rangements were conducted at 217 ± 0.5° by suspending the samples in the vapors of refluxing naphthalene in a flask with a long-necked air condenser. Samples for rearrangement were sealed in precision thin-walled nmr tubes, containing a sealed concentric capillary of hexamethyldisiloxane (lock signal), at $\leqslant 2\text{-}\mu$ pressure, after degassing by repeated freezing in liquid nitrogen and thawing. Deuterium incorporation into the 5 (terminal) position was monitored by a Varian associates HA-100 nmr spectrometer without opening the sealed sample tubes, and all rearrangements were carried to at least 65% completion. Relative peak areas were calculated from triple electronic integrals obtained with nonspinning samples, and the absorption of the proton at C_4 (—CH=) was in all cases taken as the standard and set at 1.00 proton.[36] With the exception of that of 4′-cyano-4-pentenophenone-*2-d*$_2$, the rearrangements were quite clean as indicated by the absence of any discernible extraneous peaks in the nmr spectra even after 110 hr at 217°. That a small amount of polymerization and/or decomposition was occurring under rearrangement conditions was, however, indicated by the increase in the aromatic resonance integrals and by an upward slope of the integral line in the region between δ 0.0 and 2.5 that was observed after prolonged heating. Multiple rearrangements of samples of 4-pentenophenone-*2-d*$_2$ showed good reproducibility of rate data (variations in $k \leqslant \pm 0.03 \times 10^{-2}$ hr^{-1}) and the absence of surface phenomena was demonstrated by rearrangements conducted in the presence of glass wool.

IV. Thermal Rearrangements of Alkylacylcyclopropanes. Rearrangements of 2,2-dimethyl-1-benzoylcyclopropane and 2,2-dimethyl-1-(*p*-methylbenzoyl)cyclopropane were performed using 25-μl samples sealed *in vacuo* in Pyrex tubes after degassing. Analyses were performed by glpc (3 ft × 0.25 in. 30% diethylene glycol succinate column at 130°). Separate samples were used for each analysis and peak areas were obtained by taking the average integral of three separate injections. The (peak height) × (width at one-half height) method of integration was used. Thermal ring opening of the less volatile acylcyclopropanes (**3b**,**d**,**f**,**g**, R′ = CH_3) was monitored by nmr in a manner similar to that described for the 4-pentenophenones. The absorptions used to monitor the rearrangements were the upfield methyl singlet of the acylcyclopropanes and the 4-methyl resonance of the products. Each compound was subjected to rearrangement at 125 ± 0.5° in a constant-temperature bath of refluxing 2-methoxyethanol vapors.

Infrared analyses were obtained with a Beckman IR-5A spectrophotometer; neat samples were analyzed as thin films spread between sodium chloride plates, if liquids, or as KBr pellets or Nujol mulls, if solids. Analytical glpc was performed using Beckman GC-2A and Varian Hy-Fi 600 D instruments; for preparative gas chromatography, a Wilkins A-700 (Autoprep) instrument was used. Routine nmr data were obtained using a Varian A-60 spectrometer with TMS as internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by A. Bernhardt, Mülheim, Germany.

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[36] Results reported in an earlier publication[4] show that no deuterium is incorporated into position 4 upon enolene rearrangement of 4-pentenophenone-*2-d*$_2$.

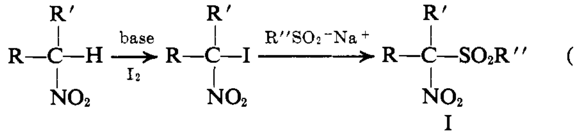
α-Nitro Sulfones

Nathan Kornblum,* Melvin M. Kestner, Steven D. Boyd, and Lawrence C. Cattran

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received October 25, 1972*

Abstract: Pure α-nitro sulfones (I) are readily obtained in 85–95% yields by treating α-iodo nitroparaffins with the salts of sulfinic acids. Inasmuch as the requisite α-iodonitro compounds are rapidly and quantitatively prepared from nitroparaffins, the overall result is a facile synthesis of α-nitro sulfones. When α-bromo nitroparaffins, α-chloro nitroparaffins, and α,α-dinitro compounds react with sulfinate salts, α-nitro sulfones (I) are again produced. Evidence is presented for the view that these reactions are chain processes in which radical anions and free radicals are intermediates.

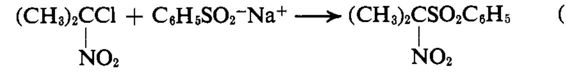
We report a new and general synthesis of α-nitro sulfones (I) in which the carbon bearing the nitro and sulfone groups is devoid of hydrogen atoms.[1] Such α-nitro sulfones are readily obtained by iodinating nitroparaffin salts and then treating the crude α-iodo nitroparaffin with the sodium salt of a sulfinic acid at −20 to 0° for several hours; the overall yields of pure products are 85–95% (Table I).



$$\mathrm{R{-}C(R')(NO_2){-}H} \xrightarrow[\mathrm{I_2}]{\text{base}} \mathrm{R{-}C(R')(NO_2){-}I} \xrightarrow{\mathrm{R''SO_2^-Na^+}} \underset{\mathrm{I}}{\mathrm{R{-}C(R')(NO_2){-}SO_2R''}} \qquad (1)$$

α-Bromo nitroparaffins also react with sulfinic acid salts to give α-nitro sulfones of the type I, but the yields are not routinely as high as when α-iodo nitroparaffins are employed, falling, instead, in the range 44–88%. Why this should be so was not investigated in view of the ready availability of the desired α-nitro sulfones *via* the sequence of eq 1.

The reaction of α-chloro nitroparaffins with sodium sulfinates at 25° is too slow to be useful. Thus, in DMF after 12 days at 25° the reaction of eq 2 is only 82% complete and a *ca.* 50% yield of the sulfone is obtained. In DMSO the reaction is faster but, even here, it is only 76% complete in 4 days.[2]



$$\mathrm{(CH_3)_2C(NO_2)Cl + C_6H_5SO_2^-Na^+ \longrightarrow (CH_3)_2C(NO_2)SO_2C_6H_5} \qquad (2)$$

α,α-Dinitro compounds can also be used to prepare α-nitro sulfones. For example, the displacement of a nitro group from 2,2-dinitropropane by benzenesulfinate ion takes place at room temperature and gives an 81% yield of the pure α-nitro sulfone after 3 days (eq

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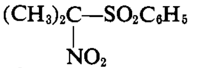
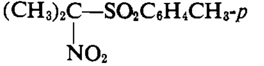
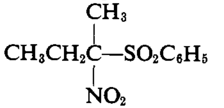
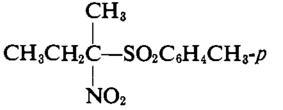
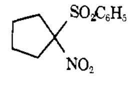
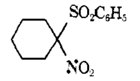
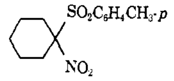
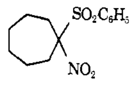
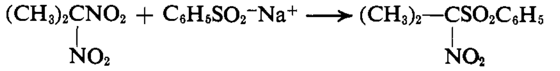
[1] Only one such compound has been prepared previously and the yield was 19%. In that preparation *p*-tolyl isopropyl sulfone was treated with *n*-butyllithium and then with ethyl nitrate: W. E. Truce, T. C. Klingler, J. E. Parr, H. Feuer, and D. K. Wu, *J. Org. Chem.*, 34, 3104 (1969).

[2] N. Kharasch and J. L. Cameron, *J. Amer. Chem. Soc.*, 73, 3864 (1951), found that 1-chloro-1-nitroethane and sodium *p*-toluenesulfinate in refluxing methanol (3 hr) give a 71% yield of α-nitroethyl *p*-tolyl sulfone; this, unlike our reactions, is presumably an SN2 displacement.

Table I. α-Nitro Sulfones Synthesized *via* α-Iodo Nitroparaffins

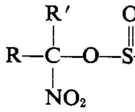
No.	α-Nitro sulfone	% yield
II	 $(CH_3)_2\underset{NO_2}{C}-SO_2C_6H_5$	87
III	 $(CH_3)_2\underset{NO_2}{C}-SO_2C_6H_4CH_3\text{-}p$	90
IV	 $CH_3CH_2\overset{CH_3}{\underset{NO_2}{C}}-SO_2C_6H_5$	93
V	 $CH_3CH_2\overset{CH_3}{\underset{NO_2}{C}}-SO_2C_6H_4CH_3\text{-}p$	85
VI		93
VII		92
VIII		95
IX		85

3).[3] But this is a relatively slow reaction and α,α-dinitro compounds, while easy to prepare,[4] are not quite as readily obtainable as α-iodo nitroparaffins; clearly, the reaction employing α-iodo nitroparaffins is the method of choice for the synthesis of α-nitro sulfones.



$$(CH_3)_2\underset{NO_2}{C}NO_2 + C_6H_5SO_2^-Na^+ \longrightarrow (CH_3)_2\underset{NO_2}{-C}SO_2C_6H_5 \qquad (3)$$

The matter of structure proof must be considered. In principle, the products of these reactions could be sulfinic esters (X) rather than sulfones and, indeed, when one considers some of the reactions of α-nitro sulfones (I),[5] it becomes apparent that this is no idle question. Fortunately, an authentic sample of α-nitro sulfone III[6] was available.[1,7] The mass spectra as well as the nmr and ir spectra, of our product and that of the authentic sulfone, are identical; in addition, the two samples have the same melting point, and the melting point of a mixture is undepressed. Furthermore, a sample of α-nitro sulfone II,[6] prepared by the procedure of Truce, *et al.*,[1] is identical with the product of the reaction of sodium benzenesulfinate with 2-bromo-2-nitropropane. There can be no doubt, then, that our products are, indeed, α-nitro sulfones (I).

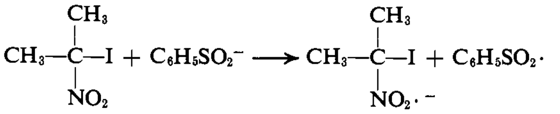


$$R-\overset{R'}{\underset{NO_2}{C}}-O-\overset{O}{\overset{\|}{S}}-R''$$

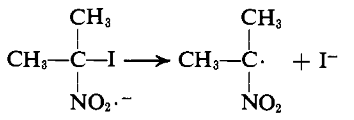
X

The reaction of an α-iodo nitroparaffin with sulfinic acid salts (eq 1) is not an SN2 process. Thus, when 2-iodo-2-nitropropane is treated with sodium *p*-toluenesulfinate in DMF at −20° for 10 min, 76% of the theoretical amount of iodide ion is liberated and a 65% yield[8] of pure α-nitro sulfone III[6] is isolated. In a duplicate experiment conducted in the presence of 10 mol % of di-*tert*-butyl nitroxide[9] only 2% of the theoretical amount of iodide ion is liberated, 75% of the 2-iodo-2-nitropropane is recovered, and none of the α-nitro sulfone III can be detected. When the reaction is repeated with *p*-dinitrobenzene present at the 10 mol % level, 22% of the theoretical amount of iodide ion is produced, 66% of the 2-iodo-2-nitropropane is recovered, and the α-nitro sulfone (III) is formed in 16% yield. Essentially the same results were obtained in an analogous set of experiments in which the reaction of 2-iodo-2-nitropropane with sodium benzenesulfinate was studied: di-*tert*-butyl nitroxide powerfully inhibits formation of the α-nitro sulfone II[6] and *p*-dinitrobenzene, while less effective, is also an inhibitor (*cf.* Experimental Section).

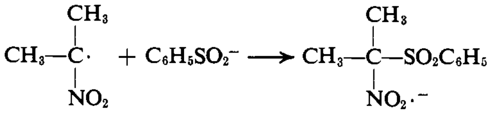
Di-*tert*-butyl nitroxide is known to scavenge free radicals,[9,10] *p*-dinitrobenzene is recognized as a diagnostic for radical anions,[11] and, manifestly, the reaction of 2-iodo-2-nitropropane with sulfinate salts is a chain process. The mechanism of eq 4–7 provides a simple rationale for these facts and is consonant with what is known about related aliphatic nitro systems.[9]



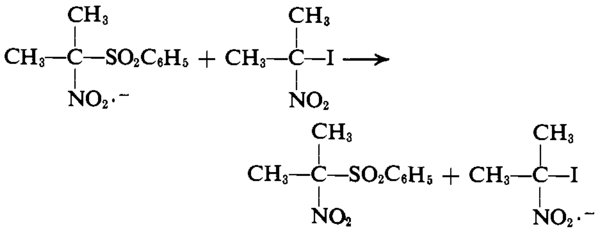
$$CH_3-\overset{CH_3}{\underset{NO_2}{C}}-I + C_6H_5SO_2^- \longrightarrow CH_3-\overset{CH_3}{\underset{NO_2\cdot^-}{C}}-I + C_6H_5SO_2\cdot \qquad (4)$$



$$CH_3-\overset{CH_3}{\underset{NO_2\cdot^-}{C}}-I \longrightarrow CH_3-\overset{CH_3}{\underset{NO_2}{C}}\cdot + I^- \qquad (5)$$



$$CH_3-\overset{CH_3}{\underset{NO_2}{C}}\cdot + C_6H_5SO_2^- \longrightarrow CH_3-\overset{CH_3}{\underset{NO_2\cdot^-}{C}}-SO_2C_6H_5 \qquad (6)$$



$$CH_3-\overset{CH_3}{\underset{NO_2\cdot^-}{C}}-SO_2C_6H_5 + CH_3-\overset{CH_3}{\underset{NO_2}{C}}-I \longrightarrow CH_3-\overset{CH_3}{\underset{NO_2}{C}}-SO_2C_6H_5 + CH_3-\overset{CH_3}{\underset{NO_2\cdot^-}{C}}-I \qquad (7)$$

The reactions of sulfinate salts with α-bromo nitroparaffins, and with α,α-dinitro compounds, also exhibit

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[3] The displacement of a nitro group from α,α-dinitro compounds by nitroparaffin anions has recently been shown to be an especially facile process: N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 5783 (1970).

[4] R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3535 (1961); also see N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *ibid.*, **93**, 4316 (1971), footnote 6.

[5] These reactions will be described in a paper with S. D. Boyd and N. Ono.

[6] See Table I.

[7] We thank Professor W. E. Truce for this.

[8] The yield based on the amount of 2-iodo-2-nitropropane actually consumed is 86%.

[9] N. Kornblum and S. D. Boyd, *J. Amer. Chem. Soc.*, **92**, 5784 (1970).

[10] A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 642 (1964); A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London, 1968, p 224; E. G. Rozantsev and V. D. Sholle, *Synthesis*, 406 (1971).

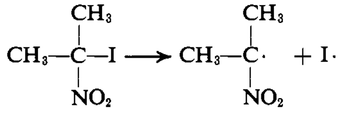
[11] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965); N. Kornblum, *Proc. Int. Congr. Pure Appl. Chem., 23rd*, **4**, 81 (1971).

the characteristics of radical anion–free radical chain processes. Thus, the reaction of 2-bromo-2-nitropropane with sodium *p*-toluenesulfinate in DMF at −20° is 95% complete in 10 min; if di-*tert*-butyl nitroxide is present at the 10 mol % level only 7% of the 2-bromo-2-nitropropane is consumed in 10 min; and in the presence of 10 mol % of *p*-dinitrobenzene the reaction proceeds only 10% to completion in 10 min.

The reaction of 2-iodo-2-nitropropane with sodium *p*-toluenesulfinate in DMF at −20° exhibits a small, but real, light effect. For example, after 4 min in the dark a 33% yield of the α-nitro sulfone III[6] is isolated; but when the system is exposed to the light of two 20-W ordinary fluorescent lamps a 66% yield of the α-nitro sulfone is obtained. An even smaller effect is observed in the reaction of 2-bromo-2-nitropropane with sodium *p*-toluenesulfinate in DMF at −20°; here, after 4 min, the dark reaction gives a 47% yield of the α-nitro sulfone III while the light reaction produces a 62% yield of III in this time.[12]

The reaction of 2,2-dinitropropane with sodium benzenesulfinate (eq 3) is strongly promoted by light. Thus, after 24 hr in the dark less than a 2% yield of the α-nitro sulfone II[6] is produced and 74% of the 2,2-dinitropropane is recovered. However, when the system is exposed to two 20-W fluorescent lights the pure α-nitro sulfone II[6] is obtained in 53% yield and only 31% of the 2,2-dinitropropane is recovered. Significantly, di-*tert*-butyl nitroxide at the 10 mol % level virtually stops the reaction; after 24 hr under the fluorescent lamps the yield of α-nitro sulfone II is less than 1%, and 80% of the 2,2-dinitropropane is recovered. Thus, α-bromonitro compounds and α,α-dinitro compounds also react with sulfinate salts by a chain mechanism and, presumably, their reactions follow a pattern fully analogous to that of the α-iodonitro compounds (eq 4–7).

With the α-iodo nitroparaffiins (and, perhaps, with α-bromo nitroparaffins) an additional possibility merits serious consideration. It well may be that here thermal and/or photochemical dissociation (eq 8) is the important initiating process.



$$\mathrm{CH_3{-}\underset{NO_2}{\overset{CH_3}{C}}{-}I} \longrightarrow \mathrm{CH_3{-}\underset{NO_2}{\overset{CH_3}{C}}\cdot} + \mathrm{I\cdot} \tag{8}$$

This affords, directly, the radical component of the chain propagating sequence.

Experimental Section

2-Nitropropane, 2-nitrobutane, and 2,2-dinitropropane were obtained from Commercial Solvents Corp., nitrocyclohexane was a Du Pont product, and DMSO was provided by the Crown Zellerbach Corp.[13] Nitrocyclopentane and nitrocycloheptane were synthesized from the bromo compounds by treatment with sodium nitrite in DMSO.[14,15] 2-Chloro-2-nitropropane was prepared by chlorinating an aqueous solution of the sodium salt of 2-nitropropane;[16] colorless liquid, bp 49° (30 mm); $n^{20}\mathrm{D}$ 1.4260; nmr ($CDCl_3$) one peak at δ 2.14.

Sodium benzenesulfinate (Matheson Coleman and Bell) and sodium *p*-toluenesulfinate (Aldrich) were recrystallized from 95% ethanol; titration with perchloric acid in glacial acetic acid showed that the salts were essentially anhydrous (neut equiv 165 and 181, respectively).

Use of α-Iodo Nitroparaffins. (A) Preparation of α-Nitro-*sec*-butyl Phenyl Sulfone (IV).[6] A solution of *ca.* 0.58 g (25 mmol) of sodium in 25 ml of methanol is prepared and then 2.57 g (25 mmol) of 2-nitrobutane is added. The resulting solution is concentrated under reduced pressure at *ca.* 25–30°, and the resulting white solid is dissolved in 75 ml of water. To the stirred, ice-cold aqueous solution of the sodium salt of 2-nitrobutane a solution of 5.08 g (20 mmol) of iodine in 50 ml of ethyl ether is rapidly added (minimal exposure to light). The resulting colorless to pale yellow ether phase is isolated, the aqueous layer is extracted twice with 50-ml portions of ethyl ether, and the combined ether solutions are washed with two 100-ml portions of water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to a yellow liquid.

Sodium benzenesulfinate (6.56 g, 40 mmol) is placed in a flask which is then cooled in a Dry Ice–carbon tetrachloride bath and swept with nitrogen for 15 min after which 80 ml of dimethylformamide (DMF) is added, and the mixture is allowed to cool to −20° before stirring is started. Without waiting, the crude 2-iodo-2-nitrobutane (precooled to *ca.* 0°) is added rapidly to the DMF suspension, 10 ml of DMF being employed to complete the transfer. The reaction is allowed to proceed under nitrogen[17] in the dark at −20 to −15° for 4 hr, and the resulting yellow mixture is then poured into water, extracted with benzene, washed with water, and dried. The light brown liquid (4.75 g) which remains after removing the benzene is dissolved in a 1:1 mixture of benzene–hexane and placed on an acid-washed alumina column. The column is eluted first with 2:1 benzene–hexane and, then, with pure benzene. In this way 4.54 g (93% yield) of the pure sulfone, $n^{20}\mathrm{D}$ 1.5414, is obtained. For analysis a small portion was distilled in a micro-still.

Anal. Calcd for $C_{10}H_{13}NSO_4$: C, 49.38; H, 5.35. Found: C, 49.67; H, 5.34.

(B) Preparation of α-Nitrocyclohexyl *p*-Tolyl Sulfone (VIII).[6] This and the following preparation demonstrate that it is not necessary to conduct the reaction of an α-iodo nitroparaffin with a sulfinate salt at −20 to −15°. When 7.12 g (40 mmol) of sodium *p*-toluenesulfinate is mixed with 70 ml of DMF at −23° (under nitrogen, in the dark) a gel forms. Even after the addition of 20 mmol of crude α-iodonitrocyclohexane (prepared as in A above) and another 10 ml of DMF, the gel cannot be stirred. However, on warming to 5° stirring occurs readily and after 4 hr at 5–7° titration for iodide ion shows that the reaction is complete. The yellow mixture is poured into 350 ml of water; the resulting white solid is isolated by filtration, dissolved in benzene, washed with water, and dried (anhydrous magnesium sulfate). Removal of the benzene gives 5.57 g of a pale yellow solid, mp 135–136.5°. Recrystallization from 95% ethanol gives 5.30 g of white crystals (95% yield), mp 135.5–136.5°.

Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.10; H, 6.05; N, 4.94; S, 11.32; mol wt, 283. Found: C, 55.11; H, 6.04; N, 4.94; S, 11.12; mol wt, 279.

(C) Preparation of α-Nitro-*sec*-butyl *p*-Tolyl Sulfone (V).[6] A reaction mixture consisting of 20 mmol of crude 2-iodo-2-nitrobutane (see A above), 80 ml of DMF, and 7.12 g (40 mmol) of sodium *p*-

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(12) It is noteworthy that 2-bromo-2-nitropropane reacts as fast as, or faster, than 2-iodo-2-nitropropane.

(13) We take pleasure in acknowledging our indebtedness to the Commercial Solvents Corp., the Crown Zellerbach Corp., and the Du Pont Co. for generous gifts of these compounds.

(14) N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957).

(15) We thank Mr. L. Cheng and Mr. T. Cole for the preparation of these nitro compounds.

(16) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 102 (1940).

(17) Although this, and all other preparations of α-nitro sulfones from α-iodonitro compounds were conducted under nitrogen (and in the dark), it is by no means established that rigorous exclusion of air (and light) is essential. Thus, a pair of experiments employing 2-iodo-2-nitropropane and sodium *p*-toluenesulfinate (in DMF at 0° in the dark) were carried out which differed only in that one was conducted under nitrogen whereas air was not excluded from the other; the flask was simply stoppered. After 1 hr, titration for iodide ion showed that the reaction under nitrogen was 96% complete while that under air had proceeded 90%. Both were complete after 1.5 hr and on work-up a 90% yield of pure α-nitro sulfone III[6] was isolated from the reaction under nitrogen and an 87% yield of pure III was obtained from the reaction which had been exposed to air; in each case the mp was 109–110°. As regards the effect of light, two reactions employing 2-iodo-2-nitropropane and sodium *p*-toluenesulfinate in DMF at −20° (under nitrogen) were carried out for 1 hr. One was conducted in total darkness and the other was exposed to ordinary room light. The dark reaction liberated 87% of the theoretical amount of iodide ion and on work-up an 82% yield of the pure α-nitro sulfone III was isolated. The "light" reaction gave 95% of the theoretical amount of iodide ion and an 87% yield of pure III. Clearly light is not deleterious; if anything, it speeds up the reaction.

toluenesulfinate could not be stirred at −20° or at 2°. It was, therefore, allowed to warm from 2 to 22° in the course of 1 hr after which iodide ion titration showed the reaction to be complete. The reaction was worked up as in B; recrystallization from 95% ethanol gave 4.40 g (85% yield) of white crystals, mp 104–104.5°.

Anal. Calcd for $C_{11}H_{15}NO_4S$: C, 51.36; H, 5.84; N, 5.45; S, 12.44; mol wt, 257. Found: C, 51.34; H, 6.14; N, 5.43; S, 12.48; mol wt, 261.

(D) **Preparation of α-Nitrocyclopentyl Phenyl Sulfone** (VI).[6] The reaction is conducted as in A at −20 to −15° using 20 mmol of crude α-iodonitrocyclopentane and 6.56 g (40 mmol) of sodium benzenesulfinate in 80 ml of DMF. After 2 hr the usual work-up gives 4.89 g of pale yellow solid which, when recrystallized from 75 ml of 95% ethanol, gives 4.73 g (93% yield) of white crystals; mp 99–100°. The analytical sample was sublimed, mp 99–100°.

Anal. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49; S, 12.56; mol wt, 255. Found: C, 51.86; H, 5.35; N, 5.30; S, 12.70; mol wt, 251.

(E) **Preparation of α-Nitrocyclohexyl Phenyl Sulfone** (VII).[6] This is obtained by carrying out the reaction of the crude α-iodonitrocyclohexane with sodium benzenesulfinate in DMF at −20 to −15° for 8 hr and then allowing the system to warm to room temperature. The crude product is white (mp 102.5–104°) and after one recrystallization from 95% ethanol melts at 103–104°; yield 5.0 g (92%).

Anal. Calcd for $C_{12}H_{15}NO_4S$: C, 53.53; H, 5.58; N, 5.20. Found: C, 53.71; H, 5.48; N, 5.18.

(F) **Preparation of α-Nitrocycloheptyl Phenyl Sulfone** (IX).[6] The reaction is conducted on the same scale and precisely as in D. After two recrystallizations from 95% ethanol there is obtained 5.0 g (85% yield) of white crystals, mp 101–102°. For analysis the product was sublimed.

Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.10; H, 6.05; N, 4.94; S, 11.32; mol wt, 283. Found: C, 55.26; H, 6.22; N, 5.23; S, 11.25; mol wt, 285.

The Use of α-Bromo Nitroparaffins. (A) **Preparation of 2-Bromo-2-nitropropane.** A solution of 42 g (1.05 mol) of sodium hydroxide in 150 ml of water is prepared under nitrogen, cooled to *ca.* 10°, and then 89 g (1.00 mol) of 2-nitropropane is added rapidly. The reaction mixture is stirred vigorously while maintaining the temperature at *ca.* 25° by occasional cooling. After about 2 hr the system becomes homogeneous; it is then cooled to *ca.* 15° and 159.8 g (1.00 mol) of bromine is added dropwise until the bromine color persists (*ca.* 1.5 hr). The reaction mixture is worked up by adding 50 ml of a saturated aqueous $NaHSO_3$ solution to destroy the excess bromine and then extracting several times with ethyl ether. The combined ether extracts are washed with 5% aqueous sodium hydroxide and with water and then dried over anhydrous magnesium sulfate. On removing the solvent and distilling under reduced pressure there was obtained 142 g (85% yield) of 2-bromo-2-nitropropane; bp 61–62° (29 mm); $n^{20}D$ 1.4639; nmr (CCl_4) δ 2.31 (s); ir (neat) 6.45 (s), 7.50 (s), 8.98 μ (s).

(B) **The Preparation of α-Nitroisopropyl *p*-Tolyl Sulfone** (III).[6] Using a hypodermic syringe, 90 ml of cold (−20°) DMF is added to a flask containing 5.34 g (30 mmol) of sodium *p*-toluenesulfinate under nitrogen[18] and a magnetic stirrer. The flask is immediately placed under the light apparatus[19] and immersed in a carbon tetrachloride–Dry Ice bath; then 3.36 g (20 mmol) of 2-bromo-2-nitropropane, dissolved in 10 ml of cold DMF, is added rapidly. After being vigorously stirred at −20°[20] for 2 hr, the reaction mixture is poured into 200 ml of benzene and 200 ml of ice–water. The aqueous DMF phase is extracted two more times with 100-ml portions of benzene after which the combined benzene extracts are washed with 100 ml of distilled water and then with three 200-ml portions of distilled water. The 100-ml portion is combined with the aqueous DMF phase and diluted with distilled water to 500 ml. Titration of 1-ml aliquots of this solution for bromide ion shows that the reaction is complete.

On removing the benzene from the organic extracts under reduced pressure, a white solid (4.67 g, mp 104–107.5°) is obtained which on one recrystallization from 95% ethanol gives 4.26 g (88% yield) of the pure α-nitro sulfone III:[6] mp and mmp (with an authentic sample)[1,7] 109–110°; for both samples nmr ($CDCl_3$) δ 1.95 (s, 6), 2.47 (s, 3), 7.59 (m, 4); ir (benzene) 6.44, 7.50, 8.72, 9.28 μ. The mass spectra (75 eV) of both samples show the molecular ion at *m/e* 243. The rest of the spectrum, in each case, consists of only three major peaks; the base peak at *m/e* 91, a peak at *m/e* 155, and a peak at *m/e* 139.

In addition, the following α-nitro sulfones were prepared from α-bromo nitroparaffins: II in 85% yield; IV in 44% yield; V in 79% yield; VII in 45% yield; VIII in 71% yield.

Reaction of 2,2-Dinitropropane with Sodium Benzenesulfinate. Using a hypodermic syringe, 180 ml of DMSO is added to a flask containing 9.84 g (60 mmol) of sodium benzenesulfinate under nitrogen. The flask is immediately placed in the light apparatus[19,21] at 25–30° and the reaction mixture is stirred until all the salt has dissolved. To the resulting solution is added 5.36 g (40 mmol) of 2,2-dinitropropane in 20 ml of DMSO. After 75 hr, the reaction mixture is poured into ice–water and extracted with benzene. The benzene extracts are washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The resulting white solid (7.87 g, mp 104–110°) after one recrystallization from 95% ethanol gives 7.44 g (81% yield) of the pure α-nitro sulfone II:[6] mp 116–117°; nmr ($CDCl_3$) δ 1.95 (s, 6), 7.71 (m, 5).

Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.14; H, 4.84; N, 6.11; S, 13.99. Found: C, 47.19; H, 4.91; N, 6.03; S, 14.00.

This product is identical (nmr and ir) with the products obtained on treating 2-bromo-2-nitropropane (and 2-iodo-2-nitropropane) with sodium benzenesulfinate; mp and mmp 116–117°.

That this product is indeed the sulfone (II), rather than the sulfinate ester, was established by direct comparison of a sample of sulfone II prepared by the alkaline nitration of isopropyl phenyl sulfone employing the procedure of Truce, Klingler, Paar, Feuer, and Wu[1] with the sample of II produced by the reaction of 2-bromo-2-nitropropane with sodium benzenesulfinate. Both products melt at 116–117° and the melting point of a mixture is not depressed. The two samples have identical nmr and ir spectra.

Reaction of 2-Chloro-2-nitropropane with Sodium Benzenesulfinate. Under nitrogen, in the light,[19] a stirred mixture of 0.687 g (5.60 mmol) of 2-chloro-2-nitropropane and 1.64 g (10 mmol) of sodium benzenesulfinate in 25 ml of DMF was allowed to react at room temperature for 12 days. At the end of this time the usual work-up showed that 82% of the theoretical amount of chloride ion had been produced. The organic product is a light yellow solid (0.755 g) whose nmr spectrum is, essentially, that of the desired sulfone II.

When 1.23 g (10 mmol) of 2-chloro-2-nitropropane is treated with 2.68 g (15 mmol) of sodium *p*-toluenesulfinate in 50 ml of DMSO, using the light apparatus,[19] only 76% of the theoretical amount of chloride ion is liberated after 4 days at room temperature. Work-up at this point gives 1.35 g (5.5 mmol, 55% yield) of crude sulfone III,[6] mp 103–108°.

Mechanistic Studies. Preparation of 2-Iodo-2-nitropropane. To a stirred, ice cold solution of 6.00 g (63 mmol) of the lithium salt of 2-nitropropane[5] in 100 ml of water is added rapidly a solution of 15.24 g (60 mmol) of iodine in 200 ml of ethyl ether (minimal exposure to light). The resulting pale yellow aqueous phase is extracted twice with 100-ml portions of ethyl ether and the combined ether extracts are dried over anhydrous magnesium sulfate. The ether solution is diluted to 450 ml with ethyl ether, divided into three equal portions, and then each of these is concentrated, under reduced pressure, to a yellow liquid: nmr δ 2.43 (s); ir (neat) 6.45 (s), 7.50 (s), 9.00 μ (s).

Reaction of 2-Iodo-2-nitropropane with Sodium *p*-Toluenesulfinate. (1) Control. Using a hypodermic syringe, 180 ml of cold (−20°) DMF is added to a flask containing 5.34 g (30 mmol) of sodium *p*-toluenesulfinate (under nitrogen) and a magnetic stirrer. The flask is maintained at −20° (carbon tetrachloride–Dry Ice bath) and is minimally exposed to light. To the DMF suspension is added 20 mmol of 2-iodo-2-nitropropane in 10 ml of cold DMF; an additional 10 ml of cold DMF is employed to complete the transfer. (Stirring is initiated only a few seconds before the 2-

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(18) Although this reaction is run under nitrogen, a parallel experiment conducted under dry air gave essentially the same result. This suggests that the reactions of α-bromonitro compounds with sulfinate salts in DMF may well be capable of being carried out routinely without a nitrogen atmosphere.

(19) The "light apparatus" consists of two 20-W ordinary fluorescent lights. Although this preparation was conducted in the light, experiments described in the mechanistic section (*vide infra*) show that light has little effect on the reaction of 2-bromo-2-nitropropane with sulfinate ions.

(20) Although this preparation is conducted at −20°, in some instances the reaction is run at −20° for 1 hr, at 0° for 1 hr and then at room temperature for 1–2 hr (until *ca.* 100% bromide ion is liberated).

(21) This reaction has a large light effect (*vide infra*).

iodo-2-nitropropane is added because prolonged stirring prior to this causes the reaction mixture to gel.) After being vigorously stirred for 10 min, the reaction mixture is poured into 200 ml of ethyl ether and 200 ml of distilled water. The aqueous DMF phase is extracted two more times with 100-ml portions of ethyl ether and the combined ether extracts are washed with three 200-ml portions of distilled water; the first 200-ml portion is combined with the aqueous DMF phase and the resulting solution is diluted with distilled water to 1 l. Titration of three 1-ml aliquots of this solution for iodide ion shows the reaction is 76% complete.

The brown solid (4.095 g, mp 103–107°) which remains after removing the ethyl ether is washed with 30 ml of cold (0°) petroleum ether (bp 35–37°). The petroleum ether is removed under reduced pressure to yield 0.832 g of a light red liquid which by vpc is 95% pure 2-iodo-2-nitropropane (18% recovery), identified by vpc, nmr, and ir.

The 3.21 g (mp 109–110°) of light yellow solid which did not dissolve in petroleum ether was recrystallized from 30 ml of 95% ethanol. This gives 3.126 g (65% yield) of pure α-nitro sulfone III,[6] identified by nmr, mp and mmp 109–110°.

(2) **Influence of 10 mol % Di-*tert*-butyl Nitroxide.** This is a duplicate of the control except that just prior to adding the 2-iodo-2-nitropropane, 0.288 g (2 mmol) of di-*tert*-butyl nitroxide in 5 ml of cold DMF is added to the reaction flask (the total amount of DMF used is 200 ml, just as in the control). After 10 min, the reaction mixture is worked up yielding 3.756 g of a red liquid. This red liquid, dissolved in 50 ml of methylene chloride, is treated with hydrogen chloride gas for a few seconds;[22] the solution, which immediately turns blue, is extracted with two 50-ml portions of water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. This gives 3.394 g of 2-iodo-2-nitropropane which by vpc is 95% pure (75% recovery); identified by vpc, nmr, and ir.

None of the α-nitro sulfone III[6] could be detected by vpc or nmr. Titration for iodide ion showed that only 2% of the theoretical amount of iodide ion had been liberated.

(3) **Influence of 10 mol % of *p*-Dinitrobenzene.** This is a duplicate of the control except that just prior to adding the 2-iodo-2-nitropropane, 0.336 g (2 mmol) of *p*-dinitrobenzene in 10 ml of cold DMF is added (total amount of DMF used is 200 ml). After 10 min, the reaction mixture is worked up, yielding 3.984 g (mp 90–124°) of a light yellow solid which is washed with 30 ml of ice-cold petroleum ether (bp 35–37°). The petroleum ether is removed under reduced pressure to yield 2.886 g of a light orange liquid which by vpc is 98% pure 2-iodo-2-nitropropane (66% recovery), identified by vpc, nmr, and ir.

The 1.053 g (mp 99–134°) of light yellow solid which does not dissolve in petroleum ether is a mixture of the α-nitro sulfone III and *p*-dinitrobenzene. Vpc and nmr analysis of the mixture showed that it contains *ca.* 0.76 g of α-nitro sulfone III and, thus, the yield of III is 15–16%. By iodide ion titration, the reaction is 22% complete.

Reaction of 2-Iodo-2-nitropropane with Sodium Benzenesulfinate. (1) Control. The lithium salt of 2-nitropropane[5] (1.0 g, 10.5 mmol) is dissolved in 50 ml of water and, while stirring, the ice-cold solution is treated with 2.53 g (10 mmol) of iodine dissolved in 50 ml of ethyl ether (minimal exposure to light). The ether layer is removed and the aqueous phase is extracted with two 50-ml portions of ether. The combined ether solutions are washed with two 100-ml portions of water, quickly dried over anhydrous magnesium sulfate, and concentrated *in vacuo*, giving clear, essentially colorless, 2-iodo-2-nitropropane.

Sodium benzenesulfinate (1.97 g, 12 mmol) is placed in a flask which is fitted with a rubber stopper and a thermometer; the flask is swept with nitrogen and then is placed in a Dry Ice–carbon tetrachloride bath. DMF (50 ml) which has had nitrogen bubbled through it to purge it of air is added and the internal temperature is maintained at −20°. At this point stirring is initiated and the 2-iodo-2-nitropropane is added using 10 ml of DMF to complete the transfer. The flask is completely wrapped in aluminum foil to protect the system from light and a positive nitrogen pressure is maintained. After 1 hr the resulting light yellow solution is poured into 400 ml of ice-cold distilled water, giving a white solid which is isolated by filtration. Titration of the aqueous solution for iodide shows 99% of the theoretical iodide ion is present. The moist white solid is recrystallized from 50 ml of 95% ethanol giving 1.92 g (8.4 mmol, 84% yield) of vpc-pure, white, α-nitroisopropyl phenyl sulfone, mp 114–116°.

(2) **Influence of 5 mol % Di-*tert*-butyl Nitroxide.** This is a duplicate of the control except that di-*tert*-butyl nitroxide (0.072 g, 0.5 mmol) is added immediately before the 2-iodo-2-nitropropane. When, after 1 hr, the reaction mixture is poured into 400 ml of ice water no precipitate forms. The aqueous DMF solution is ether extracted and then titrated for iodide ion; triplicate determinations showed that only 9% of the theoretical amount of iodide ion had been produced. The ether extracts were washed with water, dried, and concentrated *in vacuo*; this gave 1.91 g of red liquid whose nmr spectrum shows that it is *ca.* 90% 2-iodo-2-nitropropane (*ca.* 1.7 g, *ca.* 80% recovery) the major contaminant being ethyl ether; the singlet at δ 1.96 characteristic of α-nitroisopropyl phenyl sulfone (II) is absent.

(3) **Influence of 5 mol % *p*-Dinitrobenzene.** This is a duplicate of the control except that *p*-dinitrobenzene (0.084 g, 0.5 mmol) was added to the reaction flask just prior to the 2-iodo-2-nitropropane. After 1 hr the reaction mixture was poured into ice–water and ether extracted as in (2). Titration of the aqueous DMF phase showed that 33% of the theoretical amount of iodide ion had been liberated. From the ether extracts 1.49 g of a red solid was obtained; it had an nmr spectrum (in deuteriochloroform) which showed it was a 2:1 mixture of 2-iodo-2-nitropropane and α-nitroisopropyl phenyl sulfone. The red solid was dissolved in benzene and rapidly passed through an acid-washed alumina column; this gave 0.612 g (27% yield) of vpc-pure α-nitroisopropyl phenyl sulfone, mp 115–116°. The 2-iodo-2-nitropropane apparently was destroyed during chromatography for none was recovered.

Reaction of 2-Bromo-2-nitropropane with Sodium *p*-Toluenesulfinate. (1) Control. Using a hypodermic syringe, 190 ml of cold (−20°) DMF is added to a flask containing 5.34 g (30 mmol) of sodium *p*-toluenesulfinate (under nitrogen). The flask is immediately placed under the light apparatus,[19] in a −20° bath and, then, 3.36 g (20 mmol) of 2-bromo-2-nitropropane in 10 ml of cold DMF is added to the DMF suspension. (Stirring is initiated only a few seconds before the 2-bromo-2-nitropropane is added because prolonged prior stirring causes gelling.) After being vigorously stirred for 10 min, the reaction mixture is poured into 200 ml of distilled water and 200 ml of ethyl ether. The aqueous DMF phase is extracted two more times with 100-ml portions of ethyl ether. The combined ether extracts are washed with three 200-ml portions of distilled water, the first of which is added to the aqueous DMF phase. The resulting aqueous DMF solution is diluted with distilled water to 1 l.; titration of 1-ml aliquots of this solution for bromide ion shows that the reaction is 95% complete.

The white solid (4.257 g, mp 105–108°) which remains after removing the ethyl ether under reduced pressure is washed with 50 ml of ice-cold petroleum ether (35–37°); removal of the petroleum ether under reduced pressure yields 0.205 g of a colorless liquid which by vpc is 78% pure 2-bromo-2-nitropropane (5% recovery); identified by vpc and by its characteristic nmr δ 2.31 (s).

The 4.003 g (mp 108.5–110°) of white solid which is insoluble in petroleum ether is recrystallized from 30 ml of 95% ethanol. This gives 3.893 g (80% yield) of pure α-nitro sulfone III,[6] identified by nmr, mp and mmp 109–110°.

(2) **Influence of 10 mol % of Di-*tert*-butyl Nitroxide.** This is a duplicate of the control except that just prior to adding the 2-bromo-2-nitropropane, 0.288 g (2 mmol) of di-*tert*-butyl nitroxide in 5 ml of cold DMF is added to the reaction flask. After 10 min, the reaction mixture is worked up, yielding 2.707 g of red liquid containing a small amount of solid; this is washed with 50 ml of ice-cold petroleum ether (bp 35–37°). Removal of the petroleum ether under reduced pressure gives 2.624 g of a red liquid which by vpc is 92% pure 2-bromo-2-nitropropane (72% recovery). This red liquid is dissolved in 75 ml of methylene chloride and treated with dry hydrogen chloride for a few seconds. Extraction of the resulting solution with two 50-ml portions of water followed by drying and removing the solvent under reduced pressure gives 2.092 g of a yellow liquid which, by vpc, is 99% pure 2-bromo-2-nitropropane (62% recovery); it was identified by vpc and nmr. Vpc analysis shows that the 38 mg of white solid which remains after the petroleum ether wash does not contain any α-nitro sulfone III.[6] The white solid decomposes to a dark purple liquid at *ca.* 181°; it was not further examined.

Bromide ion titration of the aqueous DMF solution shows that the reaction was 7% complete.

(3) **Influence of 10 mol % *p*-Dinitrobenzene.** This is a duplicate of the control except that just prior to adding the 2-bromo-2-

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[22] The instability of di-*tert*-butyl nitroxide to hydrogen chloride was reported by A. K. Hoffmann and A. T. Henderson, *J. Amer. Chem. Soc.*, 83, 4671 (1961).

nitropropane, 0.336 g (2 mmol) of *p*-dinitrobenzene in 10 ml of cold DMF is added to the reaction flask. After 10 min, the reaction mixture is worked up as usual, yielding 2.954 g of a yellow liquid containing some solid. The mixture is washed with 50 ml of cold petroleum ether (bp 35–37°) and, then, the petroleum ether is removed under reduced pressure to yield 2.439 g of a yellow liquid which, by vpc, is 99% pure 2-bromo-2-nitropropane (72% recovery); it was identified by vpc and nmr.

The 0.455 g of yellow solid (mp 136–166°) which does not dissolve in the petroleum ether is primarily *p*-dinitrobenzene contaminated by small amounts of the α-nitro sulfone III[6] and an unknown. By vpc and nmr it appears that, at best, the yield of α-nitro sulfone III is from 1 to 2%.

By bromide ion titration of the aqueous DMF solution the reaction was found to be 10% complete.

Influence of Light on the Reactions of 2-Iodo-2-nitropropane and 2-Bromo-2-nitropropane with Sodium *p*-Toluenesulfinate. Using a hypodermic syringe, 585 ml of DMF is added to a flask containing 5.34 g (30 mmol) of sodium *p*-toluenesulfinate (under nitrogen). After stirring for *ca.* 10 min the salt dissolves completely. The flask is then cooled in a carbon tetrachloride–Dry Ice bath and placed under the light apparatus.[19] When the internal temperature reaches −20°, 4.30 g (20 mmol) of 2-iodo-2-nitropropane in 15 ml of DMF is added and the reaction is allowed to proceed for 4 min at −19 to −20°. The resulting solution is poured into a mixture of 400 ml of distilled water and 400 ml of ethyl ether. The aqueous DMF phase is extracted two more times with 200-ml portions of ethyl ether and the combined ether extracts are washed with three 200-ml portions of distilled water, the first of which is added to the aqueous DMF phase. When the ether extracts are dried and concentrated under reduced pressure 3.364 g of a light yellow solid (A) is obtained, mp 104–107°. The aqueous DMF solution is further extracted with two 200-ml portions of benzene and one 200-ml portion of ethyl ether and the combined extracts are then washed with three 200-ml portions of distilled water, the first of which is added to the aqueous DMF. The ether–benzene phase is dried and then concentrated under reduced pressure. The 0.851 g of a brown solid (mp 104–108°) so obtained is added to A and the combined solids are washed with 50 ml of ice-cold petroleum ether (bp 35–37°). This petroleum ether wash on evaporation leaves 0.731 g of a yellow liquid which, by vpc, is 98% pure 2-iodo-2-nitropropane (17% recovery); it was identified by vpc and by nmr. The 3.393 g of yellow solid (mp 108–110°) insoluble in petroleum ether is recrystallized from 30 ml of 95% ethanol; this gives 3.192 g (66% yield) of pure α-nitro sulfone III[6] (identified by nmr, mp and mmp 109–110°). Titration of three aliquots of the aqueous DMF phase for iodide ion shows that the reaction is 73% complete.

The dark reaction is a duplicate of the preceding experiment except that the flask was completely wrapped in several layers of aluminum foil to keep out light. On work-up, 3.447 g of a yellow solid (mp 95–103°) is obtained from the ether extracts and 0.521 g of a brown solid (mp 102–107°) from the benzene extracts. The combined solids are washed with 50 ml of ice-cold petroleum ether; removal of the petroleum ether gives 2.056 g of a yellow liquid which is 98% pure (by vpc) 2-iodo-2-nitropropane (47% recovery; identified by vpc and nmr). The 1.826 g of yellow solid (mp 108–110°) which does not dissolve in the petroleum ether is recrystallized from 15 ml of 95% ethanol; this gives 1.608 g (33% yield) of pure α-nitro sulfone III (identified by nmr, mp and mmp 109–110°). Iodide titration of the aqueous DMF phase shows the reaction is 39% complete.

The light[19] and the dark reactions employing 2-bromo-2-nitropropane and sodium *p*-toluenesulfinate are exact duplicates of the foregoing reactions except that 3.36 g (20 mmol) of 2-bromo-2-nitropropane is used in place of 2-iodo-2-nitropropane. On work-up of the light[19] reaction, 3.079 g of a white solid (mp 105–108°) is obtained from the ether extracts and 0.740 g of a light yellow solid (mp 108–109.5°) from the benzene extracts. The usual treatment of these combined solids with 50 ml of ice-cold petroleum ether gives 0.619 g of a light green liquid which is 97% pure (by vpc) 2-bromo-2-nitropropane (18% recovery; identified by vpc and nmr). The 3.101 g of white solid (mp 108.5–110°) insoluble in petroleum ether is recrystallized from 95% ethanol giving 2.979 g (62% yield) of pure α-nitro sulfone III (identified by nmr, mp and mmp, 109–110°). Bromide titration of the aqueous DMF phase shows the reaction is 70% complete.

The dark reaction gives 2.911 g of a white solid (mp 103–107°) from the ether extracts and 0.628 g of a light yellow solid (mp 106–108°) from the benzene extracts. When these solids are combined and treated with 50 ml of cold petroleum ether there is obtained 1.002 g of a light green liquid which (by vpc) is 98% pure 2-bromo-2-nitropropane (29% recovery; identified by vpc and nmr). The 2.444 g of petroleum ether insoluble white solid (mp 108–110°) is recrystallized from 95% ethanol; this gives 2.296 g (47% yield) of pure α-nitro sulfone III (identified by nmr, mp and mmp 109–110°). Bromide titration of the aqueous DMF phase shows the reaction is 56% complete.

Reaction of 2,2-Dinitropropane with Sodium Benzenesulfinate. (1) **Control.** By means of a hypodermic syringe, 90 ml of DMSO is added to a flask containing 6.56 g (40 mmol) of sodium benzenesulfinate (under nitrogen) and a magnetic stirrer. The flask is placed in the light apparatus[19] at 25–30° and, then, to the stirred solution is added, all at once, 2.68 g (20 mmol) of 2,2-dinitropropane in 10 ml of DMSO. After 24 hr, the reaction mixture is poured into 250 ml of ice–water and 150 ml of methylene chloride. The aqueous DMSO phase is extracted two more times with 100-ml portions of methylene chloride, and the combined extracts are washed with three 150-ml portions of water, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. A white solid (3.51 g, mp 90–102°) is obtained. Upon sublimation at room temperature and 0.15-mm pressure, 0.833 g (6.21 mmol, 31%) of unreacted 2,2-dinitropropane (indentified by vpc and nmr) is collected on the cold finger. The residual white solid (2.53 g, mp 110–113°), when recrystallized once from 95% ethanol, gives 2.42 g (10.6 mmol, 53% yield) of pure α-nitro sulfone II,[6] identified by nmr and, also, by melting point and mixture melting point with an analytically pure sample, 115–116°.

(2) **Influence of Light.** This is a duplicate of the control experiment except that the reaction flask is wrapped in aluminum foil to exclude light. On work-up after 24 hr, a light yellow-green solid is obtained (2.17 g) which, when sublimed, gives 1.97 g (14.7 mmol, 74% recovery) of unreacted 2,2-dinitropropane (identified by vpc and nmr). The 78 mg (0.34 mmol, 2% yield) of solid which does not sublime has the vpc retention time and the nmr spectrum of α-nitro sulfone II[6] and its melting point (104–109°) supports the view that it is impure II.

(3) **Influence of 10 mol % Di-*tert*-butyl Nitroxide.** This is a duplicate of the control reaction except that 228 mg (2 mmol) of di-*tert*-butyl nitroxide in 5 ml of DMSO is added immediately prior to adding the 2,2-dinitropropane. After 24 hr, work-up gives 2.54 g of an orange liquid. This liquid is placed in a sublimator which is evacuated to 0.15 mm at room temperature. From the cold finger 2.43 g of an orange mixture of 2,2-dinitropropane and di-*tert*-butyl nitroxide is obtained. The 23 mg (0.10 mmol, 1% yield) of nonvolatile solid has the vpc retention time of α-nitro sulfone II.

The 2.43 g mixture of 2,2-dinitropropane and di-*tert*-butyl nitroxide dissolved in 50 ml of CH_2Cl_2 is treated with anhydrous hydrogen chloride[22] for a few seconds. The orange solution immediately turns blue. After washing with water, drying, and removing the solvent there is obtained 1.96 g (14.6 mmol, 73% recovery) of pure 2,2-dinitropropane (identified by nmr and vpc).

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