

# Radical-Nucleophilic ( $S_{RN}1$ ) Reactions. Part 4.<sup>1</sup> Preparation, Reactions, and Electron Spin Resonance Studies of $\alpha$ -Nitro Azides

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2-Azido-2-nitropropane and 1-azido-1-nitrocyclohexane have been prepared by syntheses involving intermediate radical-anions ( $S_{RN}1$  and oxidative addition).  $S_{RN}1$  Reactions between  $\alpha$ -nitroazides and azide, benzenesulphinate, and *p*-chlorobenzenethiolate proceed with loss of nitrite. The  $S_{RN}1$  reaction between 1-azido-1-nitrocyclohexane and the anion of 2-nitropropane proceeds with loss of azide. Reactions between 2-azido-2-nitropropane and the anions of 2-nitropropane and diethyl ethylmalonate yield oxidative dimerisation. E.s.r. spectroscopy has been used to observe electron-capture by 2-azido-2-nitropropane and its dissociation to nitrite and an ill-defined radical which may be  $(Me_2CN_3)^{\cdot}$ . The addition of benzenesulphinate and the anion of 2-nitropropane to  $Me_2CNO_2$ , formed by a minor dissociation route from  $[Me_2C(N_3)NO_2]^{-\cdot}$ , has been observed by e.s.r. spectroscopy.

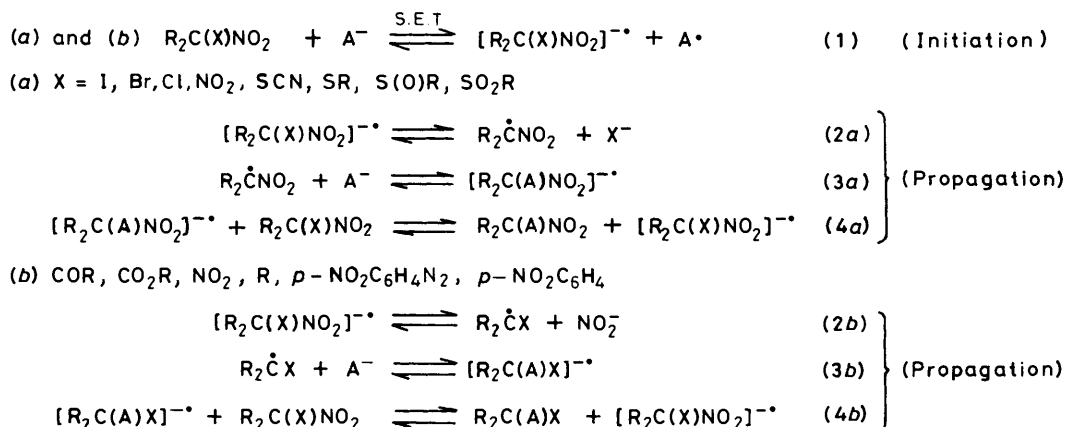
A growing number of  $\alpha$ -substituted nitroalkanes and anions have been shown<sup>2</sup> to participate in substitution reactions proceeding by the  $S_{RN}1$  mechanism. Anions ( $A^-$ ) include  $R_2CNO_2^-$ ,  $RSO_2^-$ ,  $RS^-$ ,  $SO_2^{2-}$ ,  $(RO)_2PO^-$ , and carbanions  $[RC(X)Y]^-$ , with X, Y =  $CO_2R$ ,  $COR$ ,  $SO_2R$ , and  $CN$ .  $S_{RN}1$  Reactions proceed with substitution of either the  $\alpha$ -substituent (X) (Scheme 1a) or nitrite (Scheme 1b). Initial single-electron transfer (S.E.T.) between the anion and the  $\alpha$ -substituted nitroalkanes [Equation (1)] leads to an intermediate radical-anion which dissociates to a radical and an anion [Equations (2a) and (2b)] thereby initiating the chain  $S_{RN}1$  mechanism. The direction of the  $S_{RN}1$  reaction is determined by the dissociation of the intermediate radical-anion, i.e. loss of X<sup>-</sup> or  $NO_2^-$ . Factors such as bond strength, nucleofugal properties, and overlap of the nitro  $\pi^*$  MO (holding the unpaired electron of the radical-anion) with the C-X  $\sigma^*$  MO

have been suggested<sup>3</sup> to influence the direction of dissociation of the radical-anion.

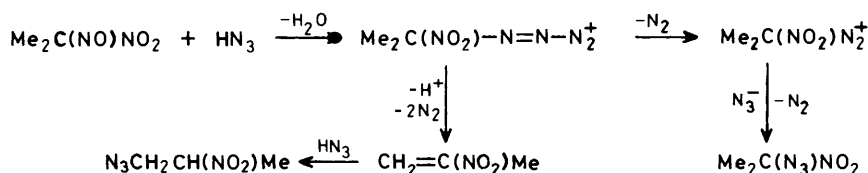
Our preliminary communication<sup>4</sup> reported the first  $S_{RN}1$  reactions of  $\alpha$ -azidonitroalkanes and the first  $S_{RN}1$  reactions of azide with  $\alpha$ -substituted nitroalkanes.  $S_{RN}1$  reactions between  $\alpha$ -substituted *p*-nitrobenzylic compounds and azide have also been reported.<sup>2a,5</sup> This paper reports the full results of our investigations of the preparation, reactions, and e.s.r. studies of  $\alpha$ -azidonitroalkanes.

## Results and Discussion

*Preparation of  $\alpha$ -Azido Nitroalkanes.*—Two methods for the preparation of  $\alpha$ -nitroazides have been reported in the literature. The first of these methods is based on the familiar preparation of phenyl azide<sup>6</sup> from the reaction between



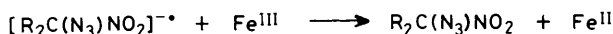
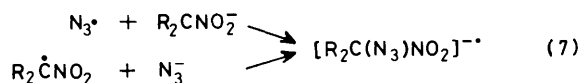
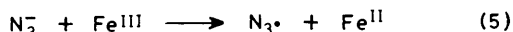
Scheme 1.



Scheme 2.

nitrosobenzene and azide, and uses 2-nitro-2-nitrosopropane and azide<sup>6</sup> (see Scheme 2). Using a similar procedure, we obtained pure 1-azido-2-nitropropane in good yield instead of the reported<sup>6</sup> 2-azido-2-nitropropane. We suggest that the product reported by Maffei and Bettinetti<sup>6</sup> is in fact 1-azido-2-nitropropane, since their evidence depends solely on combustion analysis which would equally well fit either isomer, 1- or 2-azido-2-nitropropane. We propose that the isomeric product actually obtained arises from reaction between hydrazoic acid and an intermediate nitro-olefin which is formed by elimination of a proton and two molecules of nitrogen from the cation intermediate, as shown in Scheme 2. The addition of hydrazoic acid to 2-nitropropene has been reported<sup>7</sup> to yield 1-azido-2-nitropropane in high yield.

The second method reported<sup>8</sup> for the preparation of  $\alpha$ -nitroazides uses anodic oxidation to carry out the oxidative addition of azide to the anions of nitroalkanes [Scheme 3, with



Scheme 3.

$\text{Fe}^{\text{III}}$  replaced by an anode]. The authors propose that the first step is the oxidation of azide [as exemplified in Equation (5)] rather than the oxidation of the nitro-anion [as exemplified in Equation (6)] because azide was observed to oxidise at a lower anode potential than the anion of nitrocyclohexane under the same conditions.

Our oxidative addition procedure was developed from the method of Urbanski and co-workers<sup>9</sup> using potassium ferricyanide, as shown in Scheme 3. 1-Azido-1-nitrocyclohexane was prepared by either the addition of ferricyanide to azide and the nitronate or by the addition of nitronate to ferricyanide and azide. The two-phase dichloromethane ( $\text{CH}_2\text{Cl}_2$ )-water system gave better yields than with diethyl ether-water.

The results of the oxidative addition of azide to the anion of 2-nitropropane ( $\text{Me}_2\text{CNO}_2^-$ ) are reported in Table 1. The first attempt to prepare 2-azido-2-nitropropane [ $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ ] by the ferricyanide procedure surprisingly gave pure 2,2-diazidopropane [ $\text{Me}_2\text{C}(\text{N}_3)_2$ ]. However, shorter reaction times yielded both compounds. A study of the variance of the yields of both compounds with time indicated that  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was steadily being converted into  $\text{Me}_2\text{C}(\text{N}_3)_2$ .  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was shown to react readily with azide to yield  $\text{Me}_2\text{C}(\text{N}_3)_2$  under the same reaction conditions by an  $S_{\text{RN}}1$  mechanism (see later). Wright and Ward<sup>8</sup> also commented that  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was converted into  $\text{Me}_2\text{C}(\text{N}_3)_2$  by a non-electrolytic process. Attempts to improve the yield by using only 1 equiv. of azide and reverse addition of reactants was only partially successful.

Our results indicate that  $\text{Me}_2\text{C}(\text{N}_3)_2$  is formed by an  $S_{\text{RN}}1$  mechanism from  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  and not by a rapid

Table 1. Oxidative addition of azide to  $\text{Me}_2\text{CNO}_2^-$  using  $\text{K}_3\text{Fe}(\text{CN})_6$ 

Time <sup>a</sup> (min)	0	15	20	30	40	60	20 <sup>c</sup>	30 <sup>c,d</sup>
$\text{Me}_2\text{C}(\text{N}_3)_2$ <sup>b</sup>	19	22	22	37	38	41	9	39
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ <sup>b</sup>	28	24	19	11	7	0	22	9

<sup>a</sup> Time between the end of addition of the  $\text{K}_3\text{Fe}(\text{CN})_6$  and work-up.

<sup>b</sup> The % yield based on  $\text{Me}_2\text{CNO}_2^-$ . Traces (1–2%) of  $\text{Me}_2\text{C}(\text{NO}_2)_2$  were present in all reactions. <sup>c</sup>  $\text{Me}_2\text{CNO}_2^-$  added to a solution of azide (1 equiv.) and  $\text{K}_3\text{Fe}(\text{CN})_6$ . <sup>d</sup> 1 Equiv. of  $\text{NaNO}_2$  added to the reaction mixture.

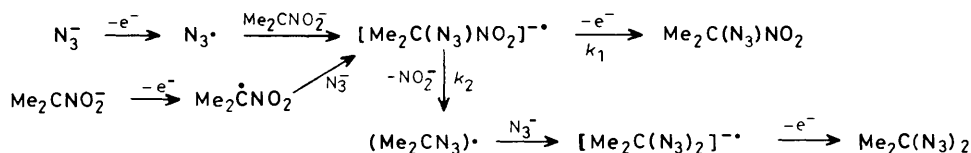
Table 2. Reaction between  $\text{Me}_2\text{C}(\text{Br})\text{NO}_2$  and azide

Inhibitor	Time (h)	% Yield	
		$\text{Me}_2\text{C}(\text{Br})\text{NO}_2$	$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$
None	24	0,0	25, 38
	1; 0.25	11; 17	22; 25
<i>p</i> -Dinitrobenzene (5 mol %)	24	0	32
	1; 0.25	11; 20,23	29; 17,18
Di- <i>t</i> -butyl nitroxide (10 mol %)	1; 0.25	13,13; 31, 25	28, 21; 24, 22
	1; 0.25	20, 14; 21, 22	20, 19; 25, 18
Dark	1; 0.25	20, 14; 21, 22	20, 19; 25, 18

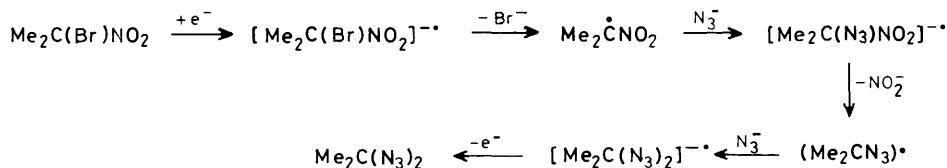
decomposition of the intermediate radical-anion [ $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2^-$ ]; i.e. the rate of electron loss by the radical-anion to ferricyanide ( $k_1$ ) is faster than the decomposition of the radical-anion ( $k_2$ ) (Scheme 4). However, the radical-anion [ $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2^-$ ] is also an intermediate in the  $S_{\text{RN}}1$  reaction between azide anion and  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ . When the ferricyanide is used up,  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2^-$  is not rapidly converted into  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ , and when formed by a single electron transfer (s.e.t.) reaction between azide anion and  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ , the slower decomposition of the radical anion to ( $\text{Me}_2\text{CN}_3$ )<sup>•</sup> and nitrite anion can take place, leading to the formation of  $\text{Me}_2\text{C}(\text{N}_3)$  by an  $S_{\text{RN}}1$  mechanism. Traces of 2,2-dinitropropane were formed in most of the reactions, but surprisingly, when an excess of nitrite was added to the reaction, the amount of 2,2-dinitropropane did not increase. However, 2,2-dinitropropane is readily formed<sup>9</sup> by oxidative addition of nitrite to  $\text{Me}_2\text{CNO}_2^-$ , and thus a probable explanation is that azide rather than  $\text{Me}_2\text{CNO}_2^-$  is initially oxidised by the ferricyanide as suggested for the electrolysis studies.<sup>8</sup> The azido radical ( $\text{N}_3^\bullet$ ) then adds to  $\text{Me}_2\text{CNO}_2^-$ . The small amount of 2,2-dinitropropane possibly arises from the addition of nitrite to the 2-nitropropan-2-yl radical which could arise from a minor dissociation route of [ $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2^-$ ] to  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  and azide.

This route therefore provides a useful synthetic method for  $\alpha$ -nitroazides. The reason for the lack of reactivity of 1-azido-1-nitrocyclohexane under the same conditions is unknown.

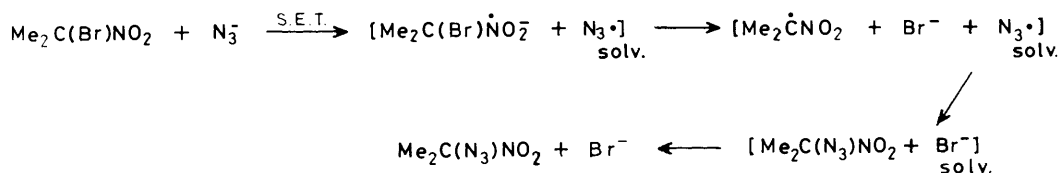
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was also prepared by a  $S_{\text{RN}}1$  reaction (Scheme 1a, X = Br, A<sup>-</sup> = N<sub>3</sub><sup>-</sup>) from 2-bromo-2-nitropropane. The results are presented in Table 2. The use of dimethylformamide (DMF) or dimethyl sulphoxide (DMSO) gave steady decomposition of product and starting material, i.e. the rate of formation of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was almost equal to its



Scheme 4.



Scheme 5.



Scheme 6.

rate of decomposition. The use of hexamethylphosphoramide (HMPA) gave a much faster reaction wherein the rate of formation of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was faster than its decomposition. Photolysis with fluorescent lamps ( $2 \times 150$  W) also gave poor results. The photolytic decomposition of azides is well known.

Light catalysis and inhibition studies were carried out to provide evidence of the mechanism of the substitution. Substitution at the carbon centre of an  $\alpha$ -substituted secondary nitroalkane is in itself a good criterion<sup>2</sup> for an  $S_{\text{RN}}1$  mechanism. The results (see Table 2) do not show significant light catalysis or inhibition by a strong radical trap (di-*t*-butylnitroxide) or a strong electron-acceptor (*p*-dinitrobenzene). A slight increase of 2-bromo-2-nitropropane and decrease of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was observed but we suggest that this is within experimental error. This lack of inhibition is unusual for what is apparently an  $S_{\text{RN}}1$  reaction.

The steady decomposition of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ , or its further reaction with azide to yield  $\text{Me}_2\text{C}(\text{N}_3)_2$  and the further decomposition of  $\text{Me}_2\text{C}(\text{N}_3)_2$ , certainly complicates the results and may explain the observed lack of inhibition. The steady reaction/decomposition of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  was shown by allowing  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  to react with azide under the same conditions (6% after 30 min and 2% after 1 h) (see later). There is competition between s.e.t. from the intermediate radical-anion  $[\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-]$  to 2-bromo-2-nitropropane and dissociation of  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  to  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  and nitrite. The results from the reaction in HMPA suggest that s.e.t. is faster than dissociation, as was observed in the ferricyanide reactions. In DMSO and DMF the rates may be similar, allowing a double substitution reaction *via* two intermediate radical-anions, as reported by Bunnett<sup>10</sup> for certain  $S_{\text{RN}}1$  reactions with dihalogenoarenes (*i.e.* Scheme 5).

The lack of inhibition can also be explained by a radical-anion reaction of short chain-length or by a non-chain mechanism (Scheme 6). A non-chain mechanism, termed  $S_{\text{ET}}2$  (substitution, electron-transfer, bimolecular), has been proposed by Russell *et al.*<sup>11</sup> to explain the lack of inhibition observed in the reactions of  $\alpha$ -substituted nitroalkanes with acetylides.

$S_{\text{RN}}1$  Reaction of 1-bromo-1-nitrocyclohexane with azide in DMSO or HMPA under identical conditions for various times gave a mixture of products in poor yield.

Characterisation of the two  $\alpha$ -nitro azides and  $\text{Me}_2\text{C}(\text{N}_3)_2$  provided a problem because their explosive properties precluded combustion analyses. An attempt to prepare crystalline derivatives of the adducts formed with norbornene<sup>12</sup> was successful for 1-azido-1-nitrocyclohexane and  $\text{Me}_2\text{C}(\text{N}_3)_2$

but the combustion analyses, although close, showed slight loss of nitrogen. Ready loss of nitrogen from norbornene adducts has been reported.<sup>12</sup> Our characterisation therefore depends on the previously reported syntheses of the compounds<sup>8</sup> (no analytical data was presented), correct spectral data, and formation of derivatives with norbornene to prove the presence of an azido group. The  $\alpha$ -nitroazides also formed derivatives with loss of nitrite or azide when treated with anions (see next section). These derivatives are either known compounds or have correct combustion analyses.

$S_{\text{RN}}1$  Reactions of  $\alpha$ -Nitro Azides.—The results of these reactions are presented in Table 3. The reaction between  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  and azide was initially studied to obtain a clearer understanding of the preparative reactions. Low yields of  $\text{Me}_2\text{C}(\text{N}_3)_2$  were obtained in HMPA but excellent yields were obtained in the same two-phase  $\text{CH}_2\text{Cl}_2$ -water system used for the ferricyanide reactions.

The exclusion of light or the addition of *p*-dinitrobenzene or di-*t*-butyl nitroxide completely inhibited the formation of  $\text{Me}_2\text{C}(\text{N}_3)_2$  and left large amounts of unaltered  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ , thereby clearly indicating an  $S_{\text{RN}}1$  radical-anion light-catalysed chain mechanism (Scheme 1b, X = A =  $\text{N}_3$ ).

Two anions (benzenesulphinate and *p*-chlorobenzenethiolate), commonly used in  $S_{\text{RN}}1$  reactions,<sup>1,2a,13</sup> were treated with both nitro azides to ascertain the extent of their  $S_{\text{RN}}1$  reactivity. Both  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  and 1-azido-1-nitrocyclohexane gave good yields of substitution products with loss of nitrite. The reaction between  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  and benzenesulphinate was carried out for different times and in the presence of inhibitors. A fast reaction took place (5 min) which was significantly inhibited by *p*-dinitrobenzene and di-*t*-butyl nitroxide, indicating an  $S_{\text{RN}}1$  mechanism (Scheme 1b, X =  $\text{N}_3$ , A =  $\text{PhSO}_2$ ).

Several important points relating to the mechanism deserve attention. Firstly, the intermediate radical-anions,  $\text{R}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ , dissociate with loss of nitrite rather than azide, which is surprising because azide is normally observed to be a better nucleofuge than nitrite. Nitrite has, however, been reported<sup>2a</sup> to have enhanced nucleofugicity in radical-anions, possibly because the unpaired electron largely resides in the  $\pi^*$  MO of the nitro group<sup>3</sup> and therefore major reorganisation of MO's is not required prior to dissociation. Whilst not strictly comparable, it should be noted that loss of nitrite has been reported<sup>5</sup> to be favoured over loss of azide in  $S_{\text{RN}}1$  substitutions in *p*-nitrocumyl systems [Equation (8)]. The reverse of this reaction is possible but was not observed.

**Table 3.**  $S_{RN}1$  reactions between  $R_2C(N_3)NO_2$  and anions

$R_2C$	Anion ( $A^-$ )	Conditions	% Yield	
			$R_2C(A)N_3^a$	$R_2C(N_3)NO_2$
$Me_2C$	$N_3^-$	HMPA, 1 h, 30 min	5 <sup>b</sup> , 10 <sup>b</sup>	2 <sup>b</sup> , 6 <sup>b,c</sup>
		$CH_2Cl_2-H_2O$ , 40 min	91 <sup>b</sup>	0 <sup>b</sup>
		$CH_2Cl_2-H_2O$	0 <sup>b</sup>	90 <sup>b</sup>
		$CH_2Cl_2-H_2O$ , 40 min <i>p</i> -dinitrobenzene (5 mol %)	0 <sup>b</sup>	91 <sup>b</sup>
$Me_2C$	$PhSO_2^-$	$CH_2Cl_2-H_2O$ , 40 min di- <i>t</i> -butyl nitroxide (10 mol %)	0 <sup>b</sup>	95 <sup>b</sup>
		DMSO, 5, 10, 40, or 180 min	70	0
		DMSO, 5 min, <i>p</i> -dinitrobenzene (5 mol %)	47	0
		DMSO, 5 min. di- <i>t</i> -butyl nitroxide (10 mol %)	47	0
		DMF, 10, 30, and 40 min, 24 h.	59, 57, 59, 46	Trace, 0, 0, 0
$(CH_2)_5C$ $Me_2C$	$PhSO_2^-$	HMPA, 2 h <sup>d</sup>	<i>e</i>	0
		DMSO, 14 h	53	0
$(CH_2)_5C$ $Me_2C$	$p-ClC_6H_4S^-$	DMSO, 40 min	34	0
		DMF, 40 min	70	0
		DMF, 40 min	20	0
		DMSO, 1 h	53	0

<sup>a</sup> % Yield after purification. <sup>b</sup> Analysis by n.m.r. spectroscopy. <sup>c</sup>  $Me_2C(NO_2)_2$  was also detected, 5 and 4% resp. <sup>d</sup> Tungsten 'white light' fluorescent lamps (2 × 150 W). <sup>e</sup> Decomposed and unidentified material.

**Table 4.** Reactions between  $R_2C(N_3)NO_2$  and  $Me_2CNO_2^-$ 

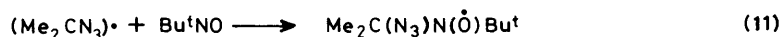
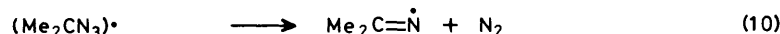
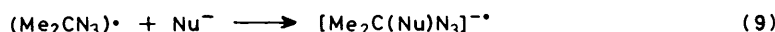
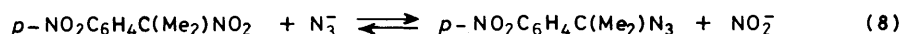
$R_2C$	Conditions	% Yield	
		$R_2C(N_3)NO_2$	$R_2C(NO_2)C(NO_2)Me_2$
$Me_2C$	HMPA, 1 h	0	24
	HMPA, 1 h, <i>p</i> -dinitrobenzene (10 mol %)	0	24
	HMPA, 1 h, di- <i>t</i> -butyl nitroxide (10 mol %) (40 mol %)	0	24
	HMPA, 1 h, dark	Trace <sup>a</sup>	Trace <sup>a</sup>
	DMSO, 2 h	0	19
$(CH_2)_5C$	DMSO, 2 h <sup>c</sup> , <i>p</i> -dinitrobenzene (10 mol %) (40 mol %)	50 <sup>a</sup>	0, (10) <sup>a,b</sup>
	DMSO, 2 h <sup>c</sup> , di- <i>t</i> -butyl nitroxide (10 mol %)	100	0
	DMSO, 2 h <sup>c</sup> , di- <i>t</i> -butyl nitroxide (10 mol %)	64	0
	DMSO, 2 h, dark	50	0

<sup>a</sup> Analysis by n.m.r. spectroscopy. <sup>b</sup> % Yield of  $Me_2C(NO_2)C(NO_2)Me_2$ . <sup>c</sup> Laboratory lighting only.

These results suggest that  $\alpha$ -nitroazides undergo s.e.t. with certain anions to form radical-anions which, in turn, undergo dissociation to nitrite and to a 2-azidopropyl radical ( $Me_2CN_3^\cdot$ ). The lifetime of this radical must be sufficiently long to allow bimolecular reaction with an anion to form a new  $\alpha$ -substituted azido radical-anion [Equation (9)]. This bimolecular reaction is apparently faster than the reported<sup>14</sup> decomposition of  $\alpha$ -azidoalkyl radicals to nitrogen and the corresponding iminyl  $\sigma$ -radicals ( $R^1R^2C=\dot{N}$ ) [Equation (10)].

No products that could be assigned to  $Me_2C=\dot{N}$  as an intermediate (e.g.  $Me_2C=N-N=CMe_2$ ) were observed. The imine ( $Me_2C=NH$ ), if formed, would have undergone hydrolysis on work-up to acetone which would have been lost by evaporation. Similarly, no 2,3-diazido-2,3-dimethylbutane<sup>15</sup> arising from possible dimerisation of ( $Me_2CN_3$ )<sup>·</sup> was observed.

Roberts and co-workers<sup>14a</sup> initially reported their failure to observe the azidoalkyl radicals by e.s.r. spectroscopy even at low temperature, but in a subsequent publication<sup>16</sup> they





**Table 5.** E.s.r. parameters for radicals obtained by electron addition to  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ ,  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{NO}_2$ ,  $\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\text{NO}_2)\text{Me}_2$ , and  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3$  in  $\text{CD}_3\text{OD}$  and MeTHF.

Source	Solvent	Radical	$^{14}\text{N}$ Hyperfine coupling (G) <sup>a</sup>		
			$A_{\parallel}$	$A_{\perp}$	$A_{\text{iso}}$
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$	$\text{CD}_3\text{OD}$	$\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$	46	17	26.7
	MeTHF	$\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$	43	15.5	24.7
$\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{NO}_2$	$\text{CD}_3\text{OD}$	$\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\dot{\text{N}}\text{O}_2^-$	41	15	23.7
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2 + \text{PhSO}_2^-$	$\text{CD}_3\text{OD}$	$\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\dot{\text{N}}\text{O}_2^-$	41	15	23.7
$\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\text{NO}_2)\text{Me}_2$	$\text{CD}_3\text{OD}$	$\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\dot{\text{N}}\text{O}_2^-)\text{Me}_2$	47.3	17.3	27.3
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2 + \text{Me}_2\text{CNO}_2^-$	$\text{CD}_3\text{OD}$	$\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\dot{\text{N}}\text{O}_2^-)\text{Me}_2$	47.3	17.3	27.3
$\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$	$\text{CD}_3\text{OD}$ or MeTHF	$\text{Me}_2\text{C}=\dot{\text{N}}$	34	$0 \pm 3$	$11.3 \pm 2$
		$\text{Me}_2\text{C}=\dot{\text{N}}$ (R.T)			$9.7^b$
$\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3$	$\text{CD}_3\text{OD}$ or MeTHF	$\text{Me}_2\text{C}=\dot{\text{N}}$	34	0	$11.3 \pm 2$

<sup>a</sup>  $G = 10^{-4}$  T. <sup>b</sup> D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Am. Chem. Soc.*, 1970, **92**, 4115

reaction routes, it is not comprehensive and does not apply to  $\alpha$ -nitro azides.

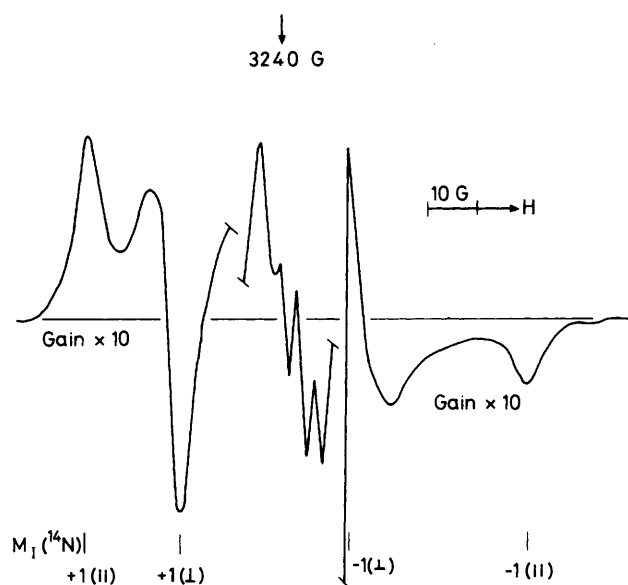
The reason for the absence of an  $S_{\text{RN}}1$  reaction with loss of nitrite in the reactions between  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  and the anions,  $\text{Me}_2\text{CNO}_2^-$  and  $\text{EtC}(\text{CO}_2\text{Et})_2^-$ , is unclear. A possible explanation is that the addition of the anion to  $(\text{Me}_2\text{CN}_3)^{\cdot}$  is much slower because of the steric bulk and low nucleophilicity of both anions as compared to  $\text{PhSO}_2^-$ ,  $\text{ArS}^-$ , and azide, and that competing reactions dominate, leading to oxidative dimerisation.

**E.s.r. Studies.**—The e.s.r. studies were carried out to provide evidence for the radical and radical-anion intermediates proposed in the preceding solution studies and to further our studies<sup>3,19</sup> of electron-capture processes of 2-substituted 2-nitropropanes [ $\text{Me}_2\text{C}(\text{X})\text{NO}_2$ ]. The e.s.r. parameters for the radicals obtained by electron addition to  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$ ,  $\text{Me}_2(\text{SO}_2\text{Ph})\text{NO}_2$ ,  $\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\text{NO}_2)\text{Me}_2$ , and  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3$  in  $\text{CD}_3\text{OD}$  and MeTHF are presented in Table 5. The only previous study in this area is the report<sup>20</sup> of the e.s.r. spectrum of the radical-anion of azidonitromethane.

In our earlier studies<sup>3,19</sup> the radical-anions of various 2-substituted 2-nitropropanes were generated by  $\gamma$ -ray irradiation in solid matrices of methyltetrahydrofuran (MeTHF) and deuteriomethanol ( $\text{CD}_3\text{OD}$ ) at low temperature (77 K) and observed by e.s.r. spectroscopy. On annealing to ca. 140 K, the dissociation of some of the radical-anions to free radicals ( $\text{Me}_2\dot{\text{C}}\text{NO}_2$  by loss of  $\text{X}^-$  or  $\text{Me}_2\dot{\text{C}}\text{X}$  by loss of  $\text{NO}_2^-$ ) was also observed by e.s.r. spectroscopy. The study of these radical-anions by e.s.r. spectroscopy has been used to predict their reactivity and direction of dissociation. For example, e.s.r. studies<sup>3</sup> of  $\text{Me}_2\text{C}(\text{SCN})\dot{\text{N}}\text{O}_2^-$  at low temperature by this method indicate that this is a relatively reactive radical-anion which readily dissociates to  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  with loss of thiocyanate. Later solution studies<sup>13</sup> of the  $S_{\text{RN}}1$  reactions of 2-nitro-2-thiocyanotropane confirmed this.

Irradiation of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  in MeTHF and  $\text{CD}_3\text{OD}$  gave electron-capture to yield the radical-anion,  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ , which was observed at 77 K. The e.s.r. spectrum of  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  (Figure 1) exhibited the asymmetric triplet characteristic of  $\text{RNO}_2^-$  radical-anions.<sup>3</sup> On annealing, the spectrum in MeTHF showed no change, but the spectrum in  $\text{CD}_3\text{OD}$  showed the conversion of the radical-anion into a novel species, together with weak features which are assigned to the radicals  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  and  $\text{Me}_2\text{C}=\dot{\text{N}}$ .

The features of the new species in the spectrum were too poorly defined for full interpretation. The best interpretation relies on the probability of considerable spin-density of the



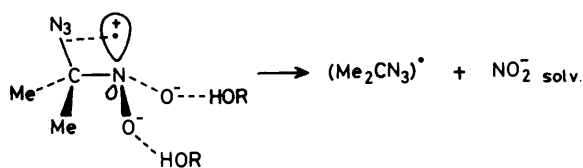
**Figure 1.** First derivative X-band e.s.r. spectrum for a dilute solution of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  in  $\text{CD}_3\text{OD}$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K showing the outer,  $M_1(^{14}\text{N}) = \pm 1$  features assigned to the radical-anion,  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ . The intense central features are from solvent radicals.

$\text{Me}_2\dot{\text{C}}$ -unit. The spectral interpretation would therefore be  $A(2\text{Me})$  ca. 15 G and  $A(\text{N})$  ca. 4 G (see Figure 2, features marked  $\beta$ ). In this case the spin-density on carbon is ca.  $100 \times \frac{1}{2} = 68\%$ . The N-splitting is ill-defined. This interpretation suggests a radical with the spin-density largely centred on carbon, i.e.  $\text{Me}_2\dot{\text{C}}\text{N}_3$ .

Supporting evidence for the formation of  $(\text{Me}_2\text{CN}_3)^{\cdot}$  is provided by the spin trapping results discussed earlier.<sup>16</sup>

The presence of features due to  $\text{Me}_2\text{C}=\dot{\text{N}}$  radicals (see Figure 2, features marked  $\alpha$ ) suggests that slow decomposition of  $(\text{Me}_2\text{CN}_3)^{\cdot}$  takes place, but that this is a minor pathway at low temperatures. Similarly, trace indications of  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  suggest that dissociation of  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  to  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  with loss of azide is a minor competing reaction.

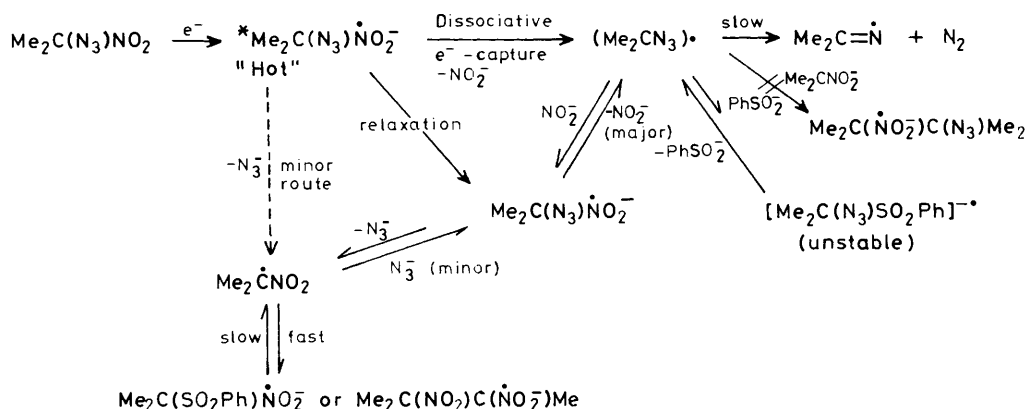
The yield of  $(\text{Me}_2\text{CN}_3)^{\cdot}$  relative to  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  is much larger in  $\text{CD}_3\text{OD}$  than in MeTHF. This phenomenon was observed in previous studies<sup>3,19</sup> and is explained by strong protic solvation of nitrite by  $\text{CD}_3\text{OD}$  (Scheme 9) which inhibits



Scheme 9.

'anion-return' [reverse of Equation (15)] in CD<sub>3</sub>OD relative to MeTHF. We postulated in our earlier publication<sup>3</sup> that protic solvation of the nitro group in Me<sub>2</sub>C(X)NO<sub>2</sub><sup>-</sup> could be expected to favour loss of nitrite relative to X<sup>-</sup> but reported that there was no clear evidence to support this proposition. The effect of protic solvation in Me<sub>2</sub>C(X)NO<sub>2</sub><sup>-</sup> is probably only marginal relative to bond strength and nucleofugal properties in determining the direction/rate of dissociation. However, in Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub><sup>-</sup> the effect of protic solvation of the nitro group does appear to influence the direction of dissociation in favour of nitrite loss, rather than azide loss. Azide has been observed to be a better nucleofuge than nitrite in most nucleophilic reactions and would be predicted to be the preferred nucleofuge. Evidence that protic solvation of Me<sub>2</sub>C(X)NO<sub>2</sub><sup>-</sup> retards the rate of dissociation by loss of X<sup>-</sup> in S<sub>RN</sub>1 reactions has been reported.<sup>21</sup>

The formation of Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub><sup>-</sup> can be explained (see Scheme 10) by either relaxation of a 'hot' radical-anion formed on electron-capture by Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub> or by dissociative electron-capture to yield (Me<sub>2</sub>CN<sub>3</sub>)• and nitrite, followed by addition ('anion-return') to (Me<sub>2</sub>CN<sub>3</sub>)•. These processes are fully discussed in our earlier publications.<sup>3,19</sup> Irradiation of higher concentrations (ca. 10%) of Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub> gave, in addition to the above species, clear features due to •NO<sub>2</sub> radicals, showing that direct damage to the substrate was occurring.<sup>22</sup>



Scheme 10.

Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub> was irradiated in CD<sub>3</sub>OD in the presence of Me<sub>2</sub>CNO<sub>2</sub><sup>-</sup> or PhSO<sub>2</sub><sup>-</sup> in order to observe the possibility of anion addition to the (Me<sub>2</sub>CN<sub>3</sub>)• free radical formed by dissociation of Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub><sup>-</sup>, i.e. the third step of the S<sub>RN</sub>1 mechanism [Equation (3b), X = N<sub>3</sub>, A<sup>-</sup> = Me<sub>2</sub>CNO<sub>2</sub><sup>-</sup> or PhSO<sub>2</sub><sup>-</sup>]. However, the expected radical-anions, [Me<sub>2</sub>C(SO<sub>2</sub>Ph)N<sub>3</sub>]<sup>-•</sup> or Me<sub>2</sub>C(NO<sub>2</sub>)C(N<sub>3</sub>)Me<sub>2</sub>, were not observed. The features for Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub><sup>-</sup> were initially observed at 77 K and on annealing features assigned to (Me<sub>2</sub>CN<sub>3</sub>)• together with features for Me<sub>2</sub>C(SO<sub>2</sub>Ph)NO<sub>2</sub><sup>-</sup> or Me<sub>2</sub>C(NO<sub>2</sub>)C(NO<sub>2</sub>)Me<sub>2</sub>, respectively, were clearly observed in the e.s.r. spectrum. [The e.s.r. spectrum of Me<sub>2</sub>C(SO<sub>2</sub>Ph)NO<sub>2</sub><sup>-</sup>,

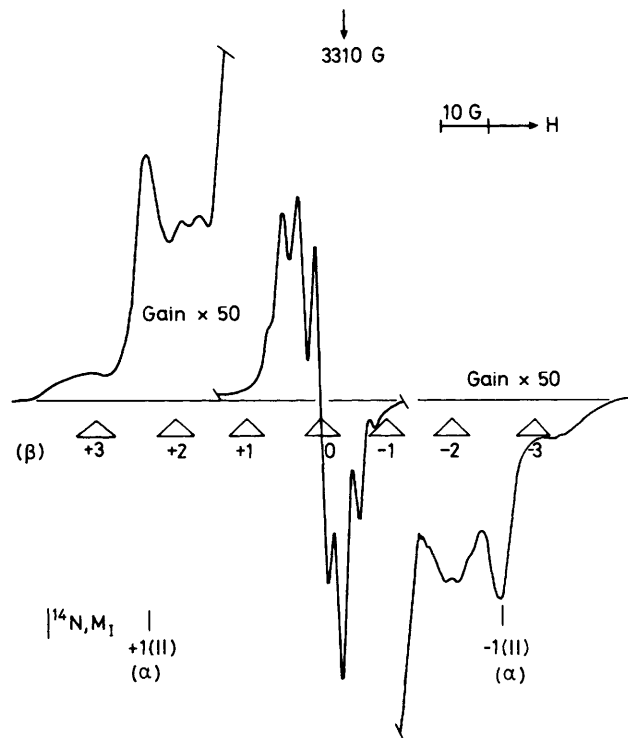


Figure 2. First derivative X-band e.s.r. spectrum for a dilute solution of Me<sub>2</sub>C(N<sub>3</sub>)SO<sub>2</sub>Ph in CD<sub>3</sub>OD after exposure to <sup>60</sup>Co γ-rays at 77 K showing outer, M<sub>1</sub>(<sup>14</sup>N) = ±1 features for Me<sub>2</sub>C=N radicals (α) and the ±2 and ±3 (<sup>1</sup>H) for a species identified as (Me<sub>2</sub>CN<sub>3</sub>) (β).

obtained by irradiation of Me<sub>2</sub>C(SO<sub>2</sub>Ph)NO<sub>2</sub> at 77 K, has been reported,<sup>3</sup> and the spectrum of Me<sub>2</sub>C(NO<sub>2</sub>)C(NO<sub>2</sub>)Me<sub>2</sub> was obtained by the same procedure.]

These results for the 'anion return' experiment with PhSO<sub>2</sub><sup>-</sup> and Me<sub>2</sub>C(N<sub>3</sub>)NO<sub>2</sub> are apparently in contradiction to those obtained from solution studies. In order to obtain an indication of the stability of the possible [Me<sub>2</sub>C(SO<sub>2</sub>Ph)N<sub>3</sub>]<sup>-•</sup> radical-anion, Me<sub>2</sub>C(SO<sub>2</sub>Ph)N<sub>3</sub> was irradiated in CD<sub>3</sub>OD at 77 K under conditions favouring electron capture. The e.s.r. spectrum (Figure 2) showed major features which are assigned to the iminyl radical, Me<sub>2</sub>C=N•, and minor features which are attributed to (Me<sub>2</sub>CN<sub>3</sub>)•. The former, intense parallel features

give  $A_{\parallel}(^{14}\text{N}) = 34$  G, and clearly,  $A_{\perp}(^{14}\text{N})$  must be small. This result is characteristic of  $\text{R}_2\text{C}=\dot{\text{N}}$  radicals and is taken as being diagnostic thereof. The latter spectrum spans the field range expected for the radical  $\text{Me}_2\text{CN}_3$ , provided this has its major spin-density on carbon. This then requires a seven-line spectrum with  $A(\text{Me}) = 17$  G. Of these, four lines are clearly seen, the remainder being concealed beneath the intense central features due to  $^1\text{CD}_2\text{OD}$  and  $^1\text{CD}_3$  radicals (Figure 2). There is extra splitting from  $^{14}\text{N}$  nuclei but unfortunately we were unable to obtain spectra of sufficient clarity to enable us to analyse these features further. We propose that our inability to observe the radical-anion  $[\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3]^-$  shows that the formation of the  $(\text{Me}_2\text{CN}_3)^\cdot$  radical occurs by a 'hot' process, *i.e.* that  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3$  undergoes dissociative electron-capture *via* a 'hot' radical-anion rather than electron capture followed by relaxation to yield  $[\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3]^-$ . Alternatively, the radical anion may be formed but is too short-lived to be observed at 77 K in the e.s.r. spectrum. In the absence of any stabilising reaction in the solid matrix, the  $(\text{Me}_2\text{CN}_3)^\cdot$  radical decomposes by loss of dinitrogen to yield the iminyl radical (see Scheme 10). We propose that this route is not observed in the solution studies because the unstable  $[\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3]^-$  radical-anion can rapidly undergo electron-transfer to  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  in the  $\text{S}_{\text{RN}}1$  reaction, thereby yielding the stable  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  radical-anion and  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3$ , and that this electron-transfer is faster than the dissociation of  $[\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3]^-$ .

**Correlation of E.s.r. and Solution Studies.**—The studies of electron-capture reactions of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  in the solid phase corroborate the solution studies, as we have previously shown for other systems.<sup>3,13,19</sup> Thus  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  undergoes electron-capture to yield a stable radical-anion,  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ , which dissociates by a major route to  $(\text{Me}_2\text{CN}_3)^\cdot$  and nitrite and by a minor route to  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  and azide. The e.s.r. studies therefore provide strong supporting evidence for the intermediacy of  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  and  $(\text{Me}_2\text{CN}_3)^\cdot$  in the solution studies.

We propose that the formation of  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\dot{\text{N}}\text{O}_2^-$  in solid-state studies as opposed to the proposed intermediacy of  $[\text{Me}_2(\text{SO}_2\text{Ph})\text{N}_3]^\cdot$  in solution  $\text{S}_{\text{RN}}1$  studies can be explained as follows (see Scheme 10).  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  undergoes electron-capture to yield a 'hot' radical-anion which undergoes both dissociation to  $\text{Me}_2\dot{\text{C}}\text{N}_3$  and relaxation to  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ . The ion  $\text{PhSO}_2^-$ , which is in close proximity in the solid matrix, can add to  $(\text{Me}_2\text{CN}_3)^\cdot$  to form  $[\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\text{N}_3]^\cdot$ , but this is thermodynamically unfavourable and is not observed in the solid state.  $(\text{Me}_2\text{CN}_3)^\cdot$  undergoes 'anion-return' with nitrite to yield  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$ , this being thermodynamically favourable. The results show that  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  also undergoes dissociation by the kinetically less favoured route with loss of azide anion to yield  $\text{Me}_2\dot{\text{C}}\text{NO}_2$ . However, this now undergoes favourable anion return<sup>19</sup> with  $\text{PhSO}_2^-$  to yield the stable  $\text{Me}_2\text{C}(\text{SO}_2\text{Ph})\dot{\text{N}}\text{O}_2^-$  radical-anion, which is the product detected by e.s.r. spectroscopy.

Likewise, the observation of  $\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\dot{\text{N}}\text{O}_2^-)\text{Me}_2$  in the solid-phase studies of  $\text{Me}_2\text{C}(\text{N}_3)\text{NO}_2$  in the presence of  $\text{Me}_2\text{CNO}_2$  can be similarly explained (see Scheme 10): addition of  $\text{Me}_2\text{CNO}_2$  to  $(\text{Me}_2\text{CN}_3)^\cdot$  to form the stable  $\text{Me}_2\text{C}(\dot{\text{N}}\text{O}_2^-)\text{C}(\text{N}_3)\text{Me}_2$  radical-anion is thermodynamically unfavourable (as observed in the solution studies), leading to dissociation of  $\text{Me}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  by the kinetically less favoured route to yield  $\text{Me}_2\dot{\text{C}}\text{NO}_2$  which undergoes 'anion return'<sup>19</sup> to yield the stable  $\text{Me}_2\text{C}(\text{NO}_2)\text{C}(\dot{\text{N}}\text{O}_2^-)\text{Me}_2$  radical-anion. The solid-state studies therefore provide good

evidence for the dual nucleofugal behaviour for  $\text{R}_2\text{C}(\text{N}_3)\dot{\text{N}}\text{O}_2^-$  radical-anions as proposed for the solution studies.

## Experimental

**General.**—DMF, DMSO, and HMPA were distilled at low pressure from calcium hydride and stored over molecular sieves. **Caution:** HMPA is a suspected carcinogen and should be handled with care. M.p.s. were determined on a Kofler block and are uncorrected. I.r. spectra were determined as Nujol mulls (solids) or thin films (liquids) on a Perkin-Elmer 177 spectrophotometer. N.m.r. spectra were determined at 90 MHz with a Perkin-Elmer R32 spectrometer or at 60 MHz on a Varian EM 360A instrument in  $\text{CDCl}_3$  using  $\text{SiMe}_4$  as internal standard. N.m.r. analyses of reaction mixtures were carried out using a known amount of an internal standard (*p*-dimethoxybenzene or phthalide). Analytical t.l.c. was carried out using Merck silica gel 60 PF<sup>254</sup>.

2-Bromo-2-nitropropane,<sup>23</sup> 2,3-dimethyl-2,3-dinitrobutane,<sup>23</sup> 1-methyl-1-nitroethyl phenyl sulphone,<sup>24</sup> 2-nitro-2-nitrosopropane,<sup>25</sup> and the sodium salts of *p*-chlorobenzenethiolate,<sup>23</sup> 2-nitropropane,<sup>23</sup> and diethyl ethylmalonate<sup>17a</sup> were prepared by literature procedures. *p*-Chlorophenyl sulphinate was prepared from *p*-chlorobenzenethiolate by aerial oxidation.

**Explosion Hazards.**—Both azido- and nitro-compounds are well known for their explosive properties. All reactions were therefore carried out in a fume cupboard behind a safety screen. A protective face shield was also worn by the researcher. All residues and unwanted products were destroyed by reaction with dilute hydrochloric acid. No explosions were encountered except with the attempted combustion analysis of 2,2-diazidopropane. Our lack of explosions should not be taken as an indication of lack of explosive properties and we caution that these compounds should be used only with **extreme care**.

**Reaction between 2-Nitro-2-nitrosopropane and Sodium Azide.**—The 2-nitro-2-nitrosopropane dimer (5.9 g, 50 mmol) was dissolved in  $\text{CHCl}_3$  (90 ml) and glacial acetic acid (6.5 ml) and cooled to 0 °C. Sodium azide (7.1 g, 110 mmol) was added portionwise over 2 h at such a rate that the temperature was kept at *ca.* 5 °C. The reaction was terminated when the bright blue colour of 2-nitro-2-nitrosopropane had disappeared. The reaction mixture was washed with water, 5% aqueous sodium carbonate, and water. The  $\text{CHCl}_3$  solution was dried ( $\text{MgSO}_4$ ) and evaporated to dryness at 0 °C. Column chromatography on silica gel with toluene yielded 1-azido-2-nitropropane (2.7 g, 46%),  $n_D^{20}$  1.46 (lit.,<sup>7</sup> 1.46);  $\nu_{\text{max}}$  (neat) 2 120 ( $\text{N}_3$ ), 1 555, and 1 355  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta_{\text{H}}$  1.55 (3 H, d), 3.75 (2 H, H, m), and 4.55 (1 H, m).

**Preparation of 1-Azido-1-nitrocyclohexane by Oxidative Addition of Azide to the Anion of 1-Nitrocyclohexane.**—1-Nitrocyclohexane (3.25 g, 25 mmol) was dissolved in a solution of sodium hydroxide (3.2 g, 80 mmol) in water (30 ml). Sodium azide (6.5 g, 100 mmol) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 80 ml) were added and the reaction mixture was cooled to 0 °C. A saturated solution of potassium ferricyanide (32.9 g, 100 mmol) was added dropwise to the reaction mixture. The layers were immediately separated and the aqueous fraction was extracted with  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  fractions were combined, washed with water, dried ( $\text{MgSO}_4$ ) and evaporated to dryness at 0 °C to yield 1-azido-1-nitrocyclohexane (2.95 g, 70%);  $\nu_{\text{max}}$  (neat film) 2 120 ( $\text{N}_3$ ), 1 550, and 1 358  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta_{\text{H}}$  1.50 (6 H, m) and 2.12 (4 H, m). G.l.c. and t.l.c. analysis showed largely one component with traces of cyclohexanone. Attempts at



purification by g.l.c. or t.l.c. failed due to decomposition. Distillation was not attempted due to the danger of explosion. The compound was used in the impure form.

A repeat reaction using diethyl ether in place of  $\text{CH}_2\text{Cl}_2$  gave a 48% yield. A repeat reaction, the anion of nitrocyclohexane being added to the mixture of azide and ferricyanide, gave a 69% yield.

*Preparation of 2-Azido-2-nitropropane by Oxidative Addition of Azide to the Anion of 2-Nitropropane.*—Freshly distilled 2-nitropropane (4.45 g, 50 mmol) was dissolved in a solution of sodium hydroxide (2.8 g, 60 mmol) in water (30 ml). Sodium azide (6.5 g, 100 mmol) and  $\text{CH}_2\text{Cl}_2$  (70 ml) was added and the reaction mixture cooled to  $0^\circ\text{C}$ . A saturated solution of potassium ferricyanide (32.9 g, 100 mmol) in water (10 ml) was added dropwise over 10 min. The reaction was stirred at  $0^\circ\text{C}$  for different periods of time. The work-up procedure was the same as detailed above.

The yields of products were analysed by n.m.r. spectroscopy. The reaction mixture, obtained from immediate work-up after the ferricyanide addition, was submitted to low pressure to remove 2,2-diazidopropane by evaporation. The residual liquid was fractionally distilled using a specially made short column and condenser. The distillate was collected in a receiver flask cooled in liquid nitrogen to yield 2-azido-2-nitropropane (1.02 g, 16%), b.p.  $35\text{--}38^\circ\text{C}$  (0.1 mmHg);  $\nu_{\text{max}}$  (neat film) 2 120 ( $\text{N}_3$ ), 1 555, and 1 550  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $\delta_{\text{H}}$  1.80 (s);  $\delta_{\text{C}}$  25.09 (q, Me) and 100.48 p.p.m. (s, quat. C);  $m/z$  84 ( $M^+ - \text{NO}_2$ , 10%) and 56 ( $M^+ - \text{NO}_2, - \text{N}_2$ , 100%). Both mass spectral fragments had correct accurate masses.

Separation and purification of the product by h.p.l.c., g.l.c., and t.l.c. failed due to extensive decomposition of both 2,2-diazidopropane and 2-azido-2-nitropropane. The results of experiments at different times and different modes of addition of reagents are shown in Table 1. Traces of 2,2-dinitropropane (1–2%) were present in most reactions.

*Preparation of 2,2-Diazidopropane.*—2,2-Diazidopropane was prepared as detailed in the procedure for the preparation of 2-azido-2-nitropropane with a period of 60 min between the end of ferricyanide addition and work-up. The reaction mixture was analysed by n.m.r. spectroscopy and showed almost pure 2,2-diazidopropane with traces of 2-azido-2-nitropropane. Fractional distillation, as detailed for 2-azido-2-nitropropane, gave pure 2,2-diazidopropane (1.21 g, 19%), b.p.  $28\text{--}30^\circ\text{C}$  (0.5 mmHg);  $\nu_{\text{max}}$  (neat film) 2 100  $\text{cm}^{-1}$  ( $\text{N}_3$ );  $\delta_{\text{H}}$  1.50 (s);  $\delta_{\text{C}}$  25.969 (q, Me) and 79.11 p.p.m. (s, quat. C);  $m/z$  111 ( $M^+ - \text{N}_3, - \text{N}_2$ , 100%). All mass spectral fragments had correct accurate masses.

*Reactions between 2-Bromo-2-nitropropane and Azide.*—(a) *General procedure for  $S_{\text{RN}}1$  reactions.* Sodium azide (0.65 g, 10 mmol) was dissolved in dry HMPA under nitrogen and anhydrous conditions in a flask with one neck covered with a rubber septum. A further 30 min was allowed for complete deoxygenation. 2-Bromo-2-nitropropane (1.68 g, 10 mmol) was added by injection *via* a syringe through the septum. The colour of the reaction mixture turned red and remained red throughout the reaction. At the end of the determined time the reaction mixture was poured into ice-cold water (100 ml) and extracted with diethyl ether. The combined ether extracts were washed with water to remove HMPA, dried ( $\text{MgSO}_4$ ), and evaporated to dryness at  $0^\circ\text{C}$ . The product was analysed by n.m.r. spectroscopy. The results are shown in Table 2. 2-Azido-2-nitropropane was purified by fractional distillation from the reaction carried out for 60 min.

1-Bromo-1-nitrocyclohexane was also allowed to react with azide for 15 min by the same procedure. Analysis of the mixture of products by g.l.c. showed 1-azido-1-nitrocyclohexane as a

major product, significant amounts of 1-bromo-1-nitrocyclohexane, cyclohexanone, two unidentified products, and traces of 1,1-dinitrocyclohexane. Further purification was not attempted.

(b) *General procedure for light catalysis and inhibition studies.* The general procedure for  $S_{\text{RN}}1$  reactions was followed except as outlined in each method detailed below. (i) Inhibition studies with di-*t*-butyl nitroxide or *p*-dinitrobenzene were carried out by adding the required amount of di-*t*-butyl nitroxide or *p*-dinitrobenzene to the reaction mixture at the same time as the anion. (ii) The studies of the effect of light catalysis were carried out by complete exclusion of light which was effected by wrapping the reaction flask in aluminium foil. The results of these studies are shown in Table 2.

2-Azido-2-nitropropane yielded no crystalline adduct with norbornene.

*Reaction between 2-Azido-2-nitropropane and Azide.*—The reactions were carried out as detailed in the general procedure for  $S_{\text{RN}}1$  reactions, for 40 min, using  $\text{CH}_2\text{Cl}_2$  (20 ml) and water (20 ml) as solvent with sodium azide (0.50 g, 7.7 mmol) and 2-azido-2-nitropropane (0.25 g, 1.9 mmol) as reactants. The residues obtained after work-up were characterised by i.r. and n.m.r. spectroscopy and shown to be pure 2,2-diazidopropane. Light catalysis and inhibition studies were carried out as detailed in the general procedure for light catalysis and inhibition studies. The results of all the reactions are presented in Table 3. All yields were measured by n.m.r. spectroscopy.

The reaction was repeated for 30 min and 1 h with HMPA in place of  $\text{CH}_2\text{Cl}_2$  and water as solvent. The results are presented in Table 3.

*Preparation of Norbornene Adducts with Azides.*—The adduct between phenyl azide and norbornene<sup>12</sup> was prepared first as a test reaction. The adduct between 1-azido-1-nitrocyclohexane and norbornene was prepared as follows: norbornene (0.5 g, 5 mmol) and 1-azido-1-nitrocyclohexane (1.27 g, 7.5 mmol) were dissolved in dry diethyl ether (10 ml) and the solution was kept overnight. The crystals were filtered off and recrystallised from ethyl acetate to yield the adduct (0.55 g, 42%), m.p.  $104\text{--}106^\circ\text{C}$ ;  $\nu_{\text{max}}$  (Nujol) 1 550 and 1 350  $\text{cm}^{-1}$  ( $\text{NO}_2$ ), no azide absorption.

2,2-Diazidopropane was allowed to react with norbornene by the same procedure [an excess of 2,2-diazidopropane (15 equiv.) was used to avoid di-adduct formation]. Recrystallisation of the product from ethyl acetate gave needles of the mono-adduct (1.02 g, 91%), m.p.  $108\text{--}110^\circ\text{C}$ ;  $\nu_{\text{max}}$  (Nujol) 2 040  $\text{cm}^{-1}$  ( $\text{N}_3$ );  $\delta_{\text{H}}$  1.40 (10 H, m, containing a strong singlet), 1.70 (2 H, s), 2.19 (2 H, br s), and 3.19 (2 H, br s).

*Preparation of  $\alpha$ -Substituted Azides by Reaction between Anions and 2-Azido-2-nitropropane and 1-Azido-1-nitrocyclohexane.*—(a) *1-Azido-1-methylethyl phenyl sulphone.* 2-Azido-2-nitropropane (0.50 g, 3.8 mmol) and sodium benzenesulphinate (1.00 g, 6 mmol) were allowed to react in DMSO for 5 min as detailed in the general procedure for  $S_{\text{RN}}1$  reactions. Recrystallisation of the crude product from hexane gave colourless crystals of 1-azido-1-methylethyl phenyl sulphone (0.60 g, 70%), m.p.  $72\text{--}73^\circ\text{C}$  (Found: C, 47.6; H, 4.6; N, 18.6.  $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  requires C, 48.0; H, 4.8; N, 18.6%);  $\nu_{\text{max}}$  (Nujol) 2 103 ( $\text{N}_3$ ), 1 595, 1 300, and 1 150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.52 (6 H, s) and 7.5 (5 H, m).

Inhibition studies were carried out as detailed in the general procedure for inhibition studies. The reaction was repeated in DMSO (for different time periods), DMF, and HMPA. The results are presented in Table 3.

(b) *1-(1-Azidocyclohexyl) phenyl sulphone.* 1-Azido-1-nitrocyclohexane (0.50 g, 2.9 mmol) and sodium benzenesulphinate (0.98 g, 6 mmol) were allowed to react in DMSO for 14 h as detailed in the general procedure for  $S_{\text{RN}}1$  reactions.

Recrystallisation of the crude product from hexane gave colourless crystals of 1-(1-azidocyclohexyl) phenyl sulphone (0.41 g, 53%), m.p. 88–89 °C (Found: C, 54.4; H, 5.6; N, 16.1.  $C_{12}H_{15}N_3O_2S$  requires C, 54.3; H, 5.6; N, 15.8%);  $\nu_{\max}$  (Nujol) 2 120 ( $N_3$ ), 1 595, 1 300, and 1 150  $cm^{-1}$ ;  $\delta_H$  1.65 (10 H, m) and 7.30 (5 H, m).

(c) 1-Azido-1-methylethyl *p*-chlorophenyl sulphone. Sodium *p*-chlorophenylsulphinat (1.59 g, 8 mmol) and 2-azido-2-nitropropane (0.50 g, 3.8 mmol) were allowed to react in DMF for 40 min as detailed in the general procedure for  $S_{RN}1$  reactions. Recrystallisation of the crude product from hexane gave colourless crystals of 1-azido-1-methylethyl *p*-chlorophenyl sulphone (0.20 g, 20%), m.p. 67–68 °C (Found: C, 41.9; H, 4.0; N, 16.55.  $C_9H_{10}N_3O_2S$  requires C, 41.6; H 3.9; N, 16.2%);  $\nu_{\max}$  (Nujol) 2 110 ( $N_3$ ), 1 600, 1 320, and 1 120  $cm^{-1}$ ;  $\delta_H$  1.60 (6 H, s) and 7.50 (4 H, ABq).

(d) 1-Azido-1-methylethyl *p*-chlorophenyl sulphide. The sodium salt of *p*-chlorobenzene thiol (1.40 g, 8.4 mmol) and 2-azido-2-nitropropane (0.50 g, 3.8 mmol) were allowed to react in DMF for 40 min as detailed in the general procedure for  $S_{RN}1$  reactions. Purification of the crude product by column chromatography on alumina with ethyl acetate–diethyl ether (9:1) as eluant yielded a clear liquid of 1-azido-1-methylethyl *p*-chlorophenyl sulphide (0.61 g, 70%) (Found: C, 47.9; H, 4.3; N, 18.0.  $C_9H_{10}ClN_3S$  requires C, 47.5; H, 4.3; N, 18.45%);  $\nu_{\max}$  (neat film) 2 110 ( $N_3$ ), 1 590, 840, and 760  $cm^{-1}$ ;  $\delta_H$  1.51 (6 H, s) and 7.30 (4 H, ABq). The reaction was repeated with DMSO in place of DMF to give a 34% yield of product.

(e) 1-(1-Azidocyclohexyl) *p*-chlorophenyl sulphide. The sodium salt of *p*-chlorobenzenethiol (1.59 g, 8 mmol) and 1-azido-1-nitrocyclohexane (0.50 g, 2.9 mmol) were allowed to react in DMSO for 1 h as detailed in the general procedure for  $S_{RN}1$  reactions. Purification of the crude product by column chromatography on alumina with ethyl acetate–diethyl ether (9:1) as eluant yielded a yellow oil of 1-(1-azidocyclohexyl) *p*-chlorophenyl sulphide (0.42 g, 53%) (Found: C, 53.5; H, 5.4; N, 15.6.  $C_{12}H_{14}ClN_3S$  requires C, 53.8; H, 5.2; N, 15.7%);  $\nu_{\max}$  (neat film) 2 110 ( $N_3$ ), 1 580, 830, and 760  $cm^{-1}$ ;  $\delta_H$  ( $CDCl_3$ ) 1.55 (10 H, m) and 7.30 (4 H, ABq).

**Reaction between the Anion of 2-Nitropropane and 2-Azido-2-nitropropane and 1-Azido-1-nitrocyclohexane.**—(a) 2-Azido-2-nitropropane. The sodium salt of 2-nitropropane (2.00 g, 18 mmol) and 2-azido-2-nitropropane (0.50 g, 3.8 mmol) were allowed to react in HMPA as detailed in the general procedure for  $S_{RN}1$  reactions with the exception that the reaction was irradiated with two 150 W fluorescent discharge lamps [mercury blended tungsten universal mounted (MBTU) lamps emitting light maximally at 430 nm from a distance of 10 cm]. Recrystallisation of the crude product from ethanol gave colourless crystals of 2,3-dimethyl-2,3-dinitrobutane (0.16 g, 24%), m.p. 206–208 °C (lit.,<sup>23</sup> 208–209 °C). The i.r. and n.m.r. spectra were identical with those of authentic material.

(b) 1-Azido-1-nitrocyclohexane. The sodium salt of 2-nitropropane (1.00 g, 9 mmol) and 1-azido-1-nitrocyclohexane (0.50 g, 2.9 mmol) were allowed to react in DMSO for 2 h as detailed in section (a). The crude product was analysed by n.m.r. spectroscopy. Recrystallisation of the crude product from ethanol yielded colourless crystals of 1-(1-methyl-1-nitroethyl)-1-nitrocyclohexane, m.p. 148–150 °C (lit.,<sup>26</sup> 149–150 °C). The i.r. and n.m.r. spectra were identical to those of authentic material.

Light catalysis and inhibition studies of both reactions were carried out as detailed in the general procedure. The results are presented in Table 4.

**Reaction between 2-Azido-2-nitropropane and the Anion of Diethyl Ethylmalonate.**—2-Azido-2-nitropropane (0.25 g, 1.9

mmol) and the anion of diethyl ethylmalonate (0.51 g, 2.4 mmol) were allowed to react in DMSO for 3 h as detailed in section (a) above. The crude product showed one spot on t.l.c. (silica gel/chloroform). Kugelrohr distillation gave pure tetraethyl hexane-3,3,4,4-tetracarboxylate (0.10 g, 22%), b.p. 173–175 °C (40 mmHg) [lit.,<sup>27</sup> 128–129 °C (0.5 mmHg)].

**E.S.R. Spectroscopy.**—Degassed samples were irradiated as dilute solutions (ca. 1% v.v.) in methanol ( $CD_3OD$  was used to avoid overlap with solvent radical features) or MeTHF. They were frozen as small beads in liquid nitrogen and irradiated at 77 K in a Vickrad  $^{60}Co$   $\gamma$ -ray source to doses of up to 1 Mrad. E.s.r. spectra were measured on a Varian E109 spectrometer. Samples were annealed to selected temperatures or until significant changes occurred in the e.s.r. spectra, and recooled to 77 K for study.

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