

(7) Public Health Service Predoctoral Fellow, 1962-1965.

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Hydrocarbon Dianion Radicals

Sir:

When Koelsch's radical¹ ($R\cdot$) is reduced with potassium in tetrahydrofuran (THF) the anion (R^-) is readily formed. The e.s.r. signal of a dilute solution² ($\sim 5 \times 10^{-5} M$) decreases in intensity with no change in spectrum as $R\cdot$ is reduced to R^- , until a trace of radical remains. The complete conversion of the pale yellow solution of $R\cdot$ to the blue R^- can also be followed spectrophotometrically where the 4860 Å. band for $R\cdot$ disappears simultaneously with the appearance of the 6010 Å. for R^- . When the e.s.r. signal of $R\cdot$ has decreased to a minimum, further reduction produces a radical with a g -value of 2.0039 and hyperfine splitting different from $R\cdot$. Whereas the spectrum of $R\cdot$ is due to eight approximately equivalent hydrogens (1.8 gauss, ref. 3) the new spectrum can be well fitted to splitting from three pairs of hydrogens (3.0, 2.0, and 0.66 gauss). The new radical gives a new band at 3750 Å. with a broad shoulder 4500 Å. region. Further reduction produces first a green solution and finally a red-orange solution. The 6040 Å. band for R^- decreases simultaneously with a decrease in e.s.r. signal. Only a trace of radical is found in the red-orange solution.

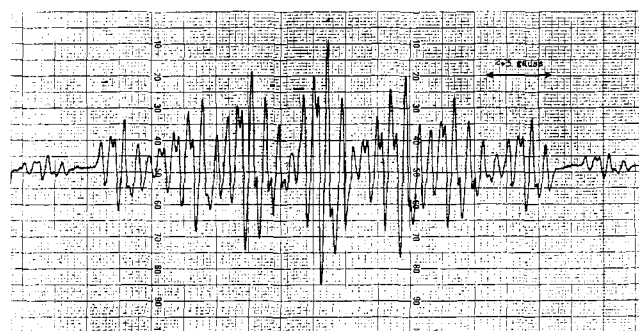


Figure 1. E.s.r. spectrum of phenanthrene-4,5-methide dianion radical in K-THF.

Solutions of the various reduction products appear to be stable for weeks. When air is admitted to the red-orange solution a rapid change of color to the blue solution of R^- is observed.⁴ If a limited amount of air is used, the same e.s.r. spectrum is obtained as produced during the reduction sequence. Koelsch¹ found that $R\cdot$

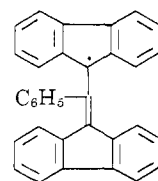
(1) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

(2) (a) The complete e.s.r. spectrum of Koelsch's radical is difficult to resolve³ although seven out of the nine groups of lines are readily obtained. (b) g -Value of Koelsch's radical = 2.0026 (J. E. Wertz, *Chem. Rev.*, **55**, 918 (1955)).

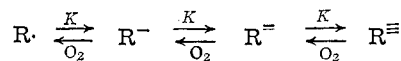
(3) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 1 (1964); K. H. Hauser, *Z. Naturforsch.*, **14A**, 425 (1959); **17A**, 158 (1962).

(4) This carbanion is relatively stable to oxygen in THF but oxidizes slowly to Koelsch's radical: J. G. Pacifici, J. F. Garst, and E. G. Janzen, *J. Am. Chem. Soc.*, **87**, 3014 (1965).

could be reduced with sodium amalgam in ether to a brick-red solution containing the trisodium derivative (R^{3-}), since upon addition of water 2-phenyl-1,3-bisbiphenylene-propane could be isolated. These observations all point to the existence of a stable dianion radical^{5,6} produced in a sequence of reductions starting from $R\cdot$.



Koelsch's radical



Because Koelsch's dianion radical has the same spectrum as fluorenone ketyl it can be concluded that the unpaired electron is localized in one biphenylene ring instead of equally in both of these rings as in the neutral radical.

Other hydrocarbon carbanions can be reduced to dianion radicals. 4,5-Methylenephenanthrene reacts with K-THF to produce the yellow carbanion.⁷ When all the hydrocarbon is converted to the anion the red dianion radical I forms rapidly⁸ (Figure 1). The orange carbanion derived from 9-phenylfluorene⁹ is also reduced to a new radical attributed to the dianion radical.¹⁰ Pentaphenylcyclopentadienyl chloride was reduced to the neutral radical¹¹ and to the orange anion. Upon further reduction a purple solution was obtained which gave a new e.s.r. spectrum of 76 lines with total line width of 21 gauss and $g = 2.0030$.¹² Quartet splitting of 0.51 gauss due to ³⁹K ($I = 3/2$) was clearly resolved. At this time we are not certain if the spectrum is due to the pentaphenyl-

(5) There has been recent interest in the chemistry of polyanion radical ions: (a) N. L. Bauld, *ibid.*, **86**, 2305 (1964); (b) *ibid.*, **86**, 3894 (1964); (c) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); (d) P. Brassem, R. E. Jesse, and G. J. Hoijsink, *Mol. Phys.*, **7**, 587 (1964).

(6) The e.s.r. spectrum of the dianion radical is essentially the same as fluorenone ketyl: (a) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); (c) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2537 (1964); (d) G. R. Luckhurst and L. E. Orgel, *Mol. Phys.*, **8**, 117 (1964). However, the g -value of Koelsch's dianion radical is higher than the g -value of fluorenone ketyl (2.0039 compared to 2.0028), and the visible absorption spectra are different (fluorenone ketyl has a strong absorption maximum at 5390 Å.). Because of the complete reversibility of the electron-transfer reactions (electron-transfer equilibria of the monoanion and dianion radical will be presented in a following paper) and isolation by Koelsch¹ of 2-phenyl-1,3-bis-biphenylene-propane from the red solution of the trisodium adduct, we are convinced the spectrum is in fact due to the dianion radical and not fluorenone ketyl.

(7) $pK_a = 22.6$: A. Streitwieser, Jr., J. I. Brauman, J. H. Hainmons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

(8) The corresponding ketyl has fewer readily resolvable lines (27) and a narrower total line width (10.6 gauss in DMF, ref. 5a).

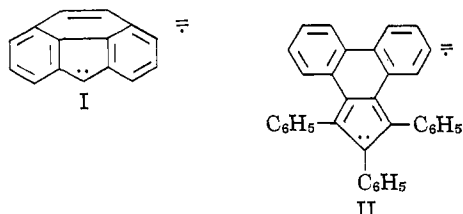
(9) $pK_a = 18.5$: C. H. Langford and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 1503 (1960).

(10) This spectrum is different from 9-phenylfluorenyl (E. G. Janzen, Abstracts of papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 12-17, 1965, p. 51S; $g = 2.0029$ in nitrobenzene) or 9-fluorenone ketyl.⁶ For 9-phenylfluorenyl dianion $g = 2.0031$; coupling constants in gauss: 4.0 (four equivalent protons) and 2.7 and 0.55 (two equivalent protons).

(11) D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961); g -value = 2.0025 (J. E. Wertz, C. F. Koelsch and J. L. Vivo, *ibid.*, **23**, 2194 (1955)).

(12) A pink solution of the corresponding ketyl gave a single unresolved line 4 gauss wide, g -value = 2.0033.

cyclopentadienide dianion radical or the corresponding ring closed compound II.¹³



All g -values were found to be higher than most previously described radicals. Anion radicals have slightly larger g -values than cation radicals of the same structure.¹⁴ The g -values for dianion radicals are consistent with the trend that the g -value of the radical increases with increase in negative charge on the radical.¹⁵

Samples were prepared in a high vacuum system and studied at room temperature in quartz tubes sealed under vacuum. Potassium mirrors were made by depositing distilled metal on the walls of a side arm under vacuum. A Varian 4502 e.p.r. spectrometer with a 12-in. magnet was used. g -Values were determined by means of a dual cavity using solid DPPH (diphenylpicrylhydrazyl) dispersed in NaCl as a g -value marker ($g = 2.0036$). By this means reported g -values could be reproduced to ± 0.0003 or better. Line widths were measured from first resolved maxima to last resolved minima.^{15a}

Acknowledgments. We are grateful to Dr. R. C. Lamb and to the Air Force Office of Scientific Research (AF-AFOSR-62-53) for their support of J. G. P. in this work.

(13) The formation of II in the reduction of pentaphenylcyclopentadienide would be analogous to the observed reduction of benzil dianion to phenanthrenequinone trianion radical (ref. 5b).

(14) M. S. Blois, Jr., H. W. Brown, and J. E. Mailing, "Free Radicals in Biological Systems," M. S. Blois, Ed., Academic Press Inc., New York, N. Y., 1961, p. 117.

(15) See A. J. Stone, *Mol. Phys.*, **6**, 507 (1963); **7**, 311 (1963).

(15a) NOTE ADDED IN PROOF. Recently cycloheptatrienide and tetraphenylallyl dianion radicals have been reported: N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, **87**, 4390 (1965); P. Dowd, *ibid.*, **87**, 4968 (1965).

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Condensation of Nitroethanol and Ribose 5-Phosphate. A Novel Route to Sedoheptulose 7-Phosphate¹

Sir:

The base-catalyzed condensation of nitroethanol with aldoses in methanol has been applied with some success as a key step in the synthesis of several ketoses.² We wish to report the first chemical synthesis of D-sedoheptulose 7-phosphate (S-7-P) using an analogous method in aqueous solution. This compound, which is unavailable commercially, is a very important metabolite³

(1) Supported in part by the Medical and Biological Research Fund of Washington State University and by Research Grant RG-5904 from the National Institutes of Health.

(2) J. C. Sowden, *Advan. Carbohydrate Chem.*, **6**, 316 (1951); J. C. Sowden and D. R. Strobach, *J. Am. Chem. Soc.*, **80**, 2532 (1958).

(3) J. S. Fruton and S. Simmonds, "General Biochemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 530, 551, and 552.

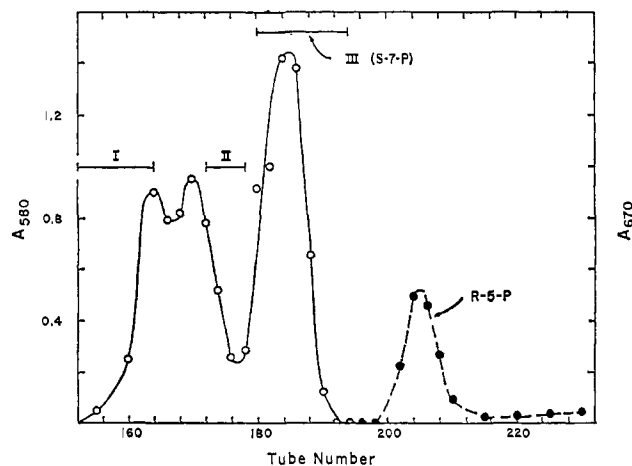


Figure 1. Column chromatography of the HBr-treated reaction mixture at an average rate of 0.7 ml./min. Fractions (22 ml./tube) were collected and 0.05 ml. was analyzed with orcinol⁸ to give: O—O, absorbancy at 580 $m\mu$ (A_{580}) due to heptulose phosphate, and ●—●, absorbancy at 670 $m\mu$ (A_{670}) due to ribose 5-phosphate. Absorbancies at 670 and 580 $m\mu$ due to heptulose phosphate and ribose 5-phosphate, respectively, are not shown.

and has been prepared by lengthy enzymatic methods^{4,5} and isolated in a partially purified state. Consequently its synthesis by more direct techniques and isolation in essentially pure form as described here are of considerable interest. Of additional interest is the likelihood that the present procedure opens an entirely new synthetic avenue to rare or unknown ketose phosphates.

An aqueous solution (97 ml.) of 6 mmoles of sodium D-ribose 5-phosphate (R-5-P) was prepared from the barium salt trihydrate (Nutritional Biochemicals Corp.). Then 1 *N* NaOH (30 mequiv.) and water were added at 2° to bring the volume to 180 ml., followed by the dropwise addition of 8.6 ml. (120 mmoles) of cold β -nitroethanol (Columbia Organic Chemicals Co.). After stirring for 24 hr. at 2° (kinetic experiments⁶ have established that the time may be shortened to 1 hr. or less), the amorphous sodium C-nitroalcohols were precipitated with ten volumes of cold acetone. The suspension was centrifuged at 2° and the supernatant solution was discarded. Cold 4 *N* HBr (250 ml.) was slowly added to the pellet which dissolved with concomitant evolution of N_2O . Then the pH was adjusted to 7.7 with LiOH, and 2.3 g. (6.9 mmoles) of $BaBr_2 \cdot 2H_2O$ was added. A small amount of precipitate was removed by filtration and the barium heptulose phosphate salts were precipitated from the filtrate by addition of five volumes of either cold acetone or cold ethanol. The barium salts were converted to a solution (80 ml.) of sodium salts with Na_2SO_4 . An aliquot assayed with transaldolase⁶ revealed that the yield of S-7-P was 30%. The solution of sodium salts was then chromatographed on a 2 \times 61 cm. Dowex 1-X8 column in the formate form by the general method of Horecker, *et al.*,^{7,8} except that

(4) B. L. Horecker, *Methods Enzymol.*, **3**, 195 (1957).

(5) J. R. Sokatch and B. A. McFadden, *Biochem. Prepn.*, **12**, in press.

(6) E. Racker in "Methods of Enzymatic Analysis," H. U. Bergmeyer, Ed., Academic Press Inc., New York, N. Y., 1963, p. 107. We are indebted to Dr. B. L. Horecker for a generous gift of highly purified transaldolase.

(7) B. L. Horecker, P. Z. Smyrniotis, H. Hiatt, and P. Marks, *J. Biol. Chem.*, **212**, 827 (1955).

(8) B. L. Horecker, *Methods Enzymol.*, **3**, 105 (1957).