted in the scheme 2).



Scheme 2.

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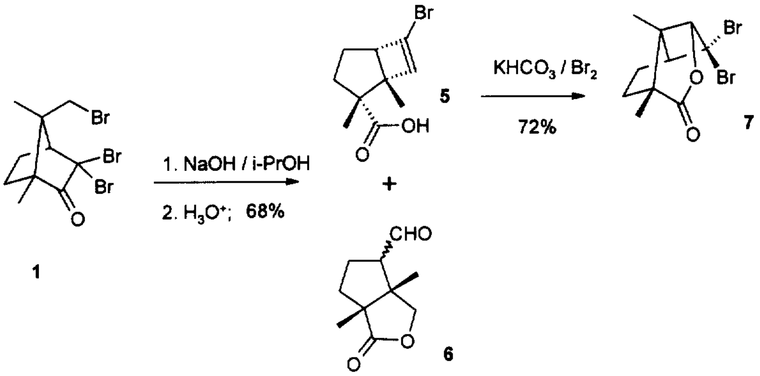
Modifying conditions for the reaction shown in the scheme 1, we observed another rearrangement leading to a sterically congested bicyclic compound. Treatment of **1** with solid NaOH in i-PrOH resulted,on acidification,in formation of a mixture of compounds **5** and **6** (scheme 3). According to a GC analysis of the mixture, the molar ratio **5**:**6** is ~1:10. Compound **5** contains fused cyclopentane and cyclobutene rings. Known approaches to this strained system usually employ photochemical [2+2] cycloaddition.[2a-c] The structure of **5** was confirmed by mass-, IR spectral data, ^{1}H-, ^{13}C-NMR, HMBC, HMQC experiments. An interesting feature of this compound is the close proximity of the carboxyl group to the C=C double bond. As a consequence, facile bromolactonization is possible, leading to 7.[3] Compound **6** is formed as a mixture of diastereomers due to epimerization under the reaction conditions (32:68 molar ratio according to a GC-MS analysis and ^{1}H-NMR); it was isolated as the 2,4-dinitrophenylhydrazone derivative.



Scheme 3.

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2. a) Eaton, P.E. *Tetrahedron Lett.* **1964**, 3695; b) Criegee, R.; Zirngibl, U.; Furer, H.; Seebach, D.; Feund, G. *Ber.* **1964**, *97*, 2942; c) Paquette, L.A. *J. Am. Chem. Soc.* **1974**, *96*, 215.
3. All new compounds gave satisfactory spectroscopic and analytical data. Selected spectral data are as follows. For **4** (m.p. 228^{0}C): ^{1}H-NMR (100 MHz, DMSO-d$_6$) δ: 6.27 (s, 1H), 4.16 (s, 1H), 2.05 (m, 4H), 1.57 (s, 3H), 1.08 (s, 3H); ^{13}C-NMR (75.43 MHz, CDCl$_3$ + DMSO-d$_6$) δ: 168.8, 57.4, 55.9, 52.3, 49.2, 44.0, 26.9, 23.9, 20.7, 16.4. Acid **5** (m.p. 106-108^{0}C): ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 11.90 (br s, 1H), 6.14 (s, 1H), 2.97 (d, J = 5.8 Hz, 1H), 2.37 (dd, J = 20.5; 12.5 Hz, 1H), 1.66 (dd, J = 13.7; 5.5 Hz, 1H), 1.60-1.51 (m, 2H), 1.34 (s, 3H), 1.19 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ: 183.1, 140.9, 119.0, 61.0, 58.3, 49.2, 34.1, 21.0, 19.3, 17.3. Compound 7 (m.p. 103^{0}C): ^{1}H-NMR (100 MHz, CDCl$_3$) δ: 4.80 (d, J = 3.4 Hz, 1H), 3.31 (m, 1H), 2.40-1.50 (m, 4H), 1.56 (s, 3H), 1.21 (s, 3H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 181.9, 88.7, 66.6, 64.0, 53.9, 51.8, 40.3, 30.8, 18.8, 17.4; IR (KBr): 1780 cm^{-1}.