ary atom which is greater than that for a tertiary atom. Second, the steric factors for these reactions are at most 10^{-3}. Dorfman and Gomer[3] reached a similar conclusion about the magnitude of the steric factors from the results of their studies of a number of similar methyl radical reactions.

(3) L. M. Dorfman and R. Gomer, *Science*, **110**, 439 (1949).

DIVISION OF CHEMISTRY A. F. TROTMAN-DICKENSON
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OTTAWA, CANADA

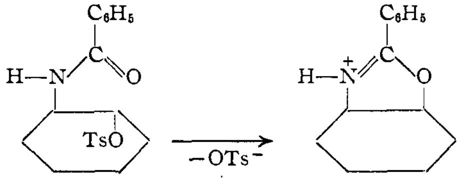
RECEIVED MARCH 29, 1950

THE NEIGHBORING BENZAMIDO GROUP IN ADDITION AND SUBSTITUTION

Sir:

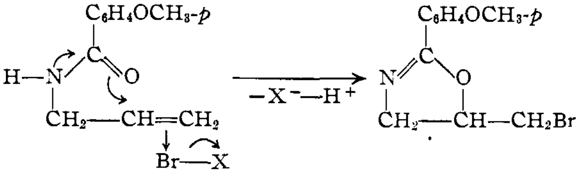
Neighboring groups which participate in nucleophilic replacement processes with relatively large driving forces[1] can be expected to participate in addition[2] to the olefinic linkage which is initiated by electrophilic attack of some reagent on the multiple linkage.

The benzamido and other acylamino groups are examples of so-called complex[2,3] neighboring groups with rather large driving forces. Benzamido can be compared with acetoxy from the first order rate of ionization of *trans*-2-benzamidocyclohexyl *p*-toluenesulfonate (I) in absolute ethanol at 74.51°, 1.78 × 10^{-3} sec.$^{-1}$, which is *ca.* 200 times the value for the *trans*-2-acetoxycyclohexyl ester[4] (and some 1000 times that of the *cis*-benzamido isomer).

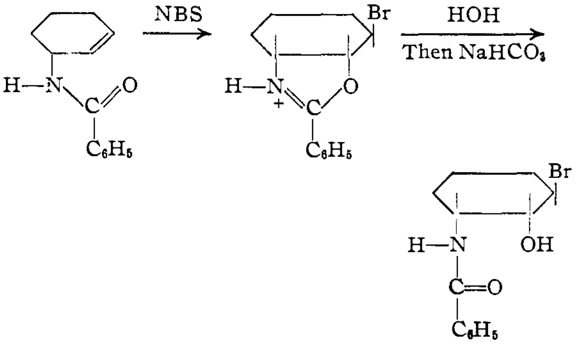

I II

Solvolysis of I in ethanol or acetic acid produces the oxazolinium ion II as the first product[3] and this may be isolated either as the water-soluble *p*-toluenesulfonate, m. p. 160–161°, as the picrate, m. p. 155.5°, or as the free oxazoline, m. p. 47°. For example, oxazolinium toluenesulfonate is obtained in 95% yield from heating I several minutes in anhydrous acetic acid.

The acylamino group turns out to participate in addition in a very useful manner. For example, N-*p*-methoxybenzoylallylamine (III) gives, on treatment in acetic acid with N-bromosuccinimide, (which, incidentally, we have used for several years as a positive bromine source in hydroxylic solvents) a 95% crude yield of the bromooxazoline IV, m. p. 91–91.5°.


IIII IV

This reaction is interesting theoretically and on the practical side constitutes a way for setting up three functional groups with a definite stereochemical relation. We illustrate with the cyclohexenyl case



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RECEIVED FEBRUARY 25, 1950

(1) Winstein and Grunwald, THIS JOURNAL, **70**, 828 (1948).

(2) Winstein, paper before Organic Division at the St. Louis meeting of the American Chemical Society, September, 1948.

(3) Winstein, paper at Eleventh National Organic Symposium, Madison, Wisconsin, June, 1949.

(4) Winstein, Hanson and Grunwald, THIS JOURNAL, **70**, 812 (1948).

THE STRUCTURE OF QUINAMINE[1]

Sir:

In 1945 quinamine, an indole alkaloid of the cinchona family,[2] was considered to have structure I.[3] In 1949 Robinson[4] suggested an alternate formulation II to account for the dihydroindole nature of quinamine (spectrum, coupling reaction with diazobenzenesulfonic acid). Very recently[5] structure III was proposed for quinamine based upon the elegant conversion of quinamine into cinchonamine (V) with lithium aluminum hydride.

We have now effected the reverse transformation of cinchonamine into quinamine with the aid of dilute peracetic acid. Since all attempts of converting indole derivatives into 2,3-epoxides by oxidation with peracids have so far failed, we should like to propose the expression IV for quinamine.

The action of peracetic acid results probably first in the formation of a *β*-hydroxyindolenine derivative (VI) in accordance with the general course of oxidation in the indole series.[6] Inter-

(1) I am indebted to Research Corporation, New York, for financial assistance of this work.

(2) Henry, Kirby and Shaw, *J. Chem. Soc.*, 524 (1945).

(3) Kirby and Shaw, *ibid.*, 528 (1945); Kirby, *ibid.*, 725 (1949).

(4) Robinson, Festschrift Paul Karrer, Zürich, 1949, p. 40; *J. Chem. Soc.*, in press (quoted from ref. 5).

(5) Goutarel, Janot, Prelog and Taylor, *Helv. Chim. Acta*, **33**, 150 (1950).

(6) Witkop, THIS JOURNAL, **72**, 1428 (1950).