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RELATIVE SOLVOLYSIS RATES OF ALLYL AND DIENYL 3,5-DINITROBENZOATES

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Of the many solvolysis rate studies involving allyl compounds, only two have examined the effect of extending conjugation. Vernon[2] has estimated that replacement of a β-methyl group by a phenyl group (1 and 2) increases the rate by a factor of ca. 140. Friedrich and Winstein[3] have studied some spirodienyl p-nitrobenzoates, and the 1.3 x 10^7 fold rate difference between compounds 3 and 4 (OPNB = p-nitrobenzoate) in 90% aqueous acetone at 25° is typical of their findings.

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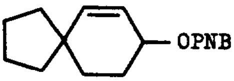

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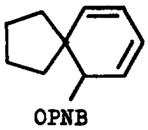

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These authors noted the unusual reactivity of the spirodienyl compounds, but Deno[4] has suggested that the rate difference is consistent with estimated relative stabilities of allyl and pentadienyl cations. We report here solvolysis rates for acyclic dienyl derivatives and their allyl analogues[5] which show that the spirodienyl compounds are indeed unusually reactive.

TABLE 1

Solvolysis Rates in 80% Aqueous Acetone[a] at 45°

Compound	k (min^{-1})[b]	k (relative)
(5) 	1.19×10^{-5} [d]	1
(6) 	$(6.6 \pm 0.9) \times 10^{-3}$	560
(7) 	$(3.08 \pm 0.05) \times 10^{-4}$	26
(8) 	$(1.4 \pm 0.04) \times 10^{-2}$	1200

a. Volume to volume at 25°.

b. Ten ml aliquots of ca. 3×10^{-3} M solution were titrated using 10^{-2} N alkali and bromothymol blue indicator.

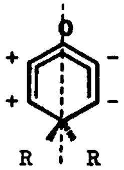
c. ODNB = 3,5-dinitrobenzoate.

d. Extrapolated from measurements in 40 and 50% aqueous acetone (m = 0.85).

Rates in Table 1 are almost certainly for S_N1 type solvolysis with alkyl oxygen fission.[6] The rate for the least reactive compound (5) exhibits the high sensitivity to solvent ionizing power (m = 0.85) characteristic of this mechanism[7] and common ion rate depression has been observed for 6. The rate increase caused by adding a second double bond in conjugation is modest, a factor of 560 for the methyl derivatives and only 46 for the more reactive phenyl derivatives. If 5 and 6 are used as the basis for an acyclic standard, an extra double bond in conjugation causes an increase in rate in the cyclic compounds that is larger than the rate increase in acyclic compounds by a factor of 2.3×10^4. The solvolysis rate of 3 seems entirely normal, as it is virtually identical to those of *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate.[8]

Assignment of the full value of a skew butane interaction (0.8 kcal./mole) to each of the two alkyl-p-nitrobenzoyloxy interactions in 4 would allow a 12-fold solvolysis rate enhancement owing to relief of steric strain in the transition state. Solvolysis of 6 may be slowed relative to 5 by loss of rotational entropy for the essential single bond of the diene in 6 on formation of the transition state. The contribution of this bond to rotational entropy cannot be large, however, since the rotational barrier in butadiene is ca. 5 kcal./mole;[9] and the consequent rate decrease certainly could be no larger than a factor of ten, and is probably much less.[10] Anchimeric assistance in 4 from ring expansion to a bicyclo [4.4.0] system[3] should not be significant for such a reactive system. Thus, even after the factors above have been taken into consideration, the spirodienyl compounds seem too reactive by a factor of 10^2 or more.

This implies some special stability for the "U" conformation (9) of pentadienyl cations relative to the "sickle" or "W" conformations[11] which we are unable to explain. Consideration of the symmetry of the highest occupied MO (HOMO) suggests that the "U" conformation should be destabilized by an antibonding 1,5-interaction (9).



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The HOMO is not stabilized by interaction with the methylene or gemdialkyl group in the way described for the pentadienyl anion[11], because it has a node which contains the spiro carbon and its substituents.

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