# Inversion of the Relative Ground and Transition State Energies for the Bicyclo[3.1.0]hexenyl Cation Circumambulation. The 5-Acylpentamethylcyclopentadiene Aluminum Trichloride Zwitterions[1,2]

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Abstract: Reaction of 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes with Al_2Cl_6 in CH_2Cl_2 is shown to take place cleanly to give zwitterions in which the Lewis acid is complexed with the ketone oxygen, RC_6=$^+OAl^-Cl_3$. A variety of these complexes have been formed in which R is either aliphatic or aromatic. These zwitterions exhibit a degenerate rearrangement in which the C_6 group migrates around the periphery of the cyclopentadienyl ring. The rate of this migration is dependent upon R, the C_6 substituent. A linear free energy relationship was found between the log of the rate constant for rearrangement and σ^+ for a series of complexes where R = phenyl or p-phenyl groups with a ρ of +4.6. It is suggested that a bicyclo[3.1.0]hexenyl zwitterion is either a high energy intermediate or the transition state in this migration. When R is electron withdrawing, the pmr spectrum indicates that there is leakage of the positive charge from C_6 onto the diene part of the complexes, although it is not known whether this is the result of a homopentadienylic or Möbius type interaction. These zwitterions are good models for the transition state (or high energy intermediate) of the degenerate rearrangement of the bicyclo[3.1.0]hexenyl cations, and the interrelationship of these systems is developed.

A noteworthy feature of the chemistry of the bicyclo[3.1.0]hexenyl cations is their degenerate rearrangement in which the cyclopropyl carbon moves around the periphery of the five-membered ring.[2,4] Each step in this circumambulation (reaction 1) may best be

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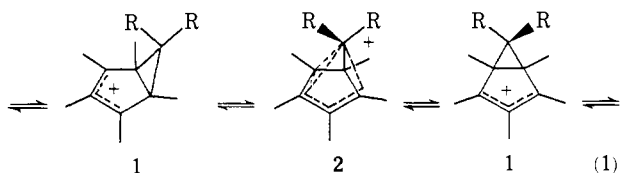
regarded as a 1,4-sigmatropic shift, it taking place with the stereochemistry requisite of such a process.[5] The ease of this migration was shown to be dependent upon the nature of the substituents on the cation and in particular to be very sensitive to substituent changes upon the migrating cyclopropyl carbon, C_6. As the rate of the rearrangement was found to be much greater when C_6 bore charge stabilizing groups, it was concluded that in the transition state of this migration C_6 becomes relatively more electron deficient.

The halfway point in this migration can be considered to be the cyclopentadiene-5-methyl cation 2, in which C_6 is equally bonded to C_1 and C_4 of the five-membered ring. While it is not yet clear whether 2 is a high energy intermediate or a transition state, it is apparent that the R groups have a much greater effect upon its stability than they do on the ground state 1.

The lowest energy barrier to migration yet measured for these cations is 10.1 kcal/mol in 1, R = Me. However, by making the C_6 substituents more electron donating it should be possible to further reduce this activation energy. Indeed, in principle, there is no reason why, with a suitable choice of R, the energies of 1 and 2 might not be very closely matched *or even inverted*. In this latter situation a degenerate migration of C_6 would still be anticipated, but 2 would then be the ground state and 1 either a transition state or high energy intermediate in the migration.

To test these ideas and further probe the mechanism of this degenerate rearrangement, we have attempted the preparation of cations with charge stabilizing substituents at C_6. In this paper the synthesis and study of systems containing an oxygen substituent are described.[6]

Results and Discussion

Three main routes have been used to prepare the bicyclo[3.1.0]hexenyl cations: the photoisomerization of the corresponding benzenonium ions,[2,4b,7] the ionization or protonation of a suitable bicyclo[3.1.0]hexene or related material,[2,4,8] and the ionization of a cyclopentadiene-5-methyl derivative.[4c,9] This latter method seemed to offer the best prospect of putting an oxygen function at C_6 of 1, e.g., reaction 2.

(2) Previous papers in this series are R. F. Childs, M. Sakai, B. D. Parrington, and S. Winstein, *J. Amer. Chem. Soc.*, 96, 6403 (1974); R. F. Childs and S. Winstein, *ibid.*, 96, 6409 (1974).
(3) Canadian International Development Agency scholarship holder.
(4) (a) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, 89, 5075 (1967); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, 91, 754 (1969); P. Vogel, M. Saunders, N. Hasty, Jr., and J. A. Berson, *ibid.*, 93, 1551 (1971); (b) I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova, and V. A. Koptyug, *Zh. Org. Khim.*, 6, 2482 (1970); (c) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969); (d) *Zh. Org. Khim.*, 6, 2258 (1970).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(6) A preliminary account of part of this work has appeared, M. Zeya and R. F. Childs, *J. Amer. Chem. Soc.*, 94, 289 (1971).

(7) B. Parrington and R. F. Childs, *Chem. Commun.*, 1581 (1970); I. S. Isaev, V. I. Mamatyuk, T. G. Egorova, L. I. Kuzubova, and V. A. Koptyug, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2089 (1969).

(8) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Zh. Org. Khim.*, 6, 1843 (1970).

(9) S. Winstein and M. Battiste, *J. Amer. Chem. Soc.*, 82, 5244 (1960); L. de Vries, *ibid.*, 82, 5242 (1960); cf. R. Criegee and H. Grüner, D. Schonleber, and R. Huber, *Chem. Ber.*, 103, 3696 (1970).

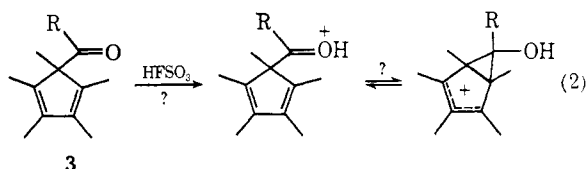$$\text{(2)}$$

3

Preparation of 5-Acylpentamethylcyclopentadienes, 3.

Whereas **3a** can be conveniently obtained from hexamethyl Dewar benzene,[10] ketones with different R groups are not available by this method. A general route to these ketones was found to be the reaction of lithium pentamethylcyclopentadienide[11,13] with the appropriate acyl halide, reaction 3. The ester **3c** was made in a similar manner.[11]

$$\text{(3)}$$
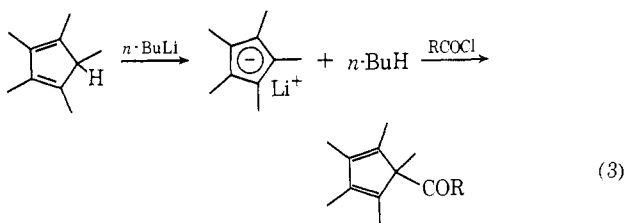
3a, R = Me; b, R = Et; c, R = OEt;
d, R = C$_6$H$_5$; e, R = p-MeOC$_6$H$_4$;
f, R = p-MeC$_6$H$_4$; g, R = p-Me$_3$CC$_6$H$_4$;
h, R = p-ClC$_6$H$_4$; i, R = p-CF$_3$C$_6$H$_4$

Reaction of 5-Acylpentamethylcyclopentadienes with Al$_2$Cl$_6$.

A simple entry to the objective 6-hydroxy cations would appear to be the oxygen protonation of **3**, reaction 2. However, solution of several derivatives of **3** in HFSO$_3$ led to protonation of both the oxygen and the diene to give a mixture of the isomeric dications **4**.[12] To eliminate the possibility of this electrophilic

4   **4**
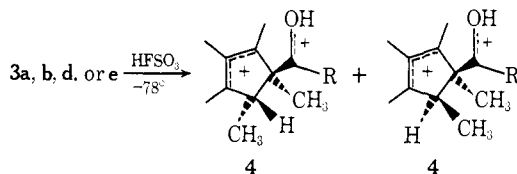
attack upon the diene, the reaction of **3** with Lewis acids was examined.[14]

A solution of **3** in anhydrous CH$_2$Cl$_2$ was added at −78° to a small excess of anhydrous Al$_2$Cl$_6$ dissolved in the same solvent. A rapid, quantitative reaction took place with the formation of a complex which was characterized spectroscopically. The complexes so obtained were stable at room temperature and could be treated with ice–water to regenerate the original ketones in high yield and purity. Provided the Lewis acid was in excess, variations in the relative ratios of **3** and Al$_2$Cl$_6$ did not have any detectable effect on the spectral

(10) H. N. Junker, W. Schäfer, and H. Neidenbruck, *Chem. Ber.*, **100**, 2508 (1967).

(11) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960). We find a more convenient route to pentamethylcyclopentadiene is the thermal fragmentation of **4** in FSO$_3$H.[12]

(12) M. Zeya, Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada.

(13) R. B. King and H. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

(14) For general reviews on the complexes of ketones with Lewis acids see I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1963; N. N. Greenwood and K. Wade in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, Chapter 7; D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, **69**, 251 (1969); *Quart. Rev., Chem. Soc.*, **25**, 171 (1971).

properties of these zwitterions.[15] To rigorously exclude trace quantities of water from these reactions, the complexes were also prepared using a high vacuum line. As the freezing point of CH$_2$Cl$_2$ limited the temperature to which the solutions of the zwitterions could be cooled, CHClF$_2$ and a mixture of CH$_2$Cl$_2$–SO$_2$ClF were used as alternative solvents in certain cases.

The ir spectrum of the complex derived from **3a** showed that the carbonyl absorption, originally at 1683 cm^{-1} in **3a**, was comparatively broad at *ca.* 1570 cm^{-1}. Similarly, the carbonyl absorption of the aromatic ketone **3e** shifted from 1655 to *ca.* 1500 cm^{-1} upon reaction with Al$_2$Cl$_6$. This very considerable shift to lower frequency is the expected result of the complexation of the carbonyl oxygen with the Al$_2$Cl$_6$. Comparable shifts have been reported for similar aliphatic and aromatic ketones.[16]

The pmr spectra of most of the complexes exhibited a variable temperature dependence; however, with the exception of the complex derived from **3i** a limiting low temperature spectrum could be obtained in each case. As is shown in Table I, all the zwitterions ex-

Table I. Pmr Spectra of 5-Acylpentamethylcyclopentadienes and Their Al$_2$Cl$_6$ Complexes^a

Compound	Temp, °C	Cyclopentadiene ring methyls 1,4	2,3	5	Av^b	Other^c
3a	+37	1.64	1.80	1.00		1.50
5a	−80	1.67	1.81	1.12	1.66	2.10
3b	+37	1.63	1.80	1.02		0.78(t), 1.79(q)
5b	−90	1.67	1.81	1.16	1.69	1.00(t), 2.28(q)
3c	+37	1.74	1.74	1.14		0.9(t) 3.99(q)
5c	−10	1.71	1.71	1.28	f	1.33(t), 4.45(q)
3d	+37	1.66	1.82	1.20		7.14–7.60
5d^d	−131	1.75	1.90	1.33	1.74	7.29–7.85
3e	+37	1.64	1.82	1.15		6.63–7.74, 3.76
5e	−75	1.67	1.77	1.27	1.68	6.68–8.13, 3.88
3f	+37	1.65	1.82	1.18		6.95–7.51, 2.28
5f	−93	1.71	1.81	1.33	1.69	7.13–7.87, 2.38
3g	+37	1.65	1.82	1.18		7.16–7.52, 1.25
5g	−95	1.64	1.85	g	1.63	7.14–7.48, 1.24
3h	+37	1.63	1.79	1.17		7.12–7.47
5h^d	−140	1.71	1.87	1.25	1.69	7.30–7.65
3i	+37	1.64	1.79	1.20		7.49–7.51
5i^{d,e}	−115				1.73	7.75–7.77

^{a} Unless otherwise stated, spectra were obtained with a Varian HA-100 spectrometer, CH$_2$Cl$_2$ solvent. Chemical shifts of complexes referred to CH$_2$Cl$_2$ taken as 5.30 ppm. ^{b} Position of averaged methyl resonances at higher temperatures. ^{c} Apart from a small, uniform upfield shift with increase in temperature, the position of these resonances was not temperature dependent. ^{d} Varian DP-60 spectrum, solvent CHClF$_2$. ^{e} Frozen spectrum could not be obtained. ^{f} Averaging not seen for this complex. ^{g} Obscured by *tert*-butyl resonance.

hibited a comparable series of resonances for the five ring methyl groups and these were not changed much from their positions in the starting ketones. In contrast, the resonance attributable to the group on C$_6$ was found to be considerably deshielded upon formation of the complex. Upon reaction of **3a** with Al$_2$Cl$_6$, the methyl group on C$_6$ moved from 1.50 to 2.10 ppm.

(15) *Cf.* R. J. Gillespie and J. S. Hartman, *Can. J. Chem.*, **46**, 2147 (1968).

(16) M. F. Lappert, *J. Chem. Soc.*, 542 (1962); I. M. Semenova and A. A. Osipov, *Zh. Obshch. Khim.*, **34**, 2702 (1964); B. P. Susz and P. Chalandon, *Helv. Chim. Acta*, **41**, 1332 (1958); A. Mohammad, D. P. N. Satchell, and R. S. Satchell, *J. Chem. Soc. B*, 723 (1967).
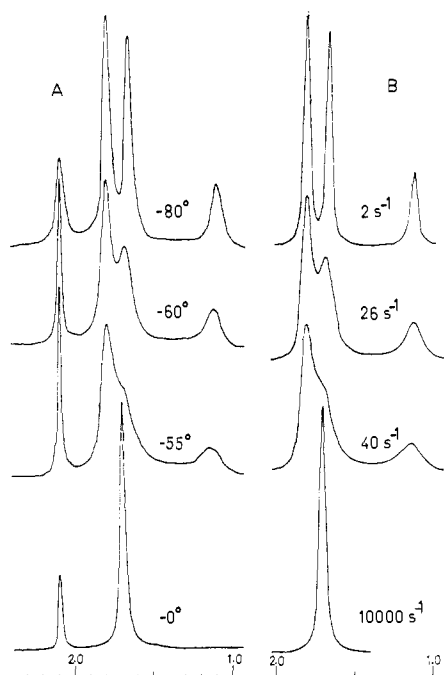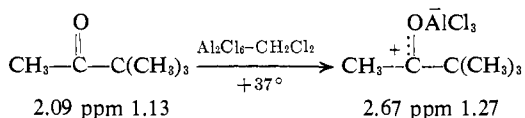
Figure 1. Observed (A) and calculated (B) pmr spectra of 5a.

Similarly the methylene protons of **3b** moved from 1.79 to 2.28 ppm. Such downfield shifts are of the magnitude to be expected for complexation of the carbonyl oxygen with the Lewis acid.[15] For example, the corresponding α-methyl group in pinacolone is deshielded by 0.58 ppm upon reaction of the ketone with Al_2Cl_6, reaction 4.[17] It is interesting that the β-methyl groups in pinacolone are moved downfield by 0.14 ppm upon complexation of the carbonyl. This is directly comparable to the downfield movement observed for the C_5 methyl group in the reaction of **3** (Table I).

$$
\begin{array}{c}
O \\
\parallel \\
CH_3-C-C(CH_3)_3 \\
2.09 \text{ ppm } 1.13
\end{array}
\xrightarrow[+37°]{Al_2Cl_6-CH_2Cl_2}
\begin{array}{c}
O\bar{A}lCl_3 \\
+ \parallel \\
CH_3-C-C(CH_3)_3 \\
2.67 \text{ ppm } 1.27
\end{array}
$$

The nmr and ir spectra of these complexes can best be understood in terms of a gross structure such as **5**, in which most of the positive charge is localized upon the C_6 assemblage. There would seem to be no evidence to support a bicyclo[3.1.0]hexenyl formulation such as **6**, in which a completely different type of nmr spectrum would be expected.[2]
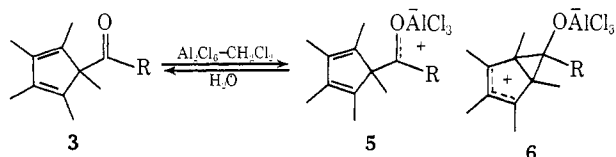
Degenerate Rearrangement of the Zwitterions. With the exception of **5c** all the complexes shown in Table I exhibited a temperature-dependent nmr spectrum. A typical set of spectra are shown in Figure 1 for **5a**.

(17) On protonation of pinacolone in $HFSO_3-SbF_5-SO_2$ the α-methyl is deshielded by 1.29 ppm and the β by 0.88 ppm. G. A. Olah, M. Calin, and D. H. O'Brian, *J. Amer. Chem. Soc.*, **89**, 3586 (1967).

Below $-80°$ the characteristic $2:2:1$ pattern for the ring methyls can be seen. As the temperature of the sample was raised, these signals broadened and coalesced and became a sharp averaged singlet. Throughout this process the resonances attributable to the C_6 group remained sharp and nonaveraged.[18] On cooling the sample the original low temperature spectrum was regenerated. While very similar changes were observed for the other complexes, it must be noted that the temperature range over which this averaging occurred was very dependent upon the substituent R.

This averaging of the five methyl groups in **5** must mean that C_6, with its attendant substituents intact, must migrate around the periphery of the five-membered ring. A very similar averaging of the five methyl groups has been observed for the σ-pentamethylcyclopentadienyl metal compounds where a comparable migration has been proposed.[19]

Theoretical line shapes for such a migration of C_6 in these complexes were computed using a Saunders many site nmr line-shape program.[20] A good fit of calculated and observed spectra was obtained only when the migration was made to proceed in such a way that the C_5 methyl exchanged first with the diene methyls resonating at the higher field. As the C_1 and C_4 methyl groups will resonate further upfield than those upon C_2 and C_3,[10,21] this means that the migration must proceed by successive 1,5-shifts rather than a series of 1,3 or random shifts.[22]

For each of the averaging systems the rate of rearrangement was determined by comparison of the calculated and observed spectra of samples made on a vacuum line. Visual line shape comparisons were made in the range where the peaks were merging, while at the slower rates a comparision of the ratios of peak heights and their positions was used. For most systems several fits were obtained and these are presented in Table II.

Precise data for **5i** could not be obtained as it was not possible to reach a sufficiently low temperature to completely stop the averaging. The value quoted is based upon the assumption that the methyl resonances in the limiting spectrum would be in the same relative positions as those of **5d**. The reverse problem occurred with the ester complex **5c**, for even at $+70°$ there was no detectable averaging of the spectrum. As at this temperature a rate of isomerization of 17 sec^{-1} could have been detected, $\Delta F^{\pm}$ for the migration must be greater than 18.2 kcal/mol.

The change of solvent from CH_2Cl_2 to $CHClF_2$ for the systems with the lower barriers to migration did not appear to produce any detectable change in the rate of rearrangement. For example, for **5d** very similar spectra were obtained at the same temperatures irrespective of whether the solvents were CH_2Cl_2, $CHClF_2$, or $CH_2Cl_2-SO_2ClF$ mixture. Any solvent effect must be smaller than the error limits in these determinations.

(18) Very small changes in the resonance positions of the non-averaged signals were observed as the temperature was changed.
(19) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970); Y. A. Ustynyuk, A. V. Kisin, and O. E. Oksinoid, *Zh. Obshch. Khim.*, **38**, 391 (1968); B. Floris, G. Illuminati, and G. Ortaggi, *Chem. Commun.*, 492 (1969); A. J. Ashe III, *J. Amer. Chem. Soc.*, **92**, 1233 (1970); F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7523 (1969).
(20) M. Saunders, *Tetrahedron Lett.*, 1699 (1963).
(21) T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **95**, 4914 (1973).
(22) *Cf.* R. B. Larrabee, *J. Amer. Chem. Soc.*, **93**, 1510 (1971).

Table II. Rate Constants for the Degenerate Rearrangement of the Zwitterions, **5**

Compd	Solv	Temp, °C	k, sec^{-1}	$\Delta F^{\ddagger}$,[a] kcal/mol	E_a,[a] kcal/mol	Log A	$\Delta S^{\ddagger}$,[a] eu
5a	CH_2Cl_2	−80	2		10.1 ± 0.8	13.5	3 ± 5
		−60	26				
		−55	40	10.9 ± 0.3			
		0	~10,000				
5b	CH_2Cl_2	−90	8		11.8 ± 2.5	b	b
		−85	17				
		−82	35				
		−80	38	9.7 ± 0.3			
5c	CH_2Cl_2	+70	⩽17	⩾18.2			
5d	$CHClF_2$	−131	1		8.2 ± 1.3	12.7	0.7 ± 9
		−126	2.5				
		−121	10				
		−116	20	8.0 ± 0.3			
		−110	42				
		−103	60				
		−90^c	710				
5e	CH_2Cl_2	−75	1.5		12.1 ± 2.9	b	b
		−60	15				
		−55	23	11.2 ± 0.3			
		−50	37				
		−90^c	0.15				
5f	CH_2Cl_2	−93	10		11.0 ± 2.1	b	b
		−90	17				
		−85	100	9.8 ± 0.3			
5g	CH_2Cl_2	−95	10		9.7 ± 3.2	b	b
		−90	15				
		−85	32	9.6 ± 0.3			
		−82	42				
		−90^c	16				
5h	$CHClF_2$	−130	4		6.4 ± 0.8	b	b
		−127	8	8.3 ± 0.3			
		−113	42				
		−108	60				
		−90^c	540				
5i	$CHClF_2$	−152	60	5.0 ± 0.6			
		−90^d	450,000				

[a] Errors quoted are based upon a temperature error of $\pm 5°$. The relative error in temperature will be much less than this. ^{b} Not quoted where temperature range is small. ^{c} Value at −90° obtained from Arrhenius plot. ^{d} Value at −90° evaluated assuming $\Delta F^{\ddagger}$ for the rearrangement is temperature independent.

An Arrhenius plot was made for those systems in which a sufficient number of rate constants at various temperatures were available. Values of E_a, log A, and $\Delta S^{\ddagger}$ so obtained are quoted in Table II. While no great accuracy may be claimed for these $\Delta S^{\ddagger}$ values, it is worth noting that they are all close to zero entropy units, which is consistent with this type of migration.[23]

The results in Table II clearly show that the C_6 substituent has a profound effect upon the rate of this degenerate migration. Considering the aliphatic groups, for example, it would appear that the ease of this migration is inversely related to the charge stabilizing ability of the C_6 substituent. Thus when R = OEt no averaging could be detected, whereas when R = Et the rate of migration is faster than when R = Me. These results are qualitatively consistent with the known abilities of these groups to stabilize positive charge.[24]

This effect is more clearly and quantitatively demonstrated by the series of phenyl substituted ketone complexes. These aromatic ketones only differ in their para substituent and, as this is far removed from the rest of the system, the complexes are all sterically comparable.

To enable a meaningful comparison, the rate constant for the migration of the C_6 group in each of the aryl ketone complexes at −90° was obtained by extrapolation of the appropriate Arrhenius plot, Table II.[25] In the case of **5i** this rate constant was evaluated by assuming $\Delta F^{\ddagger}$ for the migration to be temperature independent, an assumption validated by the very low $\Delta S^{\ddagger}$ observed for these rearrangements. Plotting log $k_{-90°}$ against σ^+ gives a straight line with a slope, ρ, of $+4.6$,[26] Figure 2. Quite clearly the rate of this rearrangement is inversely dependent upon the positive charge stabilizing ability of the C_6 substituent. The magnitude and sign of ρ show that in the transition state of the migration a substantial amount of the positive charge is transferred away from C_6 and necessarily onto the cyclopentadienyl ring.

Mechanism of the Degenerate Rearrangement. Any mechanism that is proposed for this rearrangement must be able to satisfactorily account for the large inverse rate dependence. For example, while the migration could be thought of as a [1,5] sigmatropic shift,[4] it is

(23) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(24) E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 1438 (1969); T. S. Sorensen, *ibid.*, **89**, 3782, 3794 (1967). Compare, however, D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **89**, 88 (1970).

(25) This temperature of −90° was selected as it falls midway in the range of temperatures over which averaging occurred in the aryl ketones.

(26) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957); **80**, 4979 (1958). Values used are taken from L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 356.
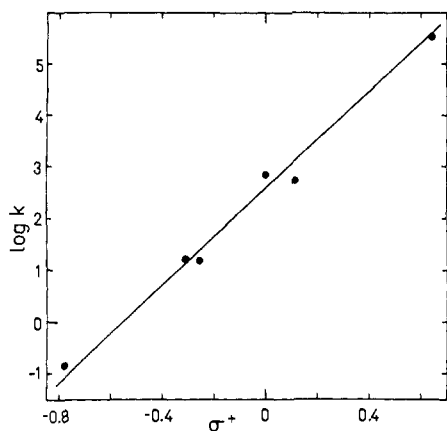
Figure 2. Plot of log k for the isomerization of the aryl substituted zwitterions, 5, at $-90°$ against σ^+.

difficult to see how such a process could account for substituent effects of this magnitude. *However, the involvement in the isomerization of a bicyclo[3.1.0]-hexenyl zwitterion as either a transition state or high energy intermediate is completely compatible with both the structure–rate relationship and the stepwise nature of the migration.* Such a process (eq 4) could proceed by

(4)
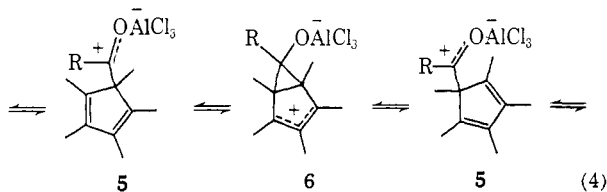
asymmetric overlap of the π electrons of the diene with the electron defficient orbital upon C_6, resulting in the transfer of the charge onto the five-membered ring. The halfway point in this process would be 6. Either of the two cyclopropane bonds of 6 could break to give the original ketone complex or the zwitterion in which the C_6 group has migrated to the adjacent carbon on the ring.

The C_6 substituent will have a much larger effect upon the charge delocalization and stability of the complex 5 than it will with 6. The greater the ability of R to stabilize the positive charge, the larger will be the energy difference between 5 and 6 and thus the slower will be the migration. A linear free energy correlation with σ^+ would be expected for such a mechanism. The magnitude of ρ is not out of line with this mechanism, particularly as the bulk of the charge stabilization in 5 will be provided by the oxygen group. Moreover, as has been discussed in an earlier paper,[2] there is delocalization of the external cyclopropyl bonds in the bicyclo-[3.1.0]hexenyl cations such as 6 and as such the charge is not completely removed from C_6.

Thus with an oxygen substituent at C_6 the relative energies of the ground and transition states or intermediate in the bicyclo[3.1.0]hexenyl degenerate migration have been inverted. The zwitterions, 5, undergo exactly the same type of circumambulation as was seen in the bicyclohexenyl cations, the only difference being the relative energy of the two forms. There has been considerable interest recently in the possibility of making the transition state of a degenerate [3,3] sigmatropic

shift to be more stable than its ground state.[27] In these present complexes we have achieved this situation for a degenerate [1,4] sigmatropic shift.

Further Consideration of the Structure of the Zwitterions. In view of the relationship of these complexes to the transition state of the bicyclo[3.1.0]hexenyl circumambulation, it is of interest to examine their structure in more detail. It will be noted in Table I that in the frozen nmr spectra of the complexes the cyclopentadiene ring methyls always exhibited a symmetry in their resonance positions. Moreover, only a single resonance or set of resonances could be detected for the substituents on C_6. Three possible situations could account for this. There could be rapid rotation around the C_5–C_6 bond as compared to the nmr time scale. Alternatively rotation could be slow and the principal rotamer be either 7 or 8 in which the substituents upon C_6 lie in the plane that runs through C_6, C_5, and the center of the C_2–C_3 bond. The third possibility is that there is rapid interconversion between two ions such as 9 and 10, the interconversion involving 8 in this case.

It will be noticed on examining the nmr data in Table I that in the aromatic series of ketones, where the anisotropy of the phenyl group might be expected to remain fairly constant, there is a steady change in the resonance positions of the dienyl methyl resonances. Thus while on formation of the complexes the C_5 methyl is deshielded by 0.12–0.15 ppm over the whole series, the C_2 and C_3 methyl resonances are moved upfield by 0.05 ppm in 5e and downfield by 0.08 ppm in 5h. Similarly the differences in the C_1 and C_4 methyl resonances show a steady progression as R becomes less able to stabilize the positive charge. While these data do not prove that one or the other of the non-classical interactions is occurring in this system, it is suggestive that there could be some homoconjugative interaction in at least the systems with the lower activation barriers to migration.

The structures 7 and 8 have a very similar geometry to that proposed for the transition state of the cyclopropyl circumambulation of the bicyclo[3.1.0]hexenyl

7   8

9   10

11
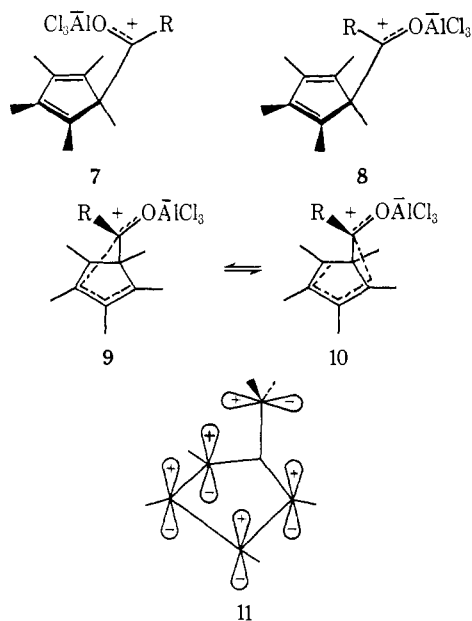
(27) R. Hoffmann and W. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971); M. J. S. Dewar and D. H. Lo, *ibid.*, **93**, 7201 (1971).

cations.[2] As such, a homoconjugative interaction of the formally vacant p orbital on C_6 with the p orbitals upon C_1 and C_4 could occur to give a delocalized cation. This interaction would be expected to result in a net stabilization as it fulfils all the requirements for Möbius aromaticity, containing a cyclic array of atomic p orbitals which possess an odd number of sign discontinuities and 4π electrons, e.g., 11.[28,29,30] However, in both of these structures, 7 and 8, there is an eclipsing between the substituents upon C_6 and the methyl group upon C_5. Moreover, as was pointed out previously the C_6 substituent, when large as in these cases, prevents the orbital on C_6 from approaching closely the p orbital on C_1 and C_4.[2]

In structures 9 and 10, there is an asymmetric overlap of C_6 with the diene to form a homopentadienyl cation.[31] This type of interaction ultimately leads to 6, the transition state for the migration; however, it is conceivable that some stability might be gained initially in such an overlap. Again with structures such as 9 and 10 the substituent and oxygen upon C_6 could be interchanged.

While the pmr evidence would seem to indicate that some leakage of the positive charge onto the diene is occurring, it is difficult at this stage to make a clear distinction between the Möbius type interaction and the rocking homopentadienylic structures such as 9 and 10. Attempts have been made to investigate the ultraviolet spectra of these complexes; however, it has not yet been possible to get completely consistent results which can uniquely be assigned to the zwitterions, 5.[32]

Conclusion

It is interesting to consider more closely the relationship between the circumambulations of the bicyclohexenyl cations and the 5–acylcyclopentadiene complexes described in this paper. This may be conveniently accomplished by plotting the energy barrier to migration in both these systems against the ability of C_6 substituents to stabilize positive charge. Of necessity this plot has to be qualitative as no data are yet available for the electron donating ability of a group such as –O–$\overline{AlCl_3}$.[30] Despite this such a graph must have the general features shown in Figure 3.

Line A represents the bicyclo[3.1.0]hexenyl cations and for this series the barrier decreases as C_6 can better support the positive charge..[2,4b] Line B represents the zwitterions discussed in this paper. In view of the common migration mechanism for these systems the two parts of the plot must intersect at that point where the energies of the two systems are equal. At this point we would expect both the monocyclic and bicyclic forms of the cation to be present and the system to exhibit a tenfold degeneracy.
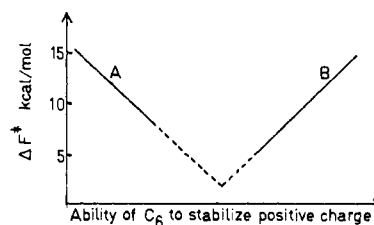

Figure 3. Barrier to migration as a function of charge stabilizing ability of C_6.

It is questionable as to what the energy barrier for migration will be when such a balance has been achieved. There is no evidence for any departure from linearity in the correlation of the rates of migration against σ^+, even when the barrier to migration is only 5 kcal/mol (5i). As such *the energy barrier to be expected when the two systems are isoenergetic must be well below 5 kcal/mol.*

Moreover, as the energies of the two systems become more closely matched, the nature of the charge delocalization will become particularly interesting. For example, the interaction of C_6 of the complexes 5 with the diene should become more important as the substituent R can less effectively stabilize the positive charge. If in fact the zwitterions, 5, gain stability from a Möbius type delocalization, this should be most pronounced as the barrier to migration is minimal.

Finally, the relationship of these results to the σ-cyclopentadienyl metal compounds merits comment. These organometallic systems are well known for their fluxional behavior which derives from the migration of the metal around the cyclopentadiene ring.[19,34] It has been suggested that these rearrangements involve the interaction of a vacant, energetically accessible orbital of the metal with the π-system of the diene in a comparable fashion to that of the carbon systems described here.[35] It is particularly interesting that the structure of the dimethyl(cyclopentadienyl)aluminum monomer, derived from its electron scattering pattern in the gas phase corresponds to that required for a Möbius type stabilization.[36] As such it may not be unreasonable to expect a similar geometry in these acylcyclopentadiene zwitterions.

Experimental Section

(28) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, 8, 1 (1969); *Accounts Chem. Res.*, 4, 272 (1971).

(29) This type of interaction is closely related to that encountered with the spirarenes; H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 89, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, 89, 5215 (1967).

(30) *Cf.* W. J. Hehre, *J. Amer. Chem. Soc.*, 94, 8908 (1972).

(31) K. Rajeswari and T. S. Sorensen, *J. Amer. Chem. Soc.*, 95, 1239 (1973); K. E. Hine and R. F. Childs, *ibid.*, 95, 3289 (1973).

(32) Solutions of these zwitterions in CH_2Cl_2 are colored (yellow to red); however, it is not yet clear what this absorption is due to.[33]

(33) *Cf.* M. Rabinovitz and A. Grinvald, *J. Amer. Chem. Soc.*, 94, 2724 (1972).

(34) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956); T. S. Piper and G. Wilkinson, *ibid.*, 3, 104 (1956); F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

(35) G. A. Shchembelor and Yu. A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, 173, 847 (1967); Yu. A. Ustynyuk, A. V. Kisin, and O. E. Oksinoid, *Zh. Obshch. Khim.*, 38, 391 (1968).

(36) D. A. Drew and A. Haaland, *J. Chem. Soc., Chem. Commun.*, 1300 (1972); W. A. Kroll and W. Naegele, *Chem. Commun.*, 246 (1969).

as 5.30 ppm) for the zwitterions. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

CH_2Cl_2 was purified by the procedure of Jones and Wood.[37] Freon 22, $CHClF_2$, and SO_2ClF were purified by double distillation on a vacuum line. The Al_2Cl_6 was sublimed *in vacuo*, mixed with aluminum powder, and resublimed.[38]

Preparation of 5-Acylpentamethylcyclopentadienes. To a solution of pentamethylcyclopentadiene (1.36 g) in anhydrous ether (100 ml) was added *n*-BuLi (3 ml of 22% in hexane). The reaction was stirred at room temperature for 30 min. The acid chloride (10 mmol) in anhydrous ether (25 ml) was added slowly, gentle refluxing being maintained. After 3 hr, water (300 ml) was added and the organic layer was separated, washed with aqueous $NaHCO_3$ (3 × 50 ml) and water (2 × 50 ml), and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on neutral alumina (activity 1), eluting with ether (5%) in pentane. The yields and properties of the 5-acylpentamethylcyclopentadienes are given in Table III. Samples for elemental analysis were prepared either by sublimation *in vacuo* (solids) or by vpc (liquids).

Preparation of Zwitterions (a). All manipulations were carried out in a drybox. Al_2Cl_6 (*ca.* 7.0 mg) was weighed out accurately into an nmr tube and dissolved in CH_2Cl_2 (1 ml) at room temperature. The solution was cooled to −78° and the acylpentamethylcyclopentadiene (0.9 of an equivalent amount of the Al_2Cl_6) dissolved in CH_2Cl_2 (0.2 ml) was added. The mixture was stirred to give a clear solution of the complex.

(37) R. E. Jones and D. E. Wood, *J. Chem. Soc. A*, 1448 (1966).
(38) T. Birchall, McMaster University, personal communication, 1969.

Table III. Properties and Analyses of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes[a]

Compound	% yield	Mp, °C	$\nu_{C=O}$, cm^{-1}	Calcd C, %	Calcd H, %	Found C, %	Found H, %	m/e
3b	65	b	1691	81.18	10.50	81.35	10.63	192
3d	68	b	1668	84.94	8.40	84.72	8.31	240
3e	66	136	1655	79.95	8.22	80.07	8.20	270
3f	60	b	1662	84.97	8.73	84.71	8.53	254
3g	71	97	1660	85.07	9.54	85.41	9.48	296
3h	69	126	1666	74.28	6.98	74.08	6.94	274
3i	58	b	1677	70.10	6.22	70.28	5.99	308

[a] Nmr spectra are given in Table I. [b] Liquid.

(b) Higher concentrations of the zwitterions could be prepared by using a suspension of Al_2Cl_6 in CH_2Cl_2. The halide went into solution upon reaction with the ketone.

(c) Vacuum line procedure. Al_2Cl_6 (*ca.* 25 mg) was weighed out accurately into a 20-ml reaction vessel containing a stirrer bar and with an attached nmr tube. The vessel was attached to a vacuum line and the appropriate solvent, CH_2Cl_2 or $CHClF_2$ (5 ml), was distilled in. The mixture was stirred until solution of the Lewis acid occurred, when it was cooled in liquid N_2 and the ketone (0.9 of an equivalent) was distilled in. The reaction vessel was warmed to −78° and stirred for 10 min. Part of the solution was transferred into the nmr tube at −78° by tilting the vessel, and the tube was sealed under vacuum.

Charge Delocalization in Saturated Systems. The Radical Cation of 1,3,6,8-Tetraazatricyclo[4.4.1.1³,⁸]dodecane

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Abstract: The photoelectron spectra of the title compound (**2**) and 1,4-diazabicyclo[2.2.2]octane (**1**) are compared, and the lone pair orbital ordering for **2** is assigned as B > E > A in energy (using S_4 molecular symmetry). The $A_1' > A_2''$ (assuming D_{3h} symmetry) ordering for **1** was previously established by Hoffmann, Heilbronner, and co-workers. The esr spectra of **1·⁺** and **2·⁺** are discussed. From the observed nitrogen and hydrogen splitting constants, it is argued that the A_2'' orbital of **1·⁺** and the E orbital of **2·⁺** are singly occupied and thus highest in energy, requiring substantial shifts of relative orbital energies in going from neutral compound to the radical cation.

McKinney and Geske[1] first reported the remarkable stability of the radical cation of 1,4-diazabicyclo[2.2.2]octane (Dabco, **1**), and found that **1·⁺** was stable enough to show a re-reduction wave in a cyclic voltammetry (cv) experiment and also to give an esr spectrum at room temperature in a slow-flow system. That the stability of **1·⁺** is really quite unusual was shown in an

1   2
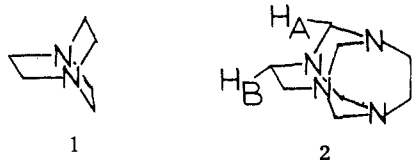
electrochemical study[2] in which several analogs of **1** in

(1) T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, 87, 3013 (1965).
(2) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 94, 7114 (1972).

which the two carbon bridges were replaced by one and three carbon bridges; most of these systems showed irreversible cv oxidation waves. One system which did show a re-reduction cv wave was 1,3,6,8-tetrazatricyclo[4.4.1.1³,⁸]dodecane (**2**). Although **2·⁺** was somewhat less stable than **1·⁺** under similar conditions, an undeciphered, weak esr signal was detected upon electrolytic oxidation of **2**.[2] In this work, we compare the photoelectron spectra (pes) of **2** and **1** and the electron spin resonance (esr) spectra of their radical cations, and discuss the orbital ordering in these systems, as a means of understanding why the cations of **1** and **2** are so much stabler than those of other saturated amines.

Results and Discussion

PES of 1 and 2. The through-bond lone pair–σ_{CC} interaction which raises the energy of the symmetric lone pair orbital of **2** (see A_1') above that of the antisymmetric (A_2'') orbital was predicted by Hoffmann