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A Study of the Formation and Reactions of Alkane Molecular Ions and Alkyl Cations with Tri-*n*-butylborane by Ion Cyclotron Resonance[1]

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Abstract: In contract to the conventional mass spectrum of tri-*n*-butylborane (**1**) which is dominated by boron-containing cationic species, the icr spectrum of **1** shows the formation of only low molecular weight ions (< *m/e* 59), including ethane, propane, and butane molecular ions, with essentially no boron-containing species (<5%). This is discussed in terms of a lesser stability of boron-containing cations relative to only C,H-containing cations. A number of reversible reactions of alkane molecular ions and/or alkyl cations with **1** have been characterized by double resonance techniques.

Mass spectral fragmentation patterns and the study of ion-molecule reactions can provide substantial information concerning structures, stabilities, and reactions of ions. The formation of new and unusual ions and the characterization of their reactions is of great current interest. In a study of the mass spectral behavior of trialkylboranes, a number of unique characteristics have been noted.[2] The mass spectra of trialkylboranes is dominated by boron-containing ions of which $C_nH_{2n+2}B^+$ is the dominant series with $C_2H_6B^+$ being, in general, the most abundant ion in the spectra. A second unique feature of the mass spectral behavior of trialkylboranes is the formation of appreciable quantities of alkane molecular ions containing up to twice the number of carbon atoms contained in a single alkyl group attached to the boron. The formation of alkane molecular ions is not observed in the mass spectra of hydrocarbons, except for the parent ion, and hydrocarbon derivatives. The formation of the $C_nH_{2n+2}B^+$ and alkane molecular ions must involve rearrangement processes,[2] and thus the structures of the ions cannot be assigned with certainty. In an attempt to derive information concerning the possible structures of the boron-containing ions and to investigate the gas-phase reactions of these species, a study of the ion cyclotron resonance behavior of tri-*n*-butylborane was undertaken.

Results and Discussion

The icr spectrum of **1** displays only peaks from *m/e* 15 to 59 (Figure 1). A detailed comparison of expanded peak shapes (Figure 2) and relative intensities over a 2×10^{-8} to 1×10^{-4} Torr pressure range indicates that boron-containing ions are present only at *m/e* 40 and 41 ($C_2H_6{}^{10}B$ and $C_2H_6{}^{11}B$) and in very low abundance (<5 and <1% of the total ion current at 2×10^{-8} and 4×10^{-7} Torr, respectively). These features of the icr spectrum are in distinct contrast to the conventional mass spectrum of **1** which contains a large number of C,H- ($C_5 \rightarrow C_8$) and boron-containing peaks above *m/e* 59, and in which boron-containing cationic species are dominant (>60% of the total ion current). The very significant lack of boron-containing cationic species in the icr spectrum of **1** must be due to a lesser stability of the boron-containing cationic species relative to only C,H-containing cationic species, an important conclusion inferred from the observed electron distributions between the products of the fragmentations of the boron-containing ions in the mass spectrometer.[2] The considerably longer residence time and the occurrence of bimolecular ion-molecule reactions in the icr cell provide for a closer approach to the equilibrium distribution of cationic charge between only C,H- and boron-containing ions.[3]

A second characteristic feature of the icr spectrum of **1** is the presence of appreciable quantities of alkane molecular ions ($C_1 \rightarrow C_4$). The intensities of the *m/e* 16, 30, 44, and 58 peaks are far too great to be due to ^{13}C-containing alkyl cations and, thus, must represent alkane molecular ions. Furthermore, some of the reactions of the *m/e* 16, 30, 44, and 58 species, characterized by double resonance techniques,[4] are different from those characterized for the alkyl cations of *m/e* 15, 29, 43, and 57.

The icr spectrum of **1** also contains an unusual peak at *m/e* 59 corresponding to $C_4H_{11}{}^+$. The assignment of this peak as representing $C_4H_{11}{}^+$ is based on the relative intensities of the *m/e* 58 and 59 species. The *m/e* 59 peak is too intense to arise solely from $C_3{}^{13}CH_{10}{}^+$ and, thus, must represent mostly $C_4H_{11}{}^+$ (~77%). Further evidence in support of this assignment is based on observed differences in the reactions of the *m/e* 58 and 59 species (*vide infra*). The intensities of the weak peaks at *m/e* 31 and 45 are consistent

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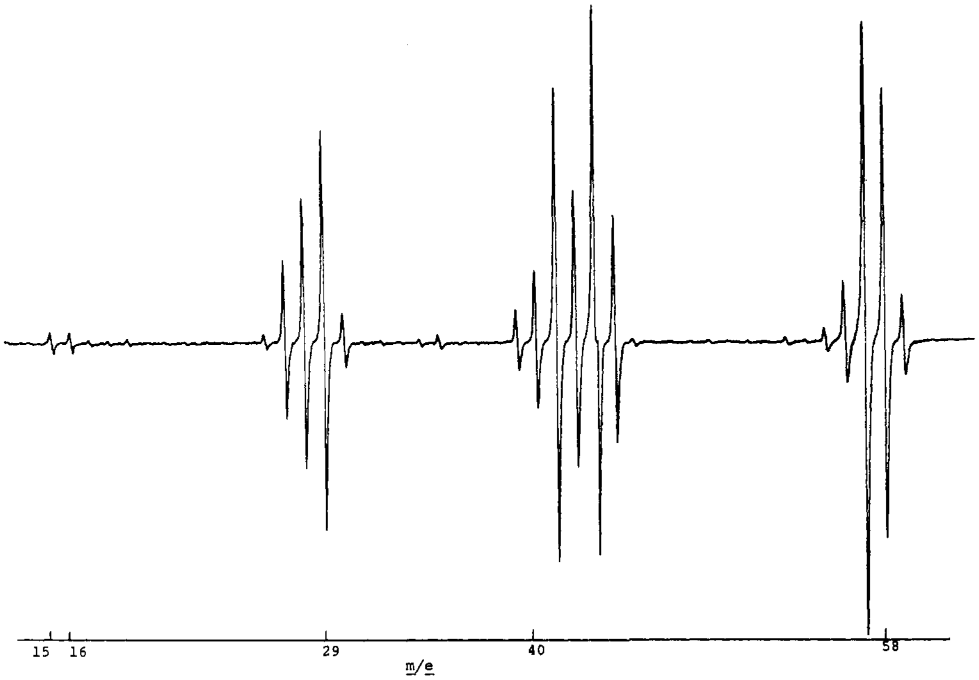


Figure 1. Icr spectrum of tri-*n*-butylborane (4×10^{-7} Torr) with ionizing voltage of 30 eV.

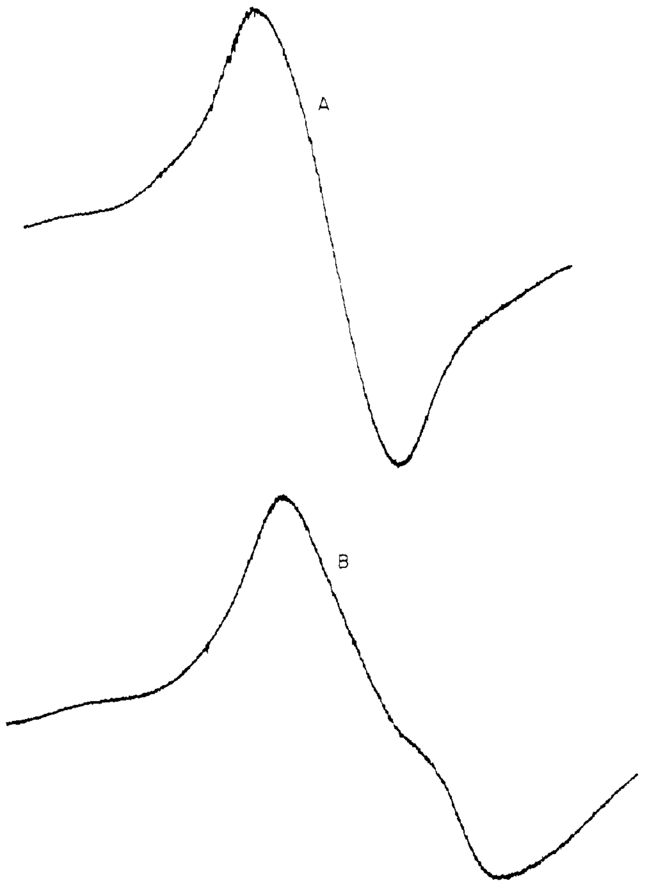


Figure 2. Peak shapes of the *m/e* 29 (A) and 41 (B) regions (5.0×10^{-7} Torr) at 30 eV.

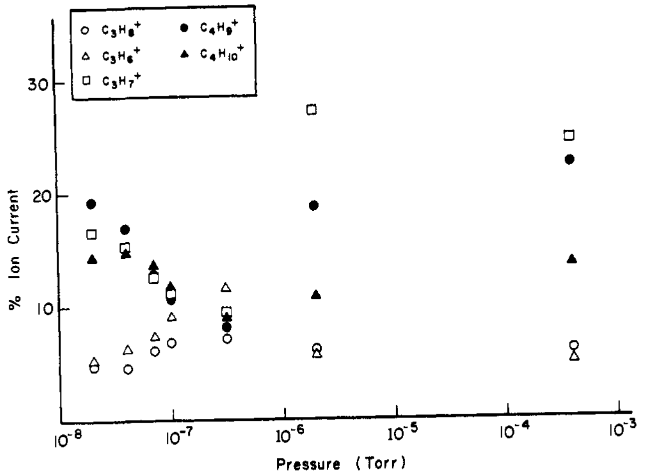


Figure 3. Plot of ion current of C_3 and C_4 species as function of pressure.

with their representing ^{13}C-labeled alkane molecular ions. The intensity of the *m/e* 17 peak appears to be too great to represent $^{13}CH_4{}^+$; however, the extremely low absolute intensity of the peak precluded further characterization.

The relative intensities of the various ions in the icr spectrum of **1** display somewhat different trends with changing pressure and ionization voltage. The $C_4H_9{}^+$ and $C_3H_7{}^+$ ions decrease in intensity on going from 2×10^{-8} to 10^{-7} Torr, whereupon they increase substantially on proceeding to 10^{-4} Torr (Figure 3). The $C_2H_5{}^+$ ion, however, displays just the opposite behavior. Of the alkane molecular ions, the intensities of $C_2H_6 \cdot {}^+$ and $C_3H_8 \cdot {}^+$ initially increase slightly and then decrease slightly, whereas the intensity of the $C_4H_{10} \cdot {}^+$ initially decreases then increases slightly. The relative intensity of the $C_4H_{11}{}^+$ ion remains fairly constant, while the intensities of the other ions initially increase and then decrease. Finally, the relative intensities of the alkyl cations and alkane molecular ions increase with decreasing ionizing voltage.

The foregoing observations can be rationalized on the basis of the dominant mode of fragmentation of the parent ion of **1** (**1**$\cdot^+$) and the factors affecting the succeeding ion-molecule reactions. At very low pressures, $C_4H_9{}^+$ is the major cationic species present.

On increasing the pressure of **1**, the reaction of $C_4H_9{}^+$ with **1** is the dominant reaction resulting in the destruction of $C_4H_9{}^+$ and production of the other ions. At the highest pressures, the dominance of $C_3H_7{}^+$ and $C_4H_9{}^+$ must reflect the formation of the most thermodynamically stable ions as

Table I. Ion–Molecule Reactions of **1**

Reaction no.	Reaction [ion (*m/e*) + **1** → ion (*m/e*)]
1	$C_3H_7^+$ (43) → CH_3^+ (15)[a]
2	$C_4H_9^+$ (57) → $C_2H_3^+$ (27)
3	$C_4H_{10}\cdot^+$ (58) → $C_2H_3^+$ (27)
4	$C_4H_{11}^+$ (59) → $C_2H_3^+$ (27)[b]
5	$C_3H_7^+$ (43) → $C_2H_4\cdot^+$ (28)
6	$C_4H_{11}^+$ (59) → $C_2H_4\cdot^+$ (28)[b]
7	$C_3H_7^+$ (43) → $C_2H_5^+$ (29)
8	$C_3H_8\cdot^+$ (44) → $C_2H_5^+$ (29)
9	$C_4H_{11}^+$ (59) → $C_2H_5^+$ (29)[b]
10	$C_3H_7^+$ (43) → $C_2H_6\cdot^+$ (30)[c]
11	$C_2H_5^+$ (29) → $C_3H_5^+$ (41)
12	$C_3H_6\cdot^+$ (42) → $C_3H_5^+$ (41)[d]
13	$C_3H_7^+$ (43) → $C_3H_5^+$ (41)
14	$C_4H_9^+$ (57) → $C_3H_5^+$ (41)
15	$C_4H_{10}\cdot^+$ (58) → $C_3H_5^+$ (41)
16	$C_4H_{11}^+$ (59) → $C_3H_5^+$ (41)
17	$C_2H_5^+$ (29) → $C_3H_6\cdot^+$ (42)
18	$C_4H_{10}\cdot^+$ (58) → $C_3H_6\cdot^+$ (42)
19	$C_4H_{11}^+$ (59) → $C_3H_6\cdot^+$ (42)
20	$C_2H_5^+$ (29) → $C_3H_7^+$ (43)
21	$C_3H_8\cdot^+$ (44) → $C_3H_7^+$ (43)[d]
22	$C_4H_9^+$ (57) → $C_3H_7^+$ (43)
23	$C_4H_{10}\cdot^+$ (58) → $C_3H_7^+$ (43)
24	$C_4H_{11}^+$ (59) → $C_3H_7^+$ (43)
25	$C_2H_9^+$ (29) → $C_3H_8\cdot^+$ (44)
26	$C_3H_5^+$ (41) → $C_3H_8\cdot^+$ (44)
27	$C_3H_6\cdot^+$ (42) → $C_3H_8\cdot^+$ (44)
28	$C_3H_7^+$ (43) → $C_3H_8\cdot^+$ (44)[d]
29	$C_4H_9^+$ (57) → $C_3H_8\cdot^+$ (44)
30	$C_4H_{10}\cdot^+$ (58) → $C_3H_8\cdot^+$ (44)
31	$C_4H_{11}^+$ (59) → $C_3H_8\cdot^+$ (44)
32	$C_2H_4\cdot^+$ (28) → $C_4H_9^+$ (57)[e]
33	$C_2H_5^+$ (29) → $C_4H_9^+$ (57)
34	$C_3H_7^+$ (43) → $C_4H_9^+$ (57)
35	$C_2H_5^+$ (29) → $C_4H_{10}\cdot^+$ (58)
36	$C_3H_7^+$ (43) → $C_4H_{10}\cdot^+$ (58)
37	$C_3H_8\cdot^+$ (44) → $C_4H_{10}\cdot^+$ (58)
38	$C_4H_9^+$ (57) → $C_4H_{10}\cdot^+$ (58)[d]
39	$C_3H_7^+$ (43) → $C_4H_{11}^+$ (59)[f]

[a] Other reactions of the *m/e* 15 (as well as the *m/e* 16) ion could not be unambiguously characterized because of the low intensity of the peak. [b] Reactions of *m/e* 57 and 58 ions with **1** producing C_2 ions could not be observed owing to interference by the first harmonic of the marginal oscillator. [c] Only reaction observed partially because of the low intensity of the peak. [d] Indicated as a shoulder on the base of the marginal oscillator peak. [e] Reactions of *m/e* 28–30 ions with **1** producing C_4 ions could barely be observed because of marginal oscillator harmonic interference. [f] Indicated by a shoulder at the base of the oscillator peak. Only reaction observed giving rise to the *m/e* 59 ion.

the end products of a sequence of ion–molecule reactions. The preference for formation of $C_nH_{2n+1}^+$ and $C_nH_{2n+2}\cdot^+$ at lower ionizing voltages reflects lower energy processes for the formation of these ions relative to the other ions.

The presence of the alkyl, alkane molecular, and $C_4H_{11}^+$ ions in the icr spectrum of **1** afforded a unique opportunity to study reactions leading to the formation and destruction of such species. A number of ion–molecule reactions of alkyl, alkane, and protonated alkane ions with alkanes have been studied in the C_1 and C_2 series. The CH_3^+ and $CH_4\cdot^+$ ions react with methane according to eq 1 and 2.[5,6] Protonated methane (CH_5^+) has been shown to react with methane to form an addition product (eq 3),[7] the reverse of

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \tag{1}$$

$$CH_4\cdot^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \tag{2}$$

$$CH_5^+ + CH_4 \longrightarrow C_2H_9^+ \tag{3}$$

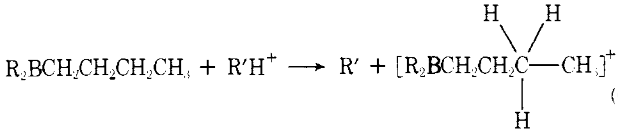
which has been observed to be collision induced.[7] Protonated methane also undergoes proton transfer reactions with other alkanes to produce a new protonated alkane ion which then undergoes fragmentation as illustrated in eq 4 and 5.[6]

$$CH_5^+ + C_8H_{14} \longrightarrow CH_4 + C_8H_{15}^+ \tag{4}$$

$$C_8H_{15}^+ \longrightarrow CH_4 + C_5H_{11}^+ \tag{5}$$

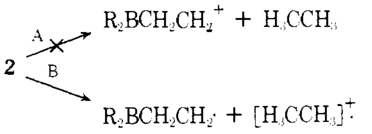
High-pressure mass spectrometric studies of ions derived from ethane (*i.e.*, $C_2H_4\cdot^+$, $C_2H_5^+$, and $C_2H_6\cdot^+$) with ethane have revealed the formation of addition intermediates ($C_4H_{10}\cdot^+$, $C_4H_{11}^+$, and $C_4H_{12}^+$) which undergo fragmentation to produce ions containing more than two carbon atoms.[8] In an attempt to characterize the ion–molecule reactions of **1** for comparison with those of alkanes, the possible reactions of the ions appearing in the icr spectrum of **1** were studied by double resonance techniques. The reactions thus detected are listed in Table I.

Most of the reactions given in Table I can be rationalized in terms of a mechanism involving the transfer of a proton to **1** from a RH^+ species to produce a variety of protonated intermediates like **2** which may then undergo fragmentation as outlined in eq 7 and 8. (In eq 6, 7, and 8, we have depicted protonation only at C_3. Similar mechanistic schemes can be written involving protonation at C_1, C_2, or C_4 which will then allow for the direct formation of C_4, C_3, or C_1 products, respectively.)[9]

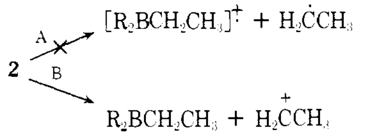


$$R_2BCH_2CH_2CH_2CH_3 + R'H^+ \longrightarrow R' + [R_2BCH_2CH_2CH_2CH_3]^+ \tag{6}$$

2



$$\mathbf{2} \xrightarrow{A} R_2BCH_2CH_2^+ + H_3CCH_3 \qquad \mathbf{2} \xrightarrow{B} R_2BCH_2CH_2\cdot + [H_3CCH_3]^{+\cdot} \tag{7}$$



$$\mathbf{2} \xrightarrow{A} [R_2BCH_2CH_3]^{+\cdot} + H_2\dot{C}CH_3 \qquad \mathbf{2} \xrightarrow{B} R_2BCH_2CH_3 + H_2\overset{+}{C}CH_3 \tag{8}$$

In each of the modes of fragmentation of **2,** the distribution of electrons between the products can be such that a boron-containing cation and a neutral are formed (eq 7A and 8A) or *vice versa* (eq 7B and 8B). The present icr results indicate that thermodynamically fragmentation occurs to produce a boron-containing neutral fragment (eq 7B and 8B). Comparison of these results with those derived from studies of ion–molecule reactions with hydrocarbons indicates that the presence of boron does not alter the type of reactions that occur but does have a substantial effect on the structures of the cationic species formed.[10]

A number of reactions were characterized in which $C_2H_3^+$, $C_2H_4\cdot^+$, $C_3H_5^+$, and $C_3H_6\cdot^+$ ions were formed (reactions 2–6 and 11–19) from ion–molecule reactions of **1**. It cannot be certain, however, whether these ions are formed as primary products of reactions involving **1** (*via* not-so-obvious pathways) or might be second generation ions formed by first-order fragmentation reactions of the primary ion products.

Experimental Section

The icr spectra of tri-*n*-butylborane were recorded on a Varian ion cyclotron resonance spectrometer at 30-eV ionization voltage at room temperature at 2 × 10^{-8} to 4 × 10^{-4} Torr. The double resonance spectra were recorded at 30 eV (5 × 10^{-7} Torr).

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References and Notes

(1) Part XXVII of a series on Transfer Reactions Involving Boron; for part XXVI, see D. J. Pasto and P. E. Timony, *J. Organometal. Chem.*, 19, (1973).

(2) D. J. Pasto and P. E. Timony, *Org. Mass Spectrom.*, in press.

(3) The almost total lack of boron-containing cationic species in the icr spectrum of **1** unfortunately precluded a study of the reactions of such species, which might have provided information concerning their structures.

(4) See J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971); G. A. Gray, *Advan. Chem. Phys.*, **19**, 141 (1971), and references therein.

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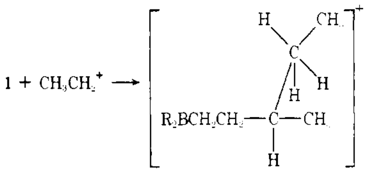
(9) The possibility of hydrogen migration in **2**, *i.e.*, leading to equilibration between the possible protonated **1** structures, cannot be dismissed. Information relating to this possibility is not available.

(10) An alternative mechanistic possibility involves the insertion of a cationic species into C–H or C–C bonds to form "addition" products[5,6,8] such as structure i which may then undergo fragmentation. However, such addition products were not detected in the present study, and, based on the reported formation of C_3 and C_4 ions from the ethane "addition" intermediates,[8] ions containing more than four carbon atoms were not formed. If intermediates similar to i had been formed, it is not obvious why product ions containing more than four carbon atoms should not have been produced.



i

Electrochemical Reduction of 1-Phenyl-1-hexyne at a Mercury Cathode in Dimethylformamide

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received June 14, 1974*

Abstract: In dimethylformamide containing 0.1 *F* tetra-*n*-butylammonium perchlorate as supporting electrolyte, 1-phenyl-1-hexyne gives a single polarographic wave corresponding to the four-electron reduction to 1-phenylhexane, the other products being tri-*n*-butylamine and 1-butene. Under certain conditions during a large-scale electrolysis, 1-phenyl-1-hexyne can rapidly isomerize to yield 1-phenyl-1,2-hexadiene. Once formed, the allene is easier to reduce than the acetylene and undergoes stepwise conversion, first to an olefin (*trans*-1-phenyl-1-hexene, *trans*-1-phenyl-2-hexene, or *cis*-1-phenyl-1-hexene) and then to 1-phenylhexane. For concentrations of 1-phenyl-1-hexyne between 0.002 and 0.01 *M*, the bimolecular acetylene-to-allene rearrangement is a dominant reaction, and the reduction of the acetylene proceeds largely *via* the allene species. For much lower concentrations of the acetylene, there is no observable formation of allene, and the electrochemical process is almost entirely the reduction of 1-phenyl-1-hexyne to 1-phenylhexane.

Relatively few investigations of the electrochemical reduction of acetylenic compounds have been reported. Diphenylacetylene and phenylacetylene have been studied polarographically in a dioxane-water solvent system[1] and in anhydrous dimethylformamide.[2] Sioda, Cowan, and Koski[3] examined the electrochemistry of phenylacetylene, diphenylacetylene, and several substituted diphenylacetylenes in dimethylformamide and presented evidence based on epr spectroscopy for the formation of relatively stable radical-anion intermediates upon reduction of these compounds. Recently, it has been confirmed by House and Kinloch[4] that nonconjugated acetylenes are polarographically inactive in dimethylformamide.

Benkeser and Tincher[5] prepared a number of trans olefins by prolonged electrolysis at a platinum cathode of methylamine–lithium chloride solutions containing different acetylenic compounds. These authors suggested that the reduction involves a homogeneous reaction between the acetylenic compound and elemental lithium formed at the cathode.

Studies of the electrochemical reduction of certain cyclizable halogen-substituted acetylene compounds at mercury electrodes in dimethylformamide have been underway in this laboratory for some time.[6] Reduction of 1-phenyl-1-hexyne was originally performed in order to prepare *cis*- and *trans*-1-phenyl-1-hexene for use as comparison samples for other investigations. A partial controlled-potential electrolysis near the half-wave potential of 1-phenyl-1-hexyne yielded the two expected olefinic products plus a small amount of 1-phenylhexane which resulted from total reduction of the triple bond. Surprisingly, a third olefin (*trans*-1-phenyl-2-hexene) was obtained, raising the possibility of an interesting rearrangement or isomerization process. In addition, the current–time behavior during the electrolysis was unusual in that, after decreasing exponentially for 10 to 15 min, the current rose to a maximum before resuming a normal decay.

Thus, the present study was undertaken to explain these intriguing observations about the electrochemical reduction of 1-phenyl-1-hexyne. Our results complement previous knowledge of the reduction of phenyl acetylenes in aprotic media and point out the important role played by the allenic isomer of a 1-phenyl-1-alkyne in the electrochemical process.