Deuterium Isotope Effects in Quenching of Aromatic Hydrocarbon Fluorescence by Conjugated Dienes

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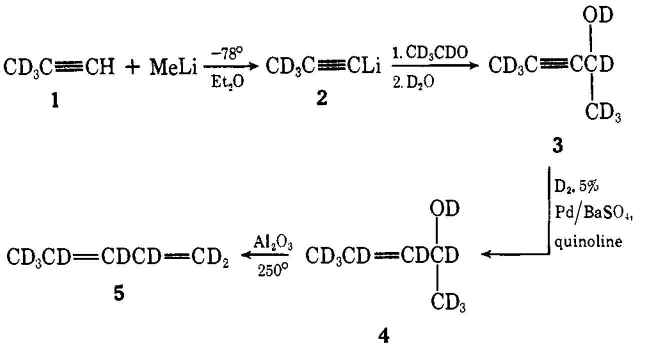
Abstract: The mechanism of quenching of the fluorescence of anthracene and naphthalene by piperylene has been investigated by looking for deuterium isotope effects. Perdeuteration of either the quencher or the quenchee results in small increases in the quenching constants and the effect is cumulative when both reactants contain deuterium. The results indicate that transfer of electronic excitation energy into C–H vibrations is not important in the rate-controlling step in quenching. We speculate that other vibrational motions become dominant in the internal conversion process. There are several ways in which the small, inverse isotope effects measured can be rationalized as arising from effects on the equilibrium constants for formation of exciplexes which may be intermediates in the decay process.

Secondary deuterium isotope effects have proved increasingly important in elucidating the mechanistic details of thermal processes.[3] Yet, until recently this tool has found little application in the photochemical arena. The notable exceptions to this situation have occurred in the areas of triplet energy transfer[4,5] and intramolecular radiationless decay processes.[6–10] We have now employed this technique in studying the intermolecular singlet quenching of aromatic hydrocarbons by conjugated dienes[11,12] and present our results in the following sections.

Synthesis. Since completely deuterated alkyl dienes are not commercially available, we were forced to develop a relatively facile synthesis for one which would quench naphthalene fluorescence at a substantial rate. Isoprene-d_8 is an obvious first choice since its synthesis had already been described.[13] However, it is a weak singlet quencher[11] thereby requiring large amounts of material to cause significant alterations in the fluorescence lifetimes or intensities, properties which we employ in measuring the quenching rate constants. Consequently, we decided to synthesize *cis*- and *trans*-piperylene-d_8 using a procedure paralleling the one mentioned above since the piperylenes quench naphthalene singlets almost ten times as fast as does isoprene. The synthetic route is outlined in Scheme I.

Scheme I



Reaction of 99.5 atom % methyl-d_3-acetylene (**1**) with an ethereal solution of methyllithium at −78° afforded a white precipitate presumed to be the lithium acetylide (**2**). Upon warming to −25° the precipitate dissolved. At this temperature condensation with 99.5 atom % acetaldehyde-d_4 occurred smoothly to give a 72% yield of the desired alcohol **3**. Reduction using a modified[14] Lindlar catalyst in the absence of solvent afforded a 90% yield of the desired reduction product **4**, contaminated with a small amount of completely reduced material. Dehydration at 250° over basic alumina, which had been deactivated with pyridine, gave a 53% yield of a mixture of *cis*- and *trans*-piperylene-d_8 (**5**). Vapor-phase chromatographic analysis showed that the substance was contaminated with 18% pentene-d_{10} (mixture of 1 and 2 isomers) and contained 29% *cis*-piperylene-d_8. Mass spectral analysis indicated the piperylene isotopic purity as 82% d_8 and 18% d_7 with a small amount of the d_6 isomer probably being present. A considerable portion of unreacted starting material was recovered from the dehydration step. Quantitative yields in this step were obtained using the protio alcohol corresponding to **4** suggesting that the lower yield obtained with deuterated material is the result of a substantial deuterium isotope effect in the dehydration step.

Results and Discussion

Our favored mechanistic model for the quenching of the fluorescence of aromatic hydrocarbons was outlined in the first paper in the present group.[15] A key step in

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the proposed mechanism is fast, radiationless decay of an exciplex.

$$(AQ)^* \xrightarrow{k_2} A^*(vib) + Q^*(vib) \qquad (1)$$

To date radiationless transition theory[6,8,9] has dealt only with intramolecular processes. However, the general ideas should be capable of extension to intermolecular energy transfer and relaxation of excited state complexes. Decay of excited triplet states of aromatic hydrocarbons is known to involve transfer of energy to the environment *via* C–H vibrational modes.[8,9] Deuteration retards the internal conversion process, thereby increasing phosphorescence yields and lifetimes. The effect has been ascribed to differences in the Franck–Condon factors controlled by the spacing of the vibrational levels and the anharmonicity of C–H and C–D stretching modes at high vibrational levels in the lower electronic state to which transition occurs.

If the exciplex energy were dissipated in a similar fashion *via* the C–H stretching modes, k_2 would decrease upon deuteration and the observed quenching rate constant $k_q = Kk_2$ should reflect this change. If the excitation energy were localized in one of the partners during the decay process, deuteration of the sensitizer and the quencher might not be expected to alter the rate constant to the same degree. On the other hand, deuteration might also result in a small change in the rate and equilibrium constants for exciplex formation.

Table I summarizes our present fluorescence quenching results in *n*-hexane solution at room temperature. The rate constants were obtained from a least-squares Stern–Volmer plot of eq 2, where τ represents

$$1/\tau = 1/\tau_0 + k_q[Q] \qquad (2)$$

the fluorescence lifetime in the presence of quencher while τ_0 is the natural fluorescence lifetime. Identical results were also obtained using fluorescence intensity data and eq 3.

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (3)$$

In the case of anthracene and anthracene-d_{10} this latter technique was the only one employed since the fluorescence lifetime of these molecules approaches the detection limits of our nanosecond lifetime device. Errors are probably inherently greater in the technique using emission intensities because of the relative instability of the intensity of the emitted light.

Table I. Effect of Deuteration on Fluorescence Quenching by Piperylene in Hexane at Room Temperature

Sensitizer[a]	Piperylene[b] isomer	$k_q \times 10^{-7}$ l. M^{-1} sec^{-1}	k_H/k_D
Naphthalene	Cis	11.1	
	Trans	12.9	
Naphthalene-d_8	Cis	12.9	0.86 ± 0.06
	Trans	13.8	0.94 ± 0.06
Anthracene	Cis	10.7	
	Trans	4.97	
Anthracene-d_{10}	Cis	12.1	0.88 ± 0.10
	Trans	5.34	0.93 ± 0.08
Naphthalene	A mixture	8.68	AB 0.94 ± 0.06
	B d_8 mixture	9.27	AC 0.87 ± 0.07
			CD 0.95 ± 0.06
Naphthalene-d_8	C mixture	9.99	BD 0.88 ± 0.08
	D d_8 mixture	10.5	AD 0.83 ± 0.07

[a] Average values of τ_0 in nanoseconds are naphthalene, 106 ± 3; naphthalene-d_8, 122 ± 4; anthracene, 5.3 ± 0.3; anthracene-d_{10}, 5.2 ± 0.3. [b] Capital letters indicate code for samples used in calculation of cumulative isotope effects. See last column and text.

As noted in the preceding section, the piperylene-d_8 consisted of a mixture of cis and trans isomers and the three possible *n*-pentene isomers. In order to obtain an accurate comparison of the piperylene-d_8 results, a stock solution mimicking the concentrations found for the deuterated material was made up from *cis*- and *trans*-piperylene and *cis*-2-pentene. The latter was substituted for the mixture of pentene isomers noted above in order to facilitate reproduction of the total olefin and diene concentrations. No effect on the quenching rate constants is expected to result from such a substitution since simple olefins quench naphthalene singlets some 10^2–10^3 times as slow as the piperylenes.[16] Analysis by vpc revealed that the percentage composition of the two samples was the same with respect to the piperylene isomer ratio and differed by less than 1% in regard to the olefin content. The piperylene sample contained slightly more olefin than did the piperylene-d_8 sample. Such differences are expected to afford errors in the k_H/k_D values much smaller than the variations actually observed.

Before commenting on the quenching data, we take note of the values of τ_0. The lifetimes for anthracene and anthracene-d_{10} are identical within experimental error. However, the values for the naphthalenes differ by an amount that exceeds probable error limits. We doubt that the effect can be due to a quenching impurity in the normal naphthalene since measured lifetimes were independent of concentration. We believe that some radiationless decay process of the excited singlet state of naphthalene must be slowed down by perdeuteration. The step effected may well be intersystem crossing to a triplet since both theory[9] and experiment[17] indicate that nonradiative decay to the ground singlet state is negligible in naphthalene. The quantum yield measurements reported by Kellog and Bennett[18] are obviously inconsistent with this view which is, therefore, advanced with some caution. However, we note that Anderson and Kistiakowsky[10] did observe higher fluorescence yields from benzene-d_6 than from normal benzene, at the high pressure limit in the vapor phase. The small decrease in the measured quantum yields of triplets on perdeuteration of naphthalene[19] is also consistent, although the difference was too close to the error limits of the method to have been taken very seriously.

The failure to observe a similar effect with anthracene can be rationalized on the basis of the very small energy gap between the lowest singlet state and the second triplet state, to which intersystem crossing apparently occurs.[20] Recent spectroscopic results[21,22] and calculations[22] for naphthalene and some of its derivatives

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reveal that such a situation is not found for this aromatic system. Figure 1 presents an outline of the energies involved. The relatively large S_1–T_1 gap for naphthalene can permit significant differences in Franck–Condon factors in the case of deuteration, thus leading to an enhanced fluorescence lifetime for the deuterated isomer.

Returning to the data in Table I, we see that deuteration of either quencher or quenchee increases the quenching rate although the exact magnitude of the effects cannot be determined with high precision because the changes are not a great deal larger than expected experimental error limits. The effect may be slightly larger for *cis*-piperylene than for the trans isomer. The last entry in Table I shows that the effects of deuteration of naphthalene and the diene are cumulative. Thus

$$(k_H/k_D)_{AB} \approx (k_H/k_D)_{CD},\ (k_H/k_D)_{AC} \approx (k_H/k_D)_{BD}$$

and

$$[(1 - (k_H/k_D)_{AB}) + (1 - (k_H/k_D)_{BD})] \approx 1 - (k_H/k_D)_{AD} \approx [(1 - (k_H/k_D)_{AC}) + (1 - (k_H/k_D)_{CD})]$$

or

$$0.18 \approx 0.17 \approx 0.18$$

The absence of large normal isotope effects permits three classes of interpretation. (1) Existing theory of radiationless decay is inadequate. (2) The rate-limiting step may be formation, rather than decay of the exciplex. (3) Modes other than C–H vibrations may become important in the internal conversion of electronic to vibrational energy.

We are reluctant to accept the first view because the theory seems reasonable and provides an attractive explanation for the isotope effects that have been observed. The second alternative, which is case 1 in the earlier introductory discussion,[15] may be correct, although we find it hard to imagine that the large reactivity variations observed in diene quenching experiments can be accounted for by variations in the rates of formation of weakly bound molecular complexes. This would be contrary to experience in the study of ground state molecular complexes and in the formation of fluorescent excimers[23] and fluorescent exciplexes of aromatic hydrocarbons with tertiary amines.[24,25] Furthermore, evidence from the study of other quenchers, such as quadricyclene[26] and aryl alkyl sulfoxides,[27] shows that in some related cases quenching is clearly accompanied by transfer of energy to the quenchers.

The notion that internal conversion of energy within the exciplex involves vibrations other than C–H modes seems most reasonable. Clearly the quencher must provide decay mechanisms which are unavailable in the quenchees, or there would be no reason for acceleration of the decay rate in the presence of the quenchers. There is no obvious reason why the high energy C–H stretching modes in the quenchers should be very different in this respect from those already available in the aromatic hydrocarbons. Thus, the very fact that quenching occurs suggests that a new channel for decay must become available. The existence of such a highly effective decay mechanism in dienes is suggested by the fact that fluorescence from open-chain dienes has never been reported, despite the fact that absorption spectra show the $S_0 \rightarrow S_1$ transitions to have large transition moments. We believe that the rapid, nonradiationless decay mechanisms available to the dienes are "borrowed" by arene–diene exciplexes.

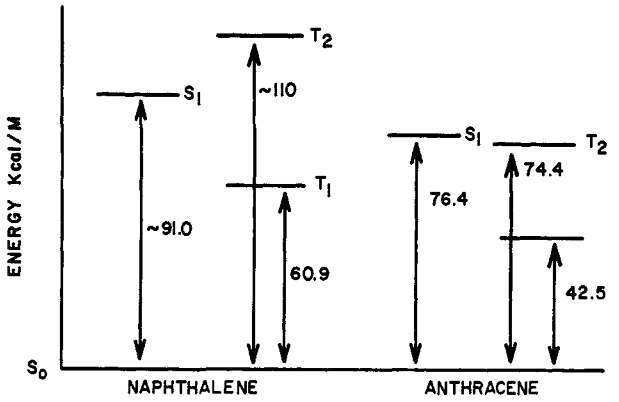

Figure 1. Energy levels of anthracene and naphthalene.

The most obvious choice for vibrational modes in the diene to mediate internal conversion is torsional motions around the carbon–carbon double bonds. At high amplitudes these motions must become highly anharmonic, perhaps allowing unusually large Franck–Condon factors connecting the ground vibrational levels with rather highly excited vibrational states. Such a theory would be directly verified if quenching were accompanied by cis–trans isomerization of the quencher. Since this does not occur,[11,12] we must speculate that insufficient energy is delivered directly to these twisting modes to carry the system over the barrier separating the geometric isomers. In a quencher such as piperylene in which only one of the carbon–carbon double bonds is a center of geometric isomerism we could beg the question by speculating that the other double bond is the sole recipient of the vibrational excitation. This is unattractive because no evidence for isomerization has appeared in the study of quenching by the isomeric 2,4-hexadienes.

We must now consider whether the small, inverse behavior can be rationalized in some way. Contribution of isotope effects to decay by the favored mechanism should be in small changes arising from changes in the reduced masses of the groups involved in the torsional motions. These effects would be expected to be "normal," that is, $k_H > k_D$. Within the framework of the model that we have adopted, such effects must be overshadowed by larger effects on the binding energies of the exciplexes. Since involvement of charge transfer from diene to aromatic has been a popular part of the exciplex interaction model,[28] it is interesting to investigate the possible relationship of this model to the isotope effect. In order to make any headway we must assume that isotopic substitution has no significant effect on binding due to excitation resonance either be-

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cause the interaction is unimportant or because deuteration does not appreciably effect singlet excitation energies. The latter view is suggested by available spectral data.[29]

Secondary deuterium isotope effects on ground state charge-transfer complexes are well known.[30] To date, only the secondary deuterium isotope effects in the electron donor have been studied. In general, deuteration of the donor produces an inverse isotope effect. Halevi and coworkers[31-34] attribute this to the inductive and polarization differences of C–D bonds. The results of Cvetanović and coworkers[35,36] on olefin and diene complexes with silver ion and iodine support these arguments. The results are a little surprising since the usually suggested direction of the inductive effect, with C–D bonds being more strongly electron donating than C–H bonds, would lead one to anticipate that ionization potentials would be decreased by deuteration. There are no data available for deuterated dienes but a small number of data for other kinds of molecules reveal a slight trend in the opposite direction.[37,38]

Although there is experimental precedent for attributing the inverse isotope effect in the dienes to charge-transfer binding, it is very difficult to explain the fact that the inverse effect is observed in both quenchers and quenchees. Unfortunately there are no relevant data available to allow us any way of directly estimating the effect of deuteration on the electron affinities of aromatic hydrocarbons. If the predicted direction of the inductive effect were controlling, we could rationalize the view that deuteration makes the electron affinities less favorable. However, this view would require that the overall electronic effect of deuteration is unfavorable to ionization in the donor and to electron acceptance in the acceptor, an unattractive combination of hypotheses. In summary, we do not think that the isotope effects can be rationalized in terms of charge-transfer binding. This does not in any way deny the importance of charge transfer but merely directs our attention elsewhere to explain the isotope effect.

We see two other approaches which quantitatively fit the experimental facts. The first of these is a trivial steric effect. Rate enhancement would occur upon deuterium substitution because of the smaller effective size of $=$C—D relative to $=$C—H. This steric isotope effect was first proposed by Bartell[39] and competes with Halevi's inductive effect model[40] of secondary deuterium isotope effects. Thornton[30] has pointed out that these competing descriptions are unnecessary since the potential energy surface is the fundamental determining factor of these vibrational effects. Nevertheless, the cases of the racemization of highly hindered substrates[41-43] appear to be representative of a direct steric isotope effect. It is apparent in these examples that severe steric interactions are required to product measurable effects. With singlet quenching *via* exciplex formation there is little likelihood that interactions involve any such severe compression at the reaction partners, although it appears that intimate contact of the partners is established.[11,12,44] Cvetanović and coworkers[35] concluded that direct steric isotope effects probably are not detectable in ground state charge-transfer complex formation. These qualitative arguments do not eliminate such an explanation and it remains, perhaps, as a conceivable possibility. One factor which favors such an explanation is that the acceleration per deuterium atom is very small for fluorescence quenching in comparison to those for instances of severe overcrowding.[43,45]

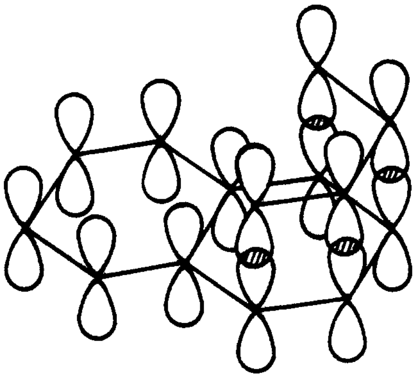

Figure 2. Postulated naphthalene–diene exciplex.

The remaining explanation of the observed isotope effects involves the postulate of partial bond formation between the sensitizer and quencher during the quenching process. Such partial bonding is pictured (Figure 2) with the bonding being represented as orbital overlap. The orientation of the diene in the s-cis form and overlapping with the naphthalene orbitals at carbons 1–4 is purely speculative.

Such bonding might be considered as inducing a hybridization change from sp^2 toward a mixture of sp^2 and sp^3. Similar changes are known to produce inverse isotope effects[45-49] which are attributed to alterations in the out-of-plane bending vibrations of the C–H bonds attached to the carbon atoms undergoing the hybridization change. Rough molecular orbital calculations of bonding interactions in excimers indicate that orbital overlap is required in order to obtain an accurate reproduction of the properties of excimers,[50]

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which are exciplexes. Conceivably, localized interaction, with rehybridization, could account for the entire effect. This theory has the attractive feature of predicting similar effects from deuteration of both the quencher and quenchee.

Conclusion

Inverse deuterium isotope effects have been found for the fluorescence quenching of aromatic hydrocarbons by conjugated dienes. The effects are of similar magnitude in either of the exciplex partners. Explanation of the results in terms of charge-transfer stabilization does not appear to be reasonable because of the inverse behavior in both partners. Steric and bonding explanations can conceivably account for the results. More experiments using specifically deuterated materials are needed to help sort out these effects. Of most importance, however, is the fact that a predicted *possibility*, based on radiationless transition theory and the assumption that exciplex decay is the slow step in the quenching process, is not realized. However, at least two views can rationalize the result without conflict with the theory: (1) the rate-determining step is formation of the complex; or (2) internal conversion in the exciplex involves modes other than carbon–hydrogen vibrations.

Experimental Section

Materials. Hexane, naphthalene, naphthalene-d_8, and *cis*- and *trans*-piperylene were purified as described previously.[44] Piperylene-d_8 was purified by distillation from lithium aluminum deuteride followed by redistillation. *cis*-2-Pentene (Aldrich) was distilled from lithium aluminum hydride prior to use. Reagent grade anthracene and anthracene-d_{10} were purified using two sublimations under vacuum.

Apparatus. Vapor-phase chromatographic analyses were performed with a Loeneo Model 70 gas chromatograph. Mass spectroscopic analyses were determined using a Consolidated Electronics Corp. Model 21-103C mass spectrometer. Fluorescence intensities were measured with an Aminco-Bowman spectrophotofluorometer. For naphthalene and naphthalene-d_8 an excitation wavelength of 320 nm was employed while 376 nm was used for anthracene and anthracene-d_{10}.

Fluorescence lifetimes were determined as described previously.[44] The naphthalene and naphthalene-d_8 emissions were filtered using a 340-nm interference filter. The filter arrangements for anthracene and anthracene-d_{10} included either a 296- or a 340-nm interference filter for absorbed light and a 320–600-nm glass filter for emitted light.

Measurements. All measurements were made at room temperature with hexane solutions in sealed Pyrex ampoules. The ampoules contained 3 ml of the appropriate solution and were constructed from 13-mm Pyrex test tubes. Each tube was degassed using three freeze–pump–thaw cycles at $<5 \times 10^{-4}$ mm. The piperylene sample mimicking the concentrations of the piperylene-d_8 sample components was prepared using *cis*-2-pentene and *cis*- and *trans*-piperylene. Analysis by vpc using a 15 ft × $^3/_8$ in. diameter column of 25% β,β-oxydipropionitrile–5% silver nitrate at 35° with a flow rate of 70 ml/min showed that the sample prepared in this fashion had a piperylene isomer ratio identical with that of the piperylene-d_8 sample. The total olefin concentration was slightly higher for the former sample with the difference being less than 1%. The concentrations of the components in the piperylene-d_8 sample were found as: *cis*-piperylene-d_8, 29%; *trans*-piperylene-d_8, 53%; and the mixture of d_{10}-pentenes, 18%.

Naphthalene concentrations used were 0.10 and 0.01 *M*, while the anthracene concentratins were all 1×10^{-4} *M*. Variations in naphthalene concentration did not alter the quenching rate constants. Quenching rate constants determined by fluorescence lifetime and intensity measurements agreed to within ±2%. Rate constants were determined from Stern–Volmer plots using a least-squares calculation.

2-Pentyn-4-ol-d_8 (3). A 1-l. three-necked, round-bottomed flask was equipped with a gas-inlet tube, an addition funnel, a low-temperature thermometer, a Dry Ice condenser to which a Friedrichs condenser bearing a drying tube was attached, and a mechanical stirrer. The system was flame dried and flushed with dry nitrogen. The gas inlet tube was connected to a three-way stopcock to which a nitrogen line and a gas sample line were attached. To the flask was added 100 ml of dry ether and both the flask and Dry Ice condenser were cooled to −78° by Dry Ice–acetone. Three 1-l. samples of methyl-d_3-acetylene (0.134 mol, 99.5% isotopic purity) obtained from Merck Sharp and Dohme were attached in succession to the sample inlet of the three-way stopcock. The contents of each were passed into the cold ether *via* a nitrogen stream, by alternative heating and cooling cycles, and by using dry ether as a chaser. To the rapidly stirred solution was added 62 ml (0.135 mol) of a freshly opened ethereal solution of methyllithium (2.16 *M* by titration) over a 30-min period followed by the addition of 25 ml of dry ether. During the addition a white precipitate, presumed to be the lithium acetylide, separated from the solution and gas was evolved. Then the stirred solution was permitted to warm to −10° while the Dry Ice condenser was maintained at −78°. The precipitate dissolved and more gas was evolved. After stirring at −10° for another 10 min the solution was cooled to −25°. Then approximately 6.45 g (0.134 mol) of 99.5% isotopically pure acetaldehyde-d_4 (Stolher Isotope Chemicals Co.) was distilled into the solution using the gas inlet tube and nitrogen carrier gas. Addition in this manner was completed in 20 min and caused warming of the ethereal solution to 10°. After stirring at this temperature for another 30 min the solution began to turn yellow and the reaction was terminated by the addition of 40 ml of deuterium oxide. The layers were separated and the ethereal portion was washed three times with 20 ml of deuterium oxide. The combined washings were extracted twice with 25 ml of ether and the combined extracts were washed three times with 10 ml of deuterium oxide. The combined ether solutions were dried over anhydrous magnesium sulfate which had been dried at 130° and stored in a desiccator prior to use. The ether was removed by distillation using a 60-cm Vigreux column and a reflux ratio of 6:1. The residue was distilled through a short-path distillation apparatus to give 8.90 g (72%) of the desired alkynol, bp 135–139°. Analysis by vpc using a 15 ft × $^3/_8$ in. Carbowax 20M column at 160° and 73 ml/min showed that the distillate consisted of only one component. Infrared analysis showed no absorption at 1970 cm^{-1} indicative of an allene structure but did exhibit the weak absorption at 2080 cm^{-1} expected for an acetylenic linkage. The spectrum also revealed the presence of trace amounts of protium in the alkyl region and more protium in the hydroxyl group.

A similar previous run using 44.6 mmol of methyl-d_3-acetylene afforded a 61% yield of the acetylenic alcohol.

2-Penten-4-ol-d_{10} (4). To a taped centrifuge bottle, which had been dried in an oven at 130° and stored in a desiccator, was added 11.3 g (0.123 mol) of 2-pentyn-4-ol-d_8 obtained from the two runs above. To this was added 0.20 ml of quinoline, which had been freshly distilled from calcium hydride, and 56.5 mg of 5% palladium on barium sulfate catalyst. The bottle was connected to a conventional Parr hydrogenation apparatus which had been previously calibrated. The apparatus was flushed four times with 99.97% isotopically pure deuterium gas and pressurized at 32 psi. Shaking was begun and deuterium uptake was permitted until 1 equiv had been consumed. The bottle was purged with argon and ether was added. The catalyst was removed by filtration and the ether was distilled through a 30-cm Vigreux column. The residue was distilled through a short-path distillation apparatus to give 10.7 g (90%) of the allylic alcohol, bp 118–122°. Vpc analysis using the Carbowax 20M column mentioned previously but at 140° and 66 ml/min revealed that the distillate consisted of 94% of the unsaturated alcohol and 6% 2-pentanol-d_{10} resulting from overreduction. No starting material was indicated by the vpc trace.

***cis*- and *trans*-1,3-Pentadiene-d_8 (5).** The dehydration apparatus employed was similar to that of Craig and coworkers.[13] It consisted of a 40 in. × 29 mm descending quartz tube equipped with a nitrogen inlet tube and a ₮ 24/40 female joint at the top, a thermocouple well extending throughout the length of the tube, and a ₮ 24/40 male joint at the outlet. Both the inlet and outlet portions of the tube were arranged vertically while the tube itself was inclined 25° to the horizontal. Heating was accomplished by wiring the tube in three sections with 22-gauge Chromel A wire. Each section was wrapped with asbestos tape and connected to a conventional power supply. By applying the proper voltages the temperature could be maintained to within ±10° throughout the length of the column and up to a maximum of 400°. The column was packed with 228 g of active alumina (No. KA-201) generously donated by the Kaiser Aluminum Corp. Temperatures were measured using iron–constantan thermocouples with ice water as a reference and a Leeds and Northrup potentiometer.

In experiments using protio material, the catalyst as obtained from the manufacturer was found to be too active giving undesirable side products. Consequently, the catalyst was further deactivated by treating the column with anhydrous pyridine at 250° under a nitrogen stream. Such treatment eliminated the undesirable side reactions.

Dehydration of deuterated material was accomplished after the catalyst had been treaed at 250° and a nitrogen flow of 200 ml/min with 50 ml of deuterium oxide, 50 ml of anhydrous pyridine, and 30 ml of deuterium oxide. The column was baked out overnight under the same conditions. A trapping system was attached to the outlet end of the column and consisted of two pentane-slush traps held at −140° and a heptane-slush trap held at −90°. The exit end of the trapping system was connected to a flow meter. The olefinic alcohol (10.7 g, 0.111 mol) was added to the top of the column using a pressure equalizing addition funnel while maintaining the system at 250 ± 10° and the nitrogen flow at 200 ml/min. The reactant was added dropwise over a 15-min period and product collection was continued for 4 hr. A total of 6.9 g of material was collected in the traps. The volatile components were distilled into another trap cooled in Dry Ice–acetone. A small portion (0.25 g) of lithium aluminum deuteride was added to the distillate and the component boiling below 50° was removed by distillation through a 15-cm Vigreux column into a flask cooled to −40°. Redistillation through a similar column gave 4.4 g (53%) of a hydrocarbon fraction boiling at 40–41°. This was taken as the piperylene-d_8 fraction. The major part of the 2.5-g residue was found to be unreacted starting material, the remainder being water. Higher temperatures are believed necessary to achieve better yields in the dehydration step using deuterated materials although temperatures of 250° gave nearly quantitative yields with protio alkenol.

Analysis by vpc using a 25 ft × $^3/_8$ in. 25% β,β′-oxydipropionitrile–5% silver nitrate column at 35° and 60 ml/min showed that the distillate consisted of 18% pentene-d_{10} (mixture of 1 and 2 isomers with *cis*-2-pentene being the major component), 29% *cis*-1,3-pentadiene-d_8, and 53% *trans*-1,3-pentadiene-d_8. The components were identified by coinjection with protio isomers of each of the compounds. Mass spectroscopic analysis revealed that the isotopic purity of the piperylenes was approximately 82% d_8 and 18% d_7 with possibly some of the d_6 isomer also being present.

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Lowest Triplet State of Substituted Benzenes. II. Phosphorescence Microwave Double Resonance Studies on the $^3\pi\pi^*$ State of *p*-Dichlorobenzene

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Abstract: Phosphorescence microwave double resonance (pmdr) spectra of *p*-dichlorobenzene have been obtained monitoring low temperature (~1.3°K) trap phosphorescence and used to make symmetry assignments of various vibronic bands present in the spectra. In addition, ratios of radiative rate constants of individual triplet spin sublevels to several vibrational states, the intrinsic lifetimes of all three triplet spin sublevels, and selective polarized phosphorescence from individual spin sublevels in various vibronic transitions have been measured. An analysis of these data is presented along with explicit considerations of the *p*-chlorine perturbation on the aromatic ring. Finally, the relationships between the orbital symmetries and the sign and magnitude of the zero-field electron spin dipolar interactions in the triplet state are presented for several halobenzenes and on these bases an assignment of the orbital symmetry of the lowest excited triplet state of *p*-dichlorobenzene is made.

The classification of the orbital symmetry of excited triplet states of aromatic and substituted aromatic molecules is a problem which has received a considerable amount of attention from theoreticians and experimentalists alike. Early investigators, while attempting to establish the assignment of the lowest triplet state of benzene from a vibrational analysis of the phosphorescence, concluded that the transition was essentially dipole forbidden and that the weak phosphorescence activity originated from a vibronic coupling of the e_{2g} vibrations.[2a] This vibronic coupling of the e_{2g} modes has been cited as evidence for either a $^3B_{1u}$ or $^3B_{2u}$ state.[2] Theorists have generally agreed that a $^3B_{1u}$ state would be lowest in energy.[3] In a classic study, Albrecht has set down the possible routes by which dipole-allowed character might find its way into the benzene $T_1 \rightarrow S_0$ transition.[4] His findings, along with the oscillator strengths and phosphorescence polarization, allowed him to propose the $^3B_{1u}$ assignment which has since gained wide acceptance.

In addition to benzene, substituted benzenes such as hexachloro-, tetrachloro-, *p*-dichloro- and *p*-dibromobenzene have been studied. A $^3B_{2u}$ assignment has

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