Free Radical Chain Nucleophilic Substitution Reactions of 1-Chloro-1-cyclopropyl-1-nitroethane and 2-Chloro-2-nitrohept-6-ene[1]

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1-Chloro-1-cyclopropyl-1-nitroethane and 2-chloro-2-nitrohept-6-ene underwent free radical chain substitution reactions in which the chlorine was replaced by the nucleophiles $Me_2C{=}NO_2^-$, c-$C_3H_5C(CH_3){=}NO_2^-$, $CH_2{=}CH(CH_2)_3C(CH_3){=}NO_2^-$, $(EtO_2C)_2CMe^-$, $Me_3C(O^-){=}CH_2$, or the enolate anion of 2-methyl-1,3-cyclopentanedione. Ring opening or closure reactions were not observed in these substitutions or in the reaction of 1-chloro-1-cyclopropyl-1-nitroethane with $(n\text{-}Bu)_3SnH$ to form 1-cyclopropyl-1-nitroethane. A 1-nitro substituent retards the rate of the cyclopropylcarbinyl radical ring opening by a factor of at least 10^4 at 40 °C.

Nucleophilic substitution proceeding by a free radical chain mechanism can occur via the $S_{RN}1$ or $S_{RN}2$ processes (Scheme I).[2] Distinction between the $S_{RN}1$ and $S_{RN}2$ routes has been made on the basis of the effect of the leaving group upon nucleophilic selectivity.[6,7] The stereochemical courses of the two processes are also probably different with the $S_{RN}1$ process leading to racemization of R.[8] Another possible experimental distinction would be the intervention of a unimolecular rearrangement of R· to R′· which is possible in the $S_{RN}1$ process but unlikely for the $S_{RN}2$ reaction. Two of the most thoroughly studied unimolecular radical reactions are the cyclization of the 5-hexenyl to cyclopentylcarbinyl radical and the ring opening of cyclopropylcarbinyl to the 3-butenyl radical, processes which occur with rate constants (25 °C) of 1.0×10^5 and 1.3×10^8 s^{-1}, respectively.[9] We have thus synthesized the chloro nitro derivatives **1** and **2** (Scheme II) and examined their reactions with nucleophiles such as $R_2C{=}NO_2^-$, $(EtO_2C)_2CCH_3^-$, $(RO)_2PO^-$, $(EtO)_2PS^-$, $Me_3COCH_2^-$, and the anion of 1-methyl-1,3-cyclopentanedione under S_{RN} conditions ($h\nu$, THF, DMF, or Me_2SO). If the radicals **1a** or **2a** undergo the same unimolecular reactions as the parent radicals, $S_{RN}1$ reactions should lead to the products derived from radicals **1b** or **2b** (Scheme III). On the other hand, $S_{RN}2$ substitutions should lead to unrearranged cyclopropylcarbinyl or Δ^5-hexenyl products. Since **1a** and **2a** contain a trisubstituted radical center stabilized by a nitro group, we were concerned that the **1a** → **1b** and **2a** → **2b** interconversions might not occur readily. However, since the tertiary alkyl derivatives of **2a** (1,1-dimethyl-5-hexenyl radical) undergoes cyclization 1.4 times as readily as 5-hexenyl radical itself[10] and 1,1-dimethylcyclopropylcarbinyl radical undergoes complete ring opening at −73 °C,[11] we felt that the rearrangements of Scheme III would probably compete with the trapping of 1a or **2a** by nucleophiles.

Scheme I

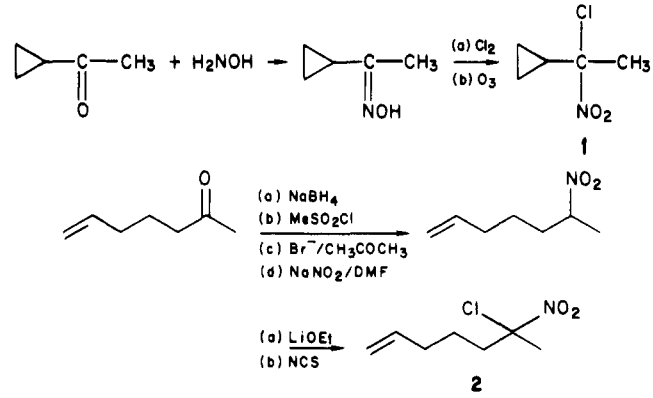
$S_{RN}1$ (ref 3-5)

$$R\cdot + N^- \longrightarrow RN^{-}\cdot$$
$$RN^{-}\cdot + RX \longrightarrow RX^{-}\cdot + RN$$
$$RX^{-}\cdot \longrightarrow R\cdot + X^-$$
$$RX + N^- \longrightarrow RN + X^-$$

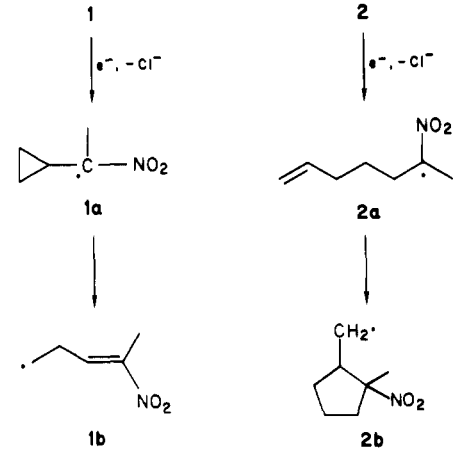
$S_{RN}2$ (ref 6)

$$RX^{-}\cdot + N^- \longrightarrow RN^{-}\cdot + X^-$$
$$RN^{-}\cdot + RX \longrightarrow RX^{-}\cdot + RN$$
$$RX + N^- \longrightarrow RN + X^-$$

Scheme II



Scheme III



Results and Discussion

Reaction of **1** with 1 equiv of $(n\text{-}Bu)_3SnH$ (1.5 M) in benzene at 40 °C with 350-nm irradiation gave after 16 h 1-cyclopropyl-1-nitroethane (46%) and unreacted **1** (23%).

(1) Electron Transfer Processes. Part 35. This work was supported by Grant CHE-8119343 from the National Science Foundation.
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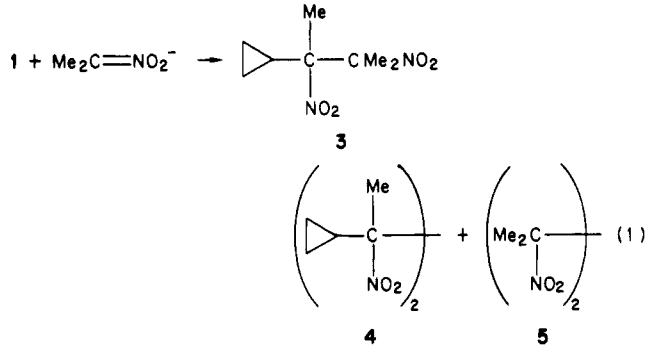
Table I. Reaction of 1 with 5 Equiv of $(n\text{-Bu})_3SnH$ (1.5 M) in Benzene-d_6 at 35–40 °C

conditns[a]	% yield 1	% yield c-$C_3H_5CH(NO_2)Me$
350 nm, 16 h	21.4	43.1
350 nm, 18 h	14.0	51.1
350 nm, 20 h	9.3	53.7
350 nm, 22 h	7.4	46.0
350 nm, 24 h	7.0	41.0
AIBN, 60 °C, 24 h	34.8	38.3
PAT, 60 °C, 24 h	37.2	19.6

[a] AIBN = azobis(isobutyronitrile); PAT = (phenylazo)triphenylmethane.

If ring opening of **1a** to give **1b** had occurred, 2-nitro-2-pentene should have been produced. Although ^1H NMR in benzene-d_6 indicated the absence of vinyl hydrogen atoms during the reduction, it is difficult to completely exclude ring opening since 2-nitro-2-pentene itself reacted completely with 1 equiv of $(n\text{-Bu})_3SnH$ in 6 h under the reaction conditions, presumably to undergo hydrostannation. Under similar conditions, 2-chloro-2-nitropropane reacted with 1 equiv of $(n\text{-Bu})_3SnH$ to form 2-nitropropane (80%) with a recovered yield of 2-chloro-2-nitropropane of 9%. 2-Chloropropane could not be detected in the reaction product. The higher reactivity of 2-chloro-2-nitropropane toward $(n\text{-Bu})_3Sn\cdot$ was confirmed by a competitive reaction of equal amounts of $(n\text{-Bu})_3SnH$, 2-chloro-2-nitropropane, and **1** which yielded, under the standard conditions, 42% of 2-nitropropane and 17% of 1-cyclopropyl-1-nitroethane. With excess $(n\text{-Bu})_3SnH$, 1-cyclopropyl-1-nitroethane was consumed (Table I), and this process may be partially responsible for the low yields of 1-cyclopropyl-1-nitroethane observed. The $(n\text{-Bu})_3SnH$ experiments gave no evidence of the occurrence of the **1a** → **1b** interconversion which we had expected to occur.

The reaction of $Me_2C{=}NO_2^-$ with primary alkyl radicals occurs with a rate constant of 10^5–10^6 L/(mol s) in H_2O or Me_2SO.[12] If ring opening of **1a** to **1b** occurs, there should be no problem in trapping **1b** by $Me_2C{=}NO_2^-$ although the stability of the resulting nitro olefin ($MeC(NO_2){=}CHCH_2CH_2CMeNO_2$) under basic conditions may pose a problem. The photostimulated $S_{RN}1$ reaction of **1** with 1 equiv of $Me_2C{=}NO_2^-$ (0.3–0.4 M) in the presence of a variety of cations and in a variety of solvents gave a mixture of **3**, **4**, and **5** (reaction 1, Table II). These



products were not observed in the dark in the presence of 10 mol % of $(t\text{-Bu})_2NO\cdot$. There was no evidence of the formation of ring-opened products from radical **1b**. The highest yield of **3** observed was 78% in DMF in the presence of $(n\text{-Bu})_4N^+$ as the counterion. In this experiment, 13.5% of the $Me_2C{=}NO_2^-$ was oxidized to **5**. A mixture of **3**, **4**, and **5** was also formed in the photostimulated reaction of 2-chloro-2-nitropropane with the anion of 1-cyclopropyl-1-nitroethane (reaction 2). Compound

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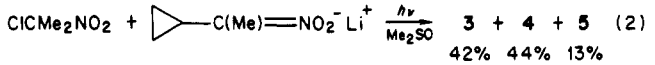
Table II. Reaction of 1 with $Me_2C{=}NO_2^-$

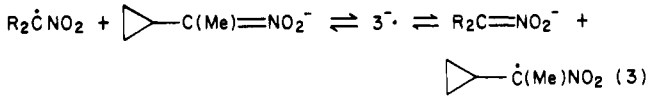
conditns[a]	% yield[b] 3	4	5
THF, Li^+, 24 h	1.2	0	7.8
EtOH, Li^+, 24 h	21.2	tr	36.2
DMF, Li^+, 48 h	57.7	8.7	22.8
Me_2SO, Li^+, 48 h	64.1	10.3	12.4
Me_2SO, Na^+, 48 h	69.9	3.6	17.1
Me_2SO, K^+, 48 h	68.1	4.7	14.7
Me_2SO, $(n\text{-Bu})_4N^+$, 48 h	74.0	tr	4.9
DMF, $(n\text{-Bu})_4N^+$, 48 h	78.1	tr	13.5
Me_2SO, $(Me)_4N^+$, 48 h	62.8	2.1	14.3
Me_2SO, $PhCH_2NMe_3^+$, 48 h	71.4	tr	23.9

[a] Reaction of a 1:1 mol ratio of 1 and $Me_2C{=}NO_2^-M^+$ (1.5–1.9 mmol) in 5 mL of solvent at 35–40 °C in a 350-nm Rayonet reactor. [b] Yield by GLC with internal standard.

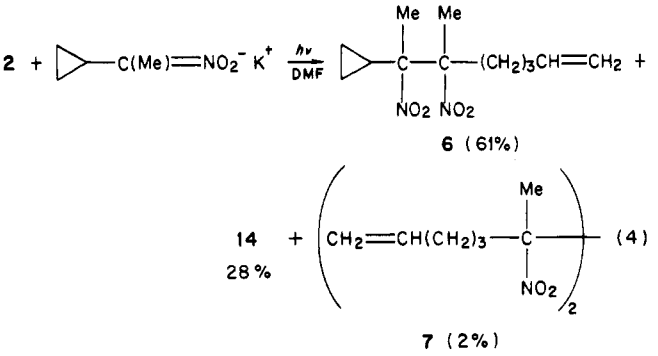


4 was also formed in high yield (89%) by the reaction of **1** with the anion of 1-cyclopropyl-1-nitroethane in Me_2SO/Li^+. In none of these reactions was there any indication of the formation of ring-opened products from radical **1b**. Assuming that $Me_2C{=}NO_2^-$ or $c\text{-}C_3H_5C(Me){=}NO_2^-$ traps **1a** with a rate constant of 10^5 L/(mol s), it follows from the yields of **3** isolated that the **1a** → **1b** interconversion cannot have a rate constant greater than 1×10^4 s^{-1}.

The formation of **4** and **5** in reactions 1 and 2 suggests that nitronate radicals and anions under electron transfer, possibly via $3^-\cdot$ as an intermediate (reaction 3).



A similar conclusion was reached in the study of the reaction of **1** with $CH_2{=}CH(CH_2)_3C(Me){=}NO_2^-$ and of **2** with $c\text{-}C_3H_5C(Me){=}NO_2^-$ in DMF/K^+. Starting from **1**, the $S_{RN}1$ coupling product **6** was observed in 56% isolated yield (sunlamp irradiation, 72 h). However, starting from **2** a considerable amount of the dimerization product **4** was also observed upon sunlamp irradiation for 72 h (reaction 4).

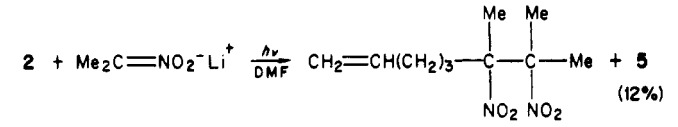


The reaction of **2** with $CH_2{=}CH(CH_2)_3C(Me){=}NO_2^-$ proceeded smoothly with sunlamp irradiation to yield a 72% isolated yield of **7** (DMF/K^+, 136 h) with no indication of the formation of cyclized products expected from the **2a** → **2b** interconversion. Reaction of **2** with $Me_2C{=}NO_2^-$ (DMF/Li^+, sunlamp, 48 h) gave a 63% isolated yield of the coupling product **8** and 12% of **5** (reaction 5). Again, there was no indication of the formation of cyclized products from radical **2b**.

Table III. Reaction of Nucleophiles with $RC(Cl)(NO_2)CH_3$

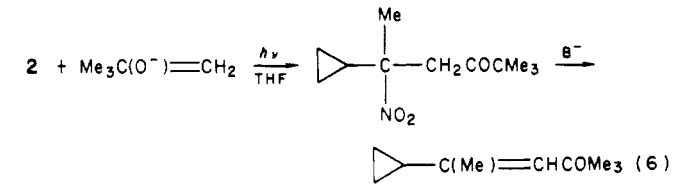
R	N^-	conditns[a]	$RC(NO_2)(N)CH_3$ (%)[b]
c-C_3H_5	$(EtO_2C)_2CMe^-$	DMF, Na^+, R, 30 h	**9** (77 I)
c-C_3H_5	$(EtO_2C)_2CMe^-$	DMF, Na^+, dark, 30 h	**9** (7 GLC)
c-C_3H_5	$(EtO_2C)_2CMe^-$	DMF, Na^+, dark, 10 mol % $(t\text{-Bu})_2NO\cdot$	**9** (0 GLC)
CH_2=$CHCH_2CH_2CH_2$	$(EtO_2C)_2CMe^-$	DMF, Na^+, R, 48 h	**10** (62 I)
c-C_3H_5	$O{=}\underline{CCH_2CH_2COCMe}^-$	Me_2SO, K^+, R, 40 h	**11** (53 I)
c-C_3H_5	$(EtO)_2PO^-$	THF, K^+, S, 48 h	**12** (64 I, 72 NMR)
CH_2=$CHCH_2CH_2CH_2$	$(EtO)_2PO^-$	THF, K^+, R, 36 h	**13** (49 I)
CH_2=$CHCH_2CH_2CH_2$	$(EtO)_2PO^-$	THF, K^+, dark, 36 h	**13** (13 NMR)
c-C_3H_5	$(MeO)_2PO^-$	THF, K^+, S, 23 h	**14** (42 I, 54 NMR)
CH_2=$CHCH_2CH_2CH_2$	$(MeO)_2PO^-$	THF, K^+, R, 36 h	**15** (63 I)
c-C_3H_5	$(EtO)_2PS^-$	THF, K^+, R, 33 h	**16** (54 I, 86 NMR)

[a] Reaction of substrate and nucleophile in a 1:1 ratio (~4 mmol of each reactant) in 10 mL of solvent at 35–40 °C; S = 275-W sunlamp at ca. 15–25 cm; R = Rayonet reactor with 350-nm irradiation. [b] I = isolated; GLC = yield with internal standard; NMR = ^1H NMR crude yield with internal standard.



(5)

Substrates **1** and **2** underwent photostimulated free radical chain reactions with a variety of other anions (Table III). In all cases, the reaction did not occur in the dark in the presence of $(t\text{-Bu})_2NO\cdot$, and GLC or ^1H NMR gave no evidence of the formation of products derived from radicals **1b** or **2b**. With $Me_3C(O^-){=}CH_2$ as the nucleophile, **1** reacted (THF/Li^+, 350 nm, 48 h) to give by ^1H NMR a mixture of 14% of the substitution product and 52% of its elimination product (reaction 6).

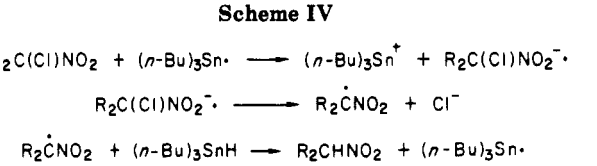


(6)

The absence of the cyclopropylcarbinyl ring opening in **1a** or the Δ^5-hexenyl ring closure in **2a** must reflect the ability of a nitro group to stabilize a radical center. Kinetically this effect reduces the rate of β-scission in the cyclopropylcarbinyl ring opening by a factor of 10^4 or greater. An α-nitro radical must have a considerably different electronic struture than a simple alkyl radical, and the delocalization of all five π-electrons should be considered. As far as spin distribution of the single electron is concerned, ESR data is ambiguous. Thus, in the series $Me_2\dot{C}H$, $Me_2\dot{C}Me$, and $Me_2\dot{C}NO_2$, the value of the unpaired spin density at carbon (ρ_c) as estimated from the hyperfine splitting constant for the methyl groups decreases from 0.84 to 0.78 to 0.68 (a_{Me}^H = 24.7, 22.7, 19.8 G).[13] On the other hand, for the series $MeCO\dot{C}HMe$, $MeCO\dot{C}Me_2$, and $MeCO\dot{C}(Me)NO_2$, the values of ρ_c are 0.77, 0.67, and 0.77 (a_{Me}^H = 22.6, 19.6, 22.6 G).[13,14] In any event, the present results indicate a fairly strong kinetic stabilization by a nitro group at the radical center. Whether this same stabilization can be utilized to promote a β-elimination in the cyclopropylcarbinyl system is under investigation.

Competitive reaction of **1** and benzyl chloride with $(n\text{-Bu})_3Sn\cdot$ in C_6H_6 at 40 °C with 350-nm irradiation indicated a comparable reactivity based on the consumption of starting materials. This might be taken as evidence that **1a** possesses resonance stabilization comparable to the benzyl radical. However, the reactivity of **1** and the approximately 2.5 times greater reactivity of $Me_2C(Cl)NO_2$ toward $(n\text{-Bu})_3Sn\cdot$ may be the result of a reaction via an electron-transfer pathway (Scheme IV).[15]

Scheme IV



Experimental Section

General Procedures. Reactions mixtures were prepared by syringing solutions of the substrate into deoxygenated solutions of the nucleophile at 0 °C. After being warmed to room temperature, the solutions were irradiated with either a Rayonet Photochemical Reactor (350 nm) or a 275-W sunlamp 15–25 cm from the Pyrex reaction flask. The light sources maintained a reaction temperature of 35–40 °C. Dark reactions were performed in an oil bath with the flask wrapped in aluminum foil. Product isolated involved hydrolysis by water or brine followed by Et_2O extraction. Residues after drying and distillation of the Et_2O were analyzed by GLC, GC/MS, and ^1H NMR. Pure reaction products were isolated by crystallization, flash chromatography, or Kugelrohr distillation.

Reagents. Diethyl thiophosphite, $Me_2C{=}NO_2Li$, $(n\text{-Bu})_3SnH$, and $(t\text{-Bu})_2NO\cdot$ were prepared by literature procedures.[16-19] Diethyl phosphite, dimethyl phosphite, pinacolone, 2-methyl-1,3-cyclopentanedione, and diethyl methylmalonate from Aldrich were converted to their salts by Me_3COK, NaH, or $(i\text{-Pr})_2NLi$.

1-Chloro-1-cyclopropyl-1-nitroethane (**1**) was prepared from the oxime of cyclopropyl methyl ketone (6.2 g) in 100 mL of CH_2Cl_2 at 0 °C by the addition of 4.4 g of Cl_2 in 100 mL of CH_2Cl_2 over a 1-h period. The blue reaction mixture was stirred an additional 2 h (0 °C) and excess Cl_2 removed by aspirator vacuum and argon purging. Ozonolysis of the CH_2Cl_2 solution of the blue chloro nitroso compound was performed at −78 °C. Distillation yield 4.7 g (51%) of **1**: bp 41–42 °C (1.8 torr); ^1H NMR ($CDCl_3$) δ 2.07 (s, 3), 2.0–1.5 (m, 1), 0.83 (br s, 2), 0.70 (br s, 2); ^{13}C NMR ($CDCl_3$) δ 105.93, 27.98, 21.53, 4.36, 3.49; IR (neat) 3020, 2900, 1565 (s), 1450, 1390 (s), 1370, 1340 (s), 1230, 1190, 1115, 1035, 850 (s) cm^{-1}; HRMS calcd for C_5H_8Cl (P − NO_2) 103.031 46, found 103.031 85. Anal. Calcd for $C_5H_8NO_2Cl$: C, 40.15; H, 5.39; N, 9.36; Cl, 23.70. Found: C, 40.39; H, 5.42; N, 9.33; Cl, 23.97.

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1-Cyclopropyl-1-nitroethane (6) was prepared from 1 (2 mmol) by reaction with Mg turnings (3.2 mmol) in THF (16 mL) with activation by $BrCH_2CH_2Br$ (1 mmol). After being stirred for 2 h under argon, the solution was decanted and treated with 8 mmol of HOAc. Hydrolysis and extraction with Et_2O gave 92% of 6: bp 80 °C (166 torr); ^1H NMR ($CDCl_3$) δ 4.06–3.96 (d × q, 1, J_d = 6.83, J_q = 6.35 Hz), 1.82 (d, 3, J = 6.35 Hz), 1.75–1.34 (m, 1), 1.04–0.051 (m, 4); ^{13}C NMR ($CDCl_3$) δ 88.22, 18.66, 15.95, 4.09; IR (neat) 3000, 1550 (s), 1450, 1400 (s), 1390, 1360 (s), 1300, 1115, 1050, 1030, 920, 865, 830 cm^{-1}; HRMS calcd for C_5H_9 (P – NO_2) 69.070 43, found 69.070 47.

6-Hepten-2-one was prepared by decarboxylation[20] of the alkylation product of ethyl acetoacetate with 4-bromo-1-butene, bp 82–84 °C (98 torr). Reduction by $NaBH_4$ formed 6-hepten-2-ol, bp 64–65 °C (13 torr), which was converted to the mesylate by reaction with $MeSO_2Cl$ in pyridine. Reaction of the mesylate in refluxing acetone with LiBr formed 2-bromo-6-heptene, bp 60–62 °C (23 torr). The bromoalkene gave a low yield of 2 (<10%) by reaction with $AgNO_2$ in Et_2O (24 h, 30 °C) while the methanesulfonate failed to react in Et_2O in a 72-h period. 2-Nitro-6-heptene was formed from 2-bromo-6-heptene by reaction with 2 equiv of $NaNO_2$ in DMF for 48 h at room temperature. Hydrolysis and ether extraction yielded a yellow oil which was purified by flash chromatography using hexane–ethyl acetate (6:1) as eluent to yield 44% of 2-nitro-6-heptene with R_f 0.61: 0.61: ^1H NMR ($CDCl_3$) δ 6.5–5.4 (m, 1), 5.2–4.8 (m, 2), 4.5 (m, 1), 1.52 (d, 3, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 137.41, 115.19, 83.26, 34.32, 32.80, 24.73, 18.98; HRMS calcd for C_3H_{13} (P – NO_2) 97.101 73, found 97.102 02. The nitroalkene (6.64 mmol) was converted to its anion by 1 equiv of EtOLi in EtOH. The lithium nitronate solution at 0 °C was saturated with O_2, and in the dark 1 equiv of *N*-chlorosuccinimide was added at 0 °C. After being stirred at room temperature for 2 days, the solution was hydrolyzed with brine and extracted with Et_2O to yield a residue purified by flask chromatography using hexane–ethyl acetate (6:1) as eluent to afford a 75% yield of 2 with R_f 0.69: ^1H NMR ($CDCl_3$) δ 6.2–5.4 (m, 1), 5.3–4.7 (m, 2), 2.7–1.0 (m, 6), 2.13 (s, 3); ^{13}C NMR ($CDCl_3$) δ 137.03, 115.74, 104.69, 42.33, 32.69, 29.28, 23.64; IR (neat) 3095, 2995, 2950, 1645, 1560 (s), 1450, 1390 (s), 1345 (s), 1095, 995, 920 (s), 850 cm^{-1}; HRMS calcd for $C_7H_{12}NO_2$ (P – Cl) 142.086 81, found: 142.087 12. Anal. Calcd for $C_7H_{12}NO_2Cl$: C, 47.33; H, 6.81; N, 7.89; 0, 18.01; Cl, 19.96. Found: C, 46.45; H, 6.82; N, 8.26; O, 18.12; Cl, 20.63.

2-Nitro-2-pentene was prepared by the reaction of proprionaldehyde (1 mol) and nitroethane (1 mol) in 50 mL of EtOH containing 4 mL of aqueous 10 N NaOH at 35 °C for 4 days. 2-Nitro-3-pentanol isolated in 66% yield, bp 99 °C (10 torr), was treated with 1 equiv of CH_3SO_2Cl (40 mmol) in CH_2Cl_2 (40 mL) to which Et_3N (16 g) was added dropwise at 0 °C.[21] Hydrolysis after 15 min with 5% aqueous HCl and brine gave by distillation 2-nitro-2-pentene: bp 85 °C (20 torr); ^1H NMR ($CDCl_3$) δ 2.13 (s, 3), 1.13 (t, 3, J = 7 Hz), 7.17 (t, 1); IR (neat) 2990, 2970, 2940, 1670, 1520 (s), 1390, 1335 cm^{-1}.

Substitution Products. 2-Cyclopropyl-3-methyl-2,3-dinitrobutane (3) was purified by GLC: ^1H NMR ($CDCl_3$) δ 2.04 (s, 3), 1.96 (s, 3), 1.54 (s, 3), 1.09–0.18 (m, 4); ^{13}C NMR ($CDCl_3$) δ 95.37; 92.71; 23.64, 23.48, 15.25, 14.28, 6.04, 2.19; IR (neat) 1550 (s), 1470, 1415, 1400, 1385, 1350 (s), 1120, 1035, 920, 735 cm^{-1}; HRMS calcd for $C_8H_{14}NO_2$ (P – NO_2) 156.102 46, found 156.103 04.

2,3-Dicyclopropyl-2,3-dinitrobutane (4) was isolated by crystallization from hexane as a mixture of diastereomers in a ratio of 5.2:1 (by ^1H NMR). Major isomer: ^1H NMR ($CDCl_3$) δ 1.80 (m, 1), 1.44 (s, 3), 0.92–0.43 (m, 4); ^{13}C NMR ($CDCl_3$) δ 96.67, 15.14, 14.87, 6.31, 2.63. Minor isomer: ^1H NMR ($CDCl_3$) δ 2.04 (m, 1), 1.36 (m, 3). Mixture: IR (KBr) 1550 (s), 1465, 1415, 1400, 1385, 1350 (s), 1120, 1040, 920, 850, 735 cm^{-1}; HRMS calcd for $C_{10}H_{15}$ (P – HN_2O_4) 136.125 20, found 136.125 27. Anal. Calcd for $C_{10}C_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.27. Found: C, 52.80; H, 7.35; N, 12.25.

2-Cyclopropyl-3-methyl-2,3-dinitro-7-octene (6) prepared from 1 or 2 was isolated as a mixture of diastereomers in a 52:48 ratio after purification by flash chromatography using hexane–ethyl acetate (10:1) as eluent: R_f 0.34; ^1H NMR ($CDCl_3$) δ 5.85–5.67 (m, 1), 5.10–4.93 (m, 2), 1.70 and 1.65 (s, 3), 1.32 and 1.34 (s, 3), 0.95–0.42 (m, 4); IR (neat) 3015, 2970, 2940, 1643, 1545 (s), 1455, 1390, 1340, 1100, 1030, 910, 840 cm^{-1}; HRMS calcd for $C_{12}H_{19}$ (P – HN_2O_4) 163.148 68, found 163.149 06.

2,3-Dimethyl-2,3-dinitro-7-octene (8) was purified by flash chromatography using hexane–ethyl acetate (6:1) as eluent: R_f 0.37; ^1H NMR ($CDCl_3$) δ 5.81–5.67 (m, 1), 5.06–4.97 (m, 2), 1.75 (s, 3), 1.69 (s, 3), 1.59 (s, 3); ^{13}C NMR ($CDCl_3$) δ 137.14, 115.63, 94.72, 92.28, 33.99, 33.23, 23.32, 23.05, 18.33; IR (neat) 3070, 2995, 2970, 2940, 2860, 1635, 1540 (s), 1450, 1400, 1380 (s), 1370, 1335 (s), 905 (s), 840, 750 (s); HRMS calcd for $C_{10}H_{17}$ (P – HN_2O_4) 137.133 03, found 137.133 34. Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.27; O, 27.79. Found: C, 51.98; H, 7.79; N, 12.03; O, 27.86.

6,7-Dimethyl-6,7-dinitrododecane-1,11-diene (7) was isolated by flash chromatography using hexane–ethyl acetate (6:1) as eluent, R_f 0.53, as a mixture of diastereomers (72:28 by ^1H NMR): ^1H NMR ($CDCl_3$) δ 5.85–5.63 (m, 1), 5.10–4.90 (m, 2), 1.62 (s, 3, 72%), 1.55 (s, 3, 28%); ^{13}C NMR ($CDCl_3$) δ 137.19, 115.74, 95.80, 34.15, 33.34, 23.48, 18.82; IR (neat) 3090, 3010, 2975, 2885, 1645, 1558 (s), 1460, 1395, 1342, 990, 920, 845, 800 cm^{-1}; HRMS calcd for $C_{13}H_{23}$ (P – HN_2O_4) 191.179 98, found 191.179 55.

Diethyl methyl(1-cyclopropyl-1-nitroethyl)malonate (9) isolated by kugelrohr distillation: bp 137 °C (2 torr); ^1H NMR ($CDCl_3$) δ 4.38–4.10 (m, 4), 1.71 (s, 3), 1.31 (s, 3), 1.29 (t, 3, J = 7.1 Hz, 1.26 (t, 3, J = 7.1 Hz), 0.77–0.50 (m, 4); IR (neat) 2995, 2950, 1730 (s), 1555 (s), 1470, 1455, 1400, 1370, 1350, 1270 (s), 1230 (s), 1100 (s), 1020, 915, 860, 840, 730 cm^{-1}; HRMS calcd for $C_{13}H_{21}O_4$ (P – NO_2) 241.143 99, found 241.143 38. Anal. Calcd for $C_{13}H_{21}NO_6$: C, 54.37; H, 7.37; N, 4.88. Found: C, 54.65; H, 7.54; N, 4.73.

Diethyl methyl(2-nitro-2-hept-6-enyl)malonate (10) was purified by flash chromatography using hexane–ethyl acetate (6:1) as eluent: R_f 0.39; ^1H NMR ($CDCl_3$) δ 6.45–5.70 (m, 1), 5.50–5.00 (m, 2), 4.40 (q, 4, J = 7 Hz), 1.79 (s, 3), 1.74 (s, 3), 1.35 (t, 6, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 169.40, 169.01, 137.34, 115.10, 94.09, 61.77, 60.80, 34.98, 33.10, 22.89, 18.98, 13.78, 13.52; IR (neat) 2890, 2930, 1730 (s), 1640, 1545, 1450, 1255 (s), 1090, 910, 850 cm^{-1}; HRMS calcd for $C_{15}H_{25}O_4$ (P – NO_2) 269.175 29, found 269.174 67.

2-Methyl-2-(1-cyclopropyl-1-nitroethyl)-1,3-cyclopentanedione (11): mp 79 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.83 (s, 3), 1.36–1.20 (m, 1), 1.18 (s, 3), 0.78–0.30 (m, 4); ^{13}C NMR ($CDCl_3$) δ 214.39, 213.04, 88.70, 54.82, 36.35, 34.66, 34.27, 23.08, 14.50, 4.88, 4.62; IR (KBr) 3000, 2985, 2965, 2935, 1740 (s), 1545 (s), 1450, 1420, 1390, 1370, 1290, 1085, 1060 (s), 1020, 990, 910, 840 cm^{-1}; HRMS calcd for $C_{10}H_{14}NO_4$ 225.100 11, found 225.099 06. The ^1H NMR singlet at δ 2.83 at 60 MHz became broad at 90 MHz and a multiplet at 300 MHz. The 300-MHz spectrum between 25 and 70 °C ($CDCl_3$) indicated partial collapse of the multiplet to a singlet, but complete collapse was not observed at 110 °C (*o*-$Cl_2C_6H_4$). The cyclopentanedione methylene groups had a very complex ^1H NMR spectrum which was not analyzed.

1-Cyclopropyl-1-nitro-1-(diethoxyphosphinyl)ethane (12) was purified by Kugelrohr distillation: bp 122 °C (0.4 torr); ^1H NMR ($CDCl_3$) δ 4.33–4.10 (m, 4), 1.8 (d, 3, J_P = 14.5 Hz), 1.37 (t, 6, J_H = 7 Hz), 1.0–0.2 (m, 4); ^{13}C NMR δ 90.22 (d, J_P = 153.8 Hz, C-1), 64.22 (d, J_P = 6.1 Hz, OCH_2), 63.9 (J_P = 7.3 Hz, OCH_2), 16.44 (s, CH_3), 16.17 (s, CH_3), 14.95 (d, J_P = 10.37 Hz, C-2), 4.09 (s), 1.49 (s), 1.06 (s); ^{13}P NMR ($CDCl_3$) δ 17.46 (s); IR (neat) 2950, 1545 (s), 1460, 1390, 1370, 1330, 1260 (s), 1160, 1090, 1030 (s), 970 (s), 855, 835, 780 cm^{-1}; HRMS calcd for $C_9H_{18}PO_3$ (P – NO_2) 205.099 37, found 205.098 68. Anal. Calcd for $C_9H_{18}NO_5P$: C, 43.03; H, 7.22; N, 5.58; P, 12.33. Found: C, 42.86; H, 7.31; N, 5.38; P, 12.50.

2-Nitro-2-(diethoxyphosphinyl)hept-6-ene (13) was purified by flash chromatography using hexane–ethyl acetate (1:1) as eluent: R_f 0.39; ^1H NMR ($CDCl_3$) δ 5.82–5.68 (m, 1), 5.06–4.97 (m, 2), 4.28–4.07 (m, 4), 1.78 (d, 3, J_P = 14.6 Hz), 1.36 (t, 6, J_H = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 137.14 (s, C-6), 115.36 (s, C-7), 89.84 (d, J_P = 149 Hz, C-2), 64.11 (d, J_P = 7.3 Hz, OCH_2), 63.95 (d, J_P = 7.3 Hz, OCH_2), 34.97 (s), 33.07 (s), 22.34 (d, J_P = 9.8 Hz, C-1), 18.93 (s), 16.33 (s, 3, OCH_2CH_3), 16.06 (s, 3, OCH_2CH_3); ^{31}P NMR ($CDCl_3$) δ 17.89 (s); IR (neat) 3075, 2980 (s), 2930, 2860, 1640, 1540 (s), 1440, 1380, 1365, 1335, 1255 (s), 1160, 1090, 1040 (s), 1015 (s),

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965, 905, 855, 785, 745 cm^{-1}; HRMS calcd for $C_{11}H_{22}O_3P$ (P - NO_2) 233.130 67, found 233.130 89. Anal. Calcd for $C_{11}H_{22}NO_5P$: C, 47.31; H, 7.94; N, 5.01; P, 11.09. Found: C, 46.95; H, 8.06; N, 4.92; P, 11.26.

1-Cyclopropyl-1-nitro-1-(dimethoxyphosphinyl)ethane (**14**) was isolated by Kugelrohr distillation at 115 °C (0.4 torr): ^1H NMR ($CDCl_3$) δ 3.91 (d, 3, J_P = 10.9 Hz), 3.88 (d, 3, J_P = 10.8 Hz), 1.47 (d, 3, J_P = 14.6 Hz), 1.0-0.2 (m, 4); ^{13}C NMR ($CDCl_3$) δ 90.06 (d, J_P = 153.8 Hz, C-1), 54.44 (d, J_P = 6.12 Hz, OCH_3), 54.14 (d, J_P = 7.32 Hz, OCH_3), 14.84 (d, J_P = 10.37 Hz, C-2), 3.87 (s), 1.44 (s), 1.00 (s); IR (neat) 1545 (s), 1460, 1390, 1335, 1260 (s), 1180, 1030 (s), 860, 830, 790, 770 cm^{-1}; HRMS calcd for $C_7H_{14}O_3P$ (P - NO_2) 177.068 06, found 177.067 79. Anal. Calcd for $C_7H_{14}NO_5P$: C, 37.67, H, 6.32. Found: C, 37.06; H, 6.68.

2-Nitro-2-(dimethoxyphosphinyl)hept-6-ene (**15**) was isolated by flash chromatography using hexane-ethyl acetate (1:1) as eluent: R_f 0.24; ^1H NMR ($CDCl_3$) δ 5.74-5.61 (m, 1), 4.99-4.90 (m, 2), 3.81 (d, 3, J_P = 11.0 Hz), 3.79 (d, 3, J_P = 11.0 Hz), 1.72 (d, 3, J_P = 14.6 Hz); ^{13}C NMR ($CDCl_3$) δ 137.19 (s, C-6), 115.58 (s, C-7), 89.98 (d, J_P = 150.1 Hz, C-2), 54.66 (d, J_P = 6.1 Hz, OCH_3), 54.39 (d, J_P = 6.1 Hz, OCH_3), 35.24 (s), 33.13 (s), 22.45 (d, J_P = 9.8 Hz, C-1), 19.20 (s); IR (neat) 3090, 2975, 2870, 1645, 1550 (s), 1465, 1390, 1345, 1270 (s), 1190, 1055 (s), 1030 (s), 920, 840 cm^{-1}; HRMS calcd for $C_9H_{18}O_3P$ (P - NO_2) 205.099 36, found 205.099 84. Anal. Calcd for $C_9H_{18}NO_5P$: C, 43.03; H, 7.22; N, 5.58; P, 12.33. Found: C, 43.35; H, 7.25; N, 5.36; P, 12.05.

1-Cyclopropyl-1-nitro-1-(diethoxythiophosphinyl)ethane (**16**) isolated by Kugelrohr distillation bp 139 °C (0.9 torr); ^1H NMR ($CDCl_3$) δ 4.55-3.80 (m, 4), 1.81 (d, 3, J_P = 16.5 Hz), 1.32 (t, 6, J_H = 6 Hz), 1.0-0.3 (m, 4); IR (neat) 2950, 1545 (s), 1460, 1390, 1335, 1160, 1095, 1030 (s), 960 (s), 860, 835, 790, 675 cm^{-1}; HRMS calcd for $C_9H_{18}O_2PS$ (P - NO_2) 221.076 52, found 221.076 35.

The reaction of **2** with $Me_3C(O^-)=CH_2$ yielded mainly 5-cyclopropyl-2,2-dimethyl-4-hexen-3-one which was isolated as a mixture of *E* and *Z* isomers in a ratio of 62:38 by Kugelrohr distillation at 50 °C (10 torr): ^1H NMR ($CDCl_3$) δ 6.28 (s, 1), 1.53 and 1.90 (d, 3, J = 1 Hz), 1.16 (s, 9), 0.95-0.60 (m, 4); IR (neat) 2960 (s), 1665 (s), 1470, 1385, 1090, 1055, 1000, 910 (s), 870, 800 cm^{-1}; HRMS calcd for $C_{11}H_{18}O$ 166.135 77, found 166.135 84. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.09; H, 10.68.

Photochemical Transformations. 38. Novel Transformations of Diarobicyclo[3.2.1]octadienes to Phenanthrenes and Dihydrophenanthrenes[1]

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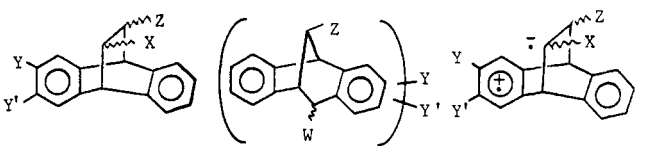
Irradiation of 2,3;6,7-diarobicyclo[3.2.1]octadienes having nucleofugal groups at C-8, in an unprecedented rearrangement, produces 9-functionalized or 9,10-difunctionalized phenanthrenes (e.g., 8-11). The reactions involve triplet excited states, as demonstrated by acetone sensitization when the C-8 substituent was Cl or Br and by quenching studies when the C-8 substituent was HgOAc. When C-8 is unsubstituted, dihydrophenanthrenes, rather than phenanthrenes, are formed. The products of the latter reaction are presumably formed from a carbene intermediate resulting via a frustrated di-π-methane rearrangement. On the other hand, the formation of the phenanthrene products is consistent with a pathway involving intramolecular electron transfer from the excited aromatic ring to the carbon-nucleofuge bond to form a zwitterionic biradical, loss of nucleofuge, and a convoluted rearrangement of the resulting biradical cation.

Our research group has been interested for some time[2] in photo-Wagner-Meerwein rearrangement and photosolvolysis reactions, in which an aromatic ring is the light-absorbing chromophore and a remote carbon-X bond is subsequently activated and is ultimately cleaved to give X^- and a carbocation. Recently, our research[1,3] has led us to a fair degree of understanding of the general requirements for such reactions to occur.

Much of the work has been carried out with diarobicyclo[2.2.2]octadiene systems **1**, in which variations in the



1 **2** **3**

nature of the auxochromic groups Y and Y′ and of the nucleofugal group X, as well as of the stereochemistry of the nucleofugal group X with respect to the light-absorbing Y-substituted ring, have been studied.

Considerations of stereochemistry, of the electron-donating ability (oxidation potential) of the photoactivated ring, and of the electron-accepting ability (reduction potential) of the carbon-nucleofuge bond have allowed considerable speculation about the course of the reactions leading to the photo-Wagner-Meerwein rearranged products **2**. Thus, we have proposed[1,3] that electron transfer from a π,π^* activated arene ring to the σ^* orbital of the carbon-nucleofuge bond is required for photoac-

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