Tetrahedron Letters No.34, pp. 4063-4066, 1966., Pergamon Press Ltd.
Printed in Great Britain.

ON THE STATUS OF ALIPHATIC RADICAL ANIONS (1)

K. W. Bowers, G. J. Nolfi, Jr., T. H. Lowry, and F. D. Greene
Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts

(Received 4 May 1966)

Some time ago the observation by e.s.r. of paramagnetic species derived from cyclopropane, adamantane, and hexamethylenetetramine was reported from these laboratories (2). Since that time we have devoted considerable effort to this area with rather conflicting results which we feel are nevertheless worth summarizing in view of the interest the work has engendered (3,4,5). Our work has been carried out in two phases (6). In the first phase the following observations were made by use of dimethoxyethane/tetrahydrofuran 1:2 and sodium-potassium alloy at low temperatures: 1) the signals from cyclopropane (seven lines of binomial intensity, a = 2.33 gauss), adamantane (five broad lines, a = 3.9 gauss), and hexamethylenetetramine (nine broadened lines, approximately fitting the intensity ratio of 1:4:10:16:19:16:10:4:1, a = 4.2 gauss) mentioned above: 2) a ten-line pattern (five lines, doubled) from spiropentane (7), $a_{\text{quintet}} = 7.1$, $a_{\text{doublet}} = 2.0$; 3) a weak four-line pattern (observed only once) from 1-methyladamantane; 4) no signals (but solution remained blue) from a number of hydrocarbons including cyclohexane, neopentane, bicyclo [2.2.2] octane, bicyclo [2.2.1] heptane, and 1,3-dimethyladamantane; 5) no signals (but occasional decolorizing of solution and frequent explosion of sample tube) from various allyl-substituted cyclopropanes. The spectra could only be observed at low temperatures (-140° and lower) and at the lowest power settings of the spectrometer.

In order to assess possible interaction of an electron on an aromatic with an adjacent cyclopropane ring, 1-methyl-1-phenylcyclopropane was examined (1-phenylcyclopropane resulted only in decolorizing the solution with no e.s.r. signal). The radical anion was very similar to that from t-butylbenzene (8), an rather than providing evidence for an electron-accepting capability for cyclopropyl, indicates that in this radical ion the cyclopropyl substituent is very weakly electron-repelling. (Apart from the suggestive indication provided by the maintenance of a weak blue color of the solution, it is not known whether the cyclopropyl ring remained intact under the conditions of this experiment.) For 1-methyl-1-phenylcyclopropane, $a_{ortho} = a_{meta} = 4.76$, $a_{para} = 1.86$, a_{methyl} is unresolved; for t-butylbenzene, $a_{ortho} = a_{meta} = 4.66$, $a_{para} = 1.74$, a_{methyl} is unresolved (8).

In the second phase of our work (6) we have been unable to duplicate the earlier observations. Also, the instability of cyclopropane-containing samples (and nortricyclene in particular) observed previously has not been encountered. One difference of possible importance between these two periods may be the state of the alloy. In the earlier work, the alloy (prepared by us) was grayish and had undergone some surface oxidation. This material, however, gave the characteristic blue color with dimethoxyethanetetrahydrofuran and gave excellent spectra with benzene and other aromatic compounds. In the second phase of the work, a highly purified commercial alloy (9) was employed, as well as alloy prepared by us. Upon failing to repeat the earlier results, we have examined a number of variables, including different treatments of the alloy (limited exposure to oxygen, etc.). All of these have failed to reproduce the earlier findings: no instability of the cyclopropane samples after preparation, and no resolved paramagnetic signals: We have also been unable to reproduce the extreme supercooling of the solvent system obtained in the earlier work.

Possibly the earlier results were due to paramagnetic species generated on (or by) the surface of the alloy. The lack of quenching by cyclopropane, adamantane and hexamethylenetetramine of the signal from the solvated electron in potassium - dimethoxyethane (5) may also point in this direction (although even in the earlier phase of our work potassium in dimethoxyethane was not a medium in which any resolved signals from aliphatic systems were observed). The lack of present reproducibility, the sensitivity of e.s.r. for detecting extremely low concentrations of paramagnetic species, and the limited amount of data do not provide an adequate basis for further discussion of the species previously observed.

1) This work was supported under contract No. AT(30-1)-905 with the Atomic Energy Commission. Reproduction is permitted for any purpose of the United States Government.

2) K. W. Bowers and F. D. Greene, J. Am. Chem. Soc., 85, 2331, (1963): K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, ibid., 85, 3707 (1963).

3) G. R. Husk and R. West, J. Am. Chem. Soc., 87, 3993 (1965).

4) M. T. Jones, J. Am. Chem. Soc., 88, 174 (1966).

5) F. Gerson, E. Heilbronner, and J. Heinzer, Tetrahedron Letters, 2095 (1966

6) The two phases were separated by a period of several months during which a new spectrometer was installed and new vacuum lines constructed. The earlier alloy preparation, solvent purification and sample handling techniques were first reproduced as closely as possible, and later some new solvent and alloy purification systems were tested.

7) Purified for heat of combustion studies and kindly provided by Bureau of Mines, National Bureau of Standards, U.S.A.

8) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, Mol. Phys., 5, 43 (1962).

9) Mine Safety Appliance Research Laboratories, Callery, Pennsylvania.