etaldehyde, the solvent was removed under vacuum at room temperature. The residue was dissolved in a small quantity of ether and 1 mol of 2-aminoethanol was added. The solution was filtered and the ether concentrated under vacuum (but not to dryness) (a drop or two of methanol will redissolve any precipitate). The product was eluted with ether from a silica gel column, concentrated by rotary evaporator, and distilled by Kugelrohr at 0.01 mmHg, 110 °C, yield 46%. (We have previously isolated this alcohol in 76% on a larger scale using *B*-siamyl-9-BBN.[5])

***p*-Dimethylaminobenzyl-*1-d* Alcohol.** The following modified procedure was used: The reaction was refluxed in THF for 8 h. The solution was then cooled to room temperature and treated with 2 mL of water, stirred for 15 min, and then extracted with 2 × 30 mL of acidified water (concentrated HCl added dropwise until the solution had a pH of 1). The aqueous solution extracts were combined, made basic to pH paper (with 3 N sodium hydroxide solution), and extracted with 2 × 20 mL of ether (saturating the water with potassium carbonate after the first extraction). The combined extracts were dried over magnesium sulfate, filtered, and concentrated under vacuum to yield the product (60%). Using *B*-siamyl-9-BBN on a larger scale, we have isolated the alcohol in 92% yield.[5]

Organoborane–Aldehyde Complex. *p*-Dimethylaminobenzaldehyde, 0.25 mmol, in 0.5 mL of THF was added to a nitrogen-flushed NMR tube. *B*-Methyl-9-BBN[20] (0.25 mmol) was added and the solution immediately became reddish orange. The aldehyde proton shifted from 9.70 to 9.45 ppm. Addition of excess *B*-methyl-9-BBN (3 mmol of borane to 0.1 mmol of aldehyde) caused an additional shift to a maximum value of 9.00 ppm.

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Electron Transfer Processes. 18. Reaction of 2-Halo-2-nitropropanes and 2,2-Dinitropropane with Resonance-Stabilized Carbanions and 1-Alkynyllithiums[1]

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Abstract: α-Substituted benzylic carbanions react with 2-X-2-nitropropane, where X = Cl, Br, or NO_2, to undergo dimerization with no evidence of formation of cross-coupling products. Lithium acetylenides (RC≡CLi, R = alkyl) react with 2-chloro-2-nitropropane or 2,2-dinitropropane to form the cross-coupled product ($RC{\equiv}CC(CH_3)_2NO_2$) by a process which does not involve a free radical chain mechanism. 2-Cyano-2-nitropropane reacts with lithium acetylenides in THF to form the cyanoacetylene (RC≡CCN).

2-Halo-2-nitropropanes, 2,2-dinitropropane, or 2-arylsulfonyl-2-nitropropane undergo a variety of reactions with carbanions. Substitution at carbon with loss of halide,[2] nitrite,[3] or arylsulfinate anions[4] can occur via a free radical chain process which has been labeled $S_{RN}1$ (Scheme I).[5]

This process has been observed with tertiary carbanions including anions derived from nitroalkanes, malonic esters, malononitriles, β-keto nitriles, cyanoacetic esters, β-keto esters, and β-diketones.[2-5]

Scheme I

$$X = Cl, Br, NO_2, ArSO_2$$

$$[XC(R)_2NO_2]^{-\cdot} \rightarrow X^- + R_2\dot{C}NO_2$$

$$R_2\dot{C}NO_2 + {>}C{:}^- \rightarrow [O_2NC(R)_2C{<}]^{-\cdot}$$

$$[O_2NC(R)_2C{<}]^{-\cdot} + XC(R)_2NO_2 \rightleftharpoons O_2NC(R)_2C{<} + [XC(R)_2NO_2]^{-\cdot}$$

A modified radical pathway leads to the dimerization of the carbanions (Scheme II).[6] The nitronate anion formed in Scheme II can react further with the substituted nitroalkane via the $S_{RN}1$ process to yield the dimer of the nitroalkane ($R_2C(NO_2)C(NO_2)R_2$). Dehydrogenation of the dimerization

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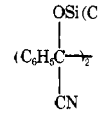
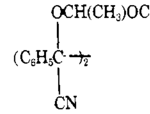
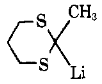
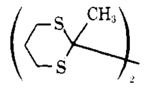
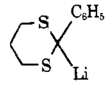
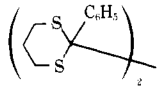
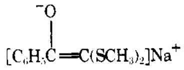
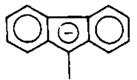
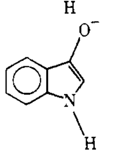
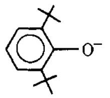
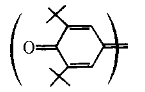
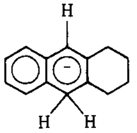
Table I. Products of Reactions of Carbanions with 2-X-2-Nitropropanes

carbanion	X	solvent (temp, °C)	product (%)	
$[C_6H_5C(OSi(CH_3)_3)CN]^-Li^+$	Cl or Br	THF (−70 to 20)	 $(C_6H_5C(OSi(CH_3)_3)(CN)\!-\!)_2$	(50)
$[C_6H_5C(OCH(CH_3)OC_2H_5)CN]^- Li^+$	Br	THF (−70 to 20)	 $(C_6H_5C(OCH(CH_3)OC_2H_5)(CN)\!-\!)_2$	(55)
$[(C_6H_5)_2CCN]^-Na^+$	Cl	CH_3OH (25)	$((C_6H_5)_2C(CN)\!-\!)_2$	(78)
	Br	THF (3-50)		(65)
	Cl, Br, or NO_2	THF (−20)		(~100)
 $[C_6H_5C(O^-)\!=\!C(SCH_3)_2]Na^+$	Br	THF (65)	$(C_6H_5COC(SCH_3)_2\!-\!)_2$	(56)
 K^+	NO_2 (excess)	Me_2SO (25)	$\Delta^{9,9'}$-bifluorene	(82)
 K^+	NO_2 or Br (excess)	*t*-BuOH (25)	indigo	(95)
 K^+	Cl (excess)	*t*-BuOH (25)		(36)
	Cl (excess)	Me_2SO/*t*-BuOH (25)	anthracene	(77)

products can also occur, presumably via Scheme III. Thus, indoxyls in basic solution react with 2-chloro-2-nitropropane to undergo oxidative dimerization and further dehydrogenation to yield indigos.[7]

Scheme II

$$XC(R)_2NO_2 + {}^-\!:\!C\!\lessdot \rightarrow [XC(R)_2NO_2]^{-\cdot} + \cdot C\!\lessdot$$
$$[XC(R)_2NO_2]^{-\cdot} \rightarrow X^- + R_2\dot{C}NO_2$$
$$R_2\dot{C}NO_2 + {}^-\!:\!C\!\lessdot \rightarrow R_2C\!=\!NO_2^- + \cdot C\!\lessdot$$
$$2\,\cdot C\!\lessdot \rightarrow \gtrdot C\!-\!C\!\lessdot$$

There also exists the possibility of an S_N2 displacement of X to yield the same coupled product formed in Scheme I, or of an E_2 elimination of HX or HNO_2.[8]

Herein we report some examples of carbanions which undergo reaction by Schemes II or III. In addition we report the reaction of lithium acetylides with 2-chloro-2-nitropropane and 2,2-dinitropropanes in which coupling occurs by what appears to be a nucleophilic substitution process not involving a free radical chain mechanism.

$$RC{\equiv}CLi + O_2NC(CH_3)_2X \rightarrow RC{\equiv}CC(CH_3)_2NO_2 + X^- \quad (1)$$

X=Cl, NO_2

1a, R=CH_3
1b, R = C_2H_5
1c, R = *n*-C_3H_7
1d, R = *n*-C_4H_9

Scheme III

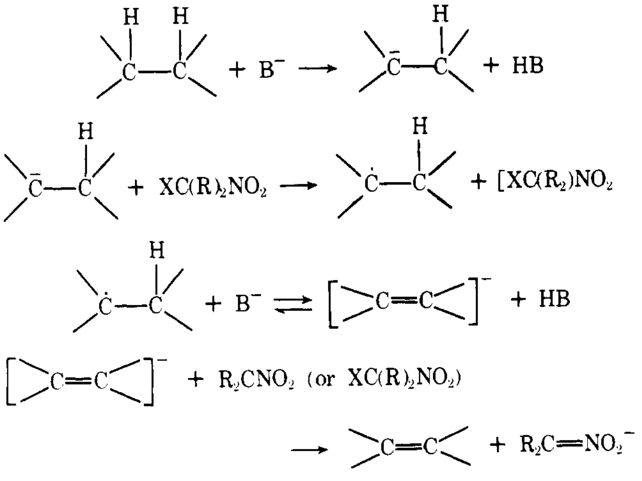
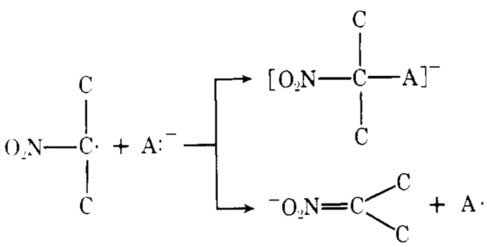


Table I lists carbanions which react by Schemes II or III. Many of the oxidative dimerizations of Table I can also be achieved using nitrobenzenes as the electron acceptor. Thus, reaction of 2-lithio-2-phenyl-1,3-dithiane with 2,4-dinitrobromobenzene yields the dimer in nearly quantitative yield,[9] while diphenylacetonitrile can be dimerized by nitrobenzene in basic solution.[10] Some 9-substituted fluorenes can be dimerized in the presence of base and nitrobenzene or 3,5-dichloronitrobenzene.[11] Coupling of the anion of ω,ω-di(methylmercapto)acetophenone by bromine to give *cis*- and *trans*-2,3-dibenzoyl-1,2-di(methylmercapto)ethylene has been previously observed.[12]

Lithium dialkylcuprates (R_2CuLi) are readily oxidized by nitrobenzene to yield the alkane R–R via a R_2Cu intermediate.[13] Similarly, 2-chloro-2-nitropropane and $(n\text{-}C_4H_9)_2CuLi$ in THF at −20 °C gave *n*-octane in 65% yield.

The scope of the $S_{RN}1$ reaction involving the 2-nitro-2-propyl radical is limited by the competition between reaction 2 (leading to substitution by Scheme I) and reaction 3 (leading to dimerization by Scheme II). When the anion A^- contains a conjugated phenyl group which can lead to a substituted benzyl radical (A·), reaction 3 greatly predominates. Other substituents which will provide resonance stabilization of A·, such as vinyl, mercapto, dialkylamino, and alkoxy, should also favor reaction 3 over 2. Occurrence of the $S_{RN}1$ process requires substituents in A which will stabilize the carbanion, but not the radical. The major group of substituents in this class are ester, nitrile, keto, nitro, sulfone, and sulfoxide functional groups. These substituents provide little or no activation relative to an alkyl group in hydrogen atom abstraction reactions for >CHX or H_2CX_2 by carbon radicals such as the phenyl radical.[14]



(2)

(3)

Carbanoid reagents without functional groups, such as butyl- or phenyllithium, react vigorously with 2-halo-2-nitropropanes or 2,2-dinitropropane to produce a variety of products with no evidence that the $S_{RN}1$ process is occurring. It was thus surprising to observe that lithium acetylenides react in THF or THF/hexane to give significant amounts of the coupling products (reaction 1). Table II summarizes the observed yields.

The sodium salts of 1-pentyne or propyne in THF or DMF, the potassium salt of 1-pentyne in Me_2SO, or the sodium salt of acetylene in liquid ammonia failed to yield the coupling product with 2-chloro-2-nitropropane. Treatment of 1-pentyne in THF with ethylmagnesium bromide followed by 2-chloro-2-nitropropane gave a low yield (<20%) of the coupling product. The reaction of 2-chloro-2-nitropropane or 2,2-dinitropropane with hexynyllithium was accompanied by the 2-nitropropane dimer ($O_2NC(CH_3)_2C(CH_3)_2NO_2$) in about 10% yield and 7,7,8,8-tetramethyl-5,9-tetradecadiyne in isolated yields up to 6% (reaction 4).

$$RC{\equiv}CC(CH_3)_2NO_2 \xrightarrow{RC{\equiv}CLi} \underset{\mathbf{2},\ R\,=\,n\text{-}C_4H_9}{RC{\equiv}CC(CH_3)_2C(CH_3)_2C{\equiv}CR} \qquad (4)$$

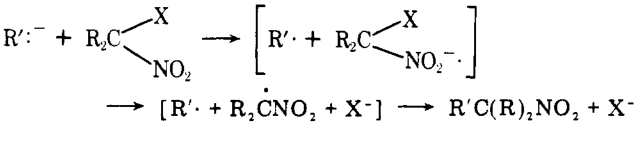
We have seen no evidence for a free radical chain mechanism for reaction 1. The presence of air or illumination with a sunlamp (Pyrex) or by UV (silica) did not have a significant effect. Addition of di-*tert*-butyl nitroxide or *p*-dinitrobenzene also had no appreciable effect on the final yield of coupled product. 2-Bromo-2-nitropropane, 2-(*p*-tolylsulfonyl)-2-nitropropane, and 2-cyano-2-nitropropane failed to give significant amounts of the coupling product.[15] In the case of 2-bromo-2-nitropropane appreciable amounts of the 2-nitropropane dimer was formed suggesting the intermediacy of $(CH_3)_2C{=}NO_2^-$. This dimer was also the only isolable product from the reaction of the potassium acetylides with 2-chloro-2-nitropropane in Me_2SO solution at 50 °C.

Table II. Reaction of $RC{\equiv}CLi + XC(CH_3)_2NO_2$ in THF

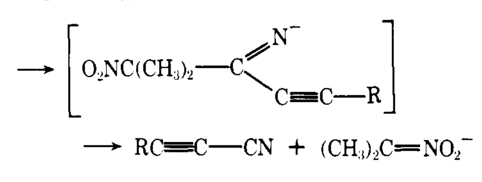
R	X	temp, °C	time, h	yield of $RC{\equiv}CC(CH_3)_2NO_2$, %
CH_3	Cl	64	5	5
CH_3	Cl	30	39	20
C_2H_5	Cl	64	6	20
C_2H_5	Cl	30	44	47
$n\text{-}C_3H_7$	Cl	55	5	43
$n\text{-}C_3H_7$	Cl	32	28	53
$n\text{-}C_3H_7$	NO_2	30	48	52[a]
$n\text{-}C_3H_7$	NO_2	55	5	48
$n\text{-}C_4H_9$	Cl	55	5	46
$n\text{-}C_4H_9$	Cl	64	12	33
$n\text{-}C_4H_9$	Cl	64	12	34.5[b]
$n\text{-}C_4H_9$	NO_2	50	5	24
$n\text{-}C_4H_9$	Cl	34	19	16[c]
$n\text{-}C_4H_9$	Cl	50	5.5	30[d]
$n\text{-}C_4H_9$	Cl	70	18	10[e]
$n\text{-}C_5H_{11}$	Cl	55	5	33
$n\text{-}C_6H_{13}$	Cl	55	5	21

[a] In the presence of 6 mol % of di-*tert*-butyl nitroxide the yield was 48%. [b] Irradiated by a sunlamp through Pyrex. [c] In Et_2O. [d] In DME. [e] In hexane.

Scheme IV. $S_{ET}2$ Mechanism



We believe that a nonchain, electron-transfer mechanism deserves serious consideration for this substitution process observed with 2-chloro-2-nitropropane or 2,2-dinitropropane (Scheme IV), wherein carbon–carbon bond formation occurs in a solvent cage.[16] This mechanism is consistent with substitution at a tertiary center and with the fact that the reaction proceeds as readily with X = NO_2 as X = Cl.[17] For the $S_{ET}2$ process to proceed the stability of $R_2C(X)NO_2^{-}\cdot$ should be such that decomposition to $R_2\dot{C}NO_2$ and X^- can occur before the initially formed radical and radical anion have diffused apart. This may be the reason why 2-cyano-2-nitropropane or 2-(*p*-tolylsulfonyl)-2-nitropropane fail to yield significant amounts of coupling products. The occurrence of other reactions may also be responsible for the failure of 2-cyano-2-nitropropane to yield the coupling product with acetylenide anions. Thus, in the case of 2-cyano-2-nitropropane yields of greater than 50% of the cyanoacetylenes have been isolated (reaction 5).



(5)

Experimental Section

Reaction of *O*-Trimethylsilylbenzaldehyde Cyanohydrin Anion with 2-Substituted 2-Nitropropanes. The anion was prepared at −70 °C by lithium disopropylamide in THF.[18] After addition of an equal molar amount of 2-bromo-2-nitropropane or 2-chloro-2-nitropropane the temperature was allowed to rise to 20 °C. After 1 h at 20 °C the reaction product was treated with water and extracted with pentane. The pentane solution was dried ($MgSO_4$) and concentrated to give di-*O*-trimethylsilylbenzil bis(cyanohydrin): mp 183°C; ^{1}H NMR (CCl_4) δ −0.19 (s, 18), 7.1–7.7 (m, 10).

Anal. Calcd for $C_{22}H_{22}N_2Si_2O_2$: C, 64.69; H, 6.90; N, 6.85. Found: C, 64.42; H, 6.82; N, 6.86.

Reaction of α-Ethoxyethyl Ether of Benzaldehyde Cyanohydrin Anion with 2-Bromo-2-nitropropane. The carbanion prepared in THF/HMPA by lithium diisopropylamide[19] was treated with an equimolar quantity of 2-bromo-2-nitropropane at −70 °C. After warming to 20 °C the mixture was poured into water and extracted with benzene to give 55% of the di-α-ethoxyethyl ether of benzil bis(cyanohydrin) as a mixture of two diastereomers: mp 125–132 °C; ^{1}H NMR (CCl_4) δ 0.6–1 (m, 6), 1.25 (d, 6, J = 5 Hz), 3.15 (q, 4, J = 5 Hz), 4.6–5 (m, 2), 7.15–7.75 (m, 10).

Anal. Calcd for $C_{24}H_{28}O_4N_2$: C, 70.56; H, 6.91; N, 6.86. Found: C, 70.59; H, 7.06; N, 7.07.

Reaction of the Anions of 2-Substituted 1,3-Dithianes with 2-Substituted 2-Nitropropanes. The lithium salt of 2-methyl-1,3-dithiane in THF[20] was reacted with an equimolar amount of 2-bromo-2-nitropropane at −3 °C to give 65% of 2,2′-dimethyl-2,2′-bis(1,3-dithiane): mp 185 °C (lit.[20] mp 184–186 °C); mass spectrum *m/e* 266 (M^+).

2-Phenyl-1,3-dithiane in ethyl ether or THF was converted to the lithium salt by *n*-butyllithium at −20 °C. An equimolar amount of the 2-X-2-nitropropane (X = Cl, Br, NO_2) was added at −20 °C and the mixture allowed to warm to room temperature over a 1-h period. The reaction product was added to water and filtered to give 2,2′-diphenyl-2,2′-bis(1,3-dithiane), mp 210–212 °C (lit.[9] mp 204 °C) in quantitative yield; ^{1}H NMR ($CHCl_3$) δ 1.75–2.2 (m, 4), 2.5–2.8 (m, 8), 7.2–7.8 (m, 10).

Reaction of the Anion of ω,ω-Di(methylmercapto)acetophenone with 2-Bromo-2-nitropropane. The enolate was prepared in THF from 10 mmol of the mercaptal by use of sodium hydride.[12] An excess (20 mmol) of 2-bromo-2-nitropropane was added dropwise at 65 °C and the mixture refluxed for 3 h. The mixture was poured into water and extracted with hexane to give 1.2 g of material, mp 117–129 °C. The ^{1}H NMR of the crude material gave a -SCH_3 singlet at δ 2.33 (ω,ω-di(methylmercapto)acetophenone, δ 2.05, 5.13; (*E*)-1,2-dibenzoyl-1,2-di(methylmercapto)ethylene, δ 2.13) and the methyl singlet of unreacted 2-bromo-2-nitropropane at δ 2.25. The mercaptal had been completely consumed and 61% of the bromide was found as bromide ion in the aqueous solution. The product could be separated from the unreacted 2-bromo-2-nitropropane by recrystallization to give material melting with decomposition at 118–127 °C and with a ^{1}H NMR consistent with 1,2-dibenzoyl-1,1,2,2-tetra(methylmercapto)ethane (δ (CCl_4) 2.33 (s, 12), 7.3–8.1 (m, 10)). This product decomposed in solution (ethyl acetate–hexane or chloroform) or when chromatographed on neutral alumina. Elution from alumina with hexane followed by 2% ether in hexane gave (*E*)-1,2-dibenzoyl-1,2-di(methylmercapto)ethylene: mp 71 °C (lit.[12] mp 69–70.5 °C), ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 6), 7.2–7.9 (m, 10). The compound of mp 118–127 °C in $CDCl_3$ after 5 days gave a ^{1}H NMR spectrum containing -SCH_3 methyl singlets in equal intensity from (*E*)-1,2-dibenzoyl-1,2-di(methylmercapto)ethylene (δ 2.1) and dimethyl disulfide (δ 2.4).

Reaction of 2-Chloro-2-nitropropane with Resonance-Stabilized Allylic Anions. 2,2-Diphenylvinylacetic acid[21] was converted to the methyl ester: bp 134 °C (0.2 Torr); ^{1}H NMR (CCl_4) δ 3.1 (d, 2), 3.65 (s, 3), 6.15 (t, 1), 7.1–7.4 (m, 10). Treatment of 2.5 g of this ester with sodium hydride in DMF followed by 1 equiv of 2-chloro-2-nitropropane gave a thick oil which could be partially crystallized from methanol to give 1 g of material, mp 157 °C, which does not contain the 2-nitro-2-propyl group by ^{1}H NMR or IR. The structure was not investigated further, but apparently the product is a dimer of the starting ester.

4,4-Diphenylacrylonitrile was prepared by the condensation of diphenylacetaldehyde and cyanoacetic acid in pyridine solution containing 3% of piperidine at 60–70 °C (exothermic reactions with evolution of carbon dioxide). After refluxing for 2 h the mixture was poured into 10% hydrochloric acid and the precipitate collected and crystallized from ethanol to give 88% of 4,4-diphenylacrylonitrile: mp 97 °C; ^{1}H NMR (CCl_4) δ 3.02 (d, 2 H), 6.0 (t, 1 H), 7.0–7.5 (m, 12 H). Reaction of 2.25 g of this material with an equimolar amount of 2-chloro-2-nitropropane in a two-phase system containing 40% aqueous sodium hydroxide and triethylbenzylammonium chloride gave 1.5 g of a bright yellow solid, mp 220 °C after crystallization from ethanol–benzene. The ^{1}H NMR spectrum contained only protons in the vinyl or aromatic region. The structure was not further investigated, but the product appears to be 1,6-dicyano-3,3,4,4-tetraphenyl-1,5-hexadiene.

Reaction of Lithium Propynide with 2-Chloro-2-nitropropane. Propyne (2.0 g, 0.05 mol) in 45 mL of THF was treated with 31 mL of 1.6 M butyllithium in THF (0.05 mol) at −40 °C. At 10 °C 6.2 g (0.05 mol) of 2-chloro-2-nitropropane was added and the mixture maintained at 30 °C for 39 h. After treatment with 500 mL of water the mixture was extracted with three 50-mL portions of hexane. The water layer contained 0.023 mol of chloride ions. The hexane solution was washed, dried ($MgSO_4$), and distilled at 50 Torr to give 1.2 g of 2-chloro-2-nitropropane and 1.0 g of 2-methyl-2-nitro-3-pentyne by GLC. Redistillation gave 0.9 g of 2-methyl-2-nitro-3-pentyne: bp 81°C (50 Torr); n_D^{20} 1.4402; ^{1}H NMR (CCl_4) δ 1.8 (s, 6), 1.92 (s, 3); IR (neat) 2250 ($C\equiv C$), 1560 and 1350 (NO_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 81 (M^+ − 46, 92), 80 (89), 79 (70), 77 (48), 65 (40), 53 (66), 51 (25), 43 (37), 41 (98), 40 (32), 39 (10), 30 (95), 27 (37).

Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.04. Found: C, 56.86; H, 7.30; N, 11.11.

2-Methyl-2-nitro-3-hexyne. Substitution of 2.7 g of 1-butyne for the propyne of the previous experiment with a reaction period of 44 h at 30 °C gave 70% of ionic chlorine, 0.3 g of recovered 2-chloro-2-nitropropane, and 3.3 g of 2-methyl-2-nitro-3-hexyne (47%): bp 84–87 °C (30 Torr); $n^{25}{}_D$ 1.4413; ^{1}H NMR (CCl_4) δ 1.17 (t, 3, J = 7 Hz), 1.8 (s, 6), 2.26 (q, 2, J = 7 Hz); IR (neat) 2240 ($C\equiv C$), 1560 and 1350 (NO_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 95 (M^+ − 46, 42), 94 (65), 93 (61), 79 (78), 77 (100), 67 (35), 55 (45), 53 (45), 51 (32), 41 (48), 39 (62), 30 (95), 29 (71), 28 (38).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.55; H, 7.86; N, 9.92. Found: C, 59.64; H, 7.71; N, 10.03.

2-Methyl-2-nitro-3-heptyne. Substitution of 3.9 g of 1-pentyne in the above experimental conditions (48 h, 30 °C) gave 4.0 g (52%) of 2-methyl-2-nitro-3-heptyne: bp 91 °C (25 Torr); $n^{25}{}_D$ 1.4451; ^{1}H NMR (CCl_4) δ 1 (t, 3, J = 6 Hz), 1.5 (m, 2, J = 6 Hz), 1.78 (s, 6), 2.2 (t, 2, J = 6 Hz); IR (neat) 2260 ($C\equiv C$), 1560 and 1350 (NO_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 109 (M^+ − 46, 27), 108 (40), 93 (30), 91 (30), 79 (38), 77 (50), 67 (35), 55 (25), 53 (25), 50 (55), 43 (38), 42 (34), 41 (56), 39 (45), 30 (100), 28 (88), 27 (34).

Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 14.01. Found: C, 61.21; H, 8.29; N, 9.46.

Reaction of pentynyllithium (0.03 mol) with 2-bromo-2-nitropropane (0.03 mol) at −20 °C followed by 2 h at 30 °C gave 1.2 g (45%) of 2,3-dinitro-2,3-dimethylbutane, mp 214 °C.

2-Methyl-2-nitro-3-octyne. Substitution of 4.1 g of 1-hexyne in the experiment described above (55 °C, 5 h) gave 80% of ionic chlorine and 3.9 g (46%) of 2-methyl-2-nitro-3-octyne: bp 61 °C (1.0 Torr); $n^{25}{}_D$ 1.4440; ^{1}H NMR (CCl_4) δ 0.8–1.1 (m, 3), 1.25–1.65 (m, 4), 1.77 (s, 6), 2.07–2.35 (m, 2); IR (neat) 2240 ($C\equiv C$), 1550 and 1340 (NO_2) cm^{-1}; mass spectrum *m/e* (rel intensity) 123 (M^+ − 46, 21), 122 (32), 107 (30), 93 (45), 91 (39), 81 (40), 79 (98), 77 (61), 67 (45), 55 (27), 53 (35), 43 (45), 41 (70), 39 (53), 30 (85), 28 (100), 27 (44).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.87; H, 8.93; N, 8.28. Found: C, 63.62; H, 8.59; N, 8.47.

Chromatography of the distillation residue from the above reaction on neutral alumina using hexane as the eluent gave 2,3-dinitro-2,3-dimethylbutane, mp 207 °C, in yields between 5 and 10%. With 2-bromo-2-nitropane yields of 2,3-dimethyl-2,3-dinitrobutane between 10 and 30% were isolated and no significant amounts of 2-methyl-2-nitro-3-octyne were found.

7,7,8,8-Tetramethyl-5,9-tetradecadiyne. Careful distillation of the high-boiling residue from the reaction of 2-chloro-2-nitropropane and 1-hexynyllithium gave 0.5 g (6%) of the decadiyne: bp 118–125 °C (0.3 Torr); $n^{25}{}_D$ 1.4753 (lit.[22] $n^{20}{}_D$ 1.4800); ^{1}H NMR (CCl_4) δ 0.92 (m), 1.2–1.6 (m), 2.0–2.3 (m); mass spectrum (70 eV) *m/e* (rel intensity) 231 (M^+ − 15, 2.9), 189 (27), 167 (100), 149 (22), 123 (25), 121 (39), 111 (51), 109 (40), 108 (28), 107 (58), 93 (43), 91 (78), 82 (25), 81 (85), 80 (23), 79 (81), 77 (60), 69 (46), 68 (26), 67 (63), 55 (87), 53 (34), 51 (34).

2-Methyl-2-nitro-1-nonyne. 1-Heptyne and 2-chloro-2-nitropropane yielded material: bp 53–54 °C (0.1 Torr); ^{1}H NMR (CCl_4) δ 0.9 (t, 3, J = 6.3 Hz), 1.39 (m, 6), 1.77 (s, 6), 2.21 (t, 2, J = 6.8 Hz); IR (neat) 2263 ($C\equiv C$), 1556 and 1352 (NO_2) cm^{-1}.

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.55; H, 9.35; N, 7.64. Found: C, 65.49; H, 9.42; N, 7.31.

2-Methyl-2-nitro-1-decyne. Reaction of 1-octyne and 2-chloro-2-nitropropane gave material: bp 62–64 °C (0.1 Torr); n^{20}_{D} 1.4452; ^{1}H NMR (CCl_4) δ 0.90 (t, 3, J = 6.1 Hz), 1.30 (m, 8), 2.12 (t, 2, J = 6.1 Hz), 1.78 (s, 6).

Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.97; H, 9.75; N, 6.80.

Reaction of 2-Cyano-2-nitropropane with 1-Pentynyllithium. To 0.05 mol of 1-pentynyllithium in THF at −50 °C was added 5.7 g (0.05 mol) of 2-cyano-2-nitropropane.[23,24] After 1 h at −50 °C the reaction mixture was diluted with water and extracted with hexane to give 3.9 g of material, bp 30–40 °C (0.1 Torr). By GC–mass spectrum tetramethylsuccinonitrile (M^+ 114) and 2-hexynenitrile (major product) [*m/e* (rel intensity) 93 (M^+, 88), 89 (27), 71 (121), 58 (28), 57 (56), 55 (33), 50 (20)] were present. Repeated distillations gave 2.8 g (60%) of 2-hexynenitrile: bp 51–53 °C (20 Torr); n^{25}_{D} 1.4385; n^{20}_{D} 1.4416 (lit.[25] bp 34–36 (11 Torr); n^{20}_{D} 1.4444); ^{1}H NMR (CCl_4) δ 1.07 (t, 3, J = 6 Hz), 1.3–1.9 (m, 2), 2.35 (t, 2, J = 6 Hz); IR (neat) 2320 ($C{\equiv}N$), 2260 ($C{\equiv}C$), 1575, 1465, 1345 cm^{-1}.

Reaction of 2-Cyano-2-nitropropane with 1-Hexynyllithium. To the hexynyllithium obtained from 4.1 g (0.05 mol) of 1-hexyne in 40 mL of THF at −50 °C, 5.7 g (0.05 mol) of 2-cyano-2-nitropropane was added slowly as the temperature increased to −30 °C. After 30 min at −30 °C the reaction mixture was quenched with water and extracted with hexane. Distillation at 1 Torr gave a fraction in which 2-cyano-2-nitropropane ($M^+ - 46 = 68$), tetramethylsuccinonitrile (M^+ 114) and 2-heptynenitrile (major component) were detected by GC–mass spectrum. The mass spectrum of 2-heptynenitrile gave *m/e* (rel intensity) 108 (M^+ + H, 10), 107 (M^+, 2.6), 106 (M^+ − H, 27), 92 ($M^+ - CH_3$, 81), 80 (M^+ − HCN, 41), 79 ($M^+ - C_2H_4$, 41), 78 ($M^+ - C_2H_5$, 12), 65 ($M^+ - C_3H_6$, 100), 56 (C_4H_8, 14), 51 (C_3HN, 40), 50 (C_3N, 27).

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Electron Transfer Processes. 19. Reaction of Aryl Radicals with Anions in Aqueous Solution[1]

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Abstract: Phenyl radicals and a variety of substituted phenyl radicals are readily trapped in aqueous solution by the anions of nitromethane, -ethane, or -propane to yield the radical anions which can be detected by ESR spectroscopy. Nitrite ion will also capture a variety of phenyl radicals in the absence of any heavy-metal ions. The *p*-nitrophenyl radical can be trapped only by oxidation-resistant anions, such as nitrite or cyanide. The trapping of radicals by anions is greatly facilitated by the presence of a nitro group which will stabilize the resulting radical anion. In the absence of a trapping agent aryldiazonium ions and sodium dithionite form a variety of unstable paramagnetic species.

The reaction of a radical with an anion to form a radical anion with a new bond, particularly a carbon–carbon bond, had not received serious consideration prior to 1966, when it was suggested as a key step in the reaction of the anion of 2-nitropropane with 2-halo-2-nitropropanes or *p*-nitrobenzyl chloride.[2] The coupling reaction has been demonstrated to occur by a free radical chain process that is most reasonably formulated as reactions 1-3,[2] and has been given the label $S_{RN}1$.[3]

$$R\cdot + (CH_3)_2C{=}NO_2^- \rightarrow RC(CH_3)_2NO_2\cdot^- \qquad (1)$$

$$R - X + RC(CH_3)_2NO_2\cdot^- \rightarrow RX\cdot^- + RC(CH_3)_2NO_2 \qquad (2)$$

$$RX\cdot^- \rightarrow R\cdot + X^- \qquad (3)$$

A number of reactions involving radicals and heavy metal salts have at times been formulated as involving addition of the

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