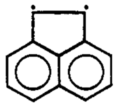
creasing ring size as does the antiaromaticity of 4*n* ring systems in the ground state.[2,3]

In a future publication, the present calculations will be extended to larger nonalternant hydrocarbons such as calicene systems and fused ring systems with multiply-connected π-electron pathways. The aromaticity analysis is more complex in many such cases, however, since the $\pi\pi^*$ excitation tends to be "localized" within a subunit of the molecule. For example, the lowest triplet of acenaphthylene (**28**) has a larger contribution from **28**a (excitation localized at an ethylenic bond) than from structures such as **28b** in which the excitation is delocalized across the entire π network.


28a


28b

Appendix

Assuming zero overlap, the energies for two conjugate MOs are $\alpha + y\beta$ and $\alpha - y\beta$ for alternant radicals. If the radical ends are joined, then by the pairing theorem, the interaction matrix elements between both the bonding and the antibonding MO with an NBMO on the second alternant radical have identical magnitude, say $k\beta$. Thus the secular determent to be solved for the three-orbital interaction is then

$$\begin{vmatrix} \alpha + y\beta - \epsilon & 0 & k\beta \\ 0 & \alpha - y\beta - \epsilon & k\beta \\ k\beta & k\beta & \alpha - \epsilon \end{vmatrix} = 0$$

The three roots are $\epsilon_1 = \alpha + \beta(y^2 + 2k)^{1/2}$, $\epsilon_2 = \alpha$, and $\epsilon_3 = \alpha - \beta(y^2 + 2k)^{1/2}$. Since ϵ_1 is occupied by two electrons and ϵ_2 by one, the net stabilization energy is

$$\begin{aligned} \Delta E^{\text{II}} &= 2\epsilon_1 - 2(\alpha + y\beta) + \epsilon_2 - (\alpha) \\ &= 2\beta[(y^2 + 2k)^{1/2} - y] \end{aligned}$$

Hydrogen Bonding of Phenol with Acetylenes and Allenes[1]

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Abstract: Hydrogen bonding between phenol and acetylene or allene derivatives was studied by measuring the hydroxyl stretching absorption band. The frequency shifts and the thermodynamic values were evaluated. The basicity of acetylenes is larger than that of allenes and olefins, which are of the same order of magnitude. The equilibrium constants and the entropy changes in the formation of complexes with acetylenes are much larger than those with olefins and allenes. Two bonded OH bands are noted with arylacetylenes, but not with aliphatic acetylenes and allenes. Arylacetylenes act as bifunctional bases toward phenol, while allenes seem to act as monofunctional bases.

It is well known that unsaturated organic compounds act as proton acceptors for hydrogen bonds.[2] Although a number of investigations have been directed toward the intermolecular hydrogen bond with aromatic hydrocarbons,[3-5] relatively little work has been done on the intermolecular hydrogen bond with olefins,[6] allenes, and acetylenes.[7-9] The authors of these papers reported only the frequency shifts of ν_{OH} due to hydrogen bond formation.

As allenes can undergo two types of double bond isomerizations, that is either acetylene and/or conjugated diene formation,[10,11] the study of hydrogen bonding with acetylenes and allenes might give useful information on their properties as carbon bases. This paper includes the frequency shifts ($\Delta\nu$) of ν_{OH} of phenol and the thermodynamic values in the hydrogen-bonded complex with acetylenes and allenes. From these results the characteristics of the complexes involving the acetylene and allene derivatives are discussed in comparison with those involving aromatic[3-5] and olefinic π bases[6] as the proton acceptor. Furthermore, the differences between acetylenes and allenes as the proton acceptor are discussed in relation to their electronic states.

Experimental Section

Materials. 2,4-Dimethyl-2,3-pentadiene, Aldrich Chemical Co., was used. The other allene derivatives were prepared by treatment of the corresponding 1,1-dibromocyclopropane derivatives with methyllithium,[12] which were obtained by addition of dibromo-

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[1] Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor. X. Part IX: Z. Yoshida and N. Ishibe, *Bull. Chem. Soc. Jap.*, **42**, 3263 (1969).

[2] For a review, see E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 259 (1963).

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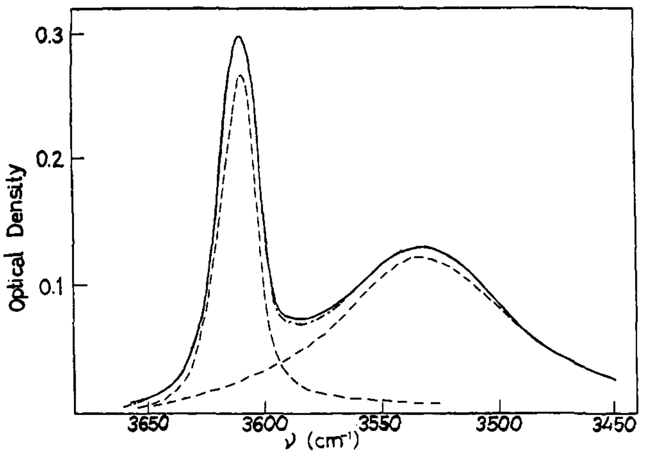

Figure 1. The ν_{OH} spectrum of phenol (0.014 *M*) in the presence of 2-methyl-2,3-pentadiene (3.94 *M*) in CCl_4 at 27°: —, the observed spectrum; ---, the resolved curve; -·-, sum of the resolved curves.

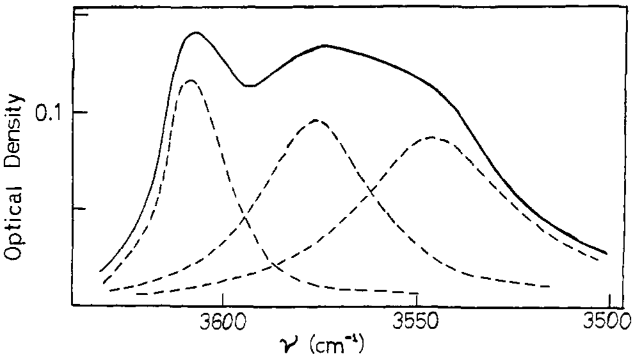

Figure 2. The ν_{OH} spectrum of phenol (0.020 *M*) in the presence of phenylacetylene (3.23 *M*) in CCl_4 at 27°: —, observed spectrum; ---, resolved curves.

carbene to the olefins.[13] Pure allenes were collected by preparative glpc[14] before use. Acetylenes, K & K Chemical Lab., were distilled over a sodium wire. Their purities, particularly the absence of water, were confirmed by analytical glpc[14] and infrared spectroscopy at the 3-μ region. Carbon tetrachloride dried over phosphorus pentoxide was fractionally distilled twice.

Measurements and Analysis of Spectra. All spectra of the hydroxyl stretching vibration were recorded on a JASCO DS-402G spectrophotometer. The experimental conditions were described in a preceding paper.[3b] Spectra were measured with both the sample and reference cells in a thermostated box.[15,16] Temperature was varied from −10 to 40° and detected with a thermistor. The transmittance (per cent) of each of three or four concentrations of the allenes and acetylenes (0.5–4.0 *M*) was studied as a function of the temperature in three or four intervals of 8–10°. In all cases, at least 15 min were allowed for temperature equilibrium. Scanning was repeated at least twice for each sample. The concentration of phenol was 0.014–0.020 *M*. The analysis of the spectra and calculations of the equilibrium constants have been described previously.[3a,b] By assuming a linear combination of the Lorentzian or Gaussian functions to the observed spectra, a Du Pont Curve Resolver was used for analysis of spectra in the case of 2-methyl-2,3-pentadiene as the proton acceptor. The enthalpies for the formation of the hydrogen-bonded complex were obtained from a plot of log *K vs.* $1/T$ (least-squares calculations).

Results

The hydroxyl stretching vibration spectra of phenol in the presence of allenes and aliphatic acetylenes were all doublets. Figure 1 shows the ν_{OH} spectrum in the presence of 2-methyl-2,3-pentadiene. On the basis of the Lorentzian function, the ν_{OH} spectrum observed was resolved into two symmetric components which fit best with the observed spectrum,[17] while in principle the unsymmetric allene, 2-methyl-2,3-pentadiene, can act as a bifunctional π base, which might show at least three symmetric components as the hydrogen-bonded spectrum. When phenyl- and diphenylacetylene were used as the proton acceptors, the ν_{OH} spectra split into a triplet as shown in Figure 2, which was resolved into three symmetric components. Multiplets were observed for the hydrogen bonding with arylfulvenes, azulenes,[3b] diphenylcyclopropenone,[18] phenylacetylene,[7] and substituted benzenes.[19] This splitting of the ν_{OH} spectra could be due to (1) self-association of the proton acceptor,[7,20] (2) the double minimum potential function of the bonded OH stretching vibration,[21] or (3) the bifunctional proton accepting properties of the proton acceptor.[3b,7,19,22] The first explanation should be excluded on the basis of the following three facts. First, only doublets were observed with other π bases involving aliphatic acetylenes which do associate,[7] a triplet was observed for diphenylacetylene where self-association cannot occur, and finally the self-association ability of acetylenes is quite smaller than that of phenol.[23] The second alternative appears improbable since such a splitting had never been observed with other π bases including aliphatic acetylenes. The third alternative seems most likely as the triplet could be explained in terms of a free OH band and two hydrogen-bonded OH bands due to the two functional centers, α and β, in the molecule (phenylacetylene and diphenylacetylene), the stretching vibrations $OH\cdots\alpha$ and $OH\cdots\beta$ absorbing at two different frequencies. Since initial mole ratios of phenol to π bases were small ([phenol]/[π base] $< 5 \times 10^{-2}$), both complexes can be assumed to be the 1:1 type complex described previously.[3b] In order to calculate the equilibrium constants, K_α and K_β, in eq 3 and 4 the concentration of the hydrogen-bonded phenol in both the α and β complexes, *i.e.* $[PhOH]_\alpha{}^b$ and $[PhOH]_\beta{}^b$, had to be evaluated. These quantities were calculated from the apparent integral intensities of the α and β bands divided by the

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[19] R. B. Wayland and R. S. Drago, *ibid.*, **86**, 5240 (1964); E. Osawa, T. Kato, and Z. Yoshida, *J. Org. Chem.*, 32, 2803 (1967).

[20] J. Hatton and R. E. Richards, *Trans. Faraday Soc.*, 57, 28 (1961); M. M. Kreevoy, H. B. Charman, and D. R. Vinard, *J. Amer. Chem. Soc.*, **83**, 1978 (1961); A. A. Petrov and N. V. Elsakov, *Opt. Spectr.*, **16**, 77 (1964); A. A. Petrov, N. V. Elsakov, and V. B. Lebedev, *ibid.*, **16**, 464, 547, 1013 (1964).

[21] S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1967).

[22] H. Fritzche, *Spectrochim. Acta*, **21**, 799 (1965).

[23] The formation constants of hydrogen-bonded complexes involving pyridine as the proton acceptor with phenol and phenylacetylene were 55 ± 10[24] and 0.1–0.2 l./mol,[25] respectively.

[24] N. Fuson, P. Pineau, and M. L. Josien, *J. Chim. Phys.*, **55**, 454 (1958).

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Table I. Frequency Shifts and Thermodynamic Values in Hydrogen Bonding of Phenol with Acetylenes and Allenes

Compound (no).	$\Delta\nu$,[a] cm^{-1}	$-\Delta H$,[b] kcal/mol	$-\Delta F°$,[c] kcal/mol	$-\Delta S°$,[d] eu
1-Hexyne (**1**)	78.5 ± 0.5	1.52	−0.48	6.7
1-Heptyne (**2**)	81 ± 1	1.56	−0.32	5.3
1-Octyne (**3**)	83 ± 1	1.62	−0.15	5.9
2-Octyne (**4**)	115 ± 1	2.15	0.12	6.8
3-Hexyne (**5**)	116.5 ± 1	2.16	0.13	6.8
3-Octyne (**6**)	120 ± 1	2.56	0.38	7.3
4-Octyne (**7**)	118.5 ± 1	2.42	0.24	7.1
2-Methyl-1-buten-3-yne (**8**)	62 ± 1	1.42	−0.32	5.9
Phenylacetylene (**9**)	α, 35 ± 1.5	0.90	−0.63	5.1
	β, 67 ± 1	1.64	−0.92	8.6
Diphenylacetylene (**10**)	α, 33.5 ± 2.0	0.93	−0.51	4.8
	β, 71.5 ± 1.5	1.66	−0.93	8.7
1,2-Hexadiene (**11**)	55.5 ± 1	1.49	−0.89	8.0
3-Methyl-1,2-pentadiene (**12**)	77.5 ± 1	1.51	−0.76	7.6
2,3-Hexadiene (**13**)	81 ± 0.5	1.59	−0.73	7.8
2-Methyl-2,3-pentadiene (**14**)	83.5 ± 1	1.61	−0.72	7.8
2,4-Dimethyl-2,3-pentadiene (**15**)	100.5 ± 1	1.78	−0.63	8.1
1,2-Cyclononadiene (**16**)	79 ± 0.5	1.57	−0.55	7.1
Phenylallene (**17**)	46 ± 1	1.54	−0.39	5.8
1-Phenyl-1-methylallene (**18**)	57 ± 1	1.50	−0.30	6.0
1,1-Diphenylallene (**19**)	52 ± 1	1.42	−0.34	5.9
1-Pentene (**20**)	58 ± 1[e]	1.71[e]	−1.10[e]	9.4[e]
Isopropylbenzene (**21**)	57 ± 1[e]	1.52[e]	−0.61[e]	7.1[e]
Styrene (**22**)	46 ± 0.5[e]	1.34[e]	−0.42[e]	5.9[e]

[a] Mean deviation from the average. [b] The maximum error is within ±0.10 kcal/mol. [c] The maximum error is within ±0.10 kcal/mol. [d] The maximum error is within 0.7 eu. [e] Reference 15.

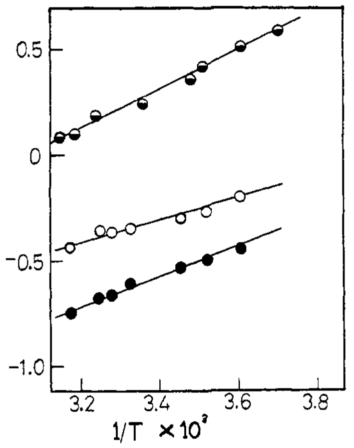

Figure 3. Plots of log K *vs.* $1/T$: ◒, 3-octyne; ○, diphenylacetylene (α band); ●, diphenylacetylene (β band).

$$\mathrm{PhOH} + \mathrm{B}_\alpha \overset{K\alpha}{\rightleftharpoons} \mathrm{PhOH}\cdots\mathrm{B}_\alpha \qquad (1)$$

$$\mathrm{PhOH} + \mathrm{B}_\beta \overset{K\beta}{\rightleftharpoons} \mathrm{PhOH}\cdots\mathrm{B}_\beta \qquad (2)$$

$$K_\alpha = \frac{[\mathrm{PhOH}]_\alpha{}^{\mathrm{b}}}{[\mathrm{PhOH}]^{\mathrm{f}}[\mathrm{base}]_\alpha{}^{\mathrm{f}}} \qquad (3)$$

$$K_\beta = \frac{[\mathrm{PhOH}]_\beta{}^{\mathrm{b}}}{[\mathrm{PhOH}]^{\mathrm{f}}[\mathrm{base}]_\beta{}^{\mathrm{f}}} \qquad (4)$$

absorption coefficients of these bands, which in turn are estimated from the $\Delta\nu$ *vs.* ΔA relationship given by Huggins and Pimentel.[26] $[\mathrm{PhOH}]^{\mathrm{f}}$ is the concentration of free phenol. $[\mathrm{Base}]^{\mathrm{f}}$ signifies the concentration of the free π base. The plots of K *vs.* $1/T$ for several π bases are shown in Figure 3. The thermodynamic data and the frequency shifts for hydrogen bonding of phenol with acetylenes and allenes are listed in Table I.

Discussion

The basicities of our compounds evaluated from the frequency shifts and the hydrogen bond energies[2,27,28] decreased in the following order: RC≡CR′ > RC≡CH (acetylenes), $R_2C{=}C{=}CR_2$ > $R_2C{=}C{=}CHR$, $R_2C{=}C{=}CH_2$, RCH=C=CHR > $RCH{=}C{=}CH_2$ (allenes), where R and R′ are alkyl substituents. The basicity of acetylenes and allenes increases with the substitution of alkyl groups for hydrogen. The same trend of the change in basicity due to the degree of alkyl substitution was observed for the hydrogen bonding of phenol with olefins.[6-8] This is expected from the known positive inductive effect of alkyl groups. As shown in Table I, $\Delta\nu_{\mathrm{OH}}$ for 1-alkynes is about 80 cm^{-1}, while it is 60 cm^{-1} for 1-alkenes[6] and 55 cm^{-1} for 1-allene (**11**). Terminal acetylenes are somewhat stronger bases toward phenol than simple terminal olefins and allenes. The basicity of 1,2-allenes is, however, nearly equal to that of 1-olefins. Moreover, internal acetylenes **4–7** give a frequency shift of about 118 cm^{-1}, while the position of the triple bond causes little effect on the frequency shifts, compared to that of 80 cm^{-1} for 2-olefins[6] and 2,3-allenes (**13**, **14**, and **16**) except 2,4-dimethyl-2,3-pentadiene. These results indicate that acetylenes are generally stronger bases than olefins and allenes, the last two being roughly equal. If the hydrogen bond of phenol to π bases is assumed to be a perturbation of the π-electron system by the proton before the proton transfer,[29] it is of interest that the more basic acetylenes, compared to olefins, have a higher reactivity toward reagents such as water and alcohols.[30] This is in good agreement with charge dis-

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(30) D. B. Killian, G. F. Hennion, and J. A. Nieuland, *J. Amer. Chem. Soc.*, **58**, 892 (1936).

Table II. Frequency Shifts in Hydrogen Bonding with Alkylallenes and ^{13}C Chemical Shifts of Alkylallenes ($R_1R_2C_\alpha{=}C_\beta{=}C_\gamma R_3R_4$)

	Substituent					^{13}C Chemical shifts (ppm)[a]		
No.	R_1	R_2	R_3	R_4	$\Delta\nu$ (cm^{-1})	δC_α[b]	δC_β[c]	δC_γ[b]
11	n-C_3H_7	H	H	H	55.5	100	−15[d]	121
12	CH_3	C_2H_5	H	H	77.5	100	−11.8	121
13	CH_3	H	C_2H_5	H	81	108	−11.8	100
14	CH_3	CH_3	CH_3	H	83.5	101	−10.1	108
15	CH_3	CH_3	CH_3	CH_3	100.5	101.1	−6.5	101.1

[a] Values in ppm relative to CS_2 external; ref 34. [b] Except for the values of 2,4-dimethyl-2,3-pentadiene, the values were calculated from those observed for similar alkylallenes[34] assuming that the alkyl substituents at the C_α have little effect on the ^{13}C chemical shift of C_γ and *vice versa*; for instance,[34] δC_γ of 3-methyl-1,2-butadiene ($R_1 = R_2 = H$; $R_3 = R_4 = CH_3$), 100.3 ppm, and δC_γ of 2,4-dimethyl-2,3-pentadiene ($R_1 = R_2 = R_3 = R_4 = CH_3$), 101.1 ppm. [c] The group contribution of alkyl is estimated as +3.3 ppm for a methyl group and +4.8 ppm for an ethyl group.[34] [d] While the group contribution of the n-propyl group is not known, the value for an ethyl group was used.

tribution calculated by the SCF-[31a] or EH–MO methods,[31b] indicating the acidic character of the proton in acetylene and the basicity of the triple bond. A similar relation was found for the protonated acetylenes and ethylenes.[32] The inductive effect of an alkyl group causes a larger relative electron density increment in acetylenes than in olefins,[31b] which corresponds with larger relative frequency shifts for acetylenes than olefins (40 cm^{-1} for acetylenes *vs.* 20 cm^{-1} for olefins[6]).

If we adopt the picture of the ground state of allenes as consisting of two overlapping and perpendicular ethylene fragments,[33] there would be two functional positions in allenes to interact with the phenolic proton. Multiplet spectra were, however, not observed. While a careful analysis of the observed spectra in the case of the unsymmetrical allene, 2-methyl-2,3-pentadiene, was carried out by using a linear combination of Lorentzian or Gaussian functions generated by a Du Pont Curve Resolver, a linear combination of two Lorentzian functions fitted best with the observed spectra as shown in Figure 1. The half band widths of interacted bands (78 cm^{-1}) are nearly equal with those in olefins (*ca.* 75 cm^{-1}),[6] suggesting that only one interaction band exists in this system. Moreover, overlap of the expected bands could be excluded since phenyl-substituted allenes did not give split spectra. This result seems to indicate that the allenes act as a monofunctional base. If the phenolic proton interacts with the more branched carbon–carbon double bond of 2-methyl-2,3-pentadiene, the expected frequency shift would be around 100 cm^{-1} as in the case of 2,4-dimethyl-2,3-pentadiene (**15**) and 2-ethyl-1-hexene.[6] The observed frequency shift is of the same magnitude as that of 2-olefins.[6] If the least substituted double bond were the site to interact with the phenolic proton, 1,2-hexadiene (**11**) should behave the same as 3-methyl-1,2-pentadiene (**12**), contrary to observation. The discrepancies can be solved by an interpretation that the hydrogen bonding is to the central sp-hybridized carbon of allenes. This interpretation can be supported by the fact that the frequency shifts for alkylallenes increase with the ^{13}C chemical shifts[34–36] of the central sp-hybridized carbon (Table II). On the other hand, there was no correlation between the frequency shifts for alkylallenes and their ^{13}C chemical shifts of the terminal sp^2-hybridized carbon. Substitution of allenic protons by the alkyl group increases the shielding of the central sp-hybridized carbon atom[34] as substitution of an olefinic proton by a methyl group increases that of the ^{13}C at the other end of the double bond.[36] The EH–MO calculation of allenes[31b] indicates that substitution of the allenic proton by a methyl group increases the electron density at the central sp-hybridized carbon. Our observation of the increased frequency shifts for alkylallenes is in good agreement with this prediction. While the ground states for alkylallenes could be only slightly perturbed by the hydrogen bond,[37] they still had the electronic properties of unperturbed ground states, which were reflected in the frequency shifts and the free energy in the hydrogen bond.

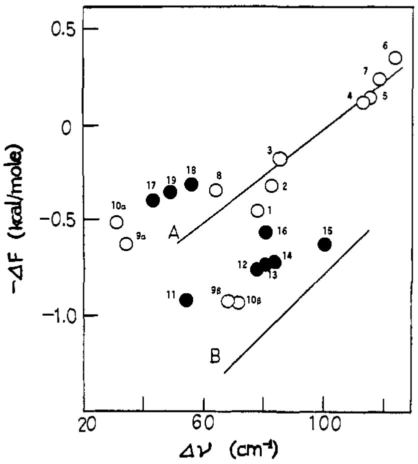

Figure 4. $-\Delta F$ *vs.* $\Delta\nu$ plot in the phenol–acetylene and phenol–allene complexes: ○, acetylenes; ●, allenes; A, alkylbenzene line; B, monoolefin line. The numbers correspond to those in Table I.

The free-energy changes, $-\Delta F$, for complex formation with alkylacetylenes **1–7** as the proton acceptor are much larger than those with olefins,[6] the former being nearly identical with alkylbenzenes.[3a] On the other hand, alkylallenes **11–16** show an intermediate behavior. These facts become evident from the plots of $-\Delta F$ *vs.* $\Delta\nu$ as shown in Figure 4. The large entropy contribution in acetylenes seems to suggest that the phenolic

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(31) (a) A. D. McLean, *J. Chem. Phys.*, **32**, 1595 (1960); L. Burnelle, *ibid.*, **32**, 1873 (1960); A. D. McLean, B. J. Ransil, and R. S. Mulliken, *ibid.*, **32**, 1873 (1960); (b) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

(32) R. Hoffmann, *ibid.*, **40**, 2480 (1964).

(33) A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965); I. M. Mills, W. L. Smith, and J. L. Duncan, *ibid.*, **16**, 349 (1965).

(34) R. Steur, J. P. C. M. van Dongen, M. J. A. de Bie, W. Drenth, J. W. de Haan, and L. J. M. van de Ven, *Tetrahedron Lett.*, 3307 (1971).

(35) Lack of data on the ^{13}C chemical shifts of phenylallenes prevents us from examining this interpretation of hydrogen bonding with phenylallenes.

(36) For a review see J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

(37) Recently a dramatic difference between proton transfer and hydrogen bonding was reported: E. M. Arnett and E. J. Mitchell, *J. Amer. Chem. Soc.*, **93**, 4052 (1971).

proton has a considerable rotational freedom around the two cylindrically symmetric π orbitals in the ground state. With arylacetylenes **9** and **10** the ν_{OH} band showed two bonded OH peaks, the α and β bands. By comparing with the frequency shifts and the thermodynamic data of alkylbenzenes[3–5,28b] and olefins,[6,15] the α and β bands seem to be due to hydrogen bonding with the aromatic π electron delocalized through the whole molecule like that of styrene and stilbene and with the double bond perpendicular to the aromatic ring, respectively. West[7] attributed the β band to the hydrogen bonding of the triple bond; our considertions, however, seem to be more reasonable since the thermodynamic values of our complexes (β band) are closer to the values of olefins than those of aliphatic acetylenes.[38] As shown in Table I, $\Delta S°$ for complex formation with alkylallenes are smaller than those for alkylacetylenes and are larger than those for olefins. This could be explained by the rotational model of the phenolic proton around the two circular p orbitals of the central sp carbon as the hydrogen bonding configuration for alkylallenes. Arylallenes **17–19** did not show splitting of the bonded ν_{OH} spectra and the frequency shifts and thermodynamic results are nearly identical with those of styrene and α-methylstyrene.[15] In arylallenes $-\Delta F$ *vs.* $\Delta\nu$ plots lie near the line obtained for phenol–alkylbenzene complexes. Such was the case for the phenol–phenylcyclopropane complex.[39] This suggests that the hydrogen bonding is to the benzene ring rather than to the terminal ethylenic linkage.[40,41] This consideration is supported from the entropy anomaly[3,4] observed for the complex involving arylallenes: $-\Delta S$ for their complex formation are smaller than the values observed for alkylallenes and olefins; their magnitudes are nearly equal to those for aryl olefins (styrene and α-methylstyrene[15]). From these results we believe that arylallenes act as monofunctional π bases, suggesting a configuration with the phenolic proton lying over the 6π-electron system of styrene and not near the terminal ethylenic fragment.

Acknowledgment. We wish to thank Professor P. v. R. Schleyer of Princeton University for valuable discussions and Mr. F. Takabayashi for taking some infrared spectra.

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(38) As pointed out by a referee, the α and β bands can be attributed to hydrogen bonding with the phenyl ring and with the triple bond, respectively. Although this interpretation cannot be ruled out from our present data, we believe that our model explains more reasonably the $-\Delta F$ *vs.* $\Delta\nu$ plots in the α and β bands for arylacetylenes (Figure 4).

(39) Z. Yoshida, N. Ishibe, and H. Kusumoto, *J. Amer. Chem. Soc.*, **91**, 2279 (1969).

(40) The possibility of interaction with the central sp-hybridized carbon of arylallene cannot be excluded.[35] However, if that were the case, $-\Delta F$ *vs.* $\Delta\nu$ plots in arylallenes would lie in a similar region to those in alkylallenes.

(41) For 1,1-diphenylallene (**19**), correction of the equilibrium constant by the statistical factor, 2, gave the ΔF value -0.62 kcal/mol. The plot of this value *vs.* $\Delta\nu$ lies more closely to the line obtained for phenol–alkylbenzene complexes.

Cyclization of 2-Azidobenzophenones to 3-Phenylanthranils. An Example of an Intramolecular 1,3-Dipolar Addition[1]

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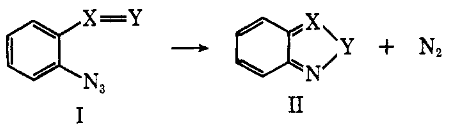
Abstract: The rate of decomposition of 4′-substituted-2-azidobenzophenones to give 4′-substituted-3-phenylanthranils has been studied in decalin over a 45° temperature range. The reaction was found to be accelerated by electron-withdrawing groups and retarded by electron-donating groups. The enthalpy of activation was found to be considerably less than reported for phenyl azide decompositions. The entropy of activation was moderately large and negative (-6 to -21 cal deg^{-1} mol^{-1}). A plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ was linear. An isokinetic temperature of 163° was calculated. The reaction was accelerated only slightly in changing the solvent from decalin to anisole to dimethylformamide. A 1,3-dipolar addition mechanism is proposed to account for these results.

Ortho-substituted phenyl azides have often been found to decompose much more rapidly than the corresponding meta or para isomers. This rate enhancement has been noted primarily in those systems where the ortho substituent has some type of α,β-unsaturation and in which the decomposition leads to



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cyclization. Several workers[3] have suggested that the reaction does not involve a nitrene intermediate (III), but instead proceeds *via* a concerted mechanism (IV) in which cyclization and loss of nitrogen are concurrent.

The evidence against the involvement of a nitrene is (a) the nitrene intermediate cannot account for the rate

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(2) (a) Abstracted in part from the M.S. Thesis of F. E. Behr, Southern Illinois University, June, 1968, and from the M.S. Thesis of R. L. Reed, Southern Illinois University, Sept, 1969; (b) American Chemical Society Fellow, summer, 1969.

(3) See L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968), and references therein.