of 3 h, and then the reaction mixture was poured into saturated aqueous sodium bicarbonate, the phases were separated, and the aqueous phase was extracted with chloroform. The combined chloroform layer was dried over anhydrous magnesium sulfate and filtered and the solution was concentrated to give an off-white solid that was further purified by medium-pressure liquid chromatography on silica gel using hexane/ethyl acetate as eluant to give 423 mg, 87%, of pure product: mp 56–58 °C; R_f 0.31 (3:1 hexane/ethyl acetate); ^{1}H NMR (90 MHz) δ 0.93 (d, 3 H, $J = 6$ Hz), 1.05 (s, 3 H), 1.35 (s, 3 H), 0.5–1.95 (m, 7 H), 2.48 (td, 1 H, $J = 10.5$ Hz, $J = 2.5$ Hz), 3.06 (dm, 1 H, $J = 12$ Hz), 4.73 (s, 1 H, exchanges with D_2O), 6.18 (dd, 1 H, $J = 8$ Hz, $J = 1.5$ Hz), 6.35 (dd, 1 H, $J = 8$ Hz, $J = 1.5$ Hz), 6.88 (t, 1 H, $J = 8$ Hz); ^{13}C NMR (200 MHz) 18.94 (q), 22.58 (q), 27.70 (q), 28.08 (d), 32.98 (t), 35.52 (t), 35.59 (d), 38.84 (t), 49.15 (d), 77.22 (s), 107.26 (d), 110.29 (d), 113.14 (s), 127.19 (d), 155.04 (s), 155.31 ppm (s); IR ($CHCl_3$) 3352, 2966, 1615, 1588, 1450, 1220, 1020 cm^{-1}; mass spectrum calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1610.

Acknowledgment. I thank Dr. Elizabeth Williams and Mr. Paul Donahue for obtaining the 200-MHz carbon-13 NMR and 300-MHz proton NMR spectra and Mr. Steve Dorn for mass spectral data.

Registry No. **9**, 55274-02-7; (*R*)-**10**, 2385-77-5; (*S*)-**10**, 5949-05-3; (1*R*,3*R*)-**11**, 95891-86-4; (1*S*,3*S*)-**11**, 95891-96-6; (1*S*,3*R*)-**12**, 95891-87-5; (1*R*,3*S*)-**12**, 95891-97-7; **13**, 95891-88-6; **14**, 95891-89-7; **18**, 81710-25-0; (1*R*,3*R*)-**19**, 95891-90-0; (1*S*,3*R*)-**19**, 95891-91-1; **20**, 95891-92-2; **21**, 95891-93-3; (1*R*,3*R*)-**22**, 95891-94-4; (1*S*,3*R*)-**22**, 95891-95-5; bis(*O*-methoxymethyl)resorcinol, 3688-89-9.

Catalyzed Oxidative Nitration of Nitronate Salts[1]

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Nitronate salts are converted to *gem*-dinitro compounds with nitrite ion and persulfate, in the presence of a catalytic amount of ferricyanide. The use of cyanide or sulfinate salts in place of nitrile gave *gem*-cyanonitro compounds and α-nitro sulfones, respectively.

A convenient laboratory procedure for the conversion of primary and secondary nitroalkanes to *gem*-dinitro compounds is the oxidative nitration reaction of Kaplan and Shechter.[2] In this reaction a nitronate salt is oxidized with silver nitrate in the presence of nitrite ion. A drawback of the reaction is the expense of the silver nitrate reagent.

$$R_1R_2C{=}NO_2^- \xrightarrow[AgNO_3]{NaNO_2} R_1R_2C(NO_2)_2$$

More recently, Mataoz, Piotrowska, and Urbanski[3] reported that potassium ferricyanide can be used in place of the silver salt with secondary nitro compounds. Subsequently, Kornblum et al.[4] found conditions that were also applicable to primary as well as secondary nitroalkanes and applied the reaction to many examples. The quantities of reagents used, however, make the method unattractive for large scale preparations.[5] The applicability of the reaction in the presence of other functional groups was not reported. We had a need for 2,2-dinitro alcohols, and attempts to apply these conditions to the preparation of 2,2-dinitropropanol and 2,2-dinitropropanediol resulted in only trace yields.

Another mild oxidant that acts on nitronate ions is persulfate ion, which has a much lower equivalent weight than ferricyanide. However, the reaction of persulfate with the salt of 2-nitropropane in the presence of nitrite ion was reported to result only in dimerization to give 2,3-dimethyl-2,3-dinitrobutane.[3] It is known, however, that persulfate oxidizes ferrous to ferric ion,[6] so it appeared conceivable that persulfate could be used as the oxidant for obtaining *gem*-dinitro compounds in the presence of a catalytic amount of ferricyanide. The reduced iron salt resulting from the nitration would be continually reoxidized.

This combination was found to be effective for the oxidative nitration of nitro compounds with a variety of functional groups. Examples are summarized in Table I.

The reactions were generally conducted at 25–35 °C in aqueous solution with ether, tetrahydrofuran, or methylene chloride as an organic cosolvent, and ice-bath cooling was used to control the initial exotherm. Optimum yields were obtained with the use of 4–5 mol of sodium nitrite per mol of nitro compound, and yields were 10–20% lower with 1–2 mol of nitrite. Stoichiometric amounts of sodium persulfate and catalytic amounts of potassium ferricyanide (0.1–0.2 equiv) were used.

2,2-Dinitropropane,[3] 1,1-dinitrocyclohexane,[3,4] 1,1-dinitrocyclopentane,[4] and 2,2-dimethyl-5,5-dinitro-1,3-dioxane[3] were reported previously with ferricyanide as the oxidant. Products listed in Table I that were previously prepared by the oxidative nitration with silver nitrate are 2,2-dinitropropane,[2] 1,1-dinitrocyclohexane,[2] 1,1-dinitroethane,[2] 1,1-dinitrobutane,[9] 4,4-dinitro-1-butene,[7] 3,3-dinitrooxetane,[8] 2,2-dinitropropanol,[2] and 2,2-dinitropropanediol.[1,9] Other syntheses of 2,2-dinitropropyl methyl ether[10] and 2,2-dimethyl-5,5-dinitro-1,3-dioxane[11]

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[1] This work was supported by the Air Force Rocket Propulsion Laboratory, Air Force Systems Command, USAF, Edwards AFB, CA 93523.

[2] Kaplan, R. B.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3535.

[3] Mataoz, Z.; Piotrowska, H.; Urbanski, T. *Rocz. Chem.* **1979**, *53*, 187.

[4] Kornblum, N.; Singh, H. K.; Kelly, W. J. *J. Org. Chem.* **1983**, *48*, 332.

[5] The nitration of 1.24 g of nitrocyclohexane[4] utilizes 16 g of potassium ferricyanide, 6.9 g of sodium nitrite, and 350 mL of solvent.

[6] Chadwick, B. M.; Sharpe, A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 114.

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0022-3263/85/1950-1699$01.50/0

Table I. Nitrations with Persulfate and Ferricyanide

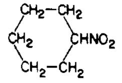
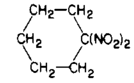
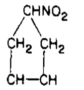
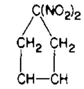
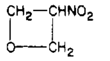
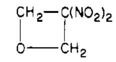
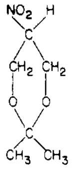
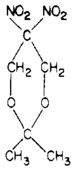
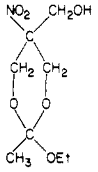
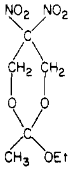
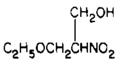
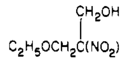
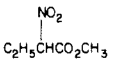
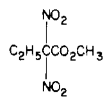
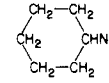
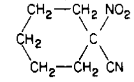
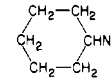
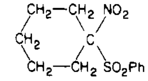
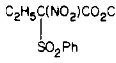
starting material	product	yield, %
$(CH_3)_2CHNO_2$	$(CH_3)_2C(NO_2)_2$	82
		88
		86
$CH_3CH_2NO_2$	$CH_3CH(NO_2)_2$	60
$CH_3(CH_2)_3NO_2$	$CH_3(CH_2)_2CH(NO_2)_2$	82
$CH_2{=}CHCH_2CH_2NO_2$	$CH_2{=}CHCH_2CH(NO_2)_2$	48
$CH_3CH(NO_2)CH_2OCH_3$	$CH_3C(NO_2)_2CH_2OCH_3$	88
		72
		92
		86
$C_2H_5O(CH_2)_2NO_2$	$C_2H_5O(CH_2)CH(NO_2)_2$	36
$(C_2H_5OCH_2)_2CHNO_2$	$(C_2H_5O\text{-}CH_2)_2C(NO_2)_2$	90
$CH_3CH(NO_2)CH_2OH$	$CH_3C(NO_2)_2CH_2OH$	67
$(HOCH_2)_2CHNO_2$	$(HOCH_2)_2C(NO_2)_2$	30
$(HOCH_2)_3CNO_2$	$(HOCH_2)_2C(NO_2)_2$	35
 $C_2H_5OCH_2CH(CH_2OH)NO_2$	 $C_2H_5OCH_2C(CH_2OH)(NO_2)_2$	20
 $C_2H_5CH(NO_2)CO_2CH_3$	 $C_2H_5C(NO_2)_2CO_2CH_3$	46

Table II. Cyanations and Sulfonations

starting material	product	yield, %
$(CH_3)_2CHNO_2$	$(CH_3)_2C(NO_2)CN$	47
		64
$(CH_3)_2CHNO_2$	$(CH_3)_2C(NO_2)SO_2Ph$	54
		64
	 $C_2H_5C(NO_2)(SO_2Ph)CO_2CH_3$	63

have been reported. 2-Nitro alcohols and 1-nitroalkanes are readily interconvertable because of the formylation–deformylation equilibrium.

Particularly noteworthy is that the oxidative nitration of nitro compounds with an adjacent electron-withdrawing group, such as a carbonyl group or another nitro group, have not been reported. The preparation of methyl 2,2-dinitrobutyrate thus extends the limits of oxidative nitrations.

The oxidative cyanation and oxidative sulfonation of nitronate salts using ferricyanide as the oxidant has been reported.[3,4] The use of sodium persulfate with a catalytic amount of ferricyanide was also found to be beneficial for these reactions, and the results are summarized in Table II. The previously reported[4] products were obtained from 2-nitropropane and nitrocyclohexane. The oxidative sulfonation of 2-nitro esters provides potentially useful trifunctional alkanes.

Experimental Section

2,2-Dinitropropane. A mixture of 4.75 g (50 mmol) of 94% 2-nitropropane, 3.00 g (75 mmol) of sodium hydroxide, and 25 mL of water was stirred until a homogeneous solution was formed. Methylene chloride (25 mL) was added and the mixture was cooled with an ice–water bath. A solution of 14.0 g (0.20 mmol) of sodium nitrite in 25 mL of water, a solution of 3.30 g (10 mmol) of potassium ferricyanide in 10 mL of water, and 11.9 g (50 mmol) of solid sodium persulfate were added consecutively with stirring. The reaction temperature rose to 42 °C before subsiding, and the mixture was then stirred for 1 h at 25 °C. The aqueous phase was separated and was extracted twice with methylene chloride, and the combined organic layers were washed with saturated sodium chloride solution, dried over magnesium sulfate, and distilled to give 5.50 g (82%) of 2,2-dinitropropane identical with an authentic sample.[2]

2,2-Dinitropropyl Methyl Ether. By this procedure, 2-nitropropyl methyl ether[12] gave an 88% yield of 2,2-dinitropropyl methyl ether, identical with an authentic sample.[10]

3,3-Dinitrooxetane. The nitration of 3-nitrooxetane[8] by this procedure gave a 72% yield of 3,3-dinitrooxetane, identical with authentic material.[8]

2,2-Dinitro-1,3-diethoxypropane. By the above procedure, nitration of 2-nitro-1,3-diethoxypropane gave a 90% yield of 2,2-dinitro-1,3-diethoxypropane: bp 70–71 °C (0.4 mm); NMR ($CDCl_3$) 1.15 (t, 6 H), 3.45 (q, 4 H), 4.10 (s, 4 H).

Anal. Calcd for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.35; N, 12.60. Found: C, 37.92; H, 6.43; N, 12.47.

The starting material was prepared in 36% yield from 3-ethoxy-2-nitro-1-propene[12] by using procedures reported[12] for related compounds: bp 76–78 °C (0.5 mm); NMR ($CDCl_3$) δ 1.15 (t, 6 H), 3.45 (q, 4 H), 3.72 (dq, 4 H), 4.85 (d pentet, 1 H).

Anal. Calcd for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90. Found: C, 47.24; H, 8.59; N, 7.78.

1,1-Dinitrocyclohexane. A mixture of 2.00 g (15.5 mmol) of nitrocyclohexane, 1.0 g (25 mmol) of sodium hydroxide, and 12 mL of 1:3 dioxane–water was stirred until a homogeneous solution was formed. A solution of 5.0 g (72 mmol) of sodium nitrite in 15 mL of water, a solution of 1.0 g (3.0 mmol) of potassium ferricyanide in 10 mL of water, and 4.0 g (17 mmol) of solid sodium persulfate were added consecutively with stirring. The reaction exotherm was controlled with an ice bath, and the mixture was stirred for 1 h at 25 °C. Product isolation, as in the 2,2-dinitropropane example, gave 2.40 g (88%) of 1,1-dinitrocyclohexane.[4]

1,1-Dinitrocyclopentane. Nitrocyclopentane was converted by this procedure to 1,1-dinitrocyclopentane (86%), identical with an authentic sample.[4]

2,2-Dimethyl-5,5-dinitro-1,3-dioxane. By the above procedure, 2,2-dimethyl-5-nitro-1,3-dioxane[11] gave 2,2-dimethyl-5,5-dinitro-1,3-dioxane (92%) with the reported[11] properties. The same yield was obtained when 2,2-dimethyl-5-nitro-5-(hydroxymethyl)-1,3-dioxane was used as the starting material.

2-Ethoxy-2-methyl-5,5-dinitro-1,3-dioxane. A solution of 12.1 g (80 mmol) of tris(hydroxymethyl)nitromethane, 13.6 g (84 mmol) of triethyl orthoacetate, and 0.030 g (0.16 mmol) of toluenesulfonic acid monohydrate in 40 mL of methylene chloride was stirred at 25 °C for 22 h. Sodium bicarbonate (0.2 g) was added and stirring was continued for 30 min. The mixture was then washed with 5% sodium bicarbonate solution, water, and brine. The solution was dried over magnesium sulfate and the solvent was removed to give 17.3 g (87%) of 2-ethoxy-2-methyl-5-nitro-5-(hydromethyl)-1,3-dioxane.

By the method of the preceding examples, 2-ethoxy-2-methyl-5-nitro-5-(hydroxymethyl)-1,3-dioxane was converted to 2-ethoxy-2-methyl-5,5-dinitro-1,3-dioxane in 86% yield. The

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[10] Grakauskas, V. *J. Org. Chem.* **1970**, *35*, 3030. Ungnade, H. E.; Kissinger, L. W. *J. Org. Chem.* **1966**, *31*, 369.

[11] Linden, G. B.; Gold, M. H. *J. Org. Chem.* **1956**, *21*, 1175.

product was purified by sublimation at 60–65 °C (0.08 mm): NMR ($CDCl_3$) δ 1.20 (t, 3 H), 1.5 (s, 3 H), 3.5 (q, 2 H), 4.60 (s, 4 H).

Anal. Calcd for $C_7H_{12}N_2O_7$: C, 35.60; H, 5.12; N, 11.85. Found: C, 35.57; H, 5.08; N, 11.75.

1,1-Dinitrobutane. A mixture of 4.75 g (46.0 mmol) of 1-nitrobutane, 4.60 g (0.115 mol) of sodium hydroxide, and 50 mL of water was stirred until a homogeneous solution was formed. A solution of 15.0 g (0.213 mol) of sodium nitrite in 40 mL of water, a solution of 3.0 g (9.1 mmol) of potassium ferricyanide in 15 mL of water, and 12.0 g (50.4 mmol) of solid sodium persulfate were added consecutively with stirring. The reaction exotherm was controlled with an ice bath, and the mixture was then stirred for 30 min at ambient temperature. Urea (10.0 g, 0.166 mol) was added and the mixture was cooled to 5 °C. The resulting red solution was stirred for 5 min with 6.5 mL (0.11 mol) of acetic acid and was extracted three times with ether. The combined organic layers were washed with water and with brine and dried over magnesium sulfate. Distillation gave 5.60 g (82%) of 1,1-dinitrobutane, identical with authentic material.[2,4]

1,1-Dinitroethane. 1,1-Dinitroethane was obtained similarly from nitroethane, in 60% yield.

1,1-Dinitro-3-butene. Nitration of 4-nitro-1-butene by the above method gave a 48% yield of 1,1-dinitro-3-butene:[7] bp 61–63 °C (0.2 mm) NMR ($CDCl_3$) δ 3.20 (t, 2 H), 5.00–5.80 (m, 3 H), 6.00 (t, 1 H); IR (neat) 1550 cm^{-1}.

Nitration of 1-Nitro-2-ethoxyethane. Nitration of 1-nitro-2-ethoxyethane[12] by the above procedure gave a 36% yield of a liquid: bp 72–78 °C (0.7 mm); NMR ($CDCl_3$) δ 1.15 (t, 3 H), 3.52 (q, 2 H), 4.20 (d, i H), 6.15 (t, 1 H); IR (neat) 1550 cm^{-1}. The spectral data are consistent with the 1,1-dinitro-2-ethoxyethane structure, but the material was too unstable for elemental analyses.

Methyl 2,2-Dinitrobutyrate. A mixture of 10.0 g (68.0 mmol) of methyl 2-nitrobutyrate[13] and 40 g (0.32 mol) of sodium carbonate hydrate in 200 mL of water was stirred vigorously until a homogeneous solution was formed. A solution of 23 g (0.33 mol) of sodium nitrite in 50 mL of water, 50 mL of methylene chloride, a solution of 10.0 g (30 mmol) of potassium ferricyanide in 30 mL of water, and 30 g (0.13 mol) of solid sodium persulfate were added consecutively with stirring, and stirring was continued for 1 h. The aqueous phase was separated and was extracted twice with methylene chloride. The combined organic layers were washed twice with 1 M sodium hydroxide and once with saturated sodium chloride solution and dried over magnesium sulfate. Distillation gave 6.0 g (46%) of methyl 2,2-dinitrobutyrate: bp 58–59 °C (0.5 mm); NMR ($CDCl_3$) δ 1.2 (t, 3 H), 2.72 (q, 2 H), 3.90 (s, 3 H); IR (CCl_4) 1770, 1570 cm^{-1}.

Anal. Calcd for $C_5H_8N_2O_6$: C, 31.26; H, 4.20; N, 14.58. Found: C, 31.28; H, 4.19; N, 14.50.

Distillation of the residue gave 1.0 g (14%) of dimethyl 2,3-diethyl-2,3-dinitrosuccinate: bp 120–125 °C (0.4 mm); NMR ($CDCl_3$) δ 1.1 (dt, 6 H), 2.4 (dq, 4 H), 3.80 (s, 6 H).

Anal. Calcd for $C_{10}H_{16}N_2O_8$: C, 41.10; H, 5.52; N, 9.58. Found: C, 40.94; H, 5.40; N, 9.66.

2,2-Dinitropropanol. A homogeneous solution, prepared from 2.75 g (68 mmol) of sodium hydroxide, 5.00 g (67 mmol) of nitroethane, and 20 mL of water, was stirred with 5.50 g (68 mmol) of 37% formalin for 2 h. Tetrahydrofuran (50 mL) and a solution of 18 g (0.26 mol) of sodium nitrite in 40 mL of water were added, and the mixture was cooled to 15 °C. A solution of 4.4 g (13 mmol) of potassium ferricyanide in 15 mL of water and a solution of 16 g (67 mmol) of sodium persulfate in 30 mL of water were added with ice bath cooling. The mixture was stirred for 1 h at 20 °C and was then extracted three times with ether. The combined organic layers were washed with brine and dried over magnesium sulfate. Distillation gave 0.40 g of a forerun, bp <80 °C (0.1 mm), consisting of 50% 2,2-dinitropropanol and 50% 1,1-dinitroethane, and 6.7 g (67%) of 2,2 dinitropropanol: bp 90–100 °C (0.1 mm); mp[2,9] 79–80 °C; NMR ($CDCl_3$) δ 2.15 (s, 3 H), 3.40, (br s, 1 H, D_2O exch), 4.30 (s, 2 H).

2,2-Dinitro-1,3-propanediol. A solution of 20.0 g (0.50 mol) of sodium hydroxide in 75 mL of water was added dropwise with stirring and to a solution of 30.0 g (0.491 mol) of nitromethane and 80 g (0.99 mol) of 37% formalin in 75 mL of water. The first 0.5-mL increment of sodium hydroxide solution resulted in a temperature rise to 52 °C, and subsequently the temperature was maintained at 5 °C until the addition was completed. The mixture was stirred at 5–8 °C for 1.5 h and then a solution of 135 g (1.96 mol) of sodium nitrite in 200 mL of water, a 125-mL portion of tetrahydrofuran, and 120 g (0.504 mol) of solid sodium persulfate were added. The reaction temperature was kept below 35 °C with ice bath cooling. After 30 min, the aqueous phase was extracted 4 times with 125-mL portions of ether. The combined organic phases were washed with 2–100-mL portions of water and with 1–100-mL portion of saturated sodium chloride solution, dried, and stripped of solvent. Washing the residue with 100-mL and 60-mL portions of cold methylene chloride gave 21.8 g of product, and an additional 3.9 g was obtained by concentrating the methylene chloride, to yield 25.7 g (30%) of 2,2-dinitropropanediol: mp 140–142 °C;[2,9] NMR (acetone-d_6) δ 4.55 (d, 4 H), 5.20 (t, 1 H, D_2O exch).

Alternatively, 10.0 g (66 mmol) of tris(hydroxymethyl)nitromethane was added to a solution of 2.70 g (67 mmol) of sodium hydroxide in 25 mL of water at 10 °C. A solution of 18 g (0.26 mol) of sodium nitrile in 40 mL of water, 25 mL of tetrahydrofuran, a solution of 4.0 (12 mmol) of potassium ferricyanide in 20 mL of water, and 17 g (71 mmol) of solid sodium persulfate were added consecutively. After 30 min, isolation by the above procedure gave 3.90 g (35%) of 2,2-dinitro-1,3-propanediol.

2-Cyano-2-nitropropane. A mixture of 5.00 g (53 mmol) of 94% 2-nitropropane, 3.0 g (75 mmol) of sodium hydroxide, and 25 mL of water was stirred until a homogeneous solution was formed. A solution of 10 g (0.20 mol) of sodium cyanide in 40 mL of water, a solution of 3.8 g (12 mmol) of potassium ferricyanide in 15 mL of water, and a 25-mL portion of methylene chloride were added. The mixture was cooled with an ice bath and 15.0 g (12.6 mmol) of solid sodium persulfate was added in increments so as to control the reaction exotherm. Distillation gave 2.80 g (47%) of 2-cyano-2-nitropropane.[4]

1-Cyano-1-nitrocyclohexane. By the same procedure, nitrocyclohexane was converted to 1-cyano-1-nitrocyclohexane (64%), identified by its physical and spectral properties.[4]

1-Nitro-1-(phenylsulfonyl)propane. A mixture of 5.00 g (52 mmol) of 94% 2-nitropropane, 5.0 g (0.125 mol) of sodium hydroxide, and 25 mL of water was stirred until a homogeneous solution was formed. A solution of 15 g (91 mmol) of benzenesulfinic acid sodium salt in 50 mL of water, 25 mL of 1,2-dichloroethane, a solution of 3.5 g (10 mmol) of potassium ferricyanide in 10 mL of water, and 15 g (63 mmol) of solid sodium persulfate were added. An ice bath was used to control the exothermic reaction, and the temperature reached 60 °C before subsiding. The mixture was stirred for 15 min at 25 °C, and the aqueous layer was extracted with methylene chloride. The combined organic phases were washed with brine and dried over magnesium sulfate. Removal of solvent and recrystallization from 50 mL of methanol gave 6.50 g (54%) of 1-nitro-1-(phenylsulfonyl)propane, with the reported[4] properties.

1-Nitro-1-(phenylsulfonyl)cyclohexane. The above procedure was used with the exception that 50 mL of 1:3 dioxane–water was used to dissolve 4.00 g (0.10 mol) of sodium hydroxide and 5.00 g (38.7 mmol) of nitrocyclohexane. The product was recrystallized from 25 mL of 5% ethanol to give 6.63 g (64%) of 1-nitro-1-(phenylsulfonyl) cyclohexane.[4]

Methyl 2-Nitro-2-(phenylsulfonyl)butanoate. A mixture of 1.0 g (6.80 mmol) of methyl 2-nitrobutyrate[13] and 4.0 g (32 mmol) of sodium carbonate hydrate in 20 mL of water was stirred vigorously until a homogeneous solution was formed. A solution of 4.0 g (24 mmol) of benzenesulfinic acid sodium salt in 15 mL of water and 20 mL of benzene were added. A solution of 6.0 g (18 mmol) of potassium ferricyanide in 25 mL of water was added dropwise with stirring. Stirring was continued for 1 h and the aqueous phase was extracted twice with ether. The combined organic layers were washed with saturated sodium chloride solution, dried over magnesium sulfate, and stripped of solvent. The residue was triturated with petroleum ether, filtered, and dried to give 1.23 g (63%) of methyl 2-nitro-2-(phenylsulfonyl)butanoate: mp 59–60 °C; IR (CCl_4) 1760, 1560, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (t, 3 H), 2.61 (q, 2 H), 3.65 (s, 3 H), 7.20–7.80 (m, 5 H).

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Anal. Calcd for $C_{11}H_{13}NO_6S$: C, 45.99; H, 4.56; N, 4.87; S, 11.16. Found: C, 46.08; H, 4.54; N, 4.88; S, 11.07.

Registry No. $CH_3CH(NO_2)CH_2OCH_3$, 95798-39-3; $C_2H_5O(CH_2)_2NO_2$, 31890-52-5; $CH_3C(NO_2)_2CH_2OCH_3$, 5917-65-7; $C_2H_5OCH_2CH(NO_2)_2$, 5946-60-1; $(C_2H_5OCH_2)_2CHNO_2$, 95798-42-8; $(HOCH_2)_3CNO_2$, 126-11-4; $C_2H_5OCH_2CH(CH_2OH)NO_2$, 95798-43-9; $C_2H_5CH(NO_2)CO_2CH_3$, 59906-50-2; $(C_2H_5OCH_2)_2C(NO_2)_2$, 95798-44-0; $CH_3C(NO_2)_2CH_2OH$, 918-52-5; $(HOCH_2)_2C(NO_2)_2$, 2736-80-3; $C_2H_5OCH_2C(NO_2)_2CH_2OH$, 95798-45-1; $C_2H_5C(NO_2)_2CO_2CH_3$, 95798-46-2; $(CH_3)_2C(NO_2)CN$, 18992-13-7; $(CH_3)_2C(NO_2)SO_2Ph$, 41774-06-5; $C_2H_5C(NO_2)(SO_2Ph)CO_2CH_3$, 95798-47-3; $(CH_3)_2CHNO_2$, 79-46-9; $CH_3CH_2NO_2$, 79-24-3; $CH_3(CH_2)_3NO_2$, 627-05-4; $CH_2{=}CHCH_2CH_2NO_2$, 32349-29-4; $(CH_3)_2C(NO_2)_2$, 595-49-3; $CH_3CH(NO_2)_2$, 600-40-8; $CH_3(CH_2)_2CH(NO_2)_2$, 3759-55-5; $CH_2{=}CHCH_2CH(NO_2)_2$, 10229-09-1; nitrocyclohexane, 1122-60-7; nitrocyclopentane, 2562-38-1; 2,2-dimethyl-5-nitro-1,3-dioxane, 4064-87-3; 1,1-dinitrocyclohexane, 4028-15-3; 1,1-dinitrocyclopentane, 10515-17-0; 3,3-dinitrooxetane, 81764-66-1; sodium nitrite, 7632-00-0; potassium ferricyanide, 13746-66-2; triethyl orthoacetate, 78-39-7; formalin, 50-00-0; nitromethane, 75-52-5; sodium cyanide, 143-33-9; 3-nitrooxetane, 86632-92-0; 2-methyl-2-ethoxy-5-nitro-5-(hydroxymethyl)-1,3-dioxane, 95798-40-6; 2,2-dimethyl-5,5-dinitro-1,3-dioxane, 5086-75-9; 2-ethoxy-2-methyl-5,5-dinitro-1,3-dioxane, 95798-41-7; 1-nitro-1-cyanocyclohexane, 58102-55-9; 1-nitro-1-(phenylsulfonyl)cyclohexane, 41774-11-2; dimethyl 2,3-diethyl-2,3-dinitrosuccinate, 95798-48-4; sodium persulfate, 7775-27-1; 3-ethoxy-2-nitro-1-propene, 95798-49-5; 2,2-dimethyl-5-nitro-5-(hydroxymethyl)-1,3-dioxane, 4728-14-7; benzenesulfinic acid sodium salt, 873-55-2.

Redox vs. Lewis Acid Catalysis. The Chemistry of 1,2-Diarylethanes in $SbCl_3$-Rich Molten Salt Media

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The product selectivity for the reactions of 1,2-diarylethanes, $ArCH_2CH_2Ar$ [Ar = phenyl (DPE), 1-naphthyl (DNE), and 9-anthryl (DAE)], in $SbCl_3$-rich molten salt media at 80–150 °C is found to be highly dependent on the nature of the aryl group. This chemistry, which has been examined primarily by in situ ^1H NMR and by quench and separation techniques, is interpreted in terms of a change in mechanism from Lewis acid catalysis to redox catalysis as the aryl group becomes more oxidizable. DPE is activated solely by the Lewis acid function of the melt, which generates a benzylic carbenium ion, ArC^+HCH_2Ar, as a reactive intermediate by hydride abstraction by $SbCl_2^+{\cdot}nSbCl_3$. This intermediate leads to transalkylation products resulting from the selective cleavage of the benzylic (sp^2–sp^3) carbon–carbon bond. DAE, on the other hand, is activated by the redox function of the melt, which generates a radical cation intermediate, $ArCH_2CH_2Ar^{+\cdot}$, by oxidation by Sb^{3+}. At 80 °C, the primary reaction pathway for the DAE radical cation is an intramolecular aryl–aryl coupling with internal hydrogen transfer to produce an unusual spiro isomer (1) of DAE in high yield. At higher temperatures (150 °C) cleavage of the ethylenic (sp^3–sp^3) carbon–carbon bond in the radical cation becomes an important process in competition with the intramolecular coupling. For DNE, combined Lewis acid catalysis (positional isomerization and transalkylation) and redox catalysis (intramolecular coupling) generates a complex product mixture. The reactions observed for $DAE^{+\cdot}$ and $DNE^{+\cdot}$ in these highly purified anhydrous $SbCl_3$-rich melts are discussed in relation to reaction pathways for alkylbenzene and diarylethane radical cations in other media.

Molecular antimony trichloride is an extremely weak Lewis acid with little ability to catalyze organic reactions when dissolved in an inert solvent.[1] However, if $SbCl_3$ is present as a continuous molten phase, it is reported to be an active catalytic medium for hydrocracking coal with a high specificity for distillate hydrocarbons.[2] In our research on molten salt catalysis with coal model compounds, we have also found $SbCl_3$-rich melts to be active catalytic media for inducing selective organic reactions.[3] These melts have been found to possess two active catalytic functions: a Lewis acid function and, perhaps more surprisingly, a redox function. Moreover, the strength of these catalytic functions can be tuned by controlled additions of chloride donors or acceptors, which produce a flexible catalyst with reproducible control over reaction rates and product selectivities.

The Lewis acid function of the melt results from the fact that in the molten state $SbCl_3$ is weakly ionized, as modeled in eq 1, with a reported ionization constant, K_i, at 99

$$SbCl_3 \rightleftarrows SbCl_2^{+}{}_{(solv)} + Cl^{-}{}_{(solv)} \qquad (1)$$

°C ranging from 3×10^{-11} to 2×10^{-8} M^2.[4] As indicated in eq 1, the ions are not present in the melt as discrete entities, but instead are complexed to neutral $SbCl_3$ molecules (or chains of $SbCl_3$ molecules) through chlorine bridge bonds as indicated from Raman[5] and electrical conductivity[6] studies. There is currently no objective ev-

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