blanketed dry-box, equipped with a moisture conductivity cell. The solution was injected with a hypodermic syringe into a small vial, capped with a self-sealing neoprene stopper. The vial was preheated in a Fisher constant temperature bath (±0.5°) and prethermostated olefin (1.22 molar) was injected into the base–solvent mixture.

The vial was removed from the bath momentarily and shaken two or three times by hand to promote mixing. The homogeneous mixture was sampled periodically by withdrawing aliquots with a hypodermic syringe. To stop the reaction, the aliquot was injected into a bottle containing ice-water as well as a small amount of extraction agent (*n*-pentane for methylenecyclohexane, methylenecycloheptane and methylenecyclooöctane isomerizations; *iso*-pentane for methylenecyclobutane and methylenecyclopentane isomerizations). The bottle was shaken and cooled to freeze the water–dimethyl sulfoxide mixture.

The supernatant pentane extract was analyzed on a Model 154 Perkin-Elmer gas chromatograph employing the following columns, temperatures and pressures. Methylenecyclobutane: DC-200, 59°, 15 p.s.i.; methylenecyclopentane: silver nitrate–diethylene glycol, 30°, 15 p.s.i.; methylenecyclohexane: 3% squalene on firebrick, 33°, 25 p.s.i.; methylenecycloheptane: silver nitrate–diethylene glycol, 30°, 15 p.s.i.; methylenecyclooöctane: silver nitrate–diethylene glycol, 30°, 15 p.s.i. Two runs were made for each olefin. Kinetic data were reproducible to ±5%.

The experimental procedure outlined by Bartlett[16] was followed in the ketone brominations. One hundred cc. of a 0.1000 *N* standard sodium hydroxide solution, 100 cc. of distilled water, and 10 cc. of a 0.0155 *M* aqueous solution of the ketone were placed in a 250-cc. glass-stoppered flask and cooled to 0° (±0.5°). Ten cc. of separately cooled 0.0398 *M* bromine water was pipetted into the base-water-ketone solution to initiate the reaction. Aliquots of 25 cc. of the reacting solution were withdrawn periodically and added to 5 cc. of 0.3 *M* acetic acid solution containing an excess of solid sodium iodide, added just before the sample. The liberated iodine was titrated with thiosulphate. At least three runs were made for each ketone. Kinetic data were reproducible to ±2%.

Materials.—Potassium *tert*-butoxide was obtained from Mine Safety Appliance Co. This material was received as the sublimed, white powder. Analysis showed it to be above 98.5% pure, with K_2CO_3 as the major impurity. Dimethyl sulfoxide was dried and distilled over 13X molecular sieves (Linde). Infrared and mass spectrometric analysis showed it to be of high purity with little, if any, water. Gas chromatographic analysis indicated only one compound.

Methylenecyclobutane was obtained from Aldrich and purified by preparative gas chromatography. The resultant material was checked against a sample supplied by Professor R. B. Turner of Rice University. Methylenecyclopentane was obtained as an API standard. Methylenecyclohexane was obtained from Columbia Organic Chemicals Co. and checked against an API standard. Both methylenecycloheptane and methylenecyclooöctane were prepared from their respective ketones by the Wittig reaction in rather low, *ca.* 5–10% overall yields. These materials were purified by preparative gas chromatography and characterized by infrared and n.m.r. techniques. In addition, the methylenecycloheptane was checked against an authentic sample supplied by Professor Turner. In all cases, the isomers showed only one peak on the gas chromatograph.

The *endo*-olefins 1-methylcyclobutene and 1-methylcycloheptene were supplied as reference samples by Professor Turner. The 1-methylcyclopentene and 1-methylcyclohexene were API reference samples. 1-Methylcyclooöctene was identified by retention time on the gas chromatograph from the isomerization of methylenecyclooöctane.

Cyclobutanone was obtained from Aldrich and was purified by preparative gas chromatography. An infrared spectrum of the resultant compound was checked against the reported spectrum. Cyclopentanone, cyclohexanone, cycloheptanone and cyclooöctanone were purchased from Columbia Organic Chemicals Co. These were dried over 13X molecular sieves (Linde) and distilled to give a material that, in each instance, showed only one peak on the gas chromatograph.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Synthesis and Stability of Some Cyclopropenyl Cations with Alkyl Substituents[1]

BY RONALD BRESLOW, HERMANN HÖVER AND HAI WON CHANG

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The dipropylcyclopropenyl cation and the tripropylcyclopropenyl cation have been synthesized. Comparison of their *pK*'s shows that the alkyl groups have a considerable effect on the stability of the cyclopropenyl cation, and this is confirmed by a comparison of the *pK*'s of diphenylcyclopropenyl cation and propyldiphenylcyclopropenyl cation. The stabilization by propyl groups is even larger than that by phenyls, and this suggests that the alkyl effect is largely inductive, rather than hyperconjugative. N.m.r. studies reinforce this interpretation. By extrapolation the *pK* of unsubstituted cyclopropenyl cation can be estimated; the relationship between this estimate and the aromaticity of cyclopropenyl cation is discussed.

I. Introduction.

—A number of aryl derivatives of the cyclopropenyl cation have recently been synthesized. The first such species, triphenylcyclopropenyl cation,[2,3] was found to be a stable carbonium ion, with pK_{R^+} 3.1, and subsequently salts of the diphenylcyclopropenyl cation[4] and of a series of *p*-methoxytriphenylcyclopropenyl cations[3] have been prepared.

The pK_{R^+}'s of these cations also have been determined, and the results can be correlated moderately well with the predictions of molecular orbital calculations.[3,4] Furthermore, both diphenylcyclopropenone[5] and dipropylcyclopropenone[6] have been synthesized. These ketones, and particularly their salts, may be considered to be derivatives of the cyclopropenyl cation as well.

The stability of these highly strained carbonium ions could at first sight be ascribed qualitatively to the substituents, since a large number of resonance forms can be written for the triphenylcyclopropenyl cation, for instance. However, it has already been shown that this effect alone cannot account for the observed stabilities, since the triphenylcyclopropenyl radical has considerably less

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[1] This work was supported by grants from the National Science Foundation, the Petroleum Research Fund and the Sloan Foundation. A preliminary report of some of this work was presented at the 17th National Organic Symposium, Bloomington, Ind., 1961, and by R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

[2] R. Breslow, *ibid.*, **79**, 5318 (1957); R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

[3] R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

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

[5] R. Breslow, R. Haynie and J. Mirra, *ibid.*, **81**, 247 (1959); M. Volpin, Yu. Koreshkov and D. Kursanov, *Izvest. Akad. Nauk SSSR*, 560 (1959).

[6] R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960).

resonance stabilization[7] and derivatives of the cyclopropenyl anion are quite unstable.[8] These observations confirm the predictions of simple molecular orbital theory, and demonstrate the special stability of the cyclopropenyl cation which is implied in Hückel's famous rule. However, it is still of interest to investigate the nature and extent of the interaction of substituents with the cyclopropenyl ring, and accordingly we have synthesized some alkyl substituted cyclopropenyl cations.

II. Synthesis of the Cations.—As part of their continued study of the reaction of ethyl diazoacetate with acetylenes, D'yakonov, *et al.*, have reported[9] the synthesis of Δ^1-1,2-dipropylcyclopropenecarboxylic acid (I). Their proof of structure is sufficient, and we have confirmed it.[10] This material was an ideal precursor, since Dewar[12] and later Farnum[13] had shown that stable carbonium ions can be prepared conveniently by decarbonylation of carboxylic acids.

Treatment of I with acetyl perchlorate afforded dipropylcyclopropenyl perchlorate (IIa). The structure follows from the usual analytical data and from the following special evidence. The compound is insoluble in non-polar solvents but dissolves in polar media, including aqueous acid. The aqueous solution gives a precipitate of potassium perchlorate in the standard test, and, as is discussed in detail below, the carbonium ion solution can be titrated with base. In the infrared, the salt shows absorption characteristic of perchlorate ion, and it also has the strong band at $7.1\ \mu$ which we find in other cyclopropenyl cations. In the n.m.r. there is found a pattern which can be ascribed to two equivalent propyl groups bearing a strongly electronegative substituent. Thus the difference in chemical shift between the α- and β-methylene groups is 1.27 p.p.m., while that for propyl bromide[14] is 1.45 p.p.m. and for propyl iodide,[14] 1.28 p.p.m. The difference for propylbenzene[14] is only 0.93 p.p.m. In addition to these bands, there is a singlet for the hydrogen on the cyclopropenyl ring which is found at -3.04 p.p.m. relative to an internal benzene standard; this very low position is expected for hydrogen on positive carbon. The n.m.r. spectra of this and the other cations prepared are discussed in more detail below.

The perchlorate salt shows only end absorption in the ultraviolet, even down to 185 mμ, and the solvent is strong acid in which the free carbonium ion is present. Although this observation is at first sight surprising, it is consistent with the predictions of molecular orbital theory. By the simple theory, the two π-electrons are in an orbital of energy $+2.0\beta$, and the next empty orbital has energy $-1.0\ \beta$. The predicted 3β of energy required to excite the system for a π–π^* transition is thus much larger than the 2β predicted for ethylene, for instance. Although the simple Hückel calculations are on particularly weak ground when an excited state is involved, excellent correlations have been found between observed spectra and those calculated by the simple treatment.[15] Accordingly, the very low wave length at which π–π^* transition occurs in our cation is to be expected. Similar considerations explain the low wave length at which dipropylcyclopropenone absorbs,[6] by contrast with open-chain unsaturated ketones.

The perchlorate salt could be transformed into a fluoroborate (IIb), which could also be synthesized directly from the cyclopropenecarboxylic acid. This material was used to prepare tripropylcyclopropene (III), either by direct reaction with propyl lithium or by conversion of the cation to dipropylcyclopropenyl methyl ether (IV) and reaction of this compound with propylmagnesium bromide. The tripropylcyclopropene was sensitive to oxygen, so the impure material was converted directly to tripropylcyclopropenyl perchlorate (V) with triphenylmethyl perchlorate.[16] This compound again had the band at $7.0\ \mu$ in the infrared expected for a cyclopropenyl cation, as well as the $9.1\ \mu$ band of perchlorate ion. The n.m.r. spectrum showed (three) equivalent propyl groups with the expected chemical shifts. In the ultraviolet the cation again showed only end absorption. The synthetic sequence is pictured in Fig. 1.

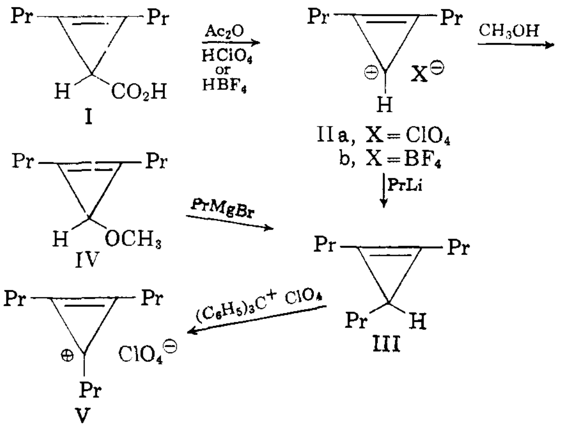

Fig. 1.

From the previously described dimeric ether of diphenylcyclopropenyl cation (VI) we also prepared propyldiphenylcyclopropenyl cation (VII) as its perchlorate and its fluoroborate salts. The route was similar to that above, involving reaction of the ether with propylmagnesium bromide and hydride abstraction from the impure propyldiphenylcyclopropene with triphenylmethyl cation. The structures of these salts are again supported

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(7) R. Breslow, W. Bahary and W. Reinmuth, *J. Am. Chem. Soc.*, **83**, 1763 (1961).

(8) R. Breslow and M. Battiste, *Chemistry & Industry*, 1143 (1958); R. Breslow, Abstracts 17th National Organic Symposium, 1961, p. 28.

(9) I. A. D'yakonov, *et al.*, *Zhur. Obshchei Khim.*, **29**, 3848 (1959).

(10) A "double-bond isomer" which is formed by the action of copper sulfate on the cyclopropene ester is also reported by them, but as we have reported elsewhere[11] this type of isomer is actually an alkoxyfuran.

(11) R. Breslow and D. Chipman, *Chemistry & Industry*, 1105 (1960).

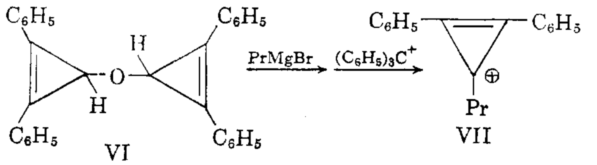
(12) M. Dewar and C. Ganellin, *J. Am. Chem. Soc.*, **81**, 2438 (1959).

(13) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(14) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1094 (1961).

(15) *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 202 ff.

(16) H. Dauben, L. Honnen and K. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).



by chemical and physical properties, including the infrared, ultraviolet and n.m.r. spectra.

III. Stabilities of the Cations.—The criterion of stability adopted was the pK_{R^+}, the pH for 50% ionization of carbinol to cation. As has been discussed previously,[3] this approach compensates as much as possible for the extreme strain in these cations by comparing their energies with the energies of the related covalent cyclopropenes. However, even in this measurement a number of factors besides π-electron stabilization will affect the position of equilibrium, so that the actual pK_{R^+} of any given cyclopropenyl ion is less easily interpreted than are the relative pK's among a series of such ions.

The method of determination of pK_{R^+} was different from that reported previously,[3,4] since the dipropyl and tripropyl cations could not be assayed by ultraviolet spectroscopy. Accordingly, a potentiometric titration was performed in aqueous acetonitrile, and this method was checked against the previous results for several already known compounds. The observed pK's are listed in Table I. It was observed that both the dipropyl (II) and tripropylcyclopropenyl cations (V) could be titrated reversibly in this medium, although the tripropyl cation showed some irreversibility much above its pK. In both cases the solutions remained clear during the titrations. Propyldiphenylcyclopropenyl cation (VII) was titrated by the spectroscopic procedure employed previously,[4] in order that it be directly comparable with diphenylcyclopropenyl cation.

TABLE I

pK_{R^+}'s OF SOME CYCLOPROPENYL CATIONS

Compound	Medium[a]	Method[b]	pK_{R^+}
Dipropylcyclopropenyl perchlorate (IIa)	A	a	2.7
Tripropylcyclopropenyl perchlorate (V)	A	a	7.2
Trianisylcyclopropenyl bromide[3]	A	a	6.5
	B	b	6.4
Dianisylphenylcyclopropenyl bromide[3]	A	a	5.2
	B	b	5.2
Triphenylcyclopropenyl bromide[3]	A	a	3.1
	B	b	2.8
Diphenylcyclopropenyl bromide[4]	B	b	−0.67
	C	b	0.32
Propyldiphenylcyclopropenyl fluoroborate (VII)	B	b	3.8

[a] A, 50% aqueous acetonitrile; B, 23% aqueous ethanol; C, water. [b] a, potentiometric titration; b, spectrophotometric titration.

Examination of the data in Table I reveals a striking fact. It is quite apparent that propyl groups stabilize the cyclopropenyl cation more effectively than do phenyl groups. This is shown by the higher pK of the tripropyl than of the triphenyl cation, the higher pK of the dipropyl cation compared with the diphenyl ion, and the fact that the pK of propyldiphenylcyclopropenyl cation (VII) is higher than that of triphenylcyclopropenyl cation.

The effects on the pK's can be ascribed to two different factors. First of all, the cations themselves are more effectively stabilized by propyl groups; secondly the covalent carbinols are more effectively stabilized by phenyl groups. Since the pK will depend on the difference in energy of cation and related carbinol, both factors must be considered. It is not surprising that the resonance energy of the stilbene system in the covalent compounds could be considerably more significant than the stabilization of a double bond by alkyl groups, and the operation of both factors is clearly discernible. Comparison of triphenylcyclopropenyl cation with the propyldiphenyl cation cancels the second factor, since in both cases the covalent carbinol has a stilbene system. Nevertheless, the pK of the propyl compound is one unit higher, and this must reflect carbonium ion stabilization. On the other hand, comparison of the symmetrically trisubstituted compounds, or the disubstituted ones, shows that here each propyl group adds more than 1 unit compared to phenyl. This difference probably reflects phenyl stabilization of the carbinols as well.

Molecular orbital calculations suggest that the effect of phenyl groups on the stability of cyclopropenyl cation should not be simply additive,[3,4] in particular because the change from the diphenyl to the triphenyl cation adds additional phenyl conjugation to the cation but not to the carbinol, whereas the first two phenyl substituents will stabilize both the cation and the covalent derivative. A similar argument could be made for nonadditivity of the effects of propyl groups. However, the data in Table I show that replacement of the remaining hydrogen atom by propyl, in two disubstituted cyclopropenyl cations, raises the pK of the cation by approximately 4.5 units. If we ignore the possibility that propyl group effects are not additive and extrapolate to unsubstituted cyclopropenyl cation, a pK_{R^+} of -6.3 is predicted. Whether or not this extrapolation is quantitatively correct, it seems likely from our data that unsubstituted cyclopropenyl cation will have a rather low pK. This may explain some of the difficulty experienced in attempts to prepare salts of this system.[17] In view of the considerable resonance energy predicted for this cation by m.o. calculations, one might well wonder whether a low pK is in accord with these predictions. However, as has been discussed in detail previously,[3] the observed pK of a cyclopropenyl cation will be influenced by many factors besides π-electron stabilization. Major destabilization will be contributed by ring strain effects ("I strain"), and some instability compared to more diffuse cations will also result from coulombic repulsion. These effects are most easily cancelled by comparing the cyclopropenyl cation with a cyclopropenyl radical or anion, as has been done,[7,8] and this comparison fully supports

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[17] J. R. Albin, Ph.D. Thesis, University of Washington, 1959.

the m.o. predictions. It is thus important to realize that the type of aromaticity predicted by Hückel's rule, or the calculations which lead to it, simply involves a particularly effective *contribution* by π-electron delocalization to the total molecular stability, and "aromatic" compounds are known, *e.g.*, benzyne, which are very unstable for other reasons (in this case, strain). The $pK_R{}^+$ of unsubstituted cyclopropenyl cation is of considerable interest, but its value can constitute a test of the m.o. predictions only if all the factors which contribute to it can be quantitatively evaluated.

IV. N.m.r. Spectra.—The ring proton of dipropylcyclopropenyl cation appears at very low field, -3.0 p.p.m. from an internal benzene standard. In our trifluoroacetic acid medium, by contrast, the protons of tropylium bromide are at -1.83 p.p.m. (they are reported[18] to be at -1.87 p.p.m. in acetonitrile, and at -1.93 p.p.m. in dimethyl sulfoxide solution). This considerable shift of the cyclopropene from benzene can be ascribed to three factors: the ring current is different for the two systems, the considerable amount of positive charge on the cyclopropenyl carbon atom should result in a large downfield shift, and the strain and consequent altered hybridization in the cyclopropenyl cation should also result in a downfield shift. These effects can be estimated from previous work.

Using Pople's free electron model,[19] and taking C–C as 1.40 Å. and C–H as 1.09 Å., the ring current effect in cyclopropenyl cation is calculated to be only 25% of that in benzene; this results both from the different geometry and, most importantly, from the presence of only two π-electrons in the small ring, so the predicted ratio is changed only slightly if, for instance, C–C is taken as 1.30 Å.[20] However, this model is known to overestimate the ring current effect, most seriously because it ignores the fact that the π-electron current is not on the plane of the ring, but is in two "doughnuts" above and below the ring. This has been taken into account in an improved model[21] and, although we have not performed the more complex calculations required to extend this case to the cyclopropenium ion, it seems likely from geometric considerations that with the improved calculation the ring current effect in our ring would be even less than 25% of the benzene value. Since the ring current effect in benzene has been estimated to be 1.50 p.p.m.,[21] we would expect our proton to be higher than the benzene protons by 1.0–1.3 p.p.m. because of the diminished ring current in our system. The rehybridization effects, involving increased *s*-character in the C–H bond of the small ring, can be estimated from Wiberg's studies on the n.m.r. spectra of cyclopropene and higher cyclic olefins.[22] The cyclopropene olefinic proton is 1.4 p.p.m. lower than are the protons of cyclopentene or cyclohexene, and since the effect of bond angle distortion in the small ring should carry over in about the same degree to the cation, a similar downfield shift of 1.4 p.p.m. can be assigned to this factor. Thus the rehybridization and ring current effects should just about cancel each other, and almost all of the net shift of the cyclopropenyl hydrogen from benzene protons can be ascribed to the effect of the positive charge. Based on a very limited number of compounds, it has been suggested[18,23] that this electrostatic chemical shift in aromatic ions will be proportional to the charge at the aromatic carbon, with a proportionality constant of $+10$ p.p.m./electron. Our unsymmetrical dipropyl cation II probably has less than one-third of the positive charge at the unsubstituted carbon, so less than 3.3 p.p.m. downfield shift is expected, but not much less. The chemical shift of the propyl groups (*vide infra*), and theoretical consideration of the stabilization they contribute compared to the total calculated resonance energy of the system, suggest that a symmetric distribution of charge will be only slightly perturbed in the dipropyl compound, so a shift of at least 3 p.p.m. is expected. Adding up all these factors, it is predicted that the proton of dipropylcyclopropenyl cation should be found at 3.1–3.7 p.p.m. downfield from benzene. This agrees well with the observed shift, 3.0 p.p.m. In view of the approximate nature of the treatment the agreement could be fortuitous, but it seems likely that no major contributing factor has been ignored.

The n.m.r. spectra of the propyl groups themselves are also revealing. First of all, the propyl groups in all three cations, dipropylcyclopropenyl, tripropylcyclopropenyl and propyldiphenylcyclopropenyl cation, are relatively shifted to the same extent. The differences between α-methylene and β-methylene are 1.27 p.p.m. for II, 1.3 p.p.m. for V, and 1.27 p.p.m. for VII. It has been shown[14] that this difference in methylene chemical shifts can be correlated roughly with the electronegativity of the substituent, and it should be noted that the difference in chemical shift between β-methylene and α-methyl protons in our three cations is also relatively constant at 0.95 p.p.m. By contrast, the α-methylene to β-methylene shift in the n.m.r. spectrum of dipropylcyclopropenecarboxylic methyl or ethyl esters in carbon tetrachloride medium is only 0.8 p.p.m., and the β-methylene to α-methyl shift is 0.6 p.p.m.[24] The considerably larger shifts in the propyl substituted cations may be due in part to a ring current effect, but it must also reflect to a large extent the fractional positive charge on the ring carbon which bears the propyl group. This supports the idea that the dipropyl- and tripropylcyclopropenyl cations have similar charge structures, with essentially one-third of the charge at each ring carbon, but it is interesting that the diphenylpropyl cation is also similar. This compound has an opportunity for considerable spreading of the charge throughout the phenyl rings, but the shift

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[18] G. Fraenkel, R. Carter, A. McLachlan and J. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[19] J. A. Pople, *Mol. Phys.*, **1**, 175 (1958).

[20] P. Kasai, R. Myers, D. Eggers and K. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

[21] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[22] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[23] H. Speisecke and W. G. Schneider, *Tetrahedron Letters*, **14**, 468 (1961).

[24] P. Wolf, unpublished work.

in the propyl group suggests that a full one-third of the positive charge is still found next to it. Actually the α-methylene group of this cation is found at even lower field than is that for the dipropyl or tripropyl cations.

The idea that not much of the charge is removed by the phenyl group is supported by the n.m.r. results on the phenyls themselves. A two-proton (per phenyl) multiplet at -1.00 p.p.m. from benzene is assigned to the *ortho* hydrogens, while a three-proton multiplet for *meta* and *para* hydrogens is centered at -0.66 p.p.m. This is similar to the spectrum of triphenylcyclopropenyl cation, whose *ortho* protons are at -1.40 p.p.m., while the *meta* and *para* multiplet is at -0.72 p.p.m. On the other hand, the *ortho* protons of diphenylcyclopropenecarboxylic ethyl ester are only 0.27 p.p.m. below the *meta* and *para* multiplet.[25] The assignment is made both from the relative areas and from the appearance of the multiplets, which resemble those of nitrobenzene and other phenyls with electron-withdrawing substituents in which this assignment has been established.[26] By contrast, the n.m.r. spectrum of triphenylmethyl cation[27,28] shows that the *para* protons in that system are at lowest field, 20 c.p.s. below the *meta* protons, as is expected if there is a large contribution[28] of quinoid forms in which the charge is delocalized into the phenyl groups. Such an effect is not observed in our compounds.

Unfortunately, it is not correct to discuss the positions of the aromatic protons only in terms of charge distribution, particularly in regard to the *ortho* protons. The considerably greater downfield shift for the *ortho* protons of triphenylcyclopropenyl cation than for propyldiphenylcyclopropenyl cation is unlikely to reflect a drastic difference in charge distribution between them. Models show that triphenylcyclopropenyl cation can be planar, but that the *ortho* protons of adjacent rings are then in contact, and there will thus be deshielding of *ortho* protons by the adjacent phenyl groups. By contrast, triphenylmethyl cation is non-planar, and models show that here the *ortho* protons may well be in the diamagnetic portion of the field from the adjacent phenyl groups. Thus the conclusion[28] that the *ortho* positions of triphenylmethyl cation carry less positive charge than do the *meta* positions need not follow from the observation that the *ortho* protons are found at highest field.

V. The Interaction between Substituents and the Cyclopropenyl Cation.—It is striking that propyl groups stabilize our cations more than phenyls do. Benzyl cation, a phenyl substituted carbonium ion, is certainly much more stable than is butyl cation, which is the analogous propyl derivative. This reversal of substituent effects can be understood if the aromatic cyclopropenyl carbon will not readily accept more electrons into its π-system, as is required for assistance by phenyls, but can receive the normal amount of assistance from inductive effects in which electron shifts occur within the σ-bonds. Thus a distinction must be drawn here between the inductive effect of an alkyl group and its hyperconjugative effect[29]; the latter would be analogous to ordinary conjugation, in that electrons would be released into the π-system. If normal conjugation by phenyls is diminished in this system because the cyclopropenyl cation, with an aromatic doublet of electrons, does not readily accept more π-electrons, hyperconjugation should also be diminished. The fact that the propyl groups are still strikingly effective suggests that they operate here primarily by a non-conjugative interaction, which is of course what is implied in the term "inductive effect."[29] Our observed difference in pK between the dipropyl and tripropylcyclopropenyl cation corresponds to a stabilization energy by the third propyl group of 5.8 kcal. As Conrow has pointed out,[30] the apparent degree of stabilization of carbonium ions by alkyl groups varies with the demands of the carbonium ion, but our value is reasonably close to that expected by interpolation on a scale[30] in which methyl adds 3.7 kcal. to the stability of tropylium ion, and at least 5.3 kcal. to the stability of allyl cation.

Accordingly, from the observed effect of phenyl on the stability of the cyclopropenyl cation and from the n.m.r. data, we conclude that phenyls contribute stabilization by conjugation, since their inductive effect is actually destabilizing, but that the extent of this conjugation is not large and not much of the charge is removed from the three-membered ring. Propyl groups contribute stabilization chiefly by a simple inductive effect, involving the single bonds, and hyperconjugation is probably unimportant. However, in carbonium ions with considerably more demand for π-electrons than is present in the cyclopropenyl cation it is of course perfectly possible that hyperconjugation could play a role as well.

Experimental[31]

2,3-Dipropylcyclopropenecarboxylic acid was prepared by a procedure similar to that previously described.[9] A mixture of 60 g. of dry octyne-4 and 0.5 g. of catalytic copper dust was stirred under a nitrogen atmosphere of 155° (oil-bath temp.) while 63 g. of ethyl diazoacetate was added dropwise (one drop/15 sec.). When the addition was complete the stirring was continued for 2 more hours, then the mixture was cooled and 70 g. of KOH in 200 ml. of 1-propanol was added. The mixture was refluxed for 4 hours, then cooled and worked up in the usual fashion. Distillation of the acidic fraction afforded 48 g. (52%) of product, b.p. 101° (0.7 mm.) (rept.[9] b.p. 92–92.5° (0.5 mm.)).

Dipropylcyclopropenyl perchlorate was prepared by decarbonylation of this acid. After treating 2.0 g. of the acid at room temperature for 5 min. with 48 g. of a solution of perchloric acid in acetic anhydride (10 g. of 70% $HClO_4$ in 280 g. of acetic anhydride) 900 ml. of cold anhydrous ether was added with shaking and the precipitated product

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was collected and washed with dry ether. Recrystallization by solution in 150 ml. of cold dry ethyl acetate and addition of 800 ml. of cold dry ether gave the pure product, which was dried in vacuum: 1.7 g. (65%), m.p. 80° dec.

Anal. Calcd. for $C_9H_{15}ClO_4$: C, 48.54; H, 6.79. Found: C, 48.62; H, 6.60.

The compound is insoluble in hexane, benzene or ether, but dissolves in ethyl acetate, acetone, acetonitrile and like solvents, and in aqueous acid. It gives a positive perchlorate ion test with potassium nitrate, and the infrared spectrum reveals a strong band at 9.1 μ characteristic of perchlorate ion. In the infrared there is also a band at 7.1 μ which we have found to be characteristic of cyclopropenyl cations. In concentrated sulfuric acid solution the compound shows only strong end absorption, the maximum occurring below 185 mμ (ϵ_{185} 4,200).

The n.m.r. spectrum in trifluoroacetic acid with an internal benzene standard (5%) showed a sharp singlet at -3.04 p.p.m. for the single proton on the ring (we find tropylium ion at -1.83 p.p.m. in the same medium), and the characteristic pattern of two equivalent propyl groups bearing a strongly electronegative substituent, with a four-proton triplet centered at $+4.11$ p.p.m., a four-proton sextuplet at $+5.38$ p.p.m. and a six-proton triplet at $+6.25$ p.p.m.; these multiplets show the expected dissymmetry from second-order effects.

Dipropylcyclopropenyl fluoroborate could be synthesized either from the above perchlorate salt or directly from the acid. In the latter case, 4.0 g. of dipropylcyclopropenecarboxylic acid was treated with 25 ml. of 10% fluoroboric acid in acetic anhydride (40 g. of 48% HBF_4 in 180 g. of acetic anhydride) for 15 min. at room temperature. Then 900 ml. of cold dry ether was added and the product was isolated as described for the perchlorate: 3.0 g. (60%), m.p. 70°. The same product could be obtained by treatment of the perchlorate salt with fluoroboric acid in acetic anhydride, then ether. Even after repeated crystallizations from acetonitrile–ether the compound could not be obtained completely pure, and for further synthetic work the crude material was ordinarily used directly.

Anal. Calcd. for $C_9H_{15}BF_4$: C, 51.46; H, 7.20. Found: C, 50.78; H, 7.27.

1,2,3-Tripropylcyclopropene could be prepared directly from the above cation. An ether suspension of 11.3 g. of the crude dipropylcyclopropenyl fluoroborate in 50 ml. of dry ether was cooled to $-80°$ under a nitrogen atmosphere, and an equivalent of freshly prepared propyllithium in 27 ml. of ether was added dropwise over 7 min. After 2 hr. further stirring, the reaction was worked up and distilled, yielding 4.0 g. of the product, b.p. 82–83° (27 mm.). The compound reacts slowly with oxygen. In the infrared the compound showed characteristic cyclopropene absorption at 1830 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 85.52; H, 13.19.

The same compound can be prepared by the following two-step sequence.

1,2-Dipropyl-3-methoxycyclopropene was synthesized by dissolving 22 g. of crude dipropylcyclopropenyl fluoroborate in 70 ml. of ice-cold methanol. After neutralization with sodium bicarbonate and ether extraction the product was isolated by distillation: 7.0 g. (43%), b.p. 94° (53 mm.). In the infrared the compound showed the characteristic cyclopropene band at 1825 cm.$^{-1}$ as well as the expected ether band at 1080 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.89; H, 11.74. Found: C, 77.84; H, 11.64.

1,2,3-Tripropylcyclopropene can be prepared from this ether. To a solution of the Grignard reagent prepared from 0.5 g. of magnesium and 2.5 g. of propyl bromide in 30 ml. of ether was added 2.0 g. of dipropylcyclopropenyl methyl ether in 20 ml. of ether. After the normal aqueous workup, the product was isolated by distillation: 0.8 g. (43%), identical with the previously described material.

Tripropylcyclopropenyl perchlorate was prepared by hydride abstraction from the tripropylcyclopropene. In a typical run, 0.5 g. of the cyclopropene was added to one equivalent of triphenylmethyl perchlorate in 30 ml. of dry acetonitrile. After a few minutes the solvent was evaporated, the residue was taken up in a few ml. of ethyl acetate and the solution was then diluted with 10 volumes of cold dry ether. The product precipitated as white needles, and after recrystallization from ethyl acetate and ether there was obtained 0.45 g. (58%) of white needles, m.p. 184–185°.

Anal. Calcd. for $C_{12}H_{11}ClO_4$: C, 54.44; H, 7.99; O, 24.18. Found: C, 54.46; H, 7.98; O, 23.45.

With potassium acetate solution the compound affords a precipitate of potassium perchlorate. This cyclopropenyl salt is soluble in ethyl acetate, acetone, and chloroform, and insoluble in hexane, benzene and ether; it can be recrystallized undecomposed from water.

In the n.m.r. spectrum (50% aqueous H_2SO_4 solvent, external benzene capillary as reference) the compound showed only one type of propyl group, again strongly shifted with the three expected multiplets centered at $+3.0$, $+4.3$ and $+5.3$ p.p.m. No other protons were present. The compound showed only end absorption in the ultraviolet, and in the infrared spectrum ($CHCl_3$ solution) it had the expected bands at 7.1 (cyclopropenyl cation) and at 9.1 μ (ClO_4^-).

The reaction of the dipropylcyclopropenyl cation with water was studied by dissolving 10 g. of purified dipropylcyclopropenyl fluoroborate in 100 ml. of 0.1 *N* HCl and adjusting to *p*H 7 by dropwise addition of 1 *N* NaOH solution. After stirring for 30 min. the organic layer was directly separated and dried with a small amount of Na_2SO_4. The liquid product, 4.8 g., had no absorption in the hydroxyl region of the infrared, but had strong absorption at 1840 (covalent cyclopropene) and at 1160 and 1070 cm.$^{-1}$ (ether). It also had weak absorption at 1680 (carbonyl) as well as the bands for a propyl group in the 2900 and 1450 cm.$^{-1}$ regions. Apparently the product was thus chiefly a dimeric ether. When 1.0 g. of this liquid was treated with a small amount of HBF_4 in acetic anhydride, followed by ether precipitation, 470 mg. of dipropylcyclopropenyl fluoroborate was formed, identical with authentic material.

1,2-Diphenyl-3-propylcyclopropenyl perchlorate was prepared by a two-step sequence. To an ethereal solution of propylmagnesium bromide, prepared from 1.48 g. of propyl bromide with 0.264 g. of magnesium in 100 ml. of ether, was added 1.76 g. of bis-Δ^1-1,2-diphenylcyclopropenyl ether[4] in 50 ml. of benzene. After 4 hours at room temperature the solution was neutralized with aqueous ammonium chloride and extracted with ether. Drying and solvent removal yielded a yellow oily liquid, impure propyldiphenylcyclopropene, which was not purified further. A solution of 1.5 g. of triphenylmethyl perchlorate in 100 ml. of dry acetonitrile was added with swirling, and after a few minutes of standing, dilution with 500 ml. of ether gave 1.03 g. (70%) of 1,2-diphenyl-3-propylcyclopropenyl perchlorate, m.p. 194–196° dec. Recrystallization from acetonitrile–ether afforded 0.9 g., m.p. 196–197° dec. In the infrared the compound had strong absorption at 7.0 (cyclopropenyl cation) and at 9.1 μ (ClO_4^-).

Anal. Calcd. for $C_{18}H_{17}ClO_4$: C, 64.96; H, 5.15. Found: C, 65.39; H, 4.92.

1,2-Diphenyl-3-propylcyclopropenyl fluoroborate was prepared similarly, using triphenylmethyl fluoroborate, in similar yield. After recrystallization from acetonitrile–ether it had m.p. 179° dec. and in the infrared showed the expected bands at 7.0 and at 9.5 μ (BF_4^-).

Anal. Calcd. for $C_{18}H_{17}BF_4$: C, 67.52; H, 5.35. Found: C, 67.18; H, 5.54.

The ultraviolet spectrum in 23% aqueous ethanol, 1 *N* in HCl, has maxima at 292 (32,000) and 305 mμ (33,000). The n.m.r. spectrum in trifluoroacetic acid with an internal benzene reference (5%) had the pattern of a strongly shifted propyl group, with a two-proton triplet at $+3.75$ p.p.m., a two-proton sextuplet at $+5.02$ p.p.m., and a three-proton triplet at $+6.00$ p.p.m. The phenyl hydrogens were separated into two multiplets, with four protons centered at -1.00 p.p.m. and six protons at -0.66 p.p.m. The pattern is identical with that for triphenylcyclopropenyl bromide[3] in the same solvent, except that in the latter the *ortho* hydrogens are centered at -1.40 p.p.m. and the *meta* and *para* hydrogens are centered at -0.72 p.p.m. These multiplets in both cases have considerable structure extending over a width of 0.16 p.p.m. Both spectra resemble the pattern for nitrobenzene in the same solvent, except that in this latter case the three-proton multiplet is centered at -0.25 p.p.m. and the *ortho* hydrogens are found at -0.75 p.p.m.

pK_{R^+} Determinations.—The dipropyl and tripropyl cations were titrated against a glass electrode, since neither they nor their neutralization products had ultraviolet spectra which could be used for the *pK* determinations. A standard method was devised, and checked against cations whose *pK* previously had been determined spectrophotometrically. To calibrate the method, 66.3 mg. of trianisylcyclopropenyl bromide[3] was added to a mixture of 20 ml. of acetonitrile and 10 ml. of 0.10 *N* HCl. The *p*H was observed on a Beckman model G *p*H meter after the stepwise addition of standardized 0.10 *N* NaOH solution. The forward titration gave an apparent *pK* of 6.54 from the usual plot, and 6.41 by back titration (reptd.[3] *pK* 6.4 in 23% aqueous ethanol by spectrophotometric titration). Similar titration of dianisylphenylcyclopropenyl bromide[3] in this 50% aqueous acetonitrile solution gave an apparent *pK* of 5.16 (rept.[3] 5.2 in 23% aqueous ethanol) and titration of triphenylcyclopropenyl bromide[3] gave *pK* 3.1 (rept.[3] 2.8).

To 20 ml. of acetonitrile containing 10.5 mg. of tripropylcyclopropenyl perchlorate was added 20 ml. of a premixed solution of 10 ml. each of 0.10 *N* NaOH and 0.10 *N* HCl (to reproduce the medium but avoid prolonged exposure of the compound to neutral aqueous solutions). Then eight portions of 0.1 *N* NaOH were added such that the total was equivalent to the cyclopropenyl cation, and the *p*H's were observed after each addition. A classical titration curve was obtained whose midpoint was taken as the *pK*. The solution remained clear during the titration, and the curve was reversible up to the *pK*, although above that point some irreversibility was observed. The *pK* observed is 7.2.

To 7.1 mg. of dipropylcyclopropenyl perchlorate in 20 ml. of acetonitrile was added a mixture of 10 ml. of 0.10 *N* HCl and 9.7 ml. of 0.10 *N* NaOH. Then the NaOH solution was added in increments of 0.1 ml. The initial and final *p*H values over this range were 2.65 and 2.92, while a standard titration in which the cation was omitted went from 2.88 to 7.0. The solution remained clear during the titration. Since at these low concentrations and *p*H's hydrolysis of the cation is appreciable, the titration curve was constructed by plotting base *consumed* by the cation against *p*H, rather than simply base *added*. When the data were plotted in this way, which required correcting the observed titration curve by use of the points of the above standard titration, a titration curve was obtained whose inflection point was taken as the *pK*. In several runs this ranged from 2.65 to 2.70.

The pK_{R^+} of propyldiphenylcyclopropenyl fluoroborate was determined in "23%" aqueous ethanol as described previously for other cations,[3] using a spectrophotometric procedure. A solution of 1.2 mg. of the cation in 5.27 ml. of 95% ethanol was diluted to 10 ml. with 0.2 *N* aqueous HCl, and 1.0 ml. of this solution was diluted to 10 ml. with 20% ethanolic acid or buffers. The ultraviolet spectra were immediately examined in 10-cm. cells, and were constant over the few minutes required for measurement. The absorbancy at 305 mμ, which is characteristic of the cation, was plotted against *p*H, determined with a Beckman model G *p*H meter calibrated against standard buffers, and the resulting titration curve had its inflection point at 3.80.

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEX.]

Studies of Ionic Elimination Reactions in the *sec*-Butyl System

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A variety of reactions which presumably proceed *via* the *sec*-butyl cation have been studied with respect to the nature of the butenes produced on elimination. In the cases of the isomerization of 1-butene over either dilute sulfuric acid or phosphoric acid and the reaction of *sec*-butyl bromide with silver nitrate in *t*-butyl alcohol the ratio of *trans*- to *cis*-2-butene was *ca.* 1. Under typical E_2 conditions *sec*-butyl bromide gives a *trans*- to *cis*-2-butene ratio of *ca.* 2.8. In none of the cases studied did the *trans* to *cis* ratio go below 1. The mechanistic implications of these results are considered.

Introduction

Cram[2] has characterized the stereochemistry of the E_1 reaction as being "vastly complicated by the multistage nature of the mechanism and by the difficulties of identifying the geometry and capabilities of the intermediates involved." The implications of this statement are nowhere more evident than in the various studies reported in recent years which purport to explain the distribution and the geometries of products obtained from the *sec*-butyl cation.

Brown and co-workers[3] have studied the acetolysis of 2-butyl tosylate at 118° and have reported a *trans* to *cis* ratio of 2-butenes as being *ca.* 1.1. Lucchesi, *et al.*,[4] have reported the stereospecific isomerization of 1-butene over a silica–alumina catalyst to give ratios of *cis-/trans*-2-butene as high as 6.5 and have proposed a hydrogen-bridged butyl cation to explain their results. Rather similar observations have been made by Pines and Haag[5] for the isomerization of 1-butene over various alumina catalysts and by phosphoric acid where values of *cis-/trans*-2-butene of 1.5 to 4.4 were reported. The dehydration of 2-butanol over the same catalysts has been observed also to lead to higher values for *cis*- than *trans*-2-butene (*cis/trans* = 3.0 at 350°).[6]

The results of Pines[5,6] and of Lucchesi[4] and their respective co-workers are considerably different from the results reported by Brown.[3] Streitwieser and Schaeffer[7] have commented on the elimination of a proton from a *sec*-butyl cation and have concluded that one should expect approximately equivalent amounts of the geometrical 2-butene isomers. In order to clear the anomaly existing in the literature, we have now investigated several systems where *sec*-butyl cations might be reasonably expected. In order to clarify further the role of steric effects in these systems some examples of the E_2 type elimination in the *sec*-butyl system were also studied.

Experimental

Gas analyses were carried out by vapor phase chromatography using a 3.7-m. column of dimethyl sulfolane and ethylene glycol saturated with silver nitrate on Chromosorb P (Johns–Manville) and then a 3.7-m. column of hexadec-

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