

Facile Substitution of Aliphatic C–H Bonds by the Tetramethylsuccinimidyl Radical during Thermal Decomposition of the *N*-Bromotetramethylsuccinimide/Tetramethylsuccinimide Anion Complex

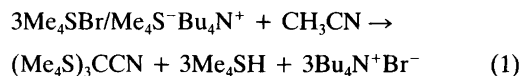
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The thermal decomposition of the *N*-bromosuccinimide/tetrabutylammonium succinimide complex in acetonitrile gives succinimide (ca. 65 % yield) and polymaleimide (ca. 10 % yield).¹ This reaction was assumed to involve electron transfer within the complex, forming a cage radical anion/radical pair. Nitrogen–bromine bond cleavage produces bromide ion and a pair of succinimidyl radicals, one of which abstracts a hydrogen from the other to give succinimide and a diradical which rearranges to maleimide.

In order to block the intraradical hydrogen abstraction pathway, we have selected the complex² between *N*-bromotetramethylsuccinimide (abbreviated Me₄SBr) and tetrabutylammonium tetramethylsuccinimide (Me₄SBr/Me₄S[−]Bu₄N⁺, **1**) and thermally decomposed it in several solvents. Much to our surprise, the expected and trivial formation of tetramethylsuccinimide was accompanied by products of substitution of solvent C–H bonds by tetramethylsuccinimidyl, highlighted by the totally unpredictable formation of tris(tetramethylsuccinimido)acetonitrile in acetonitrile according to eqn. (1)!



Reflux of **1** (0.2 M) in acetonitrile for 45 h gave bromide ion (100 %), Me₄SH (68 %), Me₄SBU (2 %) and (Me₄S)₃CCN[§] (22 %). A trace amount of Me₄SCH₂CN was also detected, indicating that the monosubstituted compound might be the precursor of the tris-substituted derivative. Reflux of **1** in benzene with pre-synthesized Me₄SCH₂CN present gave a 51 % yield of (Me₄S)₃CCN in addition to Me₄SH (59 %); an analogous run with phthalimidoacetonitrile as the second reactant gave phthalimido-bis(tetramethylsuccinimido)-acetonitrile (42 %) together with Me₄SH (65 %).

The half-life of the complex in acetonitrile was ca. 17 h at 59.4 °C, 5 h at 69.7 °C and 1.7 h at 80 °C (corresponding to an activation energy of 26 kcal mol^{−1}). In acetone, the reaction was much faster, being essentially complete after 10 min at room temperature, i.e. more than 10⁴ times faster than the acetonitrile reaction. The products, be-

[§]All new compounds were identified and characterized by elemental analysis, GLC/MS and ¹H and ¹³C NMR spectrometry.

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sides Me_4SH (52%), were $\text{Me}_4\text{SCH}_2\text{COCH}_3$ (30%) and $(\text{Me}_4\text{S})_2\text{CHCOCH}_3$ (8%). The phenomenology of this reaction is fascinating, in that an initially colourless 0.05–0.1 M solution of **1** in acetone after 4–5 min suddenly attains a blue colour which builds up to a maximum intensity (almost black solution!) within 1 min and then rapidly fades away, being replaced by an orange colour which more slowly fades to pale yellow. The blue colour corresponded to absorption at λ_{max} 557 nm, at which wavelength the trace shown in Fig. 1 was monitored. The build-up of the blue colour coincided with the onset of weak chemiluminescence (see Fig. 1), the intensity of which was proportional to the square of **[1]**, as also observed in the decomposition of the *N*-bromosuccinimide/succinimide anion complex.¹ The rate of decay of the light signal, ca. 0.3 min^{-1} , was almost the same as the rate of fading of the orange colour, ca. 0.5 min^{-1} . Finally, cyclic voltammograms run on a reacting solution showed the appearance of a new oxidation peak at 0.4 V vs. NHE during the build-up of the blue colour.

In order to prevent hydrogen abstraction by $\text{Me}_4\text{S}^\cdot$ from the solvent the reaction was run in benzene under reflux. By analogy with the known behaviour of imidyl radicals with regard to substitution of C–H bonds in benzene,³ we had expected to isolate a good yield of *N*-phenyltetramethylsuccinimide. However, no trace of this product was detectable; instead, Me_4SH (59%, evidently formed by abstracting hydrogens from primarily tetrabutylammonium ion) and a high-boiling product (11%), tentatively identified (GLC/MS) as a bis(tetramethylsuccinimido) de-

rivative of tributylamine, were obtained. Addition of an equimolar amount of tributylamine to a decomposing solution of **1** in benzene increased the yield of the latter product by at least a factor of five. Other tested compounds (diethyl malonate, toluene) undergo tetramethylsuccinimido substitution to varying degrees.

Presently, we limit ourselves to describing the phenomenology of these remarkable reactions and will discuss the reaction mechanism later in a full report. However, we note that the mechanism suggested for the *N*-bromosuccinimide/succinimide anion reaction, involving the formation of a cage succinimidyl radical pair, is equally well applicable to the reactions of **1**. In particular, the combined action of the two radicals on a solvent molecule of the cage "wall" appears to be a satisfactory way of rationalizing the facile substitution of aliphatic C–H bonds by tetramethylsuccinimidyl.

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References

1. Ebersson, L., Barry, J. E., Finkelstein, M., Moore, W. M. and Ross, S. D. *Acta Chem. Scand., Ser. B* 39 (1985) 249; Barry, J. E., Finkelstein, M., Moore,

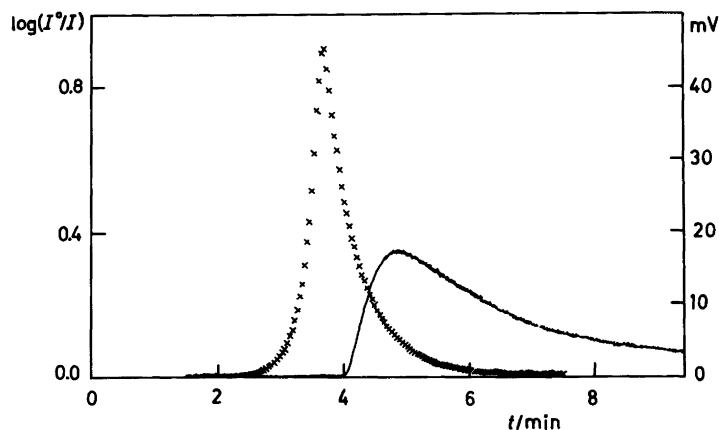


Fig. 1. The time dependence of the absorbance at 557 nm (crosses) and the light emission (solid line, measured as output/mV of the luminometer, right ordinate axis) of a 0.1 M solution of **1** in acetone at ambient temperature.

LETTER

- W. M., Ross, S. D., Ebersson, L. and Jönsson, L. J. *Org. Chem.* 47 (1982) 1292.
2. Barry, J. E., Finkelstein, M., Moore, W. M., Ross, S. D. and Ebersson, L. *Tetrahedron Lett.* 25 (1984) 2847.
3. Day, J. C., Govindaraj, N., McBain, D. S., Skell, P. S. and Tanko, J. M. *J. Org. Chem.* 51 (1986) 4959.

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