

THERMAL RING EXPANSION OF 1-AZIRINES HAVING UNSATURATED
GROUP AT 3-POSITION.

—REACTIVITIES BY THE DIFFERENCE OF SUBSTITUENT.—

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Thermal reaction of 3-benzoyl-1-azirines gave oxazole and isoxazole derivatives from the intermediates formed by C-C bond and C-N bond fission, respectively. Oxazole formation was accelerated by base in the case of the 2-unsubstituted azirine, and by acid in the case of the 2-methylazirine. Usual thermal reaction of 1-azirine by C-N bond fission also occurred in 3-benzoyl-1-azirine affording isoxazole. Oxazole formation derived from C-C bond fission was explained by ionic mechanism.

Unsaturated substituent at 3-position was usually attacked by intramolecular vinyl nitrene affording five membered ring. Methyl and Phenyl group whose substituent at cyclization position formed five membered ring, were attacked by vinyl nitrene affording six membered ring and seven membered ring respectively.

Reactivity by the difference of substituent was discussed by the stability of intermediate.