Ion Cyclotron Resonance Study of the Mechanism of the Loss of C_3H_6 from the Molecular Ion of n-Butylbenzene

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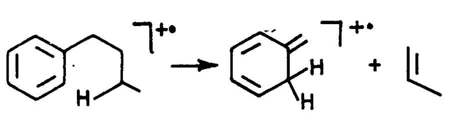
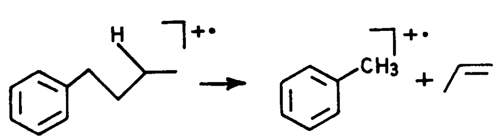
Summary The $C_7H_8{}^{+\bullet}$ ions from n-butylbenzene differ in reactivity from those of toluene, most likely because of differing structure.

THE rearrangement of alkylbenzenes involving α-cleavage with transfer of a hydrogen atom from the alkyl chain to the aromatic portion, observed in 1955,[1] has been shown to involve the γ hydrogens predominantly at 70 eV,[2] and to have a substantial kinetic shift.[3] A number of pathways may be suggested for the reaction, for example equations (1) and (2). Substituent-effect studies have been interpreted to implicate reactivity of the *ortho* position as a "driving force" for the reaction,[4,5] but it is not certain if substituent effects alter reactivity in a way which clarifies or obscures the reactivity of the unsubstituted compound.


(1)


(2)

The ionic product of equation (2) is taken as the structure of low-energy toluene molecular ion with insufficient energy to rearrange to the cycloheptatriene structure (or to decompose). Our evidence opposes equation (2).

Recently we demonstrated by ion cyclotron resonance that the $C_7H_8{}^{+\bullet}$ ion from toluene exhibits the ability to abstract NO_2 from neutral alkyl nitrates, giving a nitrated intermediate possibly reminiscent of the intermediate in nitration of toluene in solution; cycloheptatriene and norbornadiene do not undergo this reaction.[6] This $C_7H_8{}^{+\bullet}$ ion has been studied under similar conditions. At an ionizing energy of 30 eV and pressures of $0{\cdot}3\,\mu$Torr and $4{\cdot}7\,\mu$Torr for n-butylbenzene and isopropyl nitrate respectively, there is no detectable evidence of the NO_2 abstraction reaction by the rearrangement product $C_7H_8{}^{+\bullet}$. The expected product at *m/e* 138, equation (3), is formed at a rate no greater than 1% of that from toluene molecular ions; we have been unable to observe it under any conditions.

$$C_4H_9Ph^{+\bullet} \rightarrow C_7H_8{}^{+\bullet} + Pr^iONO_2 \rightarrow C_7H_8NO_2{}^{+} \qquad (3)$$

Thus the ion formed by the rearrangement of n-butylbenzene is grossly different from toluene molecular ion. Not even a detectable fraction exhibits the same reactivity, under our conditions for analysis or indeed any ionizing voltage between 14 and 70 V; under these same conditions the abstraction of NO_2 by toluene molecular ion may be detected by ion ejection techniques and forms an appreciable fraction of the *m/e* 138 ion. Our earlier result showed[6] that at least a fraction of the molecular ions formed from toluene do not have enough energy to attain a rearranged structure such as the cycloheptatriene formulation suggested by several groups,[7,8] and that this fraction can be differentiated experimentally. If the $C_7H_8^{+\cdot}$ ions from butylbenzene had the same possibilities for structures as the toluene molecular ions at a given ionizing energy, then the distribution of structures would be distorted toward those of lower internal energy, since part of the original internal energy of the butylbenzene ion must be used to form $C_7H_8^{+\cdot}$. Then an even greater fraction of the $C_7H_8^{+\cdot}$ ions from butylbenzene should not expand into the unreactive[6] cycloheptatriene form and should enter into the reaction with the nitrate. They do not. Hence our results are generally inconsistent with arguments based on different reactivities due to different internal energy distribution alone.

This is the first direct evidence that an ion with the toluene-molecular-ion structure (or any $C_7H_8^{+\cdot}$ structure reacting with isopropyl nitrate) is not formed by the loss of C_3H_6 from the molecular ion of n-butylbenzene. It is consistent with earlier contentions[9] that the reaction proceeds through a six-membered activated complex, as in equation 1.

We acknowledge support by the Alfred P. Sloan Foundation, the National Science Foundation, and the National Institute of General Medical Sciences. The Varian ICR-9 spectrometer was purchased through support by Hercules, Inc., the Shell Companies Foundation, the National Science Foundation, and the North Carolina Board of Science and Technology.

(*Received, August* 19*th*, 1971; *Com.* 1460.)

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