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RADICAL STABILIZATION: SYNTHESIS AND DECOMPOSITION OF A β-KETODIAZENE

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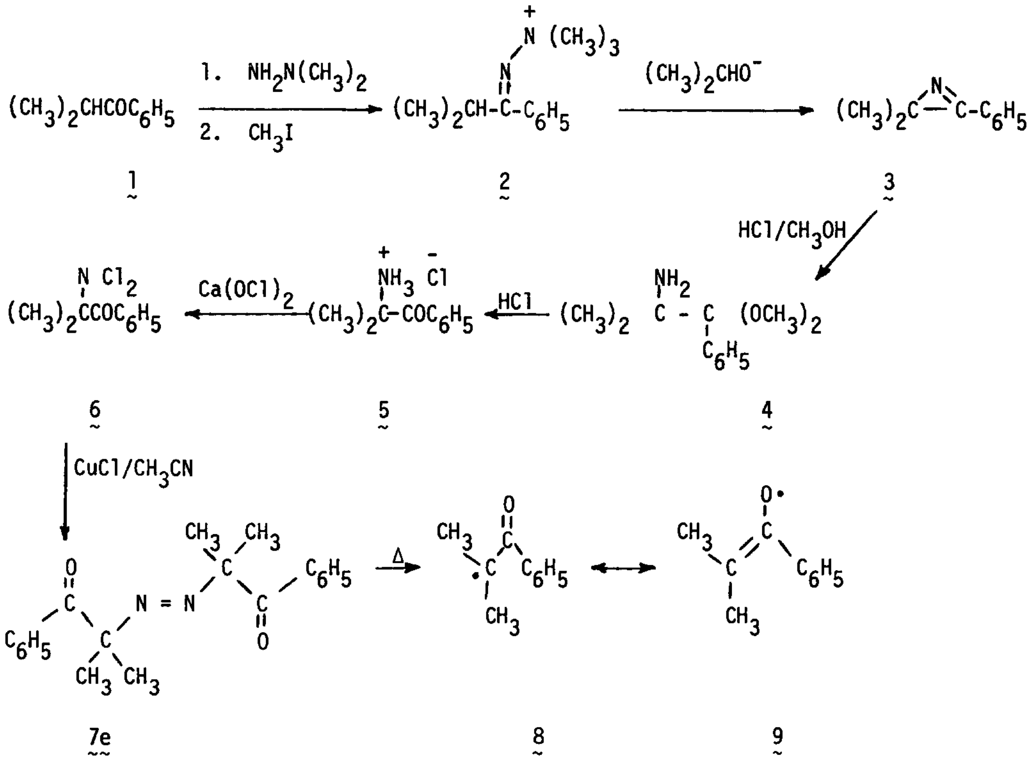
The synthesis and decomposition of bis(1,1-dimethyl-2-oxo-2-phenylethyl)diazene (7e) is described. The presence of a carbonyl group adjacent to a radical center greatly enhances the radical stability.

Substituent effects in cations and anions are well characterized and, for the most part, their rates of generation find excellent correlation with one or more of the many available substituent parameters.[1] Similar studies on radical abstractions from substituted toluenes are likewise numerous[2] but the interpretation of the results is a matter of some controversy. While the rates of hydrogen abstraction correlate with σ or σ^+, two radically different viewpoints are used to explain the results; some favor transition state effects[3] and others ground state factors.[4,5] These systems thus appear sensitive to polarization and provide little if any information regarding the effects important to stabilization of radicals.

Our approach to the study of radical substituent effects has relied on the use of substituted diazenes (7) as a model system free of polarization in which rates of decomposition have been argued to reflect differences in radical stability.[6] To a first approximation these results show that radicals are stabilized better by good anion favoring groups than by good cation favoring groups. A substituent particularly important to this interpretation is the carbonyl group which stabilizes anions but destabilizes cations.[7] Our previous attempts to prepare an appropriately labeled diazene were unsuccessful.[8]

We report here the synthesis, rates of decomposition, and the products of thermolysis of bis(1,1-dimethyl-2-oxo-2-phenylethyl)diazene (7e) which produces the radical equivalent of an acyl anion. This compound was prepared from the known ketoamine (5)[9] as shown below.



The keto diazene (7e) was characterized by: microanalysis; mp 71-72^{o}C; NMR ($CDCl_3$) δ 1.53 (s,6H) and 7.25-7.72 (m,5H); UV(hexane) 323 (ε231), 246 (ε16,175) and 196 nm (ε41,110); and the first order rates of decomposition are listed in Table 1.

The comparative data listed in Table 2 indicate that the rate of decomposition of 7e is considerably enhanced by the carbonyl group. Previous arguments[6] have ruled out, except in special cases,[16] steric ground state contributions as being major factors. It thus appears that carbonyl groups are indeed important in stabilizing radicals, presumably by delocalization into the available pi system (8<—>9). Similar resonance stabilization accounts for the enhanced rate of formation of radicals from 7d, f and g. This is supported by our preliminary molecular orbital calculations (STO-3G) which indicate substantial (slightly greater than 50%) delocalization of the odd electron into the carbonyl[12] and by ESR studies on 8 generated from phenyl isopropyl ketone and tert-butoxy radicals.[17] Of particular interest is the fact that the rate of decomposition of 7e is four times faster than AIBN (7d) a compound commonly used as a radical initiator. While this factor is real, it is small enough to avoid ruling out some amount of steric ground state acceleration of 7e over that of AIBN. It is pertinent to note that since the ESR spectrum of 8 indicates little or no spin density delocalized into the aromatic ring,[17] the phenyl group provides little electronic stabilization to this radical.

The products of thermolysis at 70°C in cumene were determined by GC using bromobenzene as an internal standard and are shown below. The relative internal balance was > 95% and the products are those expected for coupling (10) and disproportionation (11 and 12). It is interesting to contrast radical 8, which dimerizes to the extent of 70%, to those formed from thermolysis of 7a and 7f which couple to the extent < 20% and > 90% respectively.[14,18] The intermediate value of 70% for 7e is in keeping with percent dimerization reflecting radical stability.[14]

Table 1

Rates of Decomposition of (7e)

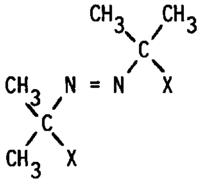
Temp °C	k, $sec^{-1} \times 10^4$ ave of three runs
70.0	1.48
79.8	5.64
90.1	17.9

$\Delta H^\ddagger = 30.0 \pm 1.2$

$\Delta S^\ddagger = 11.1 \pm 3.5$

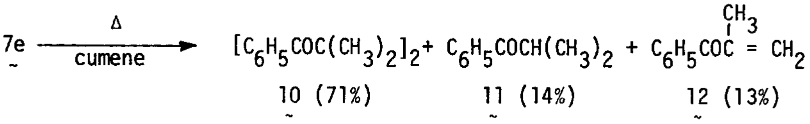
Table 2

Rates of Substituted Diazenes



7

X	Rel Rate 100°C	ref
a) CH_3	1.0	10
b) OCH_3	1.0×10^1	11
c) Cl	1.1×10^1	12
d) CN	2.9×10^5	13
e) COC_6H_5	1.1×10^6	This work
f) C_6H_5	3.9×10^6	14
g) $CH = CH_2$	9.0×10^6	15



$$7e \xrightarrow[\text{cumene}]{\Delta} [C_6H_5COC(CH_3)_2]_2 + C_6H_5COCH(CH_3)_2 + C_6H_5CO\overset{CH_3}{\overset{|}{C}} = CH_2$$

10 (71%) 11 (14%) 12 (13%)

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References

1. J.E. Leffler and E. Grunwald "Rates and Equilibria of Organic Reactions" Ch 7, John Wiley, New York 1963.
2. G.A. Russell in "Free Radicals", J.K. Kochi, Ed., Vol 3, Ch 7, John Wiley New York, 1973.
3. W.H. Davis and W.A.Pryor J. Am. Chem. Soc., 99 6365 (1977).
4. A.A. Zavitsas and J.A. Pinto, J. Am. Chem., 94, 7390 (1972).
5. A.A. Zavitsas and G.M. Hanna, J. Org. Chem., 40, 3782 (1975); D.D. Tanner, P.W. Samal, T. C-S. Rua and R. Henriquez, J. Am. Chem. Soc., 101, 1168 (1979).
6. B.K. Bandlish, A.W. Garner, M.L. Hodges, and J.W. Timberlake, J. Am. Chem. Soc., 97, 5856 (1975).
7. X. Creary, "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., September, 1979, Org. 143.
8. S.K. Chiu, M. Dube, L. Keifer, S. Szilagyi and J.W. Timberlake, J. Org. Chem., 43, 61 (1978).
9. H.E. Baumgarten, J.M. Peterson and D.C. Wolf, J. Org. Chem., 28, 2369 (1963); N.J. Leonard and B. Zwanenburg, J. Am. Chem. Soc., 89, 4456 (1967); R.F. Parcell, Chem and Ind., 1396 (1963).
10. J.C. Martin and J.W. Timberlake, J. Am. Chem. Soc., 92, 978 (1970).
11. J.W. Timberlake and M.L. Hodges, Tetrahedron Letters, 4147 (1970).
12. M.F. Dube, Ph.D. Dissertation, The University of New Orleans, New Orleans, La., 1978.
13. J.C. Roy, R.R. Williams, J.R. Nash and W.H. Harnill, J. Am. Chem. Soc., 78 519 (1958).
14. S.F. Nelsen and P.D. Bartlett J. Am. Chem. Soc., 88, 137 (1966).
15. P.S. Engel and D.J. Bishop, J. Am. Chem.Soc., 94, 2148 (1972).
16. J.W. Timberlake and A.W. Garner, J. Org. Chem., 41, 1666 (1976); A.W. Garner, J.W. Timberlake, P.S. Engel and R.A. Melaugh, J. Am. Chem. Soc., 97, 7377 (1975).
17. G. Brunton, H.C. McBay, and K.U. Ingold, J. Am. Chem. Soc., 99, 4447 (1977).
18. P. Kovacic, R.R. Flynn, J.F. Gormish, A.H. Kappelman, and J.R. Shelton, J. Org. Chem., 34, 3312 (1969).

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