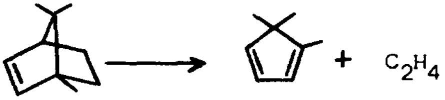
Tetrahedron Letters No.60, pp. 6327-6330, 1968. Pergamon Press. Printed in Great Britain.

THE GAS PHASE RETRO-DIELS-ALDER REACTION OF BORNYLENE. A QUESTION CONCERNING PYROLYTIC REACTIONS OF BORNYL AND ISOBORNYL HALIDES AND ESTERS (1)

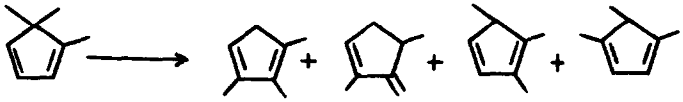
William C. Herndon (2)
Department of Chemistry, Texas Technological College, Lubbock, Texas 79409
Jerald M. Manion (3)
Department of Chemistry, University of Mississippi, University, Mississippi

(Received in USA 29 May 1968; received in UK for publication 20 November 1968)

Bornylene (3,7,7-trimethylbicyclo[2.2.1]hept-2-ene) undergoes a retro-Diels-Alder reaction at elevated temperatures in the gas phase to yield ethylene and 1,5,5-trimethylcyclopentadiene. The product 1,5,5-trimethylcyclopentadiene is unstable and a methyl shift occurs, giving rise to an equilibrium mixture of four C_8 hydrocarbons (4).



(1)



(2)

We have studied these reactions in stirred flow reactor systems which have been described in detail previously (5). We established that reactions 1 and 2 are both first-order and homogeneous in the temperature range 328-430°C. The activation parameters are $\Delta H_1^{\ddagger}$ = 44.73 (±0.86) kcal/mole, $\Delta S_1^{\ddagger}$ = 2.29 (±1.34) e.u., and $\Delta H_2^{\ddagger}$ = 43.83 (±1.25) kcal/mole, $\Delta S_2^{\ddagger}$ = 0.75 (±1.93) e.u. The indicated errors are standard deviations from a least squares regression line.

The results for the bornylene decomposition which we have outlined above raise a question concerning the reported results of the pyrolyses of bornyl and isobornyl acetates (6) and chlorides (7,8). Upon pyrolysis in the gas phase each of these compounds is said to yield a mixture of $C_{10}H_{16}$ hydrocarbons identified as tricyclene, camphene, and bornylene, with results summarized in table 1.

The identification of camphene and tricyclene as major products of these pyrolyses serves as part of the supporting evidence for "quasi-heterolytic" mechanisms (ionic transition states) in gas phase elimination reactions (8,9). We wish to question the obtention of bornylene as a major product, and thus by inference the quantities of camphene and tricyclene in the reaction mixtures.

TABLE 1

Hydrocarbon Products from Pyrolysis of Bornyl Derivatives

Product Reactant	Tricyclene	Camphene	Bornylene
Bornyl acetate (6)	23.3%	14.8%	61%
Isobornyl acetate (6)	31.5	48.4	20.1
Bornyl chloride (7)	55	25	20
Isobornyl chloride (8)	5	70	25

The rate constants at 340°C. for the pyrolysis of each of the four compounds in table 1 and for bornylene decomposition are: bornyl acetate 1.23×10^{-4} (0.75×10^{-4}), isobornyl acetate 8.02×10^{-4} (1.61×10^{-4}), bornyl chloride 1.84×10^{-4} (0.37×10^{-4}), isobornyl chloride $\sim 20 \times 10^{-4}$ ($\sim 5 \times 10^{-4}$), and bornylene 85.1×10^{-4}. These rate constants are in units of sec^{-1}, calculated from the activation parameters given in the cited papers (6-8). The parenthetical values are rate constants for formation of bornylene assuming the distribution of products given in table 1. One notes that the rate constant for decomposition of bornylene is several times larger than any of the formation constants.

If one assumes a pattern of consecutive and simultaneous reactions as outlined in eq. 3, the fraction of bornylene in the product mixture can be estimated. For this calculation the rate constants for formation of camphene, tricyclene, and bornylene are assumed proportional to the percentages given in table 1. At 340°, in the case of isobornyl chloride, at 20% total conversion to products, the product mixture should contain approximately 17% bornylene and 8% bornylene decomposition

$$\begin{tikzcd}
 & & \text{camphene (C)} & \\
\text{Bornyl acetate (A)} \arrow[urr, "k_C"] \arrow[rr, "k_A"] \arrow[drr, "k_T"] & & \text{bornylene (B)} \arrow[r, "k_B"] & \text{other products (P)} \\
 & & \text{tricyclene (T)} & (3)
\end{tikzcd}$$

$$A = A_o e\ -(k_A + k_C + k_T)\ t$$

$$B = (e^{(-k_A t)} - e^{(-k_B t)})\ (k_A A_o)/k_B - k_A)$$

products, the remainder consisting of tricyclene and camphene. These figures are in rough agreement with the literature values (6) (table 1), except for the missing bornylene decomposition products. However, the amount of bornylene in the product mixture would decrease drastically as the reaction proceeds, being only 4.9% of the products at 80% conversion. In the case of bornyl acetate, at 20% total conversion to products, the product mixture should contain only 3.9% bornylene, and over 56% of bornylene decomposition products should be obtained. Calculated results and experimental results (table 1) also do not correspond for bornyl chloride and isobornyl acetate.

One possible explanation for the discrepancies between the calculated and experimental distributions of products, is that the C_8 fragments (eq. 2) polymerized or dimerized, and were then not easily evaluated by the gas chromatographic techniques used for hydrocarbon analysis. If the samples were condensed before analysis, dimerization or polymerization becomes quite likely. In our work on the bornylene pyrolysis it proved necessary to take gas samples directly from the hot reactor in order to obtain a correct analysis of the reacting gas.

If the above explanation is correct, a reevaluation of the importance of rearrangement reactions in these gas phase pyrolytic reactions will become necessary. We believe that the rearrangement products might be the products of reactions other than the gas-phase unimolecular pyrolyses.

Acknowledgment

We gratefully acknowledge grants from the National Science Foundation (GP-247) and from the Petroleum Research Fund of the American Chemical Society (3069-A4) which helped to support this work.

References

1. Taken in part from a dissertation submitted by J. M. Manion to the faculty of the University of Mississippi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
2. Author to whom inquiries should be addressed.
3. Defense Education Act Fellow (1962-1965), present address, Department of Chemistry, State College of Arkansas, Conway, Arkansas.
4. W. C. Herndon and J. M. Manion, J. Org. Chem., in press (1968).
5. W. C. Herndon, M. B. Henley and J. M. Sullivan, J. Phys. Chem., **67**, 2843 (1963); W. C. Herndon and L. L. Lowry, J. Am. Chem. Soc. **86**, 1922 (1964).
6. E. U. Emovon, J. Chem. Soc. (B), 588 (1966).
7. R. C. Bicknell and A. Maccoll, Chem. and Ind. 1912 (1961).
8. A. Maccoll, in The Transition State, Special Publication of the Chemical Society No. 16 (1962), p. 170.
9. For the most recent review article, A. Maccoll and P. J. Thomas, Progress in Reaction Kinetics, ed., C. Porter, Pergamon Press, Oxford (1967), pp. 119-148.