repress most back hydrogen transfer of the biradical,[13] τ_{BR} values under such conditions are probably several times longer than in hydrocarbon solvents, where reverse hydrogen transfer is the dominant reaction, and typical unsolvated τ_{BR} values may be more on the order of 10^{-7} sec. In fact, we have been unable to obtain any evidence that tributylstannane can trap the biradical obtained from irradiation of valerophenone in benzene. Because the stannane very rapidly reduces triplet ketones,[14] any trapping of the type II biradical would manifest itself as a quadratic Stern–Volmer plot for quenching of the type II reaction. No curvature is apparent in such a plot out to 0.7 *M* stannane, where 85% of the reaction is quenched. Moreover, valerophenone recovered from irradiation in the presence of tributyltin deuteride shows no incorporation of deuterium. From these observations we conclude that $\tau_{BR} < 2 \times 10^{-7}$ sec in benzene, in accord with our speculations regarding solvent effects.

If these type II biradicals actually live as long as 10^{-7} sec, the partial retention of optical activity noted in the cyclization of several ketones with asymmetric γ carbons[1,15] indicates β,γ bond rotation rates on the order of 10^8 sec^{-1}. Such a value is almost as slow as those estimated by Stephenson and Brauman in their stimulating discussion of 1,4 biradicals[16] and adds support to their contention that rates of triplet → singlet spin flips are not rate determining in the reactions of triplet-derived biradicals. These results can also be construed as lending support to the biradical mechanism for the thermal polymerization of styrene.[17]

Acknowledgment. This work was supported by several NSF grants.

[13] In low concentration, thiols enhance quantum yields, presumably by solvating the biradicals as alcohols do: P. J. Wagner and J. M. McGrath, *J. Amer. Chem. Soc.*, submitted for publication.

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[18] Alfred P. Sloan Fellow, 1968–1972.

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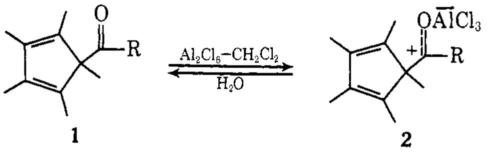
The Structure and Fivefold Degenerate Rearrangement of the 5-Acyl-1,2,3,4,5-pentamethylcyclopentadiene Aluminum Trichloride Complexes[1]

Sir:

The movement of the cyclopropyl ring around the periphery of the five-membered ring of a bicyclo[3.1.0]-hexenyl cation is a recently described molecular rearrangement.[2] We wish to report here that 5-acylpentamethylcyclopentadienes react with anhydrous aluminum trichloride to form stable zwitterions. These complexes undergo a fivefold degenerate rearrangement which is directly comparable to that exhibited by the bicyclohexenyl cations except that the relative energies of the monocyclic and bicyclic structures have been completely reversed.

When a solution of either **1**, R = Me,[3] or **1**, R = Et[4] (1 equiv), in anhydrous CH_2Cl_2 was added to a solution of Al_2Cl_6 (1.1–1.4 equiv) in CH_2Cl_2 at −78°, a complex was rapidly formed.[5] These complexes were stable at +35° for long periods and could be decomposed with ice-water to recover the ketones in high yield. The pmr spectra of these complexes would strongly suggest that they can be represented as the zwitterions **2**.[6] The infrared spectra of the complexes support this structure in that the carbonyl absorption, originally at 1695 cm^{-1} in **1**, R = Me, had been shifted very considerably to lower frequency, *ca.* 1570 cm^{-1}.



1 **2**

While below −80°, the pmr spectrum of **2**, R = Me, consisted of four sharp singlets (Table I), on warming the solution, the three resonances attributable to the ring methyl groups broadened, coalesced at *ca.* −40°, and above this temperature became an averaged singlet. During this averaging, the C_6-methyl signal remained sharp and unchanged in position. The changes in the spectrum were completely reversed on cooling the sample.

This temperature dependence, which is very similar to that exhibited by σ-pentamethylcyclopentadienyl metal compounds,[7] apparently involves a migration of C_6 with its attendant substituents around the cyclopentadiene ring. Using a Saunders many-site nmr line-shape program,[8] line shapes were calculated and plotted for a series of rate constants and a good fit of calculated and observed spectra was obtained when the averaging was assumed to proceed by successive 1,5 shifts, that is, **2a**, R = Me $\rightleftharpoons$ **2b**, R = Me $\rightleftharpoons$ **2c**, R = Me, etc.[9] The rate constant of 26 sec^{-1} at −60°, obtained in this way, corresponds to a $\Delta F^{\ddagger}$ of 10.9 kcal/mol. Comparable temperature-dependent behavior was exhibited by **2**, R = Et, $\Delta F^{\ddagger}$ for its rearrangement being 9.7 kcal/mol.

[1] This work was supported in part by the National Research Council of Canada, and the Science and Engineering Division Research Board, McMaster University.

[2] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970); V. A. Koptyug, L. K. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *ibid.*, 389 (1969); *Zh. Org. Khim.*, **6**, 2258 (1970); I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova, and V. A. Koptyug, *ibid.*, **6**, 2482 (1970); and P. Vogel, M. Saunders, N. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

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[4] All the new ketones were prepared by reaction of the appropriate acid chloride with lithium pentamethylcyclopentadienide. Elemental analyses and spectroscopic data are fully in accord with the assigned structures.

[5] The Al_2Cl_6 used was purified by two sublimations, the second being carried out after admixture of the Al_2Cl_6 with aluminum powder. The CH_2Cl_2 was purified using the procedure of R. E. Jones and D. E. Wood, *J. Chem. Soc. A*, 1448 (1966). All manipulations were carried out in a drybox.

[6] The symmetry of the nmr spectra of these zwitterions could either be due to fast rotation, compared to the nmr time scale, around the C_5–C_6 bond, or, if rotation is slow, then the principal conformations are those that maintain the required plane of symmetry.

[7] 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).

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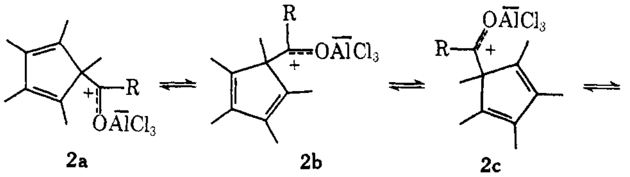
Table I. Pmr Spectra of 5-Acylpentamethylcyclopentadienes and Their $AlCl_3$ Complexes[a,b]

Compound	Temp, °C	Cyclopentadiene ring methyls 1,4	2,3	5	Av[f]	Other[g]
1, R = Me	+37	1.64	1.80	1.00		1.50
2, R = Me	−80	1.67	1.81	1.12	1.66	2.10
1, R = C_2H_5	+37	1.63	1.80	1.02		0.78 (t); 1.79 (q)
2, R = C_2H_5	−90	1.67	1.81	1.16	1.69	1.00 (t); 2.28 (q)
1, R = p-$CH_3OC_6H_4$	+37	1.64	1.82	1.15		6.63–7.74; 3.76
2, R = p-$CH_3OC_6H_4$	−75	1.67	1.77	1.27	1.68	6.78–8.13; 3.88
1, R = p-$CH_3C_6H_4$	+37	1.65	1.82	1.18		6.95–7.51; 2.28
2, R = p-$CH_3C_6H_4$	−93	1.71	1.81	1.33	1.69	7.13–7.87; 2.38
1, R = C_6H_5	+37	1.66	1.82	1.20		7.14–7.60
2, R = C_6H_5[c]	−117[d]	1.61	1.75	1.18	1.60	7.14–7.60
1, R = OC_2H_5[e]	+37	1.74	1.74	1.14		3.99 (q); 0.9 (t)
2, R = OC_2H_5[e]	−10	1.71[g]	1.71[g]	1.28[g]		4.45 (q); 1.33 (t)

[a] Unless otherwise stated, spectra obtained with a Varian HA-100 spectrometer; CH_2Cl_2 used as solvent. [b] Chemical shifts referred to CH_2Cl_2 taken as δ 5.30 ppm. [c] Solvent, CH_2Cl_2–SO_2ClF (1:1, v/v), Varian DP-60 spectra. [d] Lowest temperature attainable with CH_2Cl_2–SO_2ClF mixture, spectrum not completely frozen. [e] Varian A-60 spectrum. [f] Position of averaged cyclopentadiene methyl resonance at higher temperatures. [g] Apart from a small uniform upfield movement with increase in temperature, the position of these reasoances was not temperature dependent.



2a **2b** **2c**

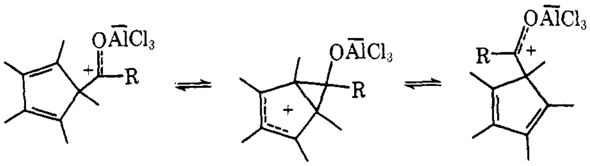
Reaction of the ester **1**, R = OEt,[10] with Al_2Cl_6 in CH_2Cl_2 at −10°, gave the zwitterion **2**, R = OEt. The pmr spectrum of this complex was not averaged on heating to +70°. As at this temperature a rate of isomerization of 17 sec^{-1} could have been detected, $\Delta F^{\ddagger}$ for the migration of C_6 must be greater than 18.2 kcal/mol. This is at least 7.6 kcal/mol more energy than is required for the migration with **2**, R = Me, and evidently the nature of the substituent R is an important factor in determining the ease of rearrangement of these zwitterions.

To systematically probe the effect of positive charge stabilization at C_6 while keeping steric factors constant a series of complexes where R = phenyl and R = para substituted phenyl has been prepared.[4] Each of the zwitterions exhibited a temperature-dependent spectrum and the rates of their degenerate rearrangements were obtained by comparison of observed and calculated spectra. For **2**, R = C_6H_5,[11] $\Delta F^{\ddagger}$ = 7.8 kcal/mol; for **2**, R = p-$CH_3C_6H_4$, $\Delta F^{\ddagger}$ = 9.8 kcal/mol; and for **2**, R = p-$CH_3OC_6H_4$, $\Delta F^{\ddagger}$ = 11.2 kcal/mol.

There is a clear trend observable in the rates of the degenerate rearrangements of these aryl ketone complexes. The greater the ability of the aryl group to stabilize the positive charge the slower the rate of migration. Although there is considerable steric congestion between the ortho hydrogens of the phenyl group and the methyls upon the five-membered ring the para substituent is well removed from the migrating center. These changes observed in the rates cannot be attributed to a changing steric requirement but must be electronic in origin.

Any mechanism that is proposed for this degenerate rearrangement must satisfactorily account for this very large dependence of the rate upon the substituent R. It is doubtful whether a 1,5-sigmatropic shift[12] process, in which C_6 moves with retention of configuration and noninvolvement of its formally vacant p orbital, can account for such a structural dependence.

More consistent with the observed substituent–rate relationship is a process in which electrons are fed from the diene to C_6 to form the bicyclic zwitterion **3**, as either a transition state or high-energy intermediate. That is, the migration proceeds by asymmetric overlap of the π electrons of the diene with the formally vacant p orbital on C_6, such that in **3**, the halfway stage, the positive charge has been very largely transferred onto the five-membered ring.[13] The greater the ability of the C_6 substituent to stabilize positive charge, the greater the energy difference between **2** and **3** and the slower rate.[14]



2a **3** **2b**

There exists a close parallel between this mechanism and that proposed for the degenerate cyclopropyl migrations observed with the bicyclo[3.1.0]hexenyl cations,[2] except that the relative energies of the monocyclic and bicyclic forms have been reversed.

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(10) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(11) Varying the ratio of Al_2Cl_6 to ketone (from 1.1:1 to 1.4:1) did not alter the rate.

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

(13) There is to a certain extent involvement of the cyclopropane of a bicyclo[3.1.0]hexenyl cation in charge delocalization.[2]

(14) The faster rate of migration of **2**, R = Et, than **2**, R = Me, is consistent with the observation that ethyl can less effectively stabilize positive charge than methyl.[15] The faster rate of **2**, R = C_6H_5, could be due to the phenyl ring being twisted out of conjugation with the carbonyl π system as a result of steric interactions with the ring methyl groups.

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

(16) Canadian International Development Agency scholarship holder.

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