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RELATIVE STABILITIES OF TRIALKYLCYCLOPROPENYL CATIONS[1]

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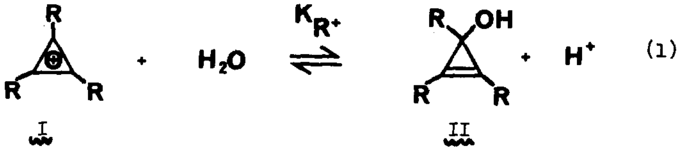
The effect of substituents on the stability of cyclopropenyl cations[3] has previously been investigated by measurement of the pK_{R+} values for the carbonium ion-carbinol equilibrium (eq. 1).[4] By this method Breslow has clearly demonstrated that the relative ability of



substituents to stabilize a cyclopropenyl cation is given by the order alkyl > phenyl > hydrogen.[5] However, little is known regarding the relative effect of methyl, primary, secondary, and tertiary alkyl groups on the pK_{R+}. Earlier we reported the synthesis of the tri-t-butylcyclopropenyl cation (Id) from di-t-butylcyclopropenone and t-butyllithium.[6] Our recent synthesis of tri-i-propylcyclopropenyl cation (Ic) from di-i-propylcyclopropenone[7] and i-propylmagnesium bromide completes this series and now permits us to comment on the relative influence of methyl, n-propyl, i-propyl, and t-butyl substitution on the pK's of cyclopropenyl cations.

Potentiometric titration[8] (glass-calomel electrodes) of trimethyl-,[9] tri-n-propyl-,[5] tri-i-propyl-, and tri-t-butylcyclopropenyl perchlorate[10] in aqueous acetonitrile solutions with 0.100N NaOH gave classical sigmoid titration curves.[11] The pK_{R+} values are presented in Table I and represent the apparent pH at half neutralization.

Table I.

Apparent pK_{R+} Values for Trialkylcyclopropenyl Perchlorates in Aqueous Acetonitrile.

Cation	$pK_{R+} \pm 0.1$[a]		
	25% H_2O	50% H_2O	75% H_2O
Ia, R = CH_3	6.9	7.4	7.8
Ib, R = $CH_3CH_2CH_2$	6.6	7.0	7.5
Ic, R = $(CH_3)_2CH$	6.0	6.4	6.9
Id, R = $(CH_3)_3C$	6.0	6.5	6.8

[a] Values represent an average of at least duplicate determinations. Each determination for a given cation fell within ± 0.1 of the mean value.

On the basis of the above data it is concluded that the effect of alkyl substituents on the stability of cyclopropenyl cations is given by the order Me>n-Pr>i-Pr≈t-Bu. Further, the trimethylcyclopropenyl cation (Ia) represents the most stable hydrocarbon cation yet reported.[12] If we assume that an increase in the electron releasing inductive ability of an alkyl substituent would result in increased stability of cyclopropenyl cations, then it is clear that the "normal" inductive order of alkyl groups (i.e., t-Bu > i-Pr > n-Pr > Me) is not reflected in the pK's of our series of cations.[13] Therefore the stability differences in this series cannot be ascribed to inductive effects.

It has been proposed that hyperconjugation is unimportant in the cyclopropenyl series because normal conjugation by phenyl is diminished. Since conjugation and hyperconjugation are analogous, both involving electron release into the π-system, the importance of the latter effect should also be diminished.[5] However, it must be pointed out that our data is consistent with the operation of hyperconjugation (hyperconjugative order: Me>n-Pr>i-Pr>t-Bu). Steric hindrance of solvation would also explain the observed results since the solvation order (i.e., Me>n-Pr>i-Pr>t-Bu) parallels the above hyperconjugative order.[13,14] Unfortunately, the present data does not permit a distinction between these two effects.

It appears from examination of models that non-bonded steric interactions are more serious in the covalent carbinols than in their respective cations. However, steric destabilization of the more hindered carbinols **IIc** and **IId** cannot be an overriding factor since this would have been reflected in higher pK's for cations **Ic** and **Id**, respectively, contrary to our experimental results. The observation of identical pK's within experimental error for the tri-*i*-propyl- and tri-*t*-butylcyclopropenyl cations is probably due to the subtle interplay of two or more of the above effects.

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(2) National Institutes of Health Predoctoral Fellow, 1969-1970.

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(7) The reaction of α,α'-dibromodiisobutyl ketone with potassium *t*-butoxide in tetrahydrofuran at -70° afforded diisopropylcyclopropenone in $\sim$20% yield; bp 70-72° (0.3 mm).

(8) Since trialkylcyclopropenyl cations show only end absorption in the ultraviolet[5], the pK's cannot be determined by ultraviolet spectroscopy.

(9) Trimethylcyclopropenyl perchlorate (**Ia**), mp 153-155°, nmr (CD$_3$CN) 2.80 δ(s), was prepared according to the procedure of Closs. The pK$_{R+}$ of this cation has not been previously reported. G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968); G. L. Closs and V. N. M. Rao, *ibid.*, **88**, 4116 (1966).

(10) All four cations can be recovered unchanged from aqueous solution as their perchlorate salts.

(11) The procedure developed by Breslow for tri-*n*-propylcyclopropenyl perchlorate (**Ib**) was duplicated for all cations. The reported pK$_{R+}$ of **Ib** is 7.2 (see ref. 5 and 6b).

(12) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1966. p. 27.

(13) For a discussion of the inductive and hyperconjugative effects of alkyl substituents see (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962; (b) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962). See also F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5686 (1969), and references cited therein.

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