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# Preferential Electrocyclic Reaction of o-Quinodimethane. New Route to Dihydronaphthalenes and Naphthalenes

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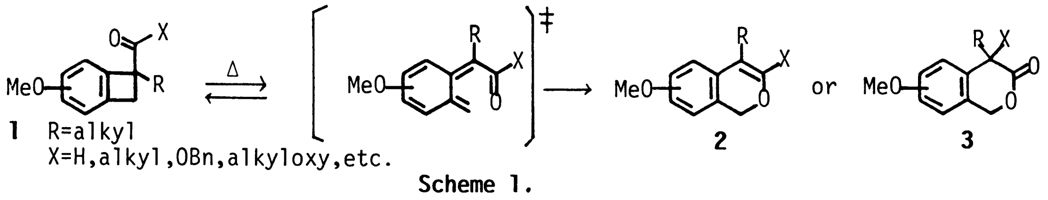
Substituted dihydronaphthalenes and naphthalenes are obtained via a preferential electrocyclic reaction of o-quinodimethanes generated by the thermolysis of 1-alkyl-1-alkenylbenzocyclobutenes.

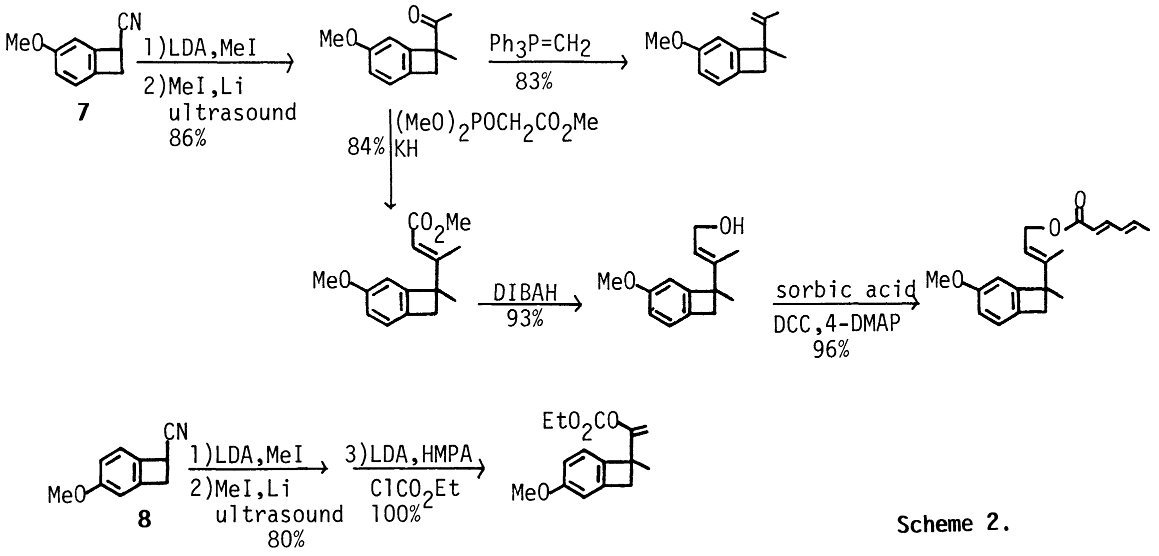
As part of program aimed toward development of new and expedient synthetic method using benzocyclobutenes,[1)] we have been interested in the competition between electrocyclic reaction (ECR) and [1,5]sigmatropic reaction (STR) during the thermolysis of 1,1-disubstituted benzocyclobutenes. In the previous publications,[2)] we have reported the preferential electrocyclic process in the thermolysis of 1-alkyl-1-carbonyl (or carbalkoxyl)substituted benzocyclobutenes (**1**). With these procedures at hand, various oxygen-containing heterocycles (**2**, **3**) could be prepared efficiently. (Scheme 1)



**Scheme 1.**

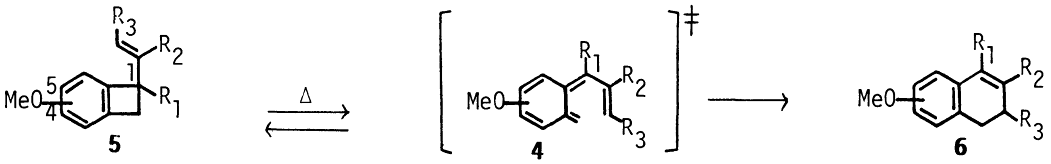
The same preference via Z-o-quinodimethane transition state (**4**) seems to be possible for the substrate, benzocyclobutenes (**5**), with olefinic functionality instead of carbonyl function at C-1, which should provide the corresponding dihydronaphthalenes (**6**), as illustrated in Scheme 3, that is the subject of the present paper.

The benzocyclobutenyl substrates[3)] for the thermolysis were prepared starting from the cyanobenzocyclobutenes (**7**[4)] and **8**[5)]), which were readily available from p- and m-anisaldehyde, respectively, by combination of several well-established standard procedures. Representative examples of the transformations are shown in Scheme 2.



**Scheme 2.**

The thermolysis of a solution of **5** in o-dichlorobenzene[6] at 180 °C proceeded cleanly and very high yields of the expected **6** could generally be obtained as a sole product. The results are shown in Table 1.



**Scheme 3.**

Table 1. Thermolysis of the benzocyclobutenes[a)]

| Entry | Substrate (**5**) OMe | $R_1$ | $R_2$ | $R_3$ | Reaction time/h | Yield/% of dihydronaphthalene(**6**) |
|---|---|---|---|---|---|---|
| 1 | C-5 | Me | Me | H | 1.3 | 95 |
| 2 | | Me | Et | H | 6.6 | 89 |
| 3 | | Et | Me | H | 3.0 | 89 |
| 4 | | Me | Me | $CO_2Me$ | 0.8 | 93 |
| 5 | | Et | Me | $CO_2Me$ | 1.0 | 86 |
| 6 | | Me | Me | $CO_2CH_2$–  | 0.8 | 95 |
| 7 | | Me | Me | $CH_2OH$ | 1.0 | 100 |
| 8 | | Me | Me |  | 2.5 | 99 |
| 9 | | Me | Me | $CO_2CH_2$–  | 1.0 | 98 |
| 10 | | Me | Me | CHO | 0.3 | 83 |
| 11 | C-4 | $^n$Pr | Me | H | 3.0 | 94 |
| 12 | | Me | $OPO(OEt)_2$ | H | 3.5 | 93 |
| 13 | | Me | $OCO_2Et$ | H | 2.0 | 94 |

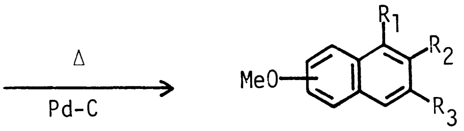
a) Thermolysis of **5** was carried out as described in text.

It should be noted that in the competition between ECR (hexatriene system) and [1,5]STR of o-quinodimethane, the electrocyclic process completely predominated over the sigmatropic process. For the substrates (entries 6, 8, and 9), it was expected to undergo sequential intramolecular Diels-Alder reaction of the resulting dihydronaphthalenes, however, we were unable to obtain any cycloadducts even for prolonged reaction time.

From the successful results described above, it is assumed that the thermolysis of the benzocyclobutenes with dehydrogenating agents should provide to access the naphthalenes in a one-pot operation. Indeed, in agreement with this assumption, effecting the thermolysis in a solution of mesitylene⁽⁶⁾ in the presence of 10% palladium on carbon at 180 °C afforded the corresponding naphthalenes in good yield, while the reaction of the substrate (**5**: $R_1$=$R_2$=Me, $R_3$=CHO; entry 6) occurred to form the deformylated product⁽⁷⁾ (**9**: $R_1$=$R_2$=Me, $R_3$=H) which was identical with the authentic material obtained from the substrate (**5**: $R_1$=$R_2$=Me, $R_3$=H; entry 1). (Table 2)

Table 2. Thermolysis of the benzocyclobutenes in the presence of 10% Pd-C[a)]

**5**



**9**

| Entry | —Substrate (**5**)— OMe | $R_1$ | $R_2$ | $R_3$ | Reaction time/h | Yield/% of naphthalene (**9**) |
|---|---|---|---|---|---|---|
| 1 | C-5 | Me | Me | H | 5 | 88 |
| 2 | | Me | Et | H | 8 | 96 |
| 3 | | Et | Me | H | 10 | 78 |
| 4 | C-4 | ${}^{n}$Pr | Me | H | 17 | 73 |
| 5 | C-5 | Me | Me | $CO_2Me$ | 12 | 74 |
| 6 | | Me | Me | CHO | 18 | 70[b)] |
| 7 | | Me | Me | COMe | 22 | 80 |

a) Commercially available 10% Pd-C (Nakarai Chemicals, Ltd.) was used.

b) The isolated product is the deformylated naphthalene (**6**: $R_1$=$R_2$=Me, $R_3$=H).

In summary, the transformations described herein which could cover both dihydronaphthalenes and naphthalenes, which are generally less available, have a significant practical value. Further studies on the extension and application of these reactions are in progress.

References

1) For reviews, see T. Kametani and K. Fukumoto, Heterocycles, 3, 29 (1975); W. Oppolzer, Angew. Chem., Int. Ed. Engl., 16, 10 (1977); Synthesis, 1978, 793; T. Kametani and K. Fukumoto, Kagaku No Ryoiki Zokan, 125, 81 (1980).
2) K. Shishido, M. Ito, S. Shimada, K. Fukumoto, and T. Kametani, Chem. Lett., 1984, 1943; K. Shishido, E. Shitara, K. Fukumoto, and T. Kametani, J. Am. Chem. Soc., 107, 5810 (1985); K. Shishido, K. Hiroya, K. Fukumoto, and T. Kametani, Tetrahedron Lett., 27, 971 (1986).
3) Correct spectral and analytical (MS or combustion) data were obtained for all new compounds.
4) T. Kametani, M. Kajiwara, and K. Fukumoto, Tetrahedron, 30, 1053 (1974).
5) T.Kametani, Y. Kato, T. Honda, and K. Fukumoto, J. Am. Chem. Soc., 98, 8185 (1976).
6) Distilled and degassed solvents were used.
7) From the fact that independent treatment of **6** (entry 10 in Table 1) and **9** ($R_1$=$R_2$=Me, $R_3$=CHO), prepared by DDQ oxidation of the former (**6**), with the same conditions as for the benzocyclobutene (**5**; $R_1$=$R_2$=Me, $R_3$=CHO) gave the deformylated product only in the case of **6**, it could be confirmed that the formyl group was removed before aromatization. It is in agreement with the previous observations; see, J. O. Hawthorne and M. H. Wilt, J. Org. Chem., 25, 2215 (1960).

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