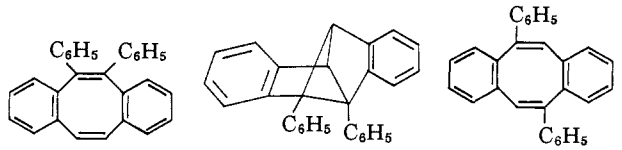
thetical scheme **1** → **3** → **4** → **2**. The rearrangement seems remarkable[16] indeed.



14 **15** **16**

Experimental Section[17]

cis,cis-1,5-Cyclooctadiene from K & K Laboratories was redistilled through a 20-cm. Vigreux column; the center cut used below, b.p. 149° (754 mm.), was estimated >99% pure by g.l.p.c. analysis. Its n.m.r. spectrum showed absorptions at τ 4.49 and 7.67 in a 1:2 area ratio.

3-Bromo-cis,cis-1,5-cyclooctadiene[9] was prepared from 47 g. (0.435 mole) of *cis,cis*-1,5-cyclooctadiene, 53 g. (0.298 mole) of N-bromosuccinimide, and 2 g. of benzoyl peroxide in 250 ml. of carbon tetrachloride under reflux with stirring for 3 hr. The reaction mixture was cooled and filtered; the filtrate was washed twice with aqueous sodium carbonate and twice with warm water. Distillation at reduced pressure gave 10 g. of unreacted diene and 30 g. (54%) of 3-bromo-*cis,cis*-1,5-cyclooctadiene, b.p. 94–95° (20 mm.). The infrared spectrum of this bromide was in good accord with the published[9] spectrum.

(17) Perkin-Elmer Model 521, Varian A-60, and Atlas CH-4 spectrometers were used for determining infrared, nuclear magnetic resonance, and mass spectra. Mass spectra of labeled and unlabeled hydrocarbons were obtained using low electron energies (<12.5 e.v.) and wide slits. A Wilkins Model A-90-P and a 6 × 300 mm. β,β'-oxydipropionitrile column at 80° were used for g.l.p.c. estimation and isolation of hydrocarbons.

3-Deuterio-cis,cis-1,5-cyclooctadiene. To 15 ml. of ether and 0.805 g. of lithium aluminium deuteride (97%, Metal Hydrides, Inc.) in a three-necked flask fitted with a reflux condenser and addition funnel was added dropwise 7.887 g. of 3-bromo-*cis,cis*-1,5-cyclooctadiene. When the initial reaction subsided, the reaction mixture was refluxed for 24 hr. Excess deuteride was destroyed through cautious dropwise addition of water; the product was extracted with ether and isolated by distillation. There was obtained 3.456 g. (75%) of 3-deuterio-*cis,cis*-1,5-cyclooctadiene, b.p. 40–41° (20 mm.). After purification and isolation by g.l.p.c., this material was analyzed by mass spectrometry (*cf.* Tables I and II).

Tricyclo[3.3.0.0^{2,6}]octane. A solution of 2 g. of *cis,cis*-1,5-cyclooctadiene in 380 ml. of ether was saturated with cuprous chloride. The saturated solution was irradiated through a Vycor filter with a Hanovia high-pressure 450-w. mercury vapor lamp for 24 hr. Ether was removed by distillation through a 20-cm. glass helix packed column. The residue was fractionated and gave 0.79 g. (39.5%) of tricyclo[3.3.0.0^{2,6}]octane, b.p. 43° (26 mm.). The product was identified by its characteristic[4] n.m.r. singlets at τ 8.18 and 8.27 in 1:2 area ratio.

Deuteriotricyclo[3.3.0.0^{2,6}]octane. Photolysis of 2.04 g. of 3-deuterio-*cis,cis*-1,5-cyclooctadiene following the procedure given above for the unlabeled diene gave 0.48 g. (24%) of product, b.p. 42° (25 mm.). The tricyclooctane and unreacted starting material were purified and isolated by g.l.p.c.; the mass spectrometric analyses for these hydrocarbons are given in Tables I and II.

The *sym*-Dibenzcyclooctatetraene Anion Radical and Dianion

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sym-Dibenzcyclooctatetraene is easily reduced in tetrahydrofuran solution to the corresponding anion radical and dianion by lithium, sodium, or potassium metal. Polarographic reduction in 96% dioxane–water proceeds at low potentials suggesting that the interaction of unsaturated centers in the anions is considerable. The e.s.r. spectrum of the anion radical and the n.m.r. spectrum of the dianion are given and analyzed.

Introduction

While conjugation between the four double bonds of cyclooctatetraene is not appreciable and while the molecule does not exhibit aromatic properties,[1] the mono- and dialkali cyclooctatetraenides formed on reaction of cyclooctatetraene with alkali metals appear to owe their stability to π-electron delocalization and do exhibit aromatic properties.[2] Thus, cyclooctatetraene is much easier to reduce than an unconjugated olefin,[2d] it forms an anion radical[2c] analogous to familiar benzenoid aromatic hydrocarbon anion radicals,[3] and the dianion shows a proton n.m.r. peak at the low fields[2a] characteristic of aromatic molecules.[4]

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(2) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) *ibid.*, **82**, 3785 (1960); (c) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); H. L. Strauss and G. K. Fraenkel, *ibid.*, **35**, 1738 (1961); H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963); (d) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, **84**, 802 (1962); (e) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961); *Chem. Ber.*, **95**, 158 (1962).

(3) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 283 (1963).

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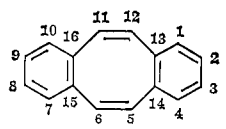
Table I. E.s.r. Splitting Constants for the *sym*-Dibenzcyclooctatetraene Anion Radical

Reducing agent	Solvent	Splitting constants (gauss) a_{H_1}	a_{H_2}	a_{H_3}
Na	THF[b]	2.55 ± 0.01[a]	1.73 ± 0.01	0.20 ± 0.02
K	THF[b]	2.51 ± 0.01	1.80 ± 0.01	0.17 ± 0.01
Li	THF[c]	2.38 ± 0.01	1.68 ± 0.01	0.18 ± 0.01
Electrolytic	DMF[d]	2.54 ± 0.00	1.80 ± 0.00	0.20 ± 0.00
Electrolytic	DMSO[d]	2.55 ± 0.01	1.81 ± 0.01	0.21 ± 0.01

[a] The error limits are average deviations of the splitting constants determined from the positions of lines in one spectrum. [b] The hydrocarbon concentration was 0.1 *M*. [c] The hydrocarbon concentration was 0.01 *M*. [d] The solution contained 0.1 *M* tetra-*n*-butylammonium perchlorate.

Like cyclooctatetraene, the related hydrocarbon *sym*-dibenzcyclooctatetraene (**1**) is nonplanar and exhibits olefinic properties.[5] It has been pointed out that derivatives of this molecule should show less propensity to aromatize than those of cyclooctatetraene itself because the delocalization of double bonds in the benzene rings should be expected to minimize delocalization in the central ring.[5a] It is probable that the benzene rings also oppose flattening of the central ring sterically, by opposing distortion of bond angles.



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The reduction of *sym*-dibenzcyclooctatetraene was, therefore, examined to see whether the anion radical or dianion could be prepared. The reduction of *sym*-dibenzcyclooctatetraene is discussed below, and the e.s.r. spectrum of the anion radical and the n.m.r. spectrum of the dianion are given.

Recently the e.s.r. spectrum of the anion radical formed on reduction of *sym*-dibenzcyclooctatetraene with lithium in tetrahydrofuran (THF) was reported, and from the agreement between observed and calculated splitting constants, it was concluded that the unpaired electron resides in a molecular orbital formed from two isolated double bonds and two benzene rings perturbed by only a weak interaction.[6]

Results

E.s.r. Spectrum of sym-Dibenzcyclooctatetraene Anion Radical. Solutions of the anion radical of *sym*-dibenzcyclooctatetraene were prepared by shaking, for a short period of time, a solution of the hydrocarbon in THF with excess sodium, potassium, or lithium metal,[7] or by reducing electrolytically[8] a solution of the hydrocarbon in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) containing tetra-*n*-butylammonium perchlorate. E.s.r. spectra of the anion radical prepared in each of these ways were determined and were found to exhibit, as expected, hyperfine splitting by three sets of four equivalent protons. The splitting constants, given in Table I, are similar for all samples, except for the one in which lithium metal was the reducing agent. The three splitting constants, 2.54, 1.80, and 0.20 gauss, in the sample prepared in DMF are presumably (see below) associated with splitting by the protons in the 5, 2, and 1 positions, respectively, and if $a_H = Q_{CH}{}^H \rho$ and $Q_{CH}{}^H = -23$ gauss,[9] the splittings imply that the absolute values of the spin densities on carbon atoms 5, 2, and 1 are 0.110, 0.078, and 0.0087.

To compare these results with theoretical expectation, we shall presume the unsaturation electrons to occupy Hückel molecular orbitals,[10] with the added condition that resonance integrals between p orbitals on atoms 12 and 13, 5 and 14, 6 and 15, and 11 and 16 are equal to β', while between orbitals on other adjacent atoms they are equal to β. We then vary β' between 0 and β. Within this theoretical framework, the spin densities at each carbon atom in the anion radical are the squares of the coefficients of the corresponding atomic orbitals in the hydrocarbon's unfilled molecular orbital of lowest energy. These are given for three values of β' in Table II.

Table II. Calculated Hückel Spin Densities in *sym*-Dibenzcyclooctatetraene Anion Radical as a Function of β'/β and Experimental Values

Carbon atom	$\beta' = 0$	$\beta' = 0.75\beta$	$\beta' = \beta$	Exptl.[b]
1	0.0	0.0138	0.0243	0.0087
2	$^1/_{16}$[a] = 0.0625	0.0441	0.0448	0.078
5	$^1/_8$ = 0.1250	0.1236	0.1172	0.110
13	$^1/_{16}$ = 0.0625	0.0686	0.0637	

[a] See ref. 6. [b] See text.

Carrington, Longuet-Higgens, and Todd[6] assert that the spin densities derived from the observed splitting constants and from the theory, assuming that β' is small, are in reasonable agreement. However, as can be seen from Table II, the agreement is essentially as good no matter what the value of β'. While the agreement is somewhat better if it is assumed that β' is small, the data do not require the interaction to be weak, but allow for the possibility that it be strong.

Polarographic Reduction. The polarographic reduction of a 1 m*M* solution of *sym*-dibenzcyclooctatetraene

heimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

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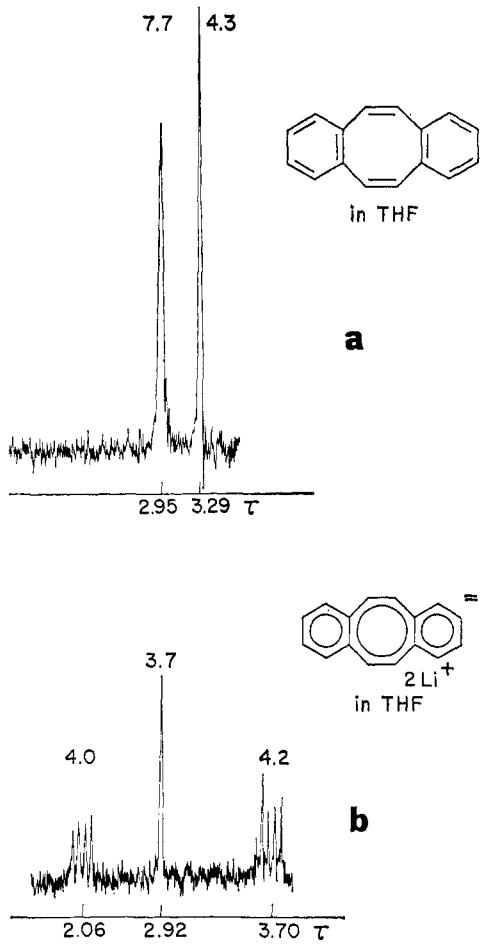

Figure 1. N.m.r. spectrum in THF of (a) *sym*-dibenzcyclooctatetraene (0.5 *M*) and (b) dilithium *sym*-dibenzcyclooctatetraenide (same sample as in a, but after reaction with excess lithium). Peak positions were determined relative to the low-field THF peak assumed to lie at τ 6.37. The n.m.r. frequency is 60 Mc. The relative intensity is given above each peak.

in 96% dioxane–water containing 0.175 mole/l. of tetra-*n*-butylammonium iodide was studied to determine the polarographic half-wave potentials for the reduction processes. This solvent system was chosen because half-wave potentials for the reduction of a large number of benzenoid aromatic hydrocarbons have been measured in it,[11] and these have been correlated with the molecular orbital theory. In particular, the half-wave potential ($E_{1/2}$), relative to the saturated calomel electrode (s.c.e.), for the first reduction wave of these hydrocarbons has been found to vary linearly with the calculated coefficient (a) of β for the energy of the hydrocarbon's lowest lying unfilled Hückel π molecular orbital, as[12]

$$E_{1/2} = -2.54a - 0.85 \quad (1)$$

If the interaction between the two benzene rings and the two double bonds in *sym*-dibenzcyclooctatetraene were weak, that is $\beta' = 0$, then a would equal 1. It follows from eq. 1 that $E_{1/2}$ for the first reduction wave should then be -3.39 v. relative to s.c.e.

The polarogram of *sym*-dibenzcyclooctatetraene exhibits two distinct reduction waves of equal (1:0.93) height at -1.971 and -2.403 v. relative to s.c.e. Two reduction waves separated in half-wave potential by about 0.4 v. are characteristically observed in the polarograms of benzenoid aromatic hydrocarbons.[11,13] In the present case the waves were not well formed and the slopes of the plots of log $(id - i)/i$ *vs.* E were both considerably greater than 0.059 (0.076 for the first and 0.097 for the second wave), which may imply that the waves are shifted in potential by kinetic complications. However, the half-wave potential for the first wave is so different from -3.39 v. as to appear inconsistent with the assumption that the interaction between the benzene rings and double bonds is weak. The value of a calculated from eq. 1 for a potential of -1.971 v. is $a = 0.441$. The value of β' that makes the energy of the lowest-lying Hückel π orbital equal to $\alpha + 0.441\beta$ is $\beta' = 0.75\beta$, considerably greater than zero.

N.m.r. Spectrum of sym-Dibenzcyclooctatetraene Dianion. A 0.5 *M* solution of *sym*-dibenzcyclooctatetraene in THF exhibits an n.m.r. spectrum (Figure 1a) of two lines, presumably attributable to the resonances of the aromatic protons in the benzene rings and the olefinic protons in the cyclooctatetraene ring, at τ 2.95 and 3.29. The relative intensity of the two lines was 7.7:4.3. When this solution is shaken with excess lithium metal a reaction takes place, and after 1 day the solution exhibits a new spectrum, one that can be interpreted to be that of the hydrocarbon dianion. This spectrum (Figure 1b) consists of three groups of lines of equal intensity, apparently a singlet at τ 2.92 and A_2X_2 multiplets[14] at τ 2.06 and 3.70. Quenching the reaction mixture with water gives 5,6-dihydro-*sym*-dibenzcyclooctatetraene, identified by its analysis and n.m.r. spectrum.[15]

The n.m.r. spectrum of the *sym*-dibenzcyclooctatetraene dianion was also determined after more dilute solutions (0.1 *M*) of the hydrocarbon in THF were shaken with either sodium, potassium, or lithium metal. In each case a spectrum similar to the one in Figure 1b was observed. The proton chemical shifts are given in Table III. The spectra are all very similar, consistent with the assumption that an ion is being observed. However, as in the case of the e.s.r. spectrum of the corresponding anion radical, the lithium salt deviates slightly from the others.[16]

The significant observation is that after addition of two electrons to the hydrocarbon, the proton chemical shifts remain at very low magnetic field and are displaced to even lower field than the corresponding resonances in the hydrocarbon precursor. The addition of electrons to an aromatic hydrocarbon should result in a displacement of the proton chemical shifts to higher magnetic field.[4b,c,f] A displacement to low fields is characteristic of aromatic molecules,[4] has been attributed to the "ring-current effect," and in the present case suggests a greater cyclic delocalization of unsatura-

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(12) G. J. Hoijtink, *ibid.*, 74, 1525 (1955).
(13) G. J. Hoijtink, *ibid.*, 73, 895 (1954); G. J. Hoijtink, E. Deboer, P. H. Van Der Meij, and W. P. Weijland, *ibid.*, 75, 487 (1956).
(14) See ref. 4a, pp. 138, 142.
(15) The proton n.m.r. spectrum in CCl_4 showed three singlets, at τ 3.02, 3.34, and 6.88 of relative intensity 8.3:2.0:3.7.
(16) This may be analogous to the change in electronic absorption spectrum with change in cation observed in other systems and attributed to weaker ion pairing when lithium, rather than sodium or potassium, is the cation: *cf.* T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 87, 669 (1965); K. H. J. Buschow and G. J. Hoijtink, *J. Chem. Phys.*, 40, 2501 (1964); J. Smid, *J. Am. Chem. Soc.*, 87, 655 (1965).

Table III. Proton Chemical Shifts of Disodium, Dipotassium, and Dilithium *sym*-Dibenzcyclooctatetraenide in THF

Cation	Chemical shifts, τ[a] A_2	Singlet	X_2
Na^+	2.12	2.82	3.77
K^+	2.12	2.82	3.80
Li^+	2.15	3.01	3.78

[a] Determined relative to the low-field THF peak, assumed to lie at τ 6.37.

tion electrons in the central ring of the *sym*-dibenzcyclooctatetraene dianion than in the hydrocarbon.

In order to indicate quantitatively some parameters of theoretical significance, the charge densities at carbon atoms 1, 2, and 5 in the dianion were estimated from the corresponding proton chemical shifts. A procedure of Schaeffer and Schneider was used,[4c] assuming that the central ring possessed regular octagonal geometry, that all carbon–carbon bond lengths were 1.397 Å., and that the magnitude of the current in the central ring was $^{10}/_{6}$ that in the benzene rings. One modification was made. We compared the chemical shift (after correction for the ring current effects of the adjacent rings) of the protons on the central ring with the chemical shift of the cyclooctatetraenyl dianion (τ 4.30),[2a] and the chemical shift of the protons on the outer rings with the chemical shift of benzene (τ 2.73), and assumed that any deviation was proportional to the difference in charge density on the carbon adjacent to the proton, the proportionality factor being 10 p.p.m./unit charge.[4b,c,e] These calculations are summarized in Table IV. For comparison, the Hückel charge densities at each carbon were calculated and are given in Table V for various values of β'/β (see above). The charge

Table IV. Electron Densities Calculated from Proton Chemical Shifts in Dipotassium *sym*-Dibenzcyclooctatetraenide

Position	Obsd. chemical shift, τ	δ', p.p.m.[a]	Cor. chemical shift	Shift owing to charge[b]	Charge
1	2.12	1.20	3.32	0.59	−0.06
2	3.80	0.48	4.28	1.55	−0.16
5	2.82	0.91	3.73	−0.57	−0.19

[a] δ' is the sum of ring current corrections (δ) for directly adjacent rings, calculated as $= (12.0)a^2/R^3$ for the effect of benzene rings and $=(20.0)a^2/R^3$ for the effect of the central ring (*cf.* ref. 4c). [b] Corrected chemical shift minus 2.73 for positions 1 and 2, and minus 4.30 for position 5.

Table V. Hückel Charge Densities at Each Carbon Atom in *sym*-Dibenzcyclooctatetraenyl Dianion

Position	$\beta' = 0$	$\beta' = 0.75\beta$	$\beta' = \beta$
1	0.0	−0.0275	−0.0487
2	−0.125	−0.0882	−0.0895
5	−0.250	−0.2471	−0.2343
13	−0.125	−0.1371	−0.1275

densities given in Table IV would be in error if the ring current correction δ' were in error. However, if this correction were wrong by a factor of two, the charge densities at carbons 1, 2, and 5 would have to be changed by only 0.06, 0.02, and 0.04. In particular it seems likely that the charge density at position 2 is large.

Conversely, the chemical shifts and probable charge densities should carry some implication about ring current effects. In particular, if the charge density at position 1 were as small as zero (unlikely because charge densities in hydrocarbon ions appear to be significantly more, not less, uniform than simple Hückel theory implies[4c,e,17]), then the ring current in the central ring would still have to be one-half that assumed above.

Electron-Exchange Reactions. In order to obtain information about the rates of electron exchange reactions,[2b,18] such as $R + R^{\overline{\cdot}} \rightarrow R^{\overline{\cdot}} + R$ (where R is the hydrocarbon *sym*-dibenzcyclooctatetraene) and related reactions involving the dianion, n.m.r. and e.s.r. spectra of solutions 0.1 *M* in *sym*-dibenzcyclooctatetraene in THF were determined after various time intervals in the course of reaction with sodium, potassium, and lithium metals.

When sodium was used, the n.m.r. spectrum of the hydrocarbon disappeared without broadening, the n.m.r. spectrum of the dianion first appeared broad, then narrowed after further reaction, and the e.s.r. spectrum of the anion radical, which had a line width[19] of 60 mgauss during most of the reaction, broadened to 120 mgauss toward the end. These data suggest that electron exchange occurs more readily between the anion radical and dianion than between the anion radical and the hydrocarbon.

However, contradictory results were obtained when potassium or lithium was used. The n.m.r. spectrum of the hydrocarbon broadened as it disappeared, and the e.s.r. spectrum of the anion radical also broadened as more metal reacted. The line width in the e.s.r. spectrum when potassium was used was 60 mgauss throughout most of the reaction, but rose to 300 mgauss near the end, and when lithium was used it was 250 mgauss at the beginning and greater than 600 mgauss near the end. The broadening of the e.s.r. spectrum of the anion radical in each case is unlike the analogous observations made for naphthalene[20] and anthracene.[21] In those cases the e.s.r. spectra are reported to appear broad at first and then to narrow, suggesting that the exchange of the anion radical with the hydrocarbon is the fast reaction.

Conclusions

The ease with which *sym*-dibenzcyclooctatetraene is reduced by electrolysis and by reaction with alkali metals to give the corresponding anion radical and dianion and the observation that the dianion's proton n.m.r. chemical shifts are at such low fields that there appears to be a large ring current in the central ring imply that the unsaturation electrons are appreciably delocalized about the central ring in the anions. The e.s.r. spectrum of the anion radical is in accord with this conclusion.

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(19) The line width is the distance between points of extreme slope.

(20) P. G. Zandstra and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4408 (1962); R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957).

(21) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

Experimental Section

sym-Dibenzcyclooctatetraene, synthesized as described in the literature, was purified by sublimation and melted at 107–108° (lit.[5c] m.p. 109°).

E.s.r. Measurements. Samples were prepared using techniques described by Bolton and Fraenkel.[22] However, in order to examine both the e.s.r. and n.m.r. spectra of the reaction mixtures as the hydrocarbon in THF reacted with the alkali metals, a different technique was used. An n.m.r. sample tube (5-mm. o.d.) with a slight constriction near the top was connected to a joint for attachment to a vacuum manifold. The hydrocarbon (10 mg.), dry THF (0.5 ml.), and a large piece of alkali metal were placed in the tube so that the metal remained above the constriction. The tube was degassed and sealed. Reaction was effected by inverting the tube and shaking, and spectra were determined at various times by reverting the tube.

The e.s.r. spectrometer was the X-band superheterodyne instrument with 1000-c.p.s. field modulation and a Varian Model V4012-3B 12-in. magnet and power supply, described by Bolton and Fraenkel.[22] The magnetic field was controlled by a Varian V3506 magnetic flux stabilizer that can scan a wide range of magnetic fields. Field measurements were made directly from calibrated strip-chart recordings.

Polarographic Measurements. High purity dioxane (Burdick and Jackson) was passed through alumina, refluxed with Na–K alloy, and distilled. A solution of 0.175 *M* tetra-*n*-butylammonium iodide in 96% dioxane–4% water was polarographically pure. The polarograms were determined against an s.c.e. electrode using a 1 m*M* solution of the hydrocarbon in this solvent. The instrument was an electronic one previously used.[2d]

N.m.r. Measurements. N.m.r. measurements were made using samples described in the e.s.r. section above and using samples in which the hydrocarbon concentration was initially greater. A 0.5 *M* solution of the hydrocarbon (0.48 mg.) in dry THF (0.5 ml.) and excess lithium metal were combined in an n.m.r. tube, similar to the one described above, the solution was degassed, and the tube was sealed. The n.m.r. spectrum, determined before the solution and metal could react, showed the spectra of THF and the hydrocarbon, but, after reacting for 1, 2, and 4 days and 1 year,[23] the solution produced the spectra of THF and the hydrocarbon dianion. Spectra were determined using a Varian A-60 instrument.

Hydrolysis of Dilithium sym-Dibenzcyclooctatetraenide. *sym*-Dibenzcyclooctatetraene (48.0 mg.), 0.5 ml. of dry THF, and a clean piece of lithium metal were combined in an n.m.r. tube that was then degassed and sealed. The reaction was monitored by periodically examining the n.m.r. spectrum. After formation of dilithium *sym*-dibenzcyclooctratetraenide was complete, the tube was opened in a nitrogen atmosphere and the solution poured into 10 ml. of 0.1 *N* hydrochloric acid. White crystals (m.p. 53–56.5°) separated and were purified by vacuum sublimation. The yield of 5,6-dihydro-*sym*-dibenzcyclooctatetraene, m.p. 58°, was 21.3 mg.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.30; H, 6.89.

The n.m.r. spectrum in CCl_4 relative to tetramethylsilane (TMS) consists of three singlets, at τ 3.02, 3.34, and 6.88, of relative intensity 8.3:2.0:3.7.

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(22) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 40, 3307 (1964).

(23) We thank William Okamura for this spectrum.

Radical Anions as Intermediates in Substitution Reactions. The Mechanism of Carbon Alkylation of Nitroparaffin Salts[1,2]

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Oxygen alkylation of the nitroparaffin anion derives simply from an SN2 displacement by the oxygen of this ambident anion. In contrast, the carbon alkylation observed on treating nitroparaffin salts with o- and p-nitrobenzyl halides is viewed as a radical-anion process (eq. a–c). Evidence in support of the radical-anion mechanism is presented; particularly striking is the ability of a powerful electron acceptor such as p-dinitrobenzene to inhibit carbon alkylation. It is suggested that other substitution reactions may proceed via radical-anion intermediates.

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(2) Paper VII in the series, "The Chemistry of Ambident Anions." A preliminary account of this work appeared in R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **86**, 3904 (1964). For the preceding paper in this series see N. Kornblum, R. Seltzer, and P. Haberfield, *ibid.*, **85**, 1148 (1963). This paper is also taken to be number XXIII in the series, "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(3) National Science Foundation Cooperative Graduate Fellow, Purdue University, 1962–1964.