dried at 80 °C under vacuum. The data are given in Table IV. ^{31}P NMR analysis showed 92% phosphine and 8% phosphine oxide sites. The second recycling of the same polymer resulted in 90% phosphine and 10% phosphine oxide sites.

Benzylpolystyryldiphenylphosphonium Salt from Recycled Polymer. The standard procedure gave a phosphonium salt content of 1.24 mequiv/g of polymer (89% yield) in the first recycle and 1.30 mequiv/g of polymer (92% yield) in the second recycle.

(*Z*)- and (*E*)-Stilbene from Recycled Polymer. The procedure described previously was followed except that the sodium ethoxide and the benzaldehyde were added dropwise simultaneously by syringe. Yields of isomeric mixtures were 96% for the first and 97% for the second recycle.

Calculation of the Percent Conversion. For the partial conversion of bromostyrene repeat units to styryldiphenylphosphine units by the lithium diphenylphosphide method with 20% cross-linked macroporous polystyrene, the percent conversion was calculated as follows. (1) With 20% divinylbenzene (DVB) cross-linking the copolymer also contains 16% ethylvinylbenzene (EVB) and 64% styrene (St) by weight, since the divinylbenzene monomer contained 55% DVB and 44% EVB by weight. The average molecular weight of one repeat unit is $[(0.20)(1\ \text{mmol}/130.2\ \text{mg of DVB}) + (0.16)(1\ \text{mmol}/132.2\ \text{mg of EVB}) + (0.64)(1\ \text{mmol}/104.1\ \text{mg of St})]^{-1} = 112.4$ mg of monomer/mmol of repeat units. (2) Assume all three kinds of repeat units are equally reactive with bromine. The brominated copolymer by elemental analysis contains 3.08 mequiv of brominated repeat units (BrSt)/g and $[1000\ \text{mg} - (3.08\ \text{mequiv})(191.4\ \text{mg of BrSt/mequiv})][112.4\ \text{mg/mequiv of nonbrominated repeat unit}]^{-1} = 3.65$ mequiv of nonbrominated repeat units/g. The brominated polystyrene has $[3.08/(3.08 + 3.65)] \times 100 = 46\%$ ring substitution. (3) After phosphination the polymer contains by elemental analysis 1.63 mequiv of BrSt/g and 0.97 phosphinated repeat units (Ph$_2$PSt)/g. Therefore $[1000\ \text{mg} - (1.63\ \text{mequiv})(191.4\ \text{mg of BrSt/mequiv}) - (0.97\ \text{mequiv of Ph}_2\text{PSt})(296.7\ \text{mg of Ph}_2\text{PSt/mequiv})][112.4\ \text{mg/mequiv of unsubstituted repeat units}]^{-1} = 3.56$ mequiv of unsubstituted repeat units/g. The polymer contains $(1.63 + 0.97 + 3.56) = 6.16$ mequiv of repeat units/g, of which $(1.63/6.16)(100) = 26\%$ are BrSt, $(0.97/6.16)(100) = 16\%$ are Ph$_2$PSt, and 58% are unsubstituted. The 42% of substituted repeat units agrees within experimental error with the 46% of BrSt units in the starting brominated polystyrene. The percent conversion of BrSt to Ph$_2$PSt repeat units was $(16/46)(100) = 35\%$.

Another calculation, which assumed that only styrene repeating units reacted with bromine, gave 27% BrSt, 16% Ph$_2$PSt, and 57% unsubstituted repeat units.

Acknowledgment. We thank the U.S. Army Research Office for financial support and Dr. S. P. McManus for sending us a copy of ref 23 prior to publication.

Registry No. PhCH$=$CHCHO, 104-55-2; (*E*)-PhCH$=$C(CH$_3$)CHO, 15174-47-7; *n*-C$_{11}$H$_{23}$CHO, 112-54-9; (*E*)-PhCH$=$CHPh, 103-30-0; (*E*,*Z*)-PhCH$=$CHCH$=$CHPh, 5808-05-9; (*Z*,*E*)-PhCH$=$C(CH$_3$)CH$=$CHPh, 83897-70-5; (*E*)-*m*-C$_{11}$H$_{23}$CH$=$CHPh, 42036-74-8; (CH$_2$)$_5$CO, 108-94-1; Ph$_2$Co, 119-61-9; (*n*-C$_{10}$H$_{21}$)$_2$CO, 19781-72-7; (CH$_2$)$_5$C$=$CH$_2$, 1192-37-6; PhC$=$CH$_2$, 530-48-3; (*n*-C$_{10}$H$_{21}$)$_2$C$=$CH$_2$, 52636-68-7; (*E*,*E*)-PhCH$=$CHCH$=$CHPh, 538-81-8; (*E*)-PhCH$=$CHCHO, 14371-10-9; (*Z*)-PhCH$=$C(CH$_3$)CHO, 66051-14-7; (*Z*)-PhCH$=$CHPh, 645-49-8; (*E*,*E*)-PhCH$=$C(CH$_3$)CH$=$CHPh, 23637-43-6; (*Z*)-*n*-C$_{11}$H$_{23}$CH$=$CHPh, 83897-71-6; (*Z*)-PhCH$=$CHCHO, 57194-69-1; PhCH$=$CHCH$=$CH$_2$, 1515-78-2; benzaldehyde, 100-52-7; cholest-4-en-3-one, 601-57-0; 3-methylenecholest-4-ene, 4561-75-5; trichlorosilane, 19165-34-5; *N*,*N*-dimethylaniline, 121-69-7.

Oxidative Substitution of Nitroparaffin Salts[1]

Nathan Kornblum,* Haribansh K. Singh, and William J. Kelly

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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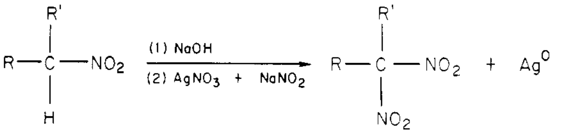
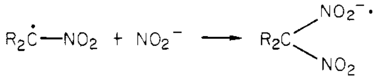
α,α-Dinitro compounds, α-nitro sulfones, and α-nitro nitriles are obtained in excellent yields when nitroparaffin salts are coupled to nitrite, benzenesulfinate, and cyanide ions by the agency of potassium ferricyanide.

Electron-transfer substitution at a saturated carbon atom is now well established.[2] Although most of the known examples are chain processes, it is of interest that the first example of an electron-transfer substitution process to be recognized (1964)[3] was the non-chain reaction of eq 1, which had been discovered in 1961.[4] The mechanism proposed in 1964 (eq 2–4) invoked collapse of a radical and an anion to give a radical anion, an idea that, while novel in 1964, is now routinely employed in any discussion of electron-transfer substitution.

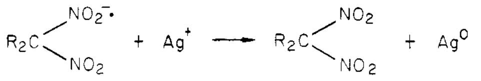


$$\mathrm{RR'CH{-}NO_2} \xrightarrow[(2)\ \mathrm{AgNO_3}\ +\ \mathrm{NaNO_2}]{(1)\ \mathrm{NaOH}} \mathrm{RR'C(NO_2){-}NO_2} + \mathrm{Ag^0} \quad (1)$$

$$\mathrm{R_2C^-{-}NO_2} + \mathrm{Ag^+} \longrightarrow \mathrm{R_2\dot{C}{-}NO_2} + \mathrm{Ag^0} \quad (2)$$



$$\mathrm{R_2\dot{C}{-}NO_2} + \mathrm{NO_2^-} \longrightarrow \mathrm{R_2C(NO_2^{-}\cdot)(NO_2)} \quad (3)$$



$$\mathrm{R_2C(NO_2^{-}\cdot)(NO_2)} + \mathrm{Ag^+} \longrightarrow \mathrm{R_2C(NO_2)_2} + \mathrm{Ag^0} \quad (4)$$

In 1979 Matacz et al.[5] reported that aqueous potassium ferricyanide is a useful reagent for oxidatively substituting secondary nitroparaffin salts but that with the salts of

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[1] This is paper 26 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". For the preceding paper see: Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1037.

[2] For reviews see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. Kornblum, N. In "The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982; p 361.

[3] N Kornblum cited by Feuer, H. *Tetrahedron Suppl.* **1964**, *20*, 107.

[4] Kaplan, R. B.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3535. See footnote 6 of the paper by Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *Ibid.* **1971**, *93*, 4316 (1971).

[5] Matacz, Z.; Piotrowska, H.; Urbanski, T. *Pol. J. Chem.* **1979**, *53*, 187.

0022-3263/83/1948-0332$01.50/0

primary nitro compounds this reagent fails. Their results are summarized in eq 5 ($A:^- = NO_2^-$, CN^-, $C_6H_5SO_2^-$, p-

$$R_2C^--NO_2 + A:^- \xrightarrow{K_3Fe(CN)_6} R_2C(A)-NO_2 \quad (5)$$

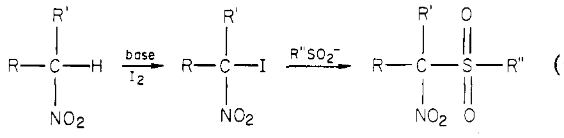
$C(C_6H_4S^-)$. As regards the matter of mechanism, the discoverers of the reaction of eq 5 made the very reasonable assumption that it proceeds by a sequence completely analogous to that of eq 2–4 with ferricyanide replacing silver as the oxidizing agent.

In connection with other studies we required α-nitro nitriles, α-nitro sulfones, and α,α-dinitroparaffins, and the possibility that potassium ferricyanide would provide a useful means of preparing these compounds was investigated. It transpires that the reaction of eq 5 is even more valuable than originally portrayed—with secondary nitro compounds the yields of pure products are very high, and contrary to the earlier report, the reaction succeeds with primary nitroparaffins. Table I summarizes our results; yields refer to pure, isolated products.

The question then arises how does the use of potassium ferricyanide compare with earlier procedures for synthesizing α,α-dinitroparaffins, α-nitro sulfones, and α-nitro nitriles?

Hitherto the most useful and general method for preparing α,α-dinitro compounds has been the reaction of eq 1, discovered by Kaplan and Shechter.[4] This reaction enables one to convert primary and secondary nitroparaffins to the geminal dinitro compounds in excellent yields by a simple procedure. The major drawback of the Kaplan–Shechter reaction is its use of silver nitrate—a reagent that has become very expensive. Our experience persuades us that for the synthesis of geminal dinitro compounds derived from primary and secondary nitroparaffins potassium ferricyanide is at least the equal of silver nitrate.

Very few methods are available for the synthesis of α-nitro sulfones in which the carbon bearing the nitro and sulfone groups is devoid of hydrogen atoms.[6] One of these, the sequence of eq 6, is extremely facile and routinely



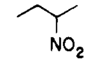
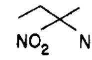
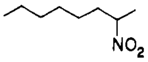
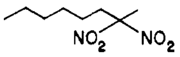
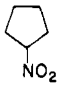
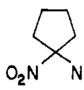
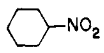
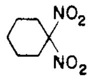
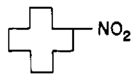
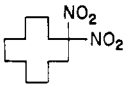
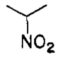
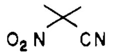
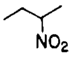
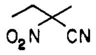
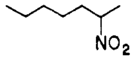
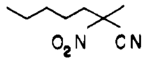
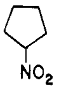
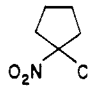
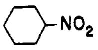
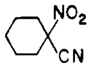
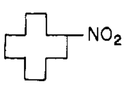
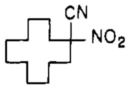
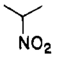
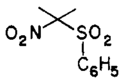
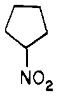
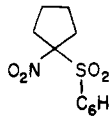
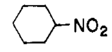
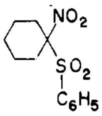
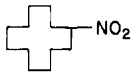
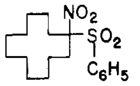
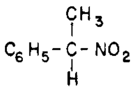
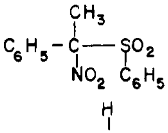
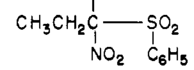
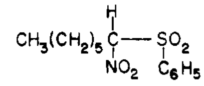
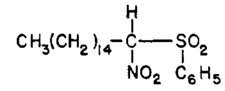
(6)

$$R-\overset{R'}{\underset{NO_2}{C}}-H \xrightarrow[I_2]{base} R-\overset{R'}{\underset{NO_2}{C}}-I \xrightarrow{R''SO_2^-} R-\overset{R'}{\underset{NO_2}{C}}-\overset{O}{\underset{O}{S}}-R'' \quad (6)$$

provides pure products in 85–95% yields;[7] while the use of potassium ferricyanide is not superior to this reaction, it is, at very minimum, a valuable alternative. Furthermore, the ferricyanide procedure provides a good way to synthesize α-nitro sulfones bearing a hydrogen on the carbon to which the nitro and sulfone groups are attached (cf. Table I); this is a capability that has not as yet been established for the reaction of eq 6.

The ferricyanide reaction of eq 5 is the only general method for preparing tertiary α-nitro nitriles. The excellent yields of pure products (Table I), the ready availability of the requisite secondary nitro compounds,[8] and the simplicity of the procedure make this an especially valuable synthetic method.[9,10]

Table I. Oxidative Substitution Reactions

nitro compd	product	yield,[a] %
		83
		90
		85
		88
		84
$CH_3(CH_2)_5CH_2NO_2$	$CH_3(CH_2)_5CH(NO_2)_2$	83
$CH_3(CH_2)_8CH_2NO_2$	$CH_3(CH_2)_8CH(NO_2)_2$	64
$CH_3(CH_2)_{16}CH_2NO_2$	$CH_3(CH_2)_{16}CH(NO_2)_2$	73
		71
		74
		83
		83
		83
		90
		86
		86
		81
		72
 $C_6H_5-\overset{CH_3}{\underset{H}{C}}-NO_2$	 $C_6H_5-\overset{CH_3}{\underset{NO_2}{C}}-\underset{C_6H_5}{SO_2}$	81
$CH_3CH_2CH_2NO_2$	 $CH_3CH_2\overset{H}{\underset{NO_2}{C}}-\underset{C_6H_5}{SO_2}$	70
$CH_3(CH_2)_5CH_2NO_2$	 $CH_3(CH_2)_5\overset{H}{\underset{NO_2}{C}}-\underset{C_6H_5}{SO_2}$	74
$CH_3(CH_2)_{14}CH_2NO_2$	 $CH_3(CH_2)_{14}-\overset{H}{\underset{NO_2}{C}}-\underset{C_6H_5}{SO_2}$	60

[a] Pure, isolated product.

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(6) In a recent paper Wade, P. A. et al. (Wade, P. A.; Hinnez, H. R.; Amin, N. V.; Vail, P. D.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S. *J. Org. Chem.* **1981**, *46*, 765) summarize the methods available for the synthesis of α-nitro sulfones.

(7) Kornblum, N.; Kestner, M. M.; Boyd, S. D.; Cattran, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3356.

(8) In this connection the conversion of amines to nitro compounds according to Gilbert and Borden (Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659) is especially noteworthy (cf. Experimental Section of the present paper). Also see: Kornblum, N. *Org. React.* **1962**, *12*, 101.

Experimental Section

Infrared spectra (IR) were recorded on a Beckman IR-33 spectrometer. Nuclear magnetic resonance spectra (NMR) were obtained on a Perkin-Elmer R-32 90-MHz spectrometer.

Nitroparaffins. 1-Nitroheptane, 1-nitrodecane, 1-nitrohexadecane, and 1-nitrooctadecane were prepared according to ref 11 from the corresponding bromides or iodides and silver nitrite. Only 1-nitrooctadecane is new; it has mp 43–44 °C. [Anal. Calcd for $C_{18}H_{37}NO_2$: C, 72.24; H, 12.37; N, 4.68. Found: C, 72.52; H, 12.18; N, 4.81].

Except for nitrocyclopentane,[12] secondary nitroparaffins were prepared by the excellent procedure due to Gilbert and Borden[13] (*m*-chloroperbenzoic acid oxidation of amines). Several of the lower nitroparaffins were gifts.[14]

Preparation of Nitrocyclododecane. To a refluxing solution (ca. 82 °C) of 175 g of *m*-chloroperbenzoic acid (technical grade, 85%, Aldrich Chemical Co.) in 1400 mL of 1,2-dichloroethane, 38.4 g (0.21 mol) of cyclododecylamine was added, *dropwise*, in the course of ca. 40 min. The initial phase of this reaction is exothermic, and care should be taken to avoid rapid addition of the amine. Refluxing was continued for another 3 h, and then the system was allowed to come to room temperature and filtered. The solids were washed with 1,2-dichloroethane, and the combined dichloroethane solutions were washed with 1 N NaOH (3 × 1 L) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a yellow oil, which was flash chromatographed on silica gel (230–400 mesh) with hexane for elution. In this way 28.6 g (64% yield) of a colorless oil was obtained, which by VPC is pure; it readily crystallized to a white solid, mp 29–30 °C.

Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.87; N, 6.57. Found: C, 67.78; H, 10.69; N, 6.59.

Preparation of 1,1-Dinitrocyclohexane. Under N_2, nitrocyclohexane (1.24 g, 0.0096 mol) was added to a rapidly stirred solution of sodium hydroxide (0.48 g, 0.012 mol) in methanol (20 mL) and water (25 mL). After 10 min a clear yellow solution was obtained, and this was added, dropwise under N_2, in the course of 30 min to a vigorously stirred solution of potassium ferricyanide (16.25 g, 0.050 mol) and sodium nitrite (6.90 g, 0.100 mol) in water (100 mL) over which pentane (200 mL) had been layered. The reaction mixture was stirred for an additional 60 min, the two phases were separated, and the aqueous phase was extracted twice with 100-mL portions of pentane. The pentane phase and extracts were combined, washed with 100 mL of water, and dried ($MgSO_4$). Removal of the pentane gave 1.79 g of crude product, which on vacuum distillation gave 1.48 g (88% yield) of VPC-pure 1,1-dinitrocyclohexane as a colorless liquid (bp 77–79 °C (1.5 mmHg)). On standing this crystallized: mp 33–34 °C; ^1H NMR ($CDCl_3$) δ 1.60 (m, 6 H), 2.50 (m, 4 H); IR ($CHCl_3$) 6.50 μm (NO_2).

Anal. Calcd for $C_6H_{10}N_2O_4$: N, 16.10. Found: N, 15.84.

Preparation of 2,2-Dinitrobutane. The procedure was the same as for 1,1-dinitrocyclohexane; 2.07 g (0.020 mol) of 2-nitrobutane was used, and consequently, twice as much of the other reagents were also employed. Distillation of the crude product (2.84 g) gave 2.48 g (83% yield) of VPC-pure 2,2-dinitrobutane as a clear liquid: bp 41–44 °C (1.5 mmHg); ^1H NMR ($CDCl_3$) δ 1.05 (t, 3 H), 2.10 (s, 3 H), 2.50 (q, 2 H); IR (neat) 6.50 μm (NO_2).

Anal. Calcd for $C_4H_8N_2O_4$: C, 32.43; H, 5.41; N, 18.92. Found: C, 32.59; H, 5.45; N, 19.15.

Preparation of 2,2-Dinitrooctane. 2-Nitrooctane (1.61 g, 0.010 mol) was treated exactly as described for 1,1-dinitrocyclohexane except that diethyl ether was employed instead of pentane. On removal of the ether 1.93 g of a pale yellow liquid remained. This on distillation gave 1.81 g (90% yield) of VPC-pure 2,2-dinitrooctane as a colorless oil: bp 93–97 °C (1.5 mmHg); ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.35 (br s, 8 H), 2.10 (s, 3 H), 2.45 (m, 2 H); IR (neat) 6.50 μm (NO_2).

Anal. Calcd for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.89; N, 13.72. Found: C, 47.29; H, 7.98; N, 13.55.

Preparation of 1,1-Dinitrocyclopentane. Nitrocyclopentane (1.15 g, 0.010 mol) was converted to the dinitro compound by following the procedure described for 1,1-dinitrocyclohexane; 1.54 g of crude product was distilled. This gave 1.40 g (85% yield) of VPC-pure 1,1-dinitrocyclopentane as a clear liquid: bp 63–64 °C (1.25 mmHg); ^1H NMR ($CDCl_3$) δ 2.00 (m, 4 H), 2.75 (t, 4 H); IR (neat) 6.47 μm (NO_2).

Anal. Calcd for $C_5H_8N_2O_4$: C, 37.50; H, 5.03; N, 17.49. Found: C, 37.74; H, 5.05; N, 17.34.

Preparation of 1,1-Dinitrocyclododecane. A 60% oil dispersion of sodium hydride (1.00 g, 0.024 mol) was washed free of oil with pentane and transferred to a nitrogen-filled flask with the aid of 35 mL of *tert*-butyl alcohol. After this was stirred for 20 min, a solution of nitrocyclododecane (4.68 g, 0.022 mol) in 25 mL of *tert*-butyl alcohol was added all at once; a heavy white precipitate formed immediately. The salt was dissolved by adding 20 mL of water. This nitro salt was added dropwise to a rapidly stirred solution of potassium ferricyanide (32.90 g, 0.100 mol) and sodium nitrite (13.80 g, 0.200 mol) in 150 mL of water over which 200 mL of diethyl ether had been layered. The reaction mixture was stirred and maintained under N_2 for an additional 60 min, the two phases were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The ether extracts and the ether phase were combined, washed with water (100 mL), and dried ($MgSO_4$). Removal of the ether gave 5.60 g of crude product. This was dissolved in 5 mL of benzene and subjected to column chromatography on a 30 × 2 cm silica gel column (Merck, 60–200 mesh) eluting with 3:1 hexane–benzene. Two major components were obtained: First, 4.82 g (84% yield) of VPC-pure 1,1-dinitrocyclododecane, a white solid: mp 63.5–64.5 °C; ^1H NMR ($CDCl_3$) δ 1.34 (br s, 18 H), 2.40 (m, 4 H); IR ($CHCl_3$) 6.50 μm (NO_2).

Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.80; H, 8.58; N, 10.84. Found: C, 56.06; H, 8.79; N, 10.92.

This was followed by 0.44 g (11% yield) of what appears to be cyclododecanone as white crystals, mp 57–59 °C (lit.[15] mp 59 °C). This material has the same VPC retention time as an authentic sample and in the infrared exhibits strong absorption at 5.80 μm (C=O).

Preparation of 1,1-Dinitroheptane. 1-Nitroheptane (1.45 g, 0.010 mol) was added to a rapidly stirred solution of sodium hydroxide (0.94 g, 0.024 mol) in methanol (20 mL) and water (30 mL) under N_2. The mixture was stirred for 1 h, by which time the nitro compound had completely dissolved. This solution was added rapidly to a vigorously stirred solution of sodium nitrite (6.90 g, 0.100 mol) and potassium ferricyanide (16.45 g, 0.050 mol) in water (100 mL), and the reaction mixture was then stirred under N_2 for 2 h; during this time a yellow precipitate formed, and the solution became dark red. Urea (10.0 g, 0.166 mol) was added, the mixture was cooled to ca. 0 °C, and glacial acetic acid was slowly introduced to a pH of ca. 6.[16] The product was extracted with pentane (3 × 100 mL), and the combined extracts were washed with 100 mL of water and dried ($MgSO_4$). Removal of

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[9] Just how valuable this method is for preparing tertiary α-nitro nitriles can only be appreciated when one realizes that α-nitroisobutyronitrile has repeatedly been prepared by decomposing azobis(isobutyronitrile) in the presence of NO_2, a reaction that gives a 31% yield (Tilney-Basset, J. F.; Waters, W. A. *J. Chem. Soc.* **1957**, 3129. Gowenlock, B. J.; Pfab, J.; Kresze, G. *Justus Liebigs Ann. Chem.* **1975**, 1903. Russell, G. A.; Jawdosiak, M.; Makosza, M. *J. Am. Chem. Soc.* **1979**, *101*, 2359]; an alternative method, the reaction of α-bromoisobutyronitrile with $NaNO_2$ gives α-nitroisobutyronitrile in 50% yield (Weaver, W. M. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1958). And the reaction of 1-bromo-1-cyanocyclopentane with sodium nitrite gave a 52% yield of 1-nitro-1-cyanocyclopentane (Boyd, S. D. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1971).

[10] In contrast, preliminary studies of the application of the ferricyanide reaction to the synthesis of secondary α-nitronitriles $RCH(NO_2)CN$ have not been successful.

[11] Kornblum, N.; Ungnade, H. E. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, 724. Also see: Kornblum, N.; Erickson, A. S.; Kelly, W. J.; Henggeler, B. J. *J. Org. Chem.*, **1982**, *47*, 4534.

[12] Prepared by treating cyclopentyl bromide with sodium nitrite: Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.

[13] Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659.

[14] Our thanks are due to the Commercial Solvents Corp. for a generous supply of 2-nitropropane and 2-nitrobutane. We are also indebted to the DuPont Co. for a generous gift of nitrocyclohexane.

[15] Ruzicka, L.; Stoll, M.; Schinz, H. *Helv. Chim. Acta* **1926**, *9*, 256.

[16] Acidification is necessary to convert the salts of 1,1-dinitro compounds into the parent dinitro compounds. However, since sodium nitrite is present, nitrosation may compete on acidification; the addition of urea is intended to prevent nitrosation.

the pentane gave 1.79 g of crude product, and this on distillation afforded 1.58 g (83% yield) of VPC-pure 1,1-dinitroheptane as a pale yellow oil: bp 74–77 °C (0.4 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.40 (m, 8 H), 2.50 (m, 2 H), 6.20 (t, 1 H); IR (neat) 6.50 μm (NO_2).

Anal. Calcd for $C_7H_{14}N_2O_4$: C, 44.21; H, 7.36; N, 14.73. Found: C, 44.45; H, 7.45; N, 14.74.

Preparation of 1,1-Dinitrodecane. Under N_2, 1-nitrodecane (1.87 g, 0.010 mol) was added to a solution of sodium hydroxide (0.96 g, 0.024 mol) in methanol (20 mL) and water (25 mL). The solution was stirred for 30 min and then added dropwise to a vigorously stirred solution of sodium nitrite (6.84 g, 0.100 mol) and potassium ferricyanide (16.50 g, 0.050 mol) in water (120 mL). After addition was complete, the solution was stirred, under N_2, for 45 min. The resulting yellow solid was filtered off, washed with ca. 200 mL of ether, and then dissolved in 200 mL of water. The aqueous solution was cooled to ca. 0 °C, and 200 mL of pentane was added. Then glacial acetic acid (ca. 15 mL) was introduced until a pH of ca. 6 was obtained.[17] The pentane layer was isolated, and the aqueous phase was extracted with two 100-mL portions of pentane. The combined pentane phase and washings were washed with water (100 mL) and dried ($MgSO_4$). Removal of the pentane afforded 1.57 g of a pale yellow oil, which on distillation gave 1.47 g (64% yield) of VPC-pure 1,1-dinitrodecane, a colorless liquid: bp 84–89 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 3 H), 1.40 (br s, 14 H), 2.50 (m, 2 H), 6.10 (t, 1 H); IR (neat) 6.47 μm (NO_2).

Anal. Calcd for $C_{10}H_{20}N_2O_4$: C, 51.72; H, 8.62; N, 12.07. Found: C, 51.93; H, 8.70; N, 12.26.

Preparation of 1,1-Dinitrooctadecane. A solution of 1-nitrooctadecane (2.99 g, 0.010 mol) in 10 mL of tetrahydrofuran was added dropwise over a 20-min period to a rapidly stirred, N_2-protected solution of sodium hydroxide (0.93 g, 0.024 mol) in 30 mL of water. After an additional 20 min of stirring, the resulting solution was transferred all at once to a well-stirred solution of sodium nitrite (7.0 g, 0.100 mol) and potassium ferricyanide (16.45 g, 0.050 mol) in 100 mL of water. The resulting red solution was stirred under N_2 for 30 min, whereupon a yellow solid appeared. Urea (20.0 g, 0.333 mol) was added to the reaction mixture, and then 200 mL of ether was introduced. After the mixture was cooled to ca. 0 °C, glacial acetic acid was added slowly until pH 6 was attained.[16] The ether phase was removed and the aqueous phase extracted with another 200 mL of ether. The ether extracts were combined, washed with 100 mL of water, and then dried ($MgSO_4$). Removal of the ether left 3.10 g of crude product, which when recrystallized from ether–methanol gave 2.57 g (73% yield) of pale yellow crystals: mp 29–30 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (m, 3 H), 1.20 (br s, 30 H), 2.45 (m, 2 H), 6.05 (t, 1 H); IR ($CHCl_3$) 6.50 μm (NO_2). For analysis a small sample was dissolved in 1:1 ether–methanol, and the solution was added to saturated aqueous sodium bicarbonate. The resulting yellow precipitate was isolated by filtration and washed thoroughly with anhydrous ether. It was then stirred with a mixture of 3 N hydrochloric acid and pentane until the yellow color was gone (ca. 20 min). The two phases were separated, and the aqueous phase was extracted with pentane. The combined pentane solutions were dried ($MgSO_4$), and the pentane was then removed. This gave pure 1,1-dinitrooctadecane as white crystals, mp 30–31 °C.[18]

Anal. Calcd for $C_{18}H_{36}N_2O_4$: C, 62.79; H, 10.46; N, 8.14. Found: C, 63.03; H, 10.46; N, 8.04.

Preparation of 2-Cyano-2-nitropropane. In a 1-L flask 3.2 g (0.080 mol) of sodium hydroxide was dissolved in 23 mL of water, and then 6.75 g (0.0758 mol) of 2-nitropropane was added; stirring and a N_2 atmosphere were maintained throughout. After ca. 30 min a clear solution was obtained, to which was added 48.75 g (0.75 mol) of potassium cyanide in 125 mL of water and 300 mL of benzene. To the resulting mixture a solution of 61.69 g (0.1875 mol) of potassium ferricyanide in 160 mL of water was added dropwise in the course of ca. 45 min. By this time a yellow precipitate had appeared. After an additional minute, stirring was discontinued. The aqueous and benzene phases were decanted from the yellow solid, and the aqueous phase was extracted twice with 100-mL portions of ethyl ether. The yellow solid was dissolved in 200 mL of water, and the solution was extracted twice with 75-mL portions of ether. The combined benzene–ether solutions were washed with 50 mL of cold water and then dried over anhydrous sodium sulfate. On removal of the solvents by simple distillation, 7.5 g of a yellow liquid was obtained. This was chromatographed on a short silica gel column with 5:95 benzene–pentane. In this way 6.045 g (71% yield) of analytically pure 2-cyano-2-nitropropane was obtained as white crystals: mp 33–34 °C (lit.[9] mp 34 °C); ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6 H); IR ($CHCl_3$) 6.49 μm (NO_2); there is no absorption in the 4–5-μm region despite the presence of a cyano group.

Anal. Calcd for $C_4H_6N_2O_2$: N, 24.56. Found: N, 24.70.

Preparation of 2-Cyano-2-nitrobutane. Under N_2, 5.15 g (0.05 mol) of 2-nitrobutane was dissolved in a stirred solution of 2.2 g (0.055 mol) of sodium hydroxide in 24 mL of water. Then 32.5 g (0.50 mol) of potassium cyanide in 100 mL of water and 300 mL of benzene were added. Finally, 49.35 g (0.15 mol) of potassium ferricyanide in 135 mL of water was added dropwise (45 min). On workup of the reaction mixture as described for 2-cyano-2-nitropropane, 5.1 g of a yellow liquid was obtained. This, on being chromatographed on a short silica gel column with pentane, gave 4.72 g (74% yield) of a colorless liquid that by VPC is pure. For analysis a sample was distilled at 81–83 °C (8 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.11 (t, 3 H), 1.98 (s, 3 H), 2.28 (m, 2 H); IR (neat) 6.50 μm (NO_2). There is no absorption in the 4–5-μm region despite the presence of a cyano group.

Anal. Calcd for $C_5H_8N_2O_2$: C, 46.87; H, 6.25; N, 21.87. Found: C, 46.87; H, 6.36; N, 21.70.

Preparation of 2-Cyano-2-nitroheptane. Under N_2, with stirring, 0.55 g (0.0139 mol) of sodium hydroxide was dissolved in 10 mL of water, and then 1.813 g (0.0125 mol) of 2-nitroheptane dissolved in 5 mL of methanol was introduced. After 30 min a clear solution was obtained, and at that time 8.125 g (0.125 mol) of potassium cyanide in 30 mL of water was added rapidly. Then a solution of 16.45 g (0.05 mol) of potassium ferricyanide in 45 mL of water was added dropwise in ca. 30 min. A yellow precipitate began to form after 15 min; 3 h after all the ferricyanide had been introduced stirring was discontinued and 100 mL of water was added. The resulting solution was extracted three times with 100-mL portions of pentane. The pentane solution was washed with 40 mL of cold water and dried over anhydrous sodium sulfate, and then the pentane was removed by distillation. This gave 2.2 g of a liquid, which was chromatographed on a short silica gel column with a 9:1 mixture of hexane–methylene chloride. In this way VPC-pure α-nitronitrile was obtained as a colorless liquid (1.757 g, 83% yield). For analysis a sample was distilled at 83–84 °C (2 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.40 (s, 6 H), 1.95 (s, 3 H), 2.20 (m, 2 H); IR (neat) 6.50 μm (NO_2). No absorption in the 4–5-μm region despite the presence of a cyano group.

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.47; H, 8.24; N, 16.47. Found: C, 56.22; H, 8.51; N, 16.70.

Preparation of 1-Cyano-1-nitrocyclopentane. A solution of 1.1 g (0.028 mol) of sodium hydroxide in 20 mL of water was treated with 2.875 g (0.025 mol) of nitrocyclopentane; stirring and a N_2 atmosphere were maintained throughout. After ca. 30 min a clear solution was obtained, and then a solution of 16.25 g (0.25 mol) of potassium cyanide in 50 mL of water was added; this was followed by 250 mL of benzene. To this mixture a solution of 20.56 g (0.0625 mol) of potassium ferricyanide in 75 mL of water was added dropwise in the course of 35 min; during the addition a yellow precipitate formed. After an additional 10 min the mixture was worked up as described for 2-cyano-2-nitropropane. Removal of ether–benzene gave 3.20 g of a brown liquid. This was chromatographed on a short silica gel column with pentane. In this way 2.905 g (83% yield) of the α-nitronitrile was isolated as a colorless liquid that by VPC is pure. For analysis a sample was distilled at 65–67 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.00 (m, 4 H), 2.60 (m, 4 H); IR (neat) 6.50 μm (NO_2). No absorption appeared in the 4–5-μm region.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.43; H, 5.72; N, 19.99. Found: C, 51.40; H, 5.89; N, 19.81.

Preparation of 1-Cyano-1-nitrocyclohexane. Under N_2, 4.837 g (0.0375 mol) of nitrocyclohexane was added to a solution of 1.65 g (0.041 mol) of sodium hydroxide in 40 mL of water; after

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(17) In this case sodium nitrite was not present, and, therefore, urea was not added (see footnote 16).

(18) There are indications that heating this *gem*-dinitro compound to 100 °C results in some decomposition.

this stirred for ca 1.5 h, a light yellow solution resulted. At this point 24.37 g (0.375 mol) of potassium cyanide in 90 mL of water was added rapidly, and then a solution of 49.35 g (0.15 mol) of potassium ferricyanide in 155 mL of water was added dropwise in the course of ca. 45 min; a yellow precipitate formed, and the solution became dark red. After a total of 3.5 h, stirring was discontinued, and 200 mL of water was added. The resulting solution was extracted three times with 150-mL portions of ethyl ether, and then the ether extracts were washed twice with 50-mL portions of cold water and dried over anhydrous sodium sulfate. Removal of ether by simple distillation gave a liquid that solidified (5.205 g, mp 41–47 °C). Chromatography on a short silica gel column with 9:1 hexane–methylene chloride gave 4.710 g (83% yield) of a colorless solid, mp 51–53 °C, that by VPC is pure. On recrystallization from methanol the melting point was 51–53 °C; ^{1}H NMR ($CDCl_3$) δ 1.91 (m, 10 H); IR ($CHCl_3$) 6.50 μm (NO_2). No absorption appeared in the 4–5-μm region.

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.55; H, 6.49; N, 18.18. Found: C, 54.78; H, 6.63; N, 17.97.

Preparation of 1-Cyano-1-nitrocyclododecane. In a nitrogen-filled flask 0.375 g (0.0094 mol) of 60% sodium hydride (washed with pentane to remove oil) was treated with 40 mL of *tert*-butyl alcohol. After the mixture was stirred for ca. 1 h, a clear solution was obtained. At this point 1.332 g (0.006 25 mol) of nitrocyclododecane was added, whereupon a white precipitate, which did not dissolve after stirring for ca. 10 min, was produced; however, on addition of 15 mL of water, a clear solution was formed. To this solution 4.06 g (0.0625 mol) of potassium cyanide in 15 mL of water was added rapidly, and then a solution of 8.23 g (0.025 mol) of potassium ferricyanide in 25 mL of water was introduced in 45 min. A yellow precipitate formed. The reaction was allowed to proceed for another 1.75 h, and then 150 mL of water was added to dissolve the yellow solid. The resulting solution was extracted three times with 100-mL portions of ether, and the ether extracts were washed with 30 mL of cold water and then dried over anhydrous sodium sulfate. Removal of the ether gave 1.65 g of solid that when chromatographed on a short silica gel column with hexane gave 1.430 g of a white solid, mp 64–66 °C. On recrystallization from methanol 1.340 g (90% yield) of white crystals, mp 65–66 °C, was obtained. This α-nitro nitrile had the following spectral data: ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 18 H), 2.30 (m, 4 H); IR ($CHCl_3$) 6.49 μm (NO_2). No absorption appeared in the 4–5-μm region.

Anal. Calcd for $C_{13}H_{22}N_2O_2$: C, 65.55; H, 9.24; N, 11.76. Found: C, 65.64; H, 9.01; N, 11.58.

Preparation of α-Nitroisopropyl Phenyl Sulfone. Under N_2, 0.837 g (0.0094 mol) of 2-nitropropane was added to a stirred solution of sodium hydroxide (0.50 g, 0.0125 mol) in 10 mL of water. After ca. 30 min a clear solution was obtained, and then 6.167 g (0.0376 mol) of sodium benzenesulfinate dissolved in 19 mL of water was added; this was followed by 200 mL of benzene. To the resulting mixture a solution of 7.732 g (0.0235 mol) of potassium ferricyanide in 21 mL of water was added dropwise in 25 min. After an additional 15 min the benzene phase was isolated, and the aqueous phase was extracted twice with 100-mL portions of ether. The combined benzene–ether solution was back-washed twice with 100-mL portions of cold water and was then dried over anhydrous sodium sulfate. Removal of solvents gave 2.55 g of solid, mp 110–115 °C. One recrystallization from methanol yielded 1.850 g of white crystals (86% yield), mp 116–117 °C (lit.[7] mp 116–117 °C). The mixed melting point with authentic α-nitroisopropyl phenyl sulfone was 116–117 °C; ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 6 H), 7.7 (m, 5 H); IR ($CHCl_3$) 6.50 (NO_2), 8.70 μm (SO_2).

Preparation of α-Nitrocyclopentyl Phenyl Sulfone. A solution of 1.081 g (0.0094 mol) of nitrocyclopentane in 13 mL of water containing 0.50 g (0.0125 mol) of sodium hydroxide was prepared as in the preceeding preparation. To this was added 6.167 g (0.0376 mol) of sodium benzenesulfinate in 19 mL of water and then 150 mL of benzene. This was followed by 7.732 g (0.0235 mol) of potassium ferricyanide in 21 mL of water (dropwise, 25 min); 15-min later the reaction mixture was worked up as in the preceding case. The crude product, ca. 3 g, had mp 96–99 °C. Recrystallization from 95% ethanol gave 2.051 g (86% yield) of the pure α-nitro sulfone as white crystals, mp 99–100 °C (lit.[7] mp 99–100 °C). A mixed melting point with authentic α-nitro sulfone was 99–100 °C; NMR ($CDCl_3$) δ 1.91 (m, 4 H), 2.70 (t, 4 H), 7.80 (m, 5 H); IR ($CHCl_3$) 6.50 μm (NO_2), 8.67 μm (SO_2).

Preparation of α-Nitrocyclohexyl Phenyl Sulfone. Under N_2, 1.212 g (0.0094 mol) of nitrocyclohexane was dissolved in a solution of 0.50 g (0.0125 mol) of sodium hydroxide in 15 mL of water (1.5 h). Then 6.167 g (0.0376 mol) of sodium benzenesulfinate in 19 mL of water, 150 mL of benzene, and 7.732 g (0.0235 mol) of potassium ferricyanide in 20 mL of water were introduced exactly as described for the preparation of α-nitrocyclopentyl phenyl sulfone. On workup a crude product (mp 99–103 °C) was obtained. Repeated recrystallization from 95% ethanol gave 2.050 g (81% yield) of pure α-nitro sulfone as white crystals, mp 103–104 °C (lit.[7] mp 103–104 °C). A mixed melting point with authentic α-nitrocyclohexyl phenyl sulfone was undepressed; NMR ($CDCl_3$) δ 2.00 (m, 10 H), 7.75 (m, 5 H); IR ($CHCl_3$) 6.50 (NO_2), 8.67 μm (SO_2).

Preparation of α-Nitrocyclododecyl Phenyl Sulfone. A 60% oil dispersion of sodium hydride (0.50 g, 0.0125 mol) was washed free of oil with pentane and then treated, under N_2, with stirring, with 50 mL of *tert*-butyl alcohol. After 40 min 10 mL of water was added, and this produced a clear solution. A solution of 1-nitrocyclodecane (2.002 g, 0.0094 mol) in 7 mL of *tert*-butyl alcohol was then added, whereupon a precipitate resulted. The mixture was stirred for ca. 25 min, and then 10 mL of water was added; this produced a clear solution. A solution of 6.167 g (0.0376 mol) of sodium benzenesulfinate in 20 mL of water was added, and then 150 mL of benzene was introduced. To this mixture a solution of potassium ferricyanide (7.732 g, 0.0235 mol) in 20 mL of water was added dropwise in ca. 20 min, and the reaction was then allowed to proceed for an additional 25 min. The aqueous phase was ether extracted, and the combined benzene–ether solution was washed with water and then dried (Na_2SO_4). Removal of solvents left a viscous liquid that, on treatment with 5 mL of cold 95% ethanol, crystallized. Repeated recrystallization from 95% ethanol gave 2.389 g (72% yield) of white crystals: mp 85–87.5 °C; NMR ($CDCl_3$) δ 1.40 (s, 18 H), 2.40 (m, 4 H), 7.70 (m, 5 H); IR ($CHCl_3$) 6.50 (NO_2), 8.73 μm (SO_2).

Anal. Calcd for $C_{18}H_{27}NO_4S$: C, 61.19; H, 7.65. Found: C, 61.31; H, 7.59.

Preparation of 1-Nitro-1-(phenylsulfonyl)-1-phenylethane. Under N_2, a 60% oil dispersion of sodium hydride (0.50 g, 0.0125 mol) was washed free of oil with pentane and then treated with 50 mL of *tert*-butyl alcohol; after stirring for 30 min a clear solution was obtained. To this 1.419 g (0.0094 mol) of α-phenylnitroethane dissolved in 5 mL of *tert*-butyl alcohol was added; this produced a precipitate that did not dissolve after stirring for 10 min. Then 10 mL of water was added, and this gave a clear solution. To this solution 6.167 g (0.0376 mol) of sodium benzenesulfinate dissolved in 19 mL of water was added, and this was followed by 150 mL of benzene. To the resulting mixture an aqueous solution of 7.732 g (0.0235 mol) of potassium ferricyanide in 20 mL of water was added dropwise in the course of 25 min, and the reaction was then allowed to proceed for an additional 15 min. The aqueous phase was ether extracted, and the combined benzene–ether solution was washed with water and then dried (Na_2SO_4). Removal of solvents produced 2.7 g of solid which melted at 101–109 °C. This, on repeated recrystallization from 95% ethanol gave 2.212 g (81% yield) of the pure α-nitro sulfone as white crystals: mp 113–114 °C; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H), 7.50 (m, 10 H); IR ($CHCl_3$) 6.49 (NO_2), 8.70 μm (SO_2).

Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.73; H, 4.47; N, 4.81; S, 11.00. Found: C, 57.55; H, 4.83; N, 4.96; S, 11.00.

Preparation of 1-Nitro-1-(phenylsulfonyl)propane. Under N_2, with stirring, 2.492 g (0.028 mol) of 1-nitropropane was dissolved in 25 mL of water containing 2.33 g (0.0583 mol) of sodium hydroxide. To this solution 18.368 g (0.112 mol) of the sodium benzenesulfinate in 50 mL of water was added. Finally, 23.03 g (0.07 mol) of potassium ferricyanide dissolved in 70 mL of water was introduced dropwise in the course of 30 min. The red solution was stirred for an additional 10 min, and the reaction mixture (now brown) was cooled to 0–5 °C and acidified (pH 5) with a solution of urea (3.696 g) in 18.8 mL of 20% aqueous acetic acid; this produced a light yellow precipitate. The mixture was then extracted twice with 200-mL portions of ethyl ether, whereupon the solid dissolved. The ether solution was washed with 30 mL of cold water and then dried (Na_2SO_4). On removal of the ether a liquid remained, which on standing at 0 °C became solid (ca.

5.9 g, mp 52–56 °C). This on repeated recrystallization from 95% ethanol gave 4.480 g (70% yield, mp 56–58 °C) of white crystals of analytically pure 1-nitro-1-(phenylsulfonyl)propane: ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 3 H), 2.30 (m, 2 H), 5.50 (AB q, 1 H), 7.80 (m, 5 H); IR (KBr) 6.51 (NO_2), 8.80 μm (SO_2).

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.16; H, 4.80; N, 6.11; S, 13.98. Found: C, 46.97; H, 4.72; N, 6.30; S, 14.10.

Further acidification of the reaction mixture with 60 mL of ice cold 2.5 N hydrochloric acid, to pH 1, gave 6.7 g of a white solid, mp 72–77 °C; this, presumably, is impure benzenesulfinic acid (mp 83–84 °C).

Preparation of 1-Nitro-1-(phenylsulfonyl)heptane. Under N_2, 0.590 g (0.0148 mol) of sodium hydroxide was dissolved in 8 mL of water, and then 1.015 g (0.007 mol) of 1-nitroheptane and 8 mL of methanol were added; after this was stirred for 30 min, a clear solution was obtained. To this 4.592 g (0.028 mol) of sodium benzenesulfinate in 15 mL of water was added, and then 5.758 g (0.0175 mol) of potassium ferricyanide in 18 mL of water was dropped in over the course of 30 min. After an additional 10 min the reaction flask was cooled in an ice bath, 150 mL of pentane was added, and the mixture was acidified (pH ca. 6) with a cold solution of urea (0.924 g) in 4.7 mL of 20% aqueous acetic acid. The product consisted of a solid phase in addition to the pentane and water phases. The pentane phase was isolated, and the aqueous solid mixture was extracted with four 50-mL portions of pentane, whereupon the solid dissolved. The combined pentane solutions were washed with 30 mL of cold water and then were dried (Na_2SO_4). On removing the pentane, a yellow solid (ca. 1.81 g, mp 44–46 °C) was obtained. This, after repeated recrystallization from pentane, gave 1.483 g (74% yield) of analytically pure 1-nitro-1-(phenylsulfonyl)heptane as white crystals: mp 47–48 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H), 1.25 (s, 8 H), 2.25 (m, 2 H), 5.54 (t, 1 H), 7.89 (m, 5 H); IR ($CHCl_3$) 6.51 (NO_2), 8.75 μm (SO_2).

Anal. Calcd for $C_{13}H_{19}NO_4S$: C, 54.73; H, 6.67; N, 4.91; S, 11.22. Found: C, 54.50; H, 6.67; N, 4.80; S, 10.99.

Further acidification of the reaction mixture with a cold solution of urea (1.848 g) in 9.4 mL of 20% aqueous acetic acid to pH 5, followed by pentane extraction, yielded no additional product, nor did further acidification to pH 1 with cold 10% hydrochloric acid, followed by extraction with pentane, give any more product.

Preparation of 1-Nitro-1-(phenylsulfonyl)hexadecane. Under N_2, a 60% oil dispersion of sodium hydride (0.56 g, 0.014 mol) was washed free of oil with pentane, and then 40 mL of *tert*-butyl alcohol was added. After this was stirred for 1 h, 10 mL of water was introduced, and this was followed by 1.897 g (0.007 mol) of 1-nitrohexadecane in 5 mL of *tert*-butyl alcohol. A precipitate formed; after 20 min of stirring 10 mL of water was added, and this gave a clear solution. At this point 4.592 g (0.028 mol) of sodium benzenesulfinate in 65 mL of water was added rapidly, and then 5.758 g (0.0175 mol) of potassium ferricyanide in 19 mL of water was added dropwise over the course of 25 min. Stirring was continued for 10 h, and the product was then acidified (pH 5) by adding a cold solution of 0.924 g of urea in 4.7 mL of 20% aqueous acetic acid over a 5-min period. The resulting mixture was extracted with pentane; the pentane extracts were washed with water and then dried (Na_2SO_4). Removal of the pentane and cooling to 0 °C gave a white solid which on repeated recrystallization from hexane yielded 1.720 g (60%) of pure 1-nitro-1-(phenylsulfonyl)hexadecane: mp 65–66 °C; ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3 H), 1.25 (s, 26 H), 2.15 (m, 2 H), 5.50 (t, 1 H), 7.75 (m, 5 H); IR (KBr) 6.50 (NO_2), 8.67 μm (SO_2).

Anal. Calcd for $C_{22}H_{37}NO_4S$: C, 64.24; H, 9.00; N, 3.40; S, 7.79. Found: C, 64.27; H, 9.08; N, 3.42; S, 8.00.

Further acidification of the reaction mixture with 20 mL of ice cold 2.5 N hydrochloric acid, followed by extraction with pentane, gave nothing.

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Registry No. 1-Nitrooctadecane, 66292-30-6; cyclododecylamine, 1502-03-0; nitrocyclododecane, 1781-70-0; nitrocyclohexane, 1122-60-7; nitrocyclopentane, 2562-38-1; 2-nitrobutane, 600-24-8; potassium ferricyanide, 13746-66-2; sodium nitrite, 7632-00-0; 1,1-dinitrocyclohexane, 4028-15-3; 2,2-dinitrobutane, 5437-66-1; 2,2-dinitrooctane, 84065-75-8; 1,1-dinitrocyclopentane, 10515-17-0; 1,1-dinitrocyclododecane, 84065-76-9; 2-nitrooctane, 4609-91-0; 1-nitroheptane, 693-39-0; 1,1-dinitroheptane, 10229-05-7; 1,1-dinitrodecane, 3759-58-8; 1-nitrodecane, 4609-87-4; 1,1-dinitrooctadecane, 84065-77-0; 2-nitropropane, 79-46-9; 2-nitroheptane, 617-72-1; 2-cyano-2-nitropropane, 18992-13-7; 2-cyano-2-nitrobutane, 84065-78-1; potassium cyanide, 151-50-8; 2-cyano-2-nitroheptane, 84065-79-2; 1-cyano-1-nitrocyclopentane, 84065-80-5; 1-cyano-1-nitrocyclohexane, 58102-55-9; 1-cyano-1-nitrocyclododecane, 84065-81-6; α-nitroisopropyl phenyl sulfone, 41774-06-5; sodium benzenesulfinate, 873-55-2; α-nitrocyclopentyl phenyl sulfone, 41774-10-1; α-nitrocyclohexyl phenyl sulfone, 41774-11-2; α-nitrocyclododecyl phenyl sulfone, 84065-82-7; α-phenylnitroethane, 7214-61-1; 1-nitropropane, 108-03-2; 1-nitro-1-(phenylsulfonyl)-1-phenylethane, 84065-83-8; 1-nitro-1-(phenylsulfonyl)propane, 21272-84-4; 1-nitro-1-(phenylsulfonyl)heptane, 78258-04-5; 1-nitro-1-(phenylsulfonyl)hexadecane, 84065-84-9; 1-nitrohexadecane, 66271-50-9.

Photoepoxidation of Propylene at Elevated Pressures Sensitized by α-Diketones

James P. Shepherd

Celanese Research Company, Summit, New Jersey 07901

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The α-diketone sensitized photooxygenation of saturated propylene solutions (*o*-dichlorobenzene) at atmospheric pressure proceeds with high selectivity to propylene oxide. The effect of changing sensitizer concentration on the rate of epoxidation was determined for biacetyl, 1-phenyl-1,2-propanedione, and benzil. A small enhancement of the rate was achieved by using mixtures of biacetyl and 1-phenyl-1,2-propanedione. Pressurization of the reaction (140–185 psia) allowed the use of greater solution concentrations of propylene and oxygen and resulted in significant rate enhancement. In concentrated propylene solutions ($\geq$3.2 M) the formation of epoxide decreased as oxidative cleavage to acetaldehyde and formaldehyde increased. Total propylene conversion remained relatively constant at these concentrations.

As part of our program to develop novel routes to chemicals of commercial importance, we have been concerned with photochemical oxidations of simple organic compounds. Photooxidations of olefins with molecular oxygen to produce the corresponding epoxides have been of particular interest. Several conversions of this type have been reported. For example, the reaction of sterically hindered alkenes like biadamantylidene and 7,7′-binor-

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