in electron density would cause the fluorine resonance to shift downfield. Thus, the shift for 3-fluoropyridine in 11.6 N hydrochloric acid is "normal," being shifted 11.8 ppm downfield from that in carbon tetrachloride. However, 2-fluoropyridine in acids exhibits upfield rather than downfield shifts; this effect has also been observed by others[22] and may be attributed to magnetic anisotropic effects.

Table V. ^{19}F Chemical Shifts of 2- and 3-Fluoropyridine in Acid Solution[a]

Acid	2-Fluoropyridine	3-Fluoropyridine
HCl	1.52	35.50
HBr	1.67	35.61
HI	0.78	35.40
HNO_3	2.56	38.07
HOAc	−7.06	46.93
$HClO_4$	1.40	36.58
H_3PO_4	1.09	34.82

[a] Relative to external trifluoroacetic acid, ±0.1 ppm.

With electron-withdrawing groups in the 5 position, para to the 2-fluoro group, the effect of the 11.6 N hydrochloric acid on chemical shifts' difference is reduced.[1] As the electron-withdrawing ability of the substituent increases, the amount of upfield shift is reduced, because the dipole of the solute molecule is reduced, and as a result so is the reaction field shielding term, S_e. This is also in accord with the solvent model.

In conclusion, solvent-induced chemical shifts in fluoropyridines do not give good correlations with functions containing the dielectric constant. The solvent parameter, E_t, has been shown to correlate very well with the chemical shifts of these compounds. The use of E_t should also be extended to other systems.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for the financial support of this project, and to Professor R. W. Taft for helpful discussions.

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(22) Professor R. W. Taft, unpublished results.

Substituent Effects on Cyclopropenium Ions

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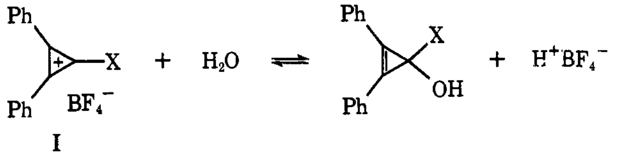
Abstract: A series of substituted diphenylcyclopropenium tetrafluoroborates, $Ph_2C_3X^+BF_4^-$ (I), has been prepared, and their pK_{R^+} values have been measured by potentiometric titration. The trend observed, $R_2N \gg$ c-C_3H_5 $>$ OEt $>$ n-$C_3H_7 \approx$ SMe $>$ Ph $>$ H, indicates conjugative effects still to be predominant in stabilizing these cations, though less so than with most other cations. No evidence of abnormal phenyl effects is found. Dicyclopropylcyclopropenone (III) has been prepared from diallylcarbinol by Simmons–Smith cyclopropanation, chromic acid oxidation, dibromination, and hydrogen bromide elimination. III is more basic ($H_0 = -1.2$) than diphenylcyclopropenone (II) ($H_0 = -2.3$).

The early finding that alkyl groups stabilized cyclopropenium ions[1] (with respect to cyclopropenols) more effectively than phenyl groups did[2-4] raised the possibility that such ions, because of their closed 2π-electron shells, were less susceptible to stabilization by conjugative electron donation than traditional open-shell carbonium ions. More recently, Ciabattoni and Nathan[5,6] reported that alkyl groups stabilize cyclopropenium ions according to the Baker–Nathan order, though they were unable to ascribe the origin (*i.e.*, hyperconjugation or steric hindrance to solvation) of this ordering.

In order to further explore stabilization of cyclopropenium ions by substituents, in particular the importance of conjugative and hyperconjugative effects, we undertook to study a greater variety of substituted cyclopropenium ions. Since we proposed to measure their stability by the standard pK_{R^+} method,[4,6] we chose to study a series of substituted diphenylcyclopropenium ions, in which electronic stabilization of the covalent cyclopropenols is potentially the same (stilbene-like) regardless of the substituent X.



I

These compounds also possess the merits that their expected pK_{R^+} values should be low enough to be significantly affected by X,[7] but yet high enough to be measured by potentiometric titration. They are also easily accessible.

Results

Substituted Diphenylcyclopropenium Ions. Reaction of appropriate Grignard reagents with diphenylcyclo-

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(1) For reviews of early work on cyclopropenium ions, see (a) A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966); (c) I. A. D'yakonov and R. R. Kostikov, *Russ. Chem. Rev.*, **36**, 557 (1967).

(2) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

(3) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(4) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(5) J. Ciabattoni and E. C. Nathan, *Tetrahedron Lett.*, 4997 (1969).

(6) J. Ciabattoni and E. C. Nathan, *J. Amer. Chem. Soc.*, **91**, 4766 (1969).

(7) A series of alkyldi-*tert*-butylcyclopropenium ions, which are much more stable (pK_R^+ = *ca.* 6.5) than alkyldiphenylcyclopropenium ions (pK_R^+ = *ca.* 3.8), showed no differentiation among the various alkyl groups.[6]

Table I. Properties of 1-X-2,3-Diphenylcyclopropenium Fluoroborates

X	Mp, °C	τ_0[a]	$\tau_{m,p}$[b]	τ_x[c]	λ_{max}, nm	$\nu_{C_3R_3^+}$
H[d]		1.55	1.92, 2.10	−0.45	307 (4.60) 305 (4.52)	
n-Pr[e]	179	1.7	2.1	6.4 (α) 7.7 (β) 8.7 (γ)	305 (4.52)	1430
c-C_3H_5	259.5–260	1.70	2.04	6.91 (α) 7.85 (β)	318 (4.22)	1425
C_6H_5	307.5–308	1.5	2.0		317 (4.13)	1420
OEt	195.5–196.5	1.65	2.06	4.55 (α) 8.15 (β)	300 (4.52)[f]	1440
NEt_2	180–181.5	1.90	2.15	5.81 (α) 8.33 (β)	315 (4.37) 313 (4.30)[f]	1410
NMePh	193–194	1.70	~2.3	5.75 (Me) ~2.3 (Ph)		1415
NPh_2	301–302	~2.25	~2.25	~2.25		1420
SMe	212–213	1.58	1.95	6.60	313 (4.40)[f]	1400
SPh	222–222.5	~2.1	~2.1	~2.1		1400
SOct	87–88.5	1.7	2.06	6.15 (α) 8.7 (β − ω)		1390

[a] Chemical shifts for ortho protons. [b] Chemical shifts for meta and para protons. [c] Chemical shifts for protons on substituent x. [d] Data on bromide and perchlorate salts from ref 3 and D. G. Farnum, A. Mostashari, and A. A. Hagedorn, III, *J. Org. Chem.*, **36**, 698 (1971); D. G. Farnum and M. Burr, *J. Amer. Chem. Soc.*, **82**, 2651 (1960). [e] Data from ref 4. [f] Data from Z. Yoshida and H. Miyahara, *Bull. Chem. Soc. Jap.*, **45**, 1919 (1972).

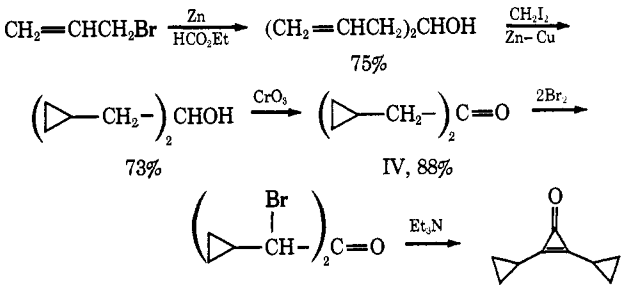
propenone (II) gave bis(cyclopropenyl) ethers, which were converted to 1-alkyl-2,3-diphenylcyclopropenium fluoroborates by treatment with fluoroboric acid in acetic anhydride. This method worked well with phenylmagnesium bromide[8] (57%) and cyclopropylmagnesium bromide (76%), but failed with *tert*-butylmagnesium bromide (91% recovered II) and methylmagnesium iodide.[8]

Reaction of II with triethyloxonium fluoroborate gave 1,2-diphenyl-3-ethoxycyclopropenium fluoroborate (I) (X = OEt). Reaction of this material with secondary amines[8] and with thiols gave a variety of 1-substituted-2,3-diphenylcyclopropenium fluoroborates I (X = NEt_2, NMePh, NPh_2, SMe, SPh, SC_8H_{17}). All are stable, high-melting crystalline materials (Table I). The infrared spectra all exhibited a strong band between 1390 and 1430 cm^{-1}, presumably a ring vibration of the cyclopropenium ring,[1b,4] and a broad fluoroborate absorption at 1020–1100 cm^{-1}. The pmr resonances of the phenyl rings of these ions (all in trifluoroacetic acid solution) are relatively insensitive to the nature of the substituent X (see Table I). In contrast, both the α and β protons of the cyclopropyl group are shifted downfield compared with cyclopropylammonium ion (τ 7.07, 9.07, respectively)[9] or cyclopropyl methyl ketone (τ 8.1, 9.2).[10] The large shift of the β protons in cyclopropylcarbonium ions has been regarded as evidence of hyperconjugative interaction of cyclopropyl groups with carbonium ion centers.[9] Similarly, the α-methylene protons on the heteroatom substituents show substantial downfield shifts, suggesting conjugative interaction of the heteroatoms with the cyclopropenium ring. However, the two phenyl groups may also contribute to the downfield shifts by virtue of their well-known anisotropic effects.

The stabilities of the various cyclopropenium ions with respect to the cyclopropenols were measured by means of the potentiometric titration procedure of Breslow,[4] in 50% aqueous acetonitrile. In all cases, classical titration curves were obtained, the midpoints of which were taken as the pK_{R^+}. The pK_{R^+} measured for tris(*tert*-butyl)cyclopropenium fluoroborate[11] using identical solutions and methods was 6.38 ± 0.1 (lit.[6] 6.5 ± 0.1). The data for the cations I are given in Table II.

Dicyclopropylcyclopropenone (III). The effectiveness of the cyclopropyl group in stabilizing the cation I (X = c-C_3H_5) led us to explore the synthesis of more highly cyclopropyl-substituted cyclopropenium ions. We chose to prepare dicyclopropylcyclopropenone as an interesting material in its own right and as a synthetic intermediate. Since dicyclopropylacetylene[12] was not known at the inception of this work, the modified Favorskii route[8,13,14] appeared most promising. The synthesis was accordingly performed as in Scheme I.

Scheme I. Synthesis of Dicyclopropylcyclopropenone (III)



Diallylcarbinol was prepared by the literature method[15] and cyclopropanated by the Simmons–Smith reaction. The success of the bis-cyclopropanation (1,5-hexadiene gives only 36% bisadduct and 18% monoadduct under

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(8) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

(9) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

(10) P. Yates and C. D. Anderson, *ibid.*, **80**, 1264 (1958).

(11) Graciously supplied by Professor J. Ciabattoni, Brown University.

(12) C. Köbrich and D. Merkel, *Angew. Chem., Int. Ed. Engl.*, **9**, 243 (1970).

(13) R. Breslow, J. Posner, and A. Krebs, *J. Amer. Chem. Soc.*, **85**, 234 (1963).

(14) R. Breslow, *et al.*, *ibid.*, **87**, 1326 (1965).

(15) M. Gaudemar, *Bull. Soc. Chim. Fr.*, 974 (1962).

Table II. pK_{R^+} Values of Substituted Diphenylcyclopropenium Cations $C_3XPh_2^+$

X	Counterion	Medium[a]	Method[b]	pK_{R^+}	Ref
H	Br	E	S	−0.67	3, 4
	Br	W	S	0.32	3, 4
Ph	Br	A	P	3.1	3, 4
	Br	W	S	3.12	3
	Br	E	S	2.80	3, 4
	BF_4	A	P	3.4	This work
SPh	BF_4	A	P	3.62	This work
SCH_3	BF_4	A	P	3.76	This work
SC_8H_{17}	BF_4	A	P	3.78	This work
C_3H_7	BF_4	E	S	3.8	4
OCH_2CH_3	BF_4	A	P	3.95 (?)	This work
p-$C_6H_4OCH_3$	Br	E	S	4.00	2
c-C_3H_5	BF_4	A	P	5.04	This work
NPh_2	BF_4	A	P	>10	This work
$NPhCH_3$	BF_4	A	P	>10	This work
$N(CH_2CH_3)_2$	BF_4	A	P	>10	This work

[a] A, 50% aqueous acetonitrile; E, 23% aqueous ethanol; W, water. [b] P, potentiometric titration; S, spectrophotometric titration.

comparable conditions)[16] is probably a result of coordination of an organozinc intermediate with the hydroxyl oxygen.[17,18] Oxidation of the secondary alcohol with Jones reagent proceeded slowly, giving the ketone IV. The mass spectrum of IV showed the expected parent ion at m/e 138 and a base peak at m/e 83 due to loss of a C_4H_7 fragment. No peak was seen at m/e 98 due to McLafferty rearrangement with loss of cyclopropene. IV was brominated while a stream of nitrogen was passed through the solution to sweep out HBr as formed. The resulting crude dibromide was treated with triethylamine to give crude III, which was purified by repeated extraction into 25% sulfuric acid.

The structure of III is confirmed by its spectroscopic properties: the infrared spectrum shows characteristic cyclopropenone bands[19] at 1850 and 1620 cm^{-1} (*cf.* di-n-propylcyclopropenone,[14] 1840 and 1639 cm^{-1}, and diphenylcyclopropenone[8] at 1840 and 1640 cm^{-1}), and bands at 1023 and 870 cm^{-1} attributable to the cyclopropyl substituents.[20] The ultraviolet spectrum showed, in addition to end absorption with a maximum below 200 nm, an $n \rightarrow \pi^*$ absorption band at 260 nm (ϵ 900); *cf.* di-n-propylcyclopropenone[14] at 252 nm (ϵ 86). The mass spectrum of III showed a parent peak at m/e 134, a peak at m/e 106 due to loss of CO, characteristic of cyclopropenones,[6,8,14] and the base peak at m/e 91 ($C_8H_{10} - CH_3$).

The pmr spectrum of III in CCl_4 shows multiplets for the α and β protons at τ 8.03 and 8.84, respectively, slightly deshielded with respect to *cis*-1,2-dicyclopropylethylene (τ 8.35, and 9.30 and 9.70).[21] When III is dissolved in chlorosulfuric acid ($H_0 = -13.8$),[22] the 1,2-dicyclopropyl-3-hydroxycyclopropenium ion is formed, as evidenced by downfield shifts of the α and β protons to τ 7.38 and 8.01. Again, the larger shift for the β protons (0.83 ppm) than for the α (0.65 ppm) may suggest hyperconjugative stabilization of the cation by the cyclopropyl groups.

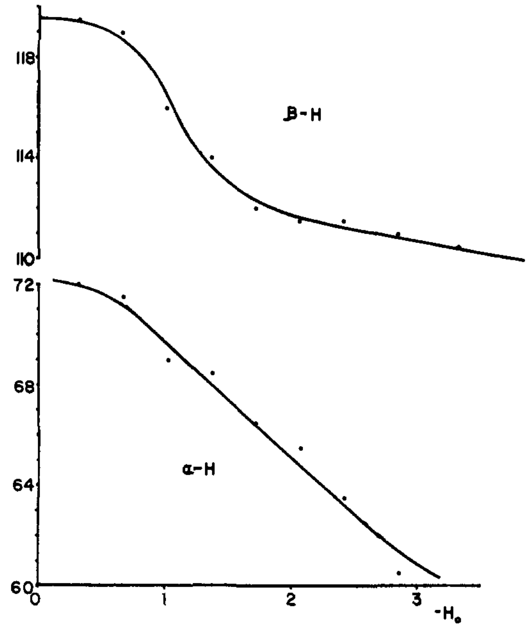

Figure 1. Chemical shift of β and α protons of III (relative to tetramethylammonium chloride) *vs.* H_0 in aqueous sulfuric acid mixtures. H_0 values from M. Paul and F. Long, *Chem. Rev.*, 57, 15 (1957).

Quantitative evaluation of the basicity of cyclopropenones is usually achieved by determination of the H_0 of a solution in which the ketone is half-protonated,[14,23] even though ketones do not behave as true Hammett bases.[24] This is most conveniently done by plotting the pmr chemical shifts of suitable protons (relative to internal tetramethylammonium chloride) *vs.* H_0 of the media used, in this case 5–50% aqueous sulfuric acid. The β protons gave a normal titration curve with a midpoint (half-protonation) at $H_0 = -1.2$. The α protons, however, changed continuously over the concentration range employed, presumably responding to medium effects differently from the standard[25] (see Figure 1). Using the value from the β protons, III appears to be

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(16) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

(17) See, for example, D. Seyferth and V. A. Mai, *ibid.*, **92**, 7412 (1970).

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(19) A. Krebs, *Tetrahedron Lett.*, 5935 (1968).

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(21) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971).

(22) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, **93**, 5083 (1971).

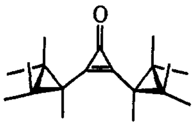
(23) R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966).

(24) C. C. Grieg and C. D. Johnson, *ibid.*, **90**, 6453 (1968).

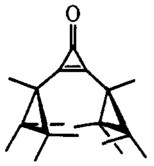
(25) Similar "misbehavior" was found for methyl- and dimethylcyclopropenones.[23]

slightly more basic than diphenylcyclopropenone ($H_0 = -2.3$, determined from uv data using the identical aqueous sulfuric acid mixtures as used above, lit.[8] $H_0 = -2.5$) or dialkylcyclopropenones (dimethyl, $H_0 = -1.5$;[23] di-*n*-propyl, $H_0 = -1.9$)[14] and much more basic than cyclopropenone itself ($H_0 = -5.2$).[26]

The higher basicity of III relative to other cyclopropenones might lead one to expect III to have a higher dipole moment. However, III has a dipole moment of 4.58 ± 0.10 D in benzene solution, compared with 5.05 for II (lit. 5.08,[27] 5.14[8]), 4.78 for dipropylcyclopropenone,[14] and 4.66 for cyclohepteno-cyclopropenone.[14] If cyclopropyl groups are involved in charge delocalization in the ground state, one may infer a preference for bisected conformer a rather than b, which has severe steric interactions of two pairs of hydrogen atoms. The observed dipole moment of conformer a, even with some positive character in the cyclopropyl rings, would be smaller than that of dialkylcyclopropenones, due to the shorter length of the resultant dipole.



IIIa



IIIb

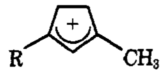
III is a stable species, which can be stored in the open for prolonged periods without evident change. The remarkable stability of cyclopropenones is demonstrated by contrasting this behavior with that of dicyclopropylcyclopropene which rapidly polymerizes at room temperature.[28]

Unfortunately, III did not react as expected with Grignard reagents, to give trisubstituted cyclopropenols or cyclopropenyl ethers. Reaction with phenylmagnesium bromide gave two major products, which were identified by gas chromatography–mass spectrometry as biphenyl and a product with parent ion at *m/e* 290, evidently formed by addition of 2 mol of phenylmagnesium bromide to 1 mol of III, perhaps 2,3-dicyclopropyl-1,3-diphenylpropan-1-one.

Discussion

From the $\mathrm{p}K_{\mathrm{R^+}}$ data of Table II it is evident that heteroatom substituents are effective in stabilizing cyclopropenium ions; indeed, the amino-substituted cations are stable at least to pH 10. This result clearly illustrates the importance of conjugative stabilization of cyclopropenium ions. Likewise, the superiority of cyclopropyl over *n*-propyl as a stabilizing substituent must be attributed to hyperconjugative interactions, the existence of which is also supported by the nmr data on the cations. In fact, evaluation of these and all the other data in the literature, including those on protonation of cyclopropenones,[8,14,23] and the $\mathrm{p}K_{\mathrm{R^+}}$ data on alkyldiphenyl-, alkyldi-*tert*-butyl,[15] and trialkylcyclopropenium ions[5] reveal in all cases the ordering $R_2N \gg c\text{-}C_3H_5 > SR > CH_3 > Et > i\text{-Pr} > t\text{-Bu} > Ph > H$ in ability to stabilize cyclopropenium ions, a conjugative order.

The seemingly anomalous position of phenyl in the above series has aroused extensive discussion,[2–4,29–32] since it contrasts with "normal" solvolytic experience, in which phenyl is much more effective than alkyl groups in stabilizing carbonium ion-like transition states,[33] as well as other experience involving ions of low intrinsic stability. However, more extensive examination of the literature reveals that in equilibria involving *stabilized* carbonium ions, such as ionic dissociation of $p\text{-RC}_6H_4CPh_2Cl$ in liquid SO_2,[34] enthalpies of transfer of ketones[35] and enols[36] from carbon tetrachloride to fluorosulfuric acid, polarographic reduction potentials of $(p\text{-RC}_6H_4)_3C^+$ ions,[37] and $\mathrm{p}K_{\mathrm{R^+}}$ measurements on cyclopentenyl cations[38] and para-substituted phenyltropylium ions,[39] $p\text{-RC}_6H_4\text{–}C_7H_6^+$, as well as in such kinetic measures as rates of protodetritiation of $p\text{-RC}_6H_4T$[40] and solvolysis of substituted cumyl chlorides,[41] *phenyl is quite generally inferior to alkyl groups* (which obey the Baker–Nathan ordering in all these cases) in stabilizing the carbonium ion relative to an uncharged equilibrant.[42] Whatever the reasons for this may be, there seems no need to invoke extraordinary phenomena in the cyclopropenium ions, which simply reflect the same qualitative trend.



Indeed, a plot of available $\mathrm{p}K_{\mathrm{R^+}}$ data for cyclopropenium ions *vs.* the summed σ^+ parameters[42] of the three substituents shows a very good linear relationship (Figure 2) (correlation coefficient 0.985) having a ρ of -15.71. The quality of the correlation is remarkable considering that the data were obtained in different solvent systems and in different laboratories. The phenyl-substituted cyclopropenium ions fit very well, with the possible exception of triphenylcyclopropenium ion, which has a *higher* $\mathrm{p}K_{\mathrm{R^+}}$ than expected. On the whole, then, phenyl substituents interact with cyclo-

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(26) R. Breslow and M. Oda, *J. Amer. Chem. Soc.*, **94**, 4787 (1972).

(27) D. N. Kursanov, M. E. Vol'pin, and Yu. D. Koreshkov, *J. Gen. Chem. USSR*, **30**, 2855 (1960).

(28) A. J. Schipperijn, *Recl. Trav. Chim. Pays-Bas*, **90**, 1110 (1971).

(29) D. G. Farnum, A. Mostashari, and A. A. Hagedorn, III, *J. Org. Chem,*, **36**, 698 (1971); D. G. Farnum and M. Burr, *J. Amer. Chem. Soc.*, **82**, 2651 (1960).

(30) (a) D. G. Farnum and C. F. Wilcox, *J. Amer. Chem. Soc.*, **89**, 5379 (1967); (b) G. J. Ray, A. K. Colter, and R. J. Kurland, *Chem. Phys. Lett.*, **2**, 324 (1968).

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(32) G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

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(36) J. W. Larsen, *ibid.*, **92**, 5136 (1970).

(37) H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969).

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(40) C. Eaborn and R. Taylor, *J. Chem. Soc.*, 247, 1012 (1961).

(41) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963); H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2052 (1966): data lead to σ_p^+ for $c\text{-}C_3H_5$ of -0.484.

(42) A referee has proposed that "when a phenyl which is *not previously conjugated with the* π *system* of a carbonium ion is brought into conjugation in the carbonium ion, it is more effective than an alkyl group in stabilizing the carbonium ion." In essentially all the systems discussed here, the phenyl groups are conjugated in the uncharged equilibrants *and* in the ions; in these systems, phenyl is a less effective stabilizer than alkyl groups. The same is apparently also true in σ-delocalized cations: C. F. Wilcox, Jr., and H. D. Banks, *J. Amer. Chem. Soc.*, **94**, 8231 (1972).

propenium ions normally, *i.e.*, as expected from their interactions with other carbonium ions.

However, some diminution in the importance of conjugative interactions in cyclopropenium ions is suggested by the deviations from the σ^+ correlation observed for cyclopropyl-, ethoxy-, and thiomethoxydiphenylcyclopropenium ions (which points were excluded from the above correlation). These ions are less stable than expected, and the deviations follow the order $CH_3CH_2O- > CH_3S- >$ c-C_3H_5. From this we infer that, while conjugative effects remain predominant in stabilizing cyclopropenium ions,[43] their relative contribution is smaller than in other carbonium ions, and the relative importance of inductive and (perhaps) steric factors is greater.

Experimental Section[44]

Diphenylcyclopropenone (II),[8] triphenylcyclopropenium fluoroborate,[8] zinc–copper couple,[45] and triethyloxonium fluoroborate[46] were prepared by literature methods.

Cyclopropyldiphenylcyclopropenium Fluoroborate (I, X = c-C_3H_5). A three-necked dropping flask (A) was fitted with a condenser with N_2 outlet, a dropping funnel with nitrogen inlet, and an ether inlet tube. A three-necked receiving flask (B) underneath (A) was fitted with the above dropping flask (A), a nitrogen inlet and a nitrogen outlet. A small amount of glass wool was packed in the dropping neck of the upper three-necked flask (A) to filter out the residual magnesium.

The required amount of magnesium turnings (1.826 g, 0.075 mol) was first placed in the upper flask; then nitrogen gas was passed through both three-necked flasks until the whole apparatus was flushed with the gas. Then the flasks were heated gently with a free flame, with continued flow of nitrogen, to ensure elimination of any moisture adhering to the surface of the glass and Mg. When the flasks had cooled completely, the nitrogen flow was reduced to a slow rate, and 7.438 g (0.06 mol) of cyclopropyl bromide in 20 ml of ether was placed in the dropping funnel. A small quantity of cyclopropyl bromide was introduced into flask A, and the mixture in flask A was heated with a heating gun. After initiation, an additional 50 ml of ether was added to the dropping funnel, and the mixture was slowly dropped into flask A. When the spontaneous boiling in flask A became slow, the mixture was heated gently to maintain the reflux until the magnesium had disintegrated and only a few small particles of metal remained. This freshly prepared cyclopropylmagnesium bromide solution was then dropped with stirring into an ice-cold mixture of 2.029 g (0.01 mol) of diphenylcyclopropenone (II) in 40 ml of ether in flask B. The solution was stirred for 1 hr, and aqueous KH_2PO_4 (6 g in 100 ml of water) was added to quench the reaction. The layers were separated, and the aqueous layer was extracted with two 30-ml portions of ether. The combined ether solution was dried over magnesium sulfate, and the ether was stripped off to yield a viscous reddish oil. The crude product had strong absorption at 1750 cm^{-1} in the ir, characteristic of covalent cyclopropenes. No strong absorption in the hydroxyl region was found; thus the product was mainly a dimeric ether. Into an ice-cold solution of this oil in 30 ml of anhydrous ether, a cold mixture of 6 g of commercial 48% HBF_4 in 18 ml of acetic anhydride was dropped with stirring. Another 100-ml portion of anhydrous ether was added, and the precipitated product was collected and washed with cold anhydrous ether. Recrystallization by solution in 20 ml of cold dry acetonitrile and addition of 200 ml of cold dry ether gave the pure product, which was dried under vacuum, yielding 2.423 g (76% yield): mp 259.5–260°; ir (KBr wafer) 3100 (m), 1601 (m), 1515 (s), 1425 (s, broad), 1350 (m), 1325 (m), 1280 (m), 1180 (m), 1050 (s, very broad), 908 (s), 862 (m), 774 (s), 708 (m), 683 (s) cm^{-1}; uv (nm, CH_3CN) λ_{max} 318 (ϵ 16,500), 303 (21,000), 288 (18,000), 264 (15,600); nmr, Table I.

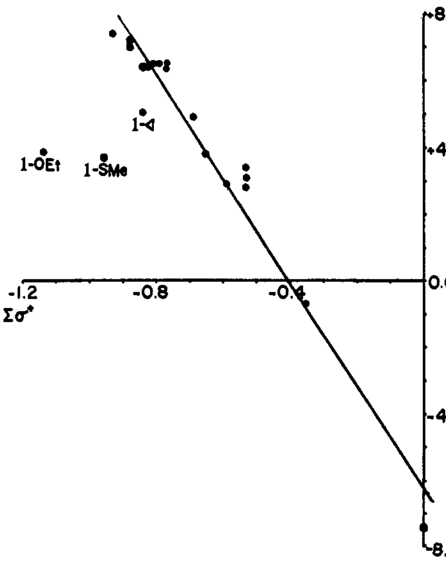

Figure 2. pK_{R^+} of cyclopropenium ions *vs.* the sum of the σ^+ parameters of the three substituents. The correlation line has a slope (σ) of -15.71. The points for I (X = c-C_3H_5, OEt, and SCH_3) were omitted from the correlation.

Anal. Calcd for $C_{18}H_{15}BF_4$: C, 67.92; H, 4.72; F, 23.90; mol wt, 318. Found: C, 67.92; H, 4.92; F, 23.78; mol wt, 328.

The compound is insoluble in hexane, benzene, or ether, but dissolves in ethyl acetate, acetone, acetonitrile, and aqueous acid.

Analogous attempts to prepare I (X = Me, *t*-Bu) failed, giving a 91% recovery of II in the latter case.

1,2-Diphenyl-3-ethoxycyclopropenium Fluoroborate (I, X = OEt).[8] A solution of 5.21 g (0.025 mol) of diphenylcyclopropenone and 4.766 g (0.025 mol) of triethyloxonium fluoroborate[48] in 45 ml of methylene chloride was allowed to stand for 2 hr, then 100 ml of dry ether was added, and the precipitated diphenylethoxycyclopropenium fluoroborate was washed successively with benzene, absolute ethanol, and ether, yielding 5.82 g of white solid (70% yield): mp 195.5–196.5° (lit.[8] 195.5–196°); ir (cm^{-1}, KBr wafer) 1840 (s), 1625 (s), 1500 (w), 1440 (s), 1330 (m), 1050 (s, broad), 765 (s). This hygroscopic compound was stored under nitrogen in a desiccator.

1,2-Diphenyl-3-(diethylamino)cyclopropenium Fluoroborate (I, X = NEt_2). To a solution of 4.653 g (0.0145 mol) of freshly prepared 1,2-diphenyl-3-ethoxycyclopropenium fluoroborate dissolved in 10 ml of methylene chloride, 1.077 g (0.0147 mol) of diethylamine in 10 ml of methylene chloride was added. The solution was stirred for about 30 min. When 150 ml of ether was added, a light yellow precipitate of 1,2-diphenyl-3-(diethylamino)-cyclopropenium fluoroborate formed and was collected (4.16 g, 83%), mp 179–182°. Recrystallization from a CH_2Cl_2–Et_2O mixture yielded white plates; mp 180–181.5°; ir (cm^{-1}, KBr wafer) 2900 (m), 1890 (s), 1600 (s), 1575 (s), 1475 (s), 1450 (s), 1400 (s), 1350 (s), 1315 (m), 1280 (m), 1200 (s), 1185 (m), 1170 (m), 1050 (s broad), 960 (m), 930 (m), 855 (w), 800 (w), 780 (s), 770 (s), 740 (w), 720 (m), 690 (s).

Anal. Calcd for $C_{19}H_{20}NBF_4$: C, 65.33; H, 5.73; N, 4.02. Found: C, 65.83; H, 6.11; N, 4.00.

1,2-Diphenyl-3-(methylphenylamino)cyclopropenium fluoroborate (I, X = NMePh) (97%) and 1,2-diphenyl-3-diphenylaminocyclopropenium fluoroborate (I, X = NPh_2) (94%) were prepared similarly.

Anal. Calcd for $C_{22}H_{18}NBF_4$: C, 63.18; H, 4.96; N, 3.65. Found: C, 64.06; H, 4.93; N, 3.12. Calcd for $C_{27}H_{20}NBF_4$: C, 72.81; H, 4.51; N, 3.01. Found: C, 72.64; N, 5.17; N, 3.20.

1,2-Diphenyl-3-(methylthio)cyclopropenium Fluoroborate (I, X = SMe). A solution of 3.23 g (0.01 mol) of I (X = OEt) in methylene chloride was treated with 0.48 g (0.01 mol) of methyl mercaptan. The mixture was stirred for 1 hr at room temperature. After addition of 100 ml of anhydrous ether, the white precipitate, 2.31 g (71%), was collected, mp 201–202°. Recrystallization from

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(43) This is also true for amino-substituted cyclopropenium ions; see Z. Yoshida and Y. Tawara, *J. Amer. Chem. Soc.*, **93**, 2573 (1971); A. T. Ku and M. Sundaralingam, *ibid.*, **94**, 1688 (1972).

(44) All melting points and boiling points are uncorrected. The nuclear magnetic resonance spectra were measured with a Varian A-60 spectrometer. Infrared spectra were determined on a Perkin-Elmer Model 137 spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., or Meade Microanalytical Laboratory, Amherst, Mass. Mass spectra were determined by Morgan-Schaffer Corp., Montreal, Quebec, Canada, on a Hitachi Perkin-Elmer RMU-6D spectrometer.

(45) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(46) N. Kornblum and R. A. Brown, *J. Amer. Chem. Soc.*, **86**, 2681 (1964).

CH_2Cl_2–Et_2O mixture yielded white plates: mp 212–213°; ir (cm^{-1}, KBr wafer) 3340 (w), 1601 (s), 1495 (m), 1400 (s), 1330 (s), 1285 (s), 1175 (m), 1100–1025 (s, broad), 788 (m), 769 (s), 678 (s).

Anal. Calcd for $C_{16}H_{13}SBF_4$: C, 59.26; H, 4.01; S, 9.88. Found: C, 59.16; H, 4.11; S, 9.54.

1,2-Diphenyl-3-(phenylthio)cyclopropenium fluoroborate (I, X = SPh) (81%) and 1,2-diphenyl-3-(*n*-octylthio)cyclopropenium fluoroborate (I, X = SC_8H_{17}) (86%) were prepared similarly.

Anal. Calcd for $C_{21}H_{15}SBF_4$: C, 65.28; H, 3.89; S, 8.29. Found: C, 64.91; H, 4.18; S, 8.20.

1,6-Heptadien-4-ol. This compound was made using allylzinc bromide and ethyl formate in THF according to the literature method.[15] The crude product thus obtained (75% yield) contained a contaminant which could not be separated by distillation through a spinning band column. Gas chromatographic isolation of the contaminant gave a material, the ir spectrum of which permitted identification as the formate ester of 1,6-heptadien-4-ol: ir 3020 (m, C=CH), 2880 (s, C–H), 1725 (s, C=O), 1640 (s, C=C), 1175 and 1000 (s, broad, C—O), 925 (s, vinyl C-H bend). Refluxing with ethanolic KOH for 2 hr gave 1,6-heptadien-4-ol.

1,3-Dicyclopropyl-2-propanol. Zinc–copper couple[46] (40.0 g, 0.6 mol), iodine crystals (1.0 g, 0.004 mol), and 250 ml of anhydrous ether were placed in a 500-ml three-necked, round-bottom flask fitted with mechanical stirrer, dropping funnel, and reflux condenser with drying tube. The mixture was stirred until the iodine color faded, then a mixture of CH_2I_2 (160.82 g, 0.600 mol) and diallylcarbinol (37.31 g, 0.300 mol) was added dropwise. The stirred solution was heated at gentle reflux for 60 hr. At the end of reaction, most of the gray couple had been replaced by finely divided copper. The mixture was cooled and then filtered. The filtrate was washed successively with cold 5% HCl, 5% sodium bicarbonate solution, and water. It was dried over anhydrous magnesium sulfate, and the ether was stripped off. A light yellow liquid (30.11 g) was obtained and purified by reduced pressure distillation (bp 46–47° (0.05 mm), yield 73%). Tlc on silica gel (eluted with 1:1 benzene–hexane mixture) showed only one spot: $n^{20}D$ 1.4496; ir (cm^{-1}) 3400 (s), 3040 (m), 2940 (s), 1440 (s), 1435 (s), 1150 (m), 1120–1020 (s, broad), 965 (s), 940 (m), 895 (m), 855 (m), 832 (s), 793 (m), 769 (m); nmr (δ, CCl_4) 0.075 (m, 4 H), 0.42 (m, 4 H), 0.68–1.10 (m, 2 H), 1.35 (q, 4 H), 3.67 (quintet, 1 H), 3.90 (s, 1 H).

1,3-Dicyclopropyl-2-propanone (IV). Jones reagent[47] [prepared from 14 g (0.135 mol) of chromium trioxide in 10 ml of water and 12 ml of concentrated sulfuric acid] was added dropwise, with mechanical stirring, to a solution of 1,3-dicyclopropyl-2-propanol (17.5 g, 0.125 mol) in 50 ml of acetone (previously purified by treatment with potassium carbonate and distillation from phosphorus pentoxide). The mixture was stirred for 6 hr at room temperature, until the original orange color was replaced by brownish green. The organic layer was separated, and the aqueous layer was extracted with two 50-ml portions of ether. Saturated $NaHSO_3$ solution was added in small portions until the initial brown color of the organic solution was discharged, and the solution was then dried over magnesium sulfate. Removal of ether on the rotary evaporator gave 15.38 g of crude 1,3-dicyclopropyl-2-propanone (88% yield). This crude product was purified by reduced pressure distillation; bp 30–31° (0.05 mm); tlc analysis on silica gel (eluted with 4:1 benzene–hexane mixture) showed only one spot; ir (cm^{-1}) 3015 (m), 2970 (m), 1725 (s), 1465 (w), 1425 (m), 1415 (m), 1380 (m), 1323 (w), 1170 (m), 1050 (w, broad), 1023 (s), 944 (m), 832 (m); nmr (δ, CCl_4) 0.13 (m, 4 H), 0.52 (m, 4 H), 0.95 (m, 2 H), 2.35 (d, 4 H). Acceptable analyses of this ketone could not be obtained, even from vpc-pure samples. The mass spectrum of IV showed important peaks at *m/e* 138 (10.7), 95 (10.0), 83 (100.0), 82 (10.9), 55 (89.7), 54 (20.3), 53 (18.3), 41 (20.6), 39 (39.3), 29 (58.1), and 28 (76.7).

The semicarbazone derivative of the ketone was prepared according to a standard procedure,[48] as a white solid, mp 136–138°. Recrystallization from 50% water–ethanol yielded a white solid, mp 137.5–138.5°.

Anal. Calcd for $C_{10}H_{17}ON_3$: N, 21.53; C, 61.53; H, 8.71. Found: N, 21.75; C, 61.64; H, 8.83.

Bromination of 1,3-Dicyclopropyl-2-propanone (IV). A solution of 1,3-dicyclopropyl-2-propanone (27.6 g, 0.2 mol) in 100 ml of methylene chloride was placed in a three-necked, round-bottom flask fitted with nitrogen inlet tube, dropping funnel, and reflux condenser with nitrogen outlet. The nitrogen inlet tube was inserted deep into the solution so that a constant nitrogen gas flow could sweep out HBr formed during the bromination. The solution was cooled in an ice bath, and a solution of bromine (67.2 g, 0.42 mol) in 50 ml of methylene chloride was added, with stirring, over 1 hr at 0°. The mixture was stirred for an additional 10 hr at 0°. Solid Na_2SO_3 was added in small portions until the initial dark red color was discharged, and the solution was then washed with distilled water. The organic phase was dried over magnesium sulfate, and the solvent was stripped off to yield on orange liquid, 56.8 g, 97% yield.

The crude product had nmr absorption at δ 0.52 (m), 0.90 (m), 1.60 (m), 3.94 (d), and 4.12 (d), in CCl_4 with relative areas of 4:4:2:1:1, which indicated a 1:1 mixture of stereoisomers of 1,3-dibromo-1,3-dicyclopropyl-2-propanone: ir (cm^{-1}): 3000 (m), 2945 (s), 1740 (s), 1450 (m), 1425 (s), 1390 (m), 1300 (s), 1265 (m), 1190 (s, broad), 1170 (s), 1025 (s), 1012 (s), 943 (s), 908 (m), 870 (m), 833 (s), 787 (m), 740 (m, broad), 692 (m). The crude dibromide darkened after refrigeration overnight.

No further purification was carried out, the unstable crude product being used directly for the elimination reaction.

Dicyclopropylcyclopropenone (III). The crude dibromide (56.8 g) was dissolved in 100 ml of methylene chloride, and the solution was added with stirring over 2 hr to 80.8 g (0.8 mol) of purified triethylamine in 200 ml of methylene chloride at room temperature. The mixture was refluxed for an additional 10 hr, then extracted with two 100-ml portions of 3 *N* HCl, which were discarded. The organic phase was cooled in an ice bath, and a cooled solution of 34 ml of H_2SO_4 and 17 ml of water was slowly added. The mixture was allowed to stand for 0.5 hr, then the aqueous phase was transferred to a 1000-ml erlenmeyer flask along with 350 ml of water and 100 ml of methylene chloride, previously purified by washing with concentrated sulfuric acid and then distilling. Na_2CO_3 was added in small portions until the pH of the solution was near 7. The organic layer was collected, and the aqueous solution was extracted with two 100-ml portions of methylene chloride. The combined organic layers were dried over $MgSO_4$, and the solvent was stripped off. The crude product was an orange liquid (1.72 g, 6%). Tlc and vpc analyses showed the presence of some minor impurities. All attempts to purify the dicyclopropylcyclopropenone by regular purification methods (column chromatography, vacuum distillation, molecular distillation) proved unsatisfactory due to decomposition.

A pure sample was obtained by two more acid extractions using 25% H_2SO_4: ir (cm^{-1}) 2950 (m), 1840 (s), 1605 (s), 1430 (m), 1383 (m), 1320 (m), 1280 (m), 1185 (w), 1100 (m), 1080 (m), 1070 (m), 1030 (m), 972 (w), 915 (s), 890 (m), 818 (m), 724 (s); uv λ_{max} (nm, 95% EtOH) 260 (ϵ 900).

Anal. Calcd for $C_9H_{10}O$: C, 80.60; H, 7.46; O, 11.94; mol wt, 134. Found: C, 80.52; H, 7.40; O, 11.90; mol wt, 137.

The mass spectrum of III showed important peaks at *m/e* 134 (23.3), 106 (32.0), 105 (36.2), 103 (10.4), 92 (35.6), 91 (100.0), 79 (44.1), 78 (82.5), 77 (42.2), 65 (29.5), 52 (42.3), 51 (38.6), 50 (32.5), 39 (45.4), and 28 (60.1).

The dipole moment of III was determined on a WTW Dipolmeter, Type DM 01, in benzene solution at 20.0°. Results on two independently synthesized samples of III gave a value of 4.58 ± 0.10 D. The dipole moment of II determined at the same time was 5.05 D (lit. 5.08,[27] 5.14[8]).

Basicity of III. Standard 50% sulfuric acid was prepared using 288.36 g of distilled water and 301.68 g of commercial reagent grade sulfuric acid (97.7%), and was standardized by titrating in triplicate with standard base. Further dilution with distilled water formed standard sulfuric acid–water solutions of concentrations 5, 10, 15, 20, 25, 30, 35, 40, and 45%, the concentration being given in per cent sulfuric acid (wt/wt).

In a typical determination, a 0.5-ml quantity of standard sulfuric acid solution was placed in a nmr tube and cooled in Dry Ice. Then a 0.025–0.05-ml sample of dicyclopropylcyclopropenone was added with a micropipet. The nmr tube was then warmed to room temperature, and a spectrum was taken within 5 min.

Tetramethylammonium chloride (TMAC) was used as an internal standard in all measurements. The chemical shift of TMAC relative to TMS varies from δ 3.20 in very dilute acid solutions (0–20%) to δ 3.18 in moderately concentrated acid solutions (25–60%).[49] The nmr chemical shifts of both α-methine and β-methylene absorp-

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(47) A. Boners, *et al.*, *J. Chem. Soc.*, 2555 (1953).

(48) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 390.

(49) G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

tions of the dicyclopropylcyclopropenone sample in different acid solutions were measured by interpolating the readings which corresponded to the midpoints of the integral curves. The results of such a measurement relative to internal tetramethylammonium chloride are shown in Figure 1. A normal titration curve was obtained for the β-methylene protons, and the midpoint, corresponding to 50% protonation, was at $H_0 = -1.2$.

As a check on the procedure, the basicity of authentic diphenylcyclopropenone was determined by the ultraviolet method,[8] using the same acid solutions. The apparent H_0 of diphenylcyclopropenone was -2.3, lit. -2.5 ± 0.3.[8]

Attempted Synthesis of Tricyclopropylcyclopropenium Fluoroborate. A Grignard reagent was prepared from 7.26 g (0.06 mol) of cyclopropyl bromide and 1.44 g (0.06 mol) of magnesium turnings in 30 ml of anhydrous ether, and dropped with stirring into an ice-cold solution of 1.31 g (0.01 mol) of dicyclopropylcyclopropenone in 40 ml of ether. After 30 min, the solution was warmed to room temperature, then stirred for another 30 min. After cooling again in an ice bath, the mixture was quenched with cold aqueous KH_2PO_4 solution. The organic layer was separated and combined with an additional ether extract. After this solution was dried and solvent-stripped, 1.71 g of syrupy reddish organic residue was obtained. The infrared spectrum showed strong absorption at 2950, 1745, 1380, and 1245 cm^{-1}, with medium peaks at 1670, 1020, 953, and 825 cm^{-1}. The residue was redissolved in 40 ml of anhydrous ether and treated with HBF_4 in acetic anhydride. The color of the solution darkened during the addition, and some white precipitate formed; however, the precipitate redissolved upon stirring. An additional 300 ml of anhydrous ether was added and the solution was cooled in an ice bath for another 30 min. No detectable amount of solid formed, so the solution was slowly neutralized with ice-cold aqueous $NaHCO_3$. The organic layer was separated and dried over $MgSO_4$, and 1.68 g of orange syrupy residue was obtained after stripping off the solvent. Tlc on silica gel (eluted with benzene) showed at least three spots (one large, two small). Vpc showed one big peak and three small peaks. A 0.5-g portion of this recovered residue was dissolved in 100 ml of anhydrous ether and treated with $HClO_4$ in acetic anhydride. Solution darkened and became turbid; however, no precipitate could be detected. Ethyl ether was then stripped off and the remaining solution was distilled at low temperature under vacuum to remove the dissolved acetic acid. After distillation, only black tar remained.

Attempted Synthesis of 1,2-Dicyclopropyl-3-phenylcyclopropenium Fluoroborate. A Grignard reagent was prepared from 6.28 g (0.04 mol) of bromobenzene and 1.2 g (0.05 mol) of magnesium turnings in 30 ml of anhydrous ether, and was added dropwise with stirring into the ice-cold solution of 1.34 g (0.01 mol) of dicyclopropylcyclopropenone in 40 ml of anhydrous ether. After 30 min, the solution was allowed to gradually warm up to room temperature, then stirred for another 30 min. After cooling again in an ice bath, the mixture was quenched with cold aqueous KH_2PO_4 solution. The organic layer was separated and combined with an additional ether extract. After the mixture was dried and solvent stripped, 1.89 g of syrupy residue was obtained. In the infrared spectrum, it showed strong absorption at 2900, 1660, 1450, 742, and 702 cm^{-1}. The residue was redissolved in 30 ml of anhydrous ether and treated with HBF_4 in acetic anhydride. The color of the solution darkened during the addition; however, no precipitate formed even after standing for 30 min in an ice bath or after addition of 300 ml of anhydrous ether. The solution was therefore slowly neutralized with ice-cold aqueous $NaHCO_3$ and the organic layer was again separated. After the solvent was stripped off, 1.85 g of syrupy orange residue was recovered. Tlc analysis on silica gel (eluted with benzene) showed two large spots and two small ones. Vapor phase chromatography (SE-30 column at 230°) showed the presence of two large and many small peaks. Preparative vpc collection of the first large peak gave a solid, mp 63–66°, which was identified by ir and mass spectral analysis as biphenyl (mp of authentic biphenyl 69–70.5°); mmp 63–66°.

Analysis by gc–ms showed the second large peak to be an adduct of 2 mol of phenylmagnesium bromide with 1 mol of III, mol wt 290. Large fragments appeared at *m/e* 289, 272, 261, 247, 233, 155, 141–143, 127–129, 105, and 77. Other peaks in the gc–ms showed apparent parent ions (in order of increasing retention time) at *m/e* 148, 146, 154 (biphenyl), 200, 212 (1 mol of III + 1 mol of PhMgBr), 290 (described above), and 286.

Determination of pK_{R^+} Values of Substituted Cyclopropenium Cations. All pH measurements were made on a Beckman Expandomatic SS-2 pH meter, equipped with glass–calomel electrodes. The pH meter was standardized with an appropriate buffer before each measurement. In a typical measurement, a solution of 0.40 mequiv of the appropriate cation was prepared in 20 ml of purified acetonitrile in a 50-ml beaker. Then 20 ml of 0.100 *N* NaCl (pH 7.0 ± 0.1) solution was added, and the solution was mixed thoroughly with a micro magnetic stirrer. The stirred aqueous acetonitrile solution was then titrated with 0.050-ml portions of 0.10 *N* NaOH from a micrometer buret, and the pH of the solution was observed 0.5 min after addition of each aliquot. As the equivalence point was approached, 0.025-ml aliquots were added. Titrations were carried out well past the equivalence point, and in many cases back-titration was performed in a similar manner.

The experimental points were plotted, giving classical titration curves whose midpoints were taken as the pK_{R^+}'s. The solutions remained clear during the titration, and the curves were reversible as shown by back-titration with 0.100 *N* HCl, as far back as the midpoint; beyond that point, irreversibility was observed in some cases.

To calibrate the method, 0.40 mequiv of tri-*tert*-butylcyclopropenyl fluoroborate[11] was titrated in the same manner. The titration curves gave an average pK_{R^+} of 6.38 ± 0.10 (lit.[5] $pK_{R^+} = 6.5 \pm 0.1$).

The observed pK_{R^+} values are listed in Table II. The reported values represent averages of duplicate or triplicate runs which did not differ by more than 0.1 p*K* unit.

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