PRJ, Vol. 4. (January 1992); P. 63–67, 5 FIGS.

Short Note

BUTADIENE REACTIONS USING THE EROS 5.0 COMPUTER PROGRAM

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تفاعلات البوتاديين باستخدام برنامج الحسوب EROS 5.0

طارق القماطي وكلاوس رافينر

تم دراسة تفاعلات البوتاديين مع متفاعلات مختلفة ، باستخدام برنامج الحسوب EROS 5.0 الذي تم برمجته وتطويره من قبل البروفسور قاستيقر ومجموعته بجامعة ميونخ التقنية .

وقد تم بالفعل الحصول على مجموعة كبيرة من النتائج الإيجابية لمجموعة من المركبات التجارية بتفاعل البوتاديين والماء والكلور والأمونيا وسيانيد الهيدروجين والهيدروجين .

INTRODUCTION

This study is intended to provide a picture of the probable products that can be produced when butadiene reacts with different reagents.

Industrial processes are largely determined by thermodynamic considerations. Only if a reaction is exothermic can the search for an appropriate catalyst begin. Therefore, as a guide to the evaluation of the different reaction pathways and products, the heats of reaction are investigated.

Butadiene is considered as one of the most important starting materials under (C_4–C_5) [1]. As a monomer and a comonomer it was used for synthesis of elastomer thermoplastics and dispersion. Also because of the fact that it is an inexpensive byproduct, makes it one of the most important starting materials in industry.

Gasteiger [5, 6] and his group have been working in writing and developing the EROS program (Elaboration of Reaction for Organic Synthesis) for the last 15 years. This program system can be used for the production of organic reactions and for the design of organic synthesis.

PREDICTION OF REACTION-DESIGN FOR SYNTHESIS

EROS [4] (Elaboration of Reactions for Organic Synthesis) is a system of computer programs which generates sequences of organic chemical reactions. It can be applied to two different types of problems depending on how the reactions are interpreted.

In a forward strategy it is assumed that the chemical reactions proceed in the same direction as they are obtained from the program. From the starting materials, that are inputs, their products in a chemical reaction can be predicted. The following types of problems can be studied.

- Prediction of the products of a chemical reaction
- Prediction of metabolic pathways
- Prediction of the degradation of a chemical in the environment
- Search for the synthetic uses of an industrial byproduct

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- Elucidation of the structure of a reaction product
- Generation of all isomers with a given empirical formula

If the reactions, as output by the program, are considered to be reverses of chemical reactions, i.e. retrosynthetic steps, then the program can be used for the planning of synthesis. In such a backward (retrosynthetic) strategy the input structure is the target of a synthesis, and one is searching for reactions and precursors leading to this compound. By such an approach, problems of synthesis design can be studied. These include:

- Design of chemical synthesis, ranging from laboratory procedures to large scale industrial processes
- Study of biochemical pathways

It is an essential feature of EROS that reactions are not taken from a database of known reactions. Rather, chemical reactions are perceived as bond-breaking and making, and electron-shifting processes. This allows the generation of all conceivable reactions, irrespective of whether a reaction is known or not. Thus, novel reactions may be found.

EROS can be applied to seek answers to two fundamental questions of major importance to an organic chemist. First, how can a desired compound be synthesized and second what is the product of such reaction?

Obviously, answering these two questions requires a deep insight into organic chemistry. Reaction prediction asks for a knowledge of the course of organic reactions, a knowledge of chemical reactivity. Synthesis design requires, on top of these capabilities, to develop strategies and plan for approaching a synthesis problem. Incomplete as our knowledge as chemists is in these fields, it cannot be expected that a computer program can solve these problems straight away.

Because of the difficulties of predicting the outcome of complex organic reactions and planning of the synthesis of organic compounds, all means to solve these problems must be considered.

Therefore, the utilization of the computer by chemists to tackle problems of reaction prediction and synthesis design is essential.

In this sense, EROS should be considered as an instrument for the chemist to analyse and seek solutions to the problems at hand. Various options are offered to the user to specify initial conditions. The more a chemist makes use of these options to specify clearly the initial conditions, the closer he gets to the optimum results.

GENERATION OF REACTIONS

An essential feature of the logic behind EROS is to use electron shifting schemes as generators for chemical reactions. The electrons that are shifted in a chemical reaction may be located in bonds (breaking or making of bonds) or they may be free electrons on atoms. Thus it becomes clear how important it is to take into account all valence electrons. Since, in chemical reactions, electrons may be converted from free electrons to bonding electrons, or vice versa. Working with formal reaction schemes allows the generation of all conceivable chemical reactions, irrespective of whether they are known or without precedence. Additionally, novel (and promising) reactions are obtained and it is up to the chemist to try to verify them in the laboratory. In this way, new inventions may be initiated.

Reaction schemes are not unfamiliar to an organic chemist. In fact, he uses them routinely in the discussion of reaction mechanisms. There, the electron shifts occurring in a reaction are indicated by curved arrows.

In EROS Version 5.0 several such reaction schemes are contained. They correspond to overall bond change patterns observed frequently and found in important organic reactions. They can be selected by the user or are invoked by default. For example, a very common reaction scheme involves the breaking and making of two bonds (reaction generator RG 22: Fig. 1).

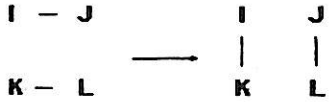


FIG. 1. An important reaction scheme: breaking and making two bonds.

GENERATION OF REACTIONS – THE OPTION "REAGEN"

Working with complete sets of formally possible reaction generators, as was done in the EROS precursor system CICLOPS, leads to reactions of various complexity (mechanistic steps and complete reactions) and varying chemical importance. Thereby, the system becomes rather inaccessible to general evaluation procedures. In EROS 5.0 therefore, only carefully selected reaction schemes are used. Although this leads to neglecting certain chemical reactions types, the selection of the schemes is such that the majority of chemically important organic reactions are encompassed. This applies to the presently known reactions but it is believed that this will also be true for new reactions. The selection of reaction schemes is supported by statistical analyses.

The reaction schemes contained in EROS comprise changes in the electron distribution which are normally considered as complete chemical reactions. Thus, starting with neutral molecules. But they are also applicable to reactions of charged and other reactive intermediates. Note that these reaction schemes give only the overall result of the electron shifts in a reaction. They are not concerned with the timing of the bond breaking and making. Thus, both concerted and stepwise processes are represented by these reacting schemes.

Presently there are two reaction schemes in EROS 5.0. Two bonds are broken and two are made in this reaction scheme (Fig. 2).

Note that both conceivable permutations for bond making are considered. This reaction scheme comprises the majority of organic reactions: substitution, addition, and elimination reactions, as well as other types, such as certain electrocyclic reactions.

In the reaction scheme (Fig. 3) three bonds are broken and three bonds are made.

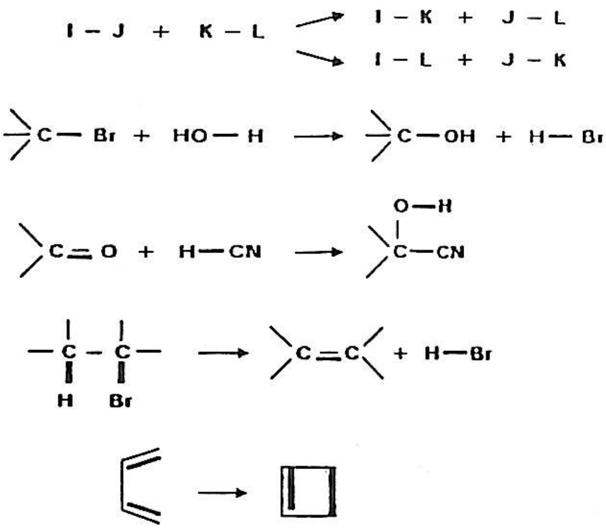


FIG. 2. Reaction scheme RG 22, breaking and making two bonds.

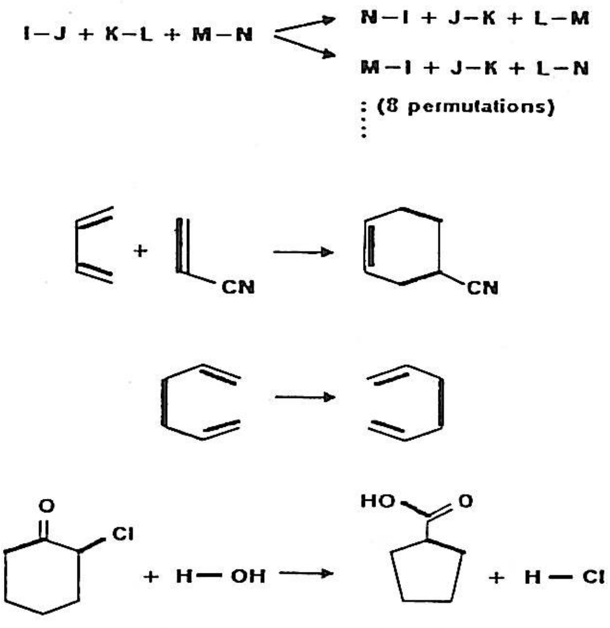


FIG. 3. Reaction scheme RG 33, breaking and making three bonds.

Many important reactions follow this electron shifting pattern e.g. the Diels–Alder reaction or the Cope rearrangement. As an example for a stepwise process the Favorski rearrangement is given.

Several reactions were studied as described in the following paragraph starting from butadiene and reacting with different reagents [2, 3]. This is shown in Fig. 4.

These reactions gave a good range of products from which we then chose the logical and the probable ones. We considered reaction enthalpy as the most important factor. Only exothermic reactions were selected, since they are thermodynamically favored. From this point of view the products were chosen as shown in Fig. 5.

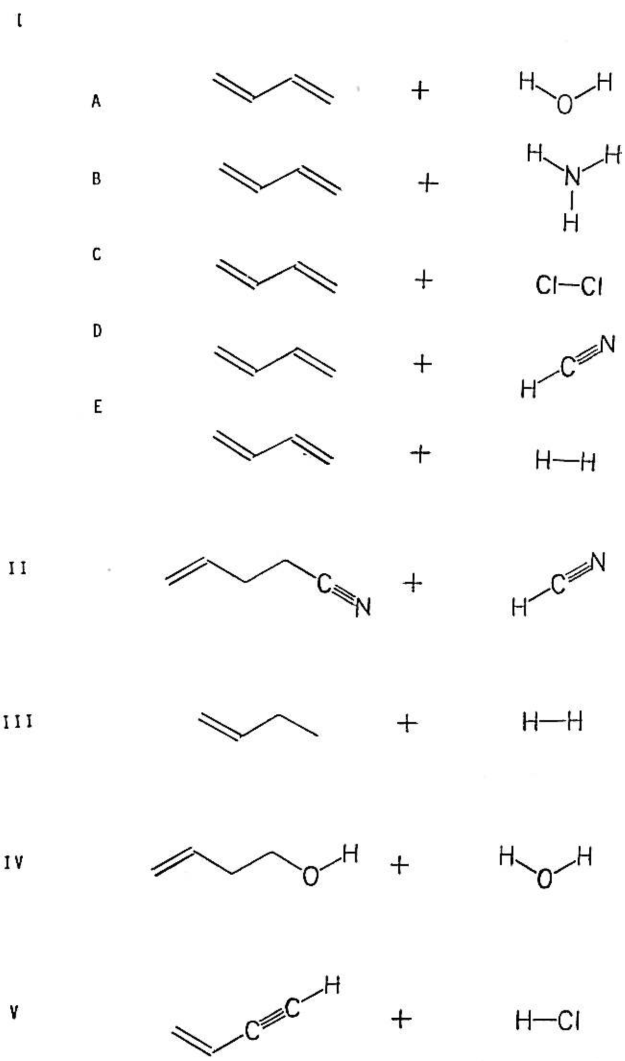


FIG. 4. The studied reaction of butadiene with different reagents and some other relevant reactions.

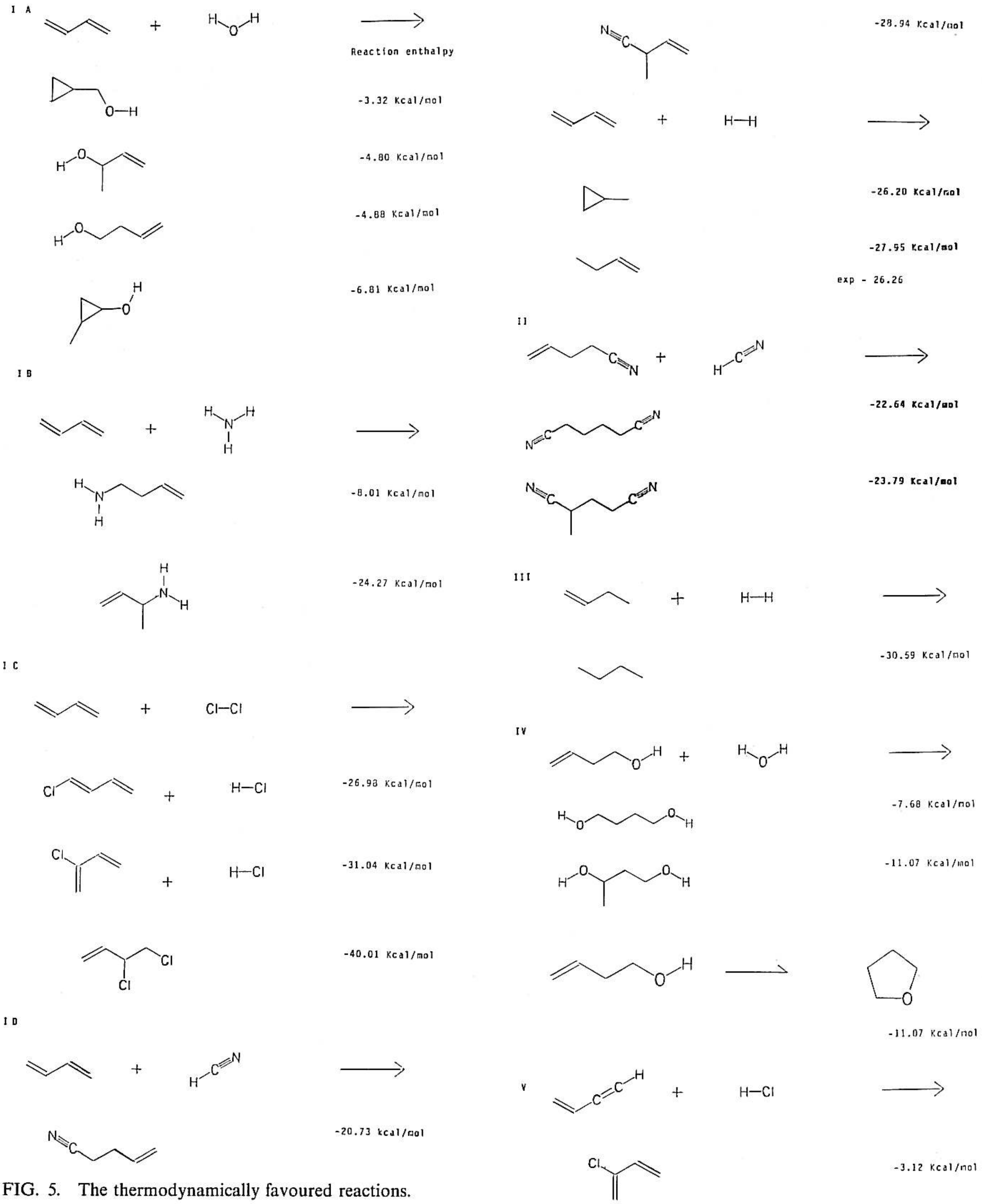


FIG. 5. The thermodynamically favoured reactions.

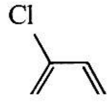
CONCLUSION

EROS can be used to study potential products derived from butadiene

(a) $+H_2O$ 1.4 butane-diole, tetrahydrofuran } commercial products

(b) $+NH_3$ incomplete study
only a first level intermediate follows reaction of these intermediates with other reagents e.g. with O_2.

(c) shows application of EROS to both addition and substitution of butadiene with chlorine.
Chloroprene commercial products.



for synthetic rubber exothermic reaction, can also be obtained in a two step procedure through addition and elimination of HCl.
Alternative processes from vinylacetylene are also favorable and commercially proven.

(d) +HCN adiponitrile commercial products.

(e) $+H_2$ for comparison with experimental Hf °

The calculated heats of reaction [2, 3] show which reactions are thermodynamically favoured (exothermic) and therefore it is of interest to look for suitable catalyst to realise such a reaction.

ACKNOWLEDGEMENT

We would like to express our deep appreciation and gratitude to Prof. Dr. J. Gasteiger for his guidance and valuable discussions in preparing this work.

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