

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 biradicals¹⁶ and adds support to their contention that rates of triplet \rightarrow 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.

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(18) Alfred P. Sloan Fellow, 1968-1972.

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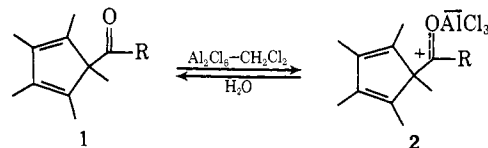
The Structure and Fivefold Degenerate Rearrangement of the 5-Acyl-1,2,3,4,5-pentamethylcyclopentadiene Aluminum Trichloride Complexes¹

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-acyl-pentamethylcyclopentadienes react with anhydrous alu-

minum 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 = Et⁴ (1 equiv), in anhydrous CH₂Cl₂ was added to a solution of Al₂Cl₆ (1.1-1.4 equiv) in CH₂Cl₂ 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.



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 C₆-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 C₆ 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 ΔF^\ddagger of 10.9 kcal/mol. Comparable temperature-dependent behavior was exhibited by 2, R = Et, ΔF^\ddagger for its rearrangement being 9.7 kcal/mol.

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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 Al₂Cl₆ used was purified by two sublimations, the second being carried out after admixture of the Al₂Cl₆ with aluminum powder. The CH₂Cl₂ 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 C₅-C₆ bond, or, if rotation is slow, then the principal conformations are those that maintain the required plane of symmetry.

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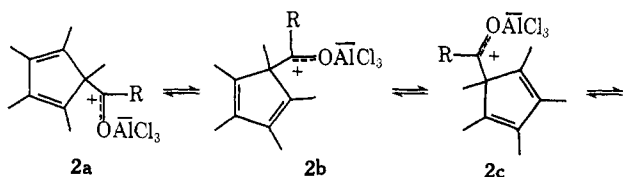
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Table I. Pmr Spectra of 5-Acylpentamethylcyclopentadienes and Their AlCl₃ Complexes^{a,b}

Compound	Temp, °C	Cyclopentadiene ring methyls				Other ^c
		1,4	2,3	5	Av ^f	
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 ₂ H ₅	+37	1.63	1.80	1.02		0.78 (t); 1.79 (q)
2, R = C ₂ H ₅	-90	1.67	1.81	1.16	1.69	1.00 (t); 2.28 (q)
1, R = <i>p</i> -CH ₃ OC ₆ H ₄	+37	1.64	1.82	1.15		6.63-7.74; 3.76
2, R = <i>p</i> -CH ₃ OC ₆ H ₄	-75	1.67	1.77	1.27	1.68	6.78-8.13; 3.88
1, R = <i>p</i> -CH ₃ C ₆ H ₄	+37	1.65	1.82	1.18		6.95-7.51; 2.28
2, R = <i>p</i> -CH ₃ C ₆ H ₄	-93	1.71	1.81	1.33	1.69	7.13-7.87; 2.38
1, R = C ₆ H ₅	+37	1.66	1.82	1.20		7.14-7.60
2, R = C ₆ H ₅ ^c	-117 ^d	1.61	1.75	1.18	1.60	7.14-7.60
1, R = OC ₂ H ₅ ^e	+37	1.74	1.74	1.14		3.99 (q); 0.9 (t)
2, R = OC ₂ H 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; CH₂Cl₂ used as solvent. ^b Chemical shifts referred to CH₂Cl₂ taken as δ 5.30 ppm. ^c Solvent, CH₂Cl₂-SO₂ClF (1:1, v/v), Varian DP-60 spectra. ^d Lowest temperature attainable with CH₂Cl₂-SO₂ClF 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 resonances was not temperature dependent.



Reaction of the ester 1, R = OEt,¹⁰ with Al₂Cl₆ in CH₂Cl₂ 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, ΔF^\ddagger for the migration of C₆ 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.

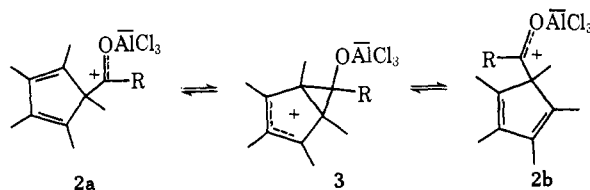
To systematically probe the effect of positive charge stabilization at C₆ while keeping steric factors constant a series of complexes where R = phenyl and R = *para* substituted phenyl has been prepared.⁴ Each of the zwitterions exhibited a temperature-dependent spectrum and the rates of their degenerate rearrangements were obtained by comparison of observed and calculated spectra. For 2, R = C₆H₅,¹¹ $\Delta F^\ddagger = 7.8$ kcal/mol; for 2, R = *p*-CH₃C₆H₄, $\Delta F^\ddagger = 9.8$ kcal/mol; and for 2, R = *p*-CH₃OC₆H₄, $\Delta F^\ddagger = 11.2$ 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 shift¹² process, in which C₆ 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 C₆ 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 C₆, 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 C₆ substituent to stabilize positive charge, the greater the energy difference between 2 and 3 and the slower rate.¹⁴



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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(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 = C₆H₅, 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.

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