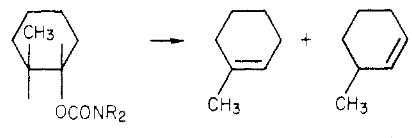
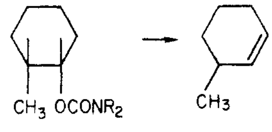
support the proposed mechanism.

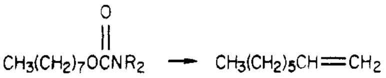


5a, R = Me
b, R = Ph



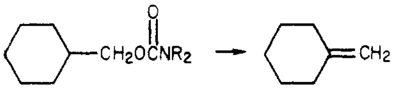
4a, R = Me
b, R = Ph

Further support for a concerted mechanism comes from the observation that carbamates of primary alcohols give terminal olefins of high purity. Thus the 1-octyl carbamates **1a** and **1b** give 1-octene with no trace of isomeric products and the cyclohexylmethyl carbamates **3a** and **3b** give methylenecyclohexane in 98% purity or better. The 2-octyl carbamates **2a** and **2b**, on the other hand, give a mixture of 1-octene and 2-octene, with the latter predominating.



$$CH_3(CH_2)_7O\overset{O}{\overset{\|}{C}}NR_2 \rightarrow CH_3(CH_2)_5CH{=}CH_2$$

1a, R = Me
b, R = Ph



3a, R = Me
b, R = Ph

Finally, this study shows that carbamate pyrolysis is similar to acetate pyrolysis both in terms of reaction conditions and product distribution[11] and that it is capable of the same degree of selectivity. Since *N,N*-dimethylcarbamates react at very nearly the same rate as acetates,[6b] they probably offer no advantage in the synthesis of olefins. *N,N*-Diphenylcarbamates, on the other hand, react more readily than acetates and hence can be pyrolyzed at lower temperatures. DePuy and King[11c] state that a pyrolysis temperature of 500–525 °C is most convenient for secondary and tertiary acetates; we employed temperatures of 375–440 °C for *N,N*-diphenylcarbamates. These carbamates should thus be preferable to acetates which require high reaction temperatures, and especially to primary acetates which must be recycled for good yields. While 1-octyl acetate is reported[11d] to require two passes at 500–515 °C to give 63.5% of olefin and 1-heptyl acetate gives only a 56% yield of olefin at 540 °C, carbamate **1b** reacts at 420 °C to give an 81% yield of olefin.

Experimental Section

Melting points were obtained on a Büchi melting-point apparatus and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 700 or a Beckman IR8 spectrophotometer. VPC analyses of olefins were performed on a Varian Aerograph 200 using the following columns: 3 ft × 0.25 in. triethylene glycol saturated with $AgNO_3$ on Chromosorb P; 6 ft × 0.25 in. 10% Apiezon P on Chromosorb P; 5 ft × 0.25 in. 20% SE-30 on Chromosorb P. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Carbamates. (a) *N,N*-Dimethylcarbamates. A 4–8 M solution of the alcohol in dry pyridine was heated to reflux with a 20% excess of *N,N*-dimethylcarbamyl chloride (possible carcinogen, Aldrich). After 22–47 h, ice–water was added and the mixture was extracted with ether. The ether extracts were washed with 2 M HCl and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was distilled at reduced pressure.

(b) *N,N*-Diphenylcarbamates. A 4 M solution of the alcohol in dry pyridine was heated to reflux with a 10% excess of *N,N*-diphenylcarbamyl chloride (Aldrich). After 16–96 h, a small amount of water was added to hydrolyze excess carbamyl chloride. The mixture was stirred a few minutes, then more water was added, and the mixture was extracted with ether or methylene chloride. The organic layer was dried with anhydrous $MgSO_4$ and decolorized with carbon. After evaporation of the solvent, the product was recrystallized from 95% ethanol.

Pyrolysis of Carbamates. Pyrolyses were performed in a 15 × 400 mm Vycor tube packed with a 350-mm bed of glass helices and heated in a tube furnace. Liquid carbamates were added dropwise to the top of the tube and solid carbamates were added in small portions from a flask connected to the tube with rubber tubing. Two receivers were employed, the first cooled in ice and the second cooled with dry ice. A flow of nitrogen was maintained through the apparatus during the course of the pyrolysis.

For carbamates which required high temperatures for complete reaction, using the procedure above, a recycling apparatus adapted from that of Johnson[9] was employed. In this apparatus the carbamate was heated to boiling in a flask at the bottom of the pyrolysis tube and was swept into the tube by a stream of nitrogen at 25 mL/min. A Vigreux column at the top of the tube separated products from unreacted starting material. The former were collected in cold traps and the latter was returned to the boiling flask through a side arm.

The products from the *N,N*-dimethylcarbamates were treated with 2 M HCl followed by removal of the water layer and drying over anhydrous $CaCl_2$. The olefinic products were distilled at reduced pressure. Olefins from the *N,N*-diphenylcarbamates were distilled directly from the reaction mixture at reduced pressure.

Products were separated by preparative VPC if necessary and identified by comparison of infrared spectra with those of authentic samples.

Registry No. 1a, 54565-65-0; **1b**, 77287-42-4; **2a**, 77287-43-5; **2b**, 77287-44-6; **3a**, 77287-45-7; **3b**, 77287-46-8; **4a**, 77287-47-9; **4b**, 77287-48-0; **5a**, 77287-49-1; **5b**, 77287-50-4; **6a**, 7541-19-7; **6b**, 77287-51-5; *N,N*-dimethylcarbamyl chloride, 79-44-7; *N,N*-diphenylcarbamyl chloride, 83-01-2; 1-octanol, 111-87-5; 2-octanol, 123-96-6; cyclohexanemethanol, 100-49-2; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; cyclohexanol, 108-93-0; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; methylenecyclohexane, 1192-37-6; 3-methylcyclohexene, 591-48-0; 1-methylcyclohexene, 591-49-1; cyclohexene, 110-83-8.

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Phenyl-Substituted Cyclopropylidenemethyl and 1-Cyclobutenyl Cations in the Gas Phase. Unusual Course of Homopropargyl Rearrangement[1]

Wilfried Franke and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, Federal Republic of Germany

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Whereas the existence of vinyl cations as intermediates in solvolysis reactions or electrophilic additions to allenyl or triple bonds in solution is now well established,[2] related

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(1) Mass spectroscopic investigation of acetylenic compounds. 26. For part 25 see: Wagner, W.; Levsen, K.; Zummack, W.; Schwarz, H. *Org. Mass Spectrom.*, in press.

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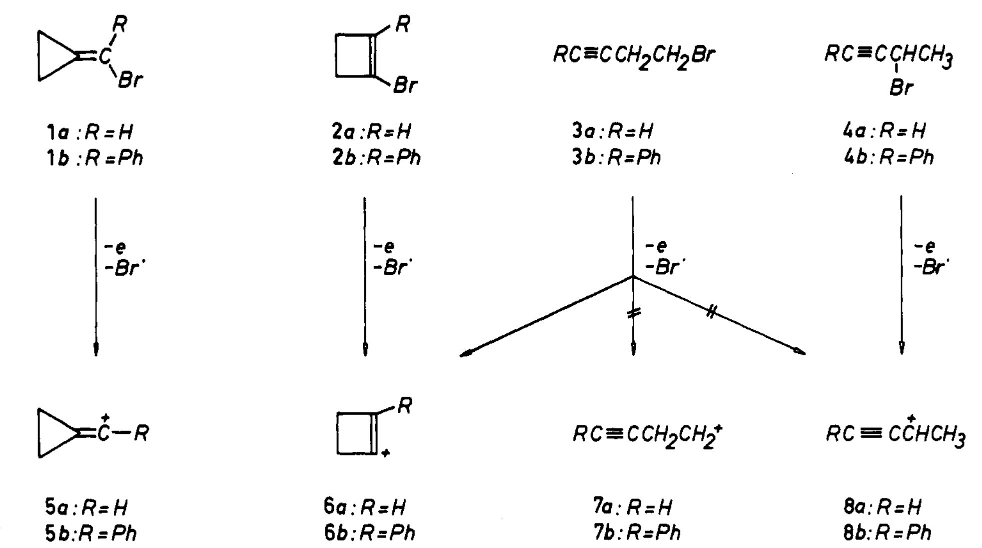
Scheme I



experimental data on *gaseous* vinyl cations are much more scarce.[2,3] However, in the last few years collisional activation (CA) mass spectrometry[4] has proved to be a useful technique to reveal the number of isomeric structures of an "isolated" ion capable of existing in significant minima on the potential-energy surface. Using this method in combination with the analysis of kinetic-energy release data, *T*, associated with unimolecular dissociation of a metastable ion,[5] we were able to demonstrate recently[6] that, for example, the highly strained cyclopropylidenemethyl (**5a**) and 1-cyclobutenyl cations (**6a**) are, indeed, stable species in the gas phase as postulated by Hanack[7] and predicted by molecular orbital theory.[8] It was also shown that dissociative ionization of the homopropargyl derivative (**3a**) did not give the primary cation **7a**, but as a result of a "homopropargyl rearrangement"[7] **6a** was identified as a stable $C_4H_5^+$ ion, from which, in condensed phase, cyclobutanone was obtained as the only reaction product[2,7] (Scheme I).

In this paper we report results of gas-phase experiments on dissociative ionization of some isomeric phenyl-substituted compounds, i.e., (1-bromo-1-phenylmethylene)cyclopropane (**1b**), 1-bromo-2-phenylcyclobutene (**2b**), 1-bromo-4-phenyl-3-butyne (**3b**), and the corresponding 2-bromo-4-phenyl-3-butyne (**4b**). The main reaction product of the solvolyses of **1b**, **2b**, and **3b** in various solvents under different conditions is phenyl cyclopropyl ketone.[9] The favored formation of this product was interpreted as direct evidence for the unusual stability of the intermediate phenyl-substituted cyclopropylidenemethyl cation (**5b**). This cation is likely to be highly stabilized both directly through a mesomeric effect of the phenyl group and, in a nonclassical way, by the overlap of the vacant p orbital of the vinyl cation with the bent bonds of the cyclopropane ring. In **6b**, however, the phenyl group does not contribute directly to the stabilization of the positive charge at C1;[2,7,9,10] the unexpected stability of **6** is likely to be a consequence of a bridging with the C2/C3 bond as is shown unambiguously to be the case for **6a** by both sophisticated ab initio and semiempiricial molecular orbital calculations.[8] For **6b** no computational results are available.

To our knowledge no gas-phase experiments on **1b**–**4b** have been described in the literature. In this paper we present experimental evidence for the existence of **5b**, **6b**, and **8b** as stable species (life time $\geq 10^{-5}$ s) in the gas phase. In addition, it is shown that unimolecular Br· loss from ionized **3b** is accompanied by triple bond participation. In contrast to the solvolysis of **3b** in condensed phase[9] it is shown, however, that the gas-phase dissociative ionization of **3b** gives rise to the exclusive formation of **6b**. We could find no experimental evidence for the existence of stable homopropargyl ion **7b** nor the formation of either **5b** or **8b**. The latter ion, however, is formed directly from the molecular ion of **4b**, whereas **5b** is generated from ionized **1b**.

Experimental Section

(1-Bromo-1-phenylmethylene)cyclopropane (**1b**) and 1-bromo-2-phenylcyclobutene (**2b**) were synthesized as described by Hanack and co-workers.[9] 1-Bromo-3-phenyl-3-butyne (**3b**)[11] was obtained by the convenient two-step procedure: 4-phenyl-3-butyn-1-ol[12] → 4-phenyl-3-butyn-1-yl tosylate → (**3b**).[13] 2-Bromo-4-phenyl-3-butyne (**4b**) was prepared according to the literature.[14] All compounds were purified by preparative gas chromatography and characterized by ^1H NMR spectroscopy. The collisional activation (CA) spectra[4] were obtained by using a Varian

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Table I. Collisional Activation Spectra of $[M - Br]^+$ Ions Formed from Isomeric Precursors 1b, 2b, 3b, and 4b

CA fragment ions, m/z[a]	$[M - Br]^+$ from precursor			
	$(1b)^{+\cdot}$	$(2b)^{+\cdot}$	$(3b)^{+\cdot}$	$(4b)^{+\cdot}$
128	56	65	64	52
127	18	20	20	17
126	2.4	2.7	2.8	1.7
115	0.7	0.3	0.2	0.2
114	0.2	0.2	0.2	1.6
113	0.2	0.2	0.2	1.1
103	0.1	0.4	0.4	1.1
102	3.1	2.1	2.2	3.1
101	1.7	1.2	1.3	2.3
100	0.3	0.2	0.2	0.5
99	0.3	0.2	0.2	0.3
98	0.3	0.2	0.2	0.3
89	0.6	0.3	0.3	0.7
88	0.3	0.1	0.2	0.6
87	0.6	0.3	0.4	0.8
86	0.4	0.2	0.3	0.5
85	0.2			0.1
78	1.1	0.5	0.6	1.0
77	3.2	1.5	1.5	3.6
76	1.2	0.6	0.7	1.2
75	1.6	0.7	0.8	2.0
74	1.3	0.7	0.8	1.5
73	0.1			0.1
65	0.1			0.1
64	0.2			0.2
63	1.4	0.6	0.6	1.4
62	0.8	0.3	0.4	1.0
61	0.3	0.1	0.1	0.3
53	0.1			0.1
52	0.3	0.1	0.1	0.3
51	1.2	0.5	0.6	1.9
50	1.1	0.5	0.5	1.2
49	0.1	0.1	0.1	0.1
39	0.4	0.1	0.1	0.3
38	0.1			0.1
37		0.1	0.1	

[a] The relative abundances are normalized to a total of 100 units over the m/z range 37-128.

MAT 311A double-focusing mass spectrometer, in which ions pass through the magnetic field (B) before entering the electric field (E). The collision cell was differentially pumped and situated in front of the energy-resolving slit. Samples were introduced via the heated all-gas inlet system. The source temperature was 150–180 °C, the uncorrected ionizing energy of the electron beam 70 and 12 eV, the emission current 1 μA, and the accelerating voltage 3 kV. The magnetic and electric fields were adjusted to transmit exclusively the $[M-Br]^+$ ions. Air was then introduced into the collision cell via a variable leak until the precursor ion abundance decreased to $^1/_3$ of its original value due to scattering and decomposition. CA spectra were then obtained by a simultaneous scanning of the magnetic and electric fields (linked B/E scan[15]). The data were directly recorded on an XY recorder and normalized to the sum of fragments. Only peak heights were measured and the abundances were not corrected for reduced multiplier response. The reported CA spectra (Table I) are mean values of at least six measurements; they are not sensitive to the ionizing energy. The reproducibility was ±2 to ±8%, depending on the abundance of the precursor ions. The kinetic-energy release, T, measurements for unimolecular ^{79}Br· loss from the molecular ions were obtained by using a Varian MAT 711 double-focusing instrument (ionizing energy 70 eV, emission current 800 μA, high-voltage scan[16]) at an energy resolution of ca. 1200. The values were derived from the half-widths of the metastable peak by using Beynon's equation[16] and are the mean values of at least five scans (reproducibility ±0.05 kcal/mol). Corrections were applied for the widths of the main beams.

Results and Discussion

The electron-impact ionization of **1b**–**4b** generates abundant molecular ions which undergo unimolecular loss of Br·. The collisional-activation (CA) mass spectra of the resulting $[M - Br]^+$ ions (m/z 129) are given in Table I. The CA data are different for the ions formed from $(\mathbf{1b})^{+\cdot}$, $(\mathbf{2b})^{+\cdot}$, and $(\mathbf{4b})^{+\cdot}$, respectively; this result indicates the generation of at least three distinct isomeric cations,[17] which do not interconvert prior to collisional activation. On the other hand, the CA spectra of the $[M - Br]^+$ ions generated from ionized **2b** and **3b** are *indistinguishable* within experimental error and insensitive to the ionizing energy, thus indicating the formation of a single ion structure from these precursors; we believe that this ion is best represented by the phenyl-substituted 1-cyclobutenyl cation **6b**. The ion **8b**, which could be generated if Br· loss from $(\mathbf{3b})^{+\cdot}$ were associated with a 1,2-hydride shift can be excluded as an alternative to **6b** due to the different CA spectra. Analogously, the substituted cyclopropylidenemethyl cation (**5b**) is not generated from $(\mathbf{3b})^{+\cdot}$. The fact that Br· loss from the molecular ion of **3b** does not give **7b** but is accompanied by an exothermic isomerization of the incipient $[M - Br]^+$ ions is also evident from the kinetic-energy release data, T. For **2b** it is found that the metastable ion peak for the process $M^{+\cdot} \rightarrow [M - Br]^+$ is characterized by a $T_{0.5}$ value of 3.2 kcal mol^{-1}, whereas Br· elimination from $(\mathbf{3b})^{+\cdot}$ corresponds to 4.1 kcal mol^{-1}. This increase in ΔT in comparing **3b** with **2b** can be interpreted as follows. If the dissociative ionization of **3b** is accompanied by an exothermic isomerization of the incipient $[M - Br]^+$ ion to a more stable species, the potential energy ΔE released during this process will be partitioned among all vibronic modes of the dissociating species. The fraction of ΔE which will fluctuate into the reaction coordinate will cause a line broadening of the metastable peak,[3,4d,5,6] which is indeed experimentally found to be the case.

Finally it should be noted that the products of solvolyses of **2b** and **3b** depend decisively on the experimental conditions. Solvolysis of **1b**, **2b**, and **3b** in condensed phase gives under various conditions for different leaving groups products which are derived from the intermediate formation of **5b**.[2,7,9,10] In the gas phase, however, **5b** is generated only from **1b**, whereas the dissociative ionization of **2b** and **3b** leads to the formation of **6b**. Whether these marked differences are due to the inherent properties of isolated ions, pronounced solvent effects, or the mode of ionization, respectively, is currently being investigated.

Acknowledgment. The financial support of this work by the Fonds der Chemischen Industrie, Frankfurt, the Gesellschaft von Freunden der Technischen Universität Berlin, and the Schering AG, Berlin, is gratefully acknowledged.

Registry No. 1b, 41893-65-6; **2b**, 41893-67-8; **3b**, 23431-56-3; **4b**, 27975-80-0; **5b**, 77305-91-0; **6b**, 60824-22-8; **8b**, 77305-92-1.

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(17) Our present knowledge of the collision-induced fragmentation behavior of these even-electron ions does not justify a detailed interpretation of the CA spectra. Nevertheless, some peaks in the complex CA mass spectra can be explained in terms of "ion structures"; for example, the enhanced loss of CH_3· in the CA spectrum of **4b** is likely to be a direct consequence of structure **8b**, which already contains an intact CH_3 group.