Electron-Transfer Processes. VIII. Coupling Reactions of Radicals with Carbanions[1]

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Abstract: It is demonstrated that the reaction of the 2-nitro-2-propyl anion with 2-chloro-2-nitropropane, 2-bromo-2-nitropropane, *p*-nitrobenzyl chloride, or *p*-nitrobenzyldimethylsulfonium bromide proceeds *via* a free-radical chain mechanism that can be initiated photochemically and can be inhibited by hexaphenylethane or *p*-dinitrobenzene. The product in all cases is the C-alkylated derivative of the 2-nitro-2-propyl anion. The presence of oxygen completely prevents the coupling reaction as might be expected if a free radical is the precursor of the coupled product. 2-Chloro-2-nitropropane also reacts with malonic ester and ethylmalonic ester to yield the C-alkylated product *via* a radical chain mechanism.

In recent years there has been a general reappraisal of the chemistry of nitroaromatic compounds in basic solution. It is now well recognized that the nitroaromatic radical anion ($\mathrm{ArNO_2}\cdot^-$) is quite stable[3] and may participate as an intermediate in numerous organic processes.[4] Nitroaromatic radical anions are readily formed by reaction of a wide variety of carbanions with the nitroaromatic,[5] or by photolysis of nitroaromatics in basic organic solvents.[6] The ability of nitroaromatics to enter into electron transfer reactions has been invoked to explain the nitroaromatic-catalyzed oxidation of fluorene anion,[7] the spontaneous disproportionation of *o*-nitrotoluene, the spontaneous dimerization of *p*-nitrotoluene in basic solution,[8] and the formation of *o*- and *p*-nitrophenols in the Wohl reaction.[8] Other easily reducible groups, such as conjugated dicarbonyl functions, nitroso groups, or azo linkages, can be expected to give rise to oxidation–reduction processes similar to the reactions observed for the nitroaromatics.

$$\mathrm{R}:^- + \mathrm{ArNO_2} \longrightarrow \mathrm{ArNO_2}\cdot^- + [\mathrm{R}\cdot]$$

$$\mathrm{ArNO_2} \xrightarrow[\mathrm{RH}]{h\nu} [\mathrm{ArNO_2H}\cdot] \xrightarrow{\mathrm{B^-}} \mathrm{ArNO_2}\cdot^-$$

The concept of electron transfer can be extended to reactions that formally appear to involve nucleophilic substitution. One possible reaction sequence is given in Scheme I. The reaction need not involve truly free radicals but may involve a radical pair in a solvent cage. This mechanism was suggested by Beringer, Galton, and Huang for processes werein R:⁻ is the 2-phenyl-1,3-diketoindanyl anion and QZ is the diphenyliodonium salt ($((\mathrm{C_6H_5})_2\mathrm{I^+})$).[9] Kerber, Urry, and Kornblum have suggested that this mechanism can be applied to the alkylation reaction wherein $\mathrm{R^-}$ is the 2-nitro-2-propyl anion and QZ is *o*- or *p*-nitrobenzyl chloride.[10] We now present evidence that in this reaction, and the analogous reaction of 2-nitro-2-propyl anion with 2-halo-2-nitropropanes, a free-radical chain mechanism occurs (Scheme II).[11] Additional support for this mechanism has been provided by Professor Kornblum and his students.[12]

Scheme I

$$\begin{array}{c}
\mathrm{R}:^- + \mathrm{QZ} \longrightarrow \mathrm{R}\cdot + \mathrm{QZ}\cdot^- \\
\mathrm{QZ}\cdot^- \longrightarrow \mathrm{Q}\cdot + \mathrm{Z}^- \\
\underline{\mathrm{Q}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{R\text{-}Q}} \\
\mathrm{R}:^- + \mathrm{QZ} \longrightarrow \mathrm{R\text{-}Q} + \mathrm{Z}^-
\end{array}$$

Scheme II

$$\begin{array}{c}
[\mathrm{RX}]\cdot^- \longrightarrow \mathrm{R}\cdot + \mathrm{X}^- \\
\mathrm{R}\cdot + \mathrm{R'}:^- \longrightarrow \mathrm{RR'}:^- \\
\mathrm{RR'}:^- + \mathrm{RX} \rightleftarrows \mathrm{RR'} + [\mathrm{RX}]\cdot^-
\end{array}$$

Our approach has been to examine, in the presence of oxygen, reactions of carbanions that are stable to molecular oxygen.[13] In the presence of oxygen, free radicals formed should be trapped to yield oxidation products rather than coupled products. Electron spin resonance (esr) spectroscopy has also aided in elucidating the course of several reactions.

Reaction of Lithium Salt of 2-Nitropropane with *p*-Nitrobenzyl Chloride. The reaction of salts of aliphatic nitro compounds with various substituted benzyl compounds has long been recognized as possessing several unique features. This uniqueness derives from characteristics peculiar to both the anion and the benzyl compound.

The anion derived from an aliphatic nitro compound is an ambident anion capable of covalency formation at either carbon or oxygen. In most instances, oxygen alkylation occurs to produce an intermediate nitronic

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[1] Reactions of Resonance Stabilized Anions. XXX. This work was supported by grants from the Petroleum Research Foundation and the National Science Foundation.

[2] National Institutes of Health Predoctoral Fellow, 1965–1967.

[3] G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

[4] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

[5] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **87**, 1807 (1965).

[6] G. A. Russell and E. J. Geels, *Tetrahedron Letters*, 1333 (1963).

[7] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

[8] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **89**, 300 (1967).

[9] F. M. Beringer, S. A. Galton, and J. J. Huang, *ibid.*, **84**, 2819 (1962).

[10] R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **87**, 4520 (1965).

[11] G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

[12] N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5662 (1966); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5606 (1966); N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 725 (1967).

[13] G. A. Russell, A. J. Moye, and K. L. Nagpal, *ibid.*, **84**, 4154 (1962).

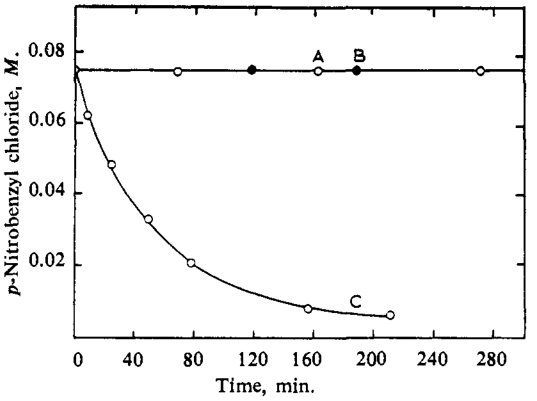

Figure 1. Concentration of *p*-nitrobenzyl chloride in a solution originally 0.075 *M* in *p*-nitrobenzyl chloride and 0.075 *M* in the lithium salt of 2-nitropropane in ethanol at 0°: A, in the dark under a nitrogen atmosphere; B, illuminated in presence of oxygen; C, illuminated under a nitrogen atmosphere.

ester which decomposes to the corresponding carbonyl compound and oxime.[14]

$$R_2C{=}NO_2^- + R'CH_2X \longrightarrow [R_2C{=}N^+(O^-)OCH_2R'] \longrightarrow R_2C{=}NOH + R'CHO$$

Carbon alkylation occurs only when the benzyl system is substituted in the *ortho* and/or *para* positions with a nitro group and a poor leaving group is present on the benzyl carbon.[14,15]

In determining the effect of molecular oxygen on the course of the reaction of the lithium salt of 2-nitropropane with *p*-nitrobenzyl chloride in ethanol or DMF, it has been found that yields of greater than 90% of carbon coupled product (p-$NO_2C_6H_4CH_2C(CH_3)_2NO_2$) are formed when the reaction is conducted in an inert atmosphere but that no detectable coupled product results in the presence of oxygen. Instead, the 2-nitro-2-propyl anion is converted to acetone and nitrite ion by a free-radical chain oxidation with the absorption of 0.5 mol of oxygen/mol of anion (Scheme III, R = 2-nitro-2-propyl).[7,16]

Scheme III

$$R^- + RH \longrightarrow R\cdot + RH\cdot^-$$
$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + R^- \longrightarrow ROO{:}^- + R\cdot$$
$$ROO{:}^- + R^- \longrightarrow 2RO{:}^-$$
$$RO{:}^- \longrightarrow (CH_3)_2CO + NO_2^-$$

In the absence of *p*-nitrobenzyl chloride, the 2-nitro-2-propyl anion is stable to oxygen. During the oxidation reaction the *p*-nitrobenzyl chloride is not consumed (Figure 1), even though the rates of the oxidation and coupling reactions are roughly equivalent. Oxygen can interrupt the chain process (*vide infra*) by trapping the intermediate radicals or by destruction of the radical anion of *p*-nitrobenzyl chloride (step 1, Scheme II).[17]

Figure 1 also illustrates the catalytic effect of light on the coupling reaction in the absence of oxygen. Note that no chloro compound is consumed when the reaction is performed in ethanol in total darkness while a quite rapid reaction occurs when the reaction solution is irradiated; the rate of the oxidation reaction is also affected profoundly by light.

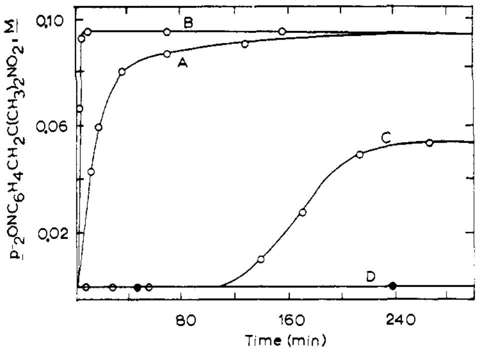

Figure 2. Concentration of p-$O_2NC_6H_4CH_2C(CH_3)_2NO_2$ (by glpc) formed in the reaction of *p*-nitrobenzyl chloride with the lithium salt of 2-nitropropane (0.20 *M*) in DMF at 0° under a nitrogen atmosphere: A, C, D, in the dark; B, illuminated; C, in presence of 0.02 *M p*-dinitrobenzene.

The coupling reaction in the absence of oxygen can be inhibited by free-radical inhibitors such as *p*-dinitrobenzene and hexaphenylethane (HPE) which acts as a source of triphenylmethyl radicals. Figure 2 demonstrates the catalytic effect of light and the inhibitory effect of *p*-dinitrobenzene and HPE on the reaction of the 2-nitro-2-propyl anion with *p*-nitrobenzyl chloride in DMF. It is seen that in this aprotic solvent there exists a dark reaction but that light causes the reaction to proceed much faster. The added *p*-dinitrobenzene completely prevents the formation of coupled product for many hours while 5% HPE inhibits the chain process for approximately 2 hr after which time the reaction proceeds quite rapidly to yield 55% carbon-alkylated product. In the absence of inhibitors, an isolated yield of 91% coupled product is formed in less than 2 hr in the dark (Figure 2). The decreased yield in product observed in the former case apparently results from consumption of *p*-nitrobenzyl chloride in a nonradical process producing *p*-nitrobenzaldehyde *via* oxygen alkylation.[15b]

These results clearly demand a free-radical chain process for the coupling reaction and exclude the nonchain mechanism of Scheme I. The effect of light could conceivably be explained as producing *p*-nitrobenzyl chloride radical anions which would eliminate chloride ion to form the chain-carrying *p*-nitrobenzyl radical (Scheme IV). The radical anions could

Scheme IV

$$p\text{-}ClCH_2C_6H_4NO_2 \xrightarrow[\text{THF or EtOH}]{h\nu} [p\text{-}ClCH_2C_6H_4NO_2H\cdot] \xrightarrow{B^-} p\text{-}ClCH_2C_6H_4NO_2\,^- \quad (1)$$

$$[p\text{-}ClCH_2C_6H_4NO_2]\cdot^- \longrightarrow Cl^- + p\text{-}NO_2C_6H_4CH_2\cdot \quad (2)$$

$$p\text{-}NO_2C_6H_4CH_2\cdot + (CH_3)_2C{=}NO_2^- \longrightarrow \underset{\mathbf{1}}{[p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2]} \quad (3)$$

$$\mathbf{1} + p\text{-}NO_2C_6H_4CH_2Cl \rightleftarrows p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + [p\text{-}NO_2C_6H_4CH_2Cl]\cdot^- \quad (4)$$

$$\mathbf{1} + p\text{-}NO_2C_6H_4NO_2 \longrightarrow p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + [p\text{-}NO_2C_6H_4NO_2]\,^- \quad (5)$$

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(14) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, 67, 1167 (1945).

(15) (a) H. B. Hass and M. L. Bender, *ibid.*, 71, 1767, 3482 (1949); (b) N. Kornblum, P. Pink, and K. V. Yorka, *ibid.*, 83, 2779 (1961).

(16) G. A. Russell, *ibid.*, 76, 1595 (1954).

(17) The nitrobenzene radical anion (potassium salt in DMSO or THF) rapidly reacts with oxygen to give potassium superoxide and nitrobenzene in quantitative yield.[3]

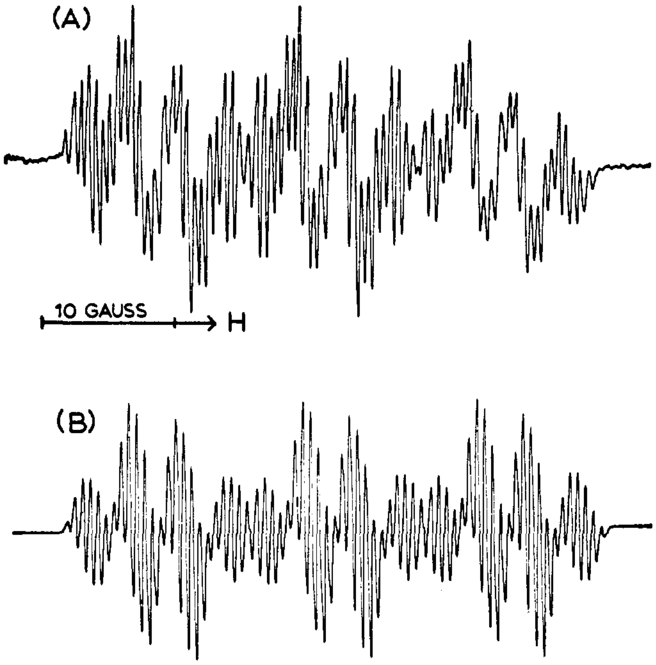


Figure 3. First derivative esr spectra attributed to **2** in ethanol solution at 25°: A, experimental spectrum formed by illumination of *m*-nitrobenzyl chloride in presence of lithium ethoxide; B, computed spectrum using hyperfine splitting constants given in text.

be formed by proton loss from the adduct resulting from hydrogen abstraction from solvent by the n $\rightarrow$ π^* excited nitro compound.[6,18]

p-Dinitrobenzene exerts its inhibitory influence presumably by competing effectively with *p*-nitrobenzyl chloride in reaction 4 (*i.e.*, reaction 4 is replaced by reaction 5).[10] Alternatively, it is well known that aromatic nitro compounds are good inhibitors for free-radical chain processes in which only neutral radicals exist,[19] and although the process by which this occurs is not known with certainty, perhaps *p*-dinitrobenzene interacts with the neutral chain-carrying *p*-nitrobenzyl radical. The triphenylmethyl radicals probably intercept and couple with *p*-nitrobenzyl radicals thus interrupting the chain process.

The unreactivity of *m*-nitrobenzyl chloride in the coupling reaction can be rationalized by considering step 2 in the chain process.[10] We have observed that the photochemical coupling reaction between 1.0 equivalent of 2-nitro-2-propyl anion and 0.5 equiv of *m*- and *p*-nitrobenzyl chlorides in ethanol proceeds until the *p*-nitrobenzyl chloride is consumed; none of the *m*-nitrobenzyl chloride is attacked. Photolysis of *m*-nitrobenzyl chloride in the presence of either the 2-nitro-2-propyl anion or ethoxide anion in ethanol produces the stable *m*-nitrobenzyl chloride radical anion **2** (Figure 3). Photolysis of *p*-nitrobenzyl chloride in the presence of the 2-nitro-2-propyl anion results only in the formation of the radical anion of the carbon alkylated product **1** (Figure 4). This radical was also formed by irradiation of the coupled product and the lithium salt of 2-nitropropane or lithium ethoxide in ethanol; no signal was detected without light. Thus

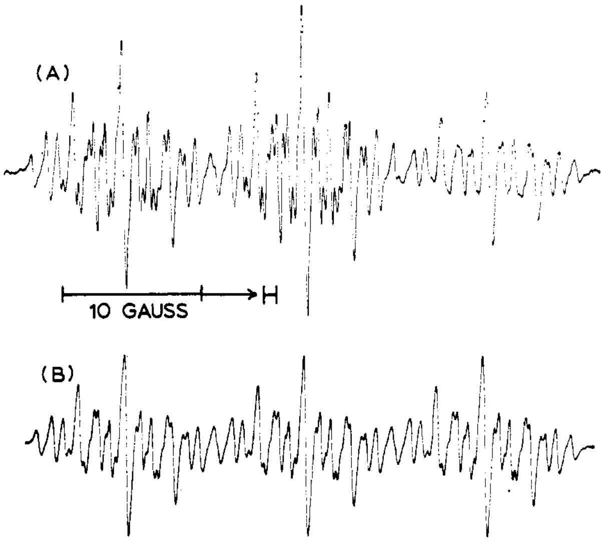
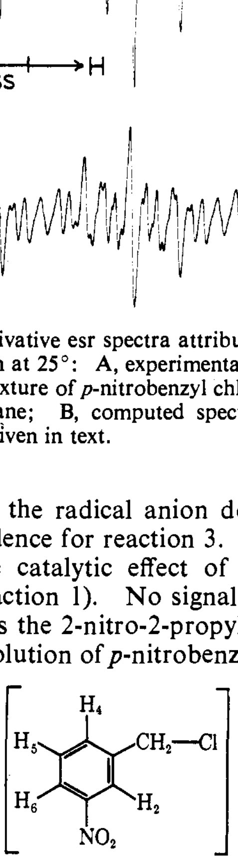


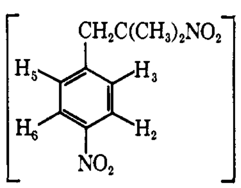
Figure 4. First derivative esr spectra attributed to lithium salt of **1** in ethanol solution at 25°: A, experimental spectrum formed by illumination of a mixture of *p*-nitrobenzyl chloride and the lithium salt of 2-nitropropane; B, computed spectrum using hyperfine splitting constants given in text.

the detection of the radical anion does not constitute unequivocal evidence for reaction 3. However, it does demonstrate the catalytic effect of light on electron transfer (*i.e.*, reaction 1). No signal is observed when ethoxide replaces the 2-nitro-2-propyl anion in an irradiated ethanol solution of *p*-nitrobenzyl chloride.[20]



2

$a^N = 12.93$ gauss
$a_{2,6}^H = 3.42$ gauss
$a_4^H = 3.58$ gauss
$a_5^H = a_{CH_2}^H = a^{Cl} = 0.57$ gauss



1

$a^N = 12.73$ gauss
$a_{2,6}^H = 3.30$ gauss
$a_{3,5}^H = 1.12$ gauss
$a_{CH_2}^H = 1.845$ gauss

These results constitute direct proof of the instability of the radical anion derived from *p*-nitrobenzyl chloride as contrasted to that derived from *m*-nitrobenzyl chloride[10] and support the proposed chain mechanism since a key step in the propagation of the chain demands that the radical anion of the chloro compound be unstable with respect to elimination of chloride ion (reaction 2).

The uniqueness of the *o*- and/or *p*-nitro benzyl chlorides in bringing about carbon alkylation in reaction

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(18) H. J. S. Winkler, H. Winkler, and R. Bollinger, *Chem. Commun.*, 70 (1966); R. Hurley and A. C. Testa, *J. Am Chem. Soc.*, 88, 4330 (1966).

(19) P. D. Bartlett and H. Kwart, *ibid.*, 74, 3969 (1952); R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1653 (1960).

(20) A short-lived species assumed to be the radical anion of *p*-nitrobenzyl chloride has been observed by workers employing a flow technique. However, no hyperfine splitting by chlorine is reported: P. L. Kolker and W. A. Waters, *Proc. Chem. Soc.*, 55 (1963).

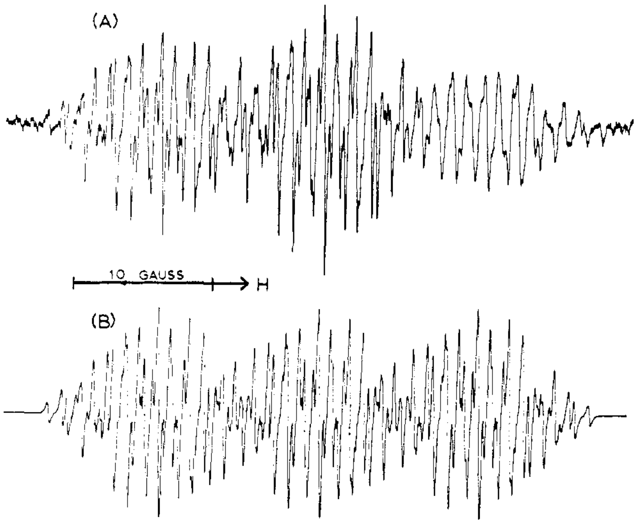
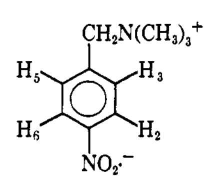


Figure 5. First derivative esr spectra attributed to the lithium salt of **3** in ethanol at 25°: A, experimental spectrum obtained by illumination of *p*-nitrobenzyltrimethylammonium bromide and the lithium salt of 2-nitropropane in ethanol at 25°; B, computed spectrum using hyperfine splitting constants given in text.

with the 2-nitro-2-propyl anion is thus readily explained by the free-radical chain mechanism schematically outlined in reactions 1–4. Apparently, only nitro substituents render the aromatic system sufficiently electronegative to accept an electron in a transfer process (reaction 1) and the positioning of the nitro group *ortho* and *para* to the carbon to which the leaving group is attached determines if the radical anion formed in the transfer process is intrinsically unstable with respect to an internal elimination of the leaving group (reaction 2). It was shown that *p*-cyanobenzyl chloride gives no carbon alkylated product in reaction with the lithium salt of 2-nitropropane even when the reaction was irradiated. This reflects the lower reducibility of cyano-substituted systems[21] as well as the inability of the cyano group to generate a radical anion when photolyzed in basic solution analogous to the nitro substituent.[6] When *p*-nitrobenzyltrimethylammonium bromide was irradiated at room temperature with 2-nitro-2-propyl anion, the radical anion of the ammonium salt (3) was observed (Figure 5). It has been demonstrated that higher temperatures are necessary before the elimination of trimethylamine and formation of carbon coupled product occurred in this case.[22]

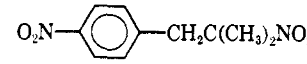


3

$a_{NO_2}{}^{N} = 11.42$ gauss
$a_{2,6}{}^{H} = 3.25$ gauss
$a_{R_4N^+}{}^{N} = 2.22$ gauss
$a_{3,5}{}^{H} = 1.01$ gauss
$a_{CH_2}{}^{H} = 1.40$ gauss

The truly unique step in the chain process is the coupling of the *p*-nitrobenzyl radical with the 2-nitro-2-propyl anion to produce the radical anion of the carbon alkylated product (reaction 3). This interaction has been suggested to occur in the photochemical coupling of phenyllithium in ethyl ether although no conclusive proof for such a process was obtained.[23] Kornblum has also suggested that the 2-nitro-2-propyl radical will attack the nitrite ion to yield the 2,2-dinitropropyl radical anion.[24] However, this radical anion would be expected to be unstable with respect to elimination of nitrite ion just as the radical anions of 2-bromo- and 2-chloro-2-nitropropane eliminate halide ion (*vide infra*). This conclusion is supported by esr results; whereas the radical anion of 2-nitropropane is sufficiently stable to be observed, no radicals were detected when 2-chloro-2-nitropropane or 2,2-dinitropropane were electrolytically reduced.[25]

The initial product of reaction 3 might be expected to be **4** rather than the observed radical anion in which the unpaired electron is delocalized throughout the



4

π system. The radical anion initially formed could rapidly isomerize intramolecularly[26] to the observed radical anion or enter into reaction 4 prior to isomerization. Alternatively, reaction 4, because of its reversibility, could provide a mechanism for intermolecular isomerization of the radical anion of the coupled product.

Reaction of Lithium Salt of 2-Nitropropane with 2-Chloro-2-nitropropane and 2-Bromo-2-nitropropane. The preparation of 2,3-dimethyl-2,3-dinitrobutane from the reaction of the sodium salt of 2-nitropropane with 2-halo-2-nitropropanes was first reported in 1940 by Seigle and Hass;[27] subsequent work resulted in a great increase in yield of the coupled dimer.[28]

We have shown that this reaction also proceeds *via* a free-radical chain process completely analogous to the reaction of the anion with *p*-nitrobenzyl chloride. In the absence of molecular oxygen an isolated yield of 86% of 2,3-dimethyl-2,3-dinitrobutane can be obtained from the reaction of the 2-nitro-2-propyl anion with 2-bromo-2-nitropropane in absolute ethanol; in the presence of oxygen, no detectable dimer is formed. Essentially none of the 2-bromo-2-nitropropane is consumed in the oxidation process; approximately 0.5 mol of oxygen/mol of 2-nitro-2-propyl anion is consumed in the oxidation and the anion is converted to acetone and nitrite ion in yields of 79 and 92%, respectively.[16]

The coupling and oxidation reactions can be catalyzed and inhibited. Figure 6 illustrates the profound effect of light on the rate of consumption of 2-chloro-2-nitropropane. A similar effect is noted for 2-bromo-2-nitropropane, although in this case a slow dark reaction persists. The addition of less than 1% of HPE completely inhibits the formation of coupled product for approximately 1 hr under our conditions of illumination

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[21] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

[22] H. Shechter and R. B. Kaplan, *ibid.*, **73**, 1883 (1951).

[23] E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **87**, 4964 (1965).

[24] H. Feuer, *Tetrahedron Suppl.*, **1**, 107 (1964) (see footnote 16).

[25] L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962).

[26] J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

[27] L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

[28] D. E. Hudgin, "Synthesis of Nitro Derivatives of Aliphatic Acids," unpublished M.S. Thesis, Library, Purdue University, 1940.

after which time a rapid reaction ensues; in the absence of this small amount of inhibitor the reaction is about 90% complete after 1 hr. In the dark at 0°, HPE will completely inhibit the coupling reactions of the 2-halo-2-nitropropanes in ethanol for days.

These results clearly demonstrate the chain character of the coupling of the 2-nitro-2-propyl anion with the 2-halo-2-nitropropanes and it is logical to assume that the same process is occurring here as was shown for the reaction of the anion with *p*-nitrobenzyl chloride.

Reaction of Other Anions with 2-Chloro-2-nitropropane. The reaction of the lithium salt of diethyl ethylmalonate with 2-chloro-2-nitropropane exhibits the usual characteristics of a free-radical chain process. There is no reaction in the dark for long periods of time but a fairly rapid consumption of chloro compound occurs when the solution is irradiated. A small amount of *p*-dinitrobenzene has a pronounced inhibitory effect on the light reaction. A preparative scale reaction gave a moderate yield of carbon alkylated product **5**.[29]

$$(CH_3CH_2O_2C)_2C(C_2H_5)C(CH_3)_2NO_2$$

5

The reaction of unsubstituted malonic ester anion with 2-chloro-2-nitropropane likewise is catalyzed by light and inhibited by *p*-dinitrobenzene; virtually no reaction occurs in the dark. However, the simple carbon alkylated coupled product is not obtained but instead the isopropylidene derivative formed by the loss of the elements of nitrous acid from the initially formed coupled product is isolated in rather poor yield.[29] It appears that the reaction of the anions derived from malonic ester and substituted malonic ester with 2-chloro-2-nitropropane is a chain process involving the coupling of the 2-nitro-2-propyl radical with the malonate anions.

The reaction of lithium thiophenoxide with 2-chloro-2-nitropropane also exhibits photolytic catalysis but all attempts to isolate the expected product, 2-nitropropyl-2-thiophenyl ether, failed. The anions derived from ω-(methylsulfinyl)acetophenone and ω,ω-diphenylacetophenone appeared to react with 2-chloro-2-nitropropane but only small amounts of unidentified oil were isolated from the reactions. However, the latter compound is known to be photochemically unstable[30] and such behavior accounts for the formation of a mixture of products when the anion with 2-chloro-2-nitropropane is irradiated. Phenyllithium reacts quite vigorously with the chloro compound to produce a small amount of biphenyl and much polymeric material apparently from 2-nitropropene generated in the reaction.[31] In any event, the expected coupled product probably could not be formed by a free-radical chain process involving the coupling of 2-nitro-2-propyl radical with the phenyl anion since it has been postulated that the 2-nitro-2-phenylpropane radical anion is an unstable species and decomposes to yield the α,α-dimethylbenzyl radical.[32]

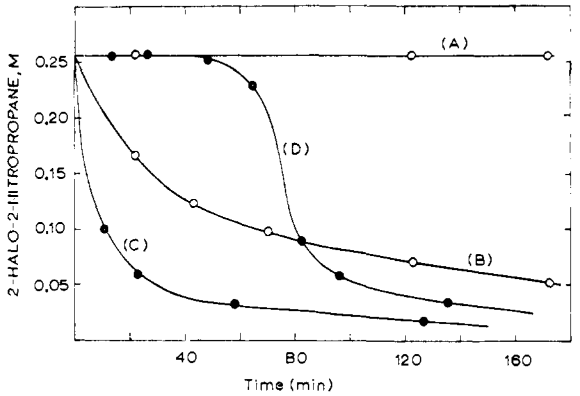

Figure 6. Concentration of 2-halo-2-nitropropane (by glpc) measured in the reaction of 2.56 mmol of 2-halo-2-nitropropanes and 2.56 mmol of the potassium salt of 2-nitropropane at 30° in ethanol solution under a nitrogen atmosphere: A, in the dark, 0.256 *M* 2-chloro-2-nitropropane; B, illuminated, 0.256 *M* 2-chloro-2-nitropropane; C, illuminated, 0.256 *M* 2-bromo-2-nitropropane; D, illuminated, 0.256 *M* 2-bromo-2-nitropropane, 0.002 *M* hexaphenylethane.

The following compounds do not react with 2-chloro-2-nitropropane in ethanol at 30° in either the light or dark: lithium salt of 2,6-dimethylphenol, lithium bromide, lithium nitrite, and ammonium thiocyanate.

In addition, the ter Meer reaction,[33] the reaction of bromomalononitrile with potassium hydroxide to produce pentacyanopropenide ion,[34] and the coupling of acetylacetone or ethyl acetoacetate by iodine and base are not affected by molecular oxygen and it can be concluded that free radicals are not intermediates in these reactions.

The reaction of 2-phenyl-1,3-indandione anion with diphenyliodonium tosylate in DMF to produce 2,2-diphenyl-1,3-indandione,[9] although strongly catalyzed by light, is only slightly affected by oxygen, *p*-dinitrobenzene, or HPE, and apparently does not proceed *via* a chain mechanism although radicals are probably involved as reaction intermediates.[9]

Reaction of Various *p*-Nitrobenzyl Sulfonium Salts with Hydroxide and 2-Nitropropane Anions. *p*-Nitrobenzyldimethylsulfonium tosylate reacts with aqueous sodium hydroxide to produce an almost quantitative yield of *p,p'*-dinitrostilbene; a mechanism involving *p*-nitrophenyl carbene has been postulated to account for the reaction (Scheme V).[35]

Scheme V

$$[p\text{-}O_2NC_6H_4CH_2S(CH_3)_2]^+ + OH^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} p\text{-}O_2NC_6H_4\overset{-}{C}H\overset{+}{S}(CH_3)_2 \quad (6)$$

$$p\text{-}O_2NC_6H_4\overset{-}{C}H\overset{+}{S}(CH_3)_2 \xrightarrow{\text{slow}} p\text{-}O_2NC_6H_4CH\colon + (CH_3)_2S \quad (7)$$

$$p\text{-}O_2NC_6H_4CH\colon + p\text{-}O_2NC_6H_4\overset{-}{C}H\overset{+}{S}(CH_3)_2 \xrightarrow{\text{fast}} p\text{-}O_2NC_6H_4CH(\overset{-}{C}HC_6H_4NO_2)\overset{+}{S}(CH_3)_2 \quad (8)$$

$$p\text{-}O_2NC_6H_4CH(\overset{-}{C}HC_6H_4NO_2)\overset{+}{S}(CH_3)_2 \xrightarrow{\text{fast}} p\text{-}O_2NC_6H_4CH{=}CHC_6H_4NO_2\text{-}p + (CH_3)_2S \quad (9)$$

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(29) E. E. van Tamelen and G. van Zyl, *J. Am. Chem. Soc.*, **71**, 835 (1949).

(30) A. Schönberg, A. K. Fateen, and S. M. A. R. Owan, *ibid.*, **78**, 1224 (1956).

(31) A. T. Blomquist, W. J. Tapp, and J. R. Johnson, *ibid.*, **67**, 1519 (1945).

(32) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. J. Jura, *ibid.*, **86**, 631 (1964).

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(35) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961); I. Rothberg and E. R. Thornton, *ibid.*, **86**, 3296 (1964).

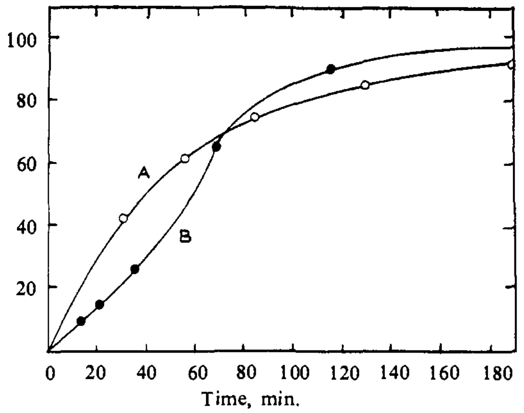
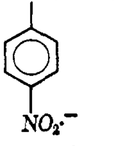


Figure 7. Reaction of 0.020 *M* *p*-nitrobenzyldimethylsulfonium bromide with 0.030 *M* hydroxide ion under a nitrogen atmosphere in ethanol-water (90:10) solution at 13°; A, illuminated; B, illuminated, 0.0016 *M* hexaphenylethane.

The reaction of *p*-nitrobenzyldimethylsulfonium bromide with aqueous base has been investigated by us to determine if the process leading to *p,p'*-dinitrostilbene might not indeed proceed *via* a free-radical chain mechanism involving the coupling of the *p*-nitrobenzyl radical with a molecule of ylide similar to the reaction of *p*-nitrobenzyl chloride with the 2-nitro-2-propyl anion.

It was found that the reaction is catalyzed markedly by light; in 50% aqueous ethanol at 12.5° the reaction is virtually complete after 8 hr when irradiated but is only about 10% complete if conducted in total darkness. However, this effect of light is not incompatible with the proposed carbene mechanism[35] for it has been demonstrated that ylides can be decomposed by light to carbenes.[36] The rate of reaction increases as the per cent of alcohol in the solvent is increased, presumably reflecting the increased concentration of ylide. However, increasing the per cent alcohol results in a decreased yield of *p,p'*-dinitrostilbene; a satisfactory yield of product is obtained when 50% alcohol is used but only 60.5% is isolated in 90% aqueous alcohol.

Application of the esr techniques satisfactory for the production and detection of **3** failed to produce **6**. Apparently **6** must decompose readily to the *p*-nitrobenzyl radical. Radical ions could not be detected under the conditions of stilbene formation perhaps because of the low solubility of the stilbene and its reduction products in aqueous solutions.



6

Employing the usual technique of determining the effect of oxygen on the reaction resulted in oxygen absorption and inhibition of stilbene formation together with the formation of 68% of *p,p'*-dinitrostilbene oxide and 23% crude *p*-nitrobenzoic acid. The formation of the stilbene oxide was not unexpected[35] and does not distinguish between the postulated carbene and free-radical mechanisms since it is not possible to ascertain if molecular oxygen attacked the *p*-nitrobenzyl radical, or the *p*-nitrophenyl carbene, or the ylide itself.

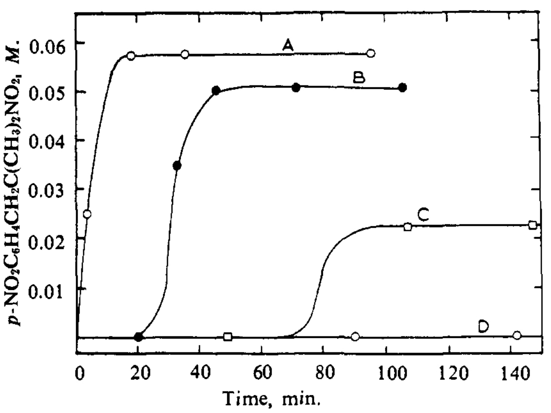


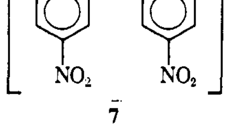
Figure 8. Concentration of p-$O_2NC_6H_4CH_2C(CH_3)_2NO_2$ formed in the reaction of the lithium salt of 2-nitropropane (0.150 *M*) with *p*-nitrobenzyldimethylsulfonium bromide (0.075 *M*) under a nitrogen atmosphere in ethanol at 30°: A, illuminated; B, illuminated, 0.0037 *M* hexaphenylethane; C, illuminated, 0.0075 *M* hexaphenylethane; D, in the dark, 0.0075 *M* hexaphenylethane.

HPE appears to inhibit the reaction in 90% aqueous ethanol somewhat at the onset but after approximately 40 min the reaction proceeds unrestrained. Figure 7 demonstrates that the initial rate of reaction is about one-half that exhibited without the triphenylmethyl inhibitor. There is no effect on the rate of reaction if a large excess of nitrobenzene is present in the reaction solution.

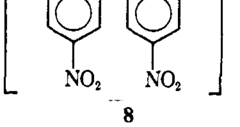
The reaction of the lithium salt of 2-nitropropane with *p*-nitrobenzyldimethylsulfonium bromide in ethanol produces the carbon alkylated coupled product in good yield. Moreover, just as with *p*-nitrobenzyl chloride, the reaction can be catalyzed by light and inhibited by HPE for periods of time dependent upon the concentration of inhibitor (Figure 8). It is noted that the yield of coupled product is also dependent upon the concentration of HPE which illustrates that another process is occurring which consumes reactants but is not affected by the free-radical inhibitor. This competing reaction results in formation of *p,p'*-dinitrostilbene, possibly *via* a carbene mechanism.[35]

The experimental evidence cited for the reaction of *p*-nitrobenzyldimethylsulfonium bromide with base suggests that a free-radical chain mechanism probably is not operative in this system while the carbene mechanism[35] is not excluded by any of the results and may, indeed, be the process by which *p,p'*-dinitrostilbene is formed.

Alternately, the formation of the stilbene can be likened to the coupling of *p*-nitrotoluene to yield *p,p'*-dinitrobibenzyl in basic solution.[8] In this process **7** has been postulated as an intermediate. In the case of the sulfonium salt a similar reaction sequence would predict **8** which would readily decompose to the stilbene. This suggestion avoids the necessity of postu-



7



8

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(36) B. M. Trost, *J. Am. Chem. Soc.*, **88**, 1587 (1966).

lating a carbene that does not react with hydroxide ion. On the other hand oxygen in general increases the yield of the bibenzyl in the coupling of *p*-nitrotoluene[37] whereas it has a major effect on the reaction products of the sulfonium salt.

Discussion

It is now apparent that the chemistry of both aliphatic and aromatic nitro compounds in basic solution can involve electron-transfer processes leading to the formation of radical anions. Such behavior might well be expected to be pronounced for aliphatic polynitro compounds. In this regard the formation of radical anions by electron transfer from a variety of carbanions to tetranitromethane or nitroform is pertinent.[38] The parent radical anions ($[(NO_2)_4C]\cdot^-$, $[(NO_2)_3CH]\cdot^-$) are unstable and apparently decompose by loss of a nitro group to yield eventually the detected species, $[(NO_2)_3C]\cdot^{2-}$ from tetranitromethane and $[(NO_2)_2CH]\cdot^{2-}$ from trinitromethane ($[(NO_2)_3C]\cdot^{2-}$ is initially formed).

Zeldin and Shechter have reported studies involving the reaction products of anions and 1,1,1-trinitroethane.[39]

Reactions of 1,1,1-trinitroethane with the anions of butyl mercaptan and 2-nitropropane lead to the dimers from the anions in yields of 71 and 87%, respectively.

$$\mathrm{CH_3C(NO_2)_3 + 2Y^- \longrightarrow NO_2^- + [CH_3C(NO_2)_2]^- + Y{-}Y} \tag{10}$$

Shechter considered the possibility of radical intermediates in reaction 10 (footnote 9, ref 39). Certainly

Scheme VI

$$\mathrm{CH_3C(NO_2)_3 + (CH_3)_2C{=}NO_2^- \longrightarrow [CH_3C(NO_2)_3]\cdot^- + (CH_3)_2\dot{C}NO_2}$$

$$\mathrm{(CH_3)_2\dot{C}NO_2 + (CH_3)_2C{=}NO_2^- \longrightarrow (CH_3)_2C(NO_2)C(CH_3)_2NO_2\cdot^-}$$

$$\mathrm{(CH_3)_2C(NO_2)C(CH_3)_2NO_2\cdot^- + CH_3C(NO_2)_3 \longrightarrow (CH_3)_2C(NO_2)C(CH_3)_2NO_2 + CH_3C(NO_2)_3^{\;-}}$$

$$\mathrm{CH_3C(NO_2)_3^{\;-}} \left[\begin{array}{l} \longrightarrow \mathrm{CH_3C(NO_2){=}NO_2^- + NO_2} \\ \longrightarrow \mathrm{CH_3\dot{C}(NO_2)_2 + NO_2^-} \end{array}\right.$$

$$\mathrm{CH_3\dot{C}(NO_2)_2 + (CH_3)_2C{=}NO_2^- \longrightarrow CH_3C(NO_2){=}NO_2^- + (CH_3)_2\dot{C}NO_2}$$

$$\mathrm{NO_2 + (CH_3)_2C{=}NO_2^- \longrightarrow NO_2^- + (CH_3)_2\dot{C}NO_2}$$

Scheme VII

$$\mathrm{CH_3C(NO_2)_3 + C_4H_8S^- \longrightarrow C_4H_8S + [CH_3C(NO_2)_3]\cdot^-}$$

$$\mathrm{[CH_3C(NO_2)_3]\cdot^-} \left[\begin{array}{l} \longrightarrow \mathrm{CH_3C(NO_2){=}NO_2^- + NO_2} \\ \longrightarrow \mathrm{CH_3\dot{C}(NO_2)_2 + NO_2^-} \end{array}\right.$$

$$\mathrm{NO_2 + C_4H_8S^- \longrightarrow NO_2^- + C_4H_8S\cdot}$$

$$\mathrm{CH_3\dot{C}(NO_2)_2 + C_4H_8S^- \rightleftarrows [CH_3C(NO_2)_2SC_4H_8]\cdot^- \rightleftarrows CH_3C(NO_2){=}NO_2^- + C_4H_8S\cdot}$$

$$\mathrm{2C_4H_8S\cdot \longrightarrow C_4H_8SSC_4H_8}$$

the reaction does not yield the products predicted by Scheme II ($CH_3C(NO_2)_2Y$). However, the stability of the 1,1-dinitro-1-ethyl anion and the instability of the intermediate radical anions predicted by Scheme II ($[CH_3C(NO_2)_2Y]\cdot^-$) may have a profound effect on the reaction. Schemes VI and VII appear to rationalize the results and at the same time are complementary to Schemes II or IV.

The participation of radical anions from dinitro compounds (α-*p*-dinitrocumene) in Scheme II, and specifically in reactions similar to reactions 2–4, has been described recently.[40]

Experimental Section

Absolute ethanol was purified by refluxing with calcium hydride for several hours and then distilling; the DMF was dried over calcium hydride for 24 hr and then vacuum distilled twice under prepurified nitrogen. Both solvents were stored over molecular sieves. 2-Nitropropane was purified by distillation through a 90-cm Todd column packed with glass helices; gas–liquid partition chromatography (glpc) and proton magnetic resonance (pmr) spectroscopy showed the compound to be pure. The lithium salt of 2-nitropropane was prepared according to the method of Kornblum.[10] The remaining chemicals employed were either commercially available or have been previously described in the literature and were purified by standard procedures when necessary.

The apparatus employed in the oxidation studies has been described elsewhere and consisted of a vigorously shaken creased flask (attached to an oxygen manometer) with a side arm for the addition of reagents.[7] Most of the reactions conducted under prepurified nitrogen were performed in a jacketed Pyrex reaction vessel kept at constant temperature by circulating thermostated water through the outer jacket. Reactants were introduced either by a 10-ml addition funnel atop the reaction vessel or by a syringe through a rubber septum. All reaction solutions were thoroughly degassed with prepurified nitrogen prior to mixing. The reactions were monitored by removing aliquots at intervals by means of a syringe, quenching with a known small amount of acid, and analyzing for the desired reactant or product by glpc employing a suitable column. In the reaction of the lithium salts of 2-nitropropane with *p*-nitrobenzyl chloride, *p*-nitrobenzyldimethylsulfonium bromide, or *p*-nitrobenzyltrimethylammonium bromide, the carbon alkylated product, 2-methyl-2-nitro-1-(*p*-nitrophenyl)propane was detected on a Perkin-Elmer Model 154 vapor fractometer with a 2-ft column of 20% GEXE-60 silicone gum nitrile on Chromosorb W at 200°. Using this same column at 136° allowed the consumption of *p*-nitrobenzyl chloride to be followed. 2-Chloro-2-nitropropane and 2-bromo-2-nitropropane were analyzed using a 2-m diisodecyl phthalate column at 100 and 125°, respectively. The reaction of *p*-nitrobenzyldimethylsulfonium bromide with sodium hydroxide was followed by potentiometric titration.

A 275-W General Electric sunlamp was the source of light for the irradiation experiments which were conducted in Pyrex equipment thus excluding wavelengths shorter than 3000 A. For the dark reactions, the reaction apparatus was wrapped with either black plastic tape or aluminum foil.

The quantitative determination of acetone and nitrite ion resulting from the oxidation of the 2-nitro-2-propyl anion in the presence of 2-bromo-2-nitropropane was performed following known procedures.[16,41]

The esr spectra shown in Figures 3 and 4 were obtained using a Varian V-4500 epr spectrometer with 100-kcps field modulation and a 9-in. magnet; the spectra shown in Figure 5 were recorded on a Varian E-3 epr spectrometer. The simulated spectra were computed on a Japanese Electron Optics Laboratory Company Model JNM-RA-1 spectrum accumulator.

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