The iodonium ion was recrystallized[37] from $CH_2Cl_2$ and $SO_2$. The halonium ions were stored as their $SbF_6^-$ salts in $SO_2$ at -80 °C until use.

Polystyryllithium (1.5-20 mequiv of Li/g) was prepared by direct lithiation of polystyrene in cyclohexane by using *n*-BuLi-TMEDA.[5] The product was washed twice with dry cyclohexane before use.

**Reaction of Halonium Ions with Polystyryllithium. Tetramethylenechloronium Ion.** To a magnetically stirred supercooled (-10 to -20 °C) suspension of polystyryllithium (2.8 g, 1.5-2.0 mequiv of Li/g) in 50 mL of dry cyclohexane under dry $N_2$ was rapidly added 50 mL of a solution of tetramethylenechloronium hexafluoroantimonate (34 mmol) in $SO_2$ at -40 °C [prepared from 1,4-dichlorobutane (4.32 g, 34 mmol) and antimony pentafluoride (7.34 g, 34 mmol)]. Stirring was continued as the temperature was allowed to slowly approach room temperature. The resin became dark brown from the initial deep reddish orange color of the aryllithium. After 1 h the resin was pressure filtered by using dry $N_2$ and was washed sequentially with nine 200-mL portions of $H_2O$, THF, and MeOH in the respective proportions 9:1:0, 7:3:0, 1:1:0, 3:7:0, 1:8:1, 0:7:3, 0:1:1, 0:3:7, 0:0:1. The chlorobutylated polystyrene was dried on the pressure filter (2 psi of $N_2$) for 0.5 h and in a drying pistol at 78 °C (0.5 mmHg) for 15 h. The product analysis is summarized in Table I.

**1,1-Dimethyltetramethylenebromonium hexafluoroantimonate** in 50 mL of $SO_2$ was prepared from 1,6-dibromohexane (9.3 g, 34 mmol) and $SbF_5$ (7.34 g, 34 mmol) and allowed to stand at -80 °C until complete rearrangement of the initially formed mixture of bromonium ions reached equilibrium.[35] Reaction with polystyryllithium and product workup was carried out as described above for the chloronium ion. The product analysis is summarized in Table I.

**Tetramethyleneiodonium hexafluoroantimonate** was recrystallized, redissolved in 100 mL of $SO_2$, and reacted with polystyryllithium, and the product was worked up as described for the chloronium ion above. The product analysis is summarized in Table I.

**Acknowledgment.** The Rohm and Haas Co. is gratefully acknowledged for a generous sample of the XE-305 resin. Dr. Paul Peterson kindly provided details of the preparation and handling of the halonium ions and served as a gracious host for S.P.M during a sabbatical at the University of South Carolina during 1974-1975 when this work was conceived. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No. 3**, 73558-10-8; **4**, 41143-82-2; **5**, 73558-49-3; 1,4-dichlorobutane, 110-56-5; 1,4-diiodobutane, 628-21-7; 1,6-dibromohexane, 629-03-8; polystyrene, 9003-53-6.

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# Nuclear Magnetic Resonance Study of the Molecular Complexes of Annelated Benzenes

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Many methods have been used to obtain the formation constants for (*K*) and properties of the weak molecular complexes (DA) between electron donors (D) and electron acceptors (A).[1,2] One procedure that has been widely used involves the evaluation of *K* from the measurement of the changes in the chemical shift of one component as the concentration of the second component is altered.[1-7] Since the rate of formation and dissociation of the complex is rapid on the NMR time scale, the observed spectra is a weighted average of the spectra of the free and complexed component. If one component is present in a large excess over the other (i.e., if $[D]_0 \gg [A]_0$ where $[D]_0$ and $[A]_0$ are the total concentration of D and A, respectively), *K* may be calculated by using eq 1. The difference between the chemical shift observed for a nucleus in A in pure solvent and A in the solvent plus D is $\Delta$, while the difference between the chemical shifts in A in pure solvent and undissociated DA is given as $\Delta_0$.

$$\Delta/[D]_0 = -K\Delta + K\Delta_0 \qquad (1)$$

Values of $\Delta_0$ for protons have been reported for a large number of complexes containing $\pi$ acceptors such as nitro-substituted benzenes[1,2] as well as polar acceptors such as dimethylformamide,[3] cyclic imides,[4] pyrimidines,[5] and purines.[6] Electron donors used in these studies have been alkyl- and methoxybenzenes, biphenyls, and stilbenes.[1-7] The results of these studies indicate that for complexes with a series of donors having similar structures but widely varying donor abilities a given acceptor has an almost constant value of $\Delta_0$. These observations can be interpreted by using eq 2[7] which is based upon an analogy with the changes in chemical shifts caused by solvent effects.

$$\Delta_0 = \Delta_w + \Delta_a + \Delta_e \qquad (2)$$

Differing contributions of dispersion forces to the chemical shift of A in the complex and A in solution are responsible for $\Delta_w$, while $\Delta_e$ represents the effect of differences in the electric fields in free A and complexed A and contains contributions to $\Delta_0$ from both charge transfer and polarization. The effect of the magnetic anisotropy of D on the chemical shift of A is represented by $\Delta_a$. In a set of similar complexes in the same solvent the contributions of $\Delta_w$ and $\Delta_e$ remain constant. Since in a series of substituted benzenes the magnetic anisotropy is almost constant, the value of $\Delta_a$ also remains constant. Biphenyl compounds do not follow this pattern because in some of these complexes the diamagnetic anisotropy of one of the benzene rings may reinforce the anisotropy of the donor ring, causing $\Delta_a$ and $\Delta_0$ to be larger than those observed for complexes of simple benzene derivatives, while steric factors in other biphenyl complexes may preclude this reinforcement.

From the above arguments it appeared to us that proton NMR studies of molecular complexes could provide a procedure by which the variation of the ring currents for a series of donor molecules could be established. Such a procedure would obviate the necessity for interpreting the chemical shifts of the free molecules in terms of the several factors besides ring current effects that can be involved. We have chosen to test this idea by examining the complexes of the small-ring benzocycloalkenes. It is well established that as the cycloalkyl ring(s) fused to the benzene ring decreases in size, the steric strain on the aromatic ring increases, and several effects on the reactivity and properties of the benzene rings may be observed.[8-10] The NMR

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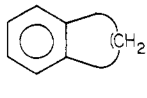
Table I. Equilibrium Constants and $\Delta_0$ for TNB and DNB Complexes with Benzocycloalkenes in $CCl_4$ at 33.5 °C

| | TNB | | DNB | |
|---|---|---|---|---|
| | $K^c$ | $\Delta_0$, ppm | $K^c$ | $\Delta_0$, ppm |
| tetralin | 1.10 ± 0.02[a] | 1.06 ± 0.04 | 0.42 ± 0.02 | 1.28 ± 0.06 |
| indan | 1.14 ± 0.04 | 0.97 ± 0.03 | 0.40 ± 0.02 | 1.30 ± 0.08 |
| benzocyclobutene | 1.27 ± 0.08 | 0.65 ± 0.04 | 0.51 ± 0.05 | 0.81 ± 0.17 |
| *o*-xylene[b] | 1.09 | 1.1 | 0.42 | 1.35 |
| benzo[1,2:4,5]dicyclopentene | 1.9 ± 0.1 | 0.84 ± 0.07 | 0.70 ± 0.1 | 1.0 ± 0.1 |
| 1,2,4,5-tetramethylbenzene[b] | 2.11 | 1.03 | 0.62 | 1.4 |
| benzo[1,2:3,4]dicyclopentene | 2.08 ± 0.08 | 0.82 ± 0.07 | 0.7 ± 0.1 | 0.9 ± 0.1 |
| 1,2,3,4-tetramethylbenzene[b] | 2.33 | 1.07 | 0.65 | 1.3 |

[a] Error limits given are the standard deviations obtained from a least-squares treatment of the data. [b] Reference 1. [c] In units of (mol/kg of solution)$^{-1}$.

of these molecules can be interpreted in terms of two opposing effects. As the strain on the benzene ring increases, the aromatic bridgehead carbons have an increased "p" character in the bonds used to construct the alkyl ring. Therefore, the remaining orbitals have more "s" character, and the carbons ortho to the strained alkyl ring are bound to orbitals of higher electronegativity. As the strain increases, the electronegativities of the ortho carbons increase, causing the shielding of the attached protons to decrease and the chemical shift to move to lower field. However, what is observed for indan and benzocyclobutene is a shift to higher field. This opposite effect is presumed to be due to an increased perturbation of the ring current and a concomitant decrease in diamagnetic anisotropy as the strain increases. Meier et al. also inferred that the ring current decreases as the strain increases from comparisons of the proton NMR spectra of the methylene group in such compounds with those in cycloalkenes and methylenecycloalkanes.[8] Such an effect is also consistent with the idea that rehybridization occurs because of strain, since such rehybridization would affect the delocalization of the $\pi$ electrons by changing the value of the Coulomb integrals for the carbon atoms of the aromatic ring.[12]

In order to obtain a direct test of the idea that ring currents decrease as the strain increases as well as to show that variations in $\Delta_0$ for molecular complexes are mainly caused by such changes in ring currents, we have obtained $K$ and $\Delta_0$ values for 1,3,5-trinitrobenzene (TNB) and 1,4-dinitrobenzene (DNB) complexes of some benzocycloalkenes and diannelated benzenes in $CCl_4$ solutions. The compounds studied have $n$ = 2–4.



## Results and Discussion

Values of $\Delta_0$, $K$, and their standard deviations obtained by applying the least-squares method to a plot of $\Delta/[D]_0$ vs. $\Delta$ are given in Table I. Before discussion of these results, it would be useful to consider some of the difficulties encountered when eq 1 or one similar to it is used. Frequently the values of $K$ obtained are inconsistent when the NMR method is applied to different nuclei in an acceptor or when they are compared with $K$ values obtained from UV spectroscopic measurements.[2] These inconsistencies are usually corrected when the presence of termolecular complexes in solution is taken into account (either $D_2A$ or $DA_2$, depending on which component is in excess). For this reason $K$ and $\Delta_0$ values obtained from eq 1 may not be the correct values. However, it has also been shown that in many cases there is a good relationship between values of $K$ and $\Delta_0$ obtained from eq 1 and values of $K$ and $\Delta_0$ obtained where the formation of 1:1 and 2:1 complexes is taken into account.[13,14] Since the $K$ and $\Delta_0$ values found for the tetralin complexes with TNB and DNB are identical (within one standard deviation) with $K$ and $\Delta_0$ values previously reported for the *o*-xylene complexes of these acceptors, we have ignored the possible formation of 2:1 complexes.

Since $\Delta_0$ is the same for the tetralin and *o*-xylene complexes, it is clear that when a six-membered ring is fused to benzene there is no strain effect on the ring current, in agreement with the conclusion of Meier et al.[12] However, as the size of the fused ring decreases from $n$ = 4 to $n$ = 2, the value of $\Delta_0$ also decreases. This effect is very small for $n$ = 3, while for the benzocyclobutene complexes the decrease in $\Delta_0$ from the $\Delta_0$ for tetralin complexes is quite large and well outside experimental error. That the decrease in $\Delta_0$ is due to a decrease in ring current and diamagnetic anisotropy of the donor may be inferred from the observation that the percent decrease in $\Delta_0$ on going from tetralin to benzocyclobutene is almost constant for the two acceptors (39% for TNB and 37% for DNB).

Complexes of the two diannelated compounds studied, benzo[1,2:3,4]dicyclopentene and benzo[1,2:4,5]dicyclopentene, show similar trends. Since only limited quantities of these compounds were available, experiments with these complexes could not cover as wide a range of concentrations or use as many different solutions as with the other donor studied, and the standard deviations given on the $\Delta_0$ values are larger than those reported for the other complexes. However, even with these limitations it is possible to conclude that with two fused rings the $\Delta_0$ for the complex and the ring currents of the donors decrease when compared with the corresponding tetramethylbenzenes or with indan. Again, for both acceptors the percent decreases in $\Delta_0$ of the diannelated complexes and those of the tetramethylbenzenes are almost the same, indicating that the decrease in $\Delta_0$ can be attributed to a decrease in ring current.

Examination of the $K$ values in Table I indicates that when one ring is fused to benzene, the $\pi$-donor ability increases slightly as the strain increases. However, if there are two rings fused to the benzene, the donor ability appears to be slightly less than that of the methyl-substituted benzenes.

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## Experimental Section

**Materials.** Spectroscopic grade $CCl_4$ was stored over molecular sieves. Commercial indan, tetralin, TNB, and DNB were purified by standard procedures. Benzocyclobutene was prepared and purified according to literature methods.[15] The diannelated compounds were a gift from Professor Randolph Thummel.

**Measurements.** All solutions were prepared by weight. A Varian EM 390 NMR spectrometer was used to obtain the $\Delta$ values. The peak positions were measured with a frequency counter and the values of $\Delta$ obtained to within ±0.1 Hz. For most compounds 10–15 solutions covering a range of $[D]_0$ from 0.08 to 0.4 mol/kg of solvent were used except where noted in the Results and Discussion section.

**Acknowledgment.** We are grateful to Professor Randolph Thummel for the gift of the two diannelated benzene compounds. This work was partially supported by an NSF undergraduate research participation program, Grant No. SMI-76-03971 A03.

**Registry No.** Tetralin-trinitrobenzene (1:1), 73506-06-6; indan-trinitrobenzene (1:1), 73506-07-7; benzocyclobutene-trinitrobenzene (1:1), 73523-12-3; *o*-xylene-trinitrobenzene (1:1), 2590-50-3; benzo[1,2:4,5]dicyclopentene-trinitrobenzene (1:1), 73512-99-9; 1,2,4,5-tetramethylbenzene-trinitrobenzene (1:1), 1095-52-9; benzo[1,2:3,4]dicyclopentene-trinitrobenzene (1:1), 73506-08-8; 1,2,3,4-tetramethylbenzene-trinitrobenzene (1:1), 2636-28-4; tetralin-dinitrobenzene (1:1), 73506-09-9; indan-dinitrobenzene (1:1), 73506-10-2; benzocyclobutene-dinitrobenzene (1:1), 73506-11-3; *o*-xylene-dinitrobenzene (1:1), 26397-19-3; benzo[1,2:4,5]dicyclopentene-dinitrobenzene (1:1), 73506-12-4; 1,2,4,5-tetramethylbenzene-dinitrobenzene (1:1), 1611-15-0; benzo[1,2:3,4]dicyclopentene-dinitrobenzene (1:1), 73506-13-5; 1,2,3,4-tetramethylbenzene-dinitrobenzene (1:1), 26397-23-9.

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# Thermolysis of 6-*endo*-(Carbomethoxy)bicyclo[3.1.0]hex-2-ene: Comparison with the Parent Compound and Effect of Different Thermolysis Techniques

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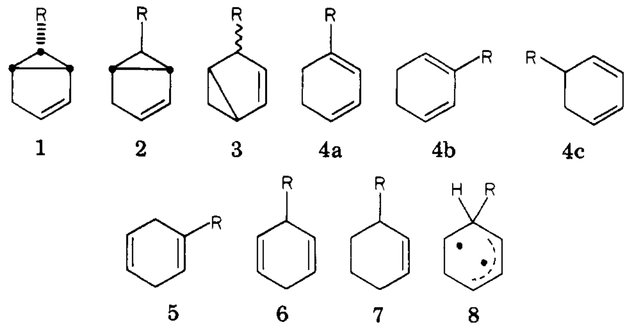
Thermal isomerizations of vinylcyclopropanes have been studied in great depth with regard to concerted vs. stepwise mechanisms.[1,2] Recent interest has focused on the thermal epimerization and rearrangements of bicyclo[3.1.0]hex-2-enes which can occur via exocyclic ($C_1$–$C_6$) and endocyclic ($C_1$–$C_5$) cyclopropyl bond cleavage.[3] We investigated the thermolysis of 6-*endo*-(carbomethoxy)bicyclo[3.1.0]hex-2-ene (1) in order to determine the mode of cleavage. We initially focused our attention on the formation of epimer **2**, using optically active compounds to demonstrate for the first time that both one-center and two-center thermal epimerization can occur competitively.[3] In the course of this investigation, we found that endocyclic bond cleavage resulted in the formation of 1,3-cyclohexadienes. *No 1,4-cyclohexadienes were observed.* In contrast, bicyclo[3.1.0]hex-2-ene (BCH) is reported to give both 1,3- and 1,4-cyclohexadienes. In view of the relative stabilities of 1,3- vs. 1,4-cyclohexadienes, the apparent absence of the 1,4 isomer prompted us to further investigate the thermolysis of **1**.



R = $CO_2CH_3$

Flash vacuum pyrolysis of **1** at 490 °C gives a pyrolysate mixture composed of ca. 38% epimer **2**, 17% 4-(carbomethoxy)bicyclo[3.1.0]hex-2-ene (**3**), 35% 1,3-cyclohexadienes (**4**), and 10% unreacted starting material, according to GLC analysis. Products were isolated via sequential preparative GLC utilizing both fluorosilicone (QF-1) and FFAP as stationary-phase materials. Proton NMR, GLC analyses, ultraviolet spectra, and comparison with known compounds[4] were used to verify the structures of isolated products. At lower temperature (460 °C), the fractional conversion of **1** is lower with only **2** and **3** appearing in approximately equal amounts (ca. 10% each). The 1,3-cyclohexadienes are not observed until a pyrolysis temperature of 475 °C and they became more significant at higher temperature with a slight decrease in formation of **3**. The rearrangement of **1** to **3** is an example of the well-known vinylcyclopropane rearrangement.[2] **3** appeared to be a mixture of both epimers in approximately equal amounts based on the proton NMR spectrum of the collected material: ($CDCl_3$) $\delta$ 0.0 (m, 0.5 H), 0.3 (m, 0.5 H), 1.0 (br m, 1 H), 2.0 (m, 2 H), 3.7 (s, 3 H), 5.4 (m, 1 H), 6.1 (m, 1 H). Since **3** was a mixture of epimers, we attempted to isomerize **3** to the conjugated ester. Treatment of **3** with 0.2 M $NaOCH_3/CH_3OH$ for 1 h at room temperature results in rearrangement to 1-(carbomethoxy)-1,4-cyclohexadiene (**5**), identified by comparison with an authentic sample.[4] This transformation can be followed by NMR by using $NaOCD_3/CD_3OD$. Integration of the peak areas in the spectrum showed the incorporation of deuterium into the methylene region of **5**. GLC analysis of the product showed it to be composed of ca. 90% **5**. Surprised by the absence of significant amounts of the 1,3-cyclohexadienes, we reacted authentic **5** with $NaOCD_3/CD_3OD$ in an NMR tube. A solid precipitated immediately. The addition of a few drops of $D_2O$ brought the material into solution and the NMR spectrum showed H–D exchange at the methylene carbon *with no observable rearrangement to a 1,3-cyclohexadiene.* Recent studies on the comparable stabilities of 1,3- vs. 1,4-cyclohexadienes lend some support to the preferred formation of the 1,4 isomer,[5-7] but its preponderance is surprising and probably

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