give the relative positions of $n^\pi$ and $\pi^\sigma$ orbitals which change with substitution, so that the $n^\pi$ orbital lies below the $\pi^\sigma$ orbital for the most basic oximes.

A similar situation is found with cyclic diazines. The (lone-pair) IP, of pyridazine which shows enhanced reactivity towards both acylating and alkylating agents\(^5,11\) is found to be ca. 0.5 eV lower than the values normally found for other nitrogen heterocycles (lying close to that of benzene (9.25 eV)) for the removal of $\pi^\sigma$ electrons.\(^12\)

References

Lytic activation as well as acid catalysis led again to the same lack of specificity and generality (7, 8, 9).

On the other hand, the determining influence of the transition metal (probably through initial formation of an EDA-metal complex) is also reflected in the first-order dependence on the rhodium concentration found by spectroscopic and volumetric measurements.

Further work is in progress to better define mechanistic and preparative aspects of this method. For instance, methylation of alcohols by gaseous diazomethane seems to be particularly promising. However, the most interesting development will be probably the formal extension of the Sandmeyer reaction to aliphatic diazo compounds, since first studies with aqueous solutions of NaCl, KBr and KI show an important competition between the nucleophilic anions and the hydroxyl group to yield the corresponding halogenoacetates.

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CONSTITUTIONAL EFFECTS ON THE COMPETING SYN- AND ANTI-PATHWAYS IN
BIMOLECULAR ELIMINATION: COMMENTS ON THE BROWN-INGOLD CONTROVERSY$^1,$$^2$

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The question whether steric$^5$ or polar$^6$ effects control the course of E2 reactions
in open-chain systems was discussed earlier during past decades and opposing views
(Brown-Ingold controversy) remained irreconcilable.$^7$ Our discovery that E2 reactions do
not always proceed homogeneously by the anti-mechanism, as it was originally anti-
cipated, but may represent a blend of two mechanistic (syn- and anti-) pathways$^6$ placed
the "old" problem into a new light. In particular, it showed that the constitutional effect in
both the competing pathways has to be examined, at least in those processes where
the dual elimination mode is pronounced.

This, obviously, poses a task of a very considerable complexity which can be
approached unambiguously only by combination of kinetic data from appropriate reaction
series and "static" data for the proportions$^8$ of the participating mechanisms to the
individual olefin-isomer formation. Earlier approaches based only on the kinetic$^3,$ and on the
"static"$^9$ data are bound to be uncertain, and, hence, eventually, to incorrect
conclusions.

We now wish to report an approximate analysis of the complex problem for the E2
reaction of the alkylbromodialkylammonium chlorides 1 with potassium t-butoxide in t-butanol.
Standard kinetic procedures employing an efficient \textit{v.p.c. technique}$^6$ allowed a quantitative
determination of the overall (syn + anti) rate constants for the individual olefin-isomer formation ($k_2\text{-}k_4$ and $k_5\text{-}k_7$). Next, the overall rate constants for the trans-alkenes
formation ($k_1$ and $k_2$) were dissected into the syn- and anti-components ($k_1\text{-}k_2\text{-}II$ \textit{and} $k_1\text{-}k_2\text{-III}$, \textit{respectively}). For some derivatives it could be par-

\[ \begin{align*}
  \text{RCH}_2\text{CH}_2\text{Bu}^+ & \xrightarrow{L\text{-BuOK}} \text{RCH}_2\text{CH}_2\text{Bu} \quad \text{(I)} \\
  \text{NMMe}_3 & \xrightarrow{t\text{-BuOM}} \\
 \end{align*} \]

\[ \begin{align*}
  k_1 & \text{trans} \quad \text{RCH}_2\text{CH}_2\text{CHBu} \text{ (I-II)} \\
  k_2 & \text{cis} \quad \text{RCH}_2\text{CH}_2\text{CHBu} \text{ (I-II)} \\
  k_3 & \text{trans} \quad \text{RCH=CH}_2\text{Bu} \text{ (I-III)} \\
  k_4 & \text{cis} \quad \text{RCH=CH}_2\text{Bu} \text{ (I-III)} \\
 \end{align*} \]

\[ R = H, \text{Me}, \text{Et}, \text{Pr}, \text{i-Pr}, \text{t-Bu} \]

formed quantitatively, on the basis of the reported$^{10}$ contributions of the two alternative
pathways to the particular isomer formation. For other derivatives, where the data were
not available, values from closely related systems$^{11,12}$ had to be used in the calculation.