*p*-benzoquinone/sulfite system, resulting in a complex set of reaction pathways and products such as suggested by Scheme II.

Although the kinetic data presented here strongly suggest Scheme I as the mechanism for sulfite addition to *p*-benzoquinone between pH 4.5 and 8.0, the behavior at higher pH is still poorly understood. Unfortunately, it is in the more alkaline solutions that the reactions of sulfite with *p*-benzoquinone are most important in photographic science. We hope the mechanistic interpretation of the well-behaved reaction in neutral solution will provide some insight into the more complex behavior in alkaline solution.

**Registry No.** $Na_2SO_3$, 7757-83-7; *p*-benzoquinone, 106-51-4.

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# Regiochemistry of Addition of Iodine Azide to 1-Arylcyclohexenes

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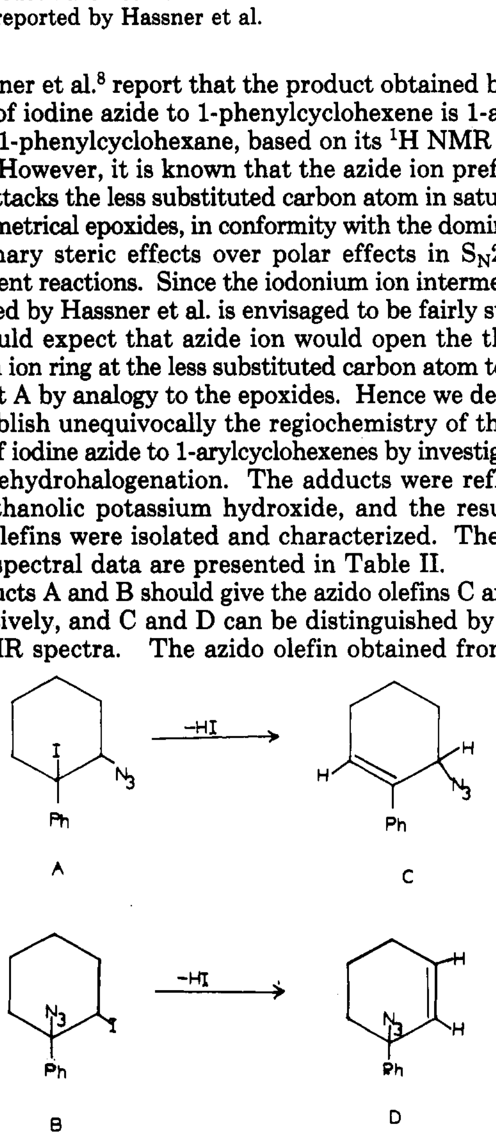
The addition products of iodine azide to several 1-arylcyclohexenes have been shown to be 2-azido-1-iodo-1-arylcyclohexanes and not 1-azido-2-iodo-1-arylcyclohexanes as reported by Hassner et al.

In connection with working out a new preparative route to the phenanthridine system[1,2] via the introduction of an azido group into 1-arylcyclohexenes, we have studied the electrophilic addition of iodine azide[3] to 1-arylcyclohexenes as a means of preparing the necessary precursors. The addition was carried out by a modification of the procedure of Hassner et al.[4] The 1-arylcyclohexene was added to iodine azide, prepared in situ from sodium azide and iodine monochloride cooled in an ice–salt bath. It was found that allowing the mixture to warm to room temperature (about 30 °C) after the addition of olefin and stirring for a further period of 8–12 h as suggested by Hassner resulted in some decomposition of the unstable iodine azide. Purer product with a better yield was obtained by maintaining the ice–salt bath temperature after the addition of olefin and stirring until the red-orange color of the slurry turned pale yellow. The yields, melting points, and $^1H$ NMR data for the products obtained by addition of iodine azide to various 1-arylcyclohexenes are presented in Table I.

The IR spectra of all these adducts show an absorption at 2100 $cm^{-1}$, characteristic of the azide group. Their $^1H$ NMR spectra show signals around $\delta$ 7.00 due to aromatic protons, a multiplet at $\delta$ 1.5–2.50 due to methylene protons, and a broad signal at $\delta$ 4.7 due to the methine hydrogen $CHN_3$. This last signal has a $W_{1/2}$ (width at half height) of 8 Hz, indicating that the $CHN_3$ proton is equatorial.[5] Confirmation of this stereochemistry was obtained from the 360-MHz spectra in which the $W$ coupling (2 Hz) of the equatorial hydrogens at $C_6$ and $C_4$ was visible. These results indicate that the stereochemistry of the addition is trans and that the adduct is a 2(a)-azido-1(a)-iodo-1-(e)-arylcyclohexane. This stereochemistry is analogous to the stereochemistry of iodine azide addition to other cyclic olefins[6] and to that observed in the addition of nitrosyl chloride to 1-arylcyclohexenes.[7]

Hassner et al.[8] report that the product obtained by addition of iodine azide to 1-phenylcyclohexene is 1-azido-2-iodo-1-phenylcyclohexane, based on its $^1H$ NMR spectrum. However, it is known that the azide ion preferentially attacks the less substituted carbon atom in saturated unsymmetrical epoxides, in conformity with the dominance of primary steric effects over polar effects in $S_N2$ displacement reactions. Since the iodonium ion intermediate proposed by Hassner et al. is envisaged to be fairly stable, we should expect that azide ion would open the the iodonium ion ring at the less substituted carbon atom to give product A by analogy to the epoxides. Hence we decided to establish unequivocally the regiochemistry of the adducts of iodine azide to 1-arylcyclohexenes by investigating their dehydrohalogenation. The adducts were refluxed with ethanolic potassium hydroxide, and the resulting azido olefins were isolated and characterized. Their $^1H$ NMR spectral data are presented in Table II.



Adducts A and B should give the azido olefins C and D, respectively, and C and D can be distinguished by their $^1H$ NMR spectra. The azido olefin obtained from the iodine azide adduct to 1-phenylcyclohexene gives signals

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**Table I. 2-Azido-1-iodo-1-arylcyclohexanes**[a]

| compd | mp, °C | yield, % | $^1$H NMR, δ Ar H | CHN$_3$ | CH$_2$ | other protons |
|---|---|---|---|---|---|---|
| 2-azido-1-iodo-1-phenylcyclohexane | 75 | 89 | 7.50 | 4.80 | 1.35–2.90 | |
| 2-azido-1-iodo-1-(4-methylphenyl)cyclohexane | 55 | 85 | 7.20 | 4.70 | 1.40–2.90 | 2.30 (Ar CH$_3$) |
| 2-azido-1-iodo-1-(3,4-dimethylphenyl)cyclohexane | 150 | 79 | 7.10 | 4.70 | 1.45–2.75 | 2.25 (Ar (CH$_3$)$_2$) |
| 2-azido-1-iodo-1-(4-methoxyphenyl)cyclohexane | 78 | 77 | 6.80–7.30 | 4.70 | 1.50–2.80 | 3.80 (Ar OCH$_3$) |
| 2-azido-1-iodo-1-(4-*tert*-butylphenyl)cyclohexane | 68 | 79 | 7.30 | 4.70 | 1.50–2.40 | 1.30 (Ar C(CH$_3$)$_3$) |

[a] Satisfactory combustion analytical data (C, H, N) were obtained for all five compounds.

**Table II. Azido Olefins**

| compd | $^1$H NMR, δ Ar H | CH$_2$ | =CH | CHN$_3$ | other protons |
|---|---|---|---|---|---|
| 3-azido-2-phenylcyclohexene | 7.20–7.45 | 1.55–2.55 | 6.10 | 3.90–4.15 | |
| 3-azido-2-(4-methylphenyl)cyclohexene | 7.10–7.47 | 1.50–2.50 | 6.12 | 3.95–4.18 | 2.35 (Ar CH$_3$) |
| 3-azido-2-(3,4-dimethylphenyl)cyclohexene | 7.10–7.35 | 1.45–2.75 | 6.05 | 3.95–4.15 | 2.25 (Ar (CH$_3$)$_2$) |
| 3-azido-2-(4-methoxyphenyl)cyclohexene | 6.80–7.45 | 1.45–2.50 | 6.05 | 3.95–4.15 | 3.78 (Ar OCH$_3$) |
| 3-azido-2-(4-*tert*-butylphenyl)cyclohexene | 7.25–7.50 | 1.55–2.52 | 6.10 | 3.95–4.15 | 1.30 (Ar C(CH$_3$)$_3$) |

at δ 6.1 (t, 1 H) and at δ 3.9–4.15 (br, 1 H). If structure D were correct then both olefinic protons should give signals in the range δ 4.6–5.9,[9] and one of them should appear as a clean doublet and the other as a multiplet, unless the anisotropic effect of the azide group should interfere. The signals obtained are not in the chemical shift range usually observed for olefinic protons, and there is no doublet as would be expected of the azido olefin D. The chemical shift values obtained and the nature of the signals agree with those expected of C. The triplet at δ 6.1 integrating to one proton accounts for the only olefinic proton of C. The methine proton, which should normally appear around δ 1.5, is deshielded to δ 3.9–4.15 because of the highly electronegative azide function attached to that carbon atom. This signal appears broad because of allylic coupling with the neighboring protons.

However, it could be argued that these data correspond to structure D because the anisotropic effect of the azide group could affect both the chemical shift and the multiplicity of the signals. In order to resolve this issue we carried out double resonance studies on the azido olefins. Decoupling studies were feasible because the two signals in which we were interested are separated by about δ 2.0. When the triplet at δ 6.1 was irradiated with the appropriate frequency, there was no significant change in the signal at δ 3.90–4.15. Similarly irradiation of the signal at δ 3.90–4.15 did not result in any significant change in the signal at δ 6.1. These results indicate that the protons giving rise to these signals are not coupled, i.e., they are not on adjacent carbon atoms, and confirm our assignment of structure C to the azido olefin.

Additional evidence that the azido olefins have structure C is provided by the UV spectra of 3-azido-2-phenylcyclohexene [$\lambda_{max}$ 247 nm ($\epsilon_{max}$ 14 439)] and 3-azido-2-(4-*tert*-butylphenyl)cyclohexene [$\lambda_{max}$ 253 nm ($\epsilon_{max}$ 15 477)]. The $\epsilon_{max}$ for structure C should be greater than 10 000, whereas that for D should be relatively weak.

The thermodynamically more stable vinyl azide 1-azido-2-phenylcyclohexene is not formed under the conditions of E$_2$ elimination. The facile elimination in the presence of base to form 1-azido-2-phenyl-2-cyclohexene indicates that the transition state requirement for E$_2$ elimination is readily met between the iodine at C$_1$ and the axial hydrogen at C$_6$.

Attempts to adduce additional evidence for the regiochemistry of the iodine azide adducts through $^{13}$C NMR spectra were not successful. The $^{13}$C NMR spectra of the adducts showed signals at 68.0 (s) and at 41.1 (d) ppm for the relevant carbons. Although these signals might indicate a 1-azido-2-iodo-1-arylcyclohexane, it has been reported[10] that 1-(iodomethyl)-1-azido-4-*tert*-butylcyclohexane and 1-(azidomethyl)-1-iodo-4-*tert*-butylcyclohexane give C$_1$ signals at 61.4 and 61.0 ppm, respectively. In the view of this chemical shift equivalence of the C$_1$ carbons the $^{13}$C NMR spectra could not be used to distinguish between structures A and B.

We conclude that the addition of iodine azide to 1-arylcyclohexenes forms 2-azido-1-iodo-1-arylcyclohexanes rather than 1-azido-2-iodo-1-arylcyclohexanes as previously reported.[8]

## Experimental Section

All melting points are uncorrected. IR spectra were determined on a Perkin-Elmer 577 instrument. $^1$H NMR spectra were determined on a R-32 Perkin-Elmer spectrometer except for the phenylcyclohexene adduct, which was obtained at 360 MHz (Bruker WM360) in CDCl$_3$ with Me$_4$Si as internal reference. $^{13}$C NMR spectra were determined at 90.56 MHz (Bruker WM360) in an approximately 0.5 M solution in acetone-$d_6$ with Me$_4$Si as internal reference. The arylcyclohexenes were prepared by addition of arylmagnesium halides to cyclohexanone. The resulting tertiary alcohols were dehydrated with 50% sulfuric acid to get the arylcyclohexenes.

**2-Azido-1-iodo-1-arylcyclohexanes.** To a stirred slurry of sodium azide (15 g, 0.23 mol) in acetonitrile (100 mL) in an ice–salt bath was added iodine monochloride (18.3 g, 0.113 mol) slowly over a period of 10–20 min. The reaction mixture was stirred for additional 10 min. The 1-arylcyclohexene (0.1 mol) was then added slowly, maintaining the ice–salt bath temperature. Stirring was continued until the yellow-orange color of the slurry just turned pale yellow. The slurry was then poured into water (250 mL), and the mixture was extracted with ether (250 mL) in three portions. These were combined and washed with 5% sodium thiosulfate until colorless. This solution was washed repeatedly with water and dried over anhydrous sodium sulfate. Removal of ether at room temperature produced the 2-azido-1-iodo-1-arylcyclohexane, now slightly colored. The compounds were recrystallized from petroleum–ether (40–60 °C). All showed an IR absorption at 2100 cm$^{-1}$ (azido group).

**3-Azido-2-arylcyclohexenes.** A mixture of 2-azido-1-arylcyclohexane (3 g) and 20% ethanolic potassium hydroxide (20 mL) was refluxed over a water bath for 1 h. The product was extracted with ether. The ether extract was washed repeatedly with water and dried over anhydrous sodium sulfate. Removal of the ether in vacuum yielded the 3-azido-2-arylcyclohexene (1.7

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g). All showed an IR absorption at 2100 cm$^{-1}$ (azido group).

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**Registry No.** 2-Azido-1-iodo-1-phenylcyclohexane, 101471-03-8; 2-azido-1-iodo-(4-methylphenyl)cyclohexane, 101471-04-9; 2-azido-1-iodo-(3,4-dimethylphenyl)cyclohexane, 101471-05-0; 2-azido-1-iodo-1-(4-methoxyphenyl)cyclohexane, 101471-06-1; 2-azido-1-iodo-1-(4-*tert*-butylphenyl)cyclohexane, 101471-07-2; 3-azido-2-phenylcyclohexene, 101471-08-3; 3-azido-2-(4-methylphenyl)cyclohexene, 101471-09-4; 3-azido-2-(3,4-dimethylphenyl)cyclohexene, 101471-10-7; 3-azido-2-(4-methoxyphenyl)cyclohexene, 101471-11-8; 3-azido-2-(4-*tert*-butylphenyl)cyclohexene, 101471-12-9; 1-phenylcyclohexene, 771-98-2; 1-(4-methylphenyl)-cyclohexene, 1821-23-4; 1-(3,4-dimethylphenyl)cyclohexene, 101471-13-0; 1-(4-methoxyphenyl)cyclohexene, 20758-60-5; 1-(4-*tert*-butylphenyl)cyclohexene, 60652-09-7; 1-azido-2-iodo-1-phenylcyclohexane, 25022-21-3; 1-azido-2-iodo-1-(4-methylphenyl)cyclohexane, 101471-14-1; 1-azido-2-iodo-1-(3,4-dimethylphenyl)cyclohexane, 101471-15-2; 1-azido-2-iodo-1-(4-methoxyphenylcyclohexane, 101471-16-3; 1-azido-2-iodo-1-(4-*tert*-butylphenyl)cyclohexane, 101471-17-4; iodine azide, 14696-82-3.

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# Crystal Structures of Isomeric (2,6-Dioxacyclohexyl)phenols: Models for Preassociation Complexes in Acid-Catalyzed Solvolysis of Acetals[1]

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The crystal structures of 2-, 3-, and 4-(2,6-dioxacyclohexyl)phenol are reported. The crystals of the 2-isomer are monoclinic, space group $P2_1/c$, with four molecules in the unit cell with dimensions $a$ = 7.520 (2) Å, $b$ = 15.593 (3) Å, $c$ = 8.550 (2) Å, and $\beta$ = 113.13 (2)°. The crystals of the 3-isomer are orthorhombic, space group $P2_12_12_1$, with four molecules in the unit cell with dimensions $a$ = 5.617 (3) Å, $b$ = 12.127 (3) Å, $c$ = 13.394 (4) Å. The crystals of the 4-isomer are monoclinic, space group $P2_1/c$, with eight molecules in the unit cell with dimensions $a$ = 18.558 (2) Å, $b$ = 5.991 (1) Å, $c$ = 18.910 (1) Å, and $\beta$ = 118.19 (1)°. For the 2-isomer $R$ = 0.033 for 1041 observed reflections, for the 3-isomer $R$ = 0.050 for 740 reflections, and for the 4-isomer $R$ = 0.040 for 1676 reflections. The analyses establish that there is intermolecular O–H···O hydrogen bonding in the 2-isomer (O1–H···O2 2.761 Å), the 3-isomer (O1–H···O2 2.730 Å), and the 4-isomer (O1–H···O2′ 2.720 Å and O1′–H···O2 2.770 Å). There is no intramolecular hydrogen bonding in the 2-isomer. Differences in the lengths of the two C–O bonds in the acetal group are sensitive to hydrogen bonding, with the longer C–O bond always containing the hydrogen-bonded oxygen. As such, the structures are models of preassociation complexes that are proposed for acid-catalyzed acetal solvolysis. Hydrogen bonding does lead to a lengthening of the C–O bond, and the orientation of this hydrogen bond appears to control the amount of lengthening. In the 2- and 4-isomers, the lengthened bond is clinal to the aromatic ring. This is consistent with the idea that maximum overlap, hence stabilization, would occur with an electron donor group. Finally, the failure to observe intramolecular catalysis[15] when the phenolic group is adjacent to the acetal because of the conflict between optimal orientation for hydrogen bonding and for stabilization of the incipient oxocarbenium ion is easily visualized in the crystal structure.

## Introduction

Crystallography has risen to prominence in recent years as a major tool for understanding chemical dynamics and reaction mechanisms. The pioneering work of Dunitz and Burgi[2] has inspired many physical organic chemists to search for correlations between molecular structure and reactivity. Indeed, several groups[3-9] have reported correlations for a variety of structures.

Crystallography is attractive for the exploration of stereoelectronic[10,11] and orientation effects in molecules that undergo catalytic reactions. Jones and Kirby,[3e] have shown a linear relationship between bond length and reactivity based on correlations of crystal structural data with hydrolytic rate constants of tetrahydropyranyl acetals. The structural data[3d] reveal that the C–OR bond lengthens and the endocyclic O–C bond shortens with decreases in the p$K_\alpha$ of the conjugate acid of the leaving group. These structural changes are greater with axial rather than equatorial OR groups, suggesting that stereoelectronic factors control the magnitude of these changes. These

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