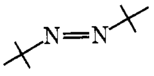
Communications

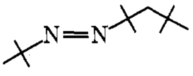
Steric Acceleration in Dialkyldiazene (Azoalkane) Decompositions. 2[1]

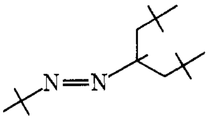
Summary: Rates of decomposition of several highly branched dialkyldiazenes have been determined; these data support a concerted mechanism of decomposition and show that tertiary alkyl radicals can be generated thermally at temperatures below 100 °C.

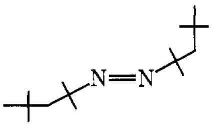
Sir: It has been shown that dialkyldiazenes are sensitive probes of radical stability and that structural changes can bring about pronounced rate enhancements.[1,2] Furthermore, these rate enhancements can be separated into electronic (resonance and inductive) and steric effects.[3] The latter were recognized as being important contributors in the work of Overberger and co-workers[4] and have more recently been examined by others.[5,6] In particular, we were intrigued by the idea that these steric effects could be enlarged to the point that alkyl radicals could be generated at relatively low temperatures, temperatures comparable with those used for azobisisobutyronitrile (AIBN) initiated reactions. These radical precursors might then be useful as polymer initiators without introducing "toxic dusting" problems.[7]

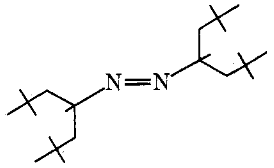
Rate constants for *tert*-butyl(2,4,4-trimethyl-2-pentyl)diazene (2), *tert*-butyl(2,2,4,6,6-pentamethyl-4-heptyl)diazene (3), and bis(2,2,4,6,6-pentamethyl-4-heptyl)diazene (5) chosen for this purpose are listed in Table I. Their activation parameters along with those for 1 and 4 reported earlier are shown in Table II. The previous study[6] was shown to be most consistent with a concerted decomposition mechanism because substitution of a methyl hydrogen in 1 with a *tert*-butyl group (2) gave a relative rate of decomposition intermediate to 1 and 4, the latter having hydrogens replaced by *tert*-butyl groups on both sides. This effect would not be expected for a stepwise decomposition.[6] The same argument can be advanced here in comparing 1, 3, and 5. The unsymmetrical analog (3) is once again intermediate in rate between the symmetrical analogs 1 and 5.

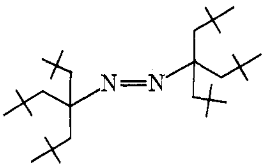

1


2


3


4


5


6

It is interesting to note that there appears to be a dilution effect as the number of *tert*-butyl replacements is monotonically increased. Thus a replacement on one side (2) and two replacements (one on each side, 4) lower $\Delta G^{\ddagger}_{100}$ by successive increments of 2.7 kcal mol^{-1}. However, two replacements on the same side (3) does not have the same effect as one replacement on each side; $\Delta\Delta G^{\ddagger}_{100}$ of 1–3 = 4.5 kcal mol^{-1} while $\Delta\Delta G^{\ddagger}_{100}$ of 1–4 = 5.4 kcal mol^{-1} (i.e., $\Delta G^{\ddagger}_{100}$ of 3 $\neq$ that of 4). It is, however, not unexpected to find a lack of additive energy since the steric requirements of these groups should be different. Even so, correction for this dilution still predicts that 6 would decompose approximately seven times faster than AIBN[8] and work is progressing toward a test of this prediction.

Comparison of steric acceleration in diazenes with those of perester decompositions is also informative. Table III shows the much greater sensitivity of diazenes toward steric changes, a result recognized earlier and reconfirmed here.[9-11] Table III also contains a comparison of solvolytic rate data with diazene thermolyses. These results are in complete agreement with Rüchardt's conclusion that steric requirements in solvolysis and diazene thermolyses are linearly related.[5]

Acknowledgment. The authors wish to thank the Petroleum Research Fund, administered by the American Chemical Society, and the Army Research Office for support of this

Table I. Rate Constants for 2, 3 and 5

Compd	Temp, °C	$k \times 10^4$, sec^{-1}	Compd	Temp, °C	$k \times 10^4$, sec^{-1}	Compd	Temp, °C	$k \times 10^4$, sec^{-1}
2	155.0	1.61	3	140.0	1.93	5	100.1	3.03
	160.0	2.52		145.4	3.29		105.1	5.03
	165.7	4.75		150.1	5.29		109.2	7.62
	170.0	7.25		155.1	8.20		115.0	15.1
	175.0	11.9		160.0	12.9		120.1	24.8
	180.0	19.8		164.8	21.8		125.0	39.0

Table II. Activation Parameters for 1, 2, 3, 4 and 5

Compd	Rel rate, 100 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, 100 °C
1	1	42.2 ± 0.3[a]	16.1 ± 0.6[a]	36.2
2	35	38.1 ± 0.6	12.3 ± 1.3	33.5
3	402	33.8 ± 0.6	5.7 ± 1.4	31.7
4	1320	31.7 ± 0.6[b,c]	2.4 ± 1.4[b,c]	30.8
5	57000	30.0 ± 0.5	5.2 ± 1.2	28.1

[a] J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.*, 92, 978 (1970). [b] Reference 3. [c] J. W. Timberlake and M. L. Hodges, *J. Am. Chem.*, 95, 634 (1973).

Table III. Comparison of Diazenes, *tert*-Butyl Peresters, and Alkyl Chlorides

R	RN=NR, rel rate, 100 °C	RCO_3-$C(CH_3)_3$, rel rate, 25 °C	RCl,[a] rel rate, 25 °C (80% ethanol)
$(CH_3)_3C$–	1	1[b]	1
$(CH_3)_3CCH_2C(CH_3)_2$–	35	4.1[b]	21
$CH_3C(CH_2C(CH_3)_3)_2$–	57000	5.7[c]	580

[a] E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 2892 (1975). [b] Reference 11. [c] Professor T. T. Tidwell, private communication.

project. The authors are grateful to Professors T. Tidwell and C. Rüchardt for unpublished results and useful discussions.

References and Notes

(1) J. W. Timberlake and M. L. Hodges, *Tetrahedron Lett.*, 4147 (1970).

(2) J. W. Timberlake, A. W. Garner, and M. L. Hodges, *Tetrahedron Lett.*, 309 (1973).

(3) B. K. Bandlish, A. W. Garner, M. L. Hodges, and J. W. Timberlake, *J. Am. Chem. Soc.*, **97**, 5856 (1975).

(4) C. G. Overberger, W. F. Hale, M. B. Berenbaum, and A. B. Finestone, *J. Am. Chem. Soc.*, **76**, 6185 (1954).

(5) W. Duismann and C. Rüchardt, *Tetrahedron Lett.*, 4517 (1974).

(6) A. W. Garner, J. W. Timberlake, P. S. Engel, and R. A. Melaugh, *J. Am. Chem. Soc.*, **97**, 7377 (1975).

(7) R. E. MacLeay and C. S. Sheppard, Canadian Patent 924299 (1973). For example, AIBN cannot be used for products by the food and drug packaging industries or as a blowing agent in the plastic foam market because of the high level of toxic residue left in the finished product.

(8) $\Delta G^\ddagger_6 \simeq \Delta G^\ddagger_1 - 2[2(\Delta G^\ddagger_1 - \Delta G^\ddagger_4) - (\Delta G^\ddagger_1 - \Delta G^\ddagger_5)] = 25.4$ kcal mol^{-1}.

(9) C Rüchardt, *Int. Congr. Pure Appl. Chem., 23rd, 1971*, **4**, 223 (1971).

(10) G. J. Abruscato and T. T. Tidwell, *J. Am. Chem. Soc.*, **94**, 672 (1972).

(11) J. A. Ernst, C. Thankachan, and T. T. Tidwell, *J. Org. Chem.*, **39**, 3614 (1974).

J. W. Timberlake,* A. W. Garner

Department of Chemistry, University of New Orleans
New Orleans, Louisiana 70122

Received January 29, 1976

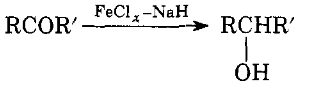
Iron Chloride–Sodium Hydride System as New Reducing Reagents of Carbonyl Compounds

Summary: Iron(II or III) chloride and sodium hydride in tetrahydrofuran provide an effective reagent system for the reduction of ketones and aldehydes to the corresponding alcohols under mild conditions.

Sir: Recently much attention has been paid toward reducing reagents consisting of a mixture of metal compounds. For example, an addition of metal salts to metal hydrides is known to modify the reducing ability.[1] Further, the reagents consisting of $TiCl_3$–$LiAlH_4$[2] or *n*-BuLi–WCl_6[3] have been demonstrated to be effective for the reductive coupling of carbonyl compounds to olefins and the reduction of epoxides to olefins. We have also described the deoxygenation of epoxides to olefins with $FeCl_3$–*n*-BuLi system using the strong affinity of iron to oxygen atom.[4] We now report the iron chloride–sodium hydride systems as effective reagents for the reduction of ketones and aldehydes to the corresponding alcohols under mild reaction conditions.

Sodium hydride is known as a strong base to abstract a proton from a carbonyl compound giving an enolate anion, but has, in general, little reducing ability for carbonyl compounds. A few exceptions reported so far are reductions of nonenolizable ketones under such drastic conditions as refluxing with sodium hydride in xylene[5] or as heating in an aprotic solvent.[6] Reductions of usual carbonyl compounds, however, were observed when they were added at room temperature to the yellow suspension generated by addition of iron(III) chloride to sodium hydride in tetrahydrofuran (THF). Table I reveals that the reagent is effective for aromatic aldehydes and ketones as well as aliphatic carbonyl compounds. The molar ratio of the hydride to the chloride seriously affected the yields of alcohols. The best result was obtained with the ratio of sodium hydride to iron(III) chloride being 3:1 and, above or below this ratio, diminished yields of alcohols were observed. It is important to note that the reducing procedure is specific, since no alcohol formation was observed when sodium hydride was added to a solution of a carbonyl compound and iron(III) chloride.

Table I. Reduction of Carbonyl Compounds



$$\mathrm{RCOR'} \xrightarrow{\mathrm{FeCl}_x\text{–NaH}} \mathrm{RC\underset{\displaystyle OH}{\underset{|}{H}}R'}$$

R	R′	$FeCl_3$–NaH[a] Time, h	$FeCl_3$–NaH[a] Yield of alcohol,[c] %	$FeCl_2$–NaH[b] Time, h	$FeCl_2$–NaH[b] Yield of alcohol,[c] %
Ph	Me	30	82	45	72
Ph	Ph	43	81	45	0
n-C_6H_{13}	Me	42	75	48	88
–$(CH_2)_5$–		24	75	30	77
Ph	H	24	85	48	48
n-C_7H_{15}	H	24	79	24	77

[a] Typically, a solution of iron(III) chloride (14 mg equiv) in THF (20 ml) was added to a suspension of sodium hydride (42 mg equiv) in THF (5 ml), and the mixture was stirred for 4 h at room temperature under an atmosphere of argon. Then a solution of a carbonyl compound (2 mmol) in THF (2 ml) was added and stirring was continued at room temperature. [b] Iron(II) chloride (20 mg equiv) and sodium hydride (40 mg equiv) were mixed in THF (15 ml) at 0–5 °C; then a solution of carbonyl compound (2 mmol) in THF (2 ml) was added with continuous stirring at the same temperature. [c] Yields were determined by GLC.

The reducing system was prepared as follows. To a stirred solution of sodium hydride in THF, was added dropwise a solution of iron(III) chloride in THF. Evolution of molecular hydrogen was observed and a yellow suspension was obtained after one third the amount of hydrogen based on the hydride used was evolved. The stability of the reducing reagent depends on the solvent used. Ether cannot be used as a solvent, since fast decomposition of the reducing reagent prevents the reduction. Even in the case of using THF as the solvent, further evolution of hydrogen was observed when carbonyl compounds were added to the suspension. Thus, to obtain satisfactory results, an excess of the reducing reagent to carbonyl compounds was necessary. The reaction mixture became dark as the reduction proceeded. Although the reducing species is not exactly identified at present, it is considered to be some kind of iron hydride,[7] because no formation of coupling product, i.e., glycol derivatives,[8] which were obtained by the reduction of carbonyl compounds with lower valent metal compound,[9] were observed in the reduction.

It is interesting to note that the use of iron(II) chloride in place of iron(III) chloride in the reduction gave different results.[10] As shown in Table I, the reduction of enolizable aliphatic carbonyl compounds with iron(II) chloride[11]–sodium hydride system in THF gave also the corresponding