Use of Toluene-*p*-sulphonylhydrazones in Electron Paramagnetic Resonance Studies of Triplet Methylenes

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RECENT electron paramagnetic resonance (e.p.r.) studies of a number of triplet methylene compounds have allowed assignments of their ground-state spin multiplicity.[1—3] In general, these methylenes were obtained in rigid-glass matrices by photolysis of appropriate diazo-compounds.

Dauben[4] has reported that alkaline salts of toluene-*p*-sulphonylhydrazones, upon irradiation with ultraviolet light at room temperature, yield products similar to those obtained by thermal decomposition,[5] presumably *via* diazo-intermediates. This led us to investigate the photolysis of toluene-*p*-sulphonylhydrazone salts of benzophenone,[5a] fluorenone,[5a] and benzaldehyde[6] in a frozen matrix since methylenes derived from the corresponding diazo-compounds have been shown to possess ground-state triplet multiplicity.[1] Lithium salts were obtained as dry solids by neutralization of cold hydrazone solutions (10% in dry tetrahydrofuran) with lithium methoxide (1·77 N in methanol) followed by precipitation with ether. Upon standing for several days at room temperature, the white salts derived from benzophenone, m.p. 100° decomp.), and benzaldehyde, m.p. 80° (decomp.), assumed the pale red colour of their diazo-compounds while the yellow fluorenone derivative, m.p. 150° (decomp.), appeared to undergo no decomposition.

Solutions of the salts (*ca.* 10^{-3} molar) in $LiAlH_4$-distilled 2-methyltetrahydrofuran were thoroughly deaerated *in vacuo* and sealed in 4 mm. O.D. quartz tubes. Photolyses were carried out at −196° in an optical-transmission cavity on a Varian V-4502-15 spectrometer, using the full or Pyrex-filtered radiation of a General Electric AH-6 high-pressure Hg lamp. The benzophenonehydrazone salt showed diphenylmethylene spin resonance absorptions after 5 min. (unfiltered irradiation) at 1062, 4655, 5420, and 7780 gauss (frequency = 9240 Mc./sec.). Two reported weak signals at 1500—2000 gauss,[1a] in addition to those observed, were not found at this sample concentration.[7] A broad line centred at 3295 gauss ($g = 2{\cdot}002 \pm 0{\cdot}003$), which grew in intensity with irradiation time, arose from photodecomposition of 2-methyltetrahydrofuran. Use of a Pyrex filter minimized the height of the absorption at $g = 2{\cdot}002$ but decreased the rate of hydrazone decomposition. Intensities of the absorptions remained nearly constant after irradiation was interrupted so long as the sample tube remained immersed in liquid nitrogen. Warming the sample sufficiently to permit diffusion through the matrix caused immediate disappearance of e.p.r. signals and the visible colour of diphenylmethylene.[7] Products recovered from the melted matrix included lithium toluene-*p*-sulphinate, λ_{max} 259, 263 mμ (H_2O).

With this general procedure the reported e.p.r. spectra of fluorenylidene (biphenylenemethylene)[1b] and phenylmethylene[1b] were obtained. Phenylmethylene was found to be short-lived in 2-methyltetrahydrofuran glass, with signals persisting for only 4—5 min. after irradiation ceased. This apparently results from our choice of matrix material since 2-methyltetrahydrofuran forms a comparatively soft glass which may allow diffusion.[1c] Its use as a solvent was dictated by its ability to dissolve lithium salts of toluene-*p*-sulphonylhydrazones.

This general method for the generation of matrix isolated carbenes and methylenes should have wide application since their diazo-precursors frequently are non-isolable or dangerously reactive.

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