DMABP, infrared spectra identical. Elution with ether, ethyl acetate, and chloroform led to starting pinacol, 0.15 g, mp and mmp 183–184°, infrared spectra identical.

Rearrangement of Di-*p*,*p*′-dimethylaminobenzpinacol. A solution of 1.0 g (0.0022 mole) of the pinacol and a few crystals of iodine in 10 ml of acetic acid was boiled under reflux for 20 min and evaporated. The residue was crystallized from alcohol, 0.91 g (0.0021 mole), 95% yield, mp 215–217°, α-phenyl-α,α-di-*p*-dimethylaminophenylacetophenone, λ_{max} 345 mμ (ε 1750).

Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.91; H, 6.96. Found: C, 83.56; H, 6.97 (Bernhardt).

Photoreduction of DMABP to the Pinacol. **a.** Aliquots (5 ml) of a solution of 0.90 g (0.0040 mole, 0.1 *M*) of *p*-DAB in 40 ml of 0.5 *N* HCl in 2-propanol were placed in eight Thunberg tubes, degassed, and irradiated under argon for 15 hr with a GE A3-85-W lamp. The solutions were combined and evaporated at room temperature. The residue, the pinacol hydrochloride, 1.19 g, mp 150–154° dec, was dissolved in water–methanol, covered with ether, and treated with aqueous bicarbonate until alkaline. The ether extract was washed with water, dried, and concentrated, leading to the pinacol, 0.86 g, 96% yield. This was crystallized from benzene–petroleum ether, mp and mmp 181–183° (a mixture with a sample prepared by the Gomberg–Bachmann reduction).

b. A solution of 1 g of DMABP in 100 ml of 2-propanol was irradiated under nitrogen in Pyrex in a Rayonet photochemical reactor for 500 hr. The solution was concentrated, and the residue was dissolved in 4:1 benzene–chloroform and placed on a column of Woelm neutral alumina wet with petroleum ether. Elution with benzene led to DMABP, 0.38 g, mp 88–90°, and chloroform led to the pinacolone, 0.37 g, mp 214–217°.

Anal. Found: C, 82.37; H, 7.20 (Nagy).

Dianion Radicals. I. Enolate and Related Systems

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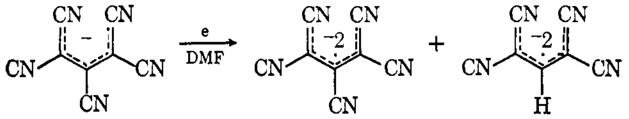
Abstract: The dibenzoylmethide dianion radical, a simple, stable, dianion radical is described and its structure proved by esr and visible spectroscopy, as well as by titration and reoxidation to dibenzoylmethane. HMO calculations of odd electron density and McLachlan calculations of spin density have been made and used, in conjunction with the McConnell and Colpa–Bolton equations, to predict the magnitudes of the hyperfine esr splittings, with fairly good success. The dianion radical can be reduced further to a stable trianion. Several other dianion radicals are also discussed. The results indicate the phenomenon to be rather general, although by no means all of the observable dianion radicals are stable.

Organic anion radicals are well known and, in fact, are currently the subject of heightened mechanistic interest.[1-3] In 1963, Reiger and Fraenkel, in a study encompassing numerous anion radicals, also described the electrolytic reduction of tetramethylammonium 1,1,2,3,3-pentacyanopropenide to a dianion radical.[4] This appears to have been the first mention of dianion radicals in the literature. In 1964, we reported on the stable dibenzoylmethide dianion radical ($DBM^{2-}\cdot$) and the corresponding trianion (DBM^{3-}), obtained by stepwise reduction of the enolate of dibenzoylmethane.[5] Several other examples of dianion radicals derived from enolate systems were also reported, thus establishing a greater generality for the phenomenon than was previously apparent. More recently, Weissman and van Willigen have published a study of the esr spectra of the dibenzoylmethide dianion radical in rigid media, as well as of its optical spectra.[6] In 1965, Bauld and Brown published a simple example of a hydrocarbon dianion radical, *viz.*, the tropenide dianion radical.[7] Since that time several additional reports of dianion radicals have accrued,[8-11] and a trianion radical has been described.[12] The purpose of the present paper is to elaborate upon the results reported earlier for the dianion radicals of enolate systems. The hydrocarbon dianion radicals, including tropenide, will be described in a companion paper.



Results and Discussion

Dibenzoylmethide Dianion Radical. A simple Hückel calculation on the dibenzoylmethyl (DBM) system with all atoms assumed planar and $\alpha_0 = \alpha + 1.0\beta$ reveals the anion to have a vacant MO at $E = \alpha - 0.66\beta$, a level considerably lower than is available in many neutral substrates capable of anion radical formation. Benzene, *e.g.*, has no vacant HMO lower than $\alpha - 1.00\beta$ but is reducible to its anion radical, which is stable below −60°. Accordingly, it seemed conceivable that the dibenzoylmethide (DBM^-) ion could be reduced to its dianion radical stage ($DBM\cdot^{2-}$) despite the additional coulombic repulsions inherent in a dianion radical (DAR). As further investigation showed, the DMB system is especially well suited for this purpose, since extremely few simple organic anions have vacant MO's as low as $\alpha - 0.66\beta$.

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(1) N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, **89**, 725 (1967).

(2) N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5660 (1966).

(3) G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

(4) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

(5) N. L. Bauld, *ibid.*, **86**, 2305 (1964).

(6) H. van Willigen and S. I. Weissman, *Mol. Phys.*, **11**, 175 (1966).

(7) N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, **87**, 4390 (1965).

(8) P. Dowd, *ibid.*, **87**, 4968 (1965).

(9) E. G. Janzen and J. G. Pacifici, *ibid.*, **87**, 5504 (1965).

(10) E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, 70, 302 (1966).

(11) N. L. Bauld and J. Zoeller, *Tetrahedron Letters*, 885 (1967).

(12) N. L. Bauld, *J. Am. Chem. Soc.*, **87**, 5504 (1965).

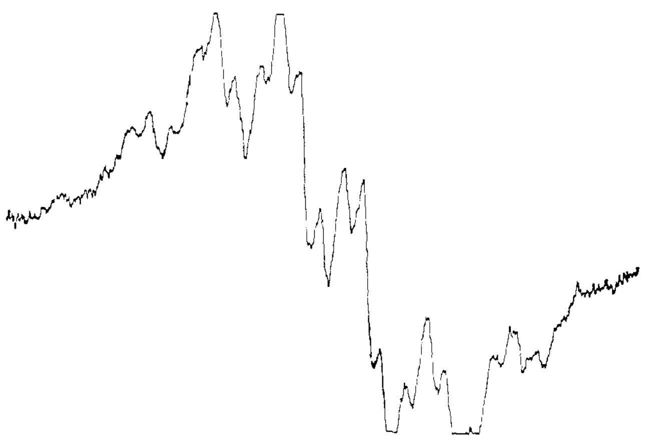
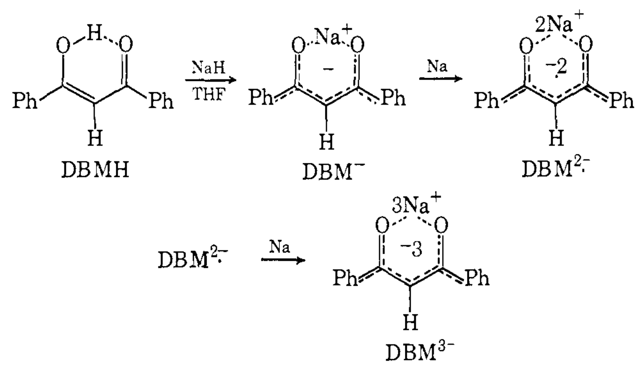


Figure 1. Partially resolved esr spectrum of DBM$^{2-}\cdot 2\text{Na}^+$ in THF solution.

Initially, large-scale experiments (0.05 mole) were carried out in THF solution under nitrogen. DBM$^-$ was prepared from dibenzoylmethane (DBMH) and excess sodium hydride dispersion. This yellow anion ($\lambda_{\max}$ 357 mμ) formed nearly instantly, as was evident from the vigorous evolution of hydrogen, and was quite stable under the conditions. Aqueous titration showed it to be a monoacidic base. That DBM$^-$ has the chelated structure has been established.[13] Addition of an equivalent of sodium (or other alkali metal) to the solutions of DBM$^-$ causes immediate formation of the green dianion radical, DBM$^{2-}\cdot$ ($\lambda_{\max}$ 756 mμ). The reaction is essentially complete within 0.5 hr, as shown by titration of DBM$^{2-}\cdot$ as a diacidic base. Neither sodium nor the other alkali metals developed any acid titer in THF alone. Addition of excess sodium then gives the trianion, DBM^{3-}, which is blue green ($\lambda_{\max}$ 695 mμ). It required 2.75 and 2.67 equiv of base for neutralization after 1 hr.



Both DBM$^{2-}\cdot$ and DBM^{3-} were oxidized back to DBMH in 90% yield by treatment with anhydrous nickel chloride followed by acidification of the chelate. Therefore, structural degradation is ruled out.

The possibility that the two colored species are conjugate acids of DBM$^{2-}\cdot$ (DBMH$^-\cdot$) and DBM^{3-} (DBMH$_2^-$) is excluded by several lines of evidence. The reductions occur with great rapidity (begin instantly) even at $-80°$. Therefore, abstraction of protons from such a relatively unacidic solvent as THF seems highly unlikely. Even benzene, a still more dubious proton donor, will serve as solvent for the reaction. Visible spectroscopy indicates that the same species are generated in both solvents. The visible absorption maximum of DBM$^{2-}\cdot$ is identical in THF and benzene with $\pm 5\ \mu$. Furthermore, DBMH$^-\cdot$ if formed would surely be unstable to hydrogen loss, in analogy to the fluorene anion radical. The latter is unstable above $-40°$.[14] In contrast, DBM$^{2-}\cdot$ is stable in refluxing THF. In both cases hydrogen loss would lead to a stable anion.

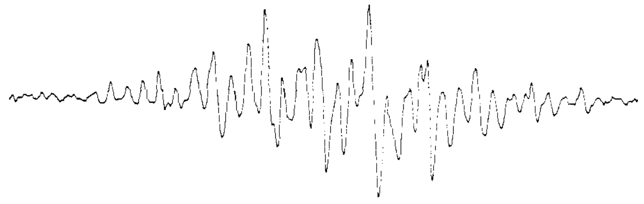


Figure 2. Esr spectrum of DBM$^{2-}\cdot$ from electrolytic reduction of DBM$^-$Na$^+$ in DMF.

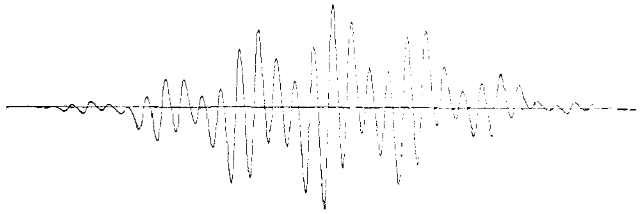
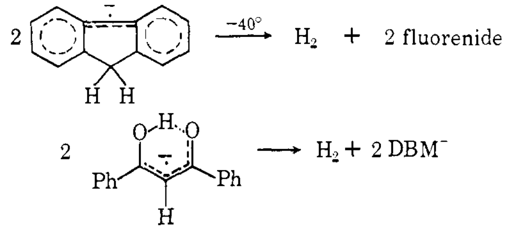


Figure 3. Simulated esr spectrum of DBM$^{2-}\cdot$ in DMF (see Figure 2).



The reduction of DBM$^-$, incidentally, is even sufficiently facile as to be brought about by calcium and magnesium. In the latter case, though, an alkyl halide is required to initiate the reaction.

Finally, whereas DBM$^-$ and DBM^{3-} are diamagnetic, DBM$^{2-}\cdot$ is paramagnetic (esr). That solutions of DBM^{3-} give no esr signal is clear proof that the reduction of DBM$^{2-}\cdot$ goes to completion, at least when alkali metals are used.

Esr Studies. Dilute samples (10^{-3}–10^{-4} *M*) of DBM$^{2-}\cdot$ for esr analysis were prepared on a vacuum line using a reaction vessel described in the Experimental Section. The spectra routinely obtained by metal reduction consisted of seven broad lines, $a_{\text{H}} = 2.3$ gauss (6 H, roughly equivalent). Occasionally a slightly better resolved spectrum was obtained, but this could not be related to concentration (10^{-2}–10^{-5} *M*), temperature ($-80°$, ambient), solvent (THF, DME, 2-methyl-THF), or metal (Na, K, Na–K, Li, Mg, and Ca), though, of course, very high concentrations were deleterious to resolution. The better spectra also consisted of seven groups of lines (Figure 1), but the enhanced resolution

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(13) H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.*, **87**, 1857 (1965).

(14) R. L. Kugel, W. G. Hodgson, and H. R. Allcock, *Chem. Ind.* (London), 1649 (1962). We have also confirmed this observation. Presumably the formation of the stable fluorenide anion provides impetus for the reaction.

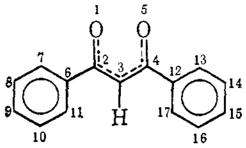
Table I. Odd Electron and Spin Densities and Hyperfine Splittings for DBM$^{2-}\cdot$

MO method	Posn	ρ_i or S_i	a_i (McConnell)	a_i (C–B)	a_i (exptl)
HMO	1	0.097	...	...	...
	2	0.134	...	...	...
	3	0.000	0.00	0.00	...
	6	0.061	...	...	...
	7	0.052	−1.40	−1.37	2.20
	8	0.009	+0.24	...	...
	9	0.085	−2.30	−2.20	2.75
McLachlan	1	0.099	...	...	...
	2	0.160	...	...	...
	3	−0.056	+1.51	+1.20	...
	6	0.058	...	...	...
	7	0.064	−1.73	−1.70	2.20
	8	−0.018	+0.49	+0.49	...
	9	0.116	−3.13	−3.03	2.75

permitted a dissection of the hyperfine splittings (hfs) into $a_H = 2.7$ (2 H) and $a_H = 2.2$ gauss (4 H). The average of these splittings (hfs) is 2.37 gauss, almost exactly that of the more poorly resolved spectra.

Electrolytic reduction of DBM$^-$Na$^+$ in DMF afforded an even better spectrum (Figures 2 and 3), again with $a_H = 2.75$ (2 H) and 2.20 (4 H).

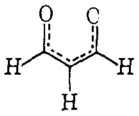
On the basis of MO calculations and symmetry, the major splittings are assigned to the *para* (2.75) and *ortho* (2.20) protons. The odd electron densities (ρ_i) at the various positions of the π systems of DBM$^{2-}\cdot$ as calculated by the HMO method are given in Table I.



Hyperfine splittings are calculated from the ρ_i by using the McConnell equation ($a_i = -27\rho_i$)[15] and the Colpa–Bolton equation ($a_i = -27\rho_i - 12.8q_i\rho_i$).[16] Note that the HMO predicted a_i are considerably less than the experimental ones. It is now established that in most radicals there are contributions to the total spin density at a position from the electrons in the MO's below that containing the unpaired electron. Thus, usually ρ_i (the odd electron density, $\psi^2{}_{(m+1)i}$) is different from the total spin density (S_i). In general, positions of high ρ_i draw spin from positions of low ρ_i. Thus $S_i > \rho_i$ in the former positions, and $S_i < \rho_i$ in the latter and, in fact, at least some of the S_i must be negative for these latter positions. At present the most convenient and well-acquitted method available for computing spin densities is that of McLachlan.[17] The results of such calculations are given in Table I and may be seen to be in much better agreement with the data than hfs obtained from Hückel ρ_i. In fact, the average *ortho,para* splitting is calculated to be 2.3, exactly as observed, though the disparity between *para* and *ortho* splittings is somewhat overestimated. The *meta*- and 3-H splittings to be expected from the small negative spin density at these positions are apparently unresolved. That none of the observed splittings arises from the 3 proton is assured by the esr spectrum of 3-deuterio-DBM$^{2-}\cdot$, which is identical with that of DBM$^{2-}\cdot$.

The breadth of the esr lines found for DBM$^{2-}\cdot$ is unusually great for solution spectra. Similar results are found for the other DAR's of this study. Undoubtedly this stems from ion agglomeration effects which must be especially pronounced in a species of such high charge density. That the visible λ_{max} of DBM$^{2-}\cdot$ is unshifted in going from benzene to ethers is proof of very tight metal ion pairing in these solvents. No doubt dimeric or higher agglomerates are also present. These give rise to the usual possibilities for hfs modulation and consequent line broadening.[6]

Simpler Dioxapentadienide DAR's. From the esr spectra of DBM$^{2-}\cdot$ it is apparent that quite a large fraction of the odd electron (*ca.* $^1/_2$) is situated on the two phenyl rings of the species. The interesting question naturally arises of whether simpler derivatives of the basic 1,5-dioxapentadienide (**1**) system can be reduced to DAR's. The prototype system has its lowest energy vacant MO at $\alpha - 1.00\beta$ and obviously should be much less readily reduced than DBM$^-$. The enolate of acetylacetone was selected as an uncross-conjugated member of the prototype family. This anion could not be reduced under any of our various conditions. However, it was apparent that the low solubility of this ion was a major problem. A more soluble enolate, that of dimedon, was thus investigated. In this case reduction occurred, but the purple DAR was insoluble and yielded a singlet esr signal. Filtration of the suspension through a fritted glass filter removed the colored paramagnetic solid, and the filtrate gave no esr signal. Finally, a nicely soluble enolate, that of 3-phenylacetylacetone (PAA$^-$), was selected. It should be noted that the phenyl group bears none of the odd electron density here, since it lies in a nodal plane of the $\alpha - 1.0\beta$ MO, which is, therefore, not lowered in energy from the prototype system. Further, it is doubtful that the phenyl group could approach planarity in this system in any case. Thus the principal and almost sole effect of the 3-phenyl substituent (unlike the 2- and 4-phenyl substituents) is to increase the solubility of the enolate in organic solvents. Indeed, reduction to PAA$^{2-}\cdot$ occurred readily. The well-resolved (but still rather broad lined) esr spectrum was a septet ($a_H = +11.04$ gauss, Figure 4). The HMO prediction is $a_H = +9.18$. No phenyl proton splittings were observed. PAA$^{2-}\cdot$ is much less stable than DBM$^{2-}\cdot$, as expected, and it is advisable to perform the reduction at −80°.



1

Intermediate between DBM$^{2-}\cdot$, which has two conjugating phenyl substituents, and PAA$^{2-}\cdot$, which has none, is the DAR of the benzoylacetone enolate system (BA$^{2-}\cdot$). It also gives a rather broad-lined septet esr, but with $a_H = 4.5$ gauss. The six approximately equivalent protons are apparently the methyl protons and the *ortho,para* ring protons. HMO calculations indicate odd electron densities of 0.10 and 0.12 at the methyl position and the averaged *ortho,para* positions, respectively. An average spin density of 0.11 would

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(15) H. M. McConnell, *J. Chem. Phys.*, 24, 764 (1956).

(16) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 6, 273 (1963).

(17) A. D. McLachlan, *ibid.*, 3, 233 (1960).

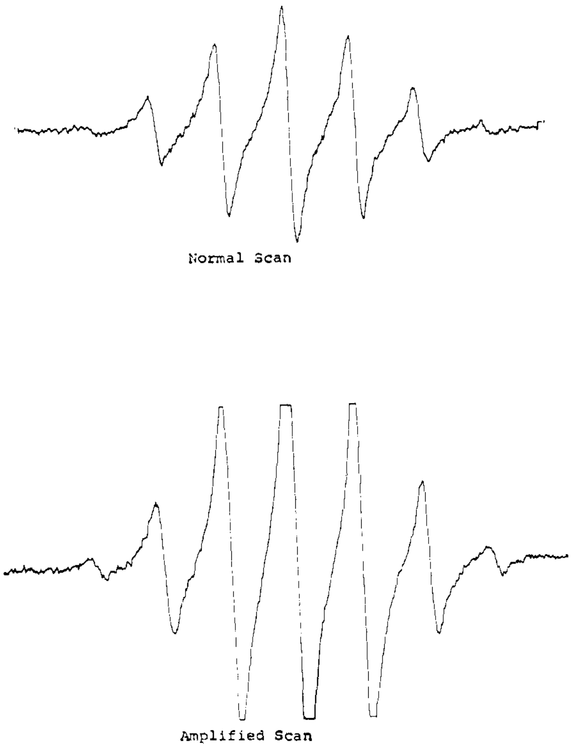
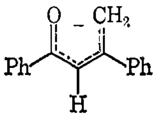


Figure 4. The esr spectrum of disodium 3-phenyl-2,4-dimethyl-1,5-dioxapentadienide.

account for an $a_H \approx 3.0$ gauss, applying the McConnell equation. Again, when negative spin densities are taken into account, the agreement should be improved.

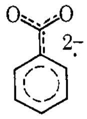
An attempt was made to verify the positional assignments by completely deuterating benzoylacetone, except for the phenyl protons, and examining the esr spectrum of the tetradeuterio DAR. This spectrum was, however, an unresolved singlet, perhaps because of the many, moderately large but unresolved, deuterium splittings. The three methyl deuterons would be expected to split each esr line into seven lines, $a_0 \approx 0.7$ gauss.

DAR's of Other Enolate Systems. Having established that the phenyl rings could be removed from conjugation with the 1,5-dioxapentadienyl system without eliminating the possibility of DAR formation, it next became of interest to see if the oxygen atoms could be replaced by carbon. Analogous, in this sense, to the dibenzoylmethide ion is the enolate of dypnone (**2**). The HMO energy level available for use in DAR formation is $\alpha - 0.69\beta$ in this system. The enolate was prepared by refluxing dypnone with excess NaH in THF. The virtually complete conversion was verified by titration and visible spectroscopy. The orange anion (λ_{max} 360 mμ) reacted rapidly with sodium or potassium giving the blue DAR (λ_{max} 580 mμ). The latter, like $DBM^{2-}\cdot$, is quite stable under the anhydrous, anaerobic conditions. The esr spectrum, unfortunately, was even more poorly resolved than $DBM^{2-}\cdot$, and discouraged any attempts at interpretation.



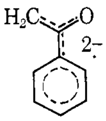
2

A large number of other monoanions have been reduced under similar conditions, and, in fact, it appears that the overwhelming majority of organic monoanions containing at least one oxygen atom is capable of DAR formation, although many of these are unstable and but few give resolved esr spectra. Particularly noteworthy is the reduction of sodium benzoate to a green, unstable DAR, from which an unresolved esr spectrum was obtained. It is assumed that this DAR is the same one presumed to be an intermediate in metal–ammonia reductions of benzoic acid (**3**). As expected, the DAR's of naphthoate salts are fairly stable, but, again, give unresolved esr spectra.



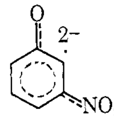
3

Acetophenone enolate also forms a green, unstable radical, presumably the indicated DAR (**4**). This adds a third radical which must be considered in reductions of ketones, in addition to the ketyl and its conjugate acid.



4

Although sodium phenoxide was not reducible, sodium *m*-nitrophenoxide formed a DAR (the *para* isomer did not).



Experimental Section

Esr spectra were obtained using a Varian V-4502 spectrometer. The vessel used to prepare esr samples was an approximately 50-ml capacity round-bottomed reaction bulb with a 10-ml, attached side-arm bulb to hold the alkali metal. The elongated neck of the flask had four or five side arms, with or without fritted glass filters, each of which was connected to a sample tube of 3-mm Pyrex tubing *ca.* 20 cm in length. It was closed with a hollow plug stopcock and attached to the vacuum manifold by a ground-glass joint. A modification replacing the esr side arms with a single side arm attached to a 1-mm quartz cell was used to obtain high-dilution visible spectra. HMO and McLachlan MO calculations and esr spectral simulations were performed on a CDC 1604 computer. The simulated spectra were plotted on a COC 165 plotter, assuming 100% Lorentzian line shape.

Esr samples were prepared by charging the side-arm bulb with excess alkali metal. The substrate was introduced into the main bulb in a capillary tube in sufficient quantity to afford concentrations in the range 5×10^{-3} to 5×10^{-4} *M*. Sodium hydride was also added to the main bulb, and the vessel was evacuated to 25–50 μ, with sufficient cooling to solidify liquid substrates. Purified solvent (20 ml), stored over potassium benzophenonide on the vacuum manifold, was then distilled into the main bulb. After allowing 15–30 min for enolate formation, the solvent was removed and alkali metal distilled over to form a mirror on the sides of the main bulb. Solvent was then distilled back into the reaction bulb and the reaction was allowed to proceed at various temperatures. Samples were taken periodically by decanting the solution into one of the capillary tubes and sealing it off. The sample tubes were stored in liquid nitrogen until analyzed. Spectra were obtained at temperatures ranging from −40 to −110°, depending upon which temperature gave optimum resolution.

1,3-Diphenyl-2,2-dideuterio-1,3-propanedione. Dibenzomethane (4 g) was dissolved in 50 ml of dry THF and 25 g of D_2O was added. The mixture was refluxed 3 hr and then stirred at room temperature 72 hr. The solvent was removed, and the crystals were filtered. The procedure was then repeated, giving 2.4 g of the dideuterated compound, mp 78°. Dideuteration was confirmed by nmr. The dianion radical gave an esr spectrum identical with that obtained from the undeuterated substrate (alkali metal generation in THF and electrolytic generation in DMF).

1,1,1,3-Tetradeuterio-2,4-diphenyl-2-buten-4-one. Dypnone (5 g) was dissolved in 50 ml of DME. Potassium *t*-butoxide (0.5 g) and D_2O (20 ml) were then added, and the mixture was refluxed 56 hr. Work-up gave 4.1 g of tetradeuterated dypnone [bp 145° (0.25 mm)]. The nmr spectrum showed only aromatic protons. The esr spectrum of the corresponding dianion radical was unresolvable.

2,2,4,4,4-Pentadeuterio-1-phenyl-1,3-butanedione. Benzoylacetone (5 g) was dissolved in 50 ml of DME. Potassium *t*-butoxide (0.5 g) and D_2O (20 ml) were then added, and the solution was refluxed for 7 days. Work-up gave 3.9 g of pentadeuterated product, which again showed only aromatic protons in the nmr.

Acknowledgments. Financial support from the National Institutes of Health and the Robert A. Welch Foundation is gratefully acknowledged.

Dianion Radicals. II. Tropenide Systems

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Received March 15, 1967

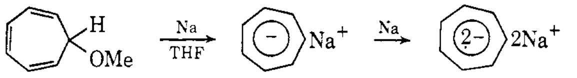
Abstract: The esr and visible spectra of the cycloheptatrienide (tropenide) dianion radical, the first and simplest reported dianion radical, are described and discussed. Disodium tropenide shows an extraordinarily large double metal splitting in its esr spectrum ($a_{2\mathrm{Na}^+} = 1.76$ gauss), at temperatures ranging from $-100°$ to ambient and in several ethereal solvents. It is thus shown to exist as contact ion triplets (or higher agglomerates) under these conditions. Dipotassium tropenide evinces no metal splitting, apparently because of rapid metal ion exchange. The proton hyperfine splitting of tropenide ($a = 3.52$) is considerably less than that for tropyl under comparable conditions, a fact predicted by the Colpa–Bolton equation. The esr spectra of the benzo- and dibenzo[1,2:4,5]tropenide dianion radicals are also reported, simulated, and correlated with HMO and McLachlan calculations.

The cycloheptatrienide (tropenide) dianion radical, the first recognized hydrocarbon dianion radical, was the subject of a recent preliminary report.[1] It is the intent of this paper to elaborate on that report and to describe also the benzotropenide and dibenzo[1,2,4,5]-tropenide dianion radicals. Since the initial report, several other, more complex, hydrocarbon radicals have been described.[2-5]

Results and Discussion

Cycloheptatrienide Dianion Radical. Solutions of tropyl methyl ether in THF, DME, or 2-methyl-THF turn blue almost immediately upon contact with alkali metal mirrors. After only a few minutes the solutions are intensely blue ($\lambda_{\max}^{\mathrm{THF}}$ 620 mμ, Na$^+$ salt), but show no esr absorption. That these initially formed solutions contain the diamagnetic tropenide ion is affirmed by the work of Dauben and Rifi.[6] In about 15 min more, the solutions have turned blue green ($\lambda_{\max}^{\mathrm{THF}}$ 570 mμ, Na$^+$ salt) and have developed a large concentration of free radicals, as shown by esr measurements. The esr spectra are essentially solvent independent for the three solvents mentioned, but do vary significantly with the nature of the alkali metal used. With potassium, an octet, $a_{\mathrm{H}} = -3.52$ gauss (7 H, sign assumed), is observed (Figure 1). When sodium is used, a more complex and well-resolved spectrum is obtained which, although a casual inspection does not necessarily reveal it, still contains the same basic octet ($a_{\mathrm{H}} = -3.52$), further split into septets ($a_{2\mathrm{Na}^+} = 1.76$ gauss). Since ^{23}Na has nuclear spin $I = {}^3/_2$, two equivalent sodium gegenions should split each esr absorptionin to $2I + 1 = 7$ lines. The experimental and computer-simulated spectra, as well as a magnified version of the former, are reproduced in Figures 2, 3, and 4, respectively. The latter, magnified, spectrum reveals exactly the right number of lines for the aforementioned interpretation. (The outermost line of the basic octet is designated by an asterisk.) These visible and esr spectral observations, in conjunction with ancillary observations to be mentioned below, confirm beyond reasonable doubt the structure of the radical as the tropenide dianion radical, formed by the sequence shown in Scheme I. No unambiguous evidence for trianion formation[7] was seen either in the form of attenuation of the esr signal after prolonged reaction time in the presence of excess metal or of alteration of the visible absorption of the dianion radical or appearance of a new maximum. It seems clear that the trianion, if formed at all, is present in quite small amounts.

Scheme I



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[1] N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, **87**, 4390 (1965).

[2] P. Dowd, *ibid.*, **87**, 4968 (1965).

[3] E. G. Janzen and J. G. Pacifici, *ibid.*, **87**, 5504 (1965).

[4] E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, **70**, 302 (1966).

[5] N. L. Bauld and J. Zoeller, *Tetrahedron Letters*, 885 (1967).

[6] H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963).

[7] R. Breslow and H. W. Chang, *ibid.*, **87**, 2200 (1965), have reported the heptaphenyltropenide ion to cleave to pentaphenylcyclopentadienide and stilbene upon reaction with potassium.