Tetrahedron Vol. 38, No. 24, pp. 3605 to 3608, 1982
Printed in Great Britain.

0040-4020/82/243605-04$03.00/0

RADICAL ANIONS AND GROUP IVB ORGANOMETALLIC ADDUCTS OF NITROPHENYLACETYLENES AND SOME HALOGENATED DERIVATIVES

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(*Received in UK* 23 *April* 1982)

Abstract—The reaction of the title compounds with several reducing agents and with a number of Group IVB organometallic radicals has been investigated by electron spin resonance spectroscopy. In reducing media the ethynyl derivatives p- and m-$NO_2C_6H_4C\equiv CH$ were found to give the corresponding radical anions, while the halogenated compounds underwent a rapid halogen-hydrogen replacement. Depending on the experimental conditions the radical from p-nitrophenylacetylene was observed in different aggregation states with the positive counterion. Easy oxidation of the ethynyl group to the carboxylic function by adventitious oxygen was also observed in basic DMSO.

On the contrary the expected organometalloxy nitroxides could be obtained in all cases, although prolonged irradiation of the p-$NO_2C_6H_4C\equiv CBr$ eventually led to substitution of Br by a H atom.

The one electron reduction of various halo-aromatics and of some vinyl halides has been investigated. Thus, electrochemical and electron spin resonance studies concerning halonitrobenzenes[1] and halonitrostyrenes[2] have provided direct evidence on the formation of the corresponding radical anions and eventually on their subsequent fragmentation to give a halide ion and a σ radical. For radical anions of alkynyl halides, on the contrary, only rare examples[3] of reactions in which these species are believed to be probable intermediates can be found in the literature.

On the other hand, several ESR studies of radical anions from acetylenic compounds have been reported.[4] As far as we know, all but one reports deal with disubstituted acetylenes. In the single study concerning a terminal acetylene,[5] ESR spectra obtained by reducing phenylacetylene with alkali metals in THF did not reveal hyperfine splitting from the ethynyl proton and were assigned to the radical dianion.

We report here ESR results for radical anions from both terminal and halogenated alkynes such as p- and m-nitrophenylacetylene and some halo derivatives. We have also investigated the reaction of these substrates with Group IVB radicals and the ESR characteristics are reported.

EXPERIMENTAL

p- (I) and m-nitrophenylacetylene (II) were prepared by reaction of the corresponding *cis* nitro-β-bromostyrenes with NaOH in ethanol following the general procedure reported by Cristol *et al.*[6] for the *para* isomer: (I) m.p. 148–149°; (II) m.p. 27–28° (Lit.[7] 27°).

The two bromo derivatives (IV and V) were obtained by direct bromination[8] of the parent acetylenes: IV m.p. 173–175° (lit.[9] 170° dec.); V m.p. 65–67°. The chloro derivative (III) was more easily obtained from IV by nucleophilic displacement with NaCl in DMSO at 80°: m.p. 152–154°.

All the halogenated acetylenes were checked for complete absence of $\equiv$C–H IR absorption at 3300 cm^{-1} ($CHCl_3$).

The nitro derivatives were reduced to radical anions by treatment with alkali alkoxides or thiomethoxides in DMSO or HMPA, and with a mirror of Na or K metal in THF or HMPA. The reduction in MeOH containing MeONa was performed photolytically.

The organometallic adducts were generated by UV irradiation of *t*-butylbenzene solns of the nitrobenzenes containing small amounts of the appropriate organometallic hydride and di-*t*-butyl peroxide (DTBP). *g*-factors were measured with respect to a sample of solid DPPH ($g = 2.0037$).

RESULTS AND DISCUSSION

Radical anions. The reduction of the title compounds with alkali metals or with bases gives origin to several different species depending on the medium and the temperature at which the reduction is performed.

Nitrophenylacetylenes (I, II). The hyperfine coupling constants of the radical anions of *p*- and *m*-nitrophenylacetylene are reported in Table 1. Apart from the nitrogen and the aromatic protons couplings characteristic of *para* and *meta* substituted nitrobenzenes, both these paramagnetic species show an additional doublet attributable to the magnetic interaction with the acetylenic proton. When the reduction is carried out in basic (*t*-BuOK)/DMSO-d_6 the ESR spectra of deuteriated anions of the two compounds are immediately observed, this indicating that a very rapid proton–deuterium exchange takes place prior to the electron transfer process. This is in agreement with the large kinetic acidity of the acetylenic hydrogen of phenylacetylene[10] which for I and II is conveniently predicted to be enhanced by the electronic effect of the nitro group.

Moreover, while at lower concentration of *t*-BuOK

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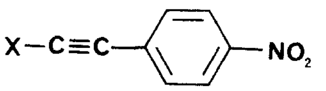
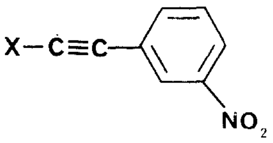


I, X = H
III, X = Cl
IV, X = Br



II, X = H
V, X = Br

Table 1. ESR parameters for the radical anions from I and II

Compound	Reducing agent and solvent	$a_{2,6}$	a_3	a_4	a_5	a_N	a_M	g
(I)	*t*-ButOLi/DMSO	3.25	1.05	2.18[a]	1.05	8.25		2.0047
(I)	*t*-ButONa/DMSO	3.25	1.04	2.18[a]	1.04	8.15		
(I)	*t*-ButOK/DMSO	3.23	1.06	2.18[a]	1.06	8.06		
(I)	*t*-ButOK/DMSO-d_6	3.20	1.04	0.32[b]	1.04	7.98		
(I)	*t*-ButONa/HMPA	3.20	0.93	2.31[a]	0.93	6.75		2.0046
(I)	*t*-ButOK/HMPA	3.20	0.98	2.30[a]	0.98	8.85		
(I)	Na/HMPA	3.14	0.91	2.36[a]	0.91	6.57		
(I)	Na/THF	3.32	1.13	2.13[a]	1.13	9.49	0.35	
(I)	Na/DB-18-C-6/THF	3.27	1.11	2.17[a]	1.11	8.75	0.37	
(I)	K/THF	3.26	1.08	2.22[a]	1.08	8.90	0.20	
(I)	K/DB-18-C-6/THF	3.28	1.11	2.16[a]	1.11	8.92		
(II)	*t*-ButOK/DMSO	3.40	0.42[a]	4.17	1.06	9.42		
(II)	*t*-ButOK/DMSO-d_6	3.40		4.18	1.07	9.42		

[a]Coupling with an acetylenic proton; [b]coupling with a deuterium nucleus.

(10^{-2}M) in partially degassed DMSO the radical anion of I remains unchanged for several days, by using higher concentrations of base (5×10^{-2}M) in the same conditions the spectrum of $I^{\cdot-}$ is replaced after some hours by the superimposition of two spectra, one with $a_N = 8.25$ and the second with $a_N = 9.72$ G, in which the acetylenic proton splitting is lacking. The first one gradually disappears and after a few days only the spectrum with the larger nitrogen splitting is observed. The latter one is almost certainly due to the *p*-nitrobenzoate dianion as the hfs constants are practically coincident with those reported for this radical.[11] Therefore the ethynyl group of I, in basic DMSO, undergoes an air oxidation process analogously to the ethyl[12] and ethenyl[11] functions in straitly related compounds. The species with the smaller value of a_N might be some intermediate formed during the oxidation of the C≡C triple bond. A hypothizable radical might be the anion of *p*-nitrophenylglioxilic acid; however the treatment of an authentic sample of this acid with *t*-BuOK in DMSO gives a spectrum with coupling constants ($a_N = 7.04$, $a_o = 2.80$ and 3.08, $a_m = 0.72$ G) different from those of the observed intermediate ($a_N = 8.25$, $a_o = 3.25$, $a_m = 1.07$ G). Although the experimental data do not allow its unambiguous identification, the latter species could be reasonably envisaged as the radical dianion [p-$NO_2C_6H_4C{\equiv}C^-]^{\cdot-}$ resulting from deprotonation of $I^{\cdot-}$.

On the contrary in the case of the *m*-nitro derivative (II) the oxidation process was never observed and the ESR spectrum of the corresponding radical anion persisted unaltered for a long time.

Different reduction systems have been investigated for I. The large variations of the nitrogen coupling (Table 1) for the species obtained in the various conditions are due to the possibility for this radical to exist in different states of aggregation with the alkali counterion, i.e. a contact ion pair, a solvated ion pair and a free ion. The latter, which could be obtained by sodium reduction in HMPA at room temperature,[13] shows the smaller value of a_N (6.57 G). The reduction by MeSNa, MeONa or *t*-BuONa in HMPA also led to spectra with very similar nitrogen couplings which are therefore assigned to the free ion.

On the contrary by reducing I with Na or K metal in THF, contact radical ion pairs are obtained as indicated by the presence of metal coupling in the corresponding spectra. These species are characterized by large values of a_N (9.49 and 8.8 G with Na^+ and K^+ as counterion respectively). Addition of the crown-ether DB-18-C-6 to THF solutions produces a reduction of a_N and a small increase of a_{Na} for the sodium ion pair, while with Potassium a_K becomes vanishingly small and a_N remains practically unchanged. These species are identified as crown complexed ion pairs.[14]

Table 2. ESR parameters for the metalloxynitroxides of general formula $XC{\equiv}CC_6H_4(\dot{O})NOMR_3$

Compound	MR_3	$a_{2,6}$	a_3	a_4	a_5	a_N	a_M	g
(I)	Et_3Si	3.18	1.20	1.72[a]	1.20	13.62		2.0046
	Ph_3Si	3.14	1.19	1.69[a]	1.19	13.87		2.0046
	Ph_3Ge	3.25	1.23	1.78[a]	1.23	13.24		2.0046
	Ph_3Sn	3.52	1.31	1.96[a]	1.31	13.63	0.67[#]	2.0041
	Ph_3Pb	3.32	1.24	1.88[a]	1.24	12.54		2.0034
(III)	Et_3Si	3.21	1.20	0.17[b]	1.20	13.49		2.0046
	Ph_3Si	3.10	1.17	0.15[b]	1.17	13.80		2.0046
	Ph_3Ge	3.20	1.19	0.15[b]	1.19	13.17		2.0045
	Ph_3Sn	3.56	1.35	0.14[b]	1.35	13.51		2.0041
	Ph_3Pb	3.46	1.22		1.22	12.69		2.0033
(IV)	Et_3Si	3.17	1.21		1.21	13.48		2.0049
	Ph_3Si	3.16	1.19		1.19	13.68		2.0049
	Ph_3Ge	3.27	1.22		1.22	13.18		2.0048
	Ph_3Sn	3.50	1.31		1.31	13.51		2.0044
(V)	Et'_3Si	3.12		3.12	1.05	14.63		
	Ph_3Si	3.16		3.16	1.06	14.88		2.0047
	Ph_3Ge	3.27		3.27	1.08	14.14		2.0045
	Ph_3Sn	3.46		3.66	1.16	14.42		2.0041
	Ph_3Pb	3.42		3.56	1.11	13.57		2.0033

[a] Coupling with an acetylenic proton; [b] coupling with a chlorine nucleus.
[#] $da_{Sn}/dT = +26\ mGK^{-1}$

When the reduction was carried out with the alkali *t*-butoxides in DMSO or with *t*-BuOK in HMPA, the nitrogen splittings were intermediate between those of the free ion and of the contact ion pairs, this being indicative that the observed species are in these cases solvated ion pairs. They can be converted to the corresponding contact ion pairs by increasing the concentration of the counter-ion in solution, this being readily obtained by adding the appropriate alkali iodide to the solutions.

In a protic solvent as MeOH, the presence of a hydrogen bonded free anion can be inferred from the large value of a_N (12.01 G).

It is worth mentioning that the comparison of the nitrogen hyperfine coupling in the radicals from I with those measured for the corresponding species from nitrobenzene, shows that the acetylenic function behaves as an electron-accepting group. For instance a_N is 6.57 and 8.48 G[13] in the free anions from I and $PhNO_2$ respectively. The electron-withdrawing ability of the C≡C triple bond is however lower than that of the C≡N triple bond, as in the free anion from p-$NO_2C_6H_4CN$, a_N is 4.90.[13]

2-(*nitrophenyl*)-1-*halo-acetylenes* (III, IV, V). By reducing the halogenated compounds (III, IV and V) with t-BuOK in DMSO only the ESR spectra of the radical anions of the corresponding unsubstituted acetylenes (I or II) could be detected. In view of the experimental conditions employed this result is not surprising as it is known that haloalkynes can readily undergo nucleophilic attack at the halogen atom followed by protonation of the resulting acetylide.[15] However initial formation of the radical anions of III, IV and V and subsequent rapid fragmentation to give, very likely, an alkynyl radical which abstracts an H atom from the medium could also justify the above result. This is what actually occurs when the considered haloalkynes are electrochemically reduced *in situ* at controlled potential (Ec = −0.9 V, vs s.c.e.) in DMSO: also in this case, in fact, the radical anion of I or II is the largely predominant species recognizable in the ESR spectra observed soon after the start of electrolysis. In this connection it should be pointed out that, contrary to our finding, the radical anions of *trans* and *cis*-β-bromo-p-nitrostyrene, under very similar conditions, did not reveal bromine elimination;[2] therefore the rupture of carbon-halogen bond, at least for this case, seems to be easier for an ethynyl than for a vinyl halide.

Organometallic adducts

p-*Nitrophenylacetylene* (I). The adducts of I with $Et_3Si\cdot$, $Ph_3Si\cdot$, and $Ph_3Ge\cdot$ were generated with a flash of light, while continuous irradiation was necessary to get intense spectra of the adducts with $Ph_3Sn\cdot$ and $Ph_3Pb\cdot$. The hyperfine splitting constants and g-factors for the resulting metalloxy-nitroxides are reported in Table 2.

It is worth mentioning that in the triphenyltin adduct from I we have been able to detect the tin satellites (^{117}Sn: $I = 1/2$, n.a. = 7.67%; ^{119}Sn: $I = 1/2$, n.a. = 8.68%), the metal splitting being negative (−0.67 G) at room temperature and showing a positive temperature coefficient of 26 mGK^{-1}. This is one of the few reports of the detection of Group IVB metal satellites in the adducts of nitro derivatives.[16] Incidentally it may be pointed out that both the value of a_{Sn} and its temperature dependence are indicative of chelation of tin by the second O atom of the nitro group.

The nitrogen hyperfine coupling (13.62 G) of the triethylsilyl adduct is intermediate between those of the corresponding adducts from nitrobenzene (14.86 G)[17] and from *p*-nitrobenzonitrile ($a_{\mathrm{N}} = 12.72$, $a_{\mathrm{o}} = 3.12$, $a_m = 1.09$, and $a_{\mathrm{N}}^{\mathrm{CN}} = 0.48$ G). Therefore, as already found in the radical anions, the electron-accepting ability of the ethynyl group is lower than that of the cyano group.

2-(*Nitrophenyl*)-1-*halo-acetylenes* (III, IV, V). The $\cdot MR_3$ radicals preferentially add to the nitro group instead of abstracting the halogen atom. This can be straightforwardly inferred from the ESR spectra of the adducts with the compound containing chlorine, which show a measurable coupling with the latter nucleus.

With the bromoacetylenes (IV and V), although no bromine splitting could be observed, the unusually large linewidth and the *g*-factors slightly greater than in the unsubstituted species suggest that we are observing the bromine containing adducts.

Prolonged irradiation of IV results in the appearance of a second spectrum due to the radical where Br has been replaced by hydrogen. The formation of the latter radical is presumably a multi-step process involving first the abstraction of bromine by $\cdot MR_3$ to give the *p*-nitrophenylethynyl radical (undetected) which in turn abstracts hydrogen from the organometallic hydride to give I:

$$(\mathrm{IV}) + \cdot\mathrm{MR_3} \longrightarrow p\text{-}\mathrm{NO_2C_6H_4C{\equiv}C\cdot} + \mathrm{BrMR_3}$$

$$p\text{-}\mathrm{NO_2C_6H_4C{\equiv}C\cdot} + \mathrm{HMR_3} \longrightarrow (\mathrm{I}) + \cdot\mathrm{MR_3}$$

$$(\mathrm{I}) + \cdot\mathrm{MR_3} \longrightarrow p\text{-}\mathrm{R_3MON(\dot{O})C_6H_4C{\equiv}CH}.$$

The ease of replacement of Br with H is dependent on the nature of the organometallic hydride employed and increases in the order: $\mathrm{HSiPh_3} < \mathrm{HGePh_3} < \mathrm{HSnPh_3} < \mathrm{HSiEt_3}$. This does not seem to be the case with the adducts of *meta* isomer (V) whose ESR spectra do not show any major modification even when irradiation is prolonged over a period of more than one hour.

Note added in proof. After the submission of this paper for publication, the detection of the *p*-nitrophenylacetylene radical anion upon reduction of *cis*- or *trans*-*p*-nitro-β-bromostyrenes has been reported by Simonetta *et al.*[18] The ESR parameters given by these authors are in good agreement with those found in the present investigation and reported in Table 1.

Acknowledgement—Financial support from C.N.R. (Rome) and Ministero P. I. of Italy is gratefully acknowledged by two of us (G.F.P. and F.C.).

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