

Reactions of Radical Anions. Part XII.¹ An Electron Spin Resonance Study of the Radical Anions of 1-Phenyl-2-trimethylsilyl-, 1-Phenyl-2-trimethylgermyl-, and 1-Phenyl-2-*t*-butyl-acetylene in Tetrahydrofuran including the Assignment of the Splitting Constants of the Phenyl Group by Deuterium Substitution

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The e.s.r. spectra of the radical anions of 1-phenyl-2-trimethylsilylacetylene with Li⁺ and Rb⁺ as gegenions, 1-phenyl-2-trimethylgermylacetylene with Na⁺, K⁺, Rb⁺, and Cs⁺ as gegenions, and 1-phenyl-2-*t*-butylacetylene with Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ as gegenions in tetrahydrofuran as solvent have been obtained and analysed. The splitting constants of the phenyl group have been unambiguously assigned in 1-phenyl-2-trimethylsilylacetylene using deuterium substitution. Except for the radical anion of 1-phenyl-2-trimethylgermylacetylene with lithium as gegenion, the radical anions were stable with time at -90°. On raising the temperature dimerisation occurred, and its rate in tetrahydrofuran was followed over a temperature range -90 to -40° using an e.s.r. spectrometer. Rate constants and thermodynamic constants of activation were calculated from these results.

We have previously studied the dimerisation reaction in tetrahydrofuran (THF) of the radical anions (*a*) of diphenylacetylene with Li⁺, Na⁺, K⁺, and Cs⁺ as gegenion² and (*b*) of 1-phenyl-2-trimethylsilylacetylene with Na⁺, K⁺, and Cs⁺ as gegenion. Well resolved e.s.r. spectra of the silylacetylenes were obtained and analysed.^{3,4}

In this paper we describe the measurement and analysis of the e.s.r. spectra in THF of the radical anions of 1-phenyl-2-trimethylsilylacetylene with Li⁺ and Rb⁺ as gegenion and 1-phenyl-2-trimethylgermyl- and 1-phenyl-2-*t*-butyl-acetylene with Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ as gegenion, together with their rates of dimerisation, using the e.s.r. technique previously described.^{4,5}

We have also measured and analysed the e.s.r. spectra of the radical anions of (*o*-, *m*-, and *p*-deuteriophenyl)-2-trimethylsilylacetylene, with K⁺ as gegenion in THF. These results enable us to assign the splitting constants for the phenyl protons in the radical anion of 1-phenyl-2-trimethylsilylacetylene which agree with what we reported earlier.⁴ Using these results we have assigned the splitting constants of the phenyl protons in the similar radical anion of 1-phenyl-2-trimethylgermylacetylene.

EXPERIMENTAL

Materials.—1-Phenyl-2-trimethylgermylacetylene was prepared under nitrogen by a method similar to that of Eaborn and Walton.⁶ The product was separated by fractionation on a spinning band micro-distillation apparatus under reduced pressure and collected at 72° and 1.5 mmHg (lit.,⁶ 73° and 1.5 mmHg). The product was purified using g.l.c. and identified by n.m.r., u.v., and i.r. spectra and b.p. 1-Phenyl-2-*t*-butylacetylene was prepared using a method similar to that of Kupin and Petrow.⁷ The product was separated using a spinning band micro-

distillation apparatus under reduced pressure and collected at 85° and 10 mmHg (lit.,⁷ 86° and 10 mmHg). The product was purified using g.l.c., and identified by n.m.r., u.v., and i.r. spectra and b.p.

1-(*o*-Deuteriophenyl)-2-trimethylsilylacetylene. *o*-Bromophenylacetylene⁸ in anhydrous ether was slowly added to ethylmagnesium bromide, boiled under reflux for 2 h, and left overnight. Chlorotrimethylsilane in ether was slowly added to the reaction mixture while stirring and the system refluxed for ca. 8 h. After cooling the mixture was worked-up with saturated aqueous ammonium chloride solution, the ether layer was separated and dried (MgSO₄), the ether extract was filtered, and the ether removed. 1-(*o*-Bromophenyl)-2-trimethylsilylacetylene was separated using a spinning band micro-distillation apparatus under reduced pressure, purified using g.l.c., and identified using mass spectrometry, and n.m.r., u.v., and i.r. spectroscopy. The pure acetylene was mixed with anhydrous ether and slowly added to clean, dry magnesium turnings over ca. 1 h, the mixture was stirred and refluxed for ca. 6 h, and after cooling, deuterium oxide was slowly added over 2 h. The ether layer was separated from the aqueous layer and dried (MgSO₄). After filtration the ether was removed and 1-(*o*-deuteriophenyl)-2-trimethylsilylacetylene was separated using a spinning band micro-distillation apparatus under reduced pressure. It was purified using g.l.c., and identified by mass spectrometry, b.p. 88° at 9 mmHg.

The *meta*-isomer was prepared similarly to the *ortho*-isomer, except that the starting material was *m*-bromophenylacetylene.⁸ The intermediate, 1-(*m*-bromophenyl)-2-trimethylsilylacetylene, b.p. 95° at 1.9 mmHg (lit.,⁸ 96° at 1.9 mmHg), was isolated and purified as before, and the *meta*-deuterio-compound was separated, purified, and identified as before. The *para*-isomer was prepared similarly, using *p*-bromophenylacetylene.^{8,9} The intermediate, 1-(*p*-bromophenyl)-2-trimethylsilylacetylene, m.p. 61.5° (lit.,¹⁰ 62°), was isolated as before and the *para*-deuterio-compound was separated, purified, and identified as before.

¹ Part XI, A. G. Evans, J. C. Evans, P. J. Emes, and S. I. Haider, *J.C.S. Perkin II*, 1974, 1121.

² D. A. Dudley and A. G. Evans, *J. Chem. Soc. (B)*, 1967, 418.

³ A. G. Evans, J. C. Evans, and T. J. Phelan, Chemical Society Autumn Meeting, Southampton, 1969, paper D11.

⁴ A. G. Evans, J. C. Evans, P. J. Emes, and T. J. Phelan, *J. Chem. Soc. (B)*, 1971, 315.

⁵ A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

⁶ C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 95.

⁷ B. S. Kupin and A. A. Petrow, *Zhur. obshechi Khim.*, 1961, **31**, 2958.

⁸ M. M. Otto, *J. Amer. Chem. Soc.*, 1934, **56**, 56.

⁹ A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1963, **41**, 1084.

¹⁰ C. Eaborn, A. R. Thomson, and D. R. M. Walton, *J. Chem. Soc. (C)*, 1967, 1364.

Tetrahydrofuran, lithium, sodium, potassium, rubidium, and caesium were purified as described earlier.¹¹

Procedure.—THF solutions of known concentrations of the acetylenes were prepared under high vacuum conditions and the radical anions were formed using methods similar to those described earlier.⁵ Except for the radical anion of 1-phenyl-2-trimethylgermylacetylene with Li⁺ as gegenion, stable, well resolved e.s.r. spectra were obtained for these solutions at -80° . At higher temperatures the radical anions dimerised and this reaction was followed by measuring the decrease in the overall e.s.r. signal with time. Each radical anion concentration was obtained by increasing the modulation on the e.s.r. spectrum until the structure was removed and then electronically doubly integrating the differential e.s.r. absorption.⁵ The absolute value of the concentration was found by comparison with diphenylpicrylhydrazyl under identical instrumental conditions. The change in concentration could be measured to within $\pm\frac{1}{2}\%$ and the absolute value to within $\pm 10\%$. The e.s.r. spectra were simulated using a JEOL R.A.1 spectrum accumulator.

RESULTS AND DISCUSSION

The Radical Anion of 1-Phenyl-2-trimethylsilylacetylene.

—**E.s.r. spectra.** The analyses of the e.s.r. spectra of this radical anion with Na⁺, K⁺, and Cs⁺ as gegenions in THF at -80° have been reported earlier.⁴ In our present work we have examined the radical anion spectra at -80° in THF for Li⁺ and Rb⁺ as gegenions, and find that the splittings of the phenyl protons (*para* 7.49, *meta* 3.16, *ortho* 0.16), the methyl protons (0.28), and ²⁹Si (4.4 G) are the same as obtained previously,⁴ and are thus independent of the nature of the gegenion. For Na⁺ and K⁺ no metal splitting was observed. Metal splitting was observed, however, for Li⁺ (2.75), Rb⁺ (2.05), and Cs⁺ (2.6 G). The spectra were analysed by superimposing a spectrum calculated from assigned splitting constants on the observed spectrum and making adjustments in the splitting constants until the best fit was obtained. The total width of the spectrum excluding metal interaction is 20.3 G (calculated 20.5 G) giving a *g* value of 2.0051.

Assignment of the splitting constants of the phenyl protons. To assign unambiguously the splitting constants of the phenyl protons the e.s.r. spectra of the radical anions of 1-(*o*-, *m*-, and *p*-deuteriophenyl)-2-trimethylsilylacetylene in THF at -80° with K⁺ as gegenion were measured and analysed. The results are given in Table 1.

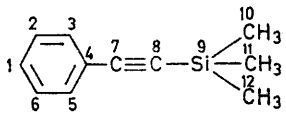
It is seen that (a) substitution of *p*-H by D removes the 7.49 doublet splitting; (b) substitution of one of the *m*-H atoms by D removes the 3.16 triplet splitting; and (c) substitution of one of the *o*-H atoms by D removes the 0.16 triplet splitting.

In this way the ring coupling constants in the 1-phenyl-2-trimethylsilylacetylene radical anion are unambiguously assigned as in Table 1. This agrees with what we found in our previous calculations,⁴ although we do not now consider that those calculations were satisfactory; a more sophisticated technique is needed, which as yet we have not been able to achieve.

E.s.r. Spectrum of the Radical Anion of 1-Phenyl-2-*t*-butylacetylene.—The analysis of the e.s.r. spectra observed at -100° in THF solution for the radical anion of 1-phenyl-2-*t*-butylacetylene with Li⁺, Na⁺, K⁺, Rb⁺,

TABLE 1

Hyperfine coupling constants (G) for the radical anions of 1-(*o*-, *m*-, and *p*-deuteriophenyl)- and 1-phenyl-2-trimethylsilylacetylene in THF with K⁺ as gegenion at -80°



Compound	Positions							
	1	2	3	5	6	9	10-12	
1-(<i>p</i> -Deuteriophenyl)-2-trimethylsilylacetylene	1.25 (D)	3.16	0.16	0.16	3.16	4.4	0.3	
1-(<i>m</i> -Deuteriophenyl)-2-trimethylsilylacetylene	7.49	0.52 (D)	0.16	0.16	3.2	4.4	0.3	
1-(<i>o</i> -Deuteriophenyl)-2-trimethylsilylacetylene	7.49	3.16	— (D)	0.2	3.16	4.4	0.3	
1-Phenyl-2-trimethylsilylacetylene *	7.49	3.16	0.16	0.16	3.16	4.4	0.28	

* Ref. 4.

and Cs⁺ as gegenion showed the following splittings: *p*-H 7.50, *m*- or *o*-H 3.2, *o*- or *m*-H 0.75 G. No hyperfine splitting is observed from the nine equivalent protons of the *t*-butyl group, showing that the unpaired electron is not transmitted or delocalised onto the methyl groups. This is in contrast to the 1-phenyl-2-trimethylsilylacetylene radical anion where hyperfine splitting due to the trimethylsilyl protons is observed by transmission of the electron through the silicon atom possibly *via* the *d* orbitals. The splitting constants of the phenyl protons in 1-phenyl-2-*t*-butylacetylene radical anions are greater than those for the 1-phenyl-2-trimethylsilylacetylene radical anion. The doublet and large triplet are slightly greater while the small triplet is greater by a factor of almost five. This would be expected if delocalisation through silicon occurs but not through carbon.

Gegenion interaction was clearly observable for Na⁺ (2.65), K⁺ (0.3), and Cs⁺ (1.25 G). In the case of Li⁺ and Rb⁺, interaction was observed but owing to the instability of the radical anion it was extremely difficult to obtain a firm value for the metal hyperfine splitting constant.

The splitting constants of the *ortho*- and *meta*-positions of the phenyl group are not dealt with on the basis of the assignment in the radical anion of 1-phenyl-2-trimethylsilylacetylene, where the coupling constants of

¹¹ J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

the ring protons were in the sequence $a_{H_1} > a_{H(a,b)} > a_{H(c,d)}$,* because the large inductive effect and the opposing delocalisation effect due to the silicon is absent in the 1-phenyl-2-t-butylacetylene radical anion, and hence the splitting constants could equally well be $a_{H_1} > a_{H(c,d)} > a_{H(a,b)}$.

The spectra were analysed by the trial and error procedure using the R.A. 1 spectrum accumulator. The total width of the spectrum excluding the metal splitting is 15.6 G (calculated 15.4 G) giving a g value of 2.0034.

E.s.r. Spectrum of the Radical Anion of 1-Phenyl-2-trimethylgermylacetylene.—E.s.r. spectra were obtained for a THF solution of 1-phenyl-2-trimethylgermylacetylene when passed over either a sodium, potassium, rubidium, or caesium film at -80° . No e.s.r. spectra were obtained for the lithium case because the red-brown colour of the radical anion disappeared before e.s.r. measurements could be made.

The analysis of the e.s.r. spectra observed in THF at -90° for Na^+ , K^+ , Rb^+ , and Cs^+ as gegenions showed the following splittings: p -H 7.50, m -H 3.20, o -H 0.1, CH_3 0.15, ^{73}Ge 1.67 G. The results show that the unpaired electron is delocalised or transmitted through the germanium onto the methyl carbon atoms, as for the corresponding silicon radical anion. The effect, however, is larger in the silicon case ($a_{H^{OH}}$ 0.28 G) than for germanium ($a_{H^{OH}}$ 0.15 G). This could be due to the greater size of the germanium resulting in a less favourable overlap of the respective orbitals. This is supported by the work of Curtis and Allred¹² and by other previous work.¹³⁻¹⁸

Gegenion interaction was observed for Rb^+ (1.50) and Cs^+ (1.54 G) but not for Na^+ and K^+ . (The resolution of the spectra was such that if the gegenions did interact with the unpaired electron, Na^+ and K^+ hyperfine splitting would have been observed.)

The splitting constants of the phenyl protons are given on the basis of the assignment in the radical anion of 1-phenyl-2-trimethylsilylacetylene. The two molecules are very similar in character, and it has been found that the $GePh_3$ and $SiPh_3$ groups have approximately the same $-I$ effect.^{19,20} It is reasonable, therefore, to assume the same assignment for the radical anions of the silyl- and germyl-acetylene. This is more valid than would be a similar assumption for the radical anion of 1-phenyl-2-t-butylacetylene.

The e.s.r. spectra were analysed by the trial and error procedure. The total width of the spectrum (excluding the metal and germanium splitting) is 17.4 G (calculated 17.0 G) giving a g value of 2.0070.

Dimerisation.—In the region -100 to -50° the dimerisation of the radical anions in THF was too fast for us to use our usual integration technique. In these

* See Table 1 for numbering.

¹² M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 1965, **87**, 2554.

¹³ H. Schmidbair, *J. Amer. Chem. Soc.*, 1963, **85**, 2336.

¹⁴ E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, 1963, **67**, 805.

¹⁵ J. S. Thayer and R. West, *Inorg. Chem.*, 1964, **3**, 889.

¹⁶ D. F. Harnisch and R. West, *Inorg. Chem.*, 1963, **2**, 1082.

cases a solution was used for which we had already measured the initial radical anion concentration by integration at a temperature at which the radical anion was stable (usually at *ca.* -90°). The change in intensity of the e.s.r. spectrum with time for this solution was followed. The radical anion solutions were stable in THF at -80° (silylacetylene), -100° (t-butylacetylene), and -90° (germylacetylene). On increasing the temperature to -40° (silylacetylene), -80° (t-butylacetylene), and -80° (germylacetylene) the intensity of the e.s.r. spectra decreased to zero and the red-brown colour of the radical anion changed to yellow. Analysis of the rate curves (*e.g.* see Figure 1) give a good

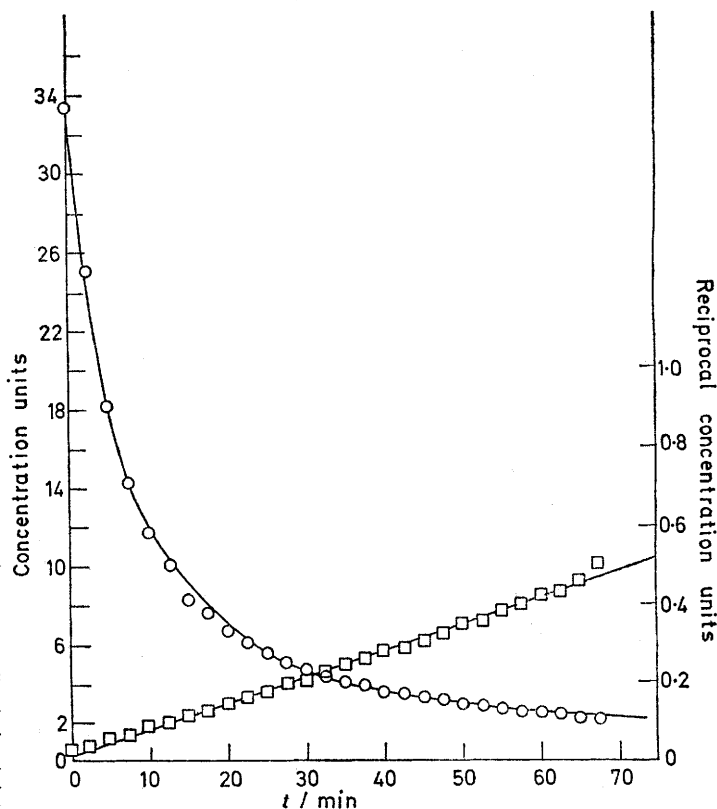


FIGURE 1 Rate curve and order plot for dimerisation of $(PhC\equiv CBut)\cdot Na^+$ in THF at -80°

second order plot over 90% of the reaction, and the plots of \log_{10} (initial rates) against \log_{10} (initial concentration of radical anion) give straight lines of slope 2.

Temperature Dependence.—The change of velocity constant with temperature was measured (see for example Figure 2). The plots of $\log_{10}k$ against $1/T$ gave reasonably straight lines and the thermodynamic constants of activation calculated for 0° are given in Tables 2–4.

¹⁷ R. West and R. H. Baney, *J. Phys. Chem.*, 1960, **64**, 822.

¹⁸ R. West, R. H. Baney, and D. L. Powell, *J. Amer. Chem. Soc.*, 1960, **82**, 6269.

¹⁹ R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421.

²⁰ R. A. Benkeser, C. E. De Boer, R. E. Robinson, and D. M. Sauve, *J. Amer. Chem. Soc.*, 1956, **78**, 682.

Reaction Products.—On hydrolysis of the reaction mixture, for the silyl radical anion reaction, one product only was found, that of 2,3-diphenyl-1,4-bis(trimethylsilyl)buta-1,3-diene (I). This was identified by n.m.r.

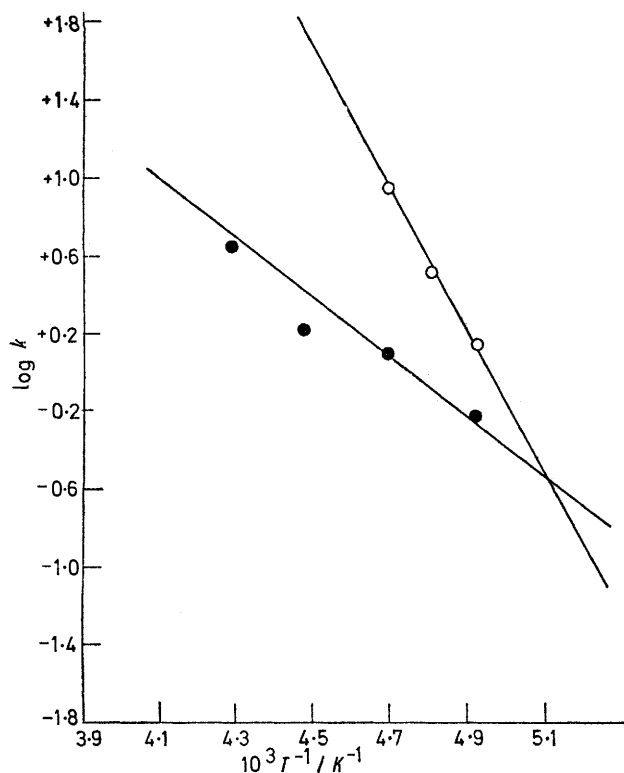


FIGURE 2 Activation energy plot for dimerisation of $(\text{PhC}\equiv\text{CSiMe}_3)\cdot\text{M}^+$ in THF: \circ , Li^+ ; \bullet , Rb^+

TABLE 2

Thermodynamic constants of activation for dimerisation of $(\text{PhC}\equiv\text{CSiMe}_3)\cdot\text{M}^+$ in THF at 0°

	Li^+	Na^+ *	K^+ *	Rb^+	Cs^+ *
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	66.9	37.6	25.9	28.0	18.4
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	41.8	47.2	64.8	58.1	69.0
$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	+92.8	-32.6	-115	-110	-186
$k/\text{l mol}^{-1} \text{s}^{-1}$	6.1×10^4	5.6×10^3	2.1	44.0	3.5×10^{-1}

The ΔH^\ddagger values are accurate to within $\pm 2.0 \text{ kJ mol}^{-1}$.

* Ref. 4.

TABLE 3

Thermodynamic constants of activation for dimerisation of $(\text{PhC}\equiv\text{CCMe}_3)\cdot\text{M}^+$ in THF at 0°

	Li^+	Na^+	K^+	Rb^+	Cs^+
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	41.4	33.4	17.9	17.9	23.0
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	41.0	45.6	49.7	50.6	53.1
$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	+1.67	-44.3	-116	-120	-110
$k/\text{l mol}^{-1} \text{s}^{-1}$	8.9×10^4	1.2×10^4	1.7×10^3	1.1×10^3	4.0×10^2

The ΔH^\ddagger values are accurate to $\pm 3.3 \text{ kJ mol}^{-1}$.

and i.r. spectroscopy, mass spectrometry, and elemental analysis.

The reaction between 1-phenyl-2-trimethylsilyl-acetylene and lithium metal was studied by Rausch and

Klemann,²¹ who also found one product only on hydrolysis of the reaction mixture. They characterised this unequivocally as (I).

TABLE 4

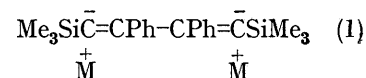
Thermodynamic constants of activation for dimerisation of $(\text{PhC}\equiv\text{CGeMe}_3)\cdot$ in THF at 0°

	Na^+	K^+	Rb^+	Cs^+
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	73.1	44.7	50.1	16.3
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	20.5	31.4	18.8	53.5
$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	+193	+49.0	+115	-136
$k/\text{l mol}^{-1} \text{s}^{-1}$	6.9×10^8	6.0×10^6	1.5×10^9	3.2×10^8

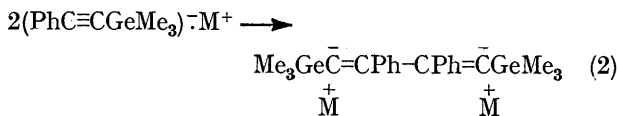
The ΔH^\ddagger values are accurate to $\pm 4.0 \text{ kJ mol}^{-1}$.

When M^+ is Li^+ the reaction was too fast to follow even at -100° .

Thus the reaction we are following is (1). As in the



case of the radical anions of 1-phenyl-2-trimethylsilyl-acetylene, only one product was found on hydrolysis. This was 2,3-diphenyl-1,4-bis(trimethylgermyl)buta-1,3-diene. This was isolated using g.l.c., and identified by n.m.r. and i.r. spectroscopy, mass spectrometry, and elemental analysis. Thus the reaction studied is the dimerisation (2).



We have not isolated the reaction products in the case of the t-butylacetylene radical anion reaction.

No results were obtained when lithium was used as gegenion in the case of the germylacetylene radical anion because on passage of the solution over the lithium film a fleeting red-brown solution was observed to change to yellow, showing that this dimerisation was too fast to measure.

When Na^+ , K^+ , and Rb^+ are the gegenions, the rate of dimerisation increases along the sequence $\text{Si} < \text{C} < \text{Ge}$. The ΔH^\ddagger value for C is less than for Si, but that for Ge is much greater than the other two, the high speed of the Ge reaction being due to an abnormally positive ΔS^\ddagger term.

When Cs^+ is the gegenion, on the other hand, the dimerisation rate increases along the sequence $\text{Si} < \text{C} \approx \text{Ge}$, and here there is no abnormality about the ΔS^\ddagger value for the Ge case.

We thank the S.R.C. for a grant to purchase the e.s.r. spectrometer and for a C.A.P.S. studentship (to T. J. P.) in association with Midland Silicones. We thank Midland Silicones for their interest and help in providing materials.

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²¹ M. D. Rausch and L. P. Klemann, 4th International Conference on Organometallic Chemistry, Bristol, 1969, Paper C8.