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A NEW AND CONVENIENT SYNTHESIS OF SUBSTITUTED BENZOBARRELENES

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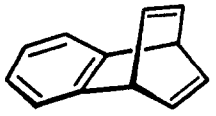
Summary: Bromination of 3-bromo-6,7-benzobicyclo [3.2.1] octa-2,6-diene at -50°C gave anti-tribromo adduct (5) in essentially quantitative yield. The double dehydrobromination of (5) was achieved using potassium tert.-butoxide to give 2-bromo-benzobarrelene (7). Reaction of (7) with n-BuLi and subsequent quenching with CH_3I, CO_2, and dimethylformamide afforded the corresponding substituted benzobarrelenes in high yield.

Benzobarrelene (1) is a molecule of considerable potential mechanistic interest. Zimmerman et al.[2] have reported that benzobarrelene (1) undergoes two types of photochemical reactions, one leading to benzocyclooctatetrane (2) proceeding from the singlet state of (1) via 2π+2π cycloaddition and the other leading to semibulvalene (3) from the triplet excited state via di-π-methane rearrangement.



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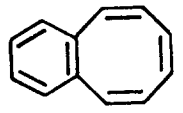

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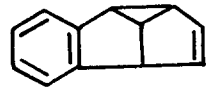
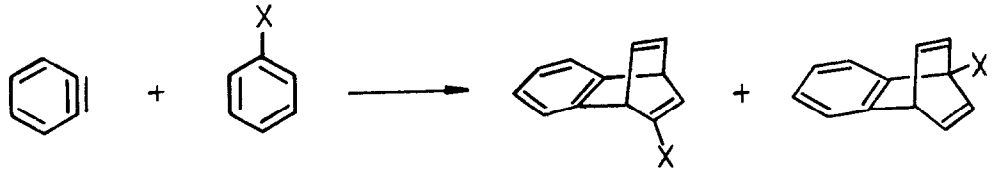


3

Furthermore, deuterium labelling studies revealed that of the two bonding routes; vinyl-vinyl bridging and vinyl-aryl bridging, the last one is mainly utilized. However, di-π-methane rearrangement was uniquely provided by the vinyl-vinyl bridging.

By the introduction of a substituent in a vinyl location the symmetry of benzobarrelene skeleton is destroyed. Therefore, the number of possible initial bonding modes is increased to three 2π+2π cycloaddition and six di-π-methane rearrangement. On this basis, vinyl substituted benzobarrelenes gain more important by elucidation of the mechanism of the 2π+2π cycloaddition reaction and di-π-methane rearrangement.

Recently, some mono-substituted benzobarrelenes have been synthesized by reaction of benzyne with substituted benzenes (anisole, chlorbenzene, brombenzene, methylbenzoate, and alkylbenzenes)[3-5].

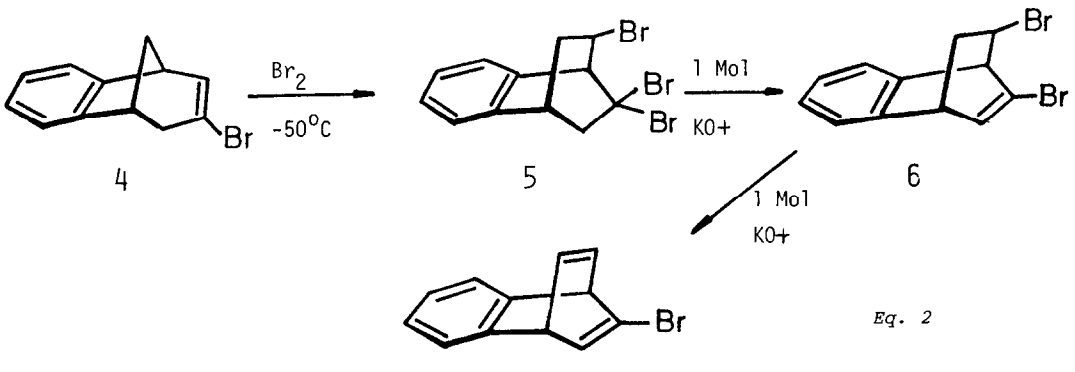


	YIELD	
X : CH_3	5 %	OTHER PRODUCTS
: CH_2CH_3	9 %	
: OCH_3	3 %	*Eq. 1*
: Cl	3.4 %	
: Br	1.7 %	
: $COOCH_3$	6 %	

From all the reactions resulted a complex mixture which could not be separated easily and the reported yields were very low for large-preparation of 2-substituted benzobarrelenes derivatives.

We now present here an alternative large-scale preparation of substituted benzobarrelenes.

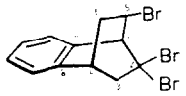
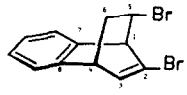
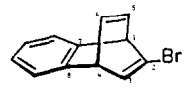
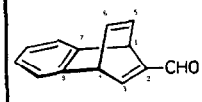
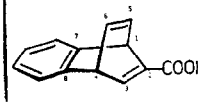
The addition of dibromocarben to the readily available benzonorbornadiene[6] gives a rearranged adduct which on reduction with $LiAlH_4$ affords the known 3-bromo-6,7-benzobicyclo [3.2.1] octa-2,6-diene (4)[6]. Bromination of bromohydrocarbon (4) in chloroform at -50°C proceeded with rearrangement to give anti-tribromoadduct (5)[7] in essentially quantitative yield. This key step serves both to bring about the requisite skeletal rearrangement and to provide the functionality which permits the easy introduction of two double bonds. In the final step, the double dehydrobromination of (5) was achieved with surprising efficiency using potassium tert.-butoxide[8]. Treatment of (5) with one mol potassium tert.-butoxide gave (6). With two mole potassium tert.-butoxide we isolated bromo-benzobarrelene (7) in a yield of 95 %. Physical data are given in Table 1.



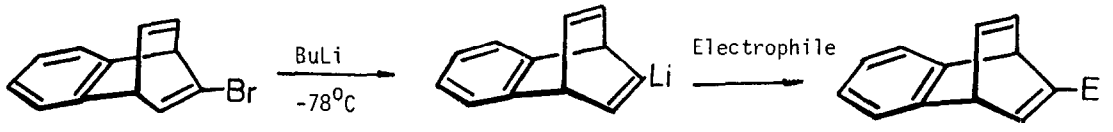
4 5 6 7

Eq. 2

Table 1. Selected physical data of compounds (5), (6), (7), (10), and (11).

	^{1}H-NMR δ ppm	^{13}C-NMR δ ppm	IR cm^{-1}
	2.0-2.45 m, $H_{66'}$, 2.8-3.65 AB-System, $H_{33'}$, 3.0 m, H_4, 4.15 d, H_1, 4.0-4.4 ddd, H_5 7.0-7.4 m, aromatic 4H	140.35, 136.98, 128.46, 127,21, 125,69, 124,51, 59.58, 58,38, 55.81, 44.95, 36,52, 34.27.	3075, 3045, 3020, 2980, 1480, 1455, 1225, 1100, 1025, 955, 850, 765.
	1.8-2.45 AB-System, $H_{66'}$, 3.7-4.15 m, H_5 and H_4, 4.25 t, H_1, 6.60 dd, H_3, 6.8-7.4 m, aromatic 4H	141.44, 139.86, 133.94, 127.04, 125.94, 124.10, 123.76, 122,97, 57.46, 46.11, 42.51, 37.94.	3060, 2970, 1610, 1470, 1455, 1210, 1000, 760.
	4.5-4.9 m, H_1 and H_4, 6.6-7.2 m, aromatic and olefinic protons 7H	145.92, 138.64, 132.23, 139.72, 139.03, 136.76, 124.19, 123.74, 122.58, 122.23, 57.89, 50.21.	3070, 3040, 3020, 2980, 1615, 1465, 1455, 1310, 1260, 1205, 1190, 1000.
	5.0 m, H_4, 5.43 m, H_1, 6.7-7.3 m, aromatic, H_5, H_6, 7.42-762 dd, H_3, 9.41 s, aldehydic		3020, 2990, 2970, 2820, 2780, 1660, 1560, 1450, 1280.
	4.95 m, H_4, 5.32 m, H_1, 6.7-7.3 m, aromatic, H_5, H_6, 7.42-7.62 dd, H_3, 9.85-10.35, OH		3400, 3000-2100, 1665, 1620, 1585, 1420, 1270, 1250.

Bromobenzobarrelene (7) was the key compound for the synthesis of tho other substituted benzobarrelene derivatives. When (7) was treated with 1.2 equivalent of n-Buli/THF at -78°C for 1/2 hour, followed by H_2O, CH_3I, CO_2, and dimethylforamide quenching, the products were as shown in Eq. 3.



7 8

E	Yield	
H	90 %	I
CH_3	80 %	9
COOH	71 %	10
CHO	48 %	11

Eq. 3

The presently described synthesis offers several advantages over previous methods. Although relatively lengthy, it begins with a readily available starting material (4) and subsequent steps are all efficient and readily applicable to large-scale preparation. On the other hand, this route offers several possibilities for isotopically labeling the bicyclic skeleton.

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