

Radical Anions of Aliphatic Diazenes

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Radical anions were generated by reduction of aliphatic diazenes with sodium-potassium alloy combined with u.v. irradiation (primary alkyl azo compounds), sodium-potassium alloy (secondary and tertiary alkyl azo compounds) and with crotylpotassium combined with u.v. irradiation (primary, secondary, and tertiary alkyl azo compounds); nitrogen hyperfine coupling constants range from 0.775 to 0.883 mT.

Radical anions of aromatic azo compounds can easily be prepared by reduction with a variety of reagents,¹ *i.e.* reaction with potassium metal in dimethoxymethane, reaction with enolates, or simply autoxidation of the corresponding hydrazine in dimethyl sulphoxide in presence of base. Except for the

radical anion of diethyl azodicarboxylate^{1,2} these procedures were not successful for aliphatic diazenes.

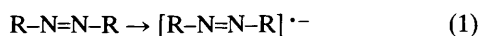
We have now found that radical anions of primary, secondary, and tertiary aliphatic azo-compounds can be generated for e.s.r. studies. Table 1 lists the hyperfine splitting

Table 1. Hyperfine splitting constants for radical anions of aliphatic azo compounds R-N=N-R.^a

R	a_N	$a_{H\alpha}$	g -Value	Line-width	Method of prep. ^b
Et	0.775	1.28	2.0042	0.17	B,C
(RR = -[CH ₂] ₃ -)	0.883	1.46	2.0043	0.23	B,C
Pr ⁱ	0.80	0.973	2.0042	0.06	A,B,C
(A) ^c	0.825	0.385	—	0.01	A,B,C
Bu ^t	0.825	0.029 ^d	2.0042	0.017	A,C
EtCMe ₂	0.809	—	2.0043	0.17	A,C
Et ₂ CMe	0.811	—	2.0041	0.11	A,C
Et ₃ C	0.807	—	2.0044	0.23	A,C
Pr ⁱ ₂ CMe	0.83	—	2.0043	0.32	A,C

^a a -Values (± 0.001) and line-width in mT; g -values ± 0.0001 . ^b A, Na-K alloy; B, Na-K alloy + $h\nu$; C, crotyl-K + $h\nu$. ^c (A) = 2,3-diazabicyclo [2.2.1]hept-2-ene; further unassigned couplings 0.255 (1H) and 0.024 mT (several H). ^d β -Hyperfine coupling.

constants of a number of such radical anions which were obtained by three different procedures at temperatures between -20 and $+20$ °C [reaction (1)].



Conditions: THF, $\text{MeCH=CHCH}_2^- \text{K}^+$, $h\nu$, or Na-K alloy, $h\nu$.

E.s.r. spectra of radical anions of primary alkyl diazenes are the most difficult to obtain. Reaction of a tetrahydrofuran (THF) solution with sodium-potassium alloy alone is not sufficient. The spectra were obtained by irradiation of a 1% (v/v) solution (1 ml) of the azo compound in THF, to which a few crystals (*ca.* 5–10 mg) of crotylpotassium³ or a small drop of Na-K alloy had been added, with light from a 1 kW Hg/Xe high-pressure lamp [Hanovia 977 B-1 with an UG-5-filter (Schott)] in the cavity of the e.s.r. spectrometer. Secondary and tertiary alkyl diazenes form radical anions also by thermal reaction with sodium-potassium alloy. Crotylpotassium in combination with u.v. illumination works also for the preparation of a number of radical anions of aromatic hydrocarbons.⁴ The role of the u.v. light in the case of crotylpotassium could be two-fold. Either an electron is transferred from an electronically excited state of the carbanion or photoioniza-

tion produces free electrons which are captured by the diazene. The latter process must occur with Na-K alloy.

The persistence of the diazene radical anions as judged from their e.s.r. spectra is tertiary > cyclic secondary \gg secondary \geq open-chain or cyclic primary. Hyperfine coupling constants for the two equivalent nitrogen atoms range from 0.775 to 0.883 mT and do not show a strong dependence on the nature of the alkyl groups. Compared with radical anions of aromatic diazenes (a_N *ca.* 0.48–0.50 mT) the magnitude of the coupling constants shows a stronger localization of the unpaired electron within the azo chromophore. The hyperfine coupling constants of the α -hydrogen atoms vary with the nature of the radical anion and reflect the respective preferred conformation.

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