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# 1-*H*-Cyclobuta[*a*]naphthalen-2-one

Horst Neudeck and Udo H. Brinker*

*Institut für Organische Chemie, Universität Wien, Währinger Strasse 38, A-1090 Wien, Austria*

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**Abstract**—1-*H*-Cyclobuta[*a*]naphthalen-2-one (**2**) was synthesized in eight steps starting from α-tetralone. With **2** the last missing compound of the three possible cyclobutanaphthalenones has been prepared.


## 1. Introduction

Of the overall three possible cyclobutanaphthalenones **1**, **2**, and **3**, only 1-*H*-cyclobuta[*a*]naphthalen-2-one (**2**) is unknown (Fig. 1). 2-*H*-Cyclobuta[*a*]naphthalen-1-one (**1**) was prepared by gas phase pyrolysis of the corresponding *ortho*-methyl-substituted naphthalene-1-carboxylic acid chloride by 1,4 elimination of HCl at 550 °C.[1] For the synthesis of cyclobuta[*b*]naphthalene-1-one (**3**) three different approaches have been described.[2] Derivatives of heterocycloalkylbenzocyclobutane and heteroarylbenzocyclobutane have been used as inhibitors of the recapture of serotonine and of noradrenaline.[3] Moreover, ketones in four-membered rings are versatile functional groups for the synthesis of carbene and carbenoid precursors.[4] such as alkali salts of tosylhydrazones,[5] diazirines,[6] but also acetals and their concomitant conversion to the corresponding geminal dibromo compounds.[7] Here the preparation of the missing 1-*H*-cyclobuta[*a*]naphthalen-2-one (**2**) is disclosed.

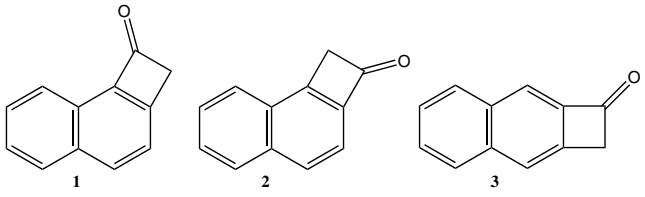


**Figure 1.**

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* Corresponding author. Tel.: +43 1 4277 52121; fax: +43 1 4277 52140; e-mail: udo.brinker@univie.ac.at

## 2. Results and discussion

Construction of the carbon framework of **2** was achieved by a regiospecific [2 + 2] cycloaddition of 1,2-dihydronaphthalene (**4**) and dichloroketene to afford **5**.[8] Compound **4** can readily be obtained from commercially available α-tetralone, reduction with $LiAlH_4$ (2.4 equiv) to the corresponding alcohol (yield 98%), followed by dehydration to **4** with *p*-toluenesulfonic acid (yield 95%). When **4** was reacted with dichloroketene, generated in situ from 1.2 equiv of trichloroacetylchloride and 2 equiv of activated zinc,[9] **5**[8] could be obtained in 86% yield after recrystallization. According to Scheme 1, target compound **2** should easily be prepared from **12** by HBr elimination, since this reaction would benefit energetically from formation of the aromatic naphthalene system. Moreover, the dehalogenation of **8** (or **9**) to yield **2** should pose no problem.

As starting material for this transformation, bromide **6** was used comprising both the four-membered ring and the bromine atom on the same side of the six-membered ring. To this end dichloroketene adduct **5** dissolved in $CCl_4$, was treated with 1.01 equiv of NBS to give **6** (*endo*:*exo* = 43:57) and **7** in a ratio of 84:16, and 22.5% of starting material **5** (yield quantitative). The mixture of **6** could be separated from the relatively unstable products **7** (consisting mainly of 67% 4,6-dibromo-8,8-dichloro-2,3-benzobicyclo[4.2.0]oct-2-en-7-one by $^1H$ NMR analysis and tribrominated products of **5**) by fractional crystallization from petrol ether/ether.

The elimination of HBr in **6** (Br *endo*) with strong organic bases like DBN or DBU proved not to be successful, since the desired compound **8** was not formed. Only a maximum of 10% of impure starting material **6** could

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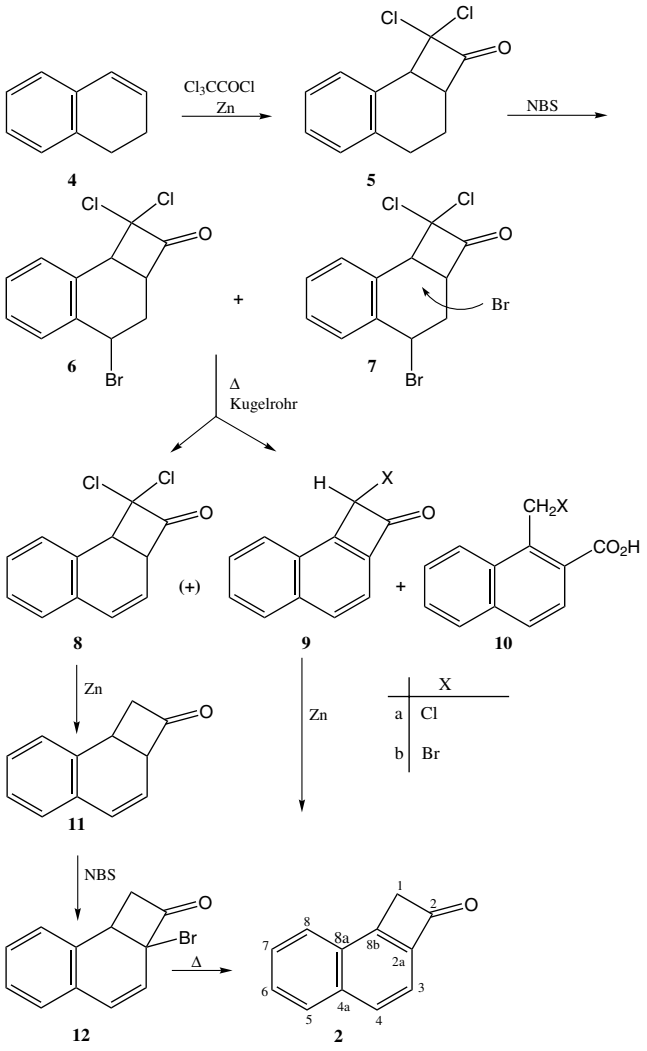


**Scheme 1.**

be recovered. The main component of this reaction probably consists of polymers of **8**. Thus, an alternative approach to **8**, that is, a thermal elimination of HBr in **6** had to be considered. For this purpose bromide **6** was distilled at a high vacuum with a Kugelrohr apparatus. The analysis of the distillate, however, revealed only partial (ca. 30%) conversion to **8**. Only after repeated distillation (three to four times) compound **8** could be obtained pure. This method, however, did not provide an optimal yield, since in each distillation some polymeric residue was produced.

To shorten this lengthy procedure, a new method for the preparation of **8** was sought. Since attempts to isolate **8** on a preparative scale either on silica gel or $Al_2O_3$ always lead to decomposition or polymerization, purification could only be achieved by crystallization. To obtain a sufficiently pure product, **8** should already be present in the product mixture in about 80–90%. Again, Kugelrohr distillation proved to be the method of choice. Thus, 75 mmol of **6** (Br *endo*) were heated in a rapidly rotating Kugelrohr first to 150 °C (0.5 Torr), to obtain partial liquefication, and thereafter the temperature was kept at 140 °C until liquefaction was complete. At high vacuum (ca. 0.005 Torr) and 130 °C, **8** was distilled over. After a repeated distillation and crystallization from petrol ether, **8** was obtained in a yield of 80%. Even the mother liquor (10% yield after a repeated Kugelrohr distillation) still contained 84% of **8**. In contrast, when a comparable amount of **6** was kept for 4 h at 20 Torr in a very slowly rotating Kugelrohr and then distilled over at high vacuum, nearly no **8** could be detected in the distillate (yield 81%). Instead the product mixture consisted of 67% of **9** (a:b = 60:40) and 33% of **10** (a:b[10] = 54:46). However, this procedure seems to be applicable only for larger amounts of **6**. Thus, when under the same conditions only 9 mmol of **6** were used, totally different results were obtained. Now the distillate consisted of 78% of **8**, besides 6% of **9a**, and 3% of **10** (a:b[10] = 79:21) plus 6% of naphthalene. Compound **9** is obviously formed from **8** by HCl elimination and subsequent aromatization, while **10** derives from a cleavage of the cyclobutenone ring in **9**. Next, the isomeric bromide **6** (*exo*) was employed, where cyclobutanone ring and bromine atom are located on opposite sides of the six-membered ring. This isomer could be obtained by crystallization of the mother liquor from reaction **5** → **6** + **7** in a purity of 93% alongside with 7% of *endo* **6**. Applying the same reaction conditions as described before with the other isomer, the composition of the distillate is now changed to 50% of **8**, 34% of **9** (a:b = 89:11), and 11% of naphthalene. After separation of the carboxylic acids **10**, obtained from reaction of **6** (Br *endo*) with $NaHCO_3$, the pure mixture of **9** was reduced to the target compound. This was achieved with 4 equiv of zinc in (a) acetic acid (heating for 3 h) or (b) in methanol and addition of 18 equiv of $NH_4Cl$ (stirring at room temperature for 6 h) in yields of 95% and 94%, respectively.

In a slightly modified approach to the title compound **2**, in principle, the aromatization of **11**[11] should pose no problem. For this purpose **8** was dehalogenated (4 equiv of zinc, acetic acid, 66 h, room temperature) to afford **11** in a yield of 90%. This product was contaminated with 2.5% of the two isomeric monochlorides of **9** in a ratio of 80:20. On the contrary, in $CH_3OH$ (4 equiv of zinc and 18 equiv of $NH_4Cl$, stirring at room temperature) the reduction to **11** was completed within 1.5 h (yield after distillation 88%). However, with the oxidizing agent 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) only 2% of **2** could be detected in the reaction mixture. Moreover, when **11** was treated with Pd/C in boiling dioxane only 14% of **2** were formed. Finally, it turned out that the best preparation of **2** from **11** consisted in another HBr elimination in **12**.[12] This compound could be obtained by allylic bromination of **11** with NBS in boiling $CCl_4$. Under these conditions HBr elimination already took place and the product mixture contained 85% of **12**. Heating this mixture for 1 h at 107 °C (decomposition of pure **12**: 100–117 °C) and subsequent two-fold Kugelrohr distillation afforded the title compound **2** in a purity of 88%. Pure crystalline **12** (yield 64% from petrol ether) after triple Kugelrohr distillation (0.5 Torr) gave pure **2**[13] in 97% yield.

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12. When using DBU in an attempt to eliminate HBr from **6** (Br *endo*) to obtain **8**, the reaction failed. By applying this method to **12**, merely 5% of a product mixture could be isolated which consisted of 46% of **2** and 9% of **12**. The reason for the low yield should be a consequence of the incorporated styrene-like structures which will lead to polymerization in the very alkaline solution used. For confirmation, pure **8** was destroyed by this procedure and only a few percent could be recovered.
13. Compound **2**: mp 70–71 °C (pillar-like needles from $CH_3OH$; recrystallization at 67 °C); $^1H$ NMR (400.1 MHz, $CDCl_3$)[†] $\delta$ 4.13 (s, 1-H), 7.33 (d, $J = 8.3$; 3-H), 7.63 (td, $J = 7.1/1.8$; 7-H), 7.66 (td, $J = 7.1/2.0$; 6-H), 7.81 (d, $J = 8.3$; 4-H), 7.86–7.90 (m; 8-H), 7.91–7.96 (m; 5-H); $^{13}C$ NMR (100.6 MHz, $CDCl_3$, *J*-mod)[‡] $\delta$ 50.0 (t; C-1), 117.1 (d; C-3), 125.5 (d; C-8), 127.7 (d; C-7), 128.7 (s; C-8a), 129.4 (d; C-6), 129.7 (d; C-5), 130.5 (d; C-4), 137.0 (s; C-4a), 144.9 (s; C-2a), 153.5 (s, C-8b), 186.2 (s; C-2); (the assignment was done by COSY, NOESY, HMQC and HMBC); $\nu_{max}/cm^{-1}$ (ATR) 2907 (w), 1788 (m), 1746 (vst), 1627 (m), 1569 (m), 1519 (w), 1450 (m), 1414 (m), 1336 (m), 1265 (w), 1217 (m), 1167 (w), 1063 (w), 957 (m), 905 (w), 875 (w), 812 (st), 771 (m), 750 (s). *m/z* (EI, pot. 50 °C) 168 ($M^+$, 60), 140 ($M^+ - CO$, 100), 139 ($M^+ - CHO$, 74), 70 (12), 69 (14), 63 (10), (found $M^+$ 168.0571 ± 5 ppm, calcd for $C_{12}H_8O$: 168.0575). Found: C, 85.41; H, 4.99 %. Anal. Calcd for $C_{12}H_8O$: C, 85.69; H, 4.79%. UV ($C_2H_5OH$) $\lambda_{max}$: 250 (628,000), 275 (78,000), 284 (79,000), 333 (38,500), and 345 (42,800).

[†] Bruker Avance DRX-400 spectrometer [$CHCl_3$ set at 7.24 ppm].
[‡] Bruker Avance DRX-400 spectrometer [$CDCl_3$ set at 77.00 ppm].