Reactions of Radical Anions. Part XIII.[1] Electron Spin Resonance Study of the Radical Anions of 1,4-Bistrimethylsilyl- and 1,4-Di-t-butylbuta-1,3-diyne

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We have studied the radical anions of the diacetylenes $(CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3$ and $(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3$ in tetrahydrofuran by e.s.r. spectroscopy. These radical anions have only one type of proton present, the 18 methyl protons. E.s.r. experiments show clearly that with the silyl radical anion, unpaired electron density occurs not only on the silicon atoms but also on the methyl groups, and this we attribute to d_{π}–p_{π} interaction. In the radical anion of 1,4-di-t-butylbuta-1,3-diyne, however, no delocalisation of the electron through to the methyl groups occurs. There is a marked difference in reactivity between the radical anions of the two diacetylenes. The silyl radical anion is very stable whereas the di-t-butyl radical anion is very reactive. This difference in reactivity is discussed in terms of electron distribution and steric hindrance.

THERE has been much discussion concerning the d_{π}–p_{π} interaction in conjugated systems containing silicon.[2] Silyl and alkyl groups have a different effect from each other, because, although both have a positive inductive effect, the silicon, on account of its vacant *d* orbitals, also has a delocalising effect due to the possibility of d_{π}–p_{π} interaction.

We have been studying the radical anions of silicon-containing acetylenic compounds of the type $PhC{\equiv}CSi(CH_3)_3$ by the e.s.r. technique to determine the extent of this d_{π}–p_{π} interaction.[3]

To investigate a system which would give a clear-cut answer concerning d_{π}–p_{π} interaction, we have now studied the radical anions of the diacetylenes. $(CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3$ and $(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3$. These radical anions have only one type of proton present, the 18 methyl protons, so e.s.r. experiments should show clearly whether or not the unpaired electron is delocalised onto the methyl groups. Furthermore, the molecules are linear and the substituent groups are fairly well removed from each other because of the two acetylenic bonds. Thus the dimerisation of these radical anions should not be as sterically hindered as that of the radical anion of $PhC{\equiv}CSi(CH_3)_3$.

EXPERIMENTAL

Materials.—Lithium, sodium, potassium, rubidium, and caesium mirrors were made as before.[1] Tetrahydrofuran (THF) (B.D.H.) was purified and dried as described previously.[4] 1,4-Di-t-butylbuta-1,3-diyne was prepared from $(CH_3)_3CC{\equiv}CC(CH_3)_3$ (Ralph Emanuel) by dimerisation, using the method of Faworsky and Morew.[5] The product gave the expected analysis and the same u.v. spectrum and m.p. (130—132°) as those obtained by Bohlmann.[6] 1,4-Bistrimethylsilylbuta-1,3-diyne was prepared from hexachlorobutadiene by the method of Ballard and Gillman.[7] It was purified by sublimation (30%) and gave m.p. 106·5° (lit.,[7] 106—107°). It was also identified by n.m.r., i.r., and u.v. spectroscopy, mass spectrometry, and elemental analysis.

Procedure.—Solutions were made up and mixed under high vacuum.[4] E.s.r. measurements were made as previously described on a Varian E.3 spectrometer with temperature control.[1] E.s.r. simulated spectra were obtained by the use of an I.C.L. 490 computer and a JEOL RA1 spectrum accumulater. *g* Values were determined by measuring the frequency of the field directly from the spectrometer.

The rate of disappearance of the radical anion in the case of di-t-butylbutadiyne was followed by measuring the concentration of radical anions at various times by a double integration method using corresponding solutions of diphenylpicrylhydrazyl for calibration purposes.[8]

RESULTS

E.s.r. Spectra.—1,4-*Bistrimethylsilylbuta*-1,3-*diyne*. A THF solution of bistrimethylsilyl butadiyne (*ca.* 10^{-3}M) was passed over metal films at −80°. The e.s.r. spectra of these solutions were measured [see for example Figure 1(a)]. Metal splittings were observed in all cases, but for Li^+ and Rb^+ these could not be accurately assigned. The splitting constants and *g* values are given in Table 1. A computer simulated spectrum is shown in Figure 1(b).

TABLE 1

Splitting constants for $[(CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3]^{-\bullet}M^+$ in THF at −80°

	Splitting constant (G)				
	Li^+	Na^+	K^+	Rb^+	Cs^+
a_H	0·15	0·15	0·16	0·17	0·17
a_{Si}	5·25	5·00	4·95	4·90	4·20
$a_{C^{13}H_3}$	~4·60	4·63	4·63	~4·60	4·50
a_{M^+}		0·40	0·30		4·10
g	2·017	2·017	2·017	2·017	2·017

1,4-*Di-t-butylbuta*-1,3-*diyne*. A THF solution of di-t-butylbutadiyne (*ca.* 10^{-3}M) was passed over metal films

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at −80° The e.s.r. spectra of these solutions were measured [see for example Figures 1(c) and 1(d)]. For each gegenion the spectrum consisted of a single line of *g* value 1·983, with two ^{13}C satellite lines of splitting 10·2 G, and no proton splitting. No gegenion splitting was observed in any case.

Rates of Reaction.—$[(CH_3)_3SiC{\equiv}C{-}C{\equiv}C{-}Si(CH_3)_3]^{-\cdot}M^+$. This radical anion is stable at room temperature. All the original butadiyne can be recovered unchanged from this system on opening to air. This was established using g.l.c. by comparison of the original solutions with those obtained by treatment with alkali metal and subsequent exposure to air. This extreme stability is unusual for a radical anion which has no aromatic groups in it.

$[(CH_3)_3C{-}C{\equiv}C{-}C{\equiv}C{-}C(CH_3)_3]^{-\cdot}M^+$. This system reacts very rapidly indeed even at −40°. The radical anion concentration decreases with time according to a second-order law (see for example Figure 2). The reaction was measured at different temperatures and the thermodynamic constants of activation obtained. These are given in Table 2, scaled up to 0° for comparison with our previous work.

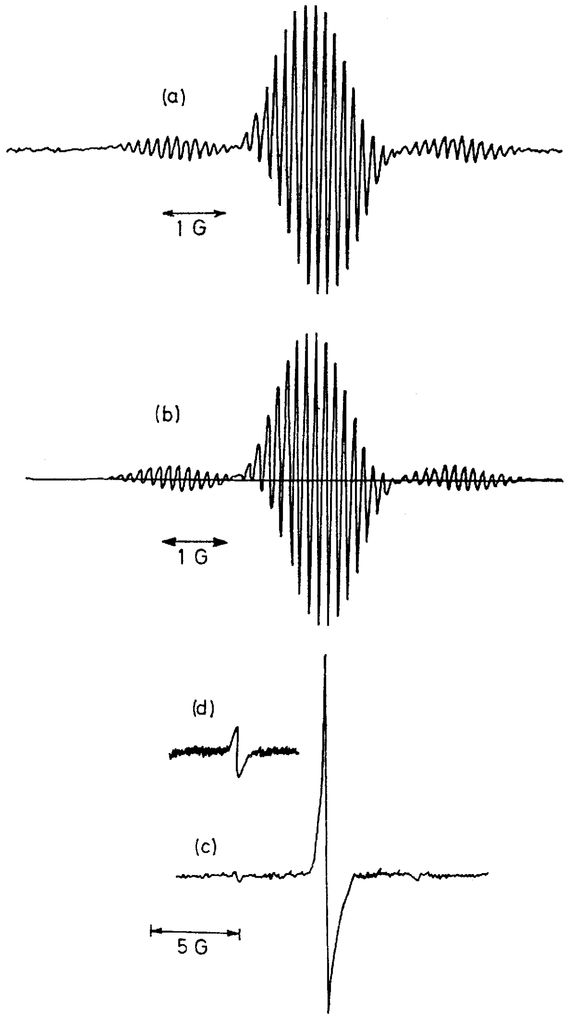

FIGURE 1 E.s.r. spectrum of $(XC{\equiv}C{-}C{\equiv}CX)^{-\cdot}$ in THF at −80° with potassium as gegenion: (a) X = $(CH_3)_3Si$; (b) computer simulated spectrum of (a); (c) X = $(CH_3)_3C$; (d) wing of curve (c) enlarged 10-fold to show ^{13}C interaction

Effect of Gegenion.—We find that for bistrimethylsilylbutadiyne, Li^+. Na^+, K^+, Rb^+, and Cs^+ ions cause splitting, showing that contact ion pairs are present.

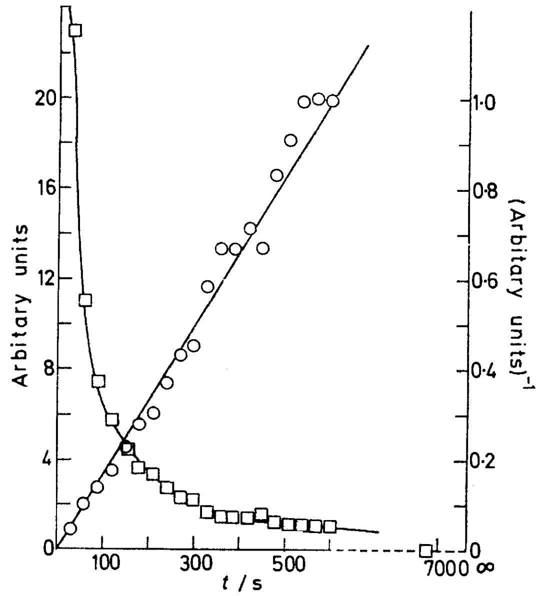

FIGURE 2 Reaction curve and second-order rate plot for $[(CH_3)_3C{-}C{\equiv}C{-}C{\equiv}C{-}C(CH_3)_3]^{-\cdot}$ Na^+ in THF at −40°

TABLE 2

Reaction **data** for $[(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3]^{-}{\cdot}M^+$ in THF scaled up to 0°

Gegen-ion	$10^{-5}k$/ l mol^{-1} s^{-1}	$\Delta G^\ddagger$/ kcal mol^{-1}	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
Li^+	9·5	8·5	5·0	−13
Na^+	8·5	8·6	4·9	−14
K^+	32·3	7·8	4·2	−13
Rb^+	8·2	8·6	5·2	−12
Cs^+	75·2	7·4	4·9	−9

For di-t-butylbutadiyne, no splitting by the gegenion can be detected, but because the rate of reaction of the radical anion varies with the nature of the gegenion, the ions must be present as solvent-separated ion pairs.

DISCUSSION

We have chosen 1,4-di-t-butyl- and 1,4-bistrimethylsilyl-buta-1,3-diyne in this study of silicon d_π–p_π interaction because of the following factors. (a) In the monoacetylenic systems, an electron cannot be given to the molecule unless there is a phenyl group present to increase the resonance stabilisation of the radical anion. In the butadiyne systems the presence of the two acetylenic groups enables an electron to be taken up even though there are no phenyl groups present. This means that in the radical anions $[(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3]^{-\cdot}M^+$ and $[(CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3]^{-\cdot}M^+$ there are 18 identical protons present, with no others to complicate the spectrum. Thus, if d_π–p_π interaction occurs with silicon and not with carbon, we should obtain a very clear distinction in the e.s.r. spectra (19 proton lines for the silyl compound and no proton lines for the t-butyl compound). (b) Since these substituted butadiynes are linear molecules, the substituent groups are well removed from each other, and so dimerisation at one of the two central carbon atoms will not involve much steric hindrance. There may, therefore, be a relationship between the reactivity of these radical anions at the central carbon atoms and the electron density on these atoms, which is unaffected by any steric effects.

E.s.r. Spectra.—The spectrum of the silyl radical ion [Figure 1(a)] shows a central line and two satellite lines, all of which are split by the 18 methyl protons. There are two ^{13}C lines each of intensity 3·3% which shows that these lines are due to the six equivalent methyl carbon atoms, since, in this case, the concentration of ^{13}C would be 6·6%. There are also two ^{29}Si lines each of intensity 4·7%, which shows that these lines are due to the two equivalent silicon atoms, since in this case the concentration of ^{29}Si would be 9·4%. The ^{13}C lines lie almost under the centres of the ^{29}Si lines, and hence the total intensity of these satellite lines is *ca.* 8% [Figure 1(a)]. In addition, the potassium gegenion splitting is almost twice that of the proton splitting. To obtain the accurate proton, ^{13}C, ^{29}Si, and M^+ splitting constants, a computer simulation was carried out. The result shown in Figure 1(b) gives a very good fit with the observed spectrum [Figure 1(a)], and the values so obtained are given in Table 1.

Thus, the d_π–p_π delocalisation effect of silicon is clearly seen from the e.s.r. spectra; the delocalisation of the electron over the methyl groups being shown both by the proton splitting and by the methyl ^{13}C splitting.

In the case of the di-t-butylbutadiyne [Figures 1(c) and 1(d)], a single line of width 0·25 G is obtained, together with two satellite lines of splitting constant 10·2 G (each of 1% intensity). The centre line is too narrow to mask 19 proton lines if the width of each of these were 0·1 G. The two satellite lines cannot be due to methyl ^{13}C (since the intensity of each line would then be 3·3% and would be more easily seen) but must be due to two of the acetylenic carbon atoms (since the intensity of each line is 1%). Since we see only one doublet of ^{13}C (10·2 G), this shows that most of the unpaired electron must be accommodated on two of the acetylenic carbon atoms, and that no delocalisation through to the methyl protons occurs.

Thus in the radical anion of the di-t-butylbutadiyne the electron resides mainly on two of the acetylenic carbon atoms, whereas in the corresponding silyl system it is smeared out over the whole radical anion, therefore reducing the proportion of the electron which resides on the acetylenic carbon atoms.

Rates of Reaction.—There is a marked difference between the reactivity of $[(CH_3)_3SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3]^{-\cdot}M^+$ and of $[(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3]^{-\cdot}M^+$. The former radical anion is stable at room temperature, whereas the latter reacts very rapidly at −40°. The radical anion $[(CH_3)_3CC{\equiv}C{-}C{\equiv}CC(CH_3)_3]^{-\cdot}M^+$ is removed by a second-order process, the second-order plot holding good up to *ca.* 80% reaction. We believe this to be due to dimerisation, since any reaction involving, for example, abstraction of a proton from the solvent, or polymerisation, would not give a second-order plot. Furthermore, we have shown that in the case of $[PhC{\equiv}C{-}Si(CH_3)_3]^{-\cdot}M^+$, where again the radical anions are removed by a second-order reaction, the product is the corresponding dimer.[3]

We believe that the marked difference in the rates of dimerisation when silicon is changed for carbon can be interpreted as follows. In the silyl compound, the inductive effect of the $(CH_3)_3Si$ group will be opposed by delocalisation of the unpaired electron, due to d_π–p_π interaction. The inductive effect of the t-butyl group, however, will not be reduced by any d_π–p_π effect. Thus, in spite of the fact that $I_{(CH_3)_3Si} > I_{(CH_3)_3C}$, there could be a smaller unpaired electron density on the acetylenic carbon atoms in the silyl case than in the case of t-butyl, and this would make the silyl radical anion more stable than the corresponding t-butyl radical anion.

The fact that the t-butyl compound reacts so rapidly suggests that the unpaired electron density is appreciable on the two central carbon atoms. (Reaction at the carbon atoms adjacent to the substituent groups would be slower because of the steric hindrance of these substituent groups.)

The fact that the silyl compound is so stable must be due to the fact that there is very little unpaired electron density at the two central carbon atoms. Electron density at the carbon atoms adjacent to the substituent groups would not lead to dimerisation because of steric hindrance at these positions.

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