Anion Radicals of a Series of [2.2]Paracyclophanes and α,ω-Diarylalkanes. I. Formation and Chemistry

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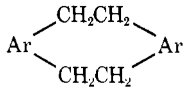
Abstract: The anion radicals of a series of [2.2]paracyclophanes (I) and α,ω-diarylalkanes, $Ar(CH_2)_nAr$, where Ar = benzene, naphthalene, and anthracene, have been prepared by chemical reduction and characterized spectroscopically. These compounds possess two identical reducible groups within the molecule, and the chemistry of their anion radicals has been determined. The anion radicals of the [2.2]paracyclophanes and the diarylethanes are stable only at low temperatures, $<-70°$, in direct contrast to their simple aromatic counterparts. Increasing the chain length in the dinaphthylalkane series increases the stability of the anion radical and the behavior approaches that of naphthalene. The anion-radical species readily accept another electron, either by disproportionation or direct reduction, to form the unstable two-electron reduced product. The two-electron reduced species undergoes decomposition accompanied by bond scission of the ethane linkage to produce the previously unreported arylmethide anions, $ArCH_2^-$, K^+ (II and III). Simple Hückel molecular orbital calculations showed that instability appears to result from the gain in π-resonance energy as the carbanions are formed. The calculations also confirm that increasing the chain length decreases the tendency of the anion radicals to decompose, in agreement with the observations for a series of dinaphthylalkanes. The structure of these carbanions was established by methanol quenching studies and by an independent synthesis from the corresponding arylmethyl methyl ethers: $ArCH_2OCH_3 \rightarrow ArCH_2^-$. The mechanism of the decomposition reaction and the products were established by optical spectroscopy. The relationship of this work to the chain degradation observed in the polyradical anions of vinyl aromatic polymers is discussed.

Anion radicals of molecules possessing more than one reducible aromatic ring have received little attention in the literature, although the chemistry of the simple aromatic species has been extensively studied. Esr spectra of the anion radicals of the α,ω-diphenylalkanes,[1-3] the [2.2]paracyclophanes,[1-4] and compounds of the type $(p\text{-}NO_2C_6H_4)_2X-$,[5] where $X = (CH_2)_n$ (n = 0, 1, and 2), O, and S, have been reported. No examples of compounds in this general class having aromatic rings higher than phenyl have been reported.

The formation and the chemical behavior of the anion radicals of a series of diarylethanes, $ArCH_2CH_2Ar$,



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and [2.2]paracyclophanes (I), where Ar = benzene, naphthalene, and anthracene, have been investigated. In addition, the anion radicals of a series of di-α-naphthylalkanes, $C_{10}H_7(CH_2)_nC_{10}H_7$, where n = 2, 3, and 4, were studied. The anion radicals were generated in tetrahydrofuran or dimethoxyethane by reduction over potassium and were characterized by optical spectroscopic techniques. The most surprising feature of the results was the unstable nature of the anion radicals of the diarylethanes and the [2.2]paracyclophanes. In order to observe the paramagnetic species, it was necessary to work at low temperatures, $<-70°$. Increasing the temperature resulted in decomposition, and the mechanism was elucidated using spectroscopic and methanol-quenching techniques.

Experimental Section

A. **Materials.** The solvents tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by fractional distillation and stored over sodium benzophenone. Final distillation into the reaction unit was carried out on a high-vacuum line.

[2.2]Paracyclophane (1) and 1,2-diphenylethane (5) (Aldrich) were purified by vacuum sublimation: **1**, mp 288–289°; **5**, mp 52°.

Dibenzo[2.2]paracyclophane was synthesized from (4-methyl-1-naphthylmethyl)trimethylammonium bromide according to the method of Wasserman and Keehn.[6] Separation into the two isomers, anti, **2**, and syn, **3**, was achieved using a chromatographic and fractional crystallization procedure supplied by Professor Wasserman. The purity of the isomers was confirmed by melting point and nmr analysis: anti, mp 299–300° (some decomposition);[7,8] syn, mp 243–245°.[6]

Tetrabenzo[2.2]paracyclophane (4) was prepared from 9,10-bis-chloromethylanthracene, using the method of Golden,[9] and recrystallized from tetrachloroethane or chloroform. Spectral analysis confirmed the structure.

1,2-Di-α,α′-naphthylethane (6) was prepared from α-chloromethylnaphthalene by treatment with sodium in isooctane,[10] mp 161–162° (lit. 161–162°[11]).

1,2-Di-9-anthrylethane (7) was formed in the lithium aluminum hydride reduction of 9-anthraldehyde in refluxing THF,[12] mp 314–316°.

1,3-Di-α,α′-naphthylpropane (8) and **1,4-di-α,α′-naphthylbutane (9)** were kindly provided by Dr. E. A. Chandross. The propane was used as received; the butane was recrystallized from ethanol.

α-Methoxymethylnaphthalene (10) was formed by treatment of α-chloromethylnaphthalene with sodium in methanol, bp 86–88° (0.5 mm).

9-Methoxymethylanthracene (11) was prepared by refluxing 9-chloromethylanthracene in methanol,[13] mp 90–91°.

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(1) S. I. Weissman, *J. Amer. Chem. Soc.*, 80, 6462 (1958).

(2) V. V. Voevodskii, S. P. Solodovnikov, and V. M. Chibrikin, *Dokl. Akad. Nauk SSSR*, 129, 1082 (1959).

(3) F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, 91, 1883 (1969).

(4) A. Ishitani and S. Nagakura, *Mol. Phys.*, 12, 1 (1967).

(5) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 39, 778 (1963).

(6) H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **91**, 2374 (1969).

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(8) D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

(9) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).

(10) E. Wolthuis and D. L. Van der Jagt, *J. Org. Chem.*, 20, 963 (1964).

(11) N. P. Buu-Hoi and N. Hoan, *ibid.*, **14**, 1023 (1949).

(12) K. C. Schreiber and W. Emerson, *ibid.*, **31**, 95 (1966).

(13) F. H. C. Stewart, *Aust. J. Chem.*, **13**, 478 (1960).

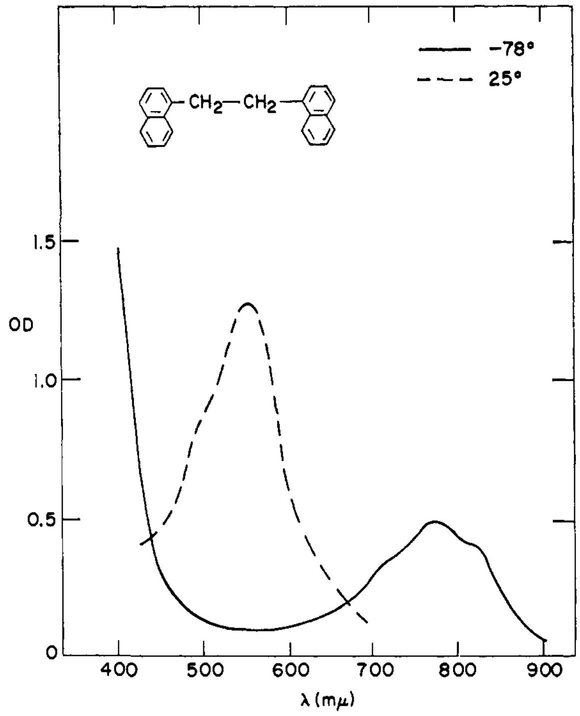

Figure 1. Optical spectrum of the anion radical of 1,2-di-α,α'-naphthylethane (6) at −78° and its decomposition product at 25°; solvent THF, counterion K^+.

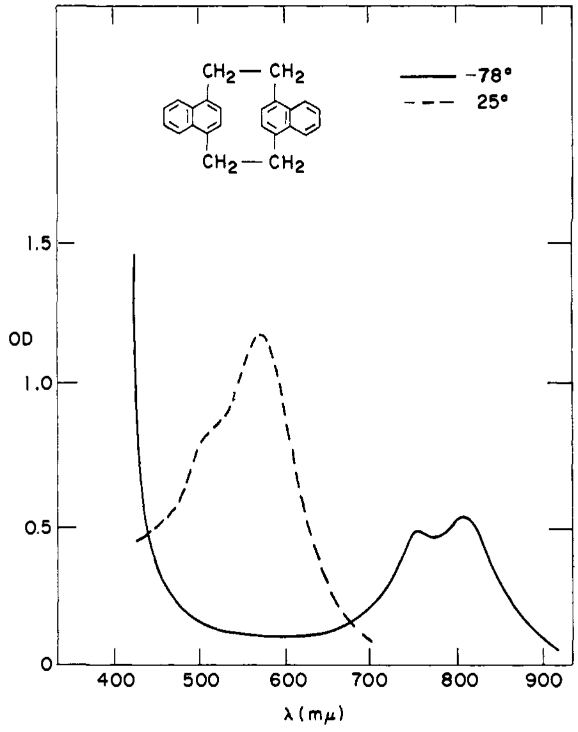

Figure 2. Optical spectra of the anion radicals of dibenzo[2.2]-paracyclophane, 2 and 3, at −78° and their decomposition products at 25°; solvent THF, counterion K^+.

B. Preparation of Radical Anions. Anion radicals of compounds **1–11** were prepared in conventional glass units under high-vacuum, anhydrous conditions. Solutions were prepared and transferred in breakseal devices. Both the alkali-metal reduction (over freshly distilled potassium metal) and the recording of the initial spectra were carried out at −78°. The optical spectra were recorded on a Cary 14 spectrophotometer, using a dewar flask equipped with optical windows, with methanol as the refrigerating liquid. The paracyclophane solutions were carefully screened from light to prevent photochemical reaction which converts them to the benzoquinene structure.[9,14]

Results

Anion Radicals of Diarylalkanes. The visible spectra of the anion radicals of the diarylalkanes of general structure, $[Ar(CH_2)_nAr]\cdot^-$, have not been reported in the literature. Esr spectra of such molecules with Ar = phenyl and $n = 1$ or 2 were reported by Weissman,[1] Voevodskii, *et al.*,[2] and Gerson and Martin.[3] The spectra of the anion radicals and the decomposition products of the naphthalene compounds **6**, **2** and **3** are shown in Figures 1 and 2 and are representative of all the systems studied. The λ_{max} values for the individual compounds are given below.

1,2-Diphenylethane (5) could be reduced to the anion radical more readily in DME than in THF. The anion radical absorbs at 680 and 408 mμ at −78° and decomposes very readily, even at −60°, to give an orange solution, λ_{max} 360 mμ. This latter solution was slowly converted at room temperature into a species absorbing in the region of 460 mμ.

1,2-Di-α,α'-naphthylethane (6). At −78° the anion radical gave a broad absorption maximum at 770 mμ, with shoulders at 810 and 710 mμ. Warming this solution, or direct reduction at room temperature, gave a solution with absorption peaks at 560, 500 (shoulder), and 360 mμ. These two spectra are shown in Figure 1. Further reduction takes place on contact with the potassium mirror, giving a solution with a complex spectrum in the 500–300-mμ region.

1,2-Di-9-anthrylethane (7). The spectrum of the anion radical at −78° exhibits a maximum at 730 mμ. Warming this solution resulted in disappearance of this band and formation of a new species absorbing at 715, 675, and 470 mμ. This species is formed by direct reduction at room temperature. On prolonged contact with the alkali metal a further reduction takes place to give a blue solution, λ_{max} 625, 600 (shoulder), 441, and 333 mμ.

1,3-Di-α,α'-naphthylpropane (8) and 1,4-Di-α,α'-naphthylbutane (9). The spectra of the anion radicals formed at −78° and, initially, at room temperature were identical; λ_{max} 780, 740, 328, and 292 mμ (*cf.* the reported spectrum[15] of the anion radical of naphthalene: λ_{max} 820, 775, 325, and 290 mμ). The anion radical of the propane decomposed slowly at room temperature to produce a complex spectrum in the 660–400-mμ region; λ_{max} 580, 515, 445 mμ. The anion radical of the butane was stable.

Anion Radicals of Paracyclophanes. The visible spectrum of the anion radical of [2.2]paracyclophane was recently reported by Ishitani and Nagakura;[4] the spectra of the naphthalene and anthracene compounds are not known.

[2.2]Paracyclophane (1). The anion radical possessed a broad absorption band at 726 mμ (ref 4, 760 mμ) which disappeared rapidly on warming to −60° to produce some species absorbing at 365 mμ. Ishitani and Nagakura report decomposition to produce a color-

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[14] H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **89**, 2770 (1967).

[15] J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

less solution in which they identified *p*-xylene. In this present work the green anion radical solution turns orange on warming.

Dibenzo[2.2]paracyclophane (*anti*-**2**, *syn*-**3**). The spectra of the anion radicals of both isomers at −78° were identical, λ_{max} 815 and 765 mμ (shoulder). The decomposition products obtained on warming to room temperature were also identical purple solutions, λ_{max} 570, 520 (shoulder), and 450 mμ. These spectra are reproduced in Figure 2. Further reduction at room temperature resulted in a complex spectrum in the 500–300-mμ region.

Tetrabenzo[2.2]paracyclophane (4). The broad absorption peak at 740 mμ of the anion radical at −78° disappears on warming and is replaced by a species with absorption bands at 710, 665, and 478 mμ.

The insolubility of the diarylalkanes and the paracyclophanes in both THF and DME at low temperatures, the instability of some of the anion radicals at temperatures as low as −65°, and the unknown conversion of the parent molecules into the anion radicals prevented any reliable estimation of the extinction coefficients. The absorption maxima are reported and the relative intensities of the bands are shown in the figures.

Discussion

Primary reduction of the diarylalkanes and [2.2]paracyclophanes studied here at −78° produces anion radical species. The esr spectra of these anion radicals and their interpretation are reported in the following paper.[16] The instability of the anion radicals of the naphthalene and anthracene paracyclophanes and diarylethanes at ambient temperatures contrasts strongly with the stable nature of the anion radicals of their simple aromatic analogs. These latter species can be generated by reduction and are extremely stable at room temperature. Apparently, the presence and relative position of two aromatic nuclei within the same molecule introduces a destabilizing influence on the anion radical species.

The diarylalkanes and paracyclophanes are examples of molecules possessing two identical reactive groups within the molecule, and, in theory, reduction of one or both groups is feasible

$$\mathrm{Ar\ X\ Ar} + 1\mathrm{e} \longrightarrow \mathrm{Ar\ X\ Ar}\cdot^-$$

$$\mathrm{Ar\ X\ Ar} + 2\mathrm{e} \longrightarrow \cdot^-\mathrm{Ar\ X\ Ar}\cdot^-$$

where X is the bridging unit linking the two aromatic nuclei, Ar.

The mechanism of the reduction may be dependent on the interaction between the reducible Ar groups. When there is no interaction, both groups should behave as isolated simple Ar molecules, but when there is interaction between the rings, the molecule will behave differently from the simple molecule case. Our electrochemical studies[16] of the reduction characteristics of these compounds indicate that there is some degree of interaction between the aromatic rings in the [2.2]paracyclophanes, the diarylethanes, and the dinaphthylpropane, and therefore, the reduction behavior and the chemistry of these molecules need not be similar to their simple aromatic analogs.

Diarylalkanes. The decomposition of the anion radicals of the diarylethanes formed at −78° results in diamagnetic products which possess spectra identical with those from the initial species produced in the reduction at room temperature. Quenching of these stable, highly colored species with methanol, isolation, and identification of the products gave toluene, 1-methylnaphthalene, and 9-methylanthracene as the major products from the respective diarylethanes. The formation of monomeric products from dimeric precursors is indicative of decomposition accompanied by C–C ethane bond scission. This observation can be rationalized by the following reaction sequence (for the sake of simplicity the counterions, K^+, have been omitted from this and the following schemes). Rupture of the C–C bond in the anion radical of the diarylethane to form the arylmethide anions, $ArCH_2^-$, requires transfer of another electron, either by disproportionation or by electron transfer from the metal.

$$\mathrm{ArCH_2CH_2Ar} \xrightarrow[-78°]{K(+1e)} \{\mathrm{ArCH_2CH_2Ar}\}\cdot^-$$

$$2\{\mathrm{ArCH_2CH_2Ar}\}\cdot^- \rightleftharpoons \{\mathrm{ArCH_2CH_2Ar}\}^{2-} + \mathrm{ArCH_2CH_2Ar}$$

$$\mathrm{ArCH_2CH_2Ar} \xrightarrow[25°]{K(+2e)} \{\mathrm{ArCH_2CH_2Ar}\}^{2-}$$

$$\{\mathrm{ArCH_2CH_2Ar}\}^{2-} \longrightarrow 2\mathrm{ArCH_2}^-$$

$$\mathrm{ArCH_2}^- + \mathrm{CH_3OH} \longrightarrow \mathrm{ArCH_3}$$

This mechanism assumes that the two-electron reduced species is unstable and undergoes decomposition with bond rupture. By analogy with the chemistry of the dianions of the simple aromatic molecules, naphthalene and anthracene, one might anticipate methanol quenching of the two-electron reduced species to give the corresponding dihydro product without bond cleavage.

$$\mathrm{ArCH_2CH_2Ar}^{2-} + \mathrm{CH_3OH} \longrightarrow \mathrm{ArCH_2CH_2Ar(H_2)}$$

However, the interaction between the aromatic rings in these systems causes delocalization of the additional electrons throughout the entire molecule and the chemical behavior is completely different from the simple molecule. The proximity of the two aromatic rings with their two additional electrons offers a convenient pathway for the formation of two carbanions accompanied by a gain in π-resonance energy at the expense of the C–C bond scission. If this energy gain is the main driving force for the reaction, then Table I provides a relative stability scale for the species which is consistent with the experimental findings. The π-resonance energies were calculated using the Hückel molecular orbital approximation with the inductive-effect parameters from Streitweiser.[17] The results in Table I predict that in the α,ω-diarylalkanes the tendency for anion formation increases in going from anthracene to naphthalene to benzene. Also, the data predict that increasing the chain length decreases the tendency for anion formation, in agreement with the experimental observations in the naphthalene series. The fate of the unstable anions, $ArCH_2CH_2^-$, shown in Table I, will not affect the calculations since only the primary bond rupture process is considered. A similar argument was invoked by Rembaum, *et al.*,[18–20] to explain the chain degradation ob-

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(16) D. J. Williams, J. M. Pearson, and M. Levy, *J. Amer. Chem. Soc.*, 93, 5483 (1971).

(17) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(18) A. Rembaum and J. Moacanin, *J. Poly. Sci., Part B-1*, 41 (1963).

(19) A. Rembaum, *ibid., Part B-2*, 117 (1964).

Table I. π-Resonance Energy Gain after Bond Scission

Ar	Energy gain, β
$\cdot^{-}ArCH_2CH_2Ar\cdot^{-} \longrightarrow 2ArCH_2^{-}$	
Phenyl	4.006
α-Naphthyl	3.526
9-Anthryl	3.404
$\cdot^{-}ArCH_2CH_2CH_2Ar\cdot^{-} \longrightarrow ArCH_2^{-} + ArCH_2CH_2^{-}$	
Phenyl	3.003
α-Naphthyl	2.434
9-Anthryl	2.167
$\cdot^{-}ArCH_2CH_2CH_2CH_2Ar\cdot^{-} \longrightarrow 2ArCH_2CH_2^{-}$	
Phenyl	2.000
α-Naphthyl	1.342
9-Anthryl	0.948

served in the polymeric anion radicals of vinyl aromatic polymers (polyradical anions).

These arylmethide anions of naphthalene and anthracene, $ArCH_2^-$, have not been reported in the literature. The benzene analog, $PhCH_2^-$, is known and can be prepared from dibenzyl mercury and alkali metal. Szwarc, *et al.*,[21] report that the anion is relatively unstable, undergoing some slow rearrangement at room temperature. The absorption maximum of benzyl sodium at 355 mμ slowly decreases to be replaced with some new species absorbing at 485 mμ. The fact that the cumyl anion is stable under similar conditions indicates that the α-H atom is involved in the rearrangement.

To establish beyond any doubt that arylmethide anions are produced in these systems, they have been prepared by an independent route. It is known that cumyl potassium can be prepared by the reaction of methyl cumyl ether with potassium. The corresponding reaction of the aromatic ethers, $ArCH_2OCH_3$, with potassium results in formation of the arylmethide anions, $ArCH_2^-$. Reaction of 9-methoxymethylanthracene (**11**) and α-methoxymethylnaphthalene (**10**) in THF at −78° with a fresh potassium mirror gives initially paramagnetic species. The esr spectrum of the anion radical of **10** is shown in Figure 3. These primary anion radicals decompose readily on warming the solution to produce highly colored diamagnetic species which have spectra identical with the initially observed products in the room-temperature reduction. Quenching of the diamagnetic solutions with methanol gave 9-methylanthracene and α-methylnaphthalene as the major products, respectively. Comparison of the visible spectra of the species formed from the diarylethanes and the benzylic-type ethers shows conclusively that the same species are formed (Table II).

The reaction sequence for the ether can be formulated.

$$ArCH_2OCH_3 \xrightarrow[-78°]{K(+1e)} \{ArCH_2OCH_3\}\cdot^{-}$$

$$2\{ArCH_2OCH_3\}\cdot^{-} \rightleftharpoons ArCH_2^{-} + OCH_3^{-} + ArCH_2OCH_3$$

$$ArCH_2OCH_3 \xrightarrow[25°]{K(+2e)} ArCH_2^{-} + OCH_3^{-}$$

Since it is highly probable that the reduction of methyl cumyl ether proceeds by the same mechanism, an attempt was made to measure the esr spectrum of the primary anion radical in THF and DME at −78°. No paramagnetic species could be detected. Since this anion radical is expected to be intrinsically less stable than the naphthalene and anthracene systems, lower temperatures may be necessary to stabilize the species.

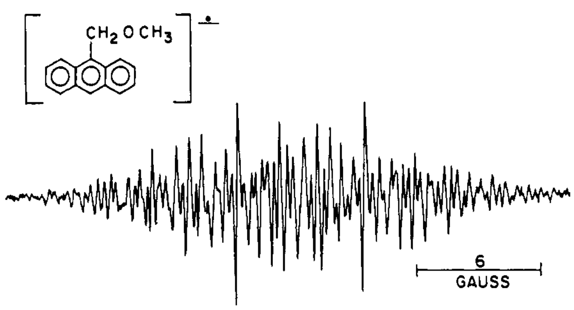
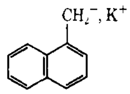
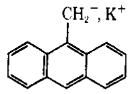


Figure 3. Esr spectrum of the anion radical of 9-methoxymethylanthracene (**11**) at −78°; solvent THF, counterion K^+.

Table II

Anion	Diarylethane, mμ	Benzylic ether, mμ
 **II**	560 500 (shoulder) 360	560 (ε ∼7000) 500 (shoulder) 362
 **III**	715 675 470	720 (ε ∼6000) 675 (ε ∼6000) 470 (ε ∼12,000)

Further reduction of these arylmethide anions takes place on contact with the alkali metal. In the case of the naphthyl anion an unstable species is produced which possesses a complex spectrum in the 500–300-mμ region. The anthracene anion is converted into a stable blue species with absorption at 625 (ε ∼20,000) 442 (ε ∼4000), and 333 mμ (ε ∼60,000). Quenching of this solution with methanol gave 9-methyl-9,10-dihydroanthracene, which is indicative of the dianion of 9-methylanthracene as the precursor anion. Since the spectrum of the dianion of 9-methylanthracene is not reported in the literature, a solution was prepared, λ_{max} 625 (ε ∼20,000), 442 (ε ∼5000), and 333 mμ (ε ∼63,000), and quenched with methanol to give the same dihydro product.

The following overall reaction scheme is consistent with these observations.

$$ArCH_2^{-} \xrightarrow[SH]{K(+2e)} (ArCH_3)^{2-}$$

Although this reaction was not investigated in any detail, the anion radical of the methyl derivative, $ArCH_3\cdot^{-}$, was identified as an intermediate by its esr spectrum. In the naphthalene system the ultimate product is the dianion of α-methylnaphthalene, a species which is known to be very unstable, giving rise to a complex spectrum in the 500–300-mμ region.

The spectra of the anion radicals of dinaphthylpropane (**8**) and butane (**9**) are identical, λ_{max} 780, 740, 328, and 292 mμ. These spectra are somewhat similar to those reported for the anion radical of naphthalene.

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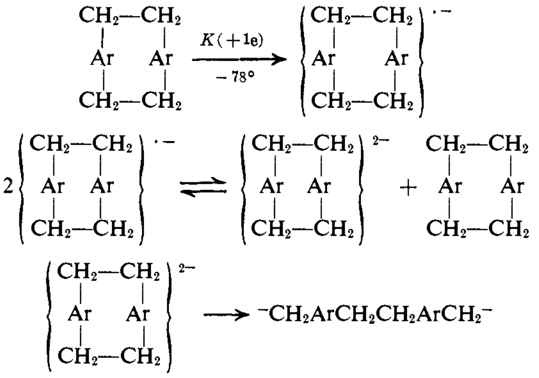
(20) A. Rembaum, J. Moacanin, and E. Cuddihy, *J. Poly. Sci., Part C-4*, 529 (1963).

(21) R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 361 (1962).

In contrast to the anion radical of dinaphthylethane, these two anion radical species are relatively stable. The anion radical of the propane undergoes slow decomposition at room temperature. The esr and electrochemical results[16] show that the 3-carbon atom chain of the propane allows those favorable molecular conformations in which the two naphthalene rings can interact. This is also confirmed by the results of Chandross and Dempster[22] in their study of intramolecular excimer formation in a series of dinaphthylalkanes. Since the ring interaction is relatively weak, the molecule is expected to behave like naphthalene rather than dinaphthylethane. The results in Table I show that the gain in π-resonance energy resulting from decomposition is less for the butane than the propane than the ethane, in agreement with our observations.

Paracyclophanes. In the [2.2]paracyclophane series of compounds the molecular geometry is such that the two aromatic rings are constrained by the methylene bridges, forcing transannular interaction. The anion radical species are very unstable and the decomposition behavior and the spectral data indicate a mechanism for decomposition similar to the diarylethanes.



The absorption spectra of these carbanions with Ar = phenyl, naphthyl, and anthryl are very similar to those formed in the decomposition of the corresponding diarylethanes. Observed spectral differences may arise from the comparison of an arylmethide anion with a dianion. One would anticipate very similar spectra with twice the extinction coefficient for the dianionic species. Unfortunately, the extremely low solubility of the paracyclophanes and other experimental problems do not permit evaluation of the ϵ values.

On contact with the alkali metal these anions reduce further, and by analogy with the diarylethanes this may involve bond cleavage. Again, insolubility problems precluded any isolation and identification of the quenched products. However, one can speculate that the mechanism is similar to that proposed earlier. In

$$^{-}CH_2ArCH_2CH_2ArCH_2^{-} \xrightarrow[SH]{K(+4e)} 2(CH_3ArCH_3)^{2-}$$

the paracyclophane system the final reduction product is the dianion of the dimethyl aromatic compound, whereas in the diarylethanes the methyl compound is formed. The dianions of the naphthalenes are unstable, but the dianions of 9-methyl- and 9,10-dimethylanthracene are known. The spectrum of the dianion of 9,10-dimethylanthracene (THF, K^+ counterion) was measured, λ_{max} 625 (ϵ ~20,000), 590 (shoulder), 460 (ϵ ~2000), and 335 mμ (ϵ ~60,000), and is slightly different from that of the dianion of 9-methylanthracene reported earlier. The spectrum is identical with the final reduction product formed in the decomposition of the tetrabenzo[2.2]paracyclophane (**4**) and provides strong evidence in favor of the proposed reaction scheme.

Conclusions

The anion radicals of the [2.2]paracyclophanes and 1,2-diarylethanes are extremely unstable, unlike their simple aromatic counterparts. It is necessary to generate and study these species at low temperatures, $< -70°$, in order to eliminate the complications which can arise from decomposition products. The facile decomposition of the anion radicals of this class of compound results from the presence of the two aromatic rings in the molecule and the existence of an energetically favorable pathway to produce stable carbanion species. The decomposition of the anion radicals of the diarylethane series was studied in detail and the formation of arylmethide anions was unequivocally established. Increasing the number of CH_2 groups between the rings increases the stability of the anion radicals and their behavior approaches that of a simple substituted aromatic molecule. Experimental problems precluded a detailed study of the decomposition of the paracyclophane series but the similarity to the diarylethanes provides strong justification for the proposed reaction scheme.

Acknowledgment. We wish to express our thanks to Dr. E. A. Chandross for samples of dinaphthylpropane and dinaphthylbutane and for a copy of his manuscript prior to publication.

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[22] E. A. Chandross and C. J. Dempster, private communication, 1970.