Anion–Cation Combination Reactions. III.[1] The Reaction of Diazonium Ions with Azide Ion in Aqueous Solution

Calvin D. Ritchie* and D. J. Wright

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.

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Abstract: The rates of reactions of ten substituted benzenediazonium ions with azide ion in aqueous solution have been measured. The reactions forming aryl azide and arylpentazole as initial products are accurately second order, first order in diazonium ion and first order in azide ion concentrations. The second-order rate constants are correlated by the Hammett equation with a ρ value of 3.2. It is argued that this ρ value indicates that the rate-determining step of the reaction is the attack of azide ion on the diazonium ion. The aryl diazoazide, which has been proposed as an intermediate in the reaction by earlier workers, was not detected in our systems. The arylpentazoles formed in the initial reactions undergo decomposition to aryl azide at rates sufficiently slow that they do not interfere with the kinetic measurements of the first stage of the reaction.

In connection with our studies of anion–cation combination reactions,[1] we wished to know the rates of attack of azide ion on diazonium ions. These reactions are sufficiently complex that a detailed kinetic study is required to obtain the desired information.

Clusius[2] and Huisgen[3] have shown that the reactions of azide ion with aromatic diazonium ions proceed entirely by attack of the azide ion on the diazonium nitrogen atom. At low temperatures, *ca.* −30°, in methanol solution, the isolable products of the reaction are the aryl azide and the arylpentazole.[4] At higher temperatures, the arylpentazoles decompose to aryl azide and nitrogen. At the high concentrations of azide ion and the low temperatures used in his studies, Huisgen[3] noted that the rate of evolution of nitrogen was independent of the concentration of azide ion. It was proposed that the formation of the aryl diazoazide was an unmeasurably fast reaction, and that the measured rate was that of the decomposition of the diazoazide to aryl azide and nitrogen.

Results

The reactions of a series of substituted benzenediazonium ions with azide ion in aqueous solution at 23° have been studied by observing both the disappearance of the absorption of the diazonium ion and the appearance of the absorption of the aryl azides in stop-flow experiments utilizing ultraviolet spectral detection. The disappearance of absorption at the λ_{max} of the diazonium ions in solutions containing at least a tenfold excess of azide ion follows strict first-order kinetics to better than 95% completion for all of the compounds studied.

In all of the cases except those of the *p*-cyano- and *p*-nitrobenzenediazonium ions, experiments in which the excess azide concentration was varied over a range of about a factor of 10 showed clearly that the reactions are strictly first order with respect to azide ion concentration. The extremely fast rates observed for the *p*-cyano and *p*-nitro compounds limited the concentration range of azide ion which could be measured to ranges of factors of 4 and 2, respectively. The precision obtained in the majority of cases is well indicated by the data for the *p*-chlorobenzenediazonium ion reaction presented in Table I.

Table I. Dependence of Rate of Reaction of *p*-Chlorobenzenediazonium Ion on Azide Ion Concentration in Aqueous Solution (23 ± 1°, $(ArN_2^+) = 2.39 \times 10^{-5}$ *M*)

$(N_3^-) \times 10^3$, *M*	k_{obsd},[a] sec^{-1}	$k \times 10^{-4}$,[b] M^{-1} sec^{-1}
2.00	20.0	1.00
1.00	11.5	1.15
0.88	9.96	1.13
0.76	8.14	1.07
0.64	6.71	1.05
0.52	5.28	1.02
0.40	4.17	1.04
0.30	3.14	1.05

[a] Pseudo-first-order rate constant for disappearance of absorption at 285 nm. [b] Calculated second-order rate constants. The average value of k is $1.06 (\pm 0.04) \times 10^4$ M^{-1} sec^{-1}.

The reaction of *p*-methoxybenzenediazonium ion was studied both under pseudo-first-order conditions, with azide ion concentrations ranging from 2×10^{-4} to 2×10^{-3} *M*, and under second-order conditions, with both azide ion and diazonium ion at 4×10^{-5} *M*. Second-order rate constants obtained from all runs agreed within 5%.

The second-order rate constants and the wavelengths used for observation are shown in Table II for all of the compounds studied.

For all of the reactions, the appearance of the absorption at the λ_{max} of the aryl azide occurs in two clearly distinguishable steps. The first step shows the same apparent rate constant as does the disappearance of the diazonium ion absorption. There then occurs a much slower further increase in aryl azide absorption which follows first-order kinetics and is independent of azide ion concentration. That this change in absorbance is due to the conversion of the arylpentazole to aryl azide is clearly shown by the following data.

The preparation of *p*-methoxyphenylpentazole was accomplished by the methods described by Ugi.[4] The ultraviolet spectrum of the compound in aqueous

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[1] Previous paper in this series: C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 2425 (1971). This work was supported by Grant GM 12832, PHS-NIH.

[2] K. Clusius and M. Vecchi, *Helv. Chim. Acta*, **39**, 1469 (1956), and earlier references cited there.

[3] I. Ugi and R. Huisgen, *Chem. Ber.*, **90**, 2914 (1957).

[4] I. Ugi, H. Perlinger, and L. Behringer, *ibid.*, **91**, 2324 (1958); see also I. Ugi, *Tetrahedron*, **19**, 1801 (1963).

Table II. Reactions of Aryldiazonium Ions with Azide Ion in Aqueous Solution at 23°

Substituent	λ_{max} (ArN_3)	λ_{max} (ArN_2^+)	k, M^{-1} sec^{-1}
p-CH_3O	253	315	54.0
p-CH_3	250	278	3.0×10^2
H	248	261	1.8×10^3
p-COO^-	268	263	2.8×10^3
p-Cl	253	280	1.1×10^4
p-Br	255	292	1.2×10^4
m-Cl	249	265	5.3×10^4
p-C_6H_5CO	300	270	5.2×10^4
p-CN	272	269	3.3×10^5
p-NO_2	320	260	8.1×10^5

methanol showed λ_{max} 275 nm (ϵ 1.2×10^4 M^{-1} cm^{-1}), and showed ϵ 8.8×10^3 M^{-1} cm^{-1} at 253 nm, the λ_{max} of the corresponding aryl azide. These values are in excellent agreement with the reported spectrum of p-ethoxyphenylpentazole.[4] The compound is extremely insoluble in water, and decomposes at an appreciable rate compared to the rate of solution in water at 0°. A portion of a moderately concentrated solution of the pentazole in methanol at −30° was added to water at 25° and the rate constant for decomposition was found to be 3.8×10^{-3} sec^{-1}.

The fortunate occurrence of an isosbestic point at 275 nm in the spectra of mixtures of p-methoxybenzenediazonium ion and p-methoxyazidobenzene allowed us to follow the formation and decomposition of the pentazole in solutions of the diazonium ion and azide ion in water. The formation of the pentazole was found to show the same apparent rate constant as that of the formation of aryl azide and of the disappearance of diazonium ion. The much slower decomposition of the pentazole occurs at precisely the same rate as the slow appearance of aryl azide. The rate constant for decomposition of the pentazole in aqueous solution at 23° was found to be 2.4×10^{-3} sec^{-1}. The slightly lower value for the rate constant in aqueous solution than that found in aqueous methanol is in accord with Ugi's observation that the decomposition rates decrease with increasing polarity of the solvent.[4]

The slow increase in absorption of the aryl azide which is due to the decomposition of the initially formed pentazole amounts to 15–18% of the total final absorbance at 253 nm. From the spectral data given above, we calculate that 42–47% of the final azide came from the pentazole. Huisgen[5] has reported that p-ethoxybenzenediazonium ion with azide ion in methanol solution at −30° produces 34.5% of the arylpentazole. Clusius[2] reports 53.6% arylpentazole formed from p-ethoxybenzenediazonium ion in aqueous acid at 0°.

For the other diazonium ion reactions, lacking spectral data for the pentazoles, we cannot calculate the amount of pentazole formed in the initial reactions. The first-order rate constants for decomposition of the arylpentazoles have been evaluated from the rate of slow increase of absorption at the λ_{max} of the aryl azides after completion of the initial reactions. The amount of absorbance increase sets a lower limit on the amount of pentazole formed.

The pertinent data are reported in Table III and are compared with data obtained by Huisgen[5] for methanol solutions at 0°. We believe that the rate constants determined in this study are accurate to 10% in the cases of the p-methoxy-, p-methyl-, p-carboxylate-, p-benzoyl-, p-cyano-, and p-nitro-substituted compounds. The other compounds show such small increases in absorbance that the rate measurements are subject to rather large uncertainty, and probably are not much better than a factor of 2 within the correct values.

Table III. Rate Constants for Decomposition of Arylpentazoles

	Aqueous soln, 23°		Methanol soln, 0°	
Substituent	ΔA, %[a]	k, sec^{-1}	% pentazole[b]	k, sec^{-1} [b]
p-CH_3O	17	2.4×10^{-3}	34.5[c]	3.0×10^{-4}
p-CH_3	9.6	2.6×10^{-3}	34.5	5.6×10^{-4}
H	2.0	1.0×10^{-2}	23.8	8.4×10^{-4}
p-COO^-	7.2	1.3×10^{-2}		
p-Cl	4.3	2.0×10^{-2}	22.2	1.2×10^{-3}
p-Br	3.5	1.0×10^{-2}		
m-Cl	4.7	7.0×10^{-2}	23.3	2.3×10^{-3}
p-C_6H_5CO	20.0	1.9×10^{-2}		
p-CN	9.8	4.7×10^{-2}		
p-NO_2	21.7	5.0×10^{-2}	14.1	5.9×10^{-3}

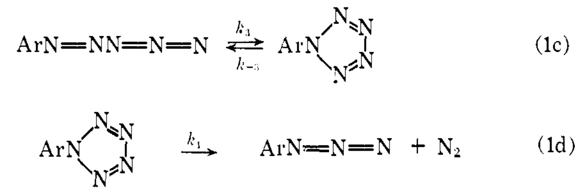
[a] The amount of the slow increase in absorbance at the λ_{max} of the aryl azide, divided by the final absorbance, times 100%. [b] Data from ref 5. The amount of pentazole formed was measured at −58°. [c] The data in methanol solution are for the p-ethoxybenzenediazonium ion reaction.

Discussion

On the basis of nitrogen isotope labeling studies and kinetic studies of nitrogen evolution, Huisgen[3] and Clusius[2] proposed that the reaction of benzenediazonium ions with azide ion followed the scheme

$$ArN_2^+ + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArN{=}NN{=}N{=}N \qquad (1a)$$

$$ArN{=}NN{=}N{=}N \xrightarrow{k_2} ArN{=}N{=}N + N_2 \qquad (1b)$$



(1c)

(1d)

At −40° in methanol solution, it was found that the rate of nitrogen evolution was independent of the concentration of azide ion. It was therefore proposed that step 1a was complete and immeasurably fast. The rate constant for evolution of nitrogen was found to be 2.5×10^{-3} sec^{-1} under these conditions.

Several questions were left unanswered by the previous studies. The data would not allow a choice for the formation of the arylpentazole between the course given above or a concerted addition of azide ion to the diazonium ion to produce the pentazole directly. Similarly, it was not possible to distinguish between reversal of step 1c followed by step 1b from the direct concerted reaction 1d for the decomposition of the arylpentazole, although Ugi favors the concerted reaction.[4] Our present data do not answer these questions.

Under our conditions, the strict second-order kinetics and the identity of the apparent rate constants for

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(5) I. Ugi and R. Huisgen, *Chem. Ber.*, **91**, 531 (1958).

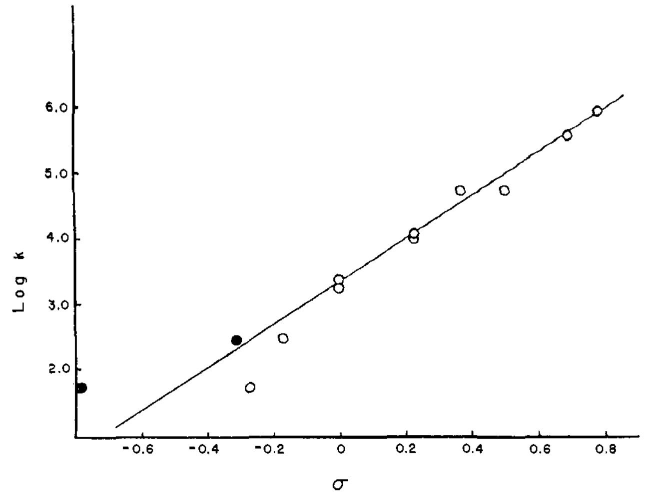

Figure 1. Hammett plot of the second-order rate constants for the reactions of aryldiazonium ions with azide ion in aqueous solution at 23°. Both σ and σ^+ values are shown for the *p*-methoxy and *p*-methyl substituents.

formation of azide and those of disappearance of the diazonium ions clearly show that the diazoazide, if present at all, behaves as a reactive intermediate. Assuming the validity of the reaction scheme shown above, the steady-state approximation shows that our observed second-order rate constants are related to the rate constants of the reaction scheme by eq 2.

$$k_{\mathrm{obsd}} = k_1(k_2 + k_3)/(k_{-1} + k_2 + k_3) \qquad (2)$$

The Hammett plot of our data for the second-order rate constants is shown in Figure 1. The ρ value is found to be 3.2. We shall now argue that this ρ value indicates that $(k_2 + k_3)$ is much greater than k_{-1}, and, therefore, that $k_{\mathrm{obsd}} = k_1$. As is the custom of logicians, we shall show that the converse argument is unreasonable.

If we assume that k_{-1} is much greater than $(k_2 + k_3)$, the observed rate constants are equal to $K_1(k_2 + k_3)$, and the observed ρ value is equal to the ρ value for the equilibrium of step 1a plus a combined ρ value correlating $k_2 + k_3$. The reaction of diazonium ions with cyanide ion in aqueous solution gives equilibrium constants which are correlated by the Hammett equation with a ρ value of 4.7.[6] It seems that the ρ value for the equilibrium of step 1a should be quite similar. In order for the observed ρ value to be 3.2, then the ρ value correlating $(k_2 + k_3)$ would have to be -1.5. Although it might not be surprising for either k_2 or k_3 to be correlated by a negative ρ value, this magnitude seems unreasonably large for such nonionic reactions.

It might be argued that the equilibria of step 1a should be more comparable to the equilibria of diazosulfone formation.[7] The small ρ value of 3.8 found in that reaction is believed to be due to the presence of appreciable positive charge on the nitrogen attached to the sulfone group. Although similar resonance structures can be drawn for the diazoazide, they are expected to be much less important than for the diazosulfones. If, counter to expectations, this resonance form were important, we would expect the ρ values of steps 1b and 1c to be less negative than otherwise. Thus, it would still be difficult to rationalize the observed ρ value of 3.2 if $k_2 + k_3$ were smaller than k_{-1}.

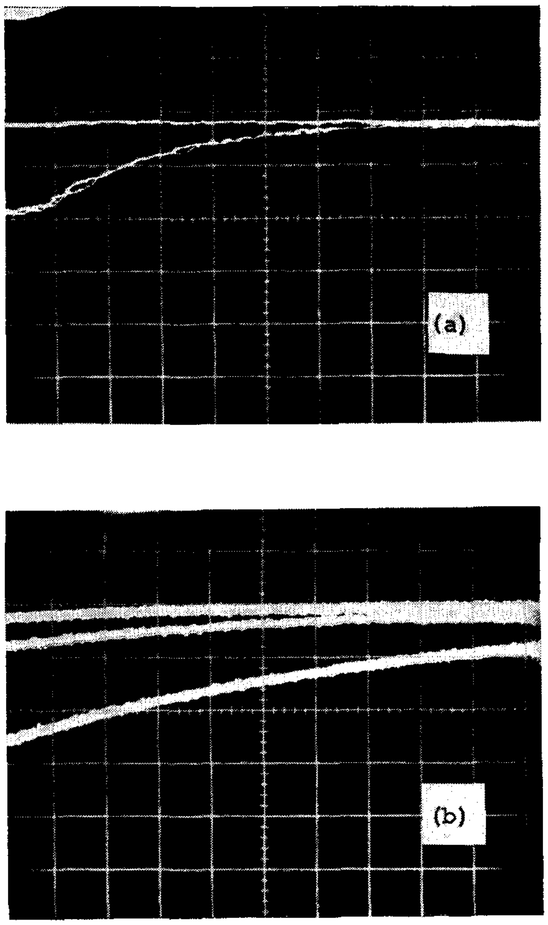

Figure 2. Oscilloscope traces obtained for the reaction of *p*-benzoylbenzenediazonium ion with azide ion in aqueous solution: $(\mathrm{ArN_2^+})_0 = 2.1 \times 10^{-5}\,M$; $(\mathrm{N_3^-})_0 = 6.45 \times 10^{-4}\,M$. (a) Normal scale trace at 10 msec/division. Top of the vertical scale is 0%, and bottom of scale is 100%, transmittance. (b) Expanded scale trace at 5 sec/division with 5 sec between successive traces. Both traces were obtained at 300 nm.

If, however, $k_2 + k_3$ is much greater than k_{-1}, the observed ρ value is easily understood. In the formation of diazosulfones,[7] the ρ value for the rates of formation is two-thirds that for the equilibrium constants. Thus, assuming the validity of the ρ value of 4.7 for the equilibria of step 1a, we expect a ρ value of 3.1 for the rates, a value embarassingly close to the 3.2 observed.

On the basis of the above arguments, therefore, we believe that our rate constants reported in Table II may be identified with k_1 of the reaction scheme shown. This identity will permit us to compare the reactivities of various nucleophiles with diazonium ions in our continuing work on anion–cation combination reactions.

Experimental Section

Materials. The diazonium tetrafluoroborates were prepared by conventional methods and were recrystallized to constancy of their ultraviolet spectra from methanol–acetone mixtures. Sodium azide was a commercial product used without further purification.

All solutions were prepared in distilled water which was stored in containers protected from carbon dioxide. Reaction solutions were not buffered, and the diazonium ion solutions were prepared fresh immediately before the kinetic run.

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(6) E. S. Lewis and H. Suhr, *Chem. Ber.*, **92**, 3043 (1959).

(7) C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

Spectra. Before carrying out the kinetic measurements on the stop-flow apparatus, spectra of the diazonium ions and of the solutions in which the reactions were complete were obtained by the use of a Cary Model 14 spectrophotometer. These spectra were used to select the wavelengths to be used in the kinetic measurements. It was found that the wavelengths of maximum absorption of the diazonium ions and of the aryl azides were those where greatest change occurred.

Kinetic Measurements. The stop-flow apparatus used for the kinetic runs has been described in earlier work.[8] Runs in which the reactions were followed at the wavelength of maximum absorption of the diazonium ions were quite routine with the time scales selected to allow observation of at least 95% completion of the reactions. For the runs in which the reactions were followed at the λ_{max} of the aryl azide, one trace was obtained on the same time scale as used when the reactions were followed at the λ_{max} of the diazonium ions. The transmittance scale of the oscilloscope was then expanded by a factor of 5 and another trace was obtained on the slowest time scale available, 5 sec/division. For those reactions in which the second step was extremely slow, the oscilloscope reading was obtained at various times measured with a stop watch. Both the fast and slow traces for the reaction of *p*-benzoylbenzenediazonium ion, followed at 300 nm, are shown in Figure 2.

Apparent rate constants for all runs were obtained from the slopes of the usual plots of ln $(A - A_\infty)$ *vs.* time.

One kinetic run with the *p*-methoxybenzenediazonium ion was carried out with both diazonium ion and azide ion at concentrations of 4.0×10^{-5} *M*. The entire spectrum of the reaction mixture, from 220 to 400 nm, was recorded at various time intervals on the Cary Model 14 spectrophotometer. Under these conditions, the arylpentazole decomposes rapidly in comparison to the rate of the overall reaction. Isosbestic points at 275 and at 237 nm were observed for the reacting solutions. After completion of the reaction (8000 sec), the final spectrum showed an absorbance at 275 nm which was slightly lower (0.175 compared to 0.195) than had been shown by the solutions during the course of the reaction. This was undoubtedly caused by a small steady-state concentration of the arylpentazole.

Preparation of *p*-Methoxyphenylpentazole. The preparation closely followed the method described by Ugi[4] except that the diazonium fluoroborate was used in place of the chloride. This caused some solubility problems. The mixture of solutions of diazonium salt and sodium azide was stirred for *ca.* 30 min at −35° to allow for the difficult solubility. The pentazole was filtered off, washed with aqueous methanol followed by pentane, and stored at −70°. Solutions were prepared in methanol at −30°, and spectra were obtained with the cells thermostated at 0°. No attempts were made to prepare the solutions accurately since the concentration of pentazole could be obtained by allowing the solutions to decompose to aryl azide and measuring the absorbance.

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[8] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 89, 2063 (1967).

Ketyls of Cyclic α,β-Unsaturated Ketones[1]

Glen A. Russell* and Gerald R. Stevenson

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received August 3, 1970*

Abstract: Ketyls can be prepared from 2-cyclopentenone, 2-cyclohexenone, 2,4- and 2,5-cyclohexadienone, and their benzo derivatives provided all hydrogen atoms α to the π system are substituted by alkyl or aryl groups. Electrolytic reduction of the ketones in dimethylformamide solution at −60 to +25° yielded the ketyls from the alkylated enones but not from the enones containing α hydrogen atoms such as 2-cyclohexenone, 4,4-dimethyl-2-cyclohexenone, or 6,6-dimethyl-2-cyclohexenone.

Ketyls with two aromatic substituents have been recognized for 80 years.[2-4] More recently electrolytic reduction has yielded the radical anions of benzaldehyde, acetophenone, 1,4-diacetylbenzene, and 1,2-dimesitylbenzene detectable by esr spectroscopy.[5]

Favorsky prepared the ketyl of di-*tert*-butyl ketone by reduction of the ketone with potassium metal.[6] Stable ketyls containing an α hydrogen are rare, although *tert*-butyl isopropyl ketyl and *tert*-butyl 3-pentyl ketyl can be detected at room temperature by esr spectroscopy.[7] Also, *tert*-butyl methyl ketyl and trimethylsilyl methyl ketyl have been examined in DME by esr spectroscopy at −90 to −70° but decompose readily at higher temperatures.[8,9] The addition of

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXII. Supported by grants from the National Institutes of Health and the National Science Foundation.

[2] E. Beckmann and T. Paul, *Justus Liebigs Ann. Chem.*, **266**, 1 (1891); W. Schlenk and T. Weickel, *Chem. Ber.*, **44**, 1182 (1911).

[3] W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 1179 (1933).

[4] E. Müller and W. Wiessemann, *Justus Liebigs Ann. Chem.*, **537**, 86 (1938); S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934).

[5] N. Steinberg and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964); P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

[6] A. Favorsky and I. N. Nazarow, *Bull. Soc. Chim. Fr.*, [5] **1**, 46 (1934).

[7] H. Hiroto and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960).

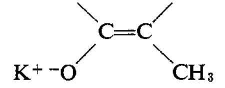
[8] P. R. Jones and R. West, *ibid.*, **90**, 6978 (1968).

[9] Decomposition of trimethylsilyl methyl ketyl in the presence of potassium ion apparently leads to the *trans*-dimethylsemidione, rather than the dimeric molecule suggested by Jones and West.[8] Jones and West overlooked the fact that acyclic semidiones can exist as cis and trans isomers, and that the predominate isomer can vary with the gegenion.[10] Thus, the observation of Jones and West that treatment of bis-1,2-trimethylsiloxy-2-butene with sodium yielded a radical anion with $a_{CH_3}{}^H = 7.43$ (2) G, does not exclude the following scheme from occurring in the presence of potassium. Similarly, the ketyl of isopropyl tri-

$$2(CH_3)_3Si\dot{C}(O^-)CH_3 \longrightarrow$$

$$(CH_3)_3SiC(O^-)(CH_3){-}C(O^-)(CH_3)Si(CH_3)_3 \xrightarrow{-2e} \xrightarrow{O_2}$$

$$(CH_3)_3SiOC(CH_3){=}C(CH_3)OSi(CH_3)_3 \xrightarrow[{[O]}]{OH^-}$$



$$a_{CH_3}{}^H = 4.5\ (2);\ a^K = 1.3\ G$$

methylsilyl ketone yielded diisopropylsemidione, $a_{CH}{}^H = 2.38$ (2) G at −40°.

[10] G. A. Russell and R. D. Stephens (*J. Phys. Chem.*, **70**, 1320 (1966)) report $a_{CH_3}{}^H = 7.0$ and 5.6 G at 25° for *cis*- and *trans*-dimethylsemidione. *trans*-Diisopropylsemidione has $a_\alpha{}^H = 2.0$ G at 25° in DMSO solution.