

Figure 1. ESR spectra of furil: (a) anion radical in 2-propanol at  $-20^{\circ}\text{C}$ ; (b) sodium ion pair in THF at  $24^{\circ}\text{C}$ ; (c) sodium triple ion in THF at  $-20^{\circ}\text{C}$ ; and (d) triphenyltin adduct in THF at  $20^{\circ}\text{C}$ .

The first step leading to an ion pair is well known among the 1,2- and 1,4-dicarbonyl compounds such as benzil,<sup>6</sup> 9,10-phenanthrenequinone (PQ),<sup>7</sup> acenaphthenequinone,<sup>8</sup> and *trans*-oxindigo.<sup>9</sup> Upon addition of an alkali metal salt such as  $\text{NaBPh}_4$ , none of the above-mentioned ion pairs proceeds in the second step to form the triple ion. However, both the furil (1,2-diketone) and the BADC (1,4-diketone) readily interact with  $\text{MBPh}_4$  to form the corresponding triple ions. The striking resolution of their ESR spectra owing to their high stability in THF revealed many valuable features which shed some light on the structure and the dynamics of ion migrations in these systems.

### Experimental Section

Alkali metal was supplied by Alfa Inorganic and was vacuum sublimated. Fisher reagent grade THF was dried repeatedly over Na-K alloy and vacuum distilled into sample tubes. Furil was received from PCR and BADC and sodium tetraphenylborate was received from Aldrich. The polyether 18-crown-6 was a gift from Professor E. Buncel. All were used as received. The preparations of potassium and lithium tetraphenylborates and samples of the ion pairs and triple ions in THF in a high vacuum line were accomplished according to the previously described procedures.<sup>4</sup>

Electron spin resonance measurements were recorded on a Bruker 420 spectrometer with 100-kHz modulation. The temperature was varied by flowing thermostated nitrogen past the sample.  $g$  factors were measured using the Bruker NMR oscillator and the potassium naphthalene ion pair in THF as an external standard.<sup>10</sup>

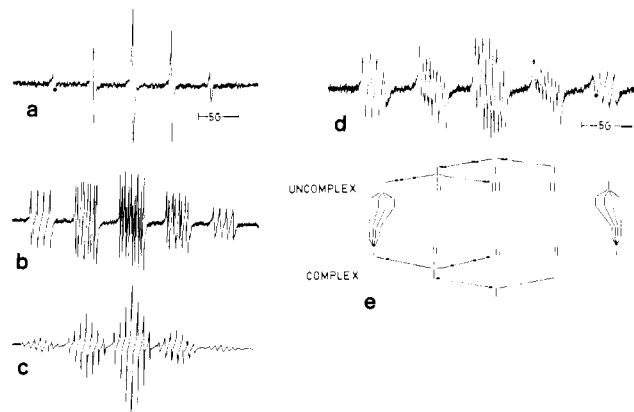
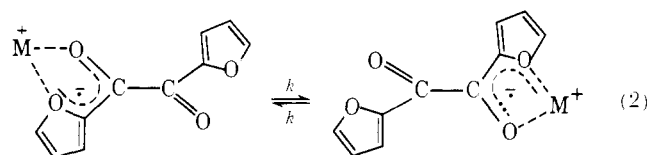


Figure 2. ESR spectra of di-*tert*-butyl azodicarboxylate: (a) anion radical in 2-propanol at  $-3^{\circ}\text{C}$ ; (b) sodium ion pair in THF at  $22^{\circ}\text{C}$ ; (c) sodium triple ion in THF at  $22^{\circ}\text{C}$ ; (d) 18-crown-6 complex sodium ion pair in THF at  $20^{\circ}\text{C}$ ; and (e) modulation diagram for the line width alternation observed in (d).

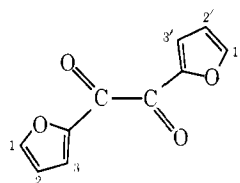
### Results and Discussion

**I. The Alkali Radical Ion Pairs of Furil and BADC. A. ESR Spectra.** The ESR spectra of the radical anions of furil and BADC are given in Figures 1a and 2a, respectively. They were generated by photochemical means in the presence of triethylamine. Their ESR parameters are reported in Tables I and II for comparison purposes. It is interesting to point out that the photochemically generated BADC anion (Figure 2a) exhibited CEDEP (EA polarization)<sup>11</sup> and a detailed polarization study is now in progress. The typical ESR spectra of sodium ion pairs of furil and BADC are illustrated in Figures 1b and 2b, respectively, and the ESR parameters, including all K, Na, and Li ion pairs, are given in Tables I and II.

**B. Intramolecular Cation Migration in Ion Pairs.** The dynamic processes of cation migration in various *p*-semiquinones and the triple ions as possible intermediates in the intermolecular cation transfer have been reviewed by Chen and Hirota.<sup>12</sup> In the alkali-furil radical ion pairs, marked line-width alternation due to intramolecular cation migration was observed. Surprisingly such line-width effect was not observed

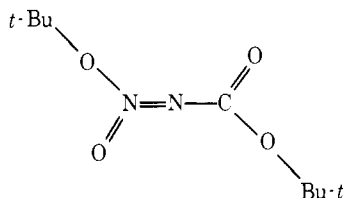


in the alkali ion pairs with other 1,2-dicarbonyl compounds, as we have repeated the previously reported alkali ion pairs of benzil, PQ, and acenaphthenequinone over a temperature range of  $-80$  to  $20^{\circ}\text{C}$ . In all probability, the failure to observe the line-width effect is due to the extremely fast cation migration rate<sup>8a</sup> in these "loose" ion pairs. Thus, marked line-width alternation has also been observed in the  $\text{Ba}^{2+}$ -acenaphthene semiquinone ion pair in DME<sup>8b</sup> when the jumping of the  $\text{Ba}^{2+}$  between the two sites was substantially slowed down compared to the alkali ion analogue. In the  $\text{Ba}(\text{ACQ})_2$  case, the four oxygen atoms adopting a "tetrahedral-like" configuration provide four equivalent sites all of which have the  $\text{Ba}^{2+}$  unsymmetrically located with respect to the two oxygen atoms of any one anion and are off the two planes of symmetry. The "jumping" is visualized as the wandering of the  $\text{Ba}^{2+}$  between these four equivalent sites. This interpretation is consistent with our conclusion that the alkali-furil ion pair is relatively tighter bound owing to the extra coordination with the strategically situated ethereal oxygen.

**Table I.** ESR Parameters of Radical Anion, Ion Pairs, Triple Ions, and Group 4B Organometal Adducts of Fural (FQ) in THF

system	$T, ^\circ\text{C}$	$g$ factor	$a_{13\text{C}}, \text{G}^a$	$a_{\text{M}}, \text{G}$	$a_1 = a_{1'}, \text{G}^c$	$a_2 = a_{2'}, \text{G}^c$	$a_3 = a_{3'}, \text{G}^c$
FQ $^{\cdot-}$	-20				1.86	0.39	2.42
K $^+$ FQ $^{\cdot-}$	20	2.004 82		n.s.	1.49	0.37	2.10
Na $^+$ FQ $^{\cdot-}$	20	2.004 76		0.50	1.62	0.42	2.18
Li $^+$ FQ $^{\cdot-}$	20	2.004 61		0.64	1.37	0.41	2.33
K $^+$ FQ $^{\cdot-}$ -K $^+$	20	2.004 72	6.25	<0.04	1.62	0.38	2.20
Na $^+$ FQ $^{\cdot-}$ -Na $^+$	20	2.004 67	6.56	0.13	1.72	0.38	2.29
Li $^+$ FQ $^{\cdot-}$ -Li $^+$	20	2.004 57	6.48	0.11	1.82	0.42	2.39
Ph $_3$ SnFQ $^{\cdot}$	20	2.003 72		5.62 $^b$	2.26	0.39	2.65
Pb $_3$ PbFQ $^{\cdot}$	20	2.003 42		7.91 $^b$	1.79	0.42	2.21

$^a$  Two equivalent  $^{13}\text{C}$  (carbonyl groups) hfs.  $^b$   $^{117}\text{Sn}$  ( $I = 1/2, 7.7\%$ ),  $^{119}\text{Sn}$  ( $I = 1/2, 8.7\%$ ),  $^{207}\text{Pb}$  ( $I = 1/2, 21.1\%$ ).  $^c$  (1) For ion pairs, fast limit average hfs are given. (2) The assignments of  $a_1$  and  $a_3$  are not absolute and can be altered.

**Table II.** ESR Parameters of Radical Anion, Ion Pairs, Triple Ions, and Group 4B Organometal Adducts of Di-*tert*-butyl Azodicarboxylate (BADC) in THF

system	$T, ^\circ\text{C}$	$g$ factor	$a_{12\text{C}}, \text{G}^a$	$a_{\text{M}}, \text{G}$	$a_{\text{N}1}, \text{G}$	$a_{\text{N}2}, \text{G}$
BADC $^{\cdot-}$	-2				4.78	4.78
K $^+$ BADC $^{\cdot-}$	22	2.004 82	4.68	n.s.	5.65	5.65
Na $^+$ BADC $^{\cdot-}$	22	2.004 80	4.07	0.79	5.54	5.86
Li $^+$ BADC $^{\cdot-}$	22	2.004 71		0.74	5.48	5.84
K $^+$ BADC $^{\cdot-}$ -K $^+$	-53	2.004 64	4.81	0.16	5.46	5.46
Na $^+$ BADC $^{\cdot-}$ -Na $^+$	22	2.004 57	4.96	0.72	5.66	5.66
Li $^+$ BADC $^{\cdot-}$ -Li $^+$	22	2.004 50		0.68	5.78	5.78
Ph $_3$ SnBADC $^{\cdot}$	20	2.003 92			7.05	7.62
Ph $_3$ PbBADC $^{\cdot}$	20	2.004 22		8.48 $^b$	6.53	8.50

$^a$  Two equivalent  $^{13}\text{C}$  (carbonyl groups) hfs.  $^b$   $^{207}\text{Pb}$ ,  $I = 1/2, 21.1\%$ .

The intramolecular cation migration in the K-fural ion pair was studied systematically as a function of temperature. This particular K-fural ion pair was chosen because of the absence of K hyperfine splittings in the ESR spectra which afforded a more precise analysis of the main lines in terms of their line-width alternation. In Figure 3a, the experimental spectrum of the K-fural ion pair at low temperature is compared with a computer-simulated spectrum (Figure 3b) assuming the migration at the *slow limit*. The computation was done on a Burrough 6700 computer using a similar program previously described by Chen and Hirota.<sup>12</sup> The experimental spectrum recorded for the K-fural ion pair at high temperature is shown in Figure 3c which is compared with a simulated spectrum (Figure 3d) assuming the cation migration at the *fast limit*. This series of experiments indicates that the rate of cation migration in the K-fural ion pair falls within the *intermediate* range. Their calculated kinetic parameters are compared with the published data of other ion-pair systems in Table III.

In the case of the alkali-BADC ion pairs, no line-width alternation was observed in a large temperature range. However, since we have argued above that the alkali-fural is tighter bound owing to the extra coordination with the ethereal oxy-

gen, it is inconceivable that the same extra coordination effect should be absent in BADC. Thus, the failure of observing any line-width alternation in the M $^+$ BADC $^{\cdot-}$  ion pairs cannot be due to a "loose" pair with a very fast cation migration rate. Rather, we suggest that the M $^+$ BADC $^{\cdot-}$  ion pairs are probably among the tightest bound pairs. To confirm this conclusion, we have examined the effect of complexation of both the Na $^+$ fural $^{\cdot-}$  and the Na $^+$ BADC $^{\cdot-}$  ion pairs by the polyether 18-crown-6 and DMF. In the former case, both the crown ether and DMF break up the Na $^+$ fural $^{\cdot-}$  ion pair by selectively "solvating" the Na $^+$  and give a spectrum identical with that of Figure 1a. In the case of Na $^+$ BADC $^{\cdot-}$ , the ion pair is very strongly bound and both the crown ether and DMF can only mildly modulate the ion-pair spectrum (Figure 2d) by the process given in eq 3.

This dynamic process is supported by the line-width analysis of the complex spectrum (Figure 2d) in which the "unusual" feature of the observed line-width effect can be explained by the modulation of both  $^{14}\text{N}$  and  $^{23}\text{Na}$  isotropic hyperfine splittings (Figure 2e). At the present time, we do not wish to speculate on the possible structure of the crown ether complexed ion pair. Nevertheless, the conclusion that M $^+$ BADC $^{\cdot-}$

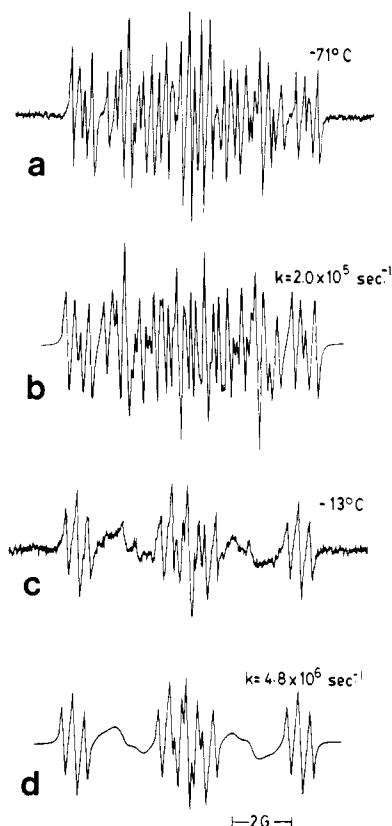
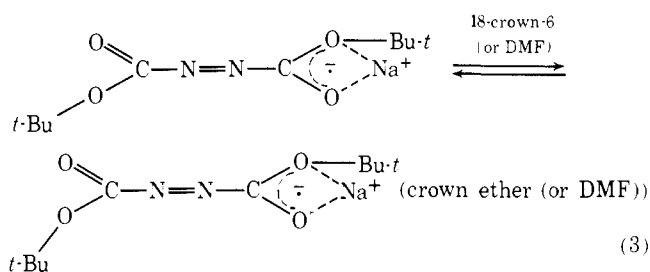
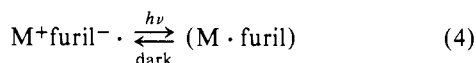


Figure 3. Experimental and calculated ESR spectra of potassium ion pair of furil in THF (see text).



is a very tight pair is confirmed and therefore the failure to observe any line-width alternation in the ion pair is due to the *absence* of any appreciable intramolecular cation migration. We may add that we also do not have a full explanation of why the  $M^+BADC^-$  should be tighter bound than the  $M^+furil^-$ , apart from the obvious recognition that the BADC system is a smaller "four-member ring" compared to the furil system with a "five-member ring". It is interesting to note that the ion pairs of 3,6-dimethylthieno[3,2-*b*]thiophene-2,5-dione in which the similarly strategic S atom provides the extra coordination do not retard the cation migration.<sup>13</sup> Another relevant experiment which we have done involving the photolysis of the  $M^+furil^-$  and the  $M^+BADC^-$  ion pairs is also rather revealing. While the  $M^+BADC^-$  ion pair is resistant to photolysis, the  $M^+furil^-$  system is sensitive to irradiation:



and one can follow the process by monitoring the modulated ESR signal intensity in a modulated photolysis. The structure of  $(M \cdot furil)$  is not known at this time and will be the subject of our future CIDNP investigations.

**C. Reactions of  $M^+Furil^-$  and  $M^+BADC^-$  Ion Pairs with Group 4B Organometals.** Alkali radical ion pairs which do not

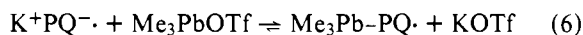
Table III. Kinetic Parameters of Intramolecular Potassium Migration in THF

system	$E_a$ , kcal/mol	log $A$	$\Delta S^\ddagger_{300K}$ , esu	log $k_{300K}$	ref
	5.7	11.5	-8.2	7.3	this work
	4.74	11.76	-6.23	8.31	13
	5.3	11.4	-8.5	7.5	12

proceed to the formation of triple ions have been shown to undergo spontaneous exchange with other types of alkali salts<sup>14</sup> such as

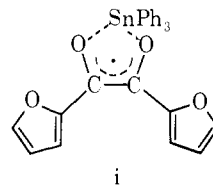


In addition, ion pairs such as  $K^+PQ^-$  can react with "ionic" organometals such as the trimethyllead trifluoromethanesulfonate ( $Me_3PbOTf$ ) via the similar exchange:<sup>14</sup>

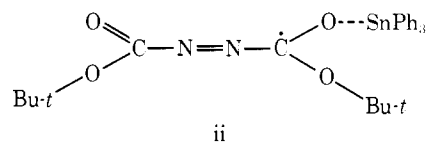


In the cases of  $K^+furil^-$  and  $K^+BADC^-$  ion pairs, the exchange with  $Na^+BPh_4^-$  even proceeds further to form the  $Na^+furil^- \cdot Na^+$  and the  $Na^+BADC^- \cdot Na^+$  triple ions. Thus, both  $K^+furil^-$  and  $K^+BADC^-$  ion pairs are expected to react with group 4B organometals. The general concept of charge transfer interactions involving the organometal as the donor has been advocated by Kochi and co-workers<sup>15</sup> and experimental confirmation leading to the formation of paramagnetic adduct has recently been obtained.<sup>16</sup>

When triphenyltin chloride was reacted with  $M^+furil^-$  and  $M^+BADC^-$  ion pairs, the expected exchange was observed with the formation of the paramagnetic adducts  $Ph_3Sn-furil$  and  $Ph_3Sn-BADC$ . It is interesting to note that in the  $Ph_3Sn-furil$  adduct, the ESR parameter suggests the structure i whereas in the  $Ph_3Sn-BADC$  case, the spectral features can



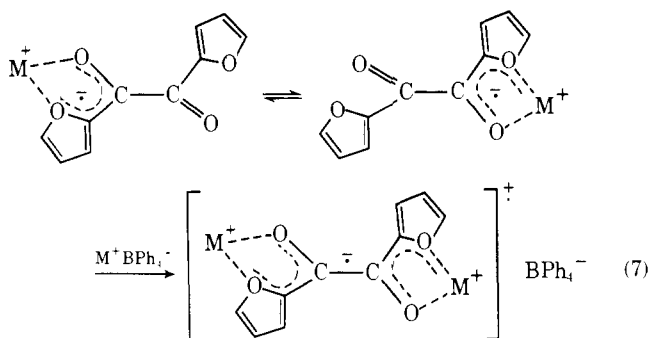
only be interpreted based on the structure ii. While the detailed structure and the nature of bonding of a series of similar adducts will be the subject of another full investigation,<sup>14</sup> the



ESR parameters of a number of the group 4B organometal adducts to furil and BADC generated via the exchanges are reported in Tables I and II, respectively. A typical spectrum of the  $Ph_3Sn-furil$  adduct is shown in Figure 1d.

**II. The  $M^+Furil^- \cdot M^+$  and  $M^+BADC^- \cdot M^+$  Triple Ions. A. Formation of the Triple Ions and the ESR Observations.** The additions of  $M^+BPh_4^-$  salts to the  $M^+furil^-$  and  $M^+BADC^-$

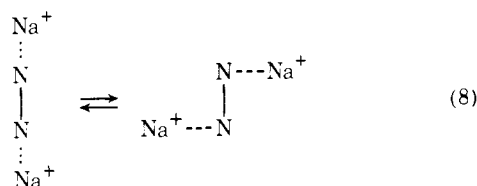
ion-pair systems induced the formation of the corresponding triple ions, e.g., eq 7. In both cases, the sodium triple ions were found to be the most stable. Thus, the addition of  $\text{Na}^+\text{BPh}_4^-$  to either the ion pair or the triple ion of another type of alkali



ions will lead to spontaneous exchange always resulting in the formation of the sodium triple ions. For the furil system the K triple ion was found to be more stable than the Li and in the BADC system the Li triple ion was more stable. Such orders of stability allow a high degree of selectivity in triple ion formation when more than one type of alkali cations is present. This may have some significance in biological systems in which K triple ions can enter a cell and exchange with  $\text{Na}^+$  ions in the cell before leaving as the Na triple ion.

Typically well-resolved spectra of the  $\text{Na}^+\text{furl}^- \cdot \text{Na}^+$  and the  $\text{Na}^+\text{BADC}^- \cdot \text{Na}^+$  triple ions are shown in Figures 1c and 2c, respectively. The ESR parameters of all  $\text{M}^+\text{furl}^- \cdot \text{M}^+$  and  $\text{M}^+\text{BADC}^- \cdot \text{M}^+$  triple ions are listed in Tables I and II.

The high stability of the  $\text{Na}^+\text{furl}^- \cdot \text{Na}^+$  triple ions allows the generation of these paramagnetic triple ions in decent concentration to afford extremely high spectral resolution. The isotropic hyperfine splitting of the  $^{13}\text{C}$  in the two carbonyl groups was readily resolved and the  $^{13}\text{C}$  hyperfine lines exhibited marked asymmetric broadening. From the observed  $g$  factor, the  $g$  anisotropy can be deduced ( $\Delta g$ ,  $g_{\parallel} - g_{\perp}$ , is negative) and a standard analysis yields a positive sign for the  $^{13}\text{C}$  splitting. On the other hand, no such asymmetric line broadening was observed among the sodium hyperfine lines. This is in contrast with most of the previous observations of other known triple ions in which the sodium septet displayed marked asymmetric line broadening.<sup>2-4</sup> More recently, Gooijer and co-workers<sup>5</sup> have established in the  $\text{Na}^+\text{pyrazine}^- \cdot \text{Na}^+$  triple ion that the observed asymmetric line broadening within the Na septet is due to the correlated modulations of the *iso-*



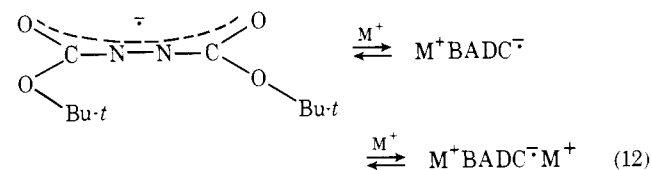
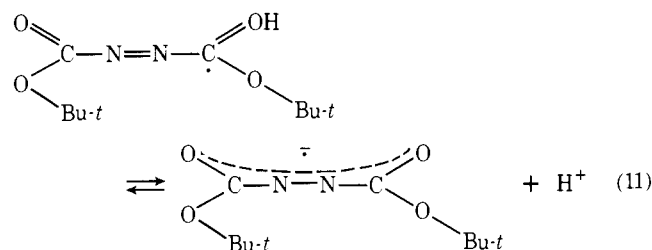
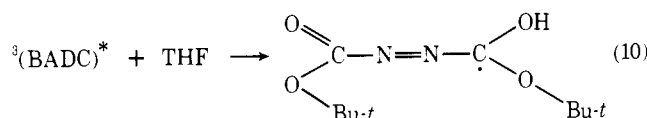
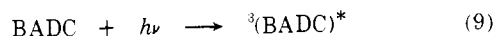
*ropic*  $g$  factor and the *isotropic* Na hyperfine splitting as a result of the intramolecular cation migration. If the sodium cations in the furil system are relatively tighter bound than the previously known triple ions owing to the extra coordination with the strategically situated ethereal oxygens, the intramolecular cation migration rate would be substantially slower to prevent any appreciable line broadening. This is confirmed by the observation of the asymmetric broadening among the lithium septet on the less tightly bound lithium triple ions of both furil and BADC systems.

The ESR analysis of the  $\text{Na}^+\text{BADC}^- \cdot \text{Na}^+$  triple ion was even simpler, since there was no interfering proton splittings. Again, clearly no asymmetric line broadening effect was observed in the Na septet. Since the  $\text{Na}^+\text{BADC}^- \cdot \text{Na}^+$  is even

more tightly bound than the corresponding furil triple ion (from a series of temperature dependence studies), it is not surprising that the intramolecular cation migration rate is negligible and no asymmetric line broadening was observed. However, a marked asymmetric line broadening effect was clearly observable among the nitrogen quintet as well as among the  $^{13}\text{C}$  hyperfine lines. The measured  $g$  factor led to a negative  $\Delta g$  and the analysis yielded a positive sign for *both* the nitrogen and the  $^{13}\text{C}$  hyperfine lines.

From the dynamic ESR features, it is conceivable that both the furil and the BADC triple ions owe part of their stability to the extra coordination with the ethereal oxygens.

**B. Photochemical Generation of the Triple Ions.** All the previously known alkali triple ions are almost exclusively generated by metal reduction together with thermal reaction with  $\text{M}^+\text{BPh}_4^-$ . Indeed, our initial study of the present furil and BADC triple ions employed such a thermal preparation, as this procedure allows the control of the separate stages in ion-pair and in triple ion formation. However, if only the formation of triple ion is of concern, we have discovered a photochemical method to generate identical triple ions. When THF solutions containing either furil or BADC in the presence of  $\text{Na}^+\text{BPh}_4^-$  were photolyzed, the identical furil or BADC sodium triple ion was readily observed. The ESR spectra of these photochemically generated triple ions are identical with the thermal spectra. Nevertheless, it was not possible to control or separate the ion-pair and the triple ion stages. These results can be explained in terms of the mechanism of eq 9-12.



The success of the photochemical generation of  $\text{M}^+\text{BADC}^- \cdot \text{M}^+$  triple ions naturally invites the attempt to apply this simpler method to other previously known triple ion forming systems. Thus, we have applied the photochemical method successfully to generate the duroquinone-sodium triple ion and the anthraquinone-sodium triple ion by the photolyses of the parent quinone in THF and in the presence of  $\text{Na}^+\text{BPh}_4^-$ . Since the photochemical reductions of these quinone systems are relatively well understood and they have been used as model systems for CIDEP and CIDNP studies,<sup>11</sup> it will be fascinating to extend the CIDEP/CIDNP studies in the photogenerated triple ion systems.

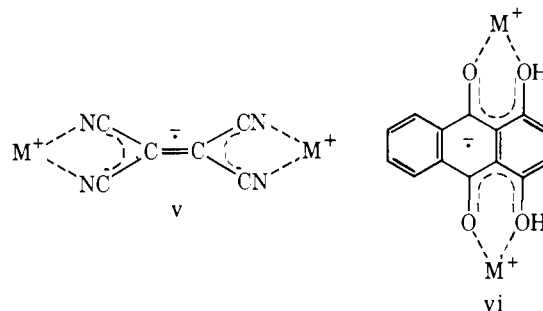
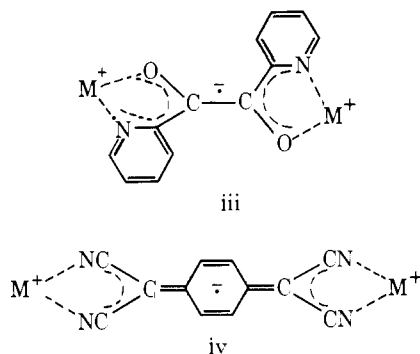
**C. Reactions of the Triple Ions with Crown Ether and Group 4B Organometals.** A parallel series of experiments was carried out to study the effect of crown ether complexation and reactions of group 4B organometals with  $\text{M}^+\text{furl}^- \cdot \text{M}$  and

$M^+BADC^- \cdot M^+$  triple ions. The addition of the 18-crown-6 polyether to the furil triple ions at low temperature appeared to have completely shifted the equilibrium to the furil anions and the "pure" furil anion ESR spectrum was observed. In the case of the BADC triple ion, the 18-crown-6 polyether seemed to be able to "remove" only one sodium cation leaving a (crown...Na<sup>+</sup>...BADC<sup>-</sup>) complex ion pair with a spectrum identical with that of Figure 2d. These results are consistent with our conclusion that both the BADC ion pair and triple ion are more stable than the corresponding furil ion pair and triple ion. A complete understanding of the crown ether effect must await further study.

Reactions of the furil and BADC triple ions with  $Ph_3SnCl$  lead to the formation of the same adducts as observed in the ion-pair reactions. The result is consistent with our interpretation that the triple ions are in equilibrium with the ion pairs and the reaction with  $Ph_3SnCl$  occurs at the ion pairs and thus shifts the equilibrium toward the adduct formation.

### Conclusion

We have generated a new series of alkali cationic ion pairs and triple ions with dicarbonyl compounds in which the higher stability is partly due to extra coordination with some strategic etheral oxygens. To further test our assumption, we have successfully prepared the alkali triple ions of compounds iii-vi. All these triple ions afford extra coordination power via the strategic nitrogen or oxygen atoms. All exhibited interesting



ESR spectra and deserved further study spectroscopically as well as chemically.

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