

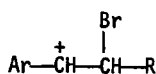
NEIGHBORING GROUP PARTICIPATION IN POLAR
BROMINATION OF STYRENE DERIVATIVES¹

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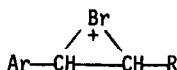
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Recent studies by Fahey and Schneider² and by Yates and Rolston^{3,4} have convincingly demonstrated that the polar bromination of styrene derivatives proceeds through open benzylic cations (1) rather than cyclic bromonium ions (2). These findings are further supported by the more recent work of Wilkins and Regulski⁵ and Yates and McDonald.⁶ Thus bromination of simple styrene derivatives proceeds nonstereoselectively^{2,3}, although the trans adduct is favored. In acetic acid, solvent attack occurs exclusively at the benzylic position³, and kinetic evidence of m- and p-substituted styrene derivatives yields ρ values characteristic of benzyl cation formation.⁴ Although modest, an α -secondary isotope effect is found for these reactions.⁵

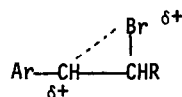
Despite the compelling evidence against bridging from studies of electronic factors, stereochemical evidence has led most researchers to favor a partially bridged species such as (3). Dubois et al.⁷, however, contend that their kinetic results on the



(1)



(2)

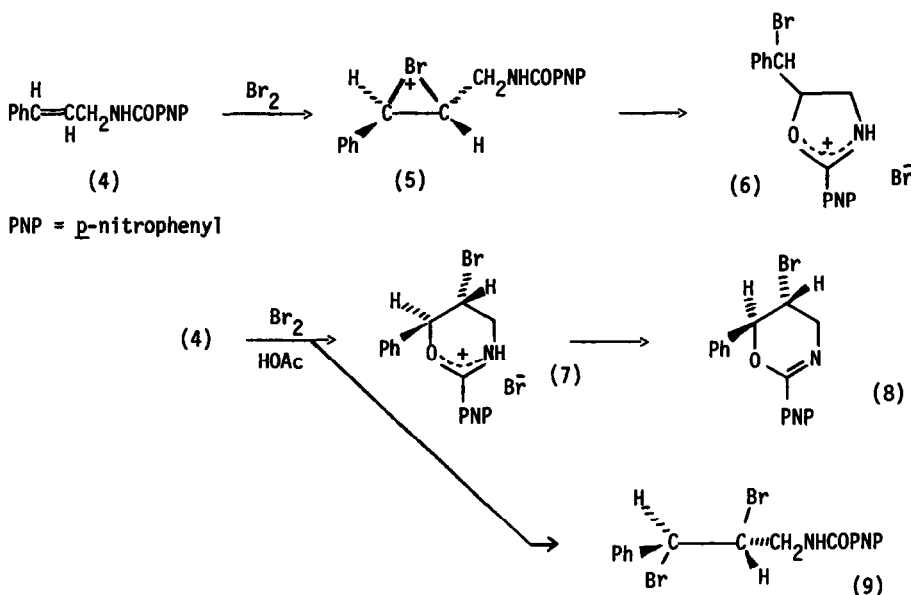


(3)

bromination of p,p'-disubstituted stilbene derivatives are satisfied by discrete carbonium ion intermediates in methanol, but the intermediates have bromonium ion character in carbon tetrachloride. Yates and McDonald⁶, from thermodynamic measurements, now favor a bridged

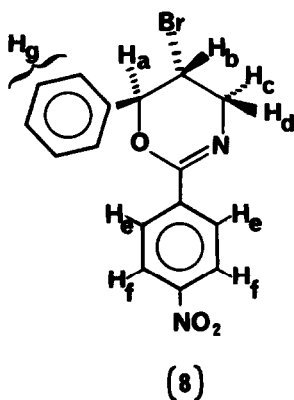
transition state and an open benzylic ion intermediate for styrene derivatives in acetic acid.

These recent disclosures prompt us to report our studies of the bromination of trans-N-cinnamyl-p-nitrobenzamide⁸ (4) in acetic acid. It is well known that five-membered ring formation is favored over six-membered ring formation because of entropy factors.⁹ On this basis the bromonium ion intermediate (5) should lead to the oxazolinium ion (6)¹⁰ upon participation by the neighboring amide group. Amide (4) rapidly consumed one equivalent of bromine in acetic acid at 18°C and a 76% yield of a brownish white precipitate of the oxazinium salt (7) was recovered. Treatment of (7) with anhydrous triethylamine gave the dihydrooxazine (8), m.p. 141-143°. From concentration of the acetic acid solution, the amide (9), m.p. 171-172°, resulting from trans addition of bromine, was isolated in



22% yield.¹¹ The nmr spectra of the products served to unequivocally identify each, and spin decoupling experiments confirmed that the cyclic product was (8) and not the isomeric oxazoline derived from (6). Thus we find no evidence to postulate (5) as an intermediate in our system. Furthermore, apparently no charge is developed on the β -carbon. The

NMR spectral data obtained in CDCl_3
(relative to TMS)

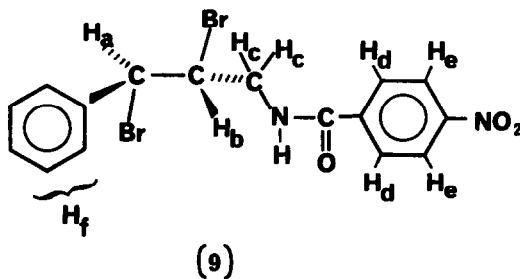


Proton	Chemical Shift (δ)	Multiplicity
H_a	5.34	doub.* ($J_{H_a H_b} = 7.2$ Hz)
H_b	4.23	multiplet
H_c & H_d	3.88	multiplet
H_e & H_f	8.00	triplet**
H_g	7.27	singlet

* irradiation at 4.23 caused the doublet to collapse to a singlet
** overlapping doublets, $J_{H_e H_f} = 9.0$ Hz

NMR spectral data obtained in $\text{CF}_3\text{CO}_2\text{H}$

(relative to TMS)



Proton	Chemical Shift (δ)	Multiplicity
H_a	4.95	doublet ($J_{H_a H_b} = 9.5$ Hz)
H_b	3.90	multiplet
H_c	4.34	multiplet
H_d	7.90	doublet ($J_{H_d H_e} = 8.2$ Hz)
H_e	8.21	doublet
H_f	7.18	singlet

efficiency of the cyclization¹² is good evidence for an open benzylic cation intermediate rather than a partially bridged ion such as (3). Based on the mechanistic conclusions of Yates and McDonald⁶, which our data supports, cyclization by a neighboring group in electrophilic addition reactions apparently occurs after the transition state.¹³ While the cyclization products would be the same for those olefins forming bridged intermediates, the results would differ in cases like the one studied here.

We are currently studying other bridging electrophiles in hopes of providing further information about bridged ions during electrophilic addition processes.

REFERENCES

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11. Acceptable elemental analyses and other spectral data were obtained on all compounds reported here.
12. Under nearly identical conditions, trans-1-phenylpropene gives 23.4% of solvent incorporation at the benzylic position, c.f. ref. 3.
13. Cyclization in solvolytic reactions, on the other hand, occurs predominantly concurrent with ionization, c.f. refs. 9 and 10b.