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Addition of Benzyne to *cis*- and *trans*-1,3-Pentadiene

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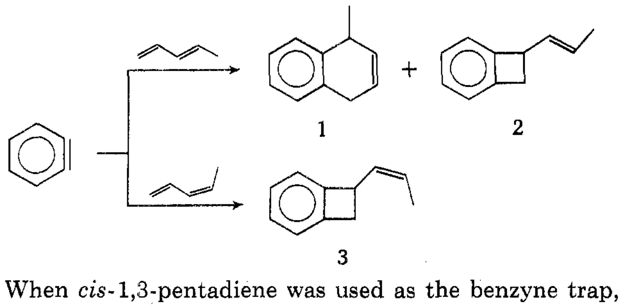
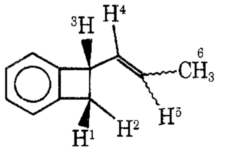
The addition of benzyne to alkyl-substituted dienes can conceivably give [2 + 2], [2 + 4], and "ene" reaction products.[1] When the diene can achieve the s-cis conformation, [2 + 4] addition predominates over [2 + 2] addition.[2] When an ene reaction is possible, it predominates over the [2 + 2] reaction path in most olefins.[3,4] We wish to report the addition of benzyne to *cis*- and *trans*-1,3-pentadiene, which surprisingly shows no ene product.

Benzyne, generated from benzenediazonium 2-carboxylate,[7] adds to *trans*-1,3-pentadiene giving two isomeric adducts, **1** (46%) and **2** (16%). Compound **1** had an NMR spectrum consistent with 1-methyl-1,4-dihydronaphthalene. In addition, oxidation of **1** with dichlorodicyanoquinone resulted in 1-methylnaphthalene, which was identical with an authentic sample. The NMR data for **2** are in Table I.



When *cis*-1,3-pentadiene was used as the benzyne trap, 2-*cis*-propenylbenzocyclobutene (**3**) was formed in 24% yield. The NMR spectrum of **3** is very similar to that of **2** (see Table I). Oxidation of **3** with $KMnO_4$–$NaIO_4$ resulted in acetic acid and benzocyclobutene-2-carboxylic acid, which was identical with authentically prepared material.[8] No **3** was observed by NMR when the trans diene was used and no **2** was found when the cis diene was used. If benzyne was produced by the reaction of *o*-bromofluorobenzene with magnesium,[2a] cis–trans isomerization of the diene occurred (GLC analysis). Thus, **1** was observed when *cis*-1,3-pentadiene was used as the benzyne trap. When benzenediazonium 2-carboxylate was used as the benzyne precursor, no cis–trans diene isomerization was observed.

Table I
Nmr Spectra of *cis*- and *trans*-2-Propenylbenzocyclobutene



	Aromatic	H_1	H_2	H_3	H_4 and H_5	H_6
2	7.13[a]	3.45	2.84	4.05	5.68	1.68
3	7.1	3.52	2.86	4.38	5.6	1.76
	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{5,6}$		
2	13.8	2.6	5.2	4.5		
3	14.0	2.7	5.3	5.2		

[a] In CCl_4/Me_4Si. Chemical shifts reported in parts per million (δ). Coupling constants reported in hertz.

The [2 + 4]/[2 + 2] ratio observed when benzyne adds to *trans*-1,3-pentadiene (3.9:1) is essentially the same as the ratio found when it adds to 1,3-butadiene (4:1[2e]). It is not surprising that the methyl group little affects the addition of benzyne to this diene. This report also shows that benzyne is unable to give a [2 + 4] addition product with *cis*-1,3-pentadiene owing to this diene's inability to achieve the required s-cis conformation.[9] In fact, maleic anhydride is the only dienophile reported to give a [2 + 4] product with the cis diene.[10,11] Since benzyne has an alternate reaction pathway ([2 + 2] addition), it is not required to partake in an inherently undesirable [2 + 4] addition to the cis diene.[12]

In dienes which have no conformational peculiarities, ene addition predominates over [2 + 2] addition. It is therefore noteworthy that no ene product is observed when benzyne adds to 1,3-pentadiene. Owing to rotation of the methyl group, a suitable conformation must be available for what is apparently a concerted ene reaction.[1b] The answer here might lie in an especially facile [2 + 2] addition of benzyne to 1,3-pentadiene. The determining factor could be a sterically less restricted approach to the terminal double bond in the pentadienes which is not possible in the other dienes that have been studied. Indeed, there could be a great inherent tendency for benzyne to undergo a [2 + 2] addition than an ene reaction with *any diene*.[14] This tendency may be masked by steric effects in most dienes.[15,16]

Experimental Section

General. The NMR spectra were obtained on a Varian Associates A-60 spectrometer. A Beckman IR-10 was used for the ir spectra. Mass spectra were determined on a Hitachi Model RMU-6E spectrometer at an ionizing voltage of 70 eV. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Gas–liquid phase chromatography was conducted on a Varian A-90P instrument. Tetrahydrofuran was distilled from lithium aluminum hydride before use. *cis*- and *trans*-1,3-pentadiene (PCR, Inc., greater than 99% geometric purity) were distilled before use.

Generation of Benzyne in the Presence of *cis*-1,3-Pentadiene. To 0.025 mol of benzenediazonium 2-carboxylate[7] was added 30 ml of chloroform and 2.04 g of *cis*-1,3-pentadiene (0.030 mol). The mixture was heated at 40–45° for 4.5 hr. After cooling, GLC analysis showed no *trans*-1,3-pentadiene. The solvent was removed under vacuum. The product, **3**, was isolated using column chromatography (alumina, *n*-pentane) and weighed 0.724 g (24%

yield). An analytical sample was isolated by preparative GLC (see Table I for NMR data): ir (neat) 3080 (w), 3020 (m), 2970 (m), 2930 (s), 1455 (m), 740 (s), 718 (m), and 700 cm^{-1} (m); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.47; H, 8.43.

Generation of Benzyne in the Presence of *trans*-1,3-Pentadiene. When the above procedure was applied using the trans diene, a mixture of 1 and 2 was isolated (62% yield combined). The ratio 1:2 was 3.9:1 (GLC). The isomers were separated by preparative GLC.

1: NMR ($CDCl_3$) 1.31 (d, J = 6.8 Hz, 3 H, methyl), 3.38 (broad s, 3 H, benzylic), 5.88 (m, 2 H, olefinic), and 7.16 ppm (m, 4 H, aromatic); ir (neat) 3035 (w), 3026 (m), 2970 (m), 2930 (m), 2880 (m), 1581 (w), 1492 (m), 1450 (m), 747 cm^{-1} (s); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.46; H, 8.43.

2: NMR, see Table I; ir 3080 (w), 3030 (m), 2970 (m), 2930 (w), 1460 (m), 965 (s), 745 cm^{-1} (s); mass spectrum *m/e* 144 (molecular ion). Anal. Calcd for $C_{11}H_{12}$: c, 91.61; H, 8.39. Found: C, 91.61; H, 8.33.

Oxidation of 3.[17] To 29 ml of a $NaIO_4$–$KMnO_4$ solution (0.38 *M* $NaIO_4$ and 0.0064 *M* $KMnO_4$) was added 20 ml of *t*-BuOH and enough K_2CO_3 to achieve a pH of 8. To this was added 20 mg of **3**. The solution was stirred at room temperature for 5 hr. After acidification with 2 *M* HCl, the solution was extracted five times with a 1:1 mixture of ether and pentane. The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed by distillation. The acetic acid in this residue was removed by vapor transfer and identified by comparing its NMR spectrum with that of authentic material. The mass spectrum of the residue showed a molecular ion (*m/e* 148) consistent with $C_9H_8O_2$. The NMR spectrum was identical with that of independently prepared benzocyclobutene-1-carboxylic acid.

Oxidation of 1. A mixture of 40 mg of **1**, 63.5 mg of dichlorodicyanoquinone, and 1 ml of benzene was brought to reflux for 15 min. After cooling, 50 ml of pentane was added and the mixture was filtered. The filtrate was then passed through a short column of alumina using pentane as the eluent. The solvent was removed under vacuum. The NMR spectrum was identical with that of commercial 1-methylnaphthalene.

Acknowledgments. We would like to acknowledge the support of the Faculty Research Fund of Georgia College. We are grateful to Dr. W. M. Jones and the Department of Chemistry of the University of Florida, where the final ir, NMR, and mass spectra were obtained.

Registry No.—1, 21564-70-5; 2, 54384-63-3; 3, 54384-64-4; benzyne, 462-80-6; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; benzenediazonium 2-carboxylate, 1608-42-0; benzocyclobutene-1-carboxylic acid, 14381-41-0; dichlorodicyanoquinone, 84-58-2; 1-methylnaphthalene, 90-12-0.

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(11) The necessary presence of picric acid in the maleic anhydride [2 + 4] addition to *cis*-1,3-pentadiene[10] obfuscates this comparison. The acid reportedly retards polymerization of the diene, but may also exert some catalytic effect.

(12) Stewart[13] has placed a relative rate limit on the addition of tetracyanoethylene to the cis and trans dienes. The ratio k_{cis}/k_{trans} = 10^{-5} was based on the rate of color fading of the complex formed between the cis diene and TCNE. No adduct was isolated.

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(14) This is not the case for monoolefins. Stepwise [2 + 2] addition[2b] to simple olefins does not result in an allylic intermediate, which is the case when a diene is the benzyne acceptor.

(15) A reviewer commented on the observed [2 + 2] addition of benzyne to disubstituted double bonds in 2,3-dimethyl-1,3-butadiene[2a] and *trans,-trans*-2,3-hexadiene.[2c] Although [2 + 2] addition was found in these systems, ene addition still predominated (although slightly with the 2,4-hexadiene). It is obviously a delicate balance of steric and electronic factors that determines the ene/[2 + 2] ratio. We thank the reviewer for his comments.

(16) In a recent publication, M. Jones, Jr., and coworkers report the thermolysis of **2** and **3**, which were prepared by the addition of benzyne (generated from the photolysis of phthaloyl peroxide) to *trans*- and *cis*-1,3-pentadiene: M. R. DeCamp, R. H. Levin, and M. Jones, Jr., *Tetrahedron Lett.*, 3575 (1974).

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Efficacious Cleavage of the Benzyl Ether Protecting Group by Electrochemical Oxidation

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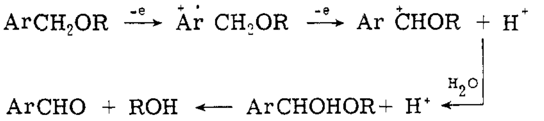
An effective way to protect an alcohol is via its benzyl ether.[2] However, the common ways used to remove this blocking group (i.e., catalytic hydrogenation or alkali metal reduction) involve conditions which may not be applied to molecules where other easily reduced functional groups are present. We wish to report a straightforward procedure whereby a benzyl group can be cleanly removed electrochemically under mild, *oxidative* conditions.[3] This provides a complementary alternative to the presently used reductive methods.

Early work by Lund[4] revealed that the oxidation potential for the benzyloxy group was low enough to allow electrochemical oxidation. This work was followed by other studies[5-7] which indicated that the oxidation of benzylic ethers, esters, or alcohols will proceed to form benzaldehyde. The probable mechanism of this reaction is as shown in Scheme I. Even though previous workers have focused attention on the formation of the aromatic aldehyde, concomitant formation of the alcohol in the above sequence has been confirmed by Miller,[5] who, in fact, suggested the possible usefulness of this reaction as a method of cleaving benzyl protecting groups. However, the generality and utility of this reaction apparently have not been tested, possibly because of Miller's observation that constant "pulsing" of the electrode potential was necessary in order to obtain reasonable yields. Without this pulsing, Miller reports that under his conditions (anhydrous acetonitrile with added

Scheme I



$$\text{ArCH}_2\text{OR} \xrightarrow{-e} \overset{+\bullet}{\text{Ar}}\,\text{CH}_2\text{OR} \xrightarrow{-e} \text{Ar}\,\overset{+}{\text{C}}\text{HOR} + \text{H}^+$$

$$\text{ArCHO} + \text{ROH} \longleftarrow \text{ArCHOHOR} + \text{H}^+ \xleftarrow{\text{H}_2\text{O}}$$