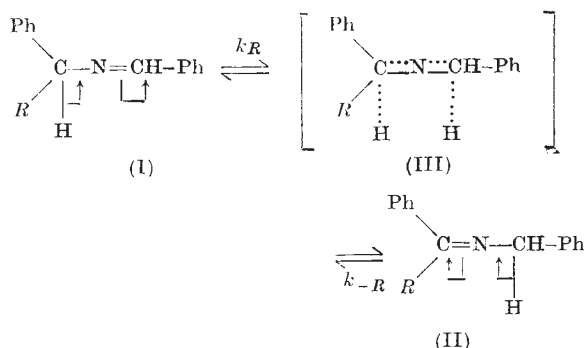


Influence of Alkyl Groups in the Prototropic Change in Methyleneazomethines

ARGUMENTS for and against control by either polar or steric effects of the course and rate of substitution and elimination reactions have recently been given¹⁻³. The concept of steric assistance has been specially stressed as an important factor in determining relative rates of unimolecular eliminations of highly branched alkyl compounds^{3,4}; in contrast to this positive steric factor, negative steric effects (connected with classical steric hindrance) play an important part in bimolecular nucleophilic substitution reactions⁵. It has been suggested³ that these steric effects can account for the known facts about nucleophilic substitutions and eliminations of alkyl compounds without need of special considerations regarding polar, particularly inductive, effects.

In connexion with these arguments, we should like to put forward some results, obtained in our laboratories, which, we think, bear on the question of the relative importance of steric and polar effects in heterolytic reactions.

Our work deals with the mechanism of prototropic change in methyleneazomethines; this is a base-catalysed synchronous S_E2' reaction⁶. The effect of alkyl groups on rate has now been examined⁷⁻¹⁰. The system under study is:



in which $R = H, Me, Et, Pr^i, Bu^t$. Reactions have been conducted under the conditions stated in Table 1, where specific first-order rate-constants are given. Alkyl derivatives have been studied by the method of loss of optical activity starting with the optically active compound (I)⁷, and by spectroscopic estimation of mixtures of isomeric azomethines starting with pure (I) or (II)⁸. The prototropic change in benzylidenebenzylamine ($I = II, R = H$) has been followed by isotopic tracer technique using azomethine labelled with carbon-14¹⁰.

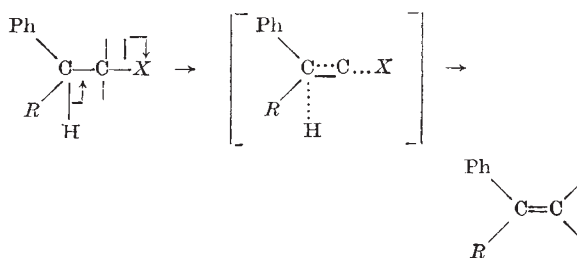
Table 1. SPECIFIC RATE-CONSTANTS (k IN HR.⁻¹) FOR THE PROTROPIC CHANGES OF METHYLENEAZOMETHINES IN 1.3 *N* SODIUM ETHOXIDE IN ETHYL ALCOHOL (60 PER CENT)-DIOXAN (40 PER CENT) AT 50°. CONCENTRATION OF AZOMETHINE, 0.4 *M*

<i>R</i>	k_R	k_{-R}
H	1.7	1.7
Me	0.132	0.096
Et	0.0112	0.0091
Pr ⁱ	0.0059	0.0046
Bu ^t	0.0034	0.0023

It can be seen that the result of introducing alkyl groups either in the carbon atom from which a proton departs, or in the one attacked by a proton, is to lower reaction-rate.

Now, if the removal of a proton by a base is considered as the important process in the prototropic

change, this could be compared with the appropriate bimolecular elimination reaction:



since, in both processes, an electron pair, forming initially a C—H bond, is shifted to form a double bond between that carbon atom and the nitrogen or carbon atom next to it, which, in turn, gives away another electron pair.

Accordingly in the forward prototropic change ($I \rightarrow II$), the inductive effect of R should oppose the departure of a proton from the R -substituted carbon atom. This will give values of k_R decreasing in the order $H > Me > Et > Pr^i > Bu^t$ in agreement with the experimental results. The electronic shift which takes place in the backward reaction ($II \rightarrow I$), as shown in (II), will be also opposed by inductive release from R , giving again a sequence of k_{-R} corresponding to that found experimentally.

On the other hand, hyperconjugation arising in the transition state of the forward reaction cannot be made responsible for the sequence of rates; since, if it were responsible, alkyl derivatives should react more quickly than benzylidenebenzylamine. In the backward reaction hyperconjugative control fails also to account for the experimental results, since it would give the minimum rate to the more hyperconjugated methyl-substituted (II). Small contributions due to hyperconjugation are considered, as will be shown in more detail elsewhere¹⁰.

Steric assistance seems to play no important part in these reactions; because, in the forward reaction, in which R is systematically changed at the proton-departing carbon atom, the sequence of rates would be opposite to that experimentally found. This could, of course, be presumed on account of the small size of the group leaving.

It can be concluded that alkyl substituents, introduced at the proton-departing or at the proton-attacked carbon atoms in these prototropic changes, exert Hofmann-type influences, which can be accounted for by inductive control.

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