

An Investigation on the Reactions of Naphtho[b]cyclopropene¹

Nurullah Saraçoğlu, İnci Durucasu and Metin Balcı*

Department of Chemistry, Faculty of Science, Atatürk University, Erzurum-TURKEY

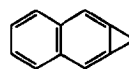
Abstract: In order to investigate the reactivity of naphtho[b]cyclopropene (**2**), the reaction with various dienophiles, dienes and electrophiles was examined. Reaction of **2** with tetracyanoethylene, 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione, 1,3-diphenylisobenzofuran and benzyne afforded the insertion products **3**, **4**, **6**, **10**. Cheletropic addition of dichlorocarbene to **2** gave 1,1-dichloronaphtho[b]cyclobutene (**11**). Hydrolysis and reductive elimination of **12** provided naphtho[b]cyclobutenone (**13**) and naphtho[b]cyclobutene (**13**), respectively. Naphtho[b]cyclopropene reacted with the different electrophiles like acetic acid, HCl, maleic acid, iodine, bromine, ethanol, and hydrogen afforded the corresponding ring-opening products **14**, **15**, **16**, **17**, **18**, **19**, **20** and **21**, respectively.

Introduction

Cycloproparenes have been found as a highly interest class in the strained organic molecules. Cycloproparene is a common name for the systems² in which a carbon bridge is fused across adjacent centers of an aromatic system and they set the feature in juxtaposition. Since the isolation of cyclopropabenzene^{3,4} (**1**) and cyclopropa[b]naphthalene⁴ (**2**) in this series, most of the efforts on this area has been directed towards the synthesis of different analogs for these compounds and the study of the physical properties of these highly strained molecules.



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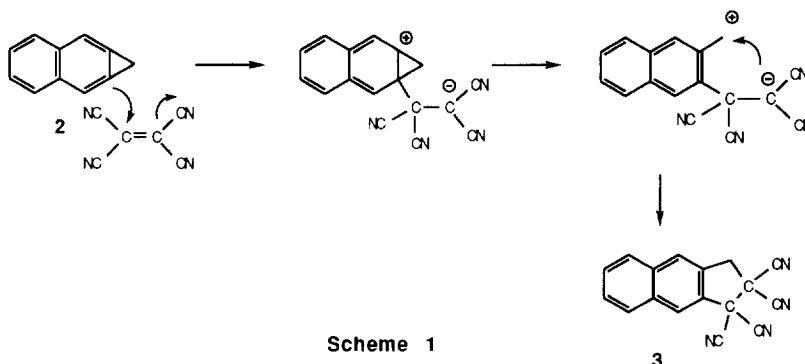
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The chemistry of the cycloproparenes has been studied systematically⁵, the bonding and energetics of the parent molecule have been reported on a theoretical basis⁶, the limits to which such stress and strain can be imposed upon the benzenoid framework. Cyclopropabenzene (**1**) is an unexpectedly stable molecule⁶ with a strain energy⁷ of ca. 68 kcal/mol. The chemistry of cyclopropabenzene (**1**) is explained by FMO theory as being dominated by its HOMO⁶ and the possibility of considerable relief of strain by ring cleavage. The HOMO of cyclopropabenzene is localized at the bridge carbons which are therefore the preferred sites for reactions with electrophiles and electron-poor dienes. In recent years, the chemistry of benzocyclopropene (**1**) has been studied in detail⁸. However, there is no detailed investigation on the reactions of naphthocyclopropene¹ (**2**) with dienophiles and electrophiles so far. In this paper, we report the results of studies on the chemistry of naphtho[b]cyclopropene with the various dienes, dienophiles and electrophiles.

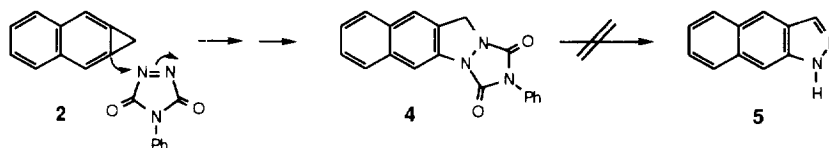
Results and Discussion

The reported synthesis⁴ of cyclopropanaphthalene **2** involves a three step sequence⁴ starting with 1,4-dihydronaphthalene⁹. In this procedure, the addition of dichlorocarbene (KOt-Bu, CHCl₃) to 1,4-dihydronaphthalene gave dichloro-carbene adduct⁴ in a yield of 27%. A marked improvement in the preparation of dichlorocarbene-adduct has been achieved by selecting by using phase-transfer catalyst (benzyltriethylammonium chloride, CHCl₃, NaOH). The yield of this step was improved up to 70%. Naphtho[b]cyclopropene (**2**) was obtained by dehydrohalogenation of 7,7-dichloro-3,4-benzobicyclo[4,1,0]-3-heptene with potassium tertiary butoxide.

The cyclopropanaphthalene (**2**) was reacted with tetracyanoethylene (TCNE), 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione (PTAD), benzyne and 1,3-diphenylisobenzofuran (DBI), respectively. When a mixture of **2** and TCNE in CHCl₃ in a sealed glass tube was reacted at 70 °C (25 h), a sole [2 π +2 σ] adduct **3** was obtained in a yield of 47%. This compound was isolated as stable crystalline solid after chromatographic purification and recrystallization. A reasonable mechanism leading to formation of **3** is shown below, the reaction may well proceed *via* zwitterion as presented by Halton et al¹⁰.

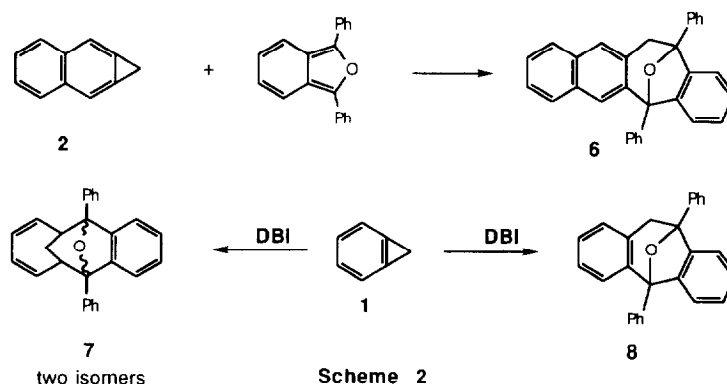


The ¹H-NMR spectrum of **3** displays the aromatic protons in the range of 7.50-8.13, and methylenic protons as a singlet at 4.0 ppm. The ¹³C-NMR spectrum of **3** is also in agreement with the proposed structure. Treatment of **2** with PTAD afforded **4**^{11a} by a similar mechanism in a yield of 77%. ¹H-NMR spectrum of the unsymmetrical adduct shows two methylenic protons (δ 5.14) and eleven aromatic protons (δ 7.30-7.97) and other data are consistent with the proposed structure. The isolated triazolindazole **4** was subjected to hydrolysis in order to synthesize [1,2-*a*]indazole **5**. Unfortunately all attempts were failed.



We also examined the behavior of **2** against to DBI as a diene. The reaction of **2** with DBI in THF at 80 °C gave ring-expanded 6,11-diphenyl-11,12-dihydro-6,11-epoxy-5H-naphthobenzo[*a, d*]cycloheptene (**6**) as sole product. The structural assignment of the product was made by comparison of spectral data with those of **8**

(Scheme 2). Methylenic protons of **6** show an AB system. The A part of the AB system appears at δ 4.03 ppm as a doublet due to geminal coupling with H_B proton (J = 16.7 Hz). Well-resolved 24 carbon signals in the aromatic range (147-122 ppm) and two bridgeheads carbons resonating at 89.86 and 85.51 ppm and methylenic carbon resonance at 38.61 ppm indicates clearly the formation of cycloadduct **6**. In contrast to this result, cyclopropabenzene reacted with DBI to afford *endo* and *exo* $[4\pi+2\pi]$ adduct **7** in THF at 20 °C, but in CHCl₃ at the same temperature, the unsymmetrical formal 5,10-epoxydibenzocycloheptene **8** was also formed¹².

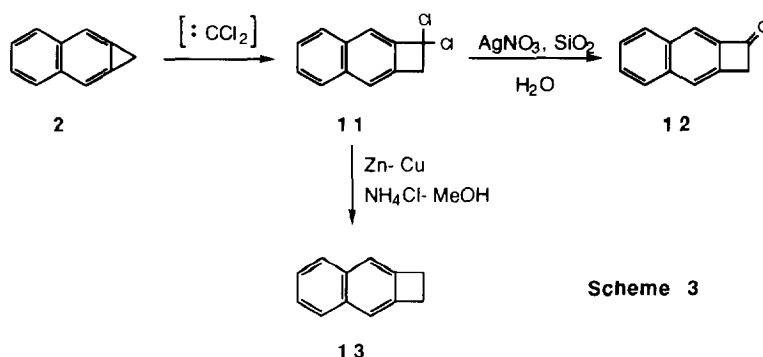


The presence of an additional fused benzenoid ring in **2** compared to **1** dictates a further loss in aromaticity in any formal Diels-Alder reaction and products analogous to **7** are deemed unlikely. Halton and Russell¹⁰ has also reacted cyclopropanaphthalene **2** with DBI at room temperature and they were not able to isolate the ring expansion product **6**. Instead, 6,13-dihydropentacene **9** was isolated in 85% yield in either tetrahydrofuran or chloroform at temperatures as low as 20 °C.



Later, we used benzyne as dienophile which was generated from benzenediazonium-2-carboxylate hydrochloride¹³ and in the presence of NaOH in refluxing dioxan and we isolated 2,3-benzofluorene (**10**) from a complex reaction mixture.

Recently the reaction of **1** with dibromo-carbene and dichloro-carbene was reported, by which the corresponding ring-expanded dihalocyclobutene derivatives was obtained in almost quantitative yield¹⁴. In an analogous manner, we have reacted naphthocyclopropene (**2**) with dichloro-carbene and isolated 1,1-dichloronaphtho[b]cyclobutene¹⁵ (**11**) in a yield of 78%. The mode of formation of **11** could well involve cheletropic addition of carbene to the bridge bonds, and proceed *via* bicyclopropane¹⁴ intermediates which has been discussed by Saito et al. The silver(I)-catalyzed hydrolysis of **11** on SiO₂ provided the corresponding ketone¹⁶ **12** in a yield of 97%. Dichloro compound **11** was easily converted to the elusive hydrocarbon¹⁷ **13** by reductive elimination¹⁸ with Zn-Cu almost quantitatively (Scheme 3).

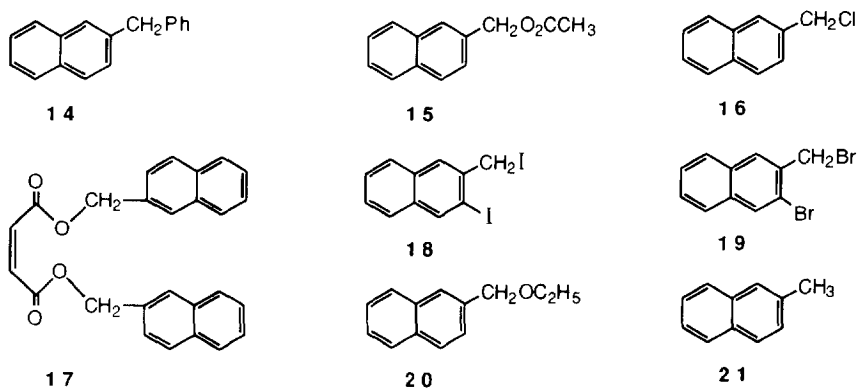


Scheme 3

Furthermore, it has been shown that 1H-cyclopropa[b]naphthalene behaves like **1**, and undergoes reactions with other electrophiles like acids and halogens giving 2,3-substituted ring-opening naphthalene derivatives as observed for benzocyclopropene¹⁹ (**1**).

To examine the behavior of the naphtho[b]cyclopropene (**2**) we reacted **2** with HCl, acetic acid, maleic acid, iodine, bromine, hydrogen, and with ethanol, benzene in the presence of acid, respectively and in every case, the corresponding naphthyl derivatives were obtained as the single reaction products. These results are best explained²⁰ by π -capture of the electrophile (E^+) at the bridge bond followed by disrotatory electrocyclic cleavage of the cyclopropyl cation thus formed. Subsequent interaction of the naphthyl cation with the nucleophile accounts for the observed product. The operation of an electrophilic attack at the strained σ -bond followed by ring cleavage and nucleophilic capture should also be considered. There are no clear-cut experiments that differentiate between those mechanisms.

It has been noted that the reaction of **1** with iodine gave small quantities of 1,6-diiodocycloheptatriene accompany the major product, o-iodobenzyl iodide^{19,21}. However, we were not able to detect any trace of cycloheptatriene derivatives by treatment of **2** with bromine and iodine. In both cases we isolated the expected addition products to cycloproparene σ -bond. By reacting of **2** with maleic anhydride we isolated **17** as the sole product. ¹H-NMR spectrum of **17** exhibits two sharp singlets. Methylenic protons of **17** appear at δ 5.29, olefinic protons at δ 6.34. Aromatic protons are resonating as multiplet in the range of δ 7.38-7.83. IR spectra of **17** showed carbonyl absorption at 1700 cm^{-1} supporting the existence of the α,β -unsaturated carbonyl group.



The investigations on cycloproparenes showed that benzocyclopropene (**1**) undergoes cycloaddition reactions with a variety of dienes, dienophiles and electrophiles. The HOMO of **1** is localized at the bridge bond, and thus the compound behaves as an electron-rich olefin and proposer in cycloadditions with inverse electron demand. However, no cycloaddition product of cyclopropa[b]naphthalene with dienes and dienophiles ($[4\pi + 2\pi]$ cycloaddition) was observed up to date. This situation can be explained by the resonance energy, and the naphtho[b]cyclopropene shows higher aromaticity compared to **1**. Nevertheless, the formation of products by way of ring expansion of **2** has no such hindrance of losing the aromaticity. This work also showed that naphtho[b]cyclopropene (**2**) could be conveniently used as a precursor in the syntheses of 2,3-disubstituted derivatives of naphthalene.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were not corrected. Solvents and starting materials were purified according to standard literature procedures. IR spectra were obtained on a Perkin-Elmer 377 Infrared recording spectrophotometer. The ^1H NMR spectra were recorded on EM 360 Varian Spectrometer using TMS as internal standard. ^{13}C NMR spectra and mass spectra were obtained by using 300 MHz ^1H -NMR General Electric QE 300 and Kratos MS TC Spectrometer, respectively. Column chromatography was performed on silica gel 60 (70-230 mesh, ASTM), aluminum oxide neutral (70-230 mesh, ASTM, Merck), TLC was carried out on silica gel (Art.741-Kieselgel, 60 HF 254+36) and aluminum oxide (PF 254+366 YPP).

2,2,3,3-Tetracyano[f]benzo-2,3H-indene (3): A mixture of naphtho[b]cyclopropene (200 mg, 1.43 mmol) and TCNE (200 mg, 1.56 mmol) in 5 mL CHCl_3 was placed into a glass tube. The tube was sealed and heated at 70 °C for 25 h. After cooling the mixture to room temperature, it was submitted to silica gel column chromatography and eluted with $\text{CHCl}_3/\text{n-hexane}$ (65:35). Crude product was obtained and recrystallized from $\text{CHCl}_3/\text{n-hexane}$ as white crystals with a yield of 47%. mp: 119-120 °C. ^1H -NMR (60 MHz, CDCl_3 , TMS) δ 4.07 (s, 2H), 7.55-8.27 (m, 6H) ; IR (KBr) 3050-3000, 2245, 1605, 1500, 1430.

2-Phenyl-1H,5H-benzo[f][1,2,4]triazolo[1,2-a]indazole-1,3-(2H)dione (4): A solution of naphtho[b]cyclopropene (520 mg, 3.7 mmol) and PTAD (650 mg, 3.71 mmol) in 25 mL CHCl_3 was stirred at room temperature. Characteristic crimson color of PTAD was disappeared in 3 h. Solvent was removed in vacuo and chromatography of the residue on silica gel eluting with $\text{CHCl}_3/\text{n-hexane}$ (3:2) afforded crude product. Recrystallization of product from CHCl_3 gave **3** as colorless needles, with a yield of 77%, mp: 186-187 °C, (lit.¹⁰, yield 92%, mp:184-185°C). ^1H -NMR (60 MHz, CDCl_3 , TMS) δ 5.54 (s, 2H), 7.97-7.30 (m, 11H) ; IR (KBr) 3045, 1725, 1600, 1500, 1015.

6,11-Diphenyl-11,12-dihydro-6,11-epoxy-5H-naphthobenzo[a,d]cycloheptene (6): A mixture of naphtho[b]cyclopropene (200 mg, 1.43 mmol) and DBI (300 mg, 1.22 mmol) in 5 ml dry THF was placed into a glass tube, the tube was sealed and heated at 70-80 °C. After 3 days, the mixture was cooled to room temperature, solvent of the mixture was removed under vacuum. The residue was dissolved in 50 mL CHCl_3 and washed with water (2x25 mL), dried over MgSO_4 . Solvent was rotoevaporated, the residue was submitted to column chromatography on silica gel eluting with $\text{CHCl}_3/\text{n-hexane}$ (35:65) and crude product was obtained. Recrystallization of product from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ gave **7** as white crystals. Yield: 42%, mp: 252-253 °C. ^1H -NMR (200 MHz, CDCl_3) δ 4.03 (A part of AB system, $J = 16.7$ Hz, 1H, H_4), 3.06 (B part of AB

system, $J = 16.7$ Hz, 1H, H₄), 8.02-7.01 (m, 20 H); ¹³C-NMR (50 MHz, CDCl₃) δ 147.41, 146.06, 143.24, 140.80, 138.93, 133.32, 132.56, 132.30, 130.07, 129.25, 129.00, 128.89, 128.42, 128.30, 128.14, 128.05, 127.41, 126.23, 126.00, 123.30, 122.43, 122.01, 89.86, 85.51, 38.62; Anal. Calcd. for C₃₁H₂₂O; C, 90.73; H, 5.36; Found; C, 90.38; H, 5.45; IR (KBr) 3040, 2920, 2895, 1595, 1490, 1440, 1325, 1280, 1180, 1050, 990, 880, 750.

11H-Benzo[b]fluorene (10): A solution of **2** (140 mg, 1 mmol), NaOH (250 mg, 6.25 mmol) and benzenediazoniumcarboxylate (1 g, 5.42 mmol) in 7.5 mL dioxane was heated at 110-120 °C. In 7 h, naphtho[b]cyclopropene was completely consumed, then solvent was removed under vacuum. The residue was applied to preparative TLC chromatography on silica gel and eluted with petroleum ether, pure compound **10** was obtained with a yield of 13%. mp: 197-199 °C (lit. Beil. 5(1) 344), yield 92%, mp: 209-210.5 °C). ¹H-NMR (60 MHz, CCl₄, TMS) δ 4.00 (s, 2H), 8.13-7.03 (m, 10H); IR (KBr) 3045, 2920, 2245, 1605, 1590.

1,1-Dichloronaphtho[b]cyclobutene (11): 100 mg of benzyltriethylammonium chloride was added to a solution of naphtho[b]cyclopropene (**2**) (200 mg, 1.43 mmol) in 25 mL CHCl₃ and the mixture was refluxed for 10 min. A solution of NaOH (5.1 g, 0.1275 mol) in water was added to this mixture by dropwise and refluxed for 24 h. Then, the mixture was poured into water and to this solution, CHCl₃ was added. Water-phase was separated from organic phase and washed with CHCl₃ (3x30 mL). Combined organic extracts were washed with water, dried on CaCl₂ and solvent was removed under reduced pressure. Chromatography of the residue on silica gel eluting with n-hexane gave **11**. Yield: 78.5 %, white crystals, mp: 131-132 °C; MS: m/e 223 (M⁺); ¹H-NMR (300 MHz, CDCl₃) δ 4.34 (s, 2H), 7.26-7.92 (m, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 129.30, 128.22, 126.63, 125.84, 122.44, 119.57, 79.10, 57.21; IR (KBr) 3060, 2945, 1625-1590, 755.

Naphtho[b]cyclobutenone (12): To a solution of **11** (140 mg, 0.63 mmol) in 50 mL CHCl₃ was added 8 g silica gel 60, 2 mL water and AgNO₃ (320 mg, 1.88 mmol) and the mixture was stirred at room temperature for 48 h. The mixture was diluted with 50 mL CHCl₃ and filtered. Evaporation of the solvent under vacuum and chromatography of the residue on silica gel eluting with n-hexane/CHCl₃ (1:1) gave **12**. The product was recrystallized from CCl₄. Yield: 96.3 %, pale-yellow crystals, mp: 157-158 °C (lit.¹⁶, mp: 162 °C); MS: m/e 168 (M⁺); ¹H-NMR (60 MHz, CCl₄, TMS) δ 4.19 (s, 2H), 7.97-7.43 (m, 6H); IR (KBr) 3020, 1755, 1600.

Naphtho[b]cyclobutene (13): A solution of CuSO₄·5H₂O (400 mg, 1.715 mmol) and dust of Zn (2 g, 0.03 mmol) in water was stirred at room temperature. Then, the mixture was left for certain time the Cu-Zn pair to settle. The precipitate was separated from organic layer and then washed with H₂O and CH₃OH, respectively. This solid was dissolved in 20 mL CH₃OH saturated with NH₄Cl and to the solution was added 1,1-dichloronaphtho[b]cyclobutene (**11**) (220 mg, 0.986 mmol). The mixture was refluxed for 2 h and then it was filtered through celite. Solvent of the mixture was evaporated in vacuo and to the residue, 50 mL CHCl₃ was added. Organic layer was washed with water, dried on CaCl₂ and recrystallized from n-hexane. Yield: 93.36 %, white crystals, mp: 86-87 °C; MS: m/e 154 (M⁺); ¹H-NMR (60 MHz, CCl₄, TMS) δ 3.34 (s, 4H), 7.47 (s, 2H), 7.93-7.20 (AA'BB' system, 4H); IR (KBr) 3045, 2910, 1600, 1410.

2-Benzyl-naphthalene (14): 2 mL concentrated H₂SO₄ and 20 mL benzene was placed into a three-necked flask, a solution of naphtho[b]cyclopropene in 15 mL benzene was dropped to this mixture in 2.5 h. Then, excess of acid was neutralized by adding 3 g NaHCO₃ and the mixture was stirred in an additional 30 min. After separation of solid-phase by filtration, organic phase was extracted by a saturated NaHCO₃ solution and water, dried over CaCl₂. Solvent was removed under vacuum, chromatography of the residue on silica gel

eluting with $\text{CHCl}_3/\text{n-hexane}$ (20: 80) gave crude product. Recrystallization of product from n-hexane gave **14** as white crystals. Yield: 46%, mp: 55-57 °C (lit. Beil. 5(3), 2237 from methanol, mp: 58 °C). MS: m/e 218 (M^+); $^1\text{H-NMR}$ (60 MHz, CCl_4 , TMS) δ 4.17 (s, 2H), 7.13-7.90 (m, 12H) ; IR (KBr) 3045-3020, 2915, 1595.

2-Naphthylmethyl acetate (15): Naphtho[b]cyclopropene (140 mg, 1 mmol) was refluxed for 30 min. in 10 mL CH_3COOH and the mixture was diluted by adding 50 mL methylene chloride and 50 mL water, respectively. Water-phase was separated from organic phase and washed with CH_2Cl_2 (2x20 mL). Combined organic phase was washed with saturated NaHCO_3 solution and water, dried over CaCl_2 . Recrystallization of **15** from CCl_4 afforded pure compound. Yield: 85%, mp: 57-58 °C. $^1\text{H-NMR}$ (60 MHz, CCl_4 , TMS) δ 2.03 (s, 3H), 5.20 (s, 2H), 7.97-7.30 (m, 7H) ; IR (KBr) 3060-3020, 2925-2890, 1730, 1600.

2-Chloromethylnaphthalene (16): Naphtho[b]cyclopropene (140 mg, 1 mmol) was dissolved in 10 mL acetone and to this solution, 250 mg concentrated HCl was added. The mixture was refluxed for 2h, then acetone was removed in vacuum, to the residue 20 mL CH_2Cl_2 was added. Organic phase was washed with saturated NaHCO_3 solution and water, dried on CaCl_2 . Chromatography of the residue on silica gel eluting with n-hexane gave **16**. Recrystallization of **16** from n-hexane afforded pure compound. Yield: 80%, mp: 47-48 °C (lit. Beil. 5(4), 1697, mp:48-49 °C).

Maleicacid bis-(2-methylnaphthyl)ester (17): Naphtho[b]cyclopropene (520 mg, 3.7 mmol) and maleic acid (329 mg, 3.37 mmol) was dissolved in 25 mL benzene and the mixture was refluxed for 5 h. The reaction mixture was allowed to warm to room temperature, to the mixture 25 mL benzene was added and washed with water (2x25 mL), dried over CaCl_2 . Solvent was removed under vacuum, and column chromatography of the residue on neutral Al_2O_3 (25 g, activity 4) eluting with $\text{CHCl}_3/\text{n-hexane}$ (20:80) gave crude product. Recrystallization of the product from $\text{CHCl}_3/\text{n-hexane}$ gave pure compound (220 mg) as white crystals. Yield: 30%, mp: 106-107 °C. MS: m/e 396 (M^+); $^1\text{H-NMR}$ (360 MHz, CDCl_3) δ 5.29 (s, 4H), 6.34 (s, 2H), 7.83-7.38 (m, 14H) ; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3) δ 164.70, 133.10, 133.07, 132.47, 129.84, 128.33, 127.95, 127.64, 127.60, 126.30, 126.27, 125.90, 67.22, IR (KBr) 3080-2820, 1700, 1625, 1595, 1500, 1460, 1390, 1360, 1300, 1280, 1210, 1150, 985.

2-Iodo-3-iodomethyl-naphthalene (18): A mixture of naphtho[b]cyclopropene (140 mg, 1 mmol) and iodine (270 mg, 1.06 mmol) in 20 mL CCl_4 was stirred for a hour at room temperature. After a hour, excess iodine in the mixture was removed by washing the mixture with a solution of $\text{Na}_2\text{S}_2\text{O}_3$ and then organic phase was washed with water, dried over MgSO_4 . Recrystallization of product gave pure compound almost quantitatively. mp: 116-117 °C (lit.^{11b}, yield 28%, mp:119.5-121 °C). $^1\text{H-NMR}$ (60 MHz, CCl_4 , TMS) δ 4.67 (s, 2H), 8.43-7.33 (m, 6H) ; IR (KBr) 3040, 1575.

2-Bromo-3-bromomethyl-naphthalene (19): To the solution of naphtho[b]cyclopropene (140 mg, 1mmol) in 10 mL CCl_4 , a solution of bromine (160 mg, 1 mmol) in 5 mL CCl_4 was added. Characteristic red color of bromine was disappeared immediately. Recrystallization of crude product from CCl_4 gave the pure compound quantitatively, mp: 108-109 °C (lit.^{11b}, yield 12%, mp:110-111.5 °C and 111-112 °C²²). $^1\text{H-NMR}$ (60 MHz, CCl_4 , TMS) δ 4.67 (s, 2H), 8.33-7.27 (m, 6H) ; IR (KBr) 3040, 1615, 1585, 750.

2-Ethoxymethylnaphthalene (20): Naphtho[b]cyclopropene (140 mg, 1mmol) was dissolved in 20 mL $\text{C}_2\text{H}_5\text{OH}$, to this solution, one drop of conc. H_2SO_4 was added. The mixture was refluxed for 2 h, then ethanol was removed and to the mixture, 30 mL CHCl_3 was added. Organic phase was washed with a solution of saturated NaHCO_3 and water, dried over CaCl_2 . The adduct was obtained quantitatively as pale-yellow liquid.

^1H -NMR (60 MHz, CCl_4 , TMS) δ 1.23 (t, 3H), 3.72 (q, 2H), 4.53 (s, 2H), 7.90-6.87 (m, 7H); IR (CCl_4) 3040-3020, 2920, 1860.

2-Methylnaphthalene (21): Naphtho[b]cyclopropene (130 mg, 0.93 mmol) and palladium-carbon (5 mg) was dissolved in 5 mL CHCl_3 and dry hydrogen gas were passed through the solution for 24 h. Then, catalyst was removed by filtration and the residue was applied on preparative TLC eluting with petroleum ether. Recrystallization of crude product from n-hexane afforded pure adduct. Yield: 61%; mp: 34-36 °C (lit. Beil. 5, 567, mp: 34-36 °C, mp: 32-33.5^{11c}).

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