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MIGRATION APTITUDES OF CYCLIC AND POLYCYCLIC BRIDGEHEAD GROUPS IN THE CRIEGEE REARRANGEMENT

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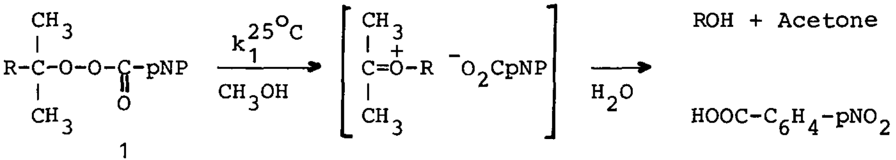
Summary: The migration aptitudes of cyclic and polycyclic bridgehead groups in the Criegee Rearrangement support σ-neighbouring group participation by pentacoordinated bonding and vertical charge stabilisation in the migrating group and therefore favour transition state 2b and not 2a.

The rates of rearrangement of 2-substituted 2-propyl-p-nitroperbenzoates 1 in methanol have been shown to reflect the relative migration aptitudes of the groups R in this type of Criegee Rearrangement$^{1,2)}$.

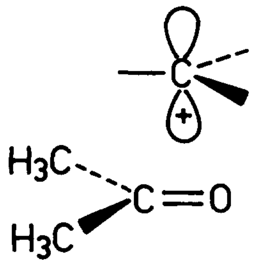


$$R{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}O{-}O{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}pNP \xrightarrow[CH_3OH]{k_1^{25^\circ C}} \left[\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{=}\overset{+}{O}{-}R \quad {}^{-}O_2CpNP\right] \xrightarrow[H_2O]{} \begin{array}{l} ROH + \text{Acetone} \\ \\ HOOC{-}C_6H_4{-}pNO_2 \end{array}$$

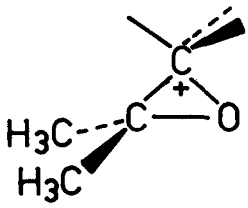
1

pNP = p-Nitrophenyl

From the relative migration aptitudes of $R=CH_3:C_2H_5:2\text{-}C_3H_7:t\text{-}C_4H_9=1:45:3000:2.3\cdot10^5$ $^{1)}$ and the ρ-value of the relative migration rates of substituted benzyl groups $(\rho=-2.1)^{2)}$, it was concluded that R is carrying an appreciable positive charge at transition state of rearrangement. The relative small migration aptitude of the benzyl group $(C_2H_5:C_6H_5CH_2=1:36)^{1,2)}$, however, does not support a high degree of carbeniumion character for R as in transition state 2a, but rather suggests a nonclassical pentacoordinated central carbon atom of R and a vertical charge delocalisation in a transition state like 2b.



2a



2b

This view was supported by the small difference in migration aptitude of R=2-exo- and R=2-endo-norbornyl2) which was interpreted to indicate that at the migrating carbon only small geometrical changes occur during the migration process. In order to get further information about the geometrical situation in the migrating group the migration aptitudes of a series of cyclic and polycyclic bridgehead groups were determined.

Table 1 Solvolysis constants of 2-substituted 2-propyl-p-nitrobenzoates **1** in methanol at 25°C a)

R	10^5k_1 b) [sec^{-1}]	$k_{rel.}$	R	10^5k_1 b) [sec^{-1}]	$k_{rel.}$
2-C_3H_7	1.30(1.03)1)	≡1.0			
t-C_4H_9	(79.4)1)	77	t-C_4H_9	(79.4)1)	≡1.0
Cyclopropyl	0.20	0.15	1-Adamantyl	156c)	19.6
Cyclobutyl	1.16	0.90	1-Bicyclo[2.2.2]octyl	40.3	0.51
Cyclopentyl	1.02	0.78	1-Bicyclo[3.2.1]octyl	14,5	0.18
Cyclohexyl	3.06	2.34	4-Camphyl		(0.06)1)
Cycloheptyl	8.31	6.39	1-Bicyclo[2.2.1]heptyl	0.14	0.002
Cyclooctyl	14.3	10.3			
Cyclononyl	14.8	11.3			
Cyclodecyl	19.1	14.7			
Cycloundecyl	12.7	9.73			
Cyclododecyl	10.1	7.7			

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a) In preparative experiments generally > 82% acetone and ROH were obtained besides an almost quantitative yield of p-nitrobenzoic acid in all examples

b) error ≤ 3% in most cases c) extrapolated from rate data in CH_2Cl_2

The results are very similar to those found in the closely related Beckmann Rearrangement$^{3)}$. The small ring size effect in table 1 is not correlated with solvolysis rate constants of 1-methyl-cycloalkyl chlorides$^{3)}$ and accordingly does not support transition state structure 2a. There is, however, a good correlation between the solvolysis constants in table 1 for the 5-12 membered cycloalkyl derivatives and the $J(^{13}C\text{-}H)$ coupling constants of the corresponding cycloalkanes.

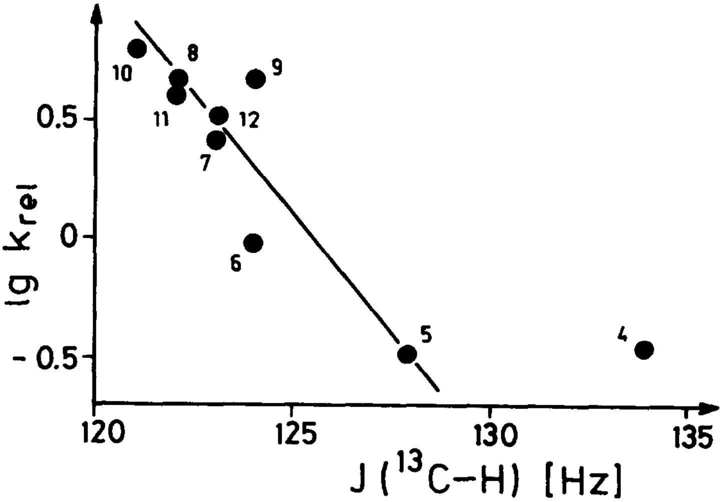

Figure 1 Correlation of the solvolysis constants of 1 (R=cycloalkyl) from table 1 and $J(^{13}C\text{-}H)$ of the corresponding cycloalkanes (ring size = n shown)

A similar correlation for the Beckmann Rearrangement has been interpreted as vertical stabilisation$^{4)}$ of charge on R in a nonclassical transition state with pyramidal geometry at the migrating carbonium center as in 2b. This interpretation is particularly supported by the deviation of the cyclobutyl group towards higher reactivity$^{3)}$. The bridgehead reactivity of table 1 points in the same direction. The higher migration aptitude of 1-adamantyl than of t-butyl and the moderately retarded rates of the small polycyclic bridgehead systems are not in agreement with a transition state like 2a, but rather with 2b. The higher reactivity of adamantyl, which was also observed in the Beckmann Rearrangement$^{3)}$, is due to charge stabilisation by 1.3-interactions (as in the cyclobutyl group mentioned above) and inductive donation by β-branching typical for vertical stabilisation[3,4]. Finally, the relative migration rates of the bridgehead groups in table 1 are linearly related to the rates of solvolysis of bridgehead bromides in 80% ethanol/H_2O (slope=+0.44)[5]. Because of the rigidity of these polycyclic ringsystems this is also compatible with vertical charge stabilisation[3].

Ando[6] and Shiner[7] quite recently concluded on the basis of isotope effects that also the transition state of the related neopentyl rearrangement is stabilized more by nonclassical bridging (transition state related to 2b) than by hyperconjugation (transition state related to 2a). The above mentioned relative large migration aptitudes of tertiary alkyl vs. primary alkyl and the comparatively large[3] rate acceleration for 1 (R=benzyl) indicate that the hyperconjugation component in the Criegee Rearrangement is probably still larger than in most other 1.2-shifts[2,3].

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