

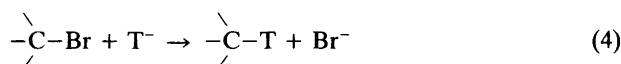
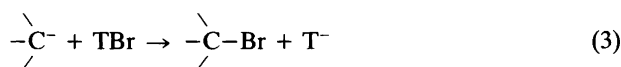
# A Reassignment of the Structure of the Persistent Radical from the Reaction between the Tetrabutylammonium *N*-Bromotetramethylsuccinimide/Tetramethylsuccinimide Complex and Acetone: An Enolate Radical

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In recent years, several novel *N*-bromomide reactivities have been identified.<sup>1</sup> As an example, *N*-bromosuccinimides form complexes with the corresponding succinimides<sup>2</sup> which are stable in crystal form and decompose fairly rapidly in solution.<sup>3,4</sup> The tetrabutylammonium *N*-bromotetramethylsuccinimide/tetramethylsuccinimide complex (**1**), lacking  $\alpha$ -hydrogens, is very stable and has been subjected to an X-ray crystallographic study<sup>5</sup> and shown to possess a linear symmetrical  $N \cdots Br \cdots N$  bond. It reacts with C–H acidic compounds with formation of *N*-tetramethylsuccinimido-substituted products via the bromo derivatives according to eqns. (1)–(4).<sup>4,6</sup> Thus acetonitrile can



T = *N*-tetramethylsuccinimidyl

be converted into tris(tetramethylsuccinimido)acetonitrile by this reagent.<sup>3,6</sup>

The reaction is sometimes accompanied by the formation of persistent radicals.<sup>7</sup> A clear-cut example is the radical from the treatment of 1,4-cyclohexanedione with **1** in acetonitrile, characterized by a nine-line EPR spectrum indicative of coupling between the odd electron and four equivalent nitrogens ( $a^N = 0.049$  mT). This radical was

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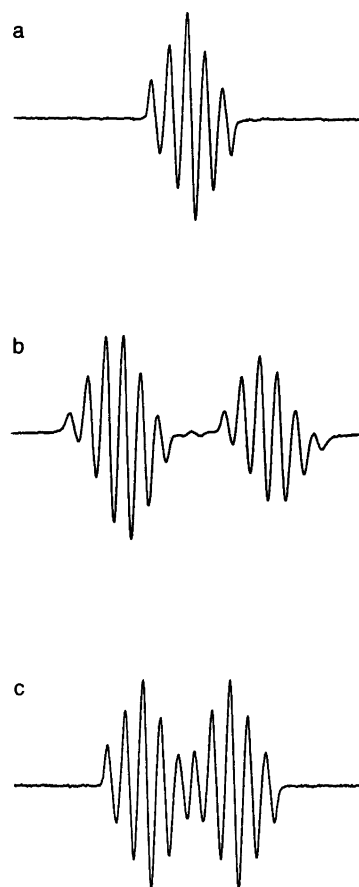
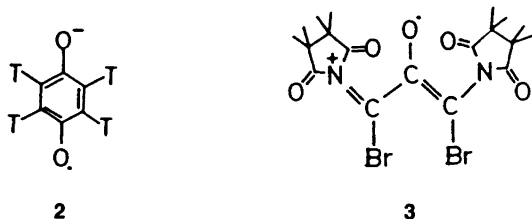


Fig. 1. EPR spectrum from a solution of **1** ( $\approx 0.34$  M) and a, acetone; b, [1,3-<sup>13</sup>C<sub>2</sub>]acetone and c, [2-<sup>13</sup>C]acetone in dichloromethane, the concentration of the appropriate acetone species being  $\approx 0.15$  M. The sweep width is 4.00 mT.

unequivocally identified as tetrakis(tetramethylsuccinimido)benzoquinone radical anion ( $T_4Q^{\cdot-}$ , **2**), accessible from independently synthesized  $T_4Q$ . Less obviously, but nevertheless rationally explicable, **2** was also formed from hexane-2,5-dione upon treatment with **1**.

The EPR signal from **1** and acetone or acetone- $d_6$  [Fig. 1a,  $a^N = 0.201$  mT (two N),  $g = 2.00462$  in dichloromethane] was initially<sup>7</sup> assigned to an oxyallyl radical cation with maximum symmetry (**3**) based upon evidence

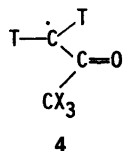


available at that time, in particular the fact that the same EPR spectrum appeared from treatment of pentabromoacetone or 1,1,3,3-tetrabromoacetone with **1**. However, additional experiments with  $[1,3-^{13}C_2]$ acetone and  $[2-^{13}C]$ acetone now unequivocally show that the radical has *two* equivalent nitrogens attached to one of the  $\alpha$  carbons of *one* acetone unit.

Thus  $[1,3-^{13}C_2]$ acetone and **1** in dichloromethane gave an EPR spectrum (Fig. 1b) consisting of a ca. 1:1 doublet of sextets (1:3:5:5:3:1, when the high- and low-field halves are averaged) with the parameters  $a^N = 0.201$  mT (two N),  $a^C = +1.737$  mT (one C),  $a^C = 0.194$  mT (one C), peak-to-peak line-width = 0.10 mT and  $g = 2.00462$ . The line-width of the low-field sextet (average 0.1001 mT) is lower than that of the high-field sextet (average 0.1015 mT), supporting the view that the largest coupling, 1.737 mT, has the positive value.

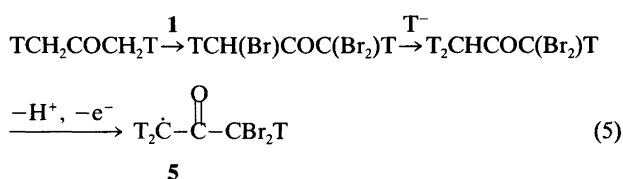
$[2-^{13}C]$ Acetone and **1** in dichloromethane gave an EPR signal (Fig. 1c) consisting of a doublet (1:1) of quintets (1:2:3:2:1) with the parameters  $a^N = 0.201$  mT (two N),  $a^C = -0.981$  mT, peak-to-peak line-width = 0.10 mT and  $g = 2.00462$ . Here the line-width of the low-field quintet (0.1029 mT) was higher than that of the high-field quintet (0.1018 mT).

Thus there is unequivocal evidence that two T groups and one of the original methyl groups of one acetone unit are connected, as shown in the enolate radical **4**. The EPR



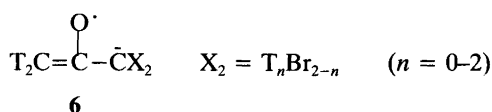
spectrum (Fig. 1a) does not reveal much about the possible structure of  $CX_3$ , since no further fine structure could be observed, in spite of much work aimed at further resolution

of the quintet. The apparent line shape of this quintet is almost purely Gaussian and the dependence of the signal upon microwave power follows qualitatively the pattern for homogeneous absorption with Lorentzian line shape of a peak-to-peak line-width of  $\approx 0.03$  mT. This phenomenon could either be explained by additional couplings of lower magnitude than the apparent line-width or by overlapping of several, very similar spectra. Both cases could be accommodated by assuming that  $CX_3$  is equal to one or several species where  $X_3 = T_nBr_{3-n}$  ( $n = 0-3$ ). Thus, for example, species **5** would be easily accessible from  $TCH_2COCH_2T$ , so far the most effective precursor of the quintet species, by triple bromination and one T substitution, as shown in eqn. (5).



This suggestion would seem to be at odds with the fact that  $T_2CHCOCH_3$  only gives a very weak EPR spectrum of the same quintet as in Fig. 1a (<0.5% of the intensity in experiments with  $TCH_2COCH_2T$ ; we initially ascribed this finding to the presence of traces of  $TCH_2COCH_2T$  in the sample of  $T_2CHCOCH_3$ , but triple recrystallization left the weak EPR spectrum intact). However, the much higher acidity of the methine group of  $T_2CHCOCH_3$  relative to that of the methyl group ensures that the first bromination occurs with high probability at  $C^1$  and thus chances of forming **5** are lost or at least strongly diminished.

A second and perhaps aesthetically more pleasing structure would be a cross-conjugated radical anion of type **6**, which, in principle, would be directly accessible from 1,1,3,3-tetrabromoacetone.



The observed  $^{13}C$  hyperfine splitting constants agree qualitatively with the calculated electronic structure of model enolate radicals (an oxy-vinyl structure of type **4**, with all three atoms  $sp^2$ ). Within the framework of the Karplus-Fraenkel theory<sup>8</sup> and using polarisation parameters of similar radicals<sup>9</sup> the spin populations in the enolate radical can be estimated from the experimental  $^{13}C$  couplings. The HMO method and McLachlan's approach<sup>10</sup> afford a similar picture; INDO calculations on model enolate radical structures, optimized by molecular mechanics calculations, parallel the experimental values of the  $^{13}C$  couplings, including the signs. Considering the approximations involved, we do not think that calculations alone can decide between structures **4** and **6**.

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