Review

Chemistry of dibenzobarallene

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This review represents a systematic and comprehensive survey of the methods of syntheses and chemical reactivity of dibenzobarallene. This compound is an important intermediate for the synthesis of useful and novel heterocycle systems.

Key Words: Dibenzobarallene, synthesis, spectroscopic and kinetic studies, thermodynamic measurements, reactions

Introduction

There is no review summarizing the literature on the synthesis and chemistry of dibenzobarallene. This review therefore aims to cover the work on the synthesis and reaction of dibenzobarallene. Cycloaddition reaction of anthracene and maleic anhydride afforded an anthracene-maleic anhydride adduct.1 Five methods were reported in the literature for the nomenclature of dibenzobarallene. Accordingly, the title compound has 3 ways for the numbering of atoms (structures 1A, 1B, and 1C). Structure 1A can be named as dibenzobarallene1 and 2,3:5,6-dibenzo-bicyclo[2,2,2]octane-7,8-dicarboxylic anhydride.2 Similarly, structure 1B was reported to have 2 methods of nomenclature, cis-9,10-dihydroanthracene-9,10-endo-α,β-succinimide anhydride3 and 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride.4 Structure 1C was named as 9,10,11,15-tetrahydro-9,10-[3′,4′]-furano-anthracene-12,14-dione.5

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Dibenzobarallene (1) has been a key starting material for the synthesis of isoindole-1,3-diones as an antibacterial agent,\textsuperscript{6,7} an antiinflammatory,\textsuperscript{5} antiarthritics,\textsuperscript{5} substituted pyrroloanthracene as immunomodulators,\textsuperscript{8} and other bioactive and novel heterocyclic systems.\textsuperscript{9,10}

Synthesis

The most convergent and well-established classical approach for the synthesis of dibenzobarallene (1) is the Diels-Alder reaction, which involves the cycloaddition reaction of anthracene (2) and maleic anhydride (3). Thus, anthracene (2) and maleic anhydride (3) were ground together and fused for 15 min to give 1.\textsuperscript{11,12} Moreover, adduct 1 was achieved through the refluxing of the same reactants in xylene,\textsuperscript{13} toluene,\textsuperscript{14} benzene,\textsuperscript{15} dioxane,\textsuperscript{16} or acetic acid\textsuperscript{17} as a solvent. The same reaction was activated by cyclopentadienyl ruthenium cations under mild conditions (83 °C).\textsuperscript{18} Microwave irradiation of anthracene (2) and maleic anhydride (3) in xylene also afforded 1.\textsuperscript{19,20} Da Cunha and Garrigues\textsuperscript{21} studied the Diels-Alder reaction of anthracene (2) and maleic anhydride (3) under ultrasonic irradiation.

Walter and Helmut reported that photolysis of 9,10-dihydro[1’;2’]cyclobutanoanthracene-13,14-dione (4) afforded compound 1.\textsuperscript{22}
Spectroscopic studies

Molecular and crystal structure of dibenzobarallene

Crystallographic data, bond lengths, and bond angles were determined for 1 by X-ray. The benzene rings are planar and the dihedral angle between them is $53.9^\circ$. The anhydride ring is also planar and forms angles of $57.5^\circ$ and $4.3^\circ$ with the benzene rings.

FTIR spectrum

The acid anhydride can be easily detected due to the appearance of 2 frequency bands in the region of 1850-1750 cm$^{-1}$. The doublet appears at 1837.63 and 1863.37 cm$^{-1}$ due to the coupled vibrations of 2 (C=O) groups. The high frequency band is assigned to symmetrical vibrations and the lower frequency band to asymmetric vibrations. The splitting of the band is due to Fermi resonance. The absorption bands between 900 and 700 cm$^{-1}$ are characteristic of C–H deformation. The absorption band at 1779.37 cm$^{-1}$ is due to C=O stretching. The absorption bands at 1231.09 and 1290.44 cm$^{-1}$ are assigned to C–O stretching. The absorption band at 3069.88 cm$^{-1}$ is characteristic of C=C–H stretching (Figure 1).

UV spectral studies

UV-visible spectral analysis revealed that the adduct was conveniently transparent at 400-1200 nm with about 75% transmission, suitable for modulation purposes (Figure 2).

The $^1$H-NMR spectrum

The $^1$H-NMR spectrum of dibenzobarallene (1) in acetone was recorded using a JEOL instrument, model GSX400 (Figure 3a). The double doublets at $\delta$ 7.5 and 7.35 ppm are assigned to the phenyl protons present in the b1 and b2 positions, respectively. The multiplet at $\delta$ 7.2 is assigned to the phenyl protons present in positions a1 and a2. The singlet at $\delta$ 4.9 ppm is assigned to the benzylic protons present in position c1, and
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the other benzylic proton present in position c2 gives a singlet at $\delta$ 3.00 ppm. The triplet at $\delta$ 3.78 ppm is assigned to the protons present in the d position. It is expected that the benzylic protons present in c1 and c2 give a doublet, but they gave 2 singlet signals at $\delta$ 4.9 and 3.00 ppm due to the electronegative phenyl group present adjacent to each proton (Figures 3a and 3b).\textsuperscript{24}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{UV-visible spectrum of 1.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{a) $^1$H-NMR spectrum of Diels-Alder adduct, b) Diels-Alder adduct.}
\end{figure}

A kinetic study

The rates of reaction of anthracene and dimethylanthracene with maleic anhydride and several of its substitution products have been followed by colorimetric procedures. In the presence of a large excess of dienophile, the reactions in chloroform are first-order with respect to diene, but the first-order rate constants are not directly proportional to the dienophile concentration. This kinetic behavior can be explained quantitatively through consideration of the fact that a substantial fraction of the diene in the reaction mixtures is bound in a molecular complex with the dienophile. The mechanism of the reaction is discussed in light of these observations and in terms of the effects of changes in temperature, solvent, and substituents in the reactant molecules on the reaction rates. The possibility that the Diels-Alder adduct may form by reaction of the diene-dienophile complex with a second dienophile molecule has been ruled out on the basis of rate studies.\textsuperscript{25}
Thermodynamic measurements

The energy of combustion of the crystalline Diels-Alder adduct of anthracene and maleic anhydride, \( \text{C}_{18}\text{H}_{12}\text{O}_{3} \), was measured with a model 1241 Parr automatic calorimeter and a model 1710 Parr calorimeter controller. The standard molar enthalpy of combustion of the anthracene and maleic anhydride adduct at \( p^\circ = 0.1 \text{ MPa} \) was determined to be \( \Delta_c H^\circ_m \text{(C}_{18}\text{H}_{12}\text{O}_{3}, \text{cr, 298.15 K}) = -(8380.0 \pm 5.9) \text{ kJ mol}^{-1} \). The molar enthalpy of fusion of this adduct at its melting temperature (534.07 K), as measured by a 910 DuPont DSC and a 9900 DuPont thermal analyzer and digital computer, was found to be \( 36.3 \pm 4.2 \text{ kJ mol}^{-1} \). The other thermodynamic properties of the anthracene and maleic anhydride adduct derived from those measured properties are: \( \Delta_f H^\circ_m \text{(C}_{18}\text{H}_{12}\text{O}_{3}, \text{cr, 298.15 K}) = -(418.2 \pm 6.4) \text{ kJ mol}^{-1} \), and \( \Delta_f H^\circ_m \text{(C}_{18}\text{H}_{12}\text{O}_{3}, \text{cr, 298.15 K}) = -(389.7 \pm 7.7) \text{ kJ mol}^{-1} \).

Reactions with

Alkali

The reaction of 1 with aqueous sodium hydroxide or potassium hydroxide solution gave corresponding cis-sodium salt 5, which afforded corresponding cis-diacid 6 upon acidification with hydrochloric acid.\(^{27,28}\)

\[
\begin{align*}
\text{COONa} & \quad \text{COONa} \\
\text{5} & \quad \text{COOH} \\
\text{COOH} & \quad \text{COOH}
\end{align*}
\]

Meanwhile, treatment of 1 with sodium ethoxide followed by acidification with hydrochloric acid gave trans-acid 7, which, upon treatment with sodium azide followed by ethyl chloroformate, yielded 8. Reaction of 8 with benzyl alcohol gave 9.\(^{29}\)

\[
\begin{align*}
\text{COOC}_{2}\text{H}_{5} & \quad \text{COOC}_{2}\text{H}_{5} \\
\text{7} & \quad \text{NHCOOC}_{2}\text{H}_{5} \\
\text{NHCOOC}_{2}\text{H}_{5} & \quad \text{NHCOOCH}_{2}\text{C}_{6}\text{H}_{5}
\end{align*}
\]

Phenols

From the reaction of 1 with phenol in the presence of concentrated sulfuric acid, phthalein-like product 10 was obtained. An analogous reaction of fluorescence-like product 11 was formed when 1 was treated with resorcinol. Treatment of 11 with bromine gave 12, like eosin.\(^{30}\)
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**Ethylene glycol**

Condensation of 1 with an equivalent amount of ethylene glycol gave polyester resin 13.30

![Chemical structure](image)

**Hydrazine hydrate**

Heating 1 with 1 equivalent of 25% hydrazine hydrate for 10 min gave N-aminodicarboximide 14. On the other hand, refluxing 1 with 85% hydrazine hydrate in ethanol gave corresponding bis-carbohydrazide 15.31

![Chemical structure](image)

Phthalazine derivative 16 was achieved via reaction of 1 with hydrazine hydrate in glacial acetic acid.1 Reaction of 16 with indene 17 in methylene chloride gave diazocyclobutane derivatives 18.

![Chemical structure](image)

Treatment of 14 with succinic anhydride in dry benzene gave 19.32 Acylation of 14 with acetic anhydride gave N,N-diacetyl derivatives 20.
Moreover, reaction of 14 with asymmetric methyl ketones in ethanol gave E-isomer hydrazones 21a, while Z-isomers 21b were achieved when the reaction took place in xylene.\textsuperscript{33,34}

\[ R = \text{Ethyl, phenyl, 2-naphthyl} \]

Reduction of both 21a and 21b with excess sodium borohydride in methanol yielded products 22.\textsuperscript{33,34} Compound 23 was obtained from the reaction of 14 with diethyl acetylene dicarboxylate in ethanol.\textsuperscript{33}

\[ R = \text{Me, Ph} \]

**Acid hydrazide**

Dibenzobarallene (1) was reacted with acid hydrazide such that hydrazide of salicylic acid, p-chlorobenzoic acid, isonicotinic acid, and benzene sulfonic acid yielded phthalazinediones 24a-c and 25, respectively. The latter phthalazinedione, 25, was treated with acetic anhydride and p-toluene sulfonyl chloride to yield O-acetylated and O-sulfonated derivatives 26a and 26b, respectively.\textsuperscript{35}

\[ 24a, \text{Ar}=2\text{-HOC}_6\text{H}_4; \quad 24b, \text{Ar}=4\text{-ClC}_6\text{H}_4; \quad 24c, \text{Ar}=4\text{-pyridyl} \]

\[ 24a, \text{Ar}=2\text{-HOC}_6\text{H}_4; \quad 24b, \text{Ar}=4\text{-ClC}_6\text{H}_4; \quad 24c, \text{Ar}=4\text{-pyridyl} \]
Phthalazinediones 27a-c were also achieved from the reaction of 1 with hydrazides of N-arylglycine, which, upon treatment with formalin in acetic acid, gave polynuclear heterocyclic system 28a-c.\(^{35}\)

\[
\begin{align*}
27a-c & \quad 28a-c \\
\text{Ar} & = p-\text{ClC}_6\text{H}_4, \text{C}_6\text{H}_5, p-\text{CH}_3\text{C}_6\text{H}_4
\end{align*}
\]

Reaction of 1 with cyanoacetic acid hydrazide afforded 3-oxo-propiononitrile 29, which, upon treatment with aromatic aldehydes, afforded the corresponding arylidene derivatives 30a and 30b.\(^{35}\) Moreover, 29\(^{36}\) underwent the Gewald reaction with cyclohexanone or cyclopentanone to yield polynuclear heterocyclic compounds 31a and 31b.\(^{35}\)

\[
\begin{align*}
29 & \quad 30a, \text{Ar} = \text{C}_6\text{H}_5 \\
30b, \text{Ar} = 4-\text{CH}_3\text{O-C}_6\text{H}_4
\end{align*}
\]

The base-catalyzed reaction of 29 with phenyl isothiocyanate in dry DMF at room temperature yields unstable potassium salt 32. Treatment of 32 with dilute HCl gave thiocarbamoyl derivative 33. Cyclization of the potassium salt of thiocarbamoyl derivative 32 with chloroacetyl chloride afforded thiazolidin-5-one derivative 34 (Scheme 1).\(^{37}\)

2-Arylideno-1,3-thiazolidinone derivatives 35a and 35b were obtained by refluxing compound 34 with the appropriate aromatic aldehydes in a mixture of DMF and glacial acetic acid in the presence of a catalytic amount of fused sodium acetate. Condensation of thiazolidin-5-one derivative 34 with isatin or ninhydrin in DMF in the presence of a catalytic amount of TEA gave corresponding aryldene derivatives 36 and 37, respectively. Thiazolidin-5-one derivative 34 gave unexpected N-substituted isoindole derivative 38 upon treatment with an excess of Vilsmeier reagent at 80 °C (Scheme 2).\(^{37}\)
Compounds 39a, 39b, and 41 were obtained in high yields by refluxing compound 33 with α-halo compounds in an EtOH/DMF mixture. Treatment of thiocarbamoyl derivatives 32 or 33 with chloroacetonitrile gave 41; this reaction may be explained by the intermediacy of 4-iminothiazolidine derivative 40. On the other hand, the base catalytic reactions of thiocarbamoyl derivative 33 with α-halo compounds gave corresponding thiophene derivatives 42a-d. Reaction of thiocarbamoyl derivative 33 with dibromoalkane in ethanol in the presence of TEA gave corresponding cyclic ketene S,N-acetals 43a and 43b. Thiocarbamoyl derivative 33 undergoes oxidative cyclization upon treatment with bromine in acetic acid to give benzothiazole derivative 44 (Scheme 3).}$^{37}$
The coupling of 29 and 34 with various aryl diazonium chlorides in pyridine afforded 3-oxo2-(4-arylhydrazono)propiononitrile and 3-oxo-2-(4-arylazo-5-oxo-3-phenyl-thiazolidin-2-ylidene)propiononitriles 45a-j and 46a-g, respectively (Scheme 4).38

**Thiosemicarbazide**

Thioamide derivative 47 was obtained from the reaction of 1 with thiosemicarbazide. Treatment of 47 with sodium hydroxide solution gave 1,2,4-triazole derivative 48, which was alkylated with n-pentyl bromide to give S-pentyl derivative 49.

Compound 47 was reacted with an equimolar amount of α-halo compounds, namely chloroacetone, phenacyl chloride, and ethyl bromoacetate, in ethanol in the presence of sodium ethoxide to afford thiazole and thiazolidinone derivatives 50a, 50b, and 51, respectively. 5-Bromothiazole derivative 52 was obtained by the bromination of 50b in glacial acetic acid at 90 °C (Scheme 5).37

The diazocoupling of 50a and 50b with appropriate diazonium chlorides 53 gave corresponding 5-arylazo-thiazole derivatives 54. The synthesized dyes were applied to polyester as disperse dyes and their antibacterial, color measurement, and fastness properties were evaluated.39
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Scheme 4.

Scheme 5.

Cyclocondensation of 29 with salicylaldehyde in boiling DMF containing a catalytic amount of TEA afforded iminocoumarin derivative 55, which, upon hydrolysis in a mixture of concentrated HCl and ethanol, gave 2-chromone derivative 56. The reaction of 29 with elemental sulfur and phenyl isothiocyanate in warmed DMF containing a catalytic amount of TEA gave thiazole derivative 57. Cyclization of 57 by refluxing with
either triethylorthoformate or acetic anhydride gave 1,2,4-triazepine derivatives 58a and 58b. When compound 58b was heated with dimethylsulfate in DMF followed by stirring with hydrazine hydrate, hydrazone derivative 59 was obtained (Scheme 6). \(^{36}\)

![Chemical structures](image)

54a, R = CH₃, X = H; 54b, R = CH₃, X = CH₃; 54c, R = CH₃, X = OCH₃; 54d, R = CH₃, X = Cl; 54e, R = CH₃, X = Br; 54f, R = CH₃, X = NO₂; 54g, R = CH₃, X = COOEt; 54h, R = Ph, X = H; 54i, R = Ph, X = CH₃; 54j, R = Ph, X = OCH₃; 54k, R = Ph, X = Cl; 54l, R = Ph, X = Br; 54m, R = Ph, X = NO₂; 54n, R = Ph, X = COOEt

The coupling of compound 29 with 4,6-dimethyl-1H-pyrazolo[3,4-b]pyridine-3-diazonium chloride (60) \(^{40}\) in pyridine at 0-5 °C afforded corresponding hydrazono compound 61, which cyclized to the corresponding triazine derivative (62) upon refluxing in glacial acetic acid. A suspension of 29 in acetic acid or chloroform reacted readily with bromine to yield dibromopropionitrile derivative 63. Meanwhile, monobromopropionitrile derivative 64 was not obtained, but when the reaction took place with N-bromosuccinamide in DMF at room temperature, compound 63 was obtained. Condensation of compound 64 with o-phenylenediamine in DMF and in the presence of TEA afforded corresponding aminoquinoxaline derivative 65 (Scheme 7). \(^{36}\)

Treatment of compound 29 with phenyl isothiocyanate in a DMF/KOH mixture at room temperature gave a nonisolated sodium salt that methylated with methyl iodide to afford novel ketene N,S-acetal 67. Reaction of 67 with hydrazine hydrate in DMF did not afford 3-aminopyrazole 68 as expected, but rather phthalazinedione derivative 16 \(^{1}\) was achieved. Propiononitrile derivative 29 treated with carbon disulfide in the presence of 2 equivalents of sodium hydride gave nonisolated sodium salt 70, which was reacted with halogenated compounds, namely methyl iodide, 1,2-dibromomethane, or 1,3-dibromopropane, to give corresponding ketene dithioacets 71, 72a, and 72b, respectively. Refluxing of 71 with hydrazine hydrate did not afford aminopyrazole derivative 69 as expected, but rather phthalazine derivative 16 was achieved. The reaction of compound 29 with carbon disulphide and 1 equivalent of sodium hydride in DMF gave nonisolated sodium dithioacetel derivative 73, which was methylated with dimethyl sulfate to give methyl dithioate derivative 74 (Scheme 8). \(^{36}\)
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Scheme 6.

Scheme 7.
Hydroxylamine hydrochloride

Refluxing 1 with hydroxylamine hydrochloride in ethanol in the presence of pyridine gave N-hydroxy-succinimide derivative 75, which, upon refluxing with 2,4-dinitrochlorobenzene, yielded 76.41
Compound 75 reacted with 1,3-dibromopropane, 1-bromobutane, and p-toluene sulfonyl chloride in the presence of TEA to give bromopropoxy, butoxy, and p-tolylsulfonate derivatives 77a-c, respectively. Compound 77a reacted with N-phenyl piperazine to yield [(4-phenyl-piperazin-1-yl)propoxy] derivative 78.

![Chemistry of dibenzobarallene, M. A. GOUDA, et al.](image)

Amino alcohols

The fusion of 1 with ethanolamine gave corresponding derivative 79. Ester derivative 80 was obtained from the reaction of 1 with ethanolamine in acetic acid.

Moreover, 2-amino-2-methylpropane-1,3-diol was reacted with 1 to give diol derivative 81 and 2-amino-2-hydroxymethyl-1,3-propanediol gave triol derivative 82.

Imide 83 was prepared by condensation of 9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride with (2S,3S)-2-amino-1-phenyl-1,3-propanediol in toluene at reflux. Corresponding amine 84 was obtained by reduction of imide 83 using LiAlH₄ as a reagent. These diols were treated with corresponding phosphorochloridite 85, prepared in situ by standard procedures, to give C₁-symmetric diphosphites 86 and 87 in good yields (80%-86%) (Scheme 9).
p-Aminophenol

Equimolar amounts of 1 and p-aminophenol were heated under reflux in DMF to give succinamide derivative 88.\(^{14}\)

\[ \text{p-Aminophenol} \]

88

o-Amino- and o-aminothiophenol

The reaction of 1 with o-aminothiophenol in acetic acid gave disulfide 89, whereas a mixture of 89 and 90 was obtained when the reaction was carried out in DMF or a dioxane/pyridine mixture instead of acetic acid. The formation of 89 may be interpreted through the autoxidation of 90. On the other hand, 2-hydroxyphenyl derivative 91 was obtained by the refluxing of 1 with o-aminophenol in acetic acid, DMF, or a dioxane/pyridine
mixture. Treatment of compound 91 with p-toluenesulfonyl chloride in DMF in the presence of a catalytic amount of TEA gave corresponding ester derivative 92 (Scheme 10).\(^7\)

\[1 + \text{arylNH}_2 \xrightarrow{\text{AcOH, DMF, or Dioxane/Pyridine}} \text{91} \]

\[\text{1} + \text{arylNH}_2 \xrightarrow{\text{AcOH, DMF, or Dioxane/Pyridine}} \text{91} \]

Scheme 10.

**Amino acids**

Reaction of 1 with some aliphatic amino acids in dioxane and sodium carbonate (20\%) gave corresponding isoindole derivatives 93a-c after acidification with dilute HCl. Analogously, aromatic amino acids were reacted with 1 in DMF to yield 94a-c.\(^{44}\)

Moreover, glycylglycine was reacted with 1 in dioxane, in the presence of sodium carbonate, to yield 95 after acidification.\(^{44}\)
Acid derivative 93b was converted to propionyl chloride derivative 96 by reaction with thionyl chloride. Treatment of acid chloride 96 with 4-alkyl piperazines, piperidine, morpholine, and aniline gave derivatives 4-alkyl-1-piperazinyl, 1-piperidinyl, 4-morpholinyl, and N-phenyl propionamide 97a, 97b, 98a, 98b, and 99, respectively.

Dibenzobarallene (1) was converted into its acid derivative by reaction with L-leucine. The cyclization reaction was carried out in situ using TEA to give succinic imide acid derivative 100. Compound 100 was converted to acid chloride 101 by reaction with thionyl chloride. The reaction of acid chloride 101 with isoeugenol (102) was carried out in chloroform and a novel, optically active isoeugenol ester derivative (103) was obtained. 4-Phenyl-1,2,4-triazolin-3,5-dione (PhTD) (104) was allowed to react with compound 103 to give only 1 diastereoisomer of 105 via Diels-Alder and ene pathways in a quantitative yield (Scheme 11).

2(S)-3-Phenyl-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoic acid (107) was synthesized from the reaction of L-phenylalanine (106) with 1 in acetic acid under refluxing conditions. Treatment of 107 with thionyl chloride afforded corresponding acid chloride 108. Compound 108 reacted with 5-aminoisophthalic acid (109) in DMAC to give 5-[3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)propanoylamino]isophthalic acid (110) as a chiral monomer in high yield and purity (Scheme 12).
A highly effective, very fast microwave method was used to synthesize optically active aromatic polyamides (PAs) 112a-g under microwave heating for only 3 min by the reaction of 110 with corresponding diamine derivatives 111a-g (Scheme 13).
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Scheme 13. Polycondensation reactions of monomer 100 with aromatic diamines.

Reaction of 1 with sarcosine methyleamide trifluoroacetate in DMF in the presence of K2CO3 yielded corresponding amide 113. Treatment of 113 with sarcosine ethyl amide trifluoroacetate in DMF in the presence of DIEA, PyBOP, and K2CO3 afforded 114.

Ethyl-2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate (115) was reacted with 1 in acetic acid/sodium acetate to yield corresponding tetrahydrobenzothiophene derivative 116.
Benzylamines

A new class of anthracene-fused proline catalysts, 125 and 126, was prepared via treatment of 1 with an equimolar amount of p-methoxybenzylamine (PMBN\(\text{H}_2\)) in hot THF, producing desired N-PMB-protected imide 117 in an almost quantitative yield. LAH reduction followed by protective-group transformation cleanly provided N-Boc-protected isoindole 119 (66% yield over 2 steps). The crucial attachment of a carboxyl function onto 119 was successfully achieved by using Beak’s protocol: N-Boc-directed lithiation/carboxylation.\(^{54,55}\) Thus, lithiation using sec-BuLi/TMEDA in dry THF at 78 °C for 5 h provided α-lithioamide intermediate 120, which, upon exposure to bubbling CO\(_2\) (gas), gave desired carboxylic acid 121 in an excellent yield. Treatment of 121 with (-)-menthol with the aid of DCC/DMAP gave menthyl ester 122. TFA-promoted deprotection of the N-Boc group gave nearly equal amounts of free amines 123 and 124 in a combined yield of 91%. Alkaline hydrolysis of the menthyl ester of 123 gave the end product, anthracene-fused proline catalyst 125, \([\alpha]_D^{22} = +57.6\) (c 0.62, MeOH), in an enantiomerically pure form in 73% yield. In the same manner, catalyst 126, \([\alpha]_D^{22} = -57.6\) (c 1.31, MeOH), was obtained from 124 (Scheme 14).\(^{56}\)

The newly formed anthracene-fused chiral proline catalysts were tested in asymmetric 3-component Mannich reactions between ketone donors (127), aldehyde acceptors (128), and p-anisidine (129) (Scheme 15).\(^{56}\)

\[
\begin{align*}
\text{O} & \quad + \quad \text{H}_2\text{C} = \text{O} \quad + \quad \text{CH}_3\text{NH}_2 \\
\text{R} & \quad \text{R}' & \quad \text{OCH}_3 \\
127 & \quad 128 & \quad 129 \\
\text{O} & \quad \text{HN} & \quad \text{PMP} \\
\text{R} & \quad \text{R} & \quad \text{PMP} \\
125 & \quad 126 & \quad 130 \\
\end{align*}
\]

Scheme 15. Asymmetric 3-component Mannich reactions between ketone, p-anisidine, and aldehyde.

N-((1S)-1-phenylethyl)-9,10-dihydro-9,10-ethanoanthracene-(11S,12S)-dicarboximide (131) was obtained by condensation of anhydride 1 and (S)-α-methylbenzylamine in toluene. Further ruthenium-assisted hydrogenation of 131 led quantitatively to the formation of 132 under mild conditions (room temperature and low hydrogen pressure).\(^{57}\)
3-[4-(4-Fluorophenyl)piperazin-1-yl]propylamine

Refluxing of 1 with 3-[4-(4-fluorophenyl)piperazin-1-yl]propyl-amine in xylene using a Dean Stark apparatus gave 133. 8

![Chemical structure of 133](image)

Substituted pyrroloanthracene or its dione derivatives (134) were prepared by imidation reaction of the corresponding substituted alkylamines with 1. 5

![Chemical structure of 134](image)

**Primary aromatic amines**

Fusion or refluxing of 1 with some primary aromatic amines in DMF gave the succinamide derivatives 135a and 135b. Treatment of 135b with Grignard compounds afforded 136 in good yield. 58,59

![Chemical structures of 135a, 135b, and 136](image)

p-Aminoarylazobenzene derivatives 137 reacted with 1 in DMF or in glacial acetic acid/anhydrous sodium acetate to afford 2-arylanil benzene isoindole derivatives 138a and 138b. 7
2-Aminopyridine

Compounds 139a and 139b were achieved by heating 1 with 2-aminopyridine derivatives at 100-140 °C for 3 h.  

Isoquinolyl amine

Fusion of dibenzobarallene (1) with isoquinolyl amine at 100-190 °C for 2 h yielded 140.  

Benzothiazole and amino-1,2,4-triazoles

Isoindoldione derivatives 141 were obtained from the reaction of adduct 1 with 2-amino-6-methylbenzothiazole in DMF. Heating of 1 with 4-amino-1,2,4-triazoles at 130-150 °C yielded 142 (R= H, Me, Et). Moreover, refluxing of 1 with 3-amino-1,2,4-triazole gave in DMF 143.
p-Aminoacetophenone

Isoindoledione derivative 144 was obtained by the reaction of 1 with 4-aminoacetophenone. Bromination of 144 in acetic acid gave dibromo derivative 145. The latter compound was reacted with o-phenylenediamine to give benzoimidazole derivative 146.7

![Chemical structures of 144, 145, and 146](image)

Diamines

Compound 1 was reacted with p-phenylenediamine in DMF to give bis-product 147.44 Reaction of 1 with ethylenediamine in acetic acid6 gave a mixture of bis-product 148 and ethyl acetamidine derivative 149.63

![Chemical structures of 147, 148, and 149](image)

The same reaction, as carried out in DMF, gave another mixture of 14864–68 and aminoethyl derivative 150.6 Compound 148 was obtained only when the reaction took place in a dioxane/pyridine mixture. Reduction of 148 with lithium aluminium hydride gave 151.67 The reaction of 1 with o-phenylenediamine in acetic acid7 gave benzoimidazole derivative 152, whereas isoindoledione derivative 153 was obtained when the reaction took
place in DMF or dioxane/pyridine. The latter derivative was treated with acetyl chloride and TEA to yield 154. Compound 152 reacted with 2-naphthoquinone-4-sulfonic acid sodium salt in DMF to give 155.\(^7\)

Adduct 1 reacted with N,N-dimethylpropane-1,3-diamine or 2,2,N,N-tetramethylpropane-1,3-diamine in toluene in the presence of a catalytic amount of p-toluene sulfonic acid to yield corresponding isoindole derivatives 156a and 156b.\(^{69}\) Isoindoledione derivatives 156 were stirred in a 10-fold excess of 1,6-dibromohexane without any solvent to give bromohexane derivative 157.\(^{69}\)

Bis-isoindoledione derivative 158 was achieved by the reflux of 1 with a half-equivalent of dibromohexane in acetonitrile in the presence of a catalytic amount of KI and K\(_2\)CO\(_3\). Furthermore, 158 was achieved by the reaction of 157 with 156 under previous conditions.\(^{69}\)
Urea

Compound 1 was fused with urea to give succinamide derivative 159, which was added to formalin to give 160.\textsuperscript{70,71} The latter compound was reacted with various amines to give 161 (R= phenyl, substituted phenyl, 1-naphthyl), which was prepared directly from the Mannich reaction of 159 with formalin and amines.

Grignard reagents

Compound 162 was prepared by reaction of 1 with Grignard reagent.\textsuperscript{72}

1,8-(Bis-trimethylsilyl)octa-2,6-diene

Adduct 1 was reacted with 1,8-(bis-trimethylsilyl)-octa-2,6-diene to yield γ-keto acid derivative 163.\textsuperscript{73}
Reduction

Hydrogenation of 1 in the presence of Raney nickel gave 164. On the other hand, treatment of 1 with hydrogen in the presence of a Ru-catalyst afforded 165. Reduction of 1 with sodium borohydride gave 166, which, upon treatment with n-butyl tin oxide and carbon disulfide, yielded 167.

 Compound 166 was prepared by reduction of 1 with lithium aluminum hydride. Reaction of 166 with p-toluenesulfonyl chloride in pyridine gave compound 168. The latter compound was refluxed with LiBr in acetone to give 9,10-ethanoanthracene derivative 169. Treatment of 168 with Na₂Se in 1-methoxy-2-(2-methoxyethoxy)ethane gave selenolane derivative 170.

9,10-Dimethyl ethanoanthracene 172 was prepared by reduction of compound 168 with LiAlH₄ in THF.
Jones and Wilson\textsuperscript{78} reported that reduction of anhydride \textbf{1} with sodium borohydride afforded lactone \textbf{172} in excellent yield. However, treatment of a slurry of lactone \textbf{172} with lithium diisopropylamide in THF at 0 °C led to complete solubilization and generation of an intense yellow solution. Addition of a slight excess of methyl iodide, allyl iodide, butenyl bromide, or benzyl bromide afforded C-alkylated lactones \textbf{173-176} in good yields. Reaction of \textbf{172} with tributylin chloride gave stannane \textbf{177} in a disappointingly low yield. However, reaction with diethyl chlorophosphate gave α-phosphonate \textbf{178} in good yield, while chlorotrimethylsilane yielded C-silyl lactone \textbf{179} as the sole product in excellent yield (84%) (Table).\textsuperscript{78}

\begin{center}
\textbf{Table.} Results of the compounds obtained from the reaction of lactone \textbf{172} with different electrophiles.
\end{center}

\begin{tabular}{|c|c|c|}
\hline
Electrophile & R & Product & Yield \\
\hline
CH\textsubscript{3}I & CH\textsubscript{3} & \textbf{173} & 76% \\
CH\textsubscript{2}=CHCH\textsubscript{2}I & CH\textsubscript{2}=CHCH\textsubscript{2} & \textbf{174} & 71% \\
CH\textsubscript{2}=CHCH\textsubscript{2}CH\textsubscript{2}Br & CH\textsubscript{2}=CHCH\textsubscript{2}CH\textsubscript{2} & \textbf{175} & 75% \\
PhCH\textsubscript{2}Br & PhCH\textsubscript{2} & \textbf{176} & 78% \\
Bu\textsubscript{3}SnCl & Bu\textsubscript{3}Sn & \textbf{177} & 21% \\
(\text{EtO})\textsubscript{2}P(O)Cl & (\text{EtO})\textsubscript{2}P(O) & \textbf{178} & 74% \\
(CH\textsubscript{3})\textsubscript{3}SiCl & (CH\textsubscript{3})\textsubscript{3}Si & \textbf{179} & 86% \\
\hline
\end{tabular}

**Nitration**

Nitration of \textbf{1} with nitric acid in the presence of concentrated sulfuric acid gave dinitro derivative \textbf{180}.\textsuperscript{79}
Sulfonation

Sulfonation of 1 with concentrated sulfuric acid in acetic anhydride afforded disulfonated product 181.\(^\text{80}\)

\[
\begin{align*}
\text{HO}_3\text{S} & \quad \text{HO}_3\text{S} \\
\text{HO}_3\text{S} & \quad \text{HO}_3\text{S}
\end{align*}
\]

Treatment of 181 with barium carbonate yielded the corresponding barium salt, which was converted to sodium carbonate 182.\(^\text{80}\)

\[
\begin{align*}
\text{NaO}_3\text{S} & \quad \text{COONa} \\
\text{NaO}_3\text{S} & \quad \text{COONa}
\end{align*}
\]

Friedel-Crafts reaction

Compounds 183a and 183b were prepared by the Friedel-Crafts reaction of 1 with benzene or toluene in the presence of AlCl\(_3\).\(^\text{81,82}\)

\[
\begin{align*}
\text{COOH} & \quad \text{R} \\
\text{183a, } R= \text{H} & \quad \text{183b, } R= \text{CH}_3
\end{align*}
\]

Esterification

Compound 1 was esterified by reaction with alcohol in the presence of concentrated sulfuric acid to give diester 185 (R= Me and Et). Treatment of 185 with hydrazine hydrate yielded diacid hydrazide 186.\(^\text{83}\) Dihydrazide 186 was reacted with acetyl acetone to afford pyrazole derivative 187. Compound 186 was also reacted with aromatic aldehydes to afford diarylidene hydrazonyl derivatives 188.\(^\text{83}\)
Moreover, the reaction of dihydrazide derivatives 186 with isothiocyanate derivatives furnished corresponding dithiosemicarbazides 189. The latter adduct, 189, cyclized with alcoholic KOH followed by acidification with dilute HCl to yield ditriazole derivative 190. Saponification of 185 (R= Me) with KOH in methanol gave the corresponding potassium salt, which, upon acidification with dilute HCl, yielded diacid 6. The refluxing of compound 6 with SOCl2 gave the acid chloride, which reacted with amines in THF to afford bis-amide ethanoanthracene derivatives 191a and 191b.

**Conclusion**

The present review has illuminated different aspects of dibenzobarallene chemistry and has outlined its importance as a valuable synthetic building block for the synthesis of a wide range of various heterocyclic systems. Five methods for dibenzobarallene’s nomenclature were reported. Synthesis of the titled compound was achieved by reacting maleic anhydride and anthracene through Diels-Alder, fusion, refluxing “in different solvent,” catalysis, microwave irradiation, and photolysis reactions. This review discussed spectroscopic and kinetic studies as well as thermodynamic measurements. Finally, the reactivity of dibenzobarallene was discussed through nucleophilic and electrophilic reactions.
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Abbreviations

FTIR, Fourier transform infrared spectroscopy; D-A, Diels-Alder; p°, standard pressure (chosen value of pressure denoted by p° in 1982); MPa, 1 MPa = 1,000,000 Pa = pascal; \( \Delta_r \text{H}^\circ_m \), standard molar enthalpy of combustion; DuPont DSC, differential scanning calorimetry; \( \Delta_f \text{H}^\circ_m \), enthalpy of fusion; LiAlH₄, lithium aluminum hydride; PhTD, 4-phenyl-1,2,4-triazoline-3,5-dione; DMAc, dimethyl acetamide; (PA)s, polyamides; DIEA, N,N-diisopropylethylamine; PyBOP, (benzotriazol-1-yloxy)tri-pyrrolidinophosphonium hexafluorophosphate; (PMBNH₂), p-methoxy-benzyl-amine p-methoxybenzylamine; N-PMB-protected imide, N-(p-methoxybenzyl)-4,9[1',2']benzeno-3a,4,9a-tetrahydro-1H-benz[f]isoindole-1,3(2H)-dione; N-Boc-directed N-(tert-butoxycarbonyl)-4,9[1',2']benzeno-1,3,3a,4,9a-hexa-hydro-1H-benz[f]isoindole; Boc₂O, di-tert-butyl dicarbonate or di-tert-butyl pyrocarbonate Boc anhydride; sec-BuLi/TMEDA, N,N,N',N'-tetramethylethylendiamine (secondary butyl lithium); DCC, N,N'-dicyclohexyl-carbodiimide C/DMAP 4-dimethylaminopyridine; \( [\alpha]_{D}^{22} \), specific rotation; Boc₂O, di-tert-butyl dicarbonate TMEDA, N,N,N',N'-tetramethyl ethylenediamine; Ru catalyst, rhodium catalyst.

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References

Chemistry of dibenzobarallene, M. A. GOUDA, et al.

15. Diels, O.; Alder, K. Ber. 1931, 64, 2194-2200; C.A. 1932, 26, 446.
Chemistry of dibenzobarallene, M. A. GOUDA, et al.

Chemistry of dibenzobarallene, M. A. GOUDA, et al.