give 3.48 g of tan crystals. The infrared spectrum appeared to be identical with that of a mixture of 2-propanesulfonamide and N-cyclohexyl-2-propanesulfonamide. Under the assumption that only these two compounds were present, the mixture was analyzed by infrared using a published method.[36] The bands used for analysis were at 1535 and 995 cm^{-1}. The results indicated that the mixture contained 94–95 mole % N-cyclohexyl-2-propanesulfonamide, a 60% yield based on 2-propanesulfonyl azide. A synthetic mixture containing 92 mole % N-cyclohexyl-2-propanesulfonamide analyzed 93%.

Reaction of *p*-Toluenesulfonyl Azide with a Mixture of Cyclohexane and Benzene. A solution of 3.50 g of *p*-toluenesulfonyl azide in 87.9 g (1.13 moles) of benzene and 97.3 g (1.16 moles) of cyclohexane was heated in a titanium-lined pressure vessel for 4 hr at 165°. The mixture was filtered and the filtrate was diluted to 500 ml with chloroform. A 200-ml aliquot was evaporated to to dryness, and the residue refluxed overnight with a mixture of 5.0 g of phenol and 35 ml of 48% hydrobromic acid.[12] The reaction mixture was continuously extracted with ether overnight, made basic with sodium hydroxide, and continuously extracted again with benzene.

Analysis of the benzene extract by gas chromatography (28% Dowfax-9N10 on 5% potassium hydroxide loaded Chromosorb W, 1-ft column) indicated 73% aniline and 27% cyclohexylamine. Repetition of the hydrolysis step yielded values of 63.5% aniline and 36.5% cyclohexylamine. In a control experiment, a mixture of 0.503 g of N-cyclohexyl-*p*-toluenesulfonamide and 0.502 g of N-phenyl-*p*-toluenesulfonamide was hydrolyzed and analyzed by the above procedure. The results were 52% aniline and 48% cyclohexylamine. Converted to mole per cent, these values are aniline, 53.5%, and cyclohexylamine, 46.5%; theoretical values are aniline, 50.5%, and cyclohexylamine, 49.5%. Correcting the average of the experimentally found values for the control, the ratio of N-phenyl-*p*-toluenesulfonamide to N-cyclohexyl-*p*-toluenesulfonamide in the azide decomposition is 1.95.

Reaction of *p*-Toluenesulfonyl Azide with a Mixture of Benzene and *p*-Xylene. A solution of 4.038 g of *p*-toluenesulfonyl azide in 78.1 g (1 mole) of benzene and 106.2 g (1 mole) of *p*-xylene was heated in a titanium-lined pressure vessel for 5 hr at 165°. The resulting mixture was filtered and evaporated to dryness. The residue, a dark semisolid mass, was cleaved with phenol and hydrobromic acid, as in the previous experiment, to give 29% aniline and 71% 2,5-dimethylaniline. In a control experiment, equal weights of the two product sulfonamides were hydrolyzed to give 56.5 mole % aniline and 43.5 mole % dimethylaniline (theoretical values are 52.5 and 47.5%). Correcting the experimentally found value for the control, the ratio of N-2,5-dimethylphenyl-*p*-toluenesulfonamide to N-phenyl-*p*-toluenesulfonamide is 2.2.

Reaction of *p*-Toluenesulfonyl Azide with Isopentane. A solution of 5.00 g of *p*-toluenesulfonyl azide in 200 ml of isopentane (Phillips Research Grade) was heated for 7 hr at 155°. The resulting solution was evaporated to dryness, the residue was dissolved in hot carbon tetrachloride, and the solution was filtered to remove black, tarry material. The carbon tetrachloride was removed under vacuum. The residue was taken up in benzene, and the resulting mixture was filtered to remove insolubles (0.252 g, 6% based on *p*-toluenesulfonyl azide), whose infrared spectrum spectrum was identical with that of *p*-toluenesulfonamide. Evaporation of the benzene left 2.00 g of an amber oil. Gas chromatography on the same column used in the above experiments indicated that 50.6% of the material was a mixture of the *p*-toluenesulfonamides of 2-amino-2-methylbutane and 2-amino-3-methylbutane, and 33% was a mixture of the *p*-toluenesulfonamides of 1-amino-2-methylbutane and 1-amino-3-methylbutane.

Decomposition of Azides in Cumene. Pressure bottles containing (a) 0.75 g of 1-pentanesulfonyl azide in 12.5 ml of cumene, (b) 1.5 g of *n*-octadecyl azidoformate[2] in 25 ml of cumene, (c) 1.0 g of *p*-toluenesulfonyl azide in 17 ml of cumene, and (d) 25 ml of cumene were flushed with nitrogen and then heated at 150° overnight. The contents of the bottles were analyzed by gas chromatography for dicumyl with the following results: a, 0.89 μg/μl; b, 1.31 μg/μl; c, none detected; d, <0.01 μg/μl. For a and b, these values correspond to 1.2 and 3.2 mole % (based on azide), respectively.

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[36] H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956).

Hydrogen Bonding between Phenol and the Cyclopropane Ring[1]

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Abstract: The hydrogen-bond interaction between phenol and the cyclopropane ring has been studied by the infrared method. The hydrogen-bond shifts of the ν_{OH} frequency of phenol are in the order of 40 cm^{-1} and the enthalpy changes for the phenol–cyclopropane complex formation are in the range of 1.3–1.5 kcal/mole. From the $-\Delta F°$ *vs.* $\Delta\nu$ plot, which is established to be a good criterion to decide the type of π base, the cyclopropane ring has been confirmed to have olefinic character. The cyclopropane ring in the bicyclic compounds has been found to be more basic than that in the alkylcyclopropanes from a comparison of the frequency shifts and the hydrogen-bond energy. The ultraviolet spectra of the iodine–cyclopropane derivatives system show the presence of a charge-transfer band at about 250 mμ.

During the past 20 years the characteristics of the cyclopropane ring were reported by using the spectroscopic methods: ultraviolet,[2] infrared,[3] nuclear magnetic resonance spectra,[4] and others.[5] Of particular interest is the fact that the cyclopropane derivatives behave as compounds having "double-bond

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[1] Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor. VIII.

[2] (a) H. Weitkamp, U. Hasserodt, and F. Korte, *Chem. Ber.*, **95**, 2280 (1962); (b) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964).

[3] (a) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); (b) R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962); M. Charton, *J. Chem. Soc.*, 1205 (1964); (c) C. Brecher, E. Krikorian, J. Blanc, and R. S. Halford, *J. Chem. Phys.*, **35**, 1097 (1961).

[4] (a) D. J. Patel, M. E. H. Howden, and J. D. Robert, *J. Am. Chem. Soc.*, **85**, 3218 (1963); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959); J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **86**, 1870 (1964); (b) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964); (c) S. Forsen and T. Norin, *Tetrahedron Letters*, 285 (1964); K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965); (d) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964); G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

[5] (a) W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, **36**, 200 (1962); R. H. Schweudeman, G. D. Jacobs, and T. M. Kraigs, *ibid.*, **40**, 1022 (1964); (b) O. Bastiansen and M. Trkttberg, *Tetrahedron*, **17**, 147 (1962); L. V. Vilkov and N. I. Sadoa, *Dokl. Akad. Nauk SSSR*, **162**, 565 (1965).

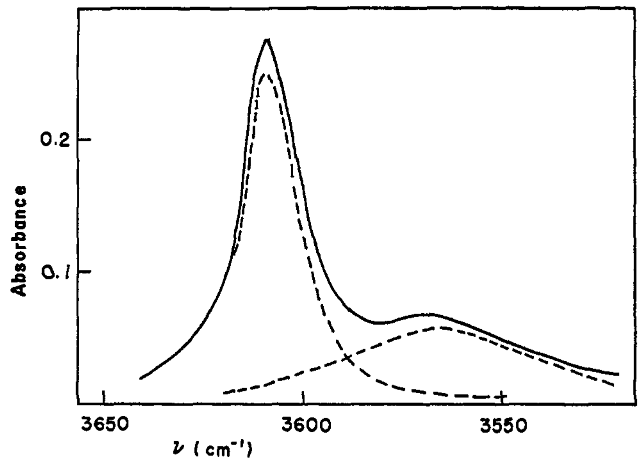

Figure 1. OH stretching absorption spectrum of 0.0205 *M* phenol in the presence of 4.58 *M* bicyclo[6.1.0]nonane in CCl_4 at 10.2°. Dotted lines are analyzed component curves.

character." To explain this peculiar behavior, quantum mechnical calculations of the electronic structure of the cyclopropane ring have been carried out;[6] Walsh suggested an sp^2 structure and Coulson proposed a bent-bond geometry. It is of interest to examine the double-bond character of the cyclopropane ring from the hydrogen-bond and charge-transfer investigations where the cyclopropane derivative can act as the electron donor. Nevertheless, little attention has been paid to the hydrogen bonding of the cyclopropanes, except for the papers of Schleyer, *et al.*,[7] which have described an intramolecular hydrogen bond in cyclopropylcarbinols. In this paper we wish to report spectroscopic evidence on the electron-donating character of the cyclopropane ring interacting with phenol and iodine. The thermodynamic values of the hydrogen-bonded complex were also evaluated by measuring the phenolic hydroxyl stretching vibration. From these results, the characteristics of the complex involving the cyclopropane derivatives could be discussed in comparison with those involving aromatic[8] and olefinic[9] π bases as the proton acceptor. Further, the interactions between iodine and the cyclopropane derivatives were studied by ultraviolet absorption spectroscopy and a new band due to charge transfer was found. By comparing these results for the charge-transfer complexes with those for the hydrogen-bonded complexes, several common properties could be discussed as it has been suggested by Mulliken.[10]

Experimental Section

Materials. The synthetic methods used for the preparation of our cyclopropane derivatives are classified as follows: (1) the reaction of methylene halide and olefins using the zinc–copper couple as the catalyst,[11] (2) the Wurz-type condensation of the 1,3-dibromo derivatives with zinc,[12] and (3) the pyrolysis of pyrazoline derivatives.[13] The cyclopropane derivatives are purified by preparative gas chromatography on an Apiezon L column. Other chemicals such as phenol and carbon tetrachloride were commercially available and purified by the usual methods.

Measurements and Analysis of Spectra. Infrared Spectra. All spectra of the hydroxyl stretching vibration were recorded on a double-pass grating infrared spectrophotometer Model DS-402G of Japan Spectroscopic Co. The experimental conditions have been described in a preceding paper.[8b,9] Spectra were measured with both sample and reference cells in a thermostated box.[14] Temperatures were varied from −10 to 40°.[15] The transmittance (%) of each of three or four concentrations of the cyclopropanes were 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.[16] The analysis of the spectra and calculations of the equilibrium constants have been described previously.[8a] In these calculations, the concentration of free phenol was corrected since the integrated absorption intensity of phenol in the absence of π bases depends not only upon its concentration but also upon the temperature.[16,17] The enthalpies for the complex formation were obtained from a plot of log *K* *vs.* $1/T$ (least-square calculations).

Ultraviolet Spectra. A Shimazu double-beam recording spectrophotometer SV-50A was employed for measuring the spectra of the solutions in fused quartz cells with light paths of 0.0114 cm. The optical path lengths of the cells were checked with standard chromate solutions.[18] Solutions of iodine in *n*-hexane (Merck "Uvasols" grade) of known concentrations were prepared by standard methods.[19] The sample temperature was kept at 27 ± 1°. The concentration of iodine and the cyclopropanes ranged from 0.002 to 0.02 mole/l. and from 0.1 to 6 mole/l., respectively. The cyclopropanes showed no tendency to form iodides during the course of the measurements, the absorption of the solutions in the visible region (*ca.* 500 mμ) remaining constant. To evaluate the extinction coefficient and the equilibrium constant of the complex, the procedure described by Benesi and Hildebrand[19a] was used.

Results

Hydrogen Bonding of Phenol with Cyclopropanes. The hydroxyl stretching vibration of phenol in the presence of bicyclo[6.1.0]nonane was a doublet as shown in Figure 1. It is apparent that there is a band due to the free OH stretching vibration at 3610 cm^{-1} and a band due to the hydrogen-bonded OH at 3566 cm^{-1}. Similar doublet spectra, well known in hydrogen bonding,[20] were observed in the other systems involving the cyclopropanes as the proton acceptor. It may be concluded that the cyclopropane ring can act as a proton acceptor in the hydrogen bonding. Table I summarizes the frequency shifts and thermodynamic values for the complexes of phenol with the cyclopropanes as well as with isopropylbenzene, styrene, and 1-pentene.

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(8) (a) Z. Yoshida and E. Ōsawa, *ibid.*, **87**, 1467 (1965); (b) Z. Yoshida and E. Ōsawa, *ibid.*, **88**, 4019 (1966).

(9) Z. Yoshida and N. Ishibe, to be published.

(10) (a) R. S. Mulliken, *J. Chim. Phys.*, **60**, 20 (1964); (b) M. R. Basila, E. L. Saier, and L. R. Cousins, *J. Am. Chem. Soc.*, **87**, 1665 (1965); (c) Z. Yoshida and N. Ishibe, to be published.

(11) (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) E. Legoff, *J. Org. Chem.*, **29**, 2048 (1964).

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(14) Z. Yoshida and N. Ishibe, *Spectrochim. Acta*, 24A, 893 (1968).

(15) M. M. Mauire and R. West, *ibid.*, 17, 369 (1961); D. L. Powell and R. West, *ibid.*, 20, 983 (1964). It is preferable to vary the temperature over a wide range especially lower than room temperature in order to obtain accurate thermodynamic data for the hydrogen bond.

(16) Details of this procedure for accurate thermodynamic data for the hydrogen bonds will be published in near future.

(17) Self-association of phenol was negligible, the plots of the integrated absorption intensity of phenol *vs.* its concentration obeying Lambert–Beer's law. Similar dependency was observed in the case of pyrrole by Mr. K. Shōbatake in our laboratory.

(18) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

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(20) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 67.

Table I. Frequency Shifts $\Delta\nu_{OH}$, Half-Band-Widths $\Delta\nu^{b}{}_{1/2}$, and Thermodynamics of Hydrogen Bonding of Phenol to Cyclopropanes in Carbon Tetrachloride

No.	Compounds	$\Delta\nu_{OH}$,[a] cm^{-1}	$\Delta\nu^{b}{}_{1/2}$,[a] cm^{-1}	$-\Delta H$,[b] kcal/mole	$-\Delta F°$,[c] kcal/mole	$-\Delta S°$,[d] eu
1	*n*-Propylcyclopropane	40 ± 1	40 ± 1	1.30	−2.09	11.4
2	*n*-Pentylcyclopropane	40 ± 1	40 ± 2	1.34	−1.92	11.3
3	Isopropylcyclopropane	40.5 ± 0.5	43 ± 1	1.39	−2.04	11.5
4	*trans*-1-Methyl-2-isopropylcyclopropane	41.5 ± 0.5	44 ± 2	1.47	−2.14	12.1
5	*cis*-1-Methyl-2-isopropylcyclopropane	41 ± 0.5	45 ± 2	1.50	−2.24	12.6
6	Bicyclo[3.1.0]hexane	42.5 ± 1	48 ± 1	1.78	−1.88	12.3
7	Bicyclo[4.1.0]heptane	42 ± 0.5	46 ± 1	1.63	−1.86	11.7
8	Bicyclo[6.1.0]nonane	44 ± 1	49 ± 1	1.76	−1.83	12.0
9	Phenylcyclopropane	53 ± 0.5	37 ± 1	1.45	−0.57	6.8
10	Styrene	46 ± 0.5	40 ± 1	1.34	−0.42	5.9
11	Isopropylbenzene	57 ± 1	48 ± 1	1.52	−0.61	7.1
12	1-Pentene	58 ± 1	72 ± 2	1.71	−1.10	9.4

[a] Mean deviation from the average. [b] The maximum error is within ±0.12 kcal/mole. [c] The maximum error is within ±0.10 kcal/mole. [d] The maximum error is within ±0.7 eu.

Charge-Transfer Complexes between Iodine and the Cyclopropanes. Figure 2 shows the ultraviolet absorption of iodine in *n*-pentylcyclopropane, from which it is appearent that there is a new absorbing species in the solution. To obtain the absorption spectrum of iodine–*n*-pentylcyclopropane complex, the absorption of uncomplexed iodine must be substracted from the spectrum shown in Figure 2. The difference[19c] between the iodine–*n*-pentylcyclopropane spectrum and the iodine–*n*-hexane plus *n*-pentylcyclopropane spectra is shown in Figure 3. This difference will represent fairly well the absorption spectrum of the iodine–*n*-pentylcyclopropane complex. The absorption peaks, the equilibrium constants, and the molar absorptivities of iodine–cyclopropane complexes are summarized in Table II.[21]

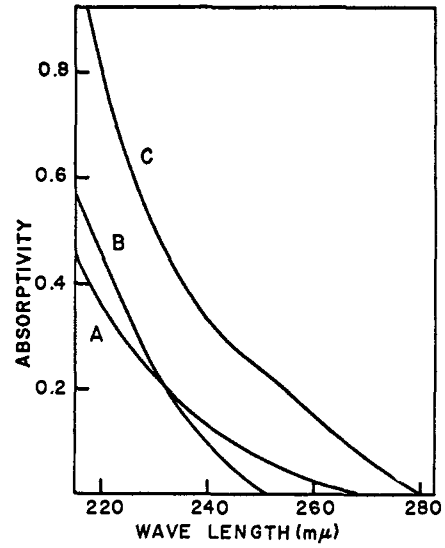

Figure 2. Ultraviolet absorption spectrum of iodine in the presence of *n*-pentylcyclopropane in *n*-hexane: (A) *n*-pentylcyclopropane in *n*-hexane, (B) iodine in *n*-hexane, (C) *n*-pentylcyclopropane and iodine in *n*-hexane.

Discussion

The frequency shifts, $\Delta\nu$, in the intermolecular hydrogen-bond complexes involving the cyclopropanes as the proton acceptor are smaller than those of alkylbenzenes and monoolefins,[8,9] but much larger than those of the intramolecular hydrogen bond of the cyclopropylcarbinols.[7,24] In other words, proton-accepting ability of the cyclopropane ring is smaller than the one of olefins and alkylbenzenes,[8,9] while the ^{13}C–H coupling constant (161 cps) of cyclopropane is nearly equal to the one (159, 157 cps) of benzene and ethylene.[4a] Such poor proton affinity of the cyclopropane ring could

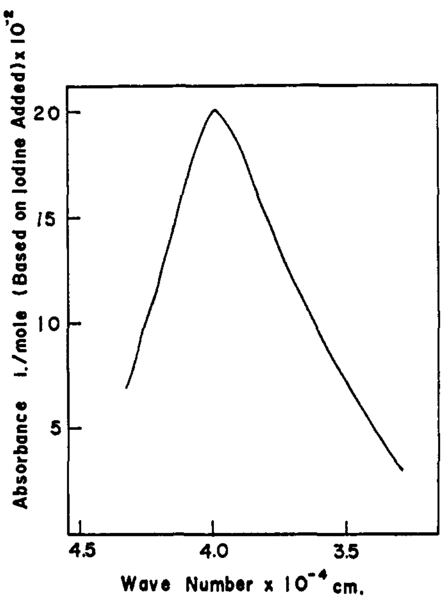

Figure 3. Charge-transfer band of *n*-pentylcyclopropane–iodine complex.

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(21) When these interactions are of the so-called contact charge-transfer complex type,[22] the equilibrium constant must be zero. The interactions of iodine with the cyclopropanes may, however, be stronger than those with alkanes.[19c,23]

(22) (a) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 483 (1957); J. N. Murrell, *ibid.*, **81**, 5037 (1959); (b) D. F. Evans, *J. Chem. Phys.*, **23**, 1424, 1426, 1429 (1955); D. F. Evans, *J. Chem. Soc.*, 4229 (1957).

(23) G. Kortüm and W. M. Vogel, *Z. Elektrochem.*, **59**, 16 (1955); K. Shinoda and J. Hildebrand, *J. Phys. Chem.*, **69**, 605 (1965).

(24) M. Ōki, H. Iwamura, K. Oka, and T. Murayama, Abstract, 19th Annual Meeting of Chemical Society of Japan, Yokohama, Japan, March 1966, 3E 307.

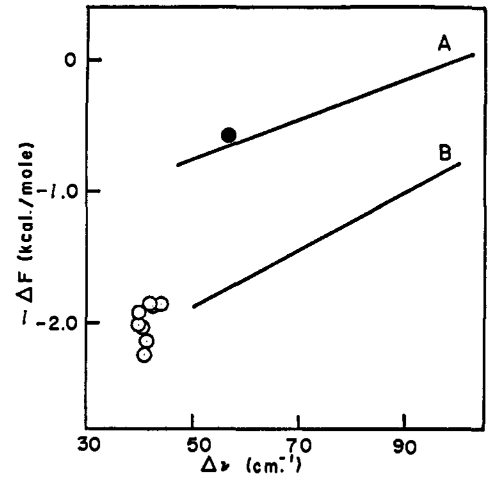

Figure 4. $-\Delta F°$ *vs.* $\Delta\nu$ plot with phenol–cyclopropanes: ○, alkylcyclopropanes and bicyclo derivatives involving the cyclopropane ring; ●, phenylcyclopropane. (A) alkylbenzene line, (B) monoolefin line.

be due to its larger ionization potential (approximately 10.0–9.7 eV) evaluated from the linear relation between the ionization potentials of the electron donors and the energy of the charge-transfer band in the iodine complexes.[19c,25,26] It is surprising that the frequency shifts are almost identical within experimental error for all the alkylcyclopropanes used in this study, because the frequency shifts increase by about 8 cm^{-1} when one alkyl group is introduced in the benzene ring or the 1-olefins as the proton acceptors.[8,9]

Table II. Absorption Peaks, λ_{max}, Equilibrium Constants, K_c, and Molar Absorptivity, ϵ_c, of the Iodine–Cyclopropane Complexes

Compound	λ_{max}, mμ	K_c, l./mole	ϵ_c	Ionization potential, eV
n-Pentylcyclopropane	253	0.053	15,000	
Isopropylcyclopropane	252	0.050	14,600	
Bicyclo[4.1.0]heptane	255	0.064	14,700	
Bicyclo[6.1.0]nonane	256.5	0.062	15,200	
Cyclohexane	238	0.021	19,400	9.88[a]
cis-Decalin	247	0.023	17,400	9.61[b]
Benzene	296[d]	0.12[d]	16,700[d]	9.56[c]

[a] K. Watanabe, *J. Chem. Phys.*, **26**, 542, 1773 (1957). [b] P. Natalis, *Nature*, **197**, 284 (1963). [c] G. F. Grable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962). [d] J. A. A. Ketelaar, *J. Phys. Radium*, **15**, 197 (1954).

The values of $-\Delta F°$ in the hydrogen-bonded complex formation are much smaller for the cyclopropane derivatives than for olefins and aromatic hydrocarbons.[8,9] Similar results were observed in the case of the iodine complexes. The equilibrium constants of the hydrogen-bonded complexes are nearly equal to those of the iodine complexes when cyclopropanes and benzene are used as the electron donor. This trend is interesting from the point of view of the various similarities observed for charge-transfer and hydrogen-bonded complexes as it has been suggested by Person[27] and Mulliken.[10a] The $-\Delta F°$ *vs.* $\Delta\nu$ plots for our cyclopropane derivatives (except for phenylcyclopropane) do not lie on the line for the phenol–alkylbenzene complexes[8] but on the line for phenol–olefin complexes[9] (Figure 4). As has been discussed in the previous paper,[8b] $-\Delta F°$ *vs.* $\Delta\nu$ plots afford information on the extent of conjugation in the π base. Therefore, it might be concluded that the cyclopropane ring would have olefinic but not aromatic "double-bond character." This conclusion corresponds well with the olefin-like properties of the cyclopropane ring observed from ultraviolet spectra[2] and reactivity.[28]

As shown in Table I, the hydrogen-bond energy increases in the order alkylcyclopropanes, isopropylbenzene, and 1-pentene, though the differences are small. The entropy change, $-\Delta S°$, is larger in the case of the alkylcyclopropanes than for 1-pentene, isopropylbenzene, and styrene. The values of $-\Delta S°$ in the cyclopropanes are nearly equal to those observed for ordinary hydrogen bonding (n hydrogen bonding) like O–H···O and N–H···N.[15,29,30] These results suggest that the freedom of the hydrogen bonding of phenol with the cyclopropane ring is similar to that of the ordinary hydrogen bonding (*e.g.*, O–H···O). Many workers[6] have proposed that the orbital having the "double-bond character" is coplanar with the cyclopropane ring. This would mean that if phenol interacts perpendicularly with the orbital of the cyclopropane ring having "double-bond character," a large decrease of the equilibrium constants should be observed for the *trans*-substituted cyclopropanes due to the steric interaction between the hydrogen-bonded phenol and the substituent of the cyclopropane ring. The values of $-\Delta F°$ and $-\Delta S°$ are, however, identical for both *cis* and *trans* isomers of 1-methyl-2-isopropylcyclopropanes. Therefore, phenol seems to interact with the orbital having the double-bond character of the cyclopropane ring on the plane coplanar with the ring.[31]

As seen in Table I, the cyclopropane ring becomes more basic toward the proton donor when it is part of a bicyclo skeleton (compare $\Delta\nu$, $-\Delta H$, and $-\Delta F°$ for no. 1–5 and no. 6–8 of Table I). Charge-transfer bands also showed a bathochromic shift when the electron donor was changed from monocyclic to bicyclic cyclopropane derivatives. This increase in basicity could be due to the increased π character of the bicyclic compounds, as is expected from the increase of the ^{13}C–H coupling constants.[32]

In phenylcyclopropane $-\Delta F°$ *vs.* $\Delta\nu$ plots lie on the line obtained for phenol–alkylbenzenes complexes.[8a] This suggests that phenol would interact with the benzene ring rather than with the cyclopropane ring. This consideration may be supported from the entropy anomaly[8] observed with the complex involving phenyl-

(25) H. M. McConnel, J. H. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(26) S. Freed and K. M. Sancier, *J. Am. Chem. Soc.*, **74**, 1273 (1952).

(27) W. B. Person, R. E. Erickson, and R. E. Buckles, *ibid.*, **82**, 29 (1960).

(28) M. S. Karasch, M. Z. Fiveman, and F. R. Mayo, *ibid.*, **61**, 2139 (1939); C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955); R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *ibid.*, 3616 (1952); S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).

(29) Reference 20, p 206.

(30) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962); D. D. Eyman and R. S. Drago, *ibid.*, **88**, 1617 (1966).

(31) This consideration is supported from quantum mechanical (extended Hückel) calculations on the total energy of the protonated cyclopropane having various configurations (T. Yonezawa, H. Katō, and K. Shimizu, private communication) and an SCF calculation on protonated cyclopropane (J. D. Petke and J. L. Whitten, *J. Am. Chem. Soc.*, **90**, 338 (1968)).

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cyclopropane: $-\Delta S^\circ$ for its complex formation is in fact much smaller than the values observed for both monocyclic and bicylic cyclopropanes; it is also roughly equal to those observed for alkylbenzenes. The frequency shift for phenylcyclopropane is larger than for benzene.[8b] Hence, the cyclopropyl group appears to be an electron-donating group. This electron-donating ability of the cyclopropyl group seems to be smaller than that of the isopropyl group from the linear relation between the frequency shifts and the Hammett $\sigma_m + \sigma_p$ constants of the substituents on benzene ring.[33]

The entropy contribution to the complex formation seems to be larger in the case of phenylcyclopropane than for isopropylbenzene, though the difference is small. This may suggest that there is a conjugation of the cyclopropyl group with the phenyl group, the degree of conjugation being smaller than the one of a vinyl group. This trend may correspond to the results observed in the dissociation constants,[34] the ultraviolet spectra,[2b,35] and the proton magnetic resonance spectra[4d] of the phenylcyclopropanes.

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Cyclopropanones. XII. Cycloaddition Reactions of Cyclopropanones[1]

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Abstract: Some cycloaddition reactions of 2,2-dimethylcyclopropanone (**3**) and the alkylcyclopropanones (**2** and **4**) are reported. Cycloadditions of the $3 + 4 \rightarrow 7$ type are observed with cyclic conjugated dienes; however, $3 + 2 \rightarrow 5$ and $2 + 2 \rightarrow 4$ cycloadditions occur when **3** is treated with dipolarophiles. The scope and mechanisms of these reactions are discussed.

Cycloaddition reactions[6] have received wide attention because of their theoretical,[7] mechanistic,[8] and synthetic[9] importance. Huisgen[7a,b] has classified cycloadditions according to the number of new σ bonds formed, the ring size, and the number of ring members contributed by each addend. The Diels–Alder reaction is thus a $4 + 2 \rightarrow 6$ cycloaddition and most 1,3-dipolar cycloadditions are of the $3 + 2 \rightarrow 5$ type.[10]

It is relatively rare for a single molecule (or class of molecules) to undergo more than one or two different types of cycloaddition reactions. We report here the cycloaddition reactions of some cyclopropanones and, in particular, 2,2-dimethylcyclopropanone (**3**), a molecule which undergoes an unusually large number of cycloaddition reactions under mild conditions.

Results

Preliminary accounts of this work have indicated the scope of cycloaddition reactions of some alkylcyclopropanones.[1a,11] Tautomers of the type **1a–c** must be considered in discussing the cycloaddition reactions of cyclopropanones. Although tautomers **1b** and **1c**

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