Chemical Consequences of Electron Impact. Neutral C_4H_8 Fragments Expelled from Molecular Ions in the Gas Phase[1]

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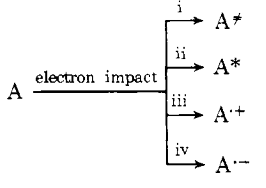
Abstract: An electron bombardment flow (EBFlow) reactor has been constructed to explore the possibility that neutral species expelled in mass spectrometric rearrangements may be collected and analyzed. Care has been taken to select a substrate whose molecular ion is expected to give products which ought not arise as a consequence of vibrational or electronic excitation. *n*-Butyl phenyl ether (**1**) has been chosen because of the variety of ways in which the ionized functionality can interact with the alkyl side chain. EBFlow radiolysis of **1** over a range of energies from 8 to 100 eV affords C_4H_8 neutral products, whose yield increases sharply between 20 and 30 eV. The isomer distribution is contrasted with that from 70-eV EBFlow radiolysis of 2-*n*-butylcyclopentanone (**5**) which undergoes a facile McLafferty rearrangement. 1-Butene is virtually the exclusive isomer from **5**, while 2-butenes compose nearly half the C_4H_8 yield from **1**. Neither pyrolysis nor 254-nm photolysis of **1** affords 2-butenes, and cation formation is proposed as the route to the C_4H_8 neutral products. The yields, in the range 2–3 μmol/(A s), and the isomer distributions are consistent with the proposal that these products from **1** arise from known mass spectrometric rearrangements of the molecular ion. A deuterium labeling experiment, 70-eV EBFlow radiolysis of **1**-β,β-d_2, shows a high yield of 1-butene-d_2, in conformity with the proposed mechanism and with published mass spectrometric studies that show much of the base peak arising via internal hydrogen transfer from the γ-methylene of the alkyl chain followed by expulsion of C_4H_8. The predominance of 1- and 2-butenes (>98% of the C_4H_8 yield) rules out the expulsion of methylcyclopropane as a major mass spectrometric rearrangement mechanism, and the expulsion of the 1,3-diradical $CH_2CH_2CHCH_3$ is suggested. On the basis of thermochemical estimates, excited states of the molecular ion of **1** observed by He(I) photoelectron spectroscopy are assigned as precursors to this expelled neutral.

In 1785, Joseph Priestley and Henry Cavendish published the first communications on the chemical consequences of electron impact.[2] Within a few months of one another, they reported separately the conversion of air into nitrogen oxides by means of an electric spark. Since then, many techniques have been developed for investigating low-energy (≤100 eV) electron bombardment of molecules, but the original method, analysis of neutral products, has remained a field of lively interest.[3-14]

Mass spectrometric investigations of ionic products of electron impact have been more numerous than neutral product studies. Identities of neutral species formed by reactions of ions are inferred from the differences between the masses of product and reactant ions. Such data do not usually lead to structures for the neutral products. Several investigators have used dual ionization for direct mass spectrometric identification of neutral species,[6,8] but mass spectrometry cannot distinguish many types of isomers, particularly structural isomers of simple hydrocarbons.

This paper reports the examination of C_4H_8 isomer distributions among neutral products collected from low-energy electron radiolyses of *n*-butyl phenyl ether. The purpose of this study has been to explore the possibility that neutral species expelled in mass spectrometric rearrangements can be collected and analyzed. Our approach has been to compare the results of electron bombardment with results of pyrolysis and photolysis, with the expectation that neutral products characteristic of ionized intermediates would result from the radiolysis experiments.



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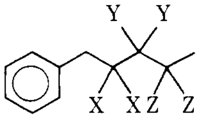
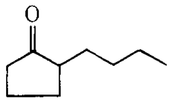
From the standpoint of the adiabatic approximation, collision between a molecule and an electron can lead to four primary processes: vibrational or rotational excitation, electronic excitation, positive ion formation, and negative ion formation, as represented by paths i–iv in reaction 1.[15] Vibrational excitation has been cited as predominant in the electrocyclic reactions of hydrocarbons in an electrical discharge,[13] while electronic excitation has been investigated in a number of aromatic compounds.[16] As a function of electron energy, the cross section for path iii reaches its maximum around 100 eV, where it is usually comparable to, if not greater than, the combined cross sections for paths i and ii.[15] Evidence for this is to be seen in the energy loss spectrum for zero-angle scattering of 100-eV electrons by acetone, in which the integrated intensity from 0.1 to 9.7 eV (the ionization potential) is less than that from 9.7 to 15 eV.[17]

Neutral products of ion–molecule reactions have been identified in the gas phase, from positive ions by means of the dual-electron beam section of a wide range radiolysis source[6c] and from negative ions by use of ion cyclotron resonance techniques.[12] The production of radicals from low-energy radiolysis of gaseous ammonia has been ascribed to positive ion–molecule reactions.[7] The present study has sought to identify the C_4H_8 species expelled during rearrangement of molecular ions of *n*-butyl phenyl ether. The neutral products from low-energy electron bombardment have been collected and the volatile hydrocarbons analyzed by gas chromatography (GLPC).

It has been desirable to select a radiolysis substrate whose molecular ion is expected to give products which ought not arise via vibrational or electronic excitation. *n*-Butyl phenyl ether (**1**) was chosen for study because of the variety of ways in which the side chain can interact with the ionized functionality.



1, X = Y = Z = H
2, X = Y = H; Z = D
3, X = Z = H; Y = D
4, X = D; Y = Z = H



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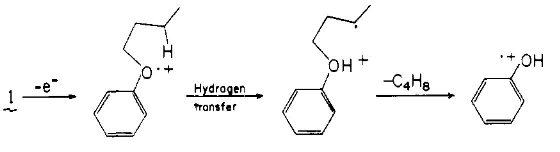
Djerassi and coworkers have demonstrated that the molecular ion rearranges to lose neutral C_4H_8, but that specifically deuterated analogues do not expel specifically deuterated neutrals. The mass spectra of compounds **1–4** all exhibit *m/e* 94 as base peak. The labeled compounds **2–4** show, in addition to this ion (M $-$ $C_4H_6D_2$), a large M $-$ C_4H_7D peak (*m/e* 95), which composes 20–40% of the base peak intensity. The high proportion of *m/e* 95 has been taken to imply that several mechanisms operate for hydrogen transfer from the alkyl chain, and not that isotopic scrambling occurs in the molecular ion prior to rearrangement. The ratio *m/e* 95:*m/e* 94 is greatest for **2**, suggesting that reaction 2, which proceeds via a five-member cyclic transition state, is the favored, but not the exclusive, pathway.[18]

The identities of the neutral C_4H_8 fragments may be surmised. Hydrogen transfer from the terminal methyl group could proceed via expulsion of two ethylene molecules.



(2)

6a 6b 7a

Transfer from the β-methylene (which would afford *m/e* 95 from **3**) would be expected to yield 1-butene. Transfer from the α-methylene (which would afford *m/e* 95 from **4**) might be followed by expulsion of *n*-propylcarbene, which ought to rearrange to give >90% 1-butene.[19]

The identity of the C_4H_8 neutral expelled following transfer from the γ-methylene, reaction 2, is harder to guess. Simple C–O bond fission in ion **6b** would afford a 1,3-diradical. Alternatively, methylcyclopropane could be expelled. Finally, more complex series of hydrogen shifts could be envisaged to rationalize other C_4H_8 isomers.

In order to investigate the identity of the C_4H_8 neutral fragments, it is necessary to collect a sufficient quantity of the neutral products to analyze the distribution of isomers. To this end, an apparatus for the collection of neutrals from low-energy (8–100 eV) electron bombardment of substrate has been constructed. This electron bombardment flow (EBFlow) reactor, which is described in detail in the Experimental Section, has permitted the isolation of volatile hydrocarbons from irradiation of gaseous *n*-butyl phenyl ether (2.5×10^{-4} Torr at 300 K) with a monoenergetic beam of electrons.

Experimental Section

Apparatus. Electron radiolyses were performed in an electron bombardment flow (EBFlow) reactor, the design of which is illustrated in Figure 1. The electron source, A, consists of a directly heated thoria-coated iridium filament, b, electrons from which are focused by a repeller, a, a control lens, c, and an anode, d. Electrons are admitted to the glass reaction vessel, D, via a 1 mm diameter aperture in the anode. The electron source region is evacuated with a Varian VHS-4 oil diffusion pump, connected at M, to prevent gas which has entered the electron source from reentering the reaction vessel. The electric potentials in the EBFlow reactor are applied to the circuit elements depicted in the inset. In the present studies, the filament, b, is grounded; the repeller, a, is biased at -1.5 V, the control lens, c, at $+180$ V, and the anode, d, at $+8$ V. The nominal energy of the bombarding electrons is determined by the potential applied to a stainless steel cage, B, lining the inner wall of the reaction vessel. Charged species are neutralized downstream of the reaction vessel on a baffle of collector grids, C, held at the same potential as the cage. Electrons and ions in the source and reaction vessel are collimated by a pair of solenoids, E, surrounding the reactor and maintained at flux densities of 10–100 G. During operation of the EBFlow reactor, gas is admitted to the reaction vessel from a sample bulb, G, via a variable leak. Pressure in the reaction vessel is monitored at F by an MKS Baratron capacitance manometer referred to a Varian VacIon 2 l./s pump.

Materials. *n*-Butyl phenyl ether (**1**) and its deuterated analogues **3** (90% d_2, 10% d_1) and **4** (>99% d_2),[18] 2-*n*-butylcyclopentanone (**5**),[20] and 2,2-dideuterio-*n*-butyl tosylate[21] were prepared by previously published procedures. Prior to EBFlow radiolysis, samples were purified by preparative GLPC on a 20 ft × 0.25 in. column of 15% SE-30 on 80–100 Chromosorb W (acid washed, DMCS treated). 2-Deuterio-1-butene was prepared by addition of the tosylate to a solution of potassium *tert*-butoxide in dimethyl sulfoxide at room temperature. Authentic samples of C_2, C_3, and C_4 hydrocarbons were purchased from Matheson Gas Products and Chem Samp Co. or were prepared via conventional routes. Reagent grade methylene chloride was distilled from phosphorus pentoxide prior to use and found to be free from impurities other than methyl chloride and chloroform. Commercial 2-methylpentane (Aldrich puriss.) was used without further purification.

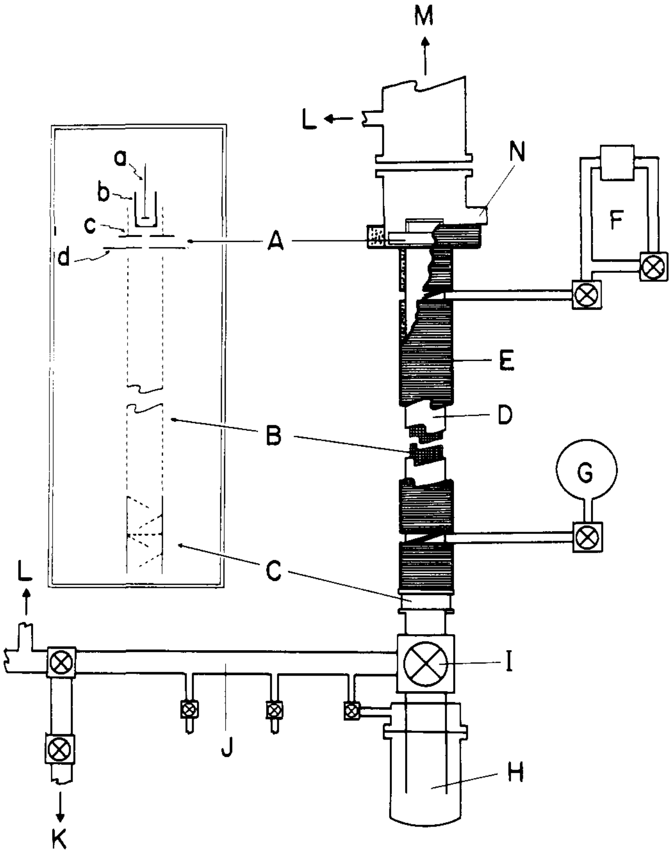
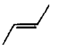
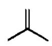
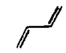


Figure 1. Schematic diagram of EBFlow reactor: A, electron source [insert: a, repeller; b, filament; c, control lens; d, anode]; B, cage within reaction vessel; C, collector; D, cylindrical glass reaction vessel; E, solenoid; F, Baratron manometer; G, gas sample bulb; H, liquid nitrogen cooled trap; I, three-way vacuum stopcock; J, vacuum line; K, to three-stage glass diffusion pump; L, Bayard-Alpert gauges; M, to 4-in. diffusion pump; N, electrical feedthrough.

Procedures. All EBFlow radiolyses were performed at a steady-state pressure of 2.5×10^{-4} Torr (measured at F), unless otherwise specified. During a radiolysis, the sample was permitted to flow continuously from G into the reaction vessel and was condensed in a liquid nitrogen cooled trap, H, filled with glass helices. Throughput of sample from G to H was found to be proportional to the steady-state pressure in the range 10^{-3} to 10^{-4} Torr, 24 mmol/(Torr s). The current with which the sample was bombarded was taken as the sum of the currents measured at B and C. Where not otherwise stated, the current for all runs was 3 ± 1 μA total, with roughly equal currents measured at the cage, B, and the collector, C. After a run of several hours, the three-way stopcock, I, connecting the reaction vessel to the trap, was turned to isolate the reaction vessel and connect the trap to the vacuum line, J. Trap H was heated to 100 °C and its contents vacuum transferred to a tube containing a known amount of methylene chloride, 0.011 M in 2-methylpentane. Tubes were sealed under vacuum for subsequent GLPC analysis on a Perkin-Elmer Model 881 instrument with flame ionization detection or GLPC-MS analysis (using a 30 ft × $\frac{1}{8}$ in. 120–150 mesh Durapak column connected to a Hitachi Perkin-Elmer RMU 6-D mass spectrometer). Isomers of C_4 hydrocarbons were

Table I. Yields of C_4 Hydrocarbons, Relative to 1-Butene (=100), from Decomposition of *n*-Butyl Phenyl Ether in the Gas Phase[a]

	Energy, eV					*n*-Butane	
EBFlow radiolysis	8	7 (2)	10 (3)	*b*	*b*	93 (33)	*b*
	10	12 (5)	9 (4)	*b*	*b*	107 (59)	*b*
	12	11 (3)	10 (2)	*b*	*b*	130 (35)	*b*
	15	6 (2)	5 (2)	*b*	*b*	105 (27)	*b*
	20	13 (1)	12 (1)	*b*	*b*	75 (9)	*b*
	30	44 (8)	40 (8)	1.3 (0.3)	1.1 (0.3)	26 (9)	4 (1)
	40	48 (6)	46 (6)	0.8 (0.2)	1.2 (0.7)	13 (2)	9 (2)
	50	48 (3)	45 (3)	2.4 (0.2)	1.6 (0.3)	13 (2)	7 (1)
	60	45 (3)	40 (3)	1.3 (0.4)	0.5 (0.2)	16 (3)	7 (1)
	70	50 (6)	45 (5)	2.2 (0.9)	0.9 (0.3)	10 (1)	8 (1)
	100	46 (1)	41 (1)	2.1 (0.5)	1.3 (0.2)	14 (1)	4 (1)
Pyrolysis	(1050 K)	0.4 (0.1)	0.3 (0.1)	*b*	*b*	23 (6)	3 (1)

[a] Numbers in parentheses are standard deviations of the mean. [b] <0.5.

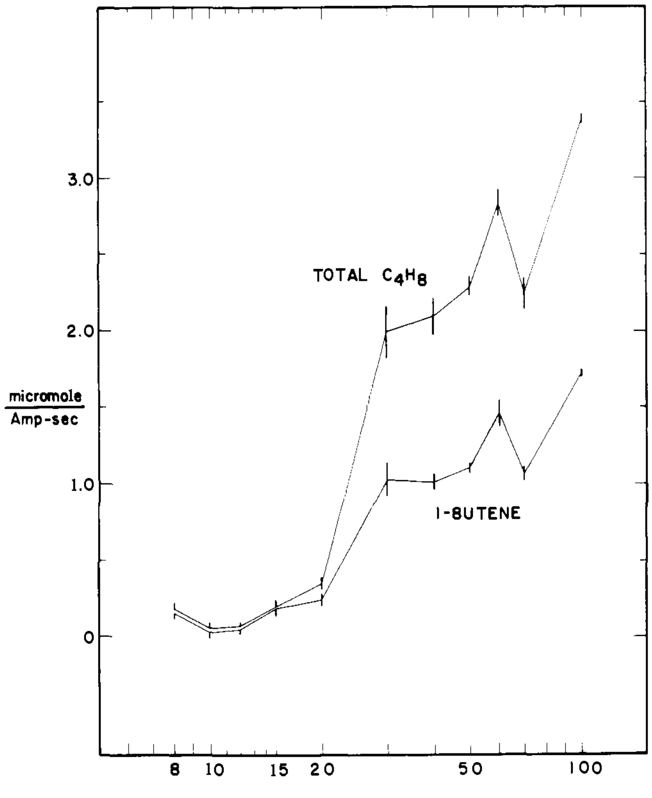


Figure 2. Yield of C_4H_8 products from EBFlow radiolyses of *n*-butyl phenyl ether as a function of cage voltage (potential at B relative to the filament, b). Correction has been made for production of 1-butene from pyrolysis on the filament. Error bars represent standard deviations of the mean.

identified by comparison of their retention times on a 30 ft × 1/8 in. column of dimethylsulfolane on 100–120 Gas-Chrom R[22] at room temperature with the retention times of authentic samples. Yields were determined by comparison of peak areas with the area of 2-methylpentane peak, for which the detector response was calibrated relative to 1-butene. All yields reported are the averages of at least three independent runs at each nominal electron energy. Control runs were performed with the filament off (affording no detectable yield of any volatile products) and with the filament on under normal operating conditions, drawing 4–5 A at a temperature of 1600 ± 100 K (brightness), but with the anode biased at −7 V, so that no electrons were entering the reaction vessel. Under these latter conditions, small quantities of volatile hydrocarbons were produced and are attributed to pyrolysis in the electron source. The only products detected were ethylene, ethane, 1-butene, and *n*-butane, in yields of 0.5, 0.015, 0.3, and 0.2 pmol/s, respectively. Yields from EBFlow radiolyses were corrected for this background contamination and are reported in micromoles/(ampere second).

Pyrolyses were performed by vacuum transfer of sample through a 30-cm quartz tube, 15 mm in diameter, heated to 1050 K. Total pressures in the range 0.1–0.8 Torr were maintained during pyrolyses, as monitored by a thermocouple vacuum gauge. Photolyses were performed by irradiating the vapor over 10–50 mg of degassed liquid in a 16 cm × 25 mm diameter quartz tube evacuated and sealed below 0.01 Torr pressure. Samples were irradiated for 20 h with a bank of germicidal lamps in a Rayonet photochemical reactor. The He(I) photoelectron spectrum of *n*-butyl phenyl ether was recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer.

Results

The most striking result from EBFlow radiolysis of *n*-butyl phenyl ether is the increase in C_4H_8 yield as electron energy is increased. Yields of C_4 hydrocarbons are summarized in Table I and Figure 2. Between 20 and 30 eV, the yield of 1-butene increases by more than a factor of 4. At the same time, the ratio of 1-butene to 2-butenes falls from 4:1 to 1.2:1. In addition to the C_4 products tabulated, traces of isobutane (yield <0.005 μmol/(A s)) were observed. Cyclobutane and 1,2-butadiene were not detected in any of the product mixtures.

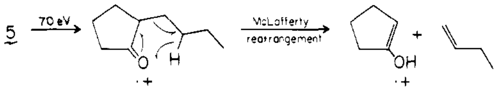
Aside from the C_4 hydrocarbons, the major volatile products from these radiolyses were propene, ethylene, and acetylene. The yield of propene relative to 1-butene increased with electron energy to a constant value of 0.20 (standard deviation = 0.02) above 40 eV. The volatility of the C_2 hydrocarbons caused large uncertainties in their analyses. The yield of ethylene was 0.3 ± 0.2 μmol/(A s), without detectable systematic variation as a function of electron energy. The yield of acetylene at electron energies $\leq$30 eV was 0.09 ± 0.06 μmol/(A s), with no apparent systematic variation. At higher energies the yield increased markedly, to roughly one-third the 1-butene yield at 40 and 50 eV and two-thirds the 1-butene yield at higher energies. Other C_2 and C_3 hydrocarbons (ethane, propane, allene, and propyne) were observed in yields $\leq$0.1 μmol/(A s).

Pyrolysis and photolysis of *n*-butyl phenyl ether gave different product distributions, with negligible yields of 2-butenes. In the former reaction, a single pass through an evacuated quartz tube at 1050 K effected 85% conversion of starting material. Of the volatile products, the two major components were ethylene (85 mol %) and 1-butene (10 mol %). In the latter reaction, photolysis at 254 nm for 20 h afforded a 2% yield of volatile products, of which butane was the major component, C_4H_8 hydrocarbons composing less than 0.01 of the *n*-butane yield. Nonvolatile products were not analyzed.

Photolysis of the deuterated compounds **3** and **4** gave roughly the same yield of butane and only traces of butenes. Mass spectrometric analysis of the major product showed it to be mostly butane-d_2, dideuterated to nearly (>90%) the same extent as the reactants **3** and **4**. A plausible mechanism involves cleavage of the oxygen–methylene bond, whose bond dissociation energy is estimated to be 2.25 eV (52 kcal/

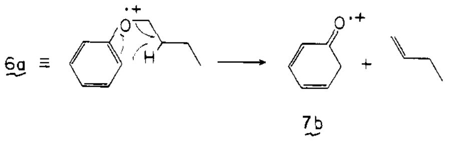
mol).[23,24] The initial products would be a phenoxyl radical, **8**, and an *n*-butyl radical. Butane formation may result from addition of **8** to unreacted starting material to generate an intermediate from which butyl radicals may abstract hydrogen. The presence of excess **8** apparently does not greatly affect the C_4 hydrocarbon ratios. Photolysis of phenyl acetate is known to form phenoxyl radicals as intermediates in the photo-Fries rearrangement;[25] irradiation at 254 nm of 2:1 mixtures of phenyl acetate and **1** in the gas phase gave proportions of C_3 and C_4 isomers comparable to the photolysis of **1** alone.

EBFlow radiolysis was also performed on 2-*n*-butylcyclopentanone (**5**) whose molecular ion is well known to undergo a facile McLafferty rearrangement, as shown in reaction 3.[26] At 70 eV, at which electron energy the mass spectrum of **5** exhibits the M − C_4H_8 rearrangement ion as its base peak, EBFlow radiolysis afforded 1-butene in a yield of 2.1 μmol/(A s). The ratio of 1-butene to all other C_4H_8 isomers was greater than 15:1. EBFlow radiolysis of methylcyclopropane, 1-butene, and *cis*- and *trans*-2-butene at 70 eV at 1 × 10^{-4} Torr pressure showed yields less than 0.1 μmol/A-sec of C_4 rearrangement products. Therefore, the C_4H_8 neutral products from EBFlow radiolyses do not rearrange under the reaction conditions.



(3)

EBFlow radiolysis of the deuterium-labeled ether **3** was performed at 20 and at 70 eV. GLPC–mass spectrometric analysis (chamber voltage = 50 V) of the 1-butene from the 20-eV run was performed, and comparison of this mass spectrum with that of an authentic sample of 2-deuterio-1-butene showed that the 1-butene produced was monodeuterated. If the C_4 hydrocarbons result only from disproportionation of pairs of butyl radicals, the butane recovered from radiolysis of **3** should be exclusively trideuterated. Analysis of the butane collected from the 20-eV run showed it to be dideuterated to the same extent as **3**, with no trideuterated component detected. These results suggest that reaction 4 and its thermal or photochemical analogues are the predominant source of 1-butene from 20-eV electron bombardment. The butane is presumed to arise via a mechanism similar to that outlined for photolysis of **1**.



(4)

At 70 eV, *cis*- and *trans*-2-butenes are produced as well as 1-butene. With an electron beam current of 13 ± 1 μA, yields of these hydrocarbons were 0.55, 0.63, and 1.28 μmol/(A s), respectively. Mass spectrometric analysis of the degree of isotopic substitution is complicated by the well-known facility of isotopic scrambling and subsequent fragmentation of C_4H_8 molecular ions.[27] Nevertheless, GLPC–mass spectrometric analysis revealed the recovered 1-butene to be at least 50% dideuterated, indicating that reaction 4 is not the exclusive pathway for 1-butene production from 70-eV electron impact on **1**.

Discussion

The production of 2-butenes from EBFlow radiolysis of **1** is the most significant result of this investigation, and the following discussion will deal primarily with this result. It is difficult to envisage mechanisms by which vibrationally or electronically excited **1** may yield 2-butenes. Reactions of *n*-butyl radicals are reported to afford 1-butene as the only C_4H_8 product,[24] and the results of our pyrolysis and photolysis experiments confirm our belief that neither path i nor path ii of reaction 1 accounts for the C_4H_8 yield from ≥30-eV electron impact on **1**. Ionization is therefore implicated as the major route to the observed products. Negative ion reactions are assumed to be negligible, for the formation of anion fragments from 100-eV electron impact has been reported to be several orders of magnitude less likely than positive ion formation.[6,15] Although negative molecular ion formation, path iv of reaction 1, has been cited in electrical discharge induced rearrangements of aromatic hydrocarbons at 1 atm pressure,[5] the necessity for third body collisional stabilization of such species renders their intermediacy at pressures below 10^{-3} Torr exceedingly improbable.[28]

Cation intermediates are the source of the 2-butenes. Two routes are possible for production of C_4H_8 from these ions: rearrangement via expulsion of a neutral fragment or neutralization. We believe that the former alternative provides the more likely explanation.

Known mass spectrometric rearrangements provide a ready explanation for production of C_4H_8 from 70-eV electron bombardment of **1** and **5**. Yields are consistent with expectation based upon estimated ionization cross sections[29] of 20–30 Å^2. Under the reaction conditions, about half of the electrons entering the reaction vessel should undergo ionizing collisions, and about half of the molecular ions decompose via reactions 2–4. Thus, one molecule of C_4H_8 is produced for every three or four electrons entering the reaction vessel, implying a theoretical C_4H_8 yield of 3 ± 0.5 μmol/(A s), in reasonable agreement with experimental observation. Reaction 2 provides an economical mechanism for production of 2-butenes and also explains the high yield of $C_4H_6D_2$ from 70-eV electron bombardment of **3**. An alternative rearrangement pathway may be proposed: reaction 4 expels excited 1-butene, which undergoes subsequent isomerization. This mechanism would imply that reaction 4 has energetics different from the seemingly analogous reaction 3, from which 1-butene is virtually the exclusive C_4H_8 isomer. This mechanism would also require that extensive hydrogen–deuterium scrambling occur in the molecular ion[21] to account for the $C_4H_6D_2$ yield from 70-eV radiolysis of **3**.

Neutralization pathways to C_4H_8 products are less attractive. Two general types of reactions can occur, charge transfer (either to a surface or to a neutral molecule) or ion–molecule reactions (e.g., proton transfer). Surface neutralization of molecular ions such as **6a** may produce neutrals in high excited states, but this does not account for the 2-butene yield. Such a mechanism, along with paths i and ii of reaction 1, may account for the yield of butane via the same mechanisms as proposed above for photolysis of **1**.

Neutralization of C_4 ions is also a conceivable pathway to the products recovered from **1**. Either charge transfer from C_4H_8 ions (*m/e* 56) or proton transfer from C_4H_9 ions (*m/e* 57) is a plausible route to C_4H_8 neutrals. Such a mechanism has two drawbacks. First, these ions compose but a small fraction of the ionization, representing 0.02 and 0.06, respectively, of the base peak intensity from **1** at 100 eV. Since the base peak, *m/e* 94, results from C_4H_8 expulsion from **6**, any neutralization route to 2-butenes would have to afford a neutral product yield from minor ions greater than the neutral product yield from the major fragmentation, which accounts for at least one-third of the total ionization. Second, these ions rearrange with facility to branched structures[30] (isobutene molecular ion and *tert*-butyl cation, respectively). This is inconsistent with the high yield of linear butenes observed.

If mass spectrometric rearrangement of **6** via reaction 2 were to be accepted as the principal route to the observed neutral products, then the distribution of C_4H_8 isomers gives some clues as to the identity of the neutral fragment expelled posterior to the hydrogen transfer. Plausible condidates include vibrationally excited methylcyclopropane (**9**) and the 1,3-diradical **10**. If the expelled species is exclusively **9**, the butene

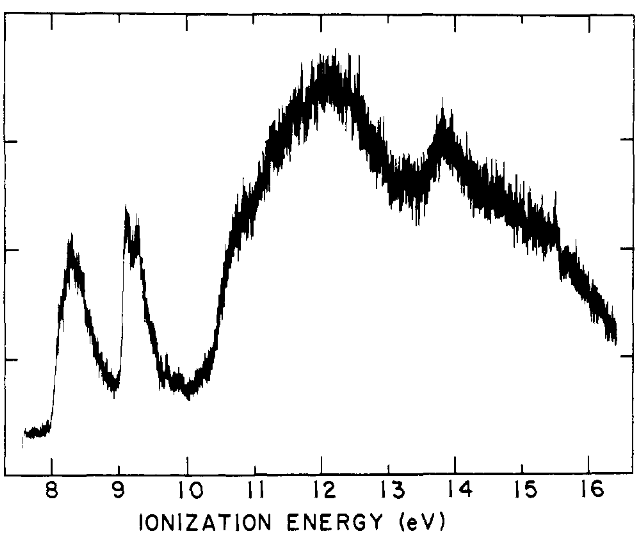
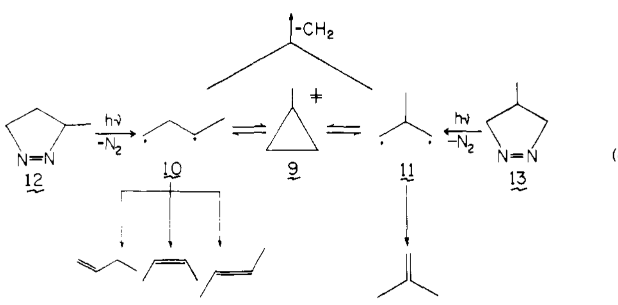


Figure 3. He(I) photoelectron spectrum of gaseous *n*-butyl phenyl ether calibrated using xenon and argon lines as reference standards. Courtesy of P. D. Mollére and K. N. Houk, Louisiana State University.

isomer distribution should resemble that from **9** generated by other means. Kistiakowsky and coworkers[31] have investigated **9** produced from a variety of reactions over a wide pressure range. At the lowest pressure studied, methylcyclopropane composed 8% of the C_4H_8 product, and the ratio of the other isomers was 1-butene:*trans*-2-butene:*cis*-2-butene:isobutene = 2.3:1.5:1.1:1.[31] The proportion of isobutene recovered in the EBFlow radiolyses is too low to be consistent with the intermediacy of **9** alone.



(5)

Intermediacy of **10** can account for the low yield of isobutene, provided that **10** does not interconvert with the isomeric diradical **11.** Dorer has examined the hydrocarbon yields from these diradicals produced by 313-nm photolysis of the pyrazolines shown in reaction 5 over a wide range of pressures. Pyrazoline **12** at a total pressure of 1.7×10^{-2} Torr yields a C_4H_8 olefin ratio of 5.2:2.6:2.4:1, while the isomeric pyrazoline **13** at a total pressure of 3.2×10^{-2} Torr gives a C_4H_8 olefin ratio of 1.8:1.1:0.8:1.[32] The differences in these product distributions imply that intermediates **10** and **11** do not interconvert rapidly on the time scale of intermolecular collisions at these pressures, at which the mean free path is on the order of centimeters. As the dimensions of the EBFlow reaction vessel are 40 cm × 3 cm diameter, we infer that the rate of collision with the wall at 2.5×10^{-4} Torr is greater than the rate of interconversion of **10** and **11.**

The intermediacy of **10** would provide mechanisms for the formation of 1,3-butadiene and the unsaturated C_3 products. Dorer has observed that **10,** when sufficiently activated, can expel methylene to form propene.[32] We estimate $\Delta H_f°(\mathbf{10}) \simeq E_a + \Delta H_f°$(methylcyclopropane), where E_a is the Arrhenius activation energy for ring opening of methylcyclopropane, 2.75 eV (63 kcal/mol).[33] Based on this estimate, $\Delta H_f°(\mathbf{10}) \simeq 3$ eV, while $\Delta H_f°$(propene) + $\Delta H_f°$(methylene) = 4.2 eV;[34] hence, **10** must have at least 1.2 eV (28 kcal/mol) excess vibrational energy to fragment to propene. Doepker[35] has observed that **10,** if produced from 147- and 124-nm photolyses of methylcyclopropane, is sufficiently activated to fragment further to 1,3-butadiene, propene, and allene. These products may also result from decomposition of excited 1-butene.[36] The ratio of 1,3-butadiene and unsaturated C_3 hydrocarbons to butene products, ≤ 0.2, suggests that only a small proportion of the expelled neutral C_4H_8 has sufficient energy content to decompose more rapidly than collide with the wall.

The yields of methylcyclopropane in reaction 5 have been reported to depend both on wavelength and on pressure. This dependence has been interpreted to reflect competition between collisional deactivation of **10** or **11** to form methylcyclopropane vs. rearrangement of the diradicals to acyclic olefins. From product ratios and from calculations of the rate of collisional deactivation, Dorer has estimated that **10** rearranges to olefins with a rate constant on the order of $10^6\ s^{-1}$ when it is excited to an energy corresponding to **9** with 3.5 eV (80 kcal/mol) vibrational energy.[32] Methylcyclopropane constitutes <1% of the C_4H_8 products from EBFlow radiolysis of *n*-butyl phenyl ether. If collision with the wall efficiently quenches vibrational excitation, the rate of rearrangement of **10** to acyclic products must be at least 100 times faster than the rate of wall collision, for which the rate constant may be estimated to be $>10^4\ s^{-1}$. Hence the rate constant for rearrangement of **10** to acyclic products must be $>10^6\ s^{-1}$, suggesting that if reaction 2 occurs, vibrationally excited **10** is produced.

The lowest electronic states of **6** do not expel C_4H_8. The *m/e* 94 ion from this rearrangement has the skeletal structure **7,** as confirmed by ^{13}C-labeling experiments of Woodgate and Djerassi.[37] Gillis and coworkers report the appearance potential for *m/e* 94 from *n*-butyl phenyl ether to be 10.05 eV, about 1 eV higher than would be expected for the production of 1-butene plus ion **7a.**[38] They suggest that this high appearance potential reflects the formation of the keto tautomer, ion **7b,** at onset by reaction 4. From the heats of formation of *n*-butyl phenyl ether and ion **7a,**[38] we estimate that the appearance potential for **10** must be at least 12 eV. The He(I) photoelectron spectrum of **1,** reproduced in Figure 3, shows the first three bands at 8.37, 9.19, and 9.31 eV (standard deviation = 0.02 eV).[39] The states of **6a** corresponding to these bands lie below the appearance potential reported for *m/e* 94.

We speculate that if reaction 2 occurs, its precursors are the states corresponding to the envelope with its maximum ~12 eV in the photoelectron spectrum. Although it is difficult to correlate photoelectron spectra quantitatively with electron impact phenomena,[15,40] we interpret the large area under the curve between 12 and 13.5 eV in Figure 3 to correspond to the large proportion of molecular ions which could undergo reaction 2. The formation of **6a** in excited levels 3.5-5 eV above its ground state is consistent with expulsion of **10** in the final step of reaction 2, and we note that there is no spin selection rule forbidding the formation of **10** in a triplet state, as total spin angular momentum may be conserved regardless of singlet or triplet multiplicity of the expelled neutral.

The present study exemplifies the connection that may be made between electron radiolysis and mass spectrometry. This apparent similarity has been noted before,[14] but our results demonstrate that molecular ionization may give neutral products that do not arise from any other mode of excitation. Current efforts are devoted to collection of neutral products from ion-molecule reactions in the gas phase.

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References and Notes

(1) Taken in part from the Ph.D. Dissertation of F. B. Burns, Brown University, 1976.

(2) (a) J. Priestley, *Philos. Trans. R. Soc. London*, **75**, 21 (1785); **78**, 313 (1788); (b) H. Cavendish, *ibid.*, **75**, 372 (1785); **78**, 261 (1788).
(3) R. R. Williams, Jr., *J. Phys. Chem.*, **63**, 776 (1959); **66**, 372 (1962).
(4) J. A. Manton and A. W. Tickner, *Can. J. Chem.*, **38**, 858 (1960).
(5) A. Streitwieser, Jr., and H. R. Ward, *J. Am. Chem. Soc.*, **85**, 539 (1963).
(6) (a) A. Niehaus, *Z. Naturforsch. A*, **22**, 690 (1967); (b) C. E. Melton and P. S. Rudolf, *J. Chem. Phys.*, **47**, 1771 (1967); (c) P. S. Rudolf and C. E. Melton, *J. Phys. Chem.*, **71**, 4572 (1967); (d) P. S. Rudolf, Volume 2, *Adv. Chem. Ser.*, **No. 82**, 101 (1968).
(7) R. Marx and G. Mauclaire, *Adv. Chem. Ser.*, **No. 82**, 212 (1968).
(8) (a) R. A. Saunders, J. T. Larkins, and F. E. Saalfeld, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 203 (1969); (b) F. Preston, M. Tsuchiya, and H. J. Svec, *ibid.*, **3**, 323 (1969); (c) J. R. Reeher, G. D. Flesch, and H. J. Svec, *Org. Mass Spectrom.*, **11**, 154 (1976).
(9) C. D. Finney and H. C. Moser, *J. Phys. Chem.*, **75**, 2405 (1971).
(10) R. R. Hutchins and R. R. Kuntz, *J. Phys. Chem.*, **75**, 2903 (1971).
(11) T. Matsushige and W. H. Hamill, *J. Phys. Chem.*, **76**, 1255 (1972).
(12) C. A. Lieder and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 4028 (1974).
(13) J. H. Kim and E. R. Thornton, *J. Am. Chem. Soc.*, **97**, 1865 (1975).
(14) H. Suhr and U. Schöch, *Chem. Ber.*, **108**, 3469 (1975), and references therein.
(15) H. S. W. Massey, "Electron and Ionic Impact Phenomena", Vol. 2, 2d ed, The Clarendon Press, Oxford, 1969, pp 801–1064.
(16) K. C. Smyth, J. A. Schiavone, and R. S. Freund, *J. Chem. Phys.*, **61**, 1782, 1789 (1974).
(17) R. H. Huebner, R. J. Celotta, S. R. Mielczarek, and C. E. Kuyatt, *J. Chem. Phys.*, **59**, 5434 (1973).
(18) (a) J. K. MacLeod and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 1840 (1966); (b) A. N. H. Yeo and C. Djerassi, *ibid.*, **94**, 482 (1972).
(19) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).
(20) G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).
(21) G. A. Smith and D. H. Williams, *J. Am. Chem. Soc.*, **91**, 5254 (1969).
(22) R. L. Churchwell, *J. Gas Chromatogr.*, **2**, 275 (1964).
(23) S. Paul and M. H. Back, *Can. J. Chem.*, **53**, 3330 (1975).
(24) W. E. Morganroth and J. G. Calvert, *J. Am. Chem. Soc.*, **88**, 5387 (1966).
(25) D. Belluš, *Adv. Photochem.*, **8**, 109 (1971).
(26) J. R. Hass, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *J. Am. Chem. Soc.*, **94**, 5095 (1972).
(27) G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Am. Chem. Soc.*, **91**, 1555 (1969).
(28) L. G. Christophorou and R. P. Blaustein, *Radiat. Res.*, **37**, 229 (1969).
(29) J. A. Beran and L. Kevan, *J. Phys. Chem.*, **73**, 3866 (1969).
(30) (a) R. W. Morgan and P. J. Derrick, *Org. Mass Spectrom.*, **10**, 563 (1975); (b) S. G. Lias and P. Ausloos, *J. Res. Natl. Bur. Stand., Sect. A*, **75**, 591 (1971); (c) L. W. Sieck, S. G. Lias, L. Hellmer, and P. Ausloos, *ibid.* **76**, 115 (1972); (d) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973).
(31) (a) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960); (b) G. B. Kistiakowsky and B. B. Saunders, *J. Phys. Chem.*, **77**, 427 (1973).
(32) F. H. Dorer, *J. Phys. Chem.*, **73**, 3109 (1969); **74**, 1142 (1970).
(33) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964, 1973 (1965).
(34) (a) W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968); (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970; (c) S. W. Benson et al., *Chem. Rev.*, **69**, 279 (1969).
(35) R. D. Doepker, *J. Phys. Chem.*, **73**, 3219 (1969).
(36) N. Harumiya, S. Shida, and S. Arai, *Bull. Chem. Soc. Jpn.*, **38**, 142 (1965).
(37) P. D. Woodgate and C. Djerassi, *Org. Mass Spectrom.*, **3**, 1093 (1970).
(38) R. G. Gillis, G. J. Long, A. G. Moritz, and J. L. Occolowitz, *Org. Mass Spectrom.*, **1**, 527 (1968).
(39) P. D. Mollère and K. N. Houk, Louisiana State University, personal communication.
(40) G. Innorta, S. Torroni, and S. Pignataro, *Org. Mass. Spectrom.*, **6**, 113 (1972); M. J. van der Wiel, W. Stoll, A. Hamnett, and C. E. Brion, *Chem. Phys. Lett.*, **37**, 240 (1976).

Stereochemistry of Electron-Impact and Lead Tetraacetate Induced Hydrogen-Abstraction Reactions

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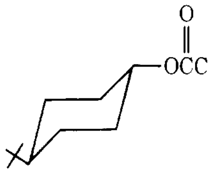
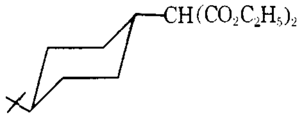
Abstract: The stereochemistry of the hydrogen-abstraction step in the electron-impact induced dehydration of a series of β-*trans*-4-*tert*-butylcyclohexyl alcohols is consistent with reaction through a chair or half-chair-like six-membered transition state and a chair conformation of the 4-*tert*-butylcyclohexyl ring system. The hydrogen-abstraction step in the lead tetraacetate induced cyclization of these alcohols exhibits parallel stereochemistry, providing further support for these conclusions. Steric arguments exclude a boat or a planar conformation of the cyclic transition state for hydrogen abstraction in either reaction. Since the lead tetraacetate induced reaction proceeds with significant trans hydrogen abstraction in every case, these observations confirm the utility of the stereochemistry of hydrogen abstraction from the 4-*tert*-butylcyclohexyl system as a probe into the concerted or nonconcerted nature of elimination reactions proceeding through six-membered cyclic transition states.

The application of mass spectrometry to stereochemical problems is made difficult by at least two factors. Most obviously, the detailed stereochemical prerequisites of most electron-impact induced fragmentations remain unknown. Of comparable importance, however, is the current dearth of knowledge concerning the prevalence of high-energy conformations after ionization. Unless the latter problem is better understood, knowledge of the former will have limited predictive value.

An effort to investigate both factors involved a study of the stereochemistry of the McLafferty rearrangements of *trans*-4-*tert*-butylcyclohexyl acetate (I) and diethyl (*trans*-4′-*tert*-butylcyclohexyl)malonate (II).[1] Both reactions exhibited a clear preference for elimination of the trans equatorial hydrogen. It was tentatively suggested that this result was attributable to steric effects in the competing transition states for hydrogen abstraction from the chair form of the 4-*tert*-butylcyclohexyl ring system. Further, it was suggested that extensive trans elimination might be characteristic of a nonconcerted elimination proceeding through a cyclic six-membered transition state.


I


II

The importance of these mechanistic proposals makes it desirable to establish more firmly the causes for and the generality of trans hydrogen abstraction in eliminations proceeding from the *trans*-4-*tert*-butylcyclohexyl ring system and to better define the conformation of the ring after electron impact. Therefore, the stereochemistry of the electron-impact induced dehydration of 2-(*trans*-4′-*tert*-butylcyclohexyl)ethanol (III), 1-(*trans*-4′-*tert*-butylcyclohexyl)-2-propanol (IV), and 2-methyl-1-(*trans*-4′-*tert*-butylcyclohexyl)-2-propanol (V) has