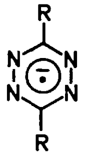
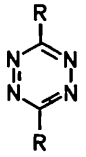
Radical Anions Derived from Alkyl-substituted 1,2,4,5-Tetrazines

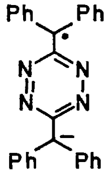
By HERBERT MALKUS, MERLE A. BATTISTE,* and ROBERT M. WHITE
(*Department of Chemistry, University of Florida, Gainesville, Florida* 32601)

Summary A new series of dialkyl-tetrazine radical anions has been prepared by a disproportionation reaction in basic Me_2SO, the mechanism apparently involving formation of two radical anion species, which have been detected in one case.

WE report a convenient procedure for generation of the previously unknown series of 3,6-dialkyl-1,2,4,5-tetrazine radical anions (**1**) by disproportionation of the corresponding dialkyl-tetrazine (**2**) in alkaline Me_2SO. In addition we report the first example (**3**) of a stable tetraza-*p*-xylylene radical anion. Previous work in the area consists of a study of the parent 1,2,4,5-tetrazine radical anion[1] and a cursory report of the radical anions of 3,6-diphenyltetrazine and 3,6-dimesitoyltetrazine.[2]


(1)


(2)

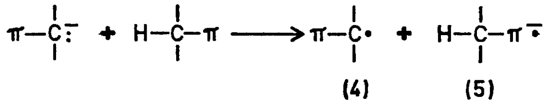

(3)

R = Me, Et, Pr^i, cyclopropyl, Ph_2CH

When tetrazine (**2**; R = Me) is added to a deoxygenated solution of $KOBu^t$ in Me_2SO, radical anion (**1**; R = Me), is formed displaying an e.s.r. spectrum consisting of 63 well defined lines (a^N = 4·87 G, a^H = 1·46 G). Similarly the radical anions (**1**; R = Et), Pr^i, cyclopropyl,† and Ph_2CH were generated. These same radicals were prepared by Na–K alloy reduction of the corresponding tetrazines in dimethoxyethane (DME) solution. The splitting constant of the radicals produced by both procedures are shown in the Table.

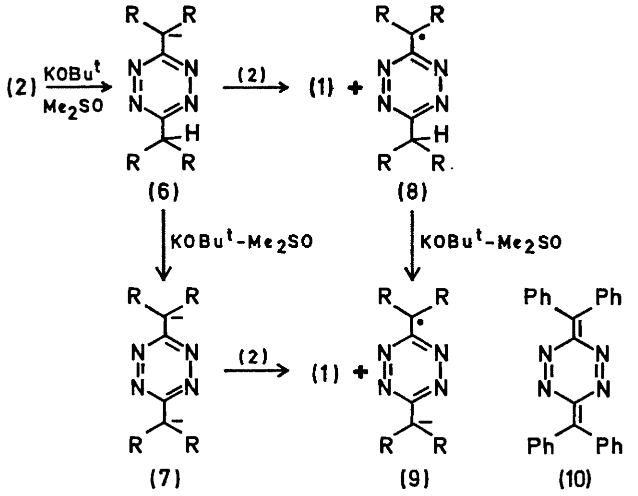
Disproportionation in basic solutions of aromatic compounds containing α hydrogen atoms proceeds through a π-electron exchange mechanism (Equation 1) as discussed by Russell and Janzen.[6] This mechanism has been shown to be of general nature in the disproportionation of substituted toluenes,[6] conjugated diketones,[7] and some heteroaromatics.[6] In each of these cases stable or relatively stable radical anions (**5**) have been detected while radicals corresponding to (**4**) have not been observed presumably due to their high reactivity. We have now observed what is apparently the first case in which two stable radical species corresponding to (**4**) and (**5**) are generated in a π-electron-transfer process.

The disproportionation of the dialkyl-tetrazines proceeds through deprotonation of (**2**) to yield either anion (**6**) or dianion (**7**) as shown in the Scheme. Electron transfer from either (**6**) or (**7**) to neutral tetrazine (**2**) yields tetrazine radical anion (**1**) and either radical (**8**) or radical anion (**9**), respectively. Radical (**8**) would be expected to deprotonate rapidly in basic solution to (**9**). In an excess of base no radicals are observed presumably due to complete ionization of (**2**). Radical anions (**9**; R = H) and/or alkyl, appear to be quite reactive as our attempts to detect these radical species by e.s.r. means have been unsuccessful. However, when aromatic substituents are present, radical anion (**9**; R = Ph) is readily observed.



$$\pi-\overset{|}{\underset{|}{C}}{:}^{-} + H-\overset{|}{\underset{|}{C}}-\pi \longrightarrow \pi-\overset{|}{\underset{|}{C}}\cdot + H-\overset{|}{\underset{|}{C}}-\pi^{\cdot -} \qquad (1)$$

(4) (5)



SCHEME

Treatment of 3,6-bis(diphenylmethyl)tetrazine (**2**; R = Ph_2CH) with deficient quantities of $KOBu^t$ in Me_2SO generates an e.s.r. spectrum comprised of two radical signals of nearly equal intensity. The broader of the two signals, a nonet of triplets (a^N = 5·07 G, a^H = 0·75 G), was independently obtained by reducing (**2**; R = Ph_2CH), with Na–K alloy in DME and is assigned to tetrazine radical anion (**1**; R = Ph_2CH). The narrower spectrum appears at a slightly lower *g* value as expected[8] for the hydrocarbon-like radical (**3**). This radical was prepared from an authentic sample of 3,6-bis(diphenylmethylene)tetrazine (**10**) by electron exchange from propiophenone in basic Me_2SO solution. The resulting e.s.r. spectrum was simulated for 12 equivalent *para* and *ortho* hydrogen atoms (a^H = 0·54 G) and four nitrogen atoms (a^N = 1·62 G). These assignments are in good agreement with the reported spectrum[9] of the radical cation of tetraphenyl-*p*-xylylene, in which the 0·69 G splitting may be assigned to the *para*- and *ortho*-phenyl

---

† The small a^H_α observed for the dicyclopropyltetrazine radical anion seems to be indicative of a bisected conformation. The larger β-splitting constant is assigned to the hydrogen atoms *cis* to the α-hydrogen atom in accord with the W-plan coupling arrangement.[3] The degree of conformational preference apparently lies between that found for the conjugated cyclopropyl group in cyclopropyl semidiones[4] and the sterically controlled conformation in cyclopropyl-nitroxides.[5]

hydrogen atoms. The decrease in a^N from 4·9 G in (**1**; R = Ph_2CH) to 1·8 G in (**3**) is due to the delocalization of approximately two-thirds of the unpaired spin into the diphenylmethylene system of the latter radical. A similar shift in spin density has been observed in the dimesitoyltetrazine radical anion.[2]

Partial support of this research by the National Science Foundation is gratefully acknowledged.

Hyperfine splitting constants of 3,6-*dialkyltetrazine radical anions,* (**1**)

R	Solvent	a^N (G)[d]	a^H_α (G)[d]	$a^H_{\beta 1}$ (G)[d]	$a^H_{\beta 2}$ (G)[d]
Me	[a]	4·87 (4)	1·46 (6)		
	[b]	5·0[c] (4)	1·6[c] (6)		
Et	[a]	4·94 (4)	1·15 (4)	0·17 (6)	
	[b]	5·05 (4)	1·25 (4)		
Pr^i	[a]	5·00 (4)	0·77 (2)	0·11 (12)	
	[b]	5·07 (4)	0·85 (2)		
Cyclopropyl	[a]	5·03 (4)	0·45 (2)	0·25 (4)	0·10 (4)
	[b]	5·05 (4)	0·5[c] (2)	0·24[c] (4)	0·12[c] (4)
Ph_2CH	[a]	5·07 (4)	0·65 (2)		
	[b]	5·07 (4)	0·75 (2)		

[a] Me_2SO–$KOBu^t$ at 30°.
[b] Na–K alloy in dimethoxyethane at 30°.
[c] Poorly resolved splitting.
[d] The number of equivalent atoms appears in parentheses.

(*Received, February* 20*th*, 1970; *Com.* 247.)

---

[1] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 1635.
[2] O. W. Maender and G. A. Russell, *J. Org. Chem.*, 1966, **31**, 442.
[3] G. A. Russell, "Radical Ions," ed., E. T. Kaiser and L. Kevan, Interscience, New York, 1968, p. 87 ff.
[4] G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, 1967, **89**, 160.
[5] G. R. Chalfont and H. Malkus, Abstracts, 158th National Meeting of the American Chemical Society, New York, Sept., 1969, ORGN 124.
[6] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1967, **89**, 307.
[7] E. R. Talaty and G. A. Russell, *J. Amer. Chem. Soc.*, 1965, **87**, 4867.
[8] M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," W. A. Benjamin, New York, 1966.
[9] H. Hart, J. S. Fleming, and J. L. Dye, *J. Amer. Chem. Soc.*, 1964, **86**, 2079.