

a Jahn-Teller distortion¹⁰ should stabilize the configuration where this orbital contains the unpaired electrons; ρ_1 may then be somewhat above 0.40.

Another feature of the electronic distribution at C-1 appears in an examination of the values of $|E|/|D|$. To a fair approximation, this ratio should equal the fractional s-character in the unfilled in-plane σ -orbital at C-1.¹¹ If the axes of the C-1 hybrids involved in bonding form an angle θ of 180° , $|E|/|D| \sim 0$, while for $\theta \approx 120^\circ$ (sp^2) $|E|/|D| \sim 1/3$. The observed ratio makes it likely that $\theta > 135^\circ$ in I, a value significantly greater than any reasonable internuclear angle at C-1. We suggest that the bonds to C-1 in I, II, and III are "bent" bonds. The angle formed by the axes of the hybrids at C-1 is greater than the internuclear angle. The interpretation is supported by an examination of the variation of the C¹³ hyperfine splittings and zero-field parameters, D and E , in I, phenylmethylene, and diphenylmethylene.² The latter two appear to be approximately planar and bent with $\theta \sim 140$ - 155° .²

To explain the smaller E for II and III in comparison with I we note that $\rho_3 = \rho_4 = 0.26$ for the stabilized Hückel orbital of II and $\rho_3 = 0.41$ in III. With respect to the unpaired σ -orbital at C-1 these spin densities have larger x -components than y -components so that they yield a negative contribution to an originally positive E and reduce its magnitude. The spin densities at atoms other than C-1 in I do not have as large an effect.

Acknowledgment.—We wish to thank Mr. R. M. R. Cramer for his assistance in obtaining the e.s.r. spectra.

(10) L. C. Snyder, *J. Chem. Phys.*, **33**, 619 (1960).

(11) Such an approximate relation is implied in the treatment of J. Higuchi [*ibid.*, **39**, 1339 (1963)] when two-center terms are included. See also H. Sternlicht, *ibid.*, **39**, 2316 (1963).

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Stable Dianion Radicals and Trianions in Substituted Pentadienyl Systems

Sir:

Not a few organic molecules have vacant MO's of sufficiently low energy to accept extra electrons forming anion radicals and dianions. Some of these are thermally stable even at room temperature and above. The naphthalene,¹ cyclooctatetraene,² semiquinone,³ benzophenone,⁴ and benzil⁵ anion radicals are some more familiar examples. Stable dianions are also formed in several of these same systems. More often, however, only the anion radical is formed and found to be unstable at room temperature. Recent work shows that even such non- π -electronic systems as cyclopropane⁶ and adamantane⁷ form unstable anion radicals. Both stable and unstable anion radicals are of considerable interest since they permit an easy check

(1) S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953).

(2) T. J. Katz and H. L. Strauss, *ibid.*, **32**, 1873 (1960).

(3) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *J. Am. Chem. Soc.*, **60**, 1678 (1938).

(4) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).

(5) H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

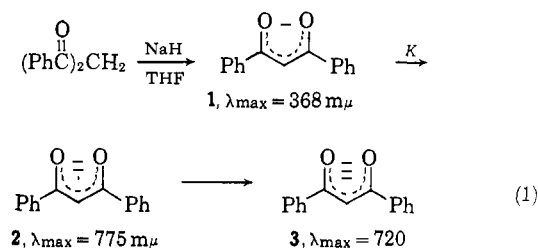
(6) K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

(7) K. W. Bowers, G. J. Nofi, and F. D. Greene, *ibid.*, **85**, 3707 (1963).

on the accuracy of trial eigenfunctions (e.s.r.) and eigenvalues (polarographic reduction potentials) of the lowest vacant MO's of these molecules.⁸

HMO calculations made in our laboratories indicate that a surprising number of organic anions have low-lying vacant MO's and could be expected to form dianion radicals and trianions. This report describes several such species which are formed with astounding ease in relatively simple systems and which possess remarkable stability. Some precedent for dianion radicals of unspecified stability already exists in the tetra- and pentacyanoallyl dianion radicals, the e.s.r. spectra of which have been obtained.⁹

Dibenzoylmethane, in THF solvent under nitrogen, reacts with excess sodium hydride to form the enolate, 2,4-diphenyl-1,5-dioxapentadienyl anion (1). This, in turn, reacts readily with either one or two atoms of potassium or sodium at temperatures from -78 to 66° to form, respectively, the deep green dianion radical 2 or the blue trianion 3, according to eq. 1. The structures of 2 and 3 are unequivocally established by



the following evidence. Aliquots of solutions of 1, 2, and 3 were filtered (to remove excess sodium hydride and any unreacted potassium) into quenching aqueous solutions and titrated to a phenolphthalein end point with 0.100 N sulfuric acid; 1 required 0.93, 0.93, 2 required 1.95, 1.87, and 3 required 2.75, 2.67 equiv. of acid to neutralize 1 mole of diketone, thus showing them to be mono-, di-, and triacidic bases, respectively. Control runs established that potassium in THF generates no appreciable acid titer under any of our conditions. Secondly, both 2 and 3 could be oxidized back to dibenzoylmethane in $>90\%$ yield by adding anhydrous nickel chloride and then acidifying the nickel chelate. Degradation is therefore excluded. Finally, whereas the enolate and trianion are both diamagnetic, the dianion radical is paramagnetic, as shown by their e.s.r. spectra.¹⁰

Solutions of 2 and 3 are stable for months at room temperature under nitrogen, and at least weeks even in refluxing THF (66°).

HMO calculations accord with the ease of the reaction, the relevant MO having $E = \alpha - 0.49\beta$.^{11,12} The 2-phenyl-4-methyl-1,5-dioxapentadienyl system has a corresponding MO at -0.57β and it too forms a dianion radical (4) which is stable at room temperature but decomposes during an hour's refluxing in THF. The parent 1,5-dioxapentadienyl system has its lowest

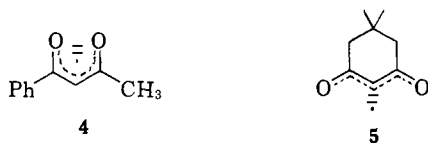
(8) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., Chapters 6 and 7.

(9) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(10) We wish to thank Professor Allen J. Bard, of this department, for e.s.r. spectra. These extremely interesting spectra will soon be discussed elsewhere.

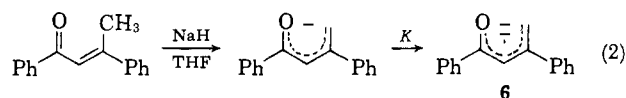
(11) Using parameters as follows¹²: $\alpha_0 = \alpha + 2\beta$; $\beta_0 = \beta\sqrt{2}$; β for phenyl to benzylic carbon overlap, 0.8.

(12) J. D. Roberts, "Notes on Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1962, p. 78.



vacant MO at -0.73β . A close facsimile, the 2,4-dimethyl-1,5-dioxapentadienyl system fails to react with potassium in THF. However, another example, dimedon enolate, does react to form a stable lavender dianion radical (5). We attribute this difference in reactivity to the fact that the more stable conformer of the dianion radical, *i.e.*, the *trans,trans* conformer, in which the negatively charged oxygens are maximally separated, can be formed directly in the cyclic case but not in the acyclic one, where the chelated enolate prefers the *cis,cis* formation, the worst for dianion radical formation.

The 2,4-diphenyl-1-oxapentadienyl dianion radical (6) has also been prepared, by sequence 2. The HMO energy level is -0.63β . Reaction stops at the



deep blue dianion radical stage (titration), at which point dypnone can be regenerated by nickel chloride treatment.

Finally, 2,4-diphenylpentadienyl anion (purple) has been prepared and treated with potassium. Here, even the dianion radical fails to form. The HMO energy level (-0.72β) is about the same as for the unsubstituted 1,5-dioxapentadienyl system, the acyclic analog of which also did not react.

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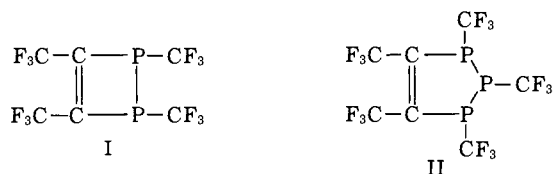
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Polyphosphine Heterocycles

Sir:

One of the more elegant synthetic applications of biphosphine chemistry is the pseudo-halogen addition to multiple bonds.^{1,2} We have extended this principle to cyclopolyposphines and thereby attained the C_2P_2 and C_2P_3 ring systems in the compounds 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphosphacyclobutene (I) and 1,2,3,4,5-pentakis(trifluoromethyl)-3,4,5-triphosphacyclopentene (II).



$(CF_3P)_4$ and $(CF_3P)_5$ in the presence of excess $CF_3C\equiv CCF_3$ at 170° for 70 hr. gave 55% of I and 31% of II.

(1) J. Chatt, F. A. Hart, and H. C. Fielding, U. S. Patent 2,922,819 (1960).

(2) A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

Anal. Calcd. for $C_6F_{12}P_2$ (I): C, 19.89; F, 62.99; P, 17.12; mol. wt., 362. Found: C, 19.82; F, 63.70; P, 17.48; mol. wt., 366 (gas density), 362 (mass spectrometer).

Anal. Calcd. for $C_7F_{15}P_3$ (II): C, 18.18; F, 61.71; P, 20.11; mol. wt., 462. Found: C, 18.25; F, 62.26; P, 20.28; mol. wt., 462 (mass spectrometer).

The vapor pressure of I is 6 mm. at 0° and 26 mm. at 25° , from which the boiling point is estimated as 110° . The vapor pressure of II is 1.5 mm. at 25° , implying a boiling point near 160° . Both I and II are colorless liquids that do not freeze at -120° . They are spontaneously flammable in air, but in isolation they are stable at 200° . The double-bond absorption for I occurs at 1625 cm.^{-1} and that for II at 1560 cm.^{-1} .

F^{19} n.m.r. of I shows two kinds of fluorine in equal amounts. The CF_3 groups attached to P have the X pattern of an $X_3AA'X_3'$ system^{3,4} in which eight lines can be resolved. From the F^{19} spectrum the coupling constants (including J_{P-P}) were derived (Table I); these values give a calculated spectrum in good

TABLE I
NUCLEAR MAGNETIC RESONANCE PARAMETERS

	$J_{P-P'}$ c.p.s.	J_{P-F} c.p.s.	$J_{P'-F}$ c.p.s.	δF , p.p.m. CF_3COOH = 0	δP , p.p.m. H_3PO_4 = 0
Compound I					
$F_3C-P-P'-CF_3'$	55	59	18	-25	+40
$F_3C-C=C-CF_3$	$J_{P-F} + J_{P'-F} = 10$			-13	
Compound II					
$(P')_2-P-CF_3$	220	60	20	-30	+41
$(CF_3-P)_2-P'$	220	65	23	-28	-55
$CF_3-C=C-CF_3$				-24	

agreement with the line positions and intensities observed. The sign of the coupling constant of F with the near P is the same as that with the far P. At high resolution there is further splitting (1.5 c.p.s.) from the other set of CF_3 groups. This F-F coupling is again seen in the F^{19} spectrum of the CF_3 groups on carbon and can be removed by double resonance. This reduces the spectrum of the carbon CF_3 groups to a triplet which is the theoretical X pattern of an $X_3AA'X_3'$ system when AA' coupling is large relative to AX couplings.⁵

The n.m.r. spectra of II are fully consistent with its structure. The resonances of the CF_3 groups attached to phosphorus appear as two triplets and two doublets in accord with expectations for first-order F-P spin-spin interactions. There are two kinds of P^{31} nuclei, in the ratio 1:2, and they appear as a triplet and doublet, as expected.

At 170° , iodine converts II to equimolar amounts of CF_3PI_2 and the diphosphacyclobutene I; the latter is resistant to further action of iodine. The P-P bonds of the heterocycles are in marked contrast to those of the homocyclic polyphosphines which are quantitatively cleaved by iodine at room temperature.⁶

(3) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

(4) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

(5) A similar situation exists in $(CH_3)_2PP(CH_3)_2$, where the proton spectrum is an almost perfect 1:2:1 triplet; the ringing of the middle line is less pronounced than that of the outer two and indicates unresolvable structure.

(6) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).