

give the relative positions of  $n^*$  and  $\pi^0$  orbitals which change with substitution, so that the  $n^*$  orbital lies below the  $\pi^0$  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<sup>5,11</sup> 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  $\pi^0$  electrons.<sup>12</sup>

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#### TRANSITION METAL CATALYSED REACTIONS OF DIAZOCOMPOUNDS - II INSERTION IN THE HYDROXYLIC BOND

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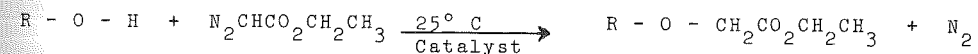
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Since the pioneer work of Meerwein and co-workers on the reaction between methylene and 2-propanol (1) and of Yates on the copper-catalysed decomposition of diazoketones in alcohols and phenols (2), insertion of various carbenes and carbenoids in hydroxylic bonds has been largely investigated. In the course of our study of the transition metal-catalysed (3) reactions of diazoalkanes, we have already succeeded in demonstrating the feasibility of a selective and quantitative cyclopropanation of olefins in the presence of palladium salts with some degree of stereocontrol (4).

We are now able to report an homogeneous rhodium-catalysed insertion of ethyl diazoacetate (EDA) in the hydroxylic bond of alcohols, water and weak acids :



These reactions are nearly quantitative at room temperature, even with very low catalyst concentrations. In each case, the balance is mainly constituted of ethyl maleate and fumarate resulting from the formal dimerization of the corresponding carbene. Some of our results are summarized in the following table.

Catalyst	EDA Catalyst	R	% Yield
Rh <sub>2</sub> (OAc) <sub>4</sub>	600	C <sub>2</sub> H <sub>5</sub> -	88
Rh <sub>2</sub> (OAc) <sub>4</sub>	600	(CH <sub>3</sub> ) <sub>2</sub> CH -	83
Rh <sub>2</sub> (OAc) <sub>4</sub>	600	(CH <sub>3</sub> ) <sub>3</sub> C -	82
Rh <sub>2</sub> (OAc) <sub>4</sub>	600	H -	80
Rh <sub>2</sub> (OAc) <sub>4</sub>	600	CH <sub>3</sub> CO -	93
Rh Cl <sub>3</sub> ·3 H <sub>2</sub> O	125	C <sub>2</sub> H <sub>5</sub> -	64
Rh Cl <sub>3</sub> ·3 H <sub>2</sub> O	125	(CH <sub>3</sub> ) <sub>3</sub> C -	58
Rh Cl(PPh <sub>3</sub> ) <sub>3</sub>	125	C <sub>2</sub> H <sub>5</sub> -	49

Reactions were carried out using the corresponding alcohol as solvent (50 cc) and adding at a constant rate  $5 \cdot 10^{-2}$  mol. of EDA in 4 h. with a dropping funnel. All the products obtained were identified by their physical properties.

As shown in the table, ethoxycarbonylcarbene is inserted with equal efficiency in the hydroxylic bond of ethanol and t-butanol. However, competitive reactions with equimolecular mixtures of alcohols gave the following relative reactivities of OH bond toward attack by the carbethoxycarbene produced by this catalytic way :  
ethanol 2.12, propan-2-ol 1.20, and t-butanol 1.00. This is also the order of decreasing acidity of the alcohols as well as the order of increasing steric hindrance.

Photolysis of diazomethane in the same alcohols give a similar order of reactivity (5) : however, by-products resulting from C - H insertion are also formed which are not found in the present catalytic reactions.

The specificity and generality of our system is to be compared also with the cupric chloride-catalysed decomposition of EDA in various alcohols which afforded OH insertion products only in low yields (6). Thermal and photo-

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 dependance 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 diazocompounds, 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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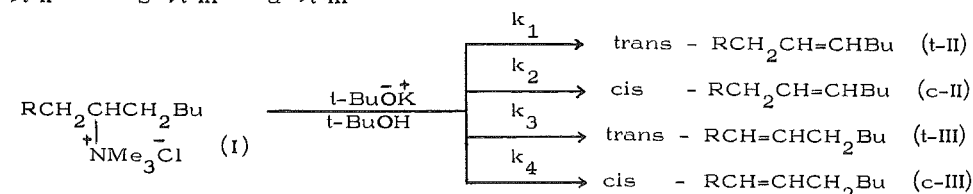
CONSTITUTIONAL EFFECTS ON THE COMPETING SYN- AND ANTI-PATHWAYS IN BIMOLECULAR ELIMINATION: COMMENTS ON THE BROWN-INGOLD CONTROVERSY<sup>1,2</sup>M. Pánková and J. Závada<sup>3\*</sup>Institute of Organic Chemistry and Biochemistry,  
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The question whether steric<sup>3</sup> or polar<sup>4</sup> effects control the course of E2 reactions in open-chain systems was discussed ardently during past decades and opposing views (Brown-Ingold controversy) remained irreconciled<sup>5</sup>. Our discovery that E2 reactions do not always proceed homogeneously by the anti-mechanism, as it was originally anticipated, but may represent a blend of two mechanistic (syn- and anti-) pathways<sup>6</sup> 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<sup>6,7</sup> of the participating mechanisms to the individual olefin-isomer formation. Earlier approaches based only on the kinetic<sup>4</sup>, or on the "static"<sup>7</sup> data are bound to be uncertain, and lead, eventually, to incorrect conclusions.

We now wish to report an approximate analysis of the complex problem for the E2 reaction of the alkyltrimethylammonium chlorides I with potassium t-butoxide in t-butanol. Standard kinetic procedures employing an efficient v.p.c. technique<sup>8</sup> allowed a quantitative determination of the overall (syn + anti) rate constants for the individual olefin-isomer formation ( $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ ). Next, the overall rate constants for the trans-alkenes formation,  $k_1$  and  $k_3$ , were dissected into the syn- and anti-components ( $k_{s \rightarrow t-II}$ ,  $k_{a \rightarrow t-II}$  and  $k_{s \rightarrow t-III}$ ,  $k_{a \rightarrow t-III}$ , respectively). For some derivatives it could be per-



R = H, Me, Et, Pr, i-Pr, t-Bu

formed quantitatively, on basis of the reported<sup>6a</sup> 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<sup>6a,7</sup> had to be used in the calculation.