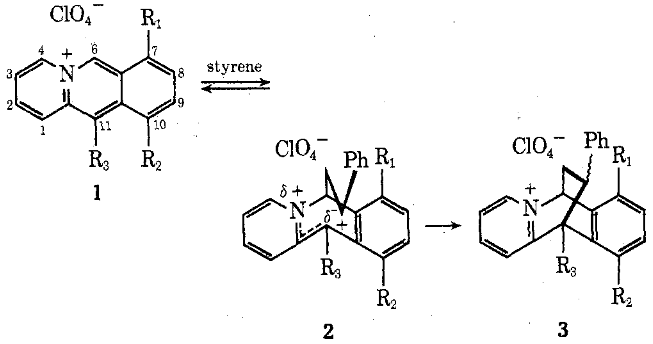
Communications

Evidence for Steric Enhancement of Rate in Cycloaddition

Summary: The acceleration in the rate of cycloaddition observed when methyl groups are introduced into the meso positions of anthracene or the acridizinium ion must be largely steric rather than electronic in origin.

Sir: Since the acridizinium ion (**1a**) is electrophilic[1] in nature, it was surprising to find that introduction of a methyl group at position 11 (see **1b**) produced over a 13-fold *increase* in the rate of cycloaddition with styrene.[2] An alternative to the earlier[2,3] electronic explanation for the rate enhancement, and one compatible with the increasing evidence[1,4] of the importance of position 6 of the acridizinium ion in the rate-controlling process, is that the methyl at position 11 is under strain as the result of peri interactions with adjacent hydrogens (at positions 1 and 10) and that this strain is relieved when the methyl group moves out of plane during cycloaddition (see **2**). If this assumption is correct, the introduction of a methyl group into a position peri to the 11-methyl should result in a further rate enhancement.



a, $R_1 = R_2 = R_3 =$ H;
b, $R_1 = R_2 =$ H, $R_3 =$ Me;
c, $R_1 = R_2 = R_3 =$ Me

For convenience in synthesis, the 7,10,11-trimethylacridizinium ion (**1c**) was studied. The observed rate of cycloaddition with styrene was more than 10 times that of the 11-methyl derivative, direct evidence of steric acceleration.[5]

Steric acceleration in the conventional Diels–Alder reaction has been overlooked because of a general inability to assess the relative importance of such acceleration when polar effects would also be expected to speed the reaction. An obvious, but hitherto unrecognized, example of such steric acceleration may be seen in published data[6] concerning anthracene derivatives. The introduction of methyl groups into both of the meso positions of anthracene results in a 218-fold acceleration of the rate of cycloaddition with maleic anhydride, while methoxyl groups at the same positions actually cause a *decrease* in rate. The suggestion,[6] "the increase in rate produced by methoxy groups is smaller than that of alkyl groups because of the impaired coplanarity (*peri*-hydrogens)," would imply that steric inhibition of resonance had rendered the methoxyl groups less electron-releasing than methyl groups. That this is not the case is evidenced by recent[7] ^{19}F substituent chemical shift data for 10-substituted 9-fluoroanthracenes. It is more likely that the greater effective size of the methyl group is largely responsible for the rapid rate of cycloaddition reported[6] for 9,10-dimethylanthracene.

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References and Notes

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