Tetrahedron, 1967. Vol. 23, pp. 2291 to 2293. Pergamon Press Ltd. Printed in Northern Ireland

RING ENLARGEMENTS—VI[1]

STERIC AND ELECTRONIC CONTROLS IN RING ENLARGEMENT REACTIONS OF THE *CIS*-8-METHYLHYDRINDANIC SYSTEM*

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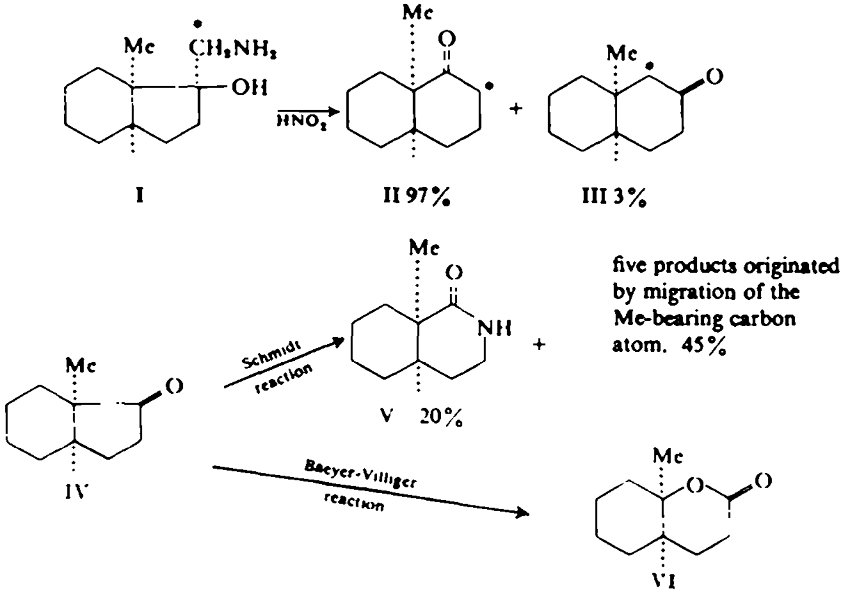
Abstract—An explanation is put forward of the observed fact that the *cis*-8-methylhydrindanic system can undergo two different ring enlargement reactions depending on the identity of the inserted group, giving either compounds where the inserted group (oxygen) is near the ring junction or compounds where the inserted group ($—CH_2—$) is far from ring junction. When the inserted group is —NH—, mixtures of compounds of both kinds are formed.

In preceding papers,[1-3] three different ring enlargement reactions of the *cis*-8-methylhydrindane system were described—the pinacolic deamination of *cis*-8-methyl-1-*exo*-aminomethylhydrindan-1-ol (I), and the Schmidt and the Baeyer-Villiger reactions on *cis*-8-methylhydrindan-1-one (IV). The results summarized in Table 1, show

Table 1



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* Thanks are due to the National Research Council for support.

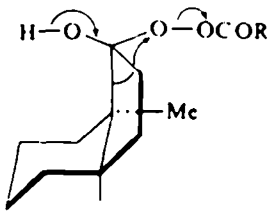
[1] Part V *Tetrahedron* **23**, 2285 (1967).

[2] G. Di Maio and V. Permutti, *Tetrahedron* **22**, 2059 (1966).

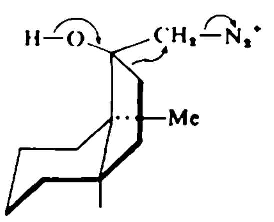
[3] G. Di Maio anc P. A. Tardella, *Tetrahedron* **22**, 2069 (1966).

that in the pinacolic deamination insertion occurs mostly far from the ring junction; in the Baeyer-Villiger reaction it occurs completely near the ring junction and the Schmidt reaction is in an intermediate situation between the former two.

Now if we assume, as is reasonable that VII[4] and VIII respectively represent the ketone-peracid adduct in the Baeyer-Villiger reaction and the intermediate of the pinacolic deamination (the two extreme cases), it is clear that VII leads to lactone VI in spite of a boat transition state, while VIII yields *cis*-9-methyldecalone-1 (II) because of a sterically favoured chair transition state.

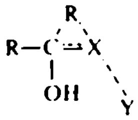


VII



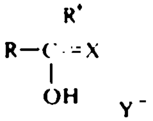
VIII

This case, we think, clearly illustrates how the relative importance of steric and electronic controls can change the passing from one ring expansion reaction to another. Perhaps the simplest and most unitary rationalization of the observed change of control can be found following and amplifying the treatment[5] for the transition state of 1,2-shifts. The American authors wrote the transition state IX as a resonance hybrid among structures IX$_{a-c}$. Each of these structures variably contributes to the hybrid IX depending on the identity of x and y. Thus, when x is a more electronegative



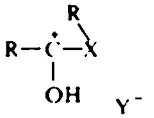
(or Y^+)

IX



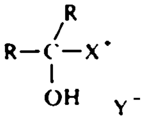
(or Y)

IX$_a$



(or Y)

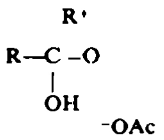
IX$_b$



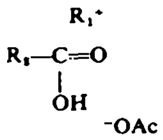
(or Y)

IX$_c$

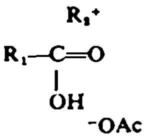
group (say —O—) and y is a weak leaving group (say MeCOO$^-$) structure IX$_a$ gives its greatest contribution to IX. On the other hand, when x is less electronegative (say —CH$_2$—) and y is an effective leaving group (say N$_2$) IX$_c$ gives its highest contribution to the hybrid IX. This means that the transition state of the Baeyer-Villiger reaction is better expressed by formula X whereas the transition state of the



X



X$_1$



X$_2$

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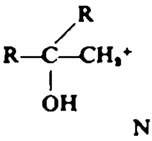
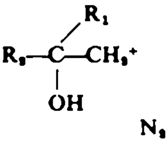
[4] See footnote 8 of the preceding paper.

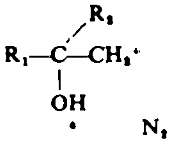
[5] J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.* **81**, 4088 (1959).



XI



XI_1

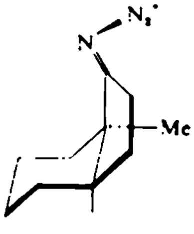


XI_2

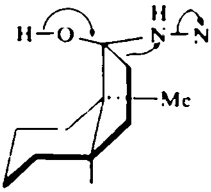
pinacolic deamination is better expressed by formula XI.

Now, if potential migratory groups R_1 and R_2 are different we must write two transition states for the Baeyer-Villiger reaction, each one corresponding to the migration of a group (X_1 and X_2). And we must do the same for the pinacolic deamination (XI_1 and XI_2). It is clear that the lowest energy transition state between X_1 and X_2 corresponds to the migration of the group that can better accommodate the positive charge i.e. the fully substituted one. Therefore the reaction products distribution will mostly be determined by the degree of substitution of the potential migratory groups.

The structures relative to the pinacolic deamination (XI_1 and XI_2) indicate that the electronic work necessary to reach the transition state i.e. to break the bond CH_2—N_2^+ is quite small and, requires no assistance from the remainder of the molecules In these circumstances the work the system must do against steric forces can be far the greatest and we can easily conceive how the lowest energy transition state between XI_1 and XI_2 corresponds to the migration of the alkyl in better steric position to migrate, thus making the degree of substitution of the migrating group of little importance. Very interestingly in the intermediate case of the Schmidt reaction[2] the conflict between migratory aptitudes and chair-boat steric controls seems to be avoided: the existence of two distinct mechanisms allows the migration of the fully substituted carbon atom to proceed *via* intermediate XII without passing through a sterically unfavourable boat transition state. On the other hand lactam V is formed through intermediate XIII because of a sterically favourable chair transition state.



XII



XIII