was then automatically chromatographed with benzene on a 2.5 × 48 in. column of Brinkmann acidic alumina. The effluent was monitored at 280 nm.

The first major fraction to be eluted was (*R,R*)-(+)-**5a** (4.34 g, 0.010 mol, 75.0%). Recrystallization from hexane gave white needles: mp 139.7–140.6°; ir (KBr) 3325 (NH), 1728, 1696, 1532, 1514, 1270, 1242, 1183, 1174, 1064, 801, and 779 cm^{-1}; nmr ($CDCl_3$) δ 1.54 (d, 3 $CHCH_3$), 5.48 (s, 1, NH), 5.54 (quartet, 1, $CHCH_3$), 7.03 (quartet, 1, $CHCF_3$), and 7.16–8.28 ppm (m, 14, both $C_{10}H_7$); $[\alpha]^{26.7}D$ +56.1 ± 1.1° (*c* 3.65, chloroform).

Anal. Calcd for $C_{25}H_{20}F_3NO_2$: C, 70.91; H, 4.76; N, 3.31. Found: C, 70.78; H, 4.77; N, 3.47.

The second major fraction to be eluted was (*S,R*)-(−)-**5b** (5.62, 0.013 mol, 97.0%), which can be recrystallized from hexane: mp 123.1–124.0°; ir 3450 (NH) 1724, 1505, 1264, 1232, 1180, 1167, 1127, 1061, 790, and 769 cm^{-1}; nmr ($CDCl_3$) δ 1.46 (d, 3, $CHCH_3$), 5.55 (s, 1, NH) 5.58 (quartet, 1, $CHCH_3$), 7.02 (quartet, 1, $CHCF_3$), and 7.20–8.28 ppm (m, 14, both $C_{10}H_7$); $[\alpha]^{24.5}D$ −12.2 ± 0.3° (*c* 15.5, chloroform).

Anal. Calcd for $C_{25}H_{20}F_3NO_2$: C, 70.91; H, 4.76; N, 3.31. Found: C, 71.05; H, 4.78; N, 3.41.

Conversion of (*R,R*)-(+)-1-(1-Naphthyl)-2,2,2-trifluoroethyl *N*-(1-[1-Naphthyl]ethyl)carbamate (5a) to (*R*)-(−)-(1-Naphthyl)-2,2,2-trifluoroethanol (3). Carbamate (*R,R*)-(+)-**5a** (4.23 g, 0.01 mol) was added to a solution of ethanolic sodium ethoxide (2.5 g sodium in 30 ml of ethanol) and refluxed for 30 min, at which time tlc (silica gel–methylene chloride) showed no remaining **5a**. The ethanol was removed at reduced pressure and excess base was neutralized with dilute hydrochloric acid. The aqueous mixture was extracted with three 50-ml portions of methylene chloride and the combined extracts were dried, concentrated, and chromatographed automatically with methylene chloride on a 2.5 × 48 in. column of Brinkmann silica gel.

The first major band to be eluted was fluoro alcohol[13] (*R*)-(−)-**3** (2.17 g, 0.0096 mol, 95.7%) identical by nmr, ir, and tlc to racemic **3**. Molecular distillation gave a waxy solid: mp 51.6–53.2°; $[\alpha]^{25.3}D$ −25.7 ± 0.7° (*c* 5.1, ethanol).

The second fraction contained, upon removal of the solvent, (*R*)-(+)-ethyl *N*-(1-[1-naphthyl]ethyl)carbamate (2.02 g, 0.0083 mol, 83.1%), identified by nmr.

A similar hydrolysis of carbamate (*S,R*)-(−)-**5b** gave, after chromatography, fluoro alcohol (*S*)-(+)-**3**: mp 51.6–53.6°; $[\alpha]^{25.7}D$ +25.8 ± 0.5° (*c* 5.1, ethanol).

Acknowledgements. This work was supported by the National Institute of Health through Research Grant GM 14518. The mass spectral data processing equipment employed was provided by National Institutes of Health Grants CA 11388 and GM 16864, from the National Cancer Institute, and the National Institute of General Medical Sciences.

Registry No.—(*R*)-**1**, 42340-98-7; (*R*)-**2**, 3886-70-2; *dl*-**3**, 17556-44-4; (*R*)-**3**, 22038-90-0; (*S*)-**3**, 33758-06-4; (*R*)-**4**, 53043-11-1; (*R,R*)-**5a**, 53043-12-2; (*S,R*)-**5b**, 53043-13-3; trifluoroacetic acid, 76-05-1; 1-bromonaphthalene, 90-11-9.

References and Notes

(1) (a) Alfred P. Sloan Foundation Research Fellow, 1970–1974. (b) Phillips Petroleum Predoctoral Fellow, 1972–1974.
(2) In view of the widespread separability of the diastereomeric derivatives of **1**, it is clear that this reagent, in conjunction with a high-pressure analytical liquid chromatography system, offers a useful tool for the determination of optical purity of those enantiomeric compounds which form derivatives with **1**.
(3) While a more comprehensive report of this resolution method will appear later, a partial list of compounds whose diastereomeric derivatives with **1** have been separated chromatographically on a preparative scale is as follows: 1-phenyl-2,2,2-trifluoroethanol; 1-phenyl-2,2,2-trichloroethanol; 1-phenyl-2,2,2-tribromoethanol; 1-(1-naphthyl)-2,2,2-trifluoroethanol; 1-(2-naphthyl-2,2,2-trifluoroethanol; 1-(3-pyrenyl)-2,2,2-trifluoroethanol; 1-(9-anthryl)-2,2,2-trifluoroethanol; 1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol; 1-phenyl-2,2,3,3,4,4,4-heptafluoro-1-butanol; 1-phenylethanol; 1-(4-nitrophenyl)ethanol; 1-(4-methoxyphenyl)ethanol; 1-(1-naphthyl)ethanol; 1-(2-naphthyl)ethanol; 1-phenylethanethiol; ethyl 2-mercaptopropanoate; methyl 2-hydroxy-3,3-dimethylbutanoate; methyl mandelate; 1-cyclohexyl-2,2,2-trifluoroethanol; 3-hydroxy-3-phenyl-4,4,4-trifluoro-1-butyne.
(4) W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 2817 (1971), and references therein.
(5) R. L. Muntz, Ph.D. Thesis, University of Illinois, Urbana, 1972.
(6) W. H. Pirkle and R. W. Anderson, *J. Org. Chem.*, **39**, 3901 (1974).
(7) The use of racemic isocyanates and chiral alcohols or, alternatively, racemic amines and chiral chloroformates, will afford diastereomeric carbamates which may be separated and hydrolyzed.
(8) The phenyl analog of this isocyanate, commercially available for several years, has previously been used [H. W. Gschwend, *J. Amer. Chem. Soc.*, **94**, 8430 (1972)] to afford diastereomers separable by crystallization. We are unaware of prior examples of chromatographic separation of diastereomeric carbamates derived from 1-phenylethyl isocyanate. In point of fact, we have found that the diastereomeric carbamates of this isocyanate do not, in general, separate as well chromatographically as those derived from **1**.
(9) T. L. Cairns, *J. Amer. Chem. Soc.*, **63**, 871 (1941).
(10) G. Greber and H. R. Kricheldorf, *Angew. Chem.*, **80**, 1028 (1968).
(11) In the event unreacted alcohol or other strongly retained materials are present in the crude product, a rough large-scale prechromatography may be desirable.
(12) Use of 1% of either *N,N*-dimethylethanolamine or di-*n*-butyltin dilaurate as a catalyst reduces reaction times to as little as *ca.* 10 hr.
(13) The absolute configuration of fluoro alcohol **3** has been established previously by the chiral nmr solvent method, using a partially resolved sample. See W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **89**, 5485 (1967). Subsequent work in these laboratories further supports the assignment.

Base-Catalyzed Decomposition of 1,2,3-Selenadiazoles and Acid-Catalyzed Formation of Diselenafulvenes

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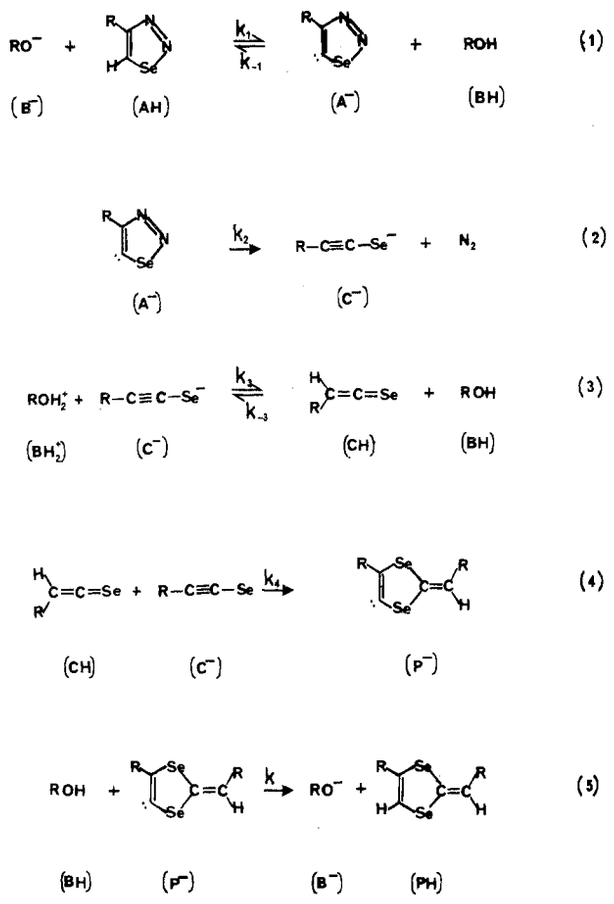
The kinetics and mechanism of the base-catalyzed decomposition of 4-aryl-1,2,3-selenadiazole with arylethynylselenolate ion as the intermediate and the subsequent hydrogen ion catalyzed formation of substituted 1,3-diselenafulvenes from this intermediate in basic alcoholic media have been investigated. Details of the mechanism, rate constants, and dependence upon the acidity function H_- are reported and discussed. An interesting coupling of the various steps in the above processes under certain conditions has been found and analyzed in some detail.

The mechanism of the formation of the 1,3-diselenafulvenes has previously been reported.[2] The steps of this reaction can be summarized as in Scheme I.

While Scheme I, deduced from our experimental observations, adequately describes the results, several points remained to be clarified. These were (a) the importance of the equilibrium in step 1 as opposed to an irreversible and concerted hydrogen abstraction–decomposition to the ethynylselenolate ion, and (b) the extent of the equilibrium in step 3 and thus a measure of the stability of the heretofore unknown selenaketene. By undertaking a kinetic study of the reaction we hoped to gain a better understanding of the

Scheme I



above as well as to find the kinetic interrelationships of this interesting and complex five-step reaction sequence in which the first step is base and some of the subsequent steps are acid catalyzed.

Furthermore, in line with the existing interest in testing the significance and validity of acidity scales in the acid- or base-catalyzed reactions of heterocyclic compounds kinetically,[3] we hoped to find a correlation of our results with the H_- scale. In this paper we wish to report our progress in the study of the above reaction.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Model T-60 Varian spectrometer. Mass spectra were obtained on a Model CH5 Varian spectrometer. Ultraviolet spectra were obtained on a Pye-Unicam SP-800 using the automatic repeat scanning facility. Melting points were determined on a Kofler hot stage. Elementary analysis was performed by Mikroanalytisches Laboratorium Dornis u. Kolbe, West Germany.

All the alcohols used were dried by refluxing over an appropriate metal alkoxide before use. The alkoxide solutions used for kinetic measurements were prepared by adding potassium metal to the respective alcohol under nitrogen.

Kinetic experiments involving volumetric gas measurements were performed using a Warburg type respirometer, Gilson Model GR14, with 14 reaction vessels. The experiments were performed as follows. From a stock solution of the selenadiazole in the appropriate solvent (typical concentration of about 60 mg/10 ml), 0.5 ml was pipeted into the side arm of a Warburg flask, and 1.5 ml of the base solution was pipeted into the main reaction compartment. The flasks were mounted on the respirometer and the apparatus was allowed to reach equilibrium for about 45 min. To start each reaction, the corresponding flask was removed from the temperature bath, its contents were rapidly mixed, and it was replaced before a lapse of about 30 sec. Readings were taken on the verniered volumeter until no appreciable gas evolution took place.

Spectrophotometric kinetic measurements were carried out by adding sufficient potassium phenylethynylselenolate to about 3 ml of the respective solvent to give a maximum absorption peak on the recorder when using a 1-mm cell. Measurements were taken at 308 and 340 nm.

The preparation of the selenadiazoles and their conversion into the 1,3-diselenafulvenes were carried out as previously described.[2,4]

ω-d_3-Acetophenone. Phenylacetylene, 3.0 g (0.03 mol), was added to a solution of 3 ml of deuterium oxide containing about 0.1 g of metallic sodium and stirred magnetically for 1 hr at room temperature. Concentrated deuteriosulfuric acid (98%), 5 ml, and 0.5 g of mercuric sulfate were mixed and the stirring was continued for 0.5 hr (until the liquid layer became homogeneous). The solution was filtered through a sintered glass funnel and washed with 2 ml of water, and the filtrate was extracted several times with ether. The combined ether layer was evaporated to give 3.2 g of an oil. The nmr spectrum of this oil showed only aromatic protons.

4-Phenyl-5-d-1,2,3-selenadiazole. The ω-d_3-acetophenone obtained in the previous preparation was converted without further purification to its semicarbazone derivative in the usual manner. The dried semicarbazone, 4.1 g (23.2 mmol), was dissolved in 10 ml of glacial acetic acid and 2.6 g (23.4 mmol) of finely powdered selenium dioxide was added and the solution heated with occasional shaking on a water bath for 1 hr. The solution was filtered hot to remove the deposited selenium and water was added to the main filtrate until turbid. The reddish-brown solid that separated upon cooling was dissolved in 40 ml of ethanol, decolorized with activated charcoal, and crystallized by the addition of water. A pure material was obtained after several recrystallizations, 3.4 g (53% yield based on the phenylacetylene used), mp 76°. Mass spectrum showed 95% deuterium content in the 102/103 fragment (Ph—C≡C—H^+).

Potassium Phenylethynylselenolate. Clean metallic potassium, 1.5 g, was added to a solution of 6 ml of absolute ethanol in 50 ml of dry dioxane. After the evolution of hydrogen gas ceased, the solution was filtered in a dry N_2 atmosphere. Freshly recrystallized selenadiazole, 0.1–0.2 g, was added to 5-ml aliquots of the above solution in centrifuge tubes. After N_2 gas evolution ceased, the precipitate was centrifuged and the supernatant decanted, and the solid was washed several times with dry ether, dried, and kept under desiccation. Typical analysis for several preparations were as follows.

Anal. Calcd for C_8H_5KSe: C, 43.83; H, 2.28; K, 17.90; Se, 36.05. Found: (a) C, 44.60; H, 4.73; K, 13.05; Se, 26.75; (b) C, 42.10; H, 4.80; K, 10.38; Se, 21.33; (c) C, 38.40; H, 3.39; K, 7.30; Se, 29.76.

The molar absorption of the potassium phenylethynylselenolate was obtained in the following way. Selenolate salt (2.0 mg) was dissolved in 10 ml of concentrated ethanolic base solution and absorption at 308 nm, its λ_{max}, was obtained. Subsequently another 2.0 mg of the salt was dissolved in 10 ml of ethanol and allowed to stand and react to form the 1,3-diselenafulvene derivative. From the ultraviolet spectrum of the resulting solution, the concentration of the pure potassium phenylethynylselenolate salt in the salt mixture was determined by measuring the optical absorption of the salt mixture at 340 nm. From several such determinations the average molar absorption of the pure potassium selenolate was determined to be 2.05×10^5.[5]

Kinetics of Deuterium Exchange at C-5 of 4-Phenyl-5-d-1,2,3-selenadiazole. 4-Phenyl-5-d-1,2,3-selenadiazole, 36 mg, was added to 3 ml of a 4×10^{-3} M solution of metallic potassium in ethanol at 22°. Aliquotes, 0.2 ml, were removed at appropriate time intervals and the reaction was quenched by adding the aliquotes to test tubes containing two drops of glacial acetic acid. The solvents were evaporated and the mass spectrum of the residue was obtained. The ratios of the fragment peaks at 102 and 103 were measured.

Kinetics of Deuterium Exchange at C-5 Position of 4-Phenyl-5H-1,2,3-selenadiazole in 1-Deuterioethanol. The same procedure as above was employed using 5H-selenadiazole and 1-deuterioethanol of 75% deuterium enrichment.

Measurement of the Acidity Function. H_- values of the various reaction media used were measured according to the method described by Schaal and Gadet.[5]

Results and Discussion

Kinetics of the reaction pathway shown in Scheme I were first studied in two separate stages as described below.

Part I. The decomposition of 4-phenyl-1,2,3-selenadiazole (AH) and production of the phenylethynylselenolate ion (C^-), steps 1 and 2, were studied under conditions of

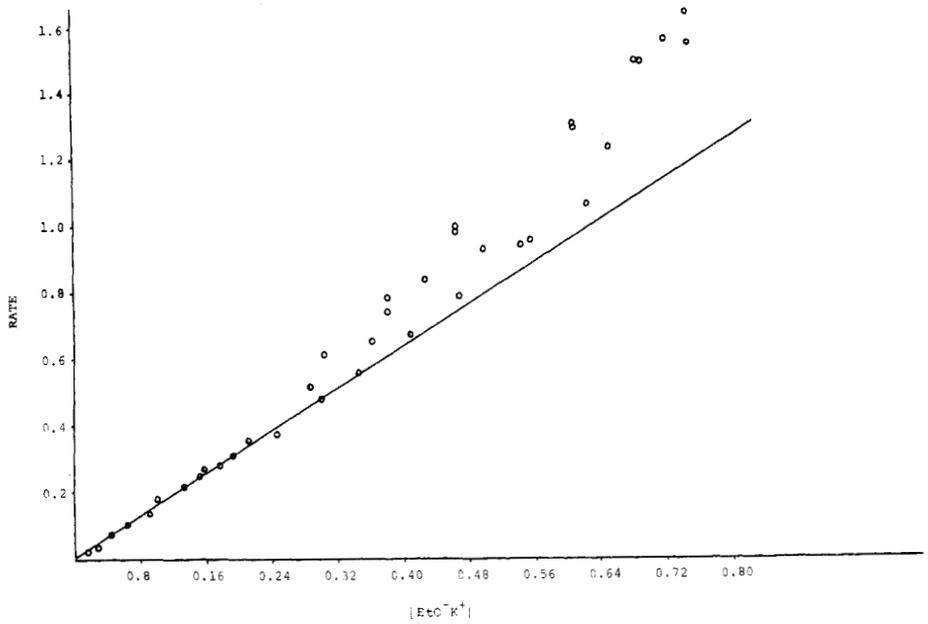


Figure 1. Observed rate *vs.* $[B^-]_0$ in ethanol at 32°.

constant basicity. This condition was realized in basic ethanolic solutions, where either the basicity of the medium was so low that the production of PH from C^- [steps 3, 4, and 5] occurred almost instantaneously thereby regenerating the consumed base and maintaining a constant base concentration, or the basicity was so high that the consumption of B^- in step 1 did not appreciably reduce the base concentration of the medium throughout the reaction. Pseudo-first-order rate constants were obtained from the following rate law[6a]

$$\log \frac{V_\infty - V_t}{V_\infty} = \frac{r}{2.303} t \qquad (6)$$

where $r = [B^-]_0 k_1 k_2 / k_{-1}'$, $k_{-1}' = k_{-1}[BH]$, $[B^-]_0$ = initial base concentration, and V_t and V_∞ are volumes of the N_2 gas evolved at time t and at the completion of the reaction, respectively. Equation 6 is obtained by assuming a fast equilibrium for step 1 and steady state condition for $[A^-]$. All experiments showed a smaller rate within the first 30 sec of the reaction. Analysis has shown that this time is substantially independent of the base concentration and is probably due to the time needed for the homogenization of the solution and equilibration of the measuring apparatus. This "time lag" therefore seems to be caused by physical conditions and not by a kinetic "build-up" period which would necessarily show a base dependence.

A plot of r *vs.* $[B^-]$ for base concentrations up to about 0.23 M gave a straight line, the slope of which determines $k_1 k_2 / k_{-1}'$ to be $1.6 \pm 0.1\ M^{-1}\ \text{min}^{-1}$. At higher base concentrations (Figure 1), r deviates upward, indicating an increase in lyate ion activity of the base.[7a] This enhancement of the lyate ion activity at high base concentration is expected, and it is attributed to a decrease in the solvent's ability to solvate. Bowden and others,[7b] however, have pointed to the fact that this increase in lyate ion activity is already appreciable at 0.1 M ethoxide concentrations, making it necessary to apply eq 7 below for the calculation of the basic strength of the solution in this region.

$$H_- = \text{const} + \log [OR^-] \qquad (7)$$

We therefore constructed an H_- scale for the region of base concentration used in this work. Figure 2 shows a plot of log $[EtO^-K^+]$ *vs.* H_- for our range of base concentrations. It can be seen that with the accuracy of the data points, a straight line of unit slope can be drawn up to a base concentration of about 0.3 M. Above this concentration, eq 7 does not seem to hold. It should be noted that our H_- values are consistently slightly higher than those reported in Bowden's review. However, such a shift has no influence on our conclusions concerning the linear relations involving H_-.

Assuming, as usual, a similarity between the indicator acid (substituted nitroanilines) and AH in strongly basic solutions, a linear relationship between log r and H_- is expected. Figure 3 shows such a plot. Although at low basicity a reasonably straight line with a near unit slope can be drawn, the linearity breaks down at higher H_- values. Interestingly, the breakdown occurs roughly at the same point as in the plot of log $[B^-]$ *vs.* H_- (Figure 2). However, when, as discussed by More O'Farrall,[8] our data are treated according to its linear free energy relationship with logarithm of the apparent rate, a straight line with a slope of about 0.53 is obtained as shown in Figure 4. Our results thus confirm the usefulness of the extension of the Bunnet and Olsen[9] approach for concentrated basic alcoholic solutions.

To further investigate the relative rates of steps 1 and 2, 4-phenyl-5-*d*-1,2,3-selenadiazole (AD) was used as a substrate. No change in the overall rate was observed, indicating a rapid and complete isotopic exchange before any gas evolution could take place. The isotopic exchange rates of AD and AH in [1-^{1}H]ethanol and [1-^{2}H]ethanol, respectively, were followed mass spectroscopically by measuring the relative peak heights of the 102 and 103, $[PhC{\equiv}CH]^+$ and $[PhC{\equiv}CD]^+$, fragment ions.[10] These experiments were carried out at a base concentration of about 0.004 M. As stated above, the amount of gas evolution [step 2] was negligible during the period of exchange. It was observed that isotopic exchange at 32° for both AD and AH was completed in less than 1 min. The fact that the reverse rate of step 1 is much larger than the forward rate (which follows from a rapid exchange) implies that the rate of the exchange reaction is given by $k_1\ [B^-]_0$. Thus k_{1H} and k_{1D} were determined. Although experimental difficulties severely limited the accuracy of the measurements, the rough results obtained are $k_{1H} = 4 \times 10^2\ M^{-1}\ \text{min}^{-1}$, and $k_{1D} = 2 \times 10^2\ M^{-1}\ \text{min}^{-1}$.

The reactions of steps 1 and 2 were further investigated by comparing the rates of the decomposition of selenadia-

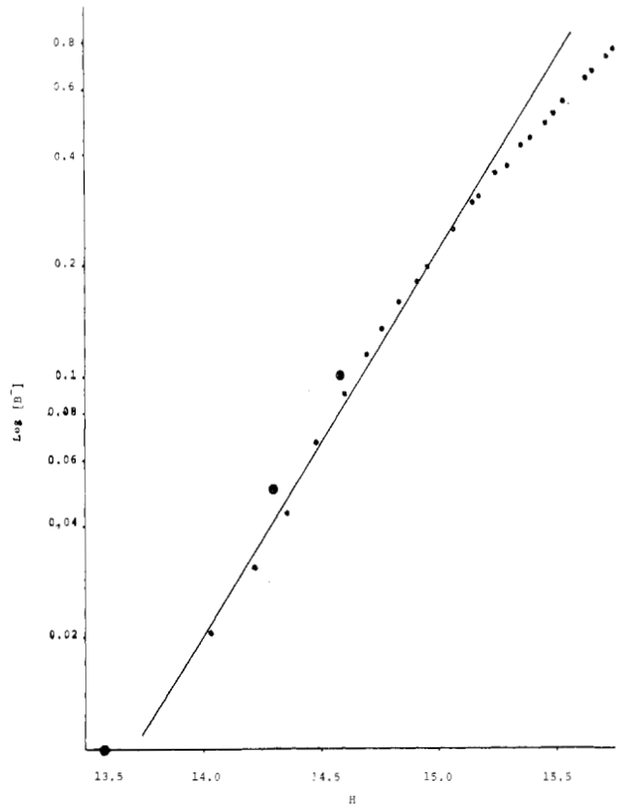


Figure 2. Logarithm of [EtO⁻] *vs.* H_-; ·, our values, ●, from Bowden's review.[7]

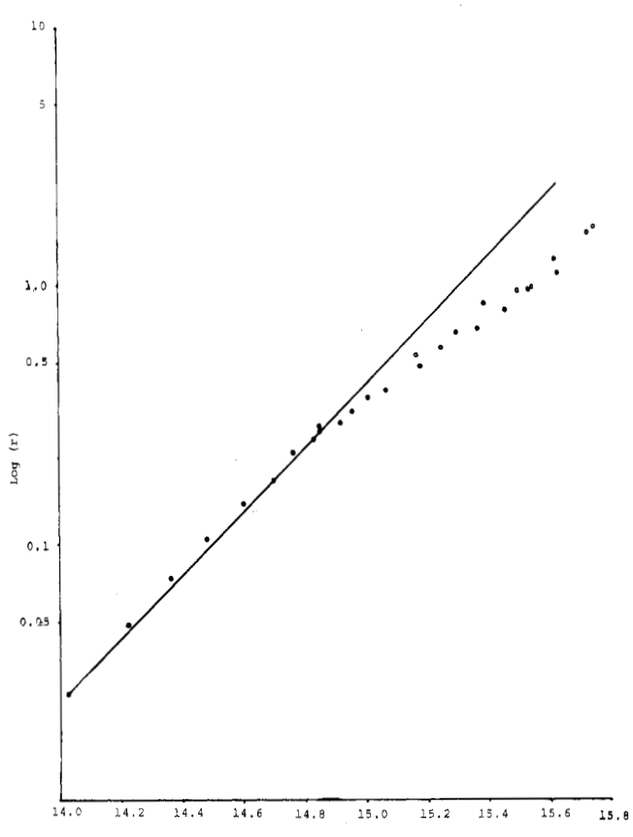


Figure 3. Logarithm of observed rate *vs.* H_- in ethanol.

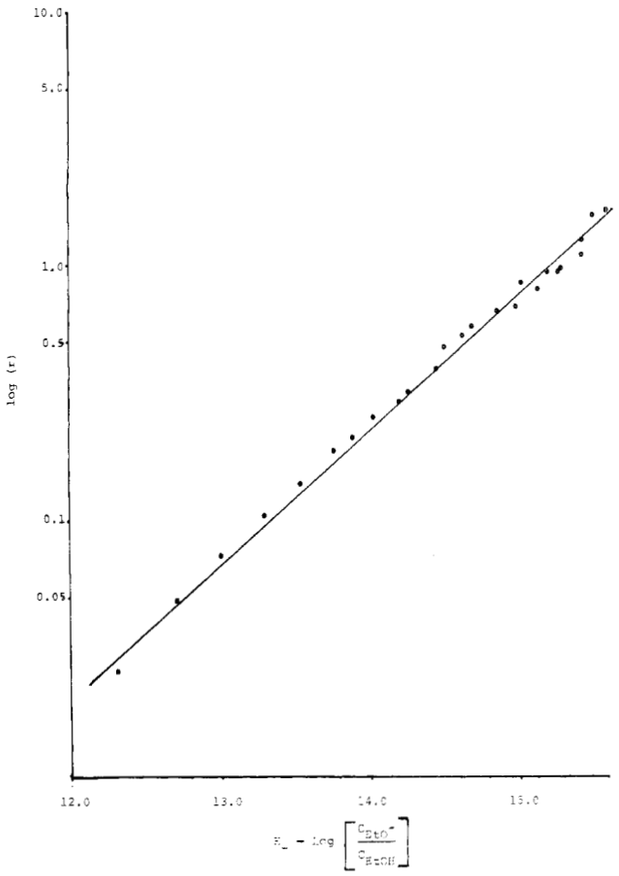


Figure 4. Logarithm of observed rate *vs.* H_- − log [EtO⁻]/[EtOH].

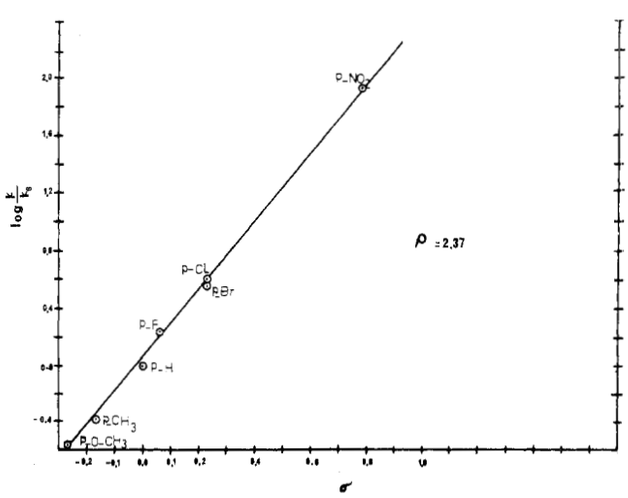


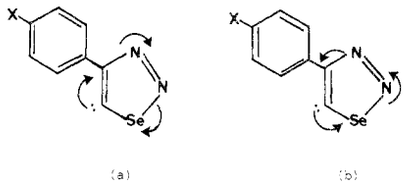
Figure 5. Hammet σ–ρ relation for the overall decomposition rate of AH at 32°.

zoles having substituents on the phenyl ring. The results, shown in Figure 5, indicate a positive ρ value of 2.4. Since isotopic exchange measurements show that step 2 is slower than the reverse direction of step 1, the relatively large positive ρ value observed could be interpreted in either of the following ways: (a) the substituents do not affect the rate of step 2, rather they shift the equilibrium to the right, thereby increasing the steady state concentration of A^- and enhancing the overall rate; (b) they act on the slower unimolecular decomposition step.

Of the two mechanisms which can be envisaged for the decomposition of A^- (Scheme II), one would not expect that in the transition state of (a) the substituents would exert any electronic effects. Hence a ρ value of zero would be expected.[11] However, since electron delocalization away from the heterocyclic ring in (b) is assumed, a relatively large ρ value should be observed. Furthermore, since in this

case electron-withdrawing groups such as a *p*-nitro group would be in direct resonance with the reaction site, a σ^-

Scheme II



value would be a better substituent constant if transition state b were operative. As can be seen from Figure 5, the ordinary σ value of 0.78 gives a much better fit than a σ^- value of 1.27. It is therefore concluded that the mode of the unimolecular decomposition is probably according to (a) as previously assumed,[2] and that the substituents shift the equilibrium as discussed above.

Part II. Steps 3 through 5 of the reaction were studied by measuring the rate of appearance of the product PH starting with the intermediate C^- (see Scheme I). In all experiments only 50 to 75% of the expected product was obtained. Since no side reaction was identified under the conditions of the experiments, it was concluded that the starting material, Ph—C≡C—Se^-, was impure. The absence of a possible side reaction was checked kinetically by measuring the rate of appearance of PH *vs.* the rate of disappearance of C^- (see Figure 6). This figure also indicates the

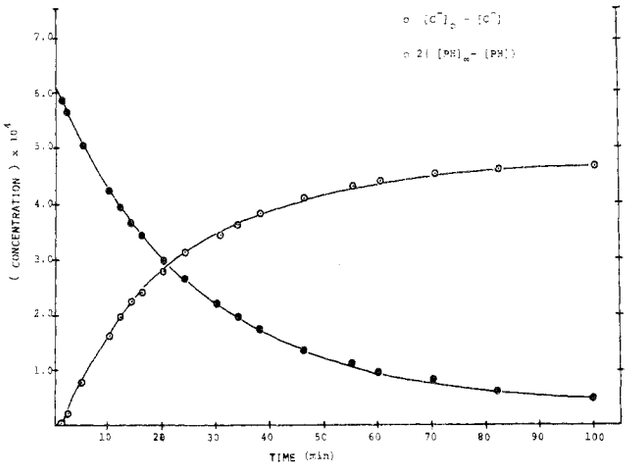


Figure 6. Disappearance of C^- and appearance of PH in 0.01 *M* EtO^-K^+ at 32°.

steady state condition of CH, and therefore implies that the selenaketene has a transient existence. The concentration of C^- was obtained by following the changes in maximum absorptions of C^- (at 308 nm) and PH (at 340 nm) as the reaction proceeded[6c] and solving two simultaneous equations for the respective concentrations.

Two different rate laws result depending on whether step 3 is general acid catalyzed (*i.e.*, $C^- + BH \rightleftharpoons CH + B^-$) or specific hydrogen ion catalyzed (*i.e.*, $C^- + BH_2^+ \rightleftharpoons CH + BH$). Denoting the rate constants for the forward and the reverse directions of step 3 by k_3 and k_{-3}, respectively, the differential rate laws obtained for the two cases are respectively

$$-\frac{d[C^-]}{dt} = 2\frac{d[PH]}{dt} = \frac{2k_3[BH][C^-]^2}{(k_{-3}/k_4)[B^-] + [C^-]} \quad (8)$$

$$-\frac{d[C^-]}{dt} = 2\frac{d[PH]}{dt} = \frac{2k_3[H^+][C^-]^2}{(k_{-3}/k_4)[BH] + [C^-]} \quad (9)$$

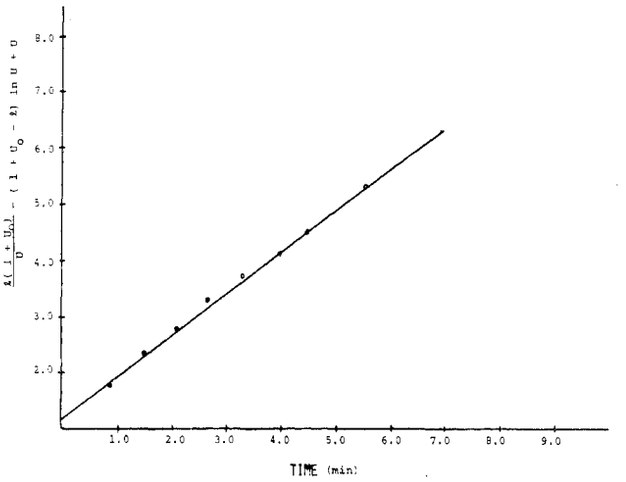


Figure 7. A plot of eq 11 with $[C^-]_0 = 1.3 \times 10^{-3}$ *M* and $[B^-]_0 = 1 \times 10^{-3}$ *M vs.* time in ethanol at 32°.

where steady state condition for CH and a rapid protonation of P^- are assumed. Preliminary analysis of the data showed that in general the two terms in the denominator of eq 8 and 9 are comparable in value and must both be retained. Hence the corresponding *initial* reaction rates

$$\frac{2k_3[BH][C^-]_0^2}{(k_{-3}/k_4)[B^-]_0 + [C^-]_0}$$

and

$$\frac{2k_3[H^+]_0[C^-]_0^2}{(k_{-3}/k_4)[BH] + [C^-]_0}$$

afford a ready distinction between eq 8 and 9 by means of their different dependencies on the initial base concentration $[B^-]_0$. Examination of the initial reaction rates obtained from the data showed an inverse proportionality to $[B^-]_0$ equivalent to a direct proportionality to $[H^+]_0$. Thus eq 9 and therefore specific hydrogen ion catalysis is clearly indicated.

To integrate eq 9, we use eq 7 to write

$$-\log [H^+] = \text{const} + \log [B^-] \quad (7')$$

Furthermore, from the stoichiometry of the reaction, the base concentration during the reaction is given by

$$[B^-] = [B^-]_0 + 2[PH]$$

The last two equations can be combined to give

$$\frac{[H^+]}{[H^+]_0} = \frac{[B^-]_0}{[B^-]} = \frac{[B^-]_0}{[B^-]_0 + 2[PH]} \quad (10)$$

which is inserted in eq 9, and the latter integrated to give

$$l(1 + U_0)\frac{1}{U} - (1 + U_0 - l)\ln U + U = 2qt + \text{const} \quad (11)$$

where

$$l = k_{-3}[BH]/k_4[B^-]_0$$

$$U = [C^-]/[B^-]_0$$

$$U_0 = [C^-]_0/[B^-]_0$$

$$q = k_3[H^+]_0$$

Figure 7 shows a typical plot corresponding to eq 11. The value of $k_{-3}BH]/k_4$ used was 3×10^{-4} *M*, which gave the best fit for the data. The maximum concentration of C^- taken was about 1×10^{-3} *M*. Therefore at base concentrations higher than about 0.01 *M*, the factors U_0 and l become negligible compared to unity, and eq 11 reduces to

Table I
Rate Constants of Step 3 in Ethanol at 32°

$[B^-]_0$, M	$2q$, min^{-1}	$2q[B^-]_0 \times 10^4$, $M\ min^{-1}$
1.1×10^{-3}	0.750	8.25
1.71×10^{-3}	0.366	6.3
3.26×10^{-3}	0.243	7.9
3.46×10^{-3}	0.233	8.2
3.83×10^{-3}	0.175	6.7
7.72×10^{-3}	0.083	6.4
8.90×10^{-3}	0.075	6.9
1.07×10^{-2}	0.064	6.8
1.22×10^{-2}	0.050	6.1
1.55×10^{-2}	0.044	6.8
1.94×10^{-2}	0.040	7.7

$$(l/U) - \ln U = 2qt + \text{const} \qquad (12)$$

The rate constants obtained using eq 11 and 12 are shown in Table I. The value of the product $2q[B^-]_0 = 2k_3[H^+]_0[B^-]_0$ nearly remains a constant in Table I, as it should for a given medium according to eq 7. It is somewhat surprising that this reaction displays a specific hydrogen ion catalysis in basic alcoholic media, where the concentration of H^+ is quite small.

Finally, the rates of phenyl-substituted Ph—C≡C—Se^- were compared and a ρ value of nearly zero was obtained. This is consistent with the interpretation that the small negative ρ value expected for step 3 is compensated by an equal and opposite ρ value for the dimerization of step 4.

When gas evolution was studied with 2-propanol as solvent, a different behavior in addition to the simple one encountered with ethanol was observed. The latter, *i.e.*, pseudo-first-order behavior described by eq 6, was observed when the initial base concentration was much greater than $[AH]_0$, so that its depletion during the reaction was negligible. However, contrary to the case of ethanol, at initial base concentrations comparable with or lower than $[AH]_0$, part II of the reaction did not occur rapidly enough to maintain a constant basicity. Thus the rate of gas evolution became dependent on the progress of part II of the reaction and *vice versa*. Therefore, contrary to the case of ethanol where parts I and II of the reaction were studied separately, 2-propanol afforded a simultaneous study of the two parts of the reaction *via* the rate of gas evolution. This difference of behavior between the two media is due to the higher inherent basicity of 2-propanol which causes a relative speed-up and slow-down of parts I and II, respectively. Although the above coupling is also possible in ethanol, the necessary conditions could not be realized with the volumetric capabilities used in the experiments.

A typical logarithmic plot of $(V_\infty - V_t)/V_\infty$ *vs.* t in 2-propanol displaying variable basicity is shown in Figure 8. This plot indicates that the basicity, which controls the rate of gas evolution, decreases from its initial value to a minimum (where it assumes a steady state) and then starts increasing to its initial value as the reaction proceeds to completion. Clearly parts I and II of the reaction are coupled *via* base concentration, and must be treated simultaneously. This is accomplished by combining the differential rate laws of the two parts [*cf.* eq 6 and 9], taking due account of the coupling.

$$-\frac{d[AH]}{dt} = \frac{d[N_2]}{dt} = k_2[A^-] = \frac{k_1k_2}{k_{-1}'}[B^-][AH] \qquad (13)$$

$$2\frac{d[PH]}{dt} = \frac{2k_3[H^+][C^-]^2}{(k_{-3}/k_4)[BH] + [C^-]} \qquad (9')$$

As before, $[H^+]$ is obtained by means of eq 7′ and the stoichiometric conditions

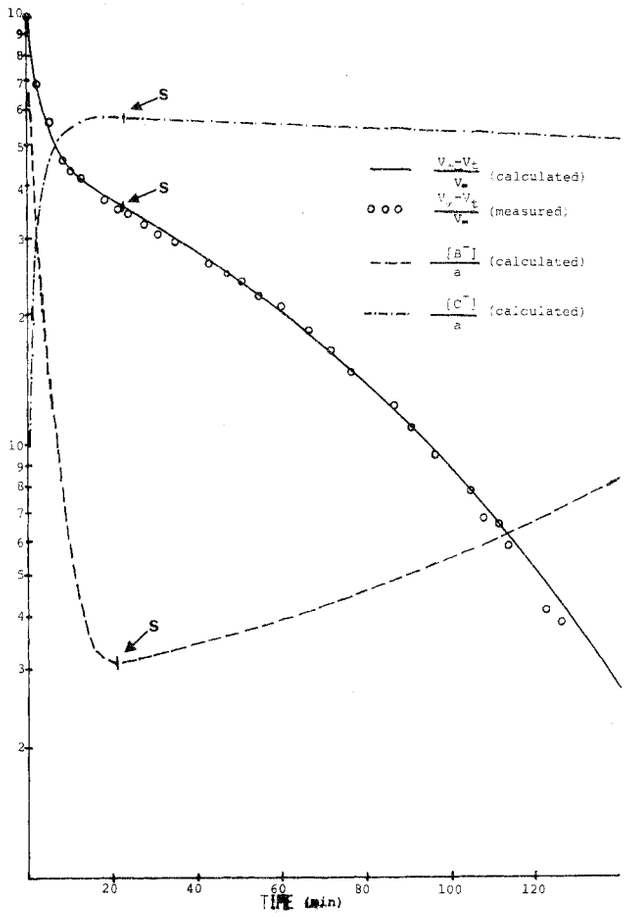


Figure 8. Overall reaction progress in dilute basic 2-propanolic solution at 32°.

$$\frac{[H^+]}{[H^+]_0} = \frac{[B^-]_0}{[B^-]} = \frac{[B^-]_0}{[B^-]_0 + 2[PH] - [N_2]} \qquad (14)$$

Denoting $[AH]_0$ and $[B^-]_0$ by a and b, and the amount of N_2 gas evolved and the concentration of C^- at time t by x and y, respectively, we obtain from eq 14

$$[H^+] = [H^+]_0\frac{b}{b - y} \qquad (15)$$

Equations 13 and 9′ then take the form of eq 16 and 17, respectively.

$$\frac{dx}{dt} = (k_1k_2/k_{-1}')(a - x)(b - y) \qquad (16)$$

$$\frac{d(x - y)}{dt} = \frac{2qby^2}{(b - y)(k_{-3}/k_4[BH] + y)} \qquad (17)$$

The differential eq 16 and 17 were integrated numerically on a CDC 6400 computer using Taylor's method.[12] The results of the computations for a typical experiment are shown in Figure 8, where the measured and calculated values for $(V_\infty - V_t)/V_\infty$ are compared, and the calculated values of $[B^-]/a$ and $[C^-]/a$ are also drawn in for reference.

In obtaining the calculated results displayed in Figure 8, the values $a = [AH]_0 = 7 \times 10^{-3}\ M$ (measured value) and $k_3[BH]/k_4 = 3 \times 10^{-4}\ M$ (obtained from the data of part II in ethanol) were used. The remaining parameters, *i.e.*, $b = [B^-]_0$, k_1k_2/k_{-1}', and q, were treated as free and were determined by a mean-square fit. The reason for treating b as a free parameter is the inaccuracy in its measurement at the concentrations used (*i.e.*, about $5 \times 10^{-3}\ M$). The reason for treating q as free is the unavoidable presence in small and variable concentrations of water in the alcohol used, which, because of the extreme sensitivity of the H_- value of 2-propanol to the addition of small amounts of

Table II
Parameters Obtained by Fitting Volumetric Data with 2-propanol as Solvent

Expt no.	$[B^-]_0 \times 10^3$, M	k_1k_2/k_{-1}' min^{-1} M^{-1}	$2q[B^-]_0 \times 10,^6$ M min^{-1}	$(2k_1k_2/k'_{-1}) \cdot q[B^-]_0 \times 10^4$, min^{-2}
1	5.5	79	1.8	1.4
2	6.1	69	2.0	1.4
3	4.9	67	1.6	1.0
4	4.4	61	2.1	1.3
5	4.7	41	3.2	1.3

water,[7] has a decisive effect on the value of this parameter. Table II shows the parameters obtained by fitting five representative experiments with apparently variable water content (experiment no. 2 is the one displayed in Figure 8). All fits were about equally good as judged from the mean-square deviation. Table II has been arranged in the order of decreasing values of k_1k_2/k_{-1}' and thus increasing water content. The value of $q = k_3[H^+]_0$ is thus expected to increase with increasing aqueous component. With the exception of experiment 3, this expectation is verified. Finally the product qk_1k_2/k_{-1}' should approximately remain constant, as the two factors are oppositely influenced by the increase of the aqueous component. Again, with the exception of experiment 3, this product is seen to be roughly constant. The above observations also serve to show that the fitting procedure s a fairly reliable one and yields meaningful results with very little input data.

We now proceed to give a qualitative interpretation of the results displayed in Figure 8. The initial decrease of basicity is accounted for by observing that, under these conditions, C^- accumulates to an appreciable concentration, thereby preventing the complete regeneration of the base consumed in step 1. Thus concurrent with the accumulation of C^- as the reaction proceeds, $[B^-]$ decreases, and consequently part I of the reaction is hindered while part II is enhanced. The changes just mentioned continue until the two parts of the reaction equilibrate, at which time $[B^-]$ and $[C^-]$ reach their minimum and maximum values, respectively. This stage corresponds to the points S of Figure 8, where the rate of gas evolution is clearly at its minimum. The "steady state" just described will subsequently be disturbed as the depletion of B^- causes a corresponding decrease in the rate of the production of C^-, thereby forcing the latter to decrease and $[B^-]$ to increase. Thus the last stage of the reaction is characterized by increasing basicity and rate of gas evolution. Finally at the completion of the reaction, [AH] and $[C^-]$ go to zero while $[B^-]$ returns to its initial value. Note that Figure 8 does not continue to completion, since the rate of gas evolution becomes unmeasureably small long before the accumulated C^- converts into the final product. As is evident from Figure 8, the complete conversion of C^- will take several hours.

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Supplementary Material Available. Plots of gas evolution *vs.* time, observed rate *vs.* $[B^-]_0$ and changes in absorbance maxima of C^- and PH will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3906.

Registry No.—ω-d_3-Acetophenone, 17537-31-4; phenylacetylene, 536-74-3; deuterium oxide, 7789-20-0; 4-phenyl-5-*d*-1,2,3-selenadiazole, 53060-19-8; potassium phenylethynylselenolate, 36928-61-7; 4-phenyl-5*H*-1,2,3-selenadiazole, 25660-64-4; 1-deuterioethanol, 1624-36-8.

References and Notes

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(6) Figures a, b, and c will appear following this article in the microfilm edition of this journal. See paragraph at end of paper regarding supplementary material.
(7) (a) At higher base concentrations than about 0.7 *M*, the reaction is too rapid to be measured in ethanol. Actually, the excessive heat of solution of the base at about 1 *M* concentration disturbs the thermal equilibrium of the medium and thus prohibits measurements in the otherwise suitable medium methanol. (b) K. Bowden, *Chem. Rev.*, **66**, 119 (1966).
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(10) The *m/e* 102 rather than the molecular ion was chosen for the measurement, since (a) it was the base peak in the spectrum and (b) it contained no selenium. The latter, because of its multiple natural abundance peaks, would have complicated ratio measurements.
(11) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).
(12) The accuracy of the computation was controlled and set to be uniformly better than three significant figures.