

CYCLOPROPYLNITRENIUM IONS AND SUBSTITUENT EFFECTS

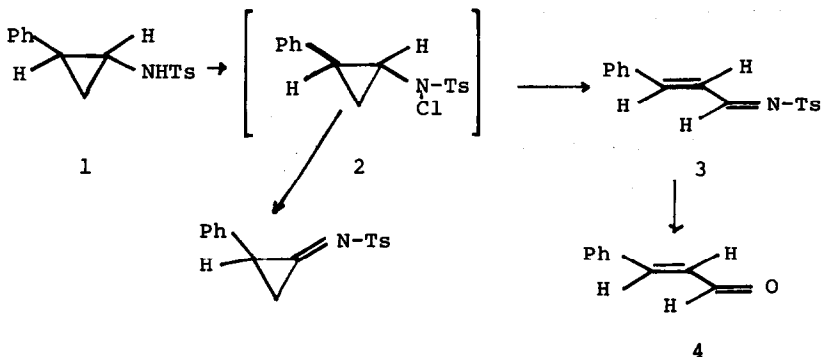
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Extensive recent investigations have sought to define the role of electron deficient nitrogen atoms in transition states and as intermediates.<sup>3</sup> It now appears certain that significant positive charge does develop on nitrogen in many reactions. We would like to report in this communication our observations concerning the effects of substituents on potential precursors of cyclopropyl nitrenium ions. These observations seem to reveal a not unexpected spectrum of mechanistic types.

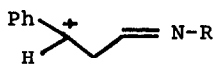
Our interest in N-chlorocyclopropylamines was prompted by our hope that elimination of HCl might provide a simple route to cyclopropanone imines.<sup>4</sup> For this purpose a CHCl<sub>3</sub> solution of 1 was reacted with 5% NaOCl saturated with Na<sub>2</sub>CO<sub>3</sub> at room temperature.<sup>5</sup> Immediate monitoring of the CHCl<sub>3</sub> layer by nmr spectroscopy revealed a total destruction of the cyclopropane ring hydrogen peaks and the formation of a single new substance. This substance (m.p. 79-80°, 81%) was assigned structure 3 on the basis of analytical and spectral data.<sup>6</sup> Confirmation of this assignment was obtained by hydrolysis of 3 to cinnamadehyde 4.



Formation of 3 is similar in consequence to the recently reported  $\text{Pb}(\text{OAc})_4$  oxidation of cis- and trans-2-phenylcyclopropylamine to 4.<sup>7</sup> Nitrenium ion 5b and cation 6a were proposed as possible intermediates in the oxidation. Cyclopropylnitrenium ions have been invoked by Gassman in the solvolysis of N-chloro-

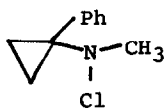


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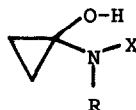


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N-methyl-1-phenyl cyclopropylamine (7)<sup>8</sup> and suggested by Wasserman in a series of cyclopropane ring expansions.<sup>9</sup>

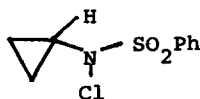


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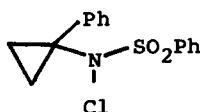


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In order to compare this recent work of Nozaki, Gassman and Wasserman with the observed chemistry of 2, we prepared 9 and 10. These compounds were obtained from the corresponding N-H precursors by the above procedure. In contrast to 1, 9 and 10 were quite inert, could be isolated and failed to react under a variety of conditions (e.g.,  $\text{KOt-Bu}$   $\text{HOT-Bu}$ ).



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The powerful electron withdrawing properties of the arylsulfonyl group should oppose positive charge development on nitrogen. The facility of the fragmentation of 2 would thus suggest that 5b is concertedly by-passed in favor of the stabilized cation 6b.<sup>10</sup> The failure of 9 to undergo fragmentation substantiates the importance of the ring phenyl group in charge stabilization. Equally interesting is the effect of the arylsulfonyl group on the rearrangement observed by Gassman. The inertness of 9 strongly suggests the absence of a concerted by-pass of nitrogen in the ionization of 7 and supports the proposed<sup>8</sup> transition state positive charge leading from 7.

Thus, we conclude from these substituent effects that the nitrenium ion designation seems appropriate to the rearrangement of 7 and inappropriate to the decomposition of 2. It is apparent that other substituent studies may be of further use in the study of nitrenium ions.

#### ACKNOWLEDGMENT

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#### FOOTNOTES

1. Present Address: Polaroid Corporation, Cambridge, Massachusetts
2. A portion of this work was originally described in the Ph.D. Thesis of Richard B. Greenwald, Harvard University, Cambridge, Massachusetts, 1965.
3. P. G. Gassman, Accts. Chem. Res., 3, 26 (1970).
4. cf. J. A. Deyrup and R. B. Greenwald, Tetrahedron Letters, 5091 (1966); H. Quastand, W. Rissler, Angew. Chem. Internat. Ed., 12, 414 (1973).
5. cf. F. D. Chattaway, J. Chem. Soc., 145 (1905).
6. Satisfactory analytical data was obtained for all new compounds reported with the exception of the N-halo compounds.
7. T. Hiyama, H. Koide and H. Nozaki, Tetrahedron Letters, 2144 (1973).
8. P. G. Gassman and A. Carrasquillo, Chem. Comm., 495 (1969).
9. H. H. Wasserman, R. E. Cochoy and M. S. Baird, J. Am. Chem. Soc., 91, 2375 (1969); H. H. Wasserman, H. W. Adickes, O. E. deOchoa, ibid., 93, 5586 (1971)
10. We use the term "concerted by-pass" to describe a transition state in which most of the positive charge develops elsewhere in the molecule and relatively little on nitrogen.