

Polar Substituent Effects on 1,5-Homodienyl Hydrogen Migrations in (*E*)-1-Aryl-2-[(*E*)-2,2-dimethyl-3-phenylcyclopropyl]-ethenes

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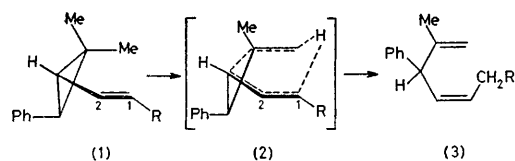
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Summary 1,5-Homodienyl hydrogen migrations in the title compounds are accelerated by electron-withdrawing aryl substituents, with a systematic rate dependence on σ constants (Hammett equation) and on $\sigma_{R(BA)}$ or σ_R^+ constants (Taft dual-substituent parameter equation).

THE strict stereoelectronic demands on the transition state for concerted 1,5-homodienyl hydrogen migration have been well documented for vinylcyclopropanes constrained into medium-ring systems¹ and for the parent monocyclic

systems.² To our knowledge, the demonstration of polar substituent effects on the rates of these sigmatropic migrations has not been reported. Such effects have been observed for the analogous 1,5-dienyl shifts in a limited number of cases.³

Herein we report preliminary kinetic data which demonstrate a small but systematic polar electronic effect on the rates of 1,5-homodienyl hydrogen shifts (Scheme) in the (*E*)-1-aryl-2-[(*E*)-2,2-dimethyl-3-phenylcyclopropyl]-ethenes (**1**).



a ; R = 4-MeOC ₆ H ₄	g ; R = 3-ClC ₆ H ₄
b ; R = 4-MeC ₆ H ₄	h ; R = 3-NCC ₆ H ₄
c ; R = Ph	i ; R = 4-MeOC ₆ H ₄ CO ₂
d ; R = 4-ClC ₆ H ₄	j ; R = PhCO ₂
e ; R = 4-NCC ₆ H ₄	k ; R = 4-O ₂ NC ₆ H ₄ CO ₂
f ; R = 4-O ₂ NC ₆ H ₄	

SCHEME

In *o*-dichlorobenzene (ODCB) at 453.5 K compounds (**1a–h**) rearrange to (*Z*)-hexa-1,4-diene products (**3a–h**). Kinetic data (Table) were obtained by the sealed glass ampoule technique employing flame ionisation g.l.c. analysis and electronic integration. Linear first order kinetics were observed for at least three half lives in each case.

TABLE. Kinetic data for thermal rearrangement of (**1**) to (**3**) in ODCB at 453.5 K

Compound	(1a)	(1b)	(1c)	(1d)	(1e)	(1f)	(1g)	(1h)
$k \times 10^5/s^{-1}$ ^a	1.80	2.01	2.32	2.88	4.32	4.50	3.53	3.77
Error ^b	0.04	0.02	0.02	0.03	0.06	0.09	0.03	0.02

^a Rate constant for appearance of (**3**). ^b Standard deviation from weighted least-squares analysis.

Electron-withdrawing substituents moderately accelerate the rate of rearrangement. Moreover, an acceptable correlation ($R = 0.994$) of $\log k$ with Hammett σ values[†] was obtained ($\rho = 0.38$) for (**1a–h**). Analysis of the kinetic data for the *para*-substituted analogues (**1a–f**) by Taft's dual-substituent parameter (DSP) approach⁴ gave the best fit with $\sigma_{R(BA)}$ ($f = 0.03$, $\lambda = 0.93$) or σ_R ($f = 0.06$, $\lambda = 1.18$) resonance constants. Correlation was significantly poorer with σ_R values ($f = 0.12$). A similar depend-

ence of rate on the electronic nature of the substituent has been observed for the phenyl ester analogues (**1i–k**) so far studied. Thus the nitro ester (**1k**) rearranges approximately twice as rapidly as its methoxy congener (**1i**).

The rate factor (*ca.* 2.5) separating the extremes of the series (**1a–h**), while small in magnitude, contrasts significantly with the negligible (<5%) rate-substituent effect reported for the retro-ene fragmentation of benzyl allyl ethers.⁵ Also, the apparently electronic basis for the rate variation (Hammett, DSP analyses) argues against it being due to ground state entropy effects.[‡] Activation parameters for the rearrangements of (**1a–h**) are currently being determined.

Detailed mechanistic interpretation of our kinetic results is not yet possible. However, a reasonable first hypothesis is that the observed rate variations do reflect partial negative charge development in the transition state (**2**)² for suprafacial 1,5-homodienyl hydrogen migration. The moderate ρ value (0.38) and poor rate correlations with σ^- or σ_R^- indicate such charge development to be at C-2 rather than at C-1. To test this point, analogues of (**1**) substituted at C-2 are being synthesised, as is a series of

compounds designed to detect any polar substituent effect at the migration origin.

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[†] The kinetic data correlated poorly with σ^+ ($R = 0.979$) or σ^- ($R = 0.949$).

[‡] Differences in internal rotational barriers in the ground state have been cited (ref. 5) to explain the fourfold increase in the rate of retro-ene fragmentation of allyl benzyl ether over its allyl methyl counterpart.

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⁵ H. Kwart, S. F. Sarner, and J. Slutsky, *J. Amer. Chem. Soc.*, 1973, 96, 5234.