

solution of 180 mg (1 mmol) of **23** and 0.2 ml of TMEDA in 1 ml of ether was treated at 5° with 1.2 ml (2.1 mmol) of 1.75 M BuLi-hexane. The mixture was left for 16 hr at room temperature then hydrolyzed and worked up as usual to give 165 mg of crude product. Gc analysis indicated the presence of ca. 45% of **23**, 25% of **28**, and 30% of **27**. Separation was achieved by gc collection. Starting material **23** and β -cyclogeraniol (**28**) were identified by comparison of their spectra with authentic ones; ketone **27**: ir 1720 cm⁻¹; nmr (90 MHz, CDCl₃) δ 3.17 (br s, 2), 2.16 (s, 3), 2.02 (br t, 2), 1.53 (br s, 3), 1.35–1.80 (m, 4), 0.93 (s, 6); mass spectrum *m/e* (rel intensity) 180 (26), 95 (73), 81 (59), 43 (100).

(*Z*)- and (*E*)-Propenyl Benzyl Sulfides (**30** and **32**). A solution of 5.0 g (30 mmol) of allyl benzyl sulfide and 1.08 g (9.6 mmol) of potassium *tert*-butoxide in 11 ml of DMSO was left for 11 days at 39°. The mixture was poured into water and extracted with ether. The organic layer was washed with water, dried (MgSO₄), and concentrated. The residue was applied to a dry column containing 50 ml of alumina (Woelm, neutral). The column was washed with 400 ml of pentane. The eluate was concentrated and distilled to give 4.39 g (88%) of a mixture of **30** and **32**: bp 111–114° (12 mm); nmr δ 7.18 (s, 5), 5.0–5.9 (m, 2), 3.70 (s, 2), 1.64 (d with fur-

ther fine structure, 3); ir 1600, 700 cm⁻¹; mass spectrum *m/e* (rel intensity) 164 (20), 91 (100).

Reaction of (*Z*)- and (*E*)-Propenyl Benzyl Sulfides (**30** and **32**) with BuLi. A solution of 253 mg (1.54 mmol) of a mixture of **30** and **32** in 3 ml of THF was treated at -75° with 1.1 ml (1.7 mmol) of 1.75 M BuLi-hexane. After 15 hr of standing at 23°, the mixture was treated at -75° with 1.52 g (10.8 mmol) of methyl iodide then stirred at -75° for 10 min and at 25° for 5 min. Water was added, and the mixture was extracted with ether. The ether layer was washed with water, dried (MgSO₄), and concentrated. Distillation afforded 110 mg (40%) of a mixture of **31** and **33**, bp ca. 115° (12 mm). A sample of **31** + **33** was isolated by gc collection: ir 1600, 700 cm⁻¹; nmr δ 7.20 (s, 5), 5.6–6.0 (m, 2), 3.95 (q, *J* = 7 Hz, 1), 1.4–1.8 (m, 6); mass spectrum *m/e* (rel intensity) 178 (9), 105 (100), 91 (13).

Lithiation as described above, but at -75° for 1.5 hr, followed by methylation as described, gave a mixture of **31** and **33** in 85% yield.

Acknowledgment. The group in Cambridge is indebted to Firmenich, S. A. for generous financial support.

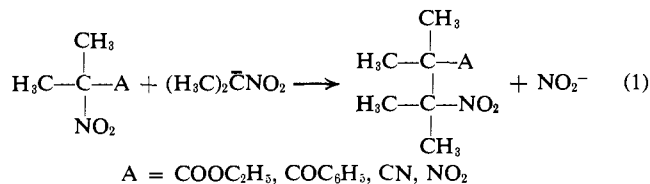
Displacement of the Sulfone Group from α -Nitro Sulfones¹

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Abstract: At room temperature the sulfone group of α -nitro sulfones is readily displaced by a variety of nucleophiles. These new reactions all appear to be radical anion-free radical chain processes.

In 1970 a new reaction, the displacement of a nitro group from α -nitro esters, α -nitro ketones, α -nitro nitriles, and α,α -dinitro compounds by nitroparaffin salts, was described.² These displacements, which are exemplified by the reactions of eq 1, take place at room

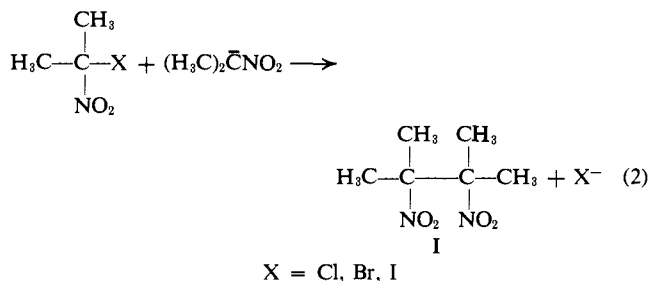


temperature and give excellent yields of pure products.

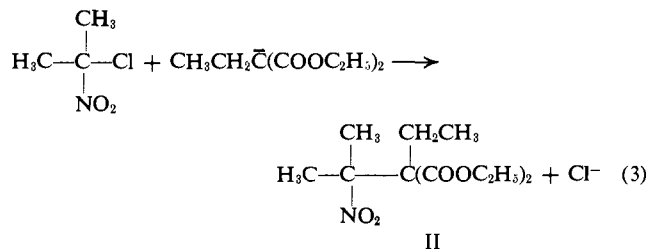
It has been known for some time, however, that the closely related α -halo nitro compounds undergo an alternative type of displacement in which the halogen atom, rather than the nitro group, is displaced. The first report of such a reaction appears to have been made by Seigle and Hass in 1940; they found that 2-chloro-2-nitropropane, 2-bromo-2-nitropropane, and 2-iodo-2-nitropropane react with the sodium salt of 2-nitropropane according to eq 2; *i.e.*, the vicinal

(1) Paper XV in the series "Substitution Reactions which Proceed via Radical Anion Intermediates." For the preceding paper see N. Kornblum, M. M. Kestner, S. D. Boyd, and L. C. Cattran, *J. Amer. Chem. Soc.*, **95**, 3356 (1973). The first paper of this series is by R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **86**, 3904 (1964). Except for paper XIII (N. Kornblum, *Proc. Int. Congr. Pure Appl. Chem.*, **23rd**, **4**, 81 (1971)), all the papers of this group have appeared in the *J. Amer. Chem. Soc.*

(2) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 5783 (1970); N. Kornblum and S. D. Boyd, *ibid.*, **92**, 5784 (1970).



dinitro compound (I) is produced.^{3,4} Another early example is the reaction of 2-chloro-2-nitropropane with the anion of diethyl ethylmalonate which gives a 68% yield of II (eq 3).⁵ In 1971 further instances of re-



actions in which the halogen atom rather than the nitro group is displaced were described.^{4b} These in-

(3) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

(4) This result has been confirmed and extended: (a) N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *J. Amer. Chem. Soc.*, **93**, 4316 (1971); (b) G. A. Russell, R. K. Norris, and E. J. Panek, *ibid.*, **93**, 5839 (1971).

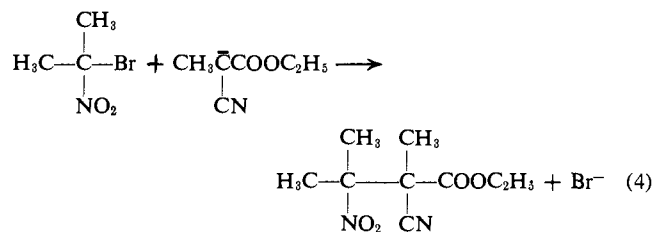
(5) E. E. van Tamelen and G. Van Zyl, *J. Amer. Chem. Soc.*, **71**, 835 (1949).

Table I. The Reaction of α -Nitro Sulfones with Nitroparaffin Salts

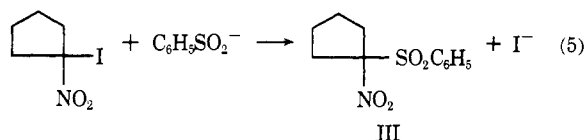
α -Nitro sulfone	Lithium salt of	Product	% yield ^a
$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{SO}_2\text{C}_6\text{H}_5$ (IV)	2-Nitropropane	$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{C}(\text{CH}_3)_2$	83
IV	Nitrocyclohexane		83
$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3-p$	Nitrocyclohexane	VIII	86
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{C}(\text{NO}_2)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3-p$	Nitrocyclohexane		86 ^b
	2-Nitropropane		85
VII	Nitrocyclohexane		60
	2-Nitropropane		85
XVIII	Nitrocyclohexane		82
	Nitrocyclohexane		85

^a Yields refer to pure products unless otherwise stated. ^b Contaminated with *ca.* 2% of 1,1'-dinitro-bicyclohexane.

volve 2-bromo-2-nitropropane and the anions derived from a malononitrile, a cyanoacetic ester, and a β -keto nitrile, *e.g.*, the reaction of eq 4. And, very recently



it has been found that the salts of sulfonic acids readily displace iodide (and bromide) ion from a variety of α -iodo (and α -bromo) nitro compounds. Thus, the reaction of eq 5 is complete in 2 hr at -20° and gives a 93%



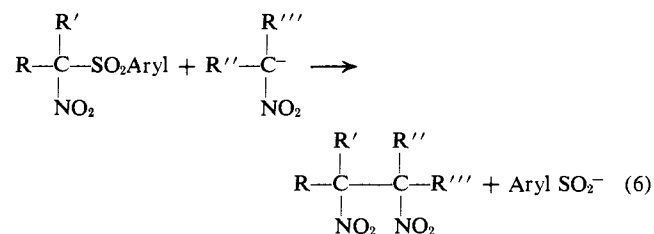
yield of the pure α -nitro sulfone (III).⁶

The present paper is concerned with two questions: do α -nitro sulfones react with nucleophiles and, if they do, which group is displaced, the nitro or the sulfone? It transpires that α -nitro sulfones react readily with a variety of anions and that it is the sulfone group which is displaced.

(6) N. Kornblum, M. M. Kestner, S. D. Boyd, and L. C. Cattran, *J. Amer. Chem. Soc.*, **95**, 3356 (1973).

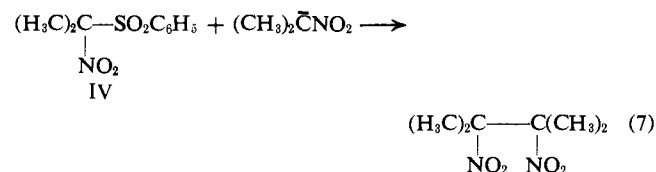
Reactions with Nitroparaffin Salts

At room temperature α -nitro sulfones react rapidly with nitroparaffin salts to give *vicinal* dinitro compounds (eq 6). As can be seen from Table I, the yields are



excellent.

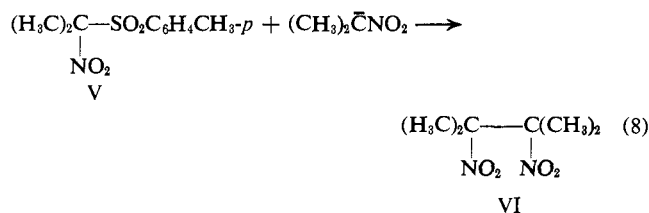
The reactions of nitroparaffin salts with α -nitro sulfones possess the characteristics of radical anion-free radical processes. Thus, the lithium salt of 2-nitropropane reacts completely with the α -nitro sulfone IV in 1 hr and gives an 83% yield of pure 2,3-dimethyl-2,3-dinitrobutane (eq 7), but if *p*-dinitro-



benzene (*p*-DNB) is present at the 5 mol % level the reaction proceeds only 13% to completion in 1 hr and 70% of the α -nitro sulfone is recovered. Five mole per

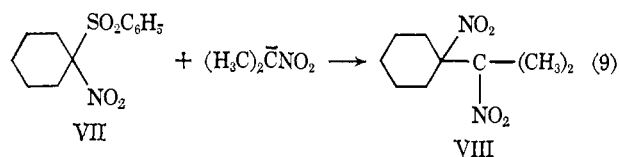
cent of di-*tert*-butyl nitroxide produces an even more dramatic result; after 4 hr less than 1% reaction occurs and 89% of the pure α -nitro sulfone IV is recovered.

A second set of experiments is concerned with the reaction of eq 8, which is complete in 15 min and which



gives an 80% yield of pure 2,3-dimethyl-2,3-dinitrobutane (VI).^{7,7a} One hundred mole per cent of nitrobenzene produces a small, but real, rate retardation; in 15 min the reaction is 88% complete, the yield of product is only 63%, and 8% of the α -nitro sulfone V is recovered. *m*-Dinitrobenzene (*m*-DNB) is a distinctly better inhibitor; at the 10 mol % level only 29% reaction occurs, the yield of the dinitro compound VI falls to 15%, and the recovery of α -nitro sulfone V amounts to 59%. Consonant with what is observed with other radical anion processes,⁸ *p*-DNB is the most effective of the nitro aromatics in slowing down the reaction of eq 8; at the 5 mol % level only 7% reaction takes place in 15 min and 83% of the α -nitro sulfone V is recovered.

In the same way, when α -nitro sulfone VII is treated with the lithium salt of 2-nitropropane at room temperature it reacts completely in 1.5 hr and gives an 85% yield of the *vicinal* dinitro compound VIII (eq 9). But



if 5 mole % of *p*-DNB is present the reaction goes only 11% in 1.5 hr and 87% of the starting α -nitro sulfone is recovered. Once again, di-*tert*-butyl nitroxide proves extraordinarily effective; at the 5 mol % level it virtually stops the reaction; even after 4.5 hr only *ca.* 2% reaction occurs and 91% of the α -nitro sulfone VII is recovered.

p-DNB is recognized as a diagnostic for radical anions,⁸ di-*tert*-butyl nitroxide is a free radical scavenger,^{2,9} and, clearly, the reactions of eq 7, 8, and 9 are chain processes. The following mechanism (eq 10–13) provides a simple basis for understanding the foregoing facts and is consistent with what is known about related aliphatic nitro systems.^{2, 4b, 6, 10}

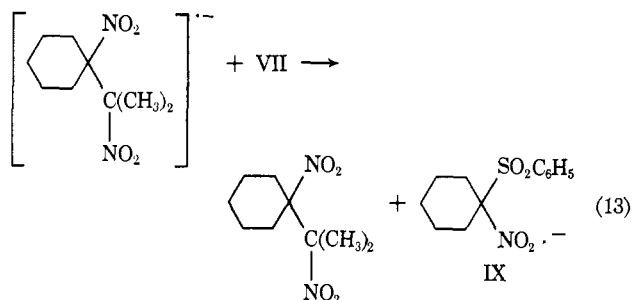
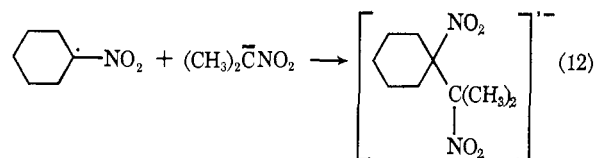
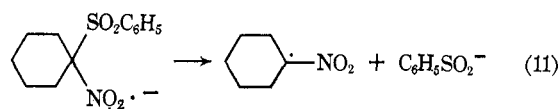
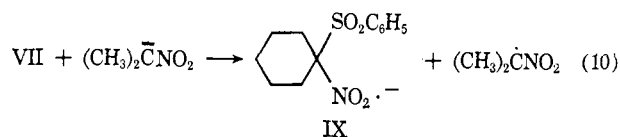
(7) It is quite likely that the somewhat greater speed of this reaction as compared to that of eq 7 derives from the greater care with which oxygen was purged from the system (see Experimental Section).

(7a) NOTE ADDED IN PROOF. J. J. Zeilstra and J. B. F. Engberts have recently decried the reaction of eq 8; *Recl. Trav. Chim. Pays-Bas*, **92**, 954 (1973).

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

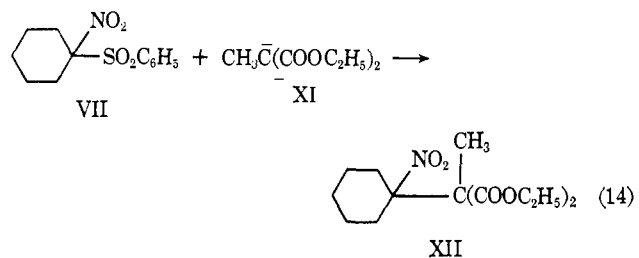
(9) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 642 (1964); A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London 1968, p 224; E. G. Rozantsev and V. D. Sholle, *Synthesis*, 406 (1971).

(10) Very small amounts of symmetrical *vicinal* dinitro compounds are occasionally formed as by-products (*e.g.*, entry 4 in Table I). They

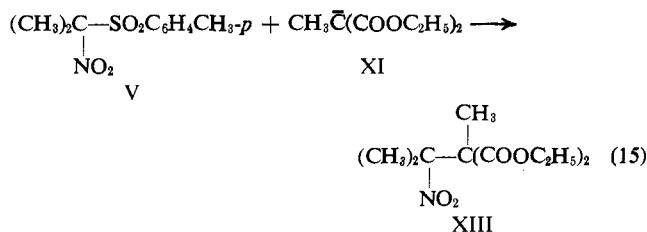


Reactions with the Sodium Salt of Diethyl Methylmalonate

α -Nitro sulfones react readily at room temperature with the sodium salt of diethyl methylmalonate. Thus, the reaction of eq 14 is complete in 3 hr and the β -



nitromalonic ester XII is isolated in 87% yield; similarly, the reaction between α -nitro sulfone V and the diethyl methylmalonate anion (eq 15) is complete in 2



hr and gives an 82% yield of the pure β -nitromalonic ester XIII.

Table II summarizes the results of a set of experiments in which the reaction of eq 15 was allowed to proceed

apparently derive from the reaction of nitroparaffin radicals produced in the initiation step (eq 10) with the nitroparaffin anion employed (eq i and ii), a process completely analogous to that of eq 12 and 13.

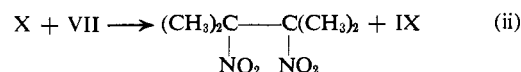
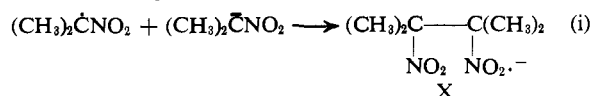


Table II. The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of Diethyl Methylmalonate (XI)^a

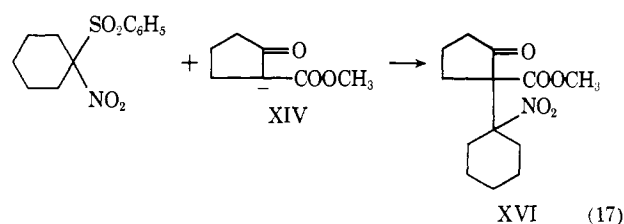
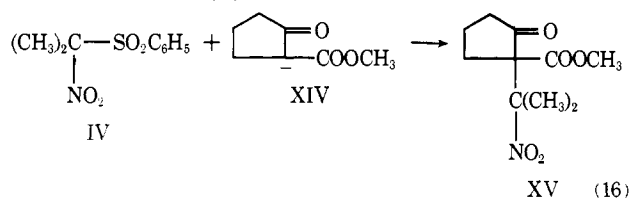
Inhibitor (mol %)	% reaction
None	95
Nitrobenzene (100)	16
<i>m</i> -Dinitrobenzene (10)	4
<i>p</i> -Dinitrobenzene (5)	2
Di- <i>tert</i> -butyl nitroxide (5)	0

^a All reactions conducted in DMSO at room temperature for 30 min.

for 30 min in the presence of various inhibitors. From these results it is clear that the displacement of a sulfone group by the diethyl methylmalonate anion (XI) exhibits the characteristics of a chain reaction in which radical anions and free radicals are intermediates. We conclude, therefore, that the displacement of a sulfone group by the malonate anion (XI) proceeds by a chain sequence completely analogous to that of eq 10–13.

Reactions with the Sodium Salt of 2-Carbomethoxycyclopentanone

In view of the facility with which α -nitro sulfones react with the sodium salt of a malonic ester it comes as no surprise to find that they also react with the sodium salt of a β -keto ester (XIV). In DMSO, at room temperature, the reaction of eq 16 is complete in 6 hr and gives an 84% yield of pure XV; that of eq 17



proceeds equally rapidly to give the nitro keto ester XVI (77% yield).

The reaction of α -nitroisopropyl *p*-tolyl sulfone (V) with the β -keto ester salt (XIV) was studied as regards the matter of mechanism; the findings are summarized in Table III. Here, too, there can be little doubt that the displacement of a sulfone group from an α -nitro sulfone is a chain process involving radical anions and free radicals¹¹ and that the mechanism of these reactions is completely analogous to that of eq 10–13.

Table III. The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of 2-Carbomethoxycyclopentanone (XIV)^a

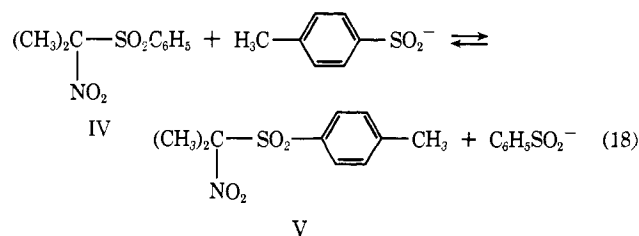
Inhibitor (mol %)	% reaction
None	83
Nitrobenzene (100)	74
<i>m</i> -Dinitrobenzene (10)	10
Di- <i>tert</i> -butyl nitroxide (5)	0

^a All reactions run in DMSO at room temperature for 1 hr.

(11) Consonant with this conclusion is the observation that light significantly speeds up these reactions (*cf.* Experimental Section).

Reactions with the Salts of Sulfinic Acids

Two reactions of α -nitro sulfones with sulfinate salts were investigated, namely, those of eq 18. When



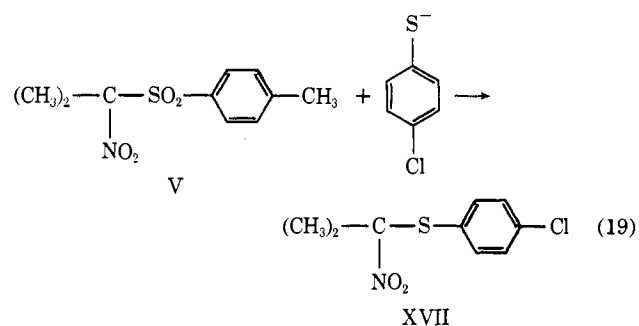
α -nitro sulfone IV is treated with 6 equiv of sodium *p*-toluenesulfinate in hexamethylphosphoramide (HM-PA) in the dark no reaction occurs after 22 hr at room temperature. However, if the reaction flask is exposed to two 20-W fluorescent lights, 25% of α -nitro sulfone IV is converted into α -nitro sulfone V in 22 hr. A duplicate of the light experiment, except that 5 mol % of di-*tert*-butyl nitroxide is present, results in no reaction whatsoever.

The back reaction of eq 18 exhibits the same characteristics. Treatment of α -nitro sulfone V with 6 equiv of sodium benzenesulfinate produces no reaction after 29 hr in the dark, but on exposure to two 20-W fluorescent lights 12% of α -nitro sulfone V is transformed into IV. And, as before, di-*tert*-butyl nitroxide at the 5 mol % level completely stops the reaction.

Clearly, the reactions of eq 18 are free radical chain processes and it seems likely that they proceed by a mechanism fully analogous to that of eq 10–13.

The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of *p*-Chlorothiophenol

The reaction of eq 19 has a large light effect. In the



dark, even after 2 hr at 25°, there is no reaction. In contrast, exposure to two 20-W fluorescent lights results in 95% reaction after 2 hr and the isolation of α -nitro sulfide (XVII) in 59% yield.¹²

The influence of inhibitors on the reaction between α -nitro sulfone V and the sodium salt of *p*-chlorothiophenol was examined and the results are presented in Table IV. Once again it is clear that the assignment of a chain mechanism involving radical anions and free radicals, fully analogous to that of eq 10–13, is warranted.

Experimental Section

The α -nitro sulfones were prepared as described by Kornblum, Kestner, Boyd, and Cattran.⁶

Preparation of the Lithium Salt of 2-Nitropropane. A 500-ml

(12) The chemistry of α -nitro sulfides will be discussed in a forthcoming paper by N. Kornblum and N. Ono.

Table IV. The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of *p*-Chlorothiophenol^a

Inhibitor (mol %)	% reaction
None	54
<i>m</i> -Dinitrobenzene (10)	13
Di- <i>tert</i> -butyl nitroxide (5)	0
None ^b	0

^a All reactions run in DMSO at 25° for 6 min. ^b In the dark.

round-bottom flask containing 215 ml of absolute methanol and a magnetic stirring bar is cooled in an ice bath while sweeping with nitrogen. Lithium wire cut into *ca.* 1-in. lengths is washed in low-boiling petroleum ether, then in absolute methanol to remove the dark coating, and then placed into low-boiling petroleum ether. While stirring, 2.17 g (0.313 mol) of clean lithium wire is added to the flask in the course of *ca.* 30 min; after most of the lithium has reacted the ice bath is removed to bring the reaction to completion. To the resulting colorless solution 29.08 g (0.325 mol) of 2-nitropropane¹³ is added and stirring is continued for 5 min. The nitrogen sweep is terminated and the methanol is removed under reduced pressure while maintaining the flask in a bath at 30–35° until a viscous solution develops. About 250 ml of cyclohexane is then added and the cyclohexane-methanol azeotrope is removed under reduced pressure. Two additional 250-ml portions of cyclohexane are added and the azeotrope repeated. The resulting white solid is subjected to a vacuum of 1 mm for *ca.* 2 hr while still on the rotary evaporator and, then, the free flowing white powder is transferred to a coarse 250-ml sintered glass funnel protected by a nitrogen blanket and washed with anhydrous ethyl ether (lumps are broken up with a flattened glass rod); the ether is then sucked through the funnel under vacuum. This ether washing procedure is repeated several times (a total of *ca.* 500 ml of ether is used). The resulting solid, while still moist with ether, is placed in a round-bottom flask which is then attached to a rotary evaporator. The system is evacuated to *ca.* 1 mm and the flask is immersed in an oil bath heated to *ca.* 55–60° and kept there for 2 to 3 hr. This produces a finely divided, free flowing white powder; potentiometric titration using perchloric acid in acetic acid¹⁴ gives a neutral equivalent of 95.4, theoretical 95.1.

Preparation of the Lithium Salt of Nitrocyclohexane. To begin with the procedure is the same as that used to prepare the lithium salt of 2-nitropropane but the work-up is significantly different. Absolute methanol (150 ml), *ca.* 1 g (0.14 mol) of clean lithium wire, and 18.8 g (0.146 mol) of du Pont nitrocyclohexane are employed as above. Methanol is then removed from the resulting yellow solution under reduced pressure (bath temperature below 35°) until a thick yellow oil remains. At this point 300 ml of anhydrous ethyl ether is added. The resulting yellow solid is isolated by suction filtration using a 400-ml sintered glass funnel (coarse); while still on the funnel it is washed with an additional 300 ml of ether, the final stages of the filtration process being conducted under a nitrogen blanket. (If sufficient methanol is not removed prior to adding the ethyl ether the salt fails to crystallize.) The resulting pale yellow solid is transferred to a round-bottom flask and rotated under a vacuum of *ca.* 1 mm at 55–60° for 5 hr; this gives a pale yellow, free flowing powder; potentiometric titration gives a neutral equivalent of 136.8, theoretical 135.1.¹⁵

Displacements Employing Nitroparaffin Salts. (A) **The Reaction of α -Nitroisopropyl Phenyl Sulfone (IV) with the Lithium Salt of 2-Nitropropane.** The lithium salt of 2-nitropropane (1.90 g, 20 mmol) and α -nitroisopropyl phenyl sulfone (2.29 g, 10 mmol) are placed in a flask which is then fitted with a rubber stopple and swept with nitrogen for *ca.* 30 min by means of inlet and outlet hypodermic needles. Following this, 90 ml of dimethyl sulfoxide (DMSO)¹⁶ is added, magnetic stirring is instituted, and the flask is placed under the light apparatus.¹⁷ The reaction is allowed to proceed for 1 hr at room temperature (a slight positive pressure of nitrogen is main-

(13) We thank the Commercial Solvents Corp. for a gift of 99.9% pure 2-nitropropane.

(14) H. Feuer and B. F. Vincent, *Anal. Chem.*, **35**, 598 (1963).

(15) We are indebted to Dr. M. M. Kestner for assistance with this preparation.

(16) We thank the Crown Zellerbach Corp. for a generous supply of DMSO.

(17) The "light apparatus" consists of two 20 W ordinary fluorescent lights.

tained in the reaction flask) and the resulting yellow solution is then poured into 400 ml of cold water layered with 50 ml of benzene. After several more extractions with benzene the combined benzene extracts are washed with water and dried over anhydrous magnesium sulfate and the benzene then removed under reduced pressure. By vpc the white solid thus obtained is free of starting α -nitro sulfone and one recrystallization from 95% ethanol gives 1.46 g (83% yield) of vpc pure 2,3-dimethyl-2,3-dinitrobutane; mp 210–211°, lit. mp 208–209°. Its nmr spectrum consists of a singlet at δ 1.75.

A duplicate experiment was carried out simultaneously with the above reaction, the only difference being that light was excluded by wrapping the reaction flask in four layers of aluminum foil. Here the reaction was only 61% complete after 1 hr (vpc analysis) and the crude product, when chromatographed on acid washed alumina (using hexane-benzene mixtures), gave 0.88 g (50% yield) of 2,3-dimethyl-2,3-dinitrobutane, mp 208–210° (which by vpc and nmr is pure), followed by 0.85 g (37% recovery) of α -nitroisopropyl phenyl sulfone, mp 115–116° (which by vpc and nmr is pure). This difference in rates between the dark and light reactions, while small, is reproducible; it has, however, not been excluded that the small difference in rates may derive from small differences in reaction temperature rather than being due to the light. What is certain is that if light speeds up this reaction it does so only to a small extent.

(B) **The Reaction of α -Nitroisopropyl Phenyl Sulfone (IV) with the Lithium Salt of Nitrocyclohexane.** This experiment employed 150 ml of DMSO, 4.45 g (33 mmol) of the lithium salt of nitrocyclohexane, and 6.85 g (30 mmol) of α -nitroisopropyl phenyl sulfone and was conducted under the light apparatus¹⁷ as described in experiment A. After 22 hr the reaction mixture was worked up as above and the crude product was recrystallized several times from carbon tetrachloride; this gave 5.41 g (83% yield) of pure dinitroisopropylcyclohexane (VIII), white crystals, mp 149–150°.

Anal. Calcd for C₅H₁₆N₂O₄: C, 49.91; H, 7.45; N, 12.95; mol wt, 216. Found: C, 50.21; H, 7.42; N, 12.65; mol wt, 212.

(C) **The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone with the Lithium Salt of Nitrocyclohexane.** Duplicate experiments employing the procedure of A were carried out: one in the light apparatus,¹⁷ the other in the dark. In each case 50 ml of DMSO, 4.85 g (20 mmol) of α -nitroisopropyl *p*-tolyl sulfone, and 3.38 g (25 mmol) of the lithium salt of nitrocyclohexane were used. The reaction in the light was complete in 5 hr and was worked up in the usual way at that time. The dark reaction was 65% complete after 5 hr and, consequently, was allowed to run for a total of 20 hr before being worked up.

The crude product from the light reaction (mp 141–145°) after two recrystallizations from methanol gave 3.49 g (82% yield) of white crystals, mp 148.5–149.5°; the nmr spectrum of this dinitroisopropylcyclohexane (VIII) is identical with that of the analytical sample obtained in B, but vpc analysis reveals the presence of a trace of 1,1'-dinitrobicyclohexane. In contrast, the crude product from the dark reaction (mp 141–145°) after one recrystallization from methanol gives 3.87 g (90% yield) of the dinitroisopropylcyclohexane which has mp 148.5–149.5°, exhibits the nmr spectrum of the analytical sample, and which by vpc is pure. Conceivably the dark reaction, albeit a little slower, may be the better way to obtain pure unsymmetrical *vicinal* dinitro compounds.

(D) **The Reaction of α -Nitro-*sec*-butyl *p*-Tolyl Sulfone with the Lithium Salt of Nitrocyclohexane.** The α -nitro sulfone (5.14 g, 20 mmol) and the nitrocyclohexane salt (3.38 g, 25 mmol) were allowed to react in 50 ml of DMSO as in A for 5 hr under the light apparatus. The crude obtained on work-up gave, after two recrystallizations from methanol, 3.95 g (86% yield) of dinitro-*sec*-butylcyclohexane, mp 129–130°; vpc analysis showed that it was contaminated with *ca.* 2% of 1,1'-dinitrobicyclohexane. The dinitro-*sec*-butylcyclohexane prepared by treating 1,1-dinitrocyclohexane with the lithium salt of 2-nitrobutane² is analytically and vpc pure and melts at 127.5–128°.¹⁸

(E) **The Reaction of α -Nitrocyclohexyl Phenyl Sulfone with the Lithium Salt of Nitrocyclohexane.** The reaction was conducted as in A using 2.69 g (10 mmol) of the α -nitro sulfone, 1.69 g (12.5 mmol) of the salt, and 50 ml of DMF. After 16 hr under the light apparatus the reaction mixture was poured into water and worked up. The crude product, on recrystallization from acetone, gave 1.53 g (60% yield) of pure 1,1'-dinitrobicyclohexane, mp 216–217° dec (lit.¹⁹ mp 216–217°).

(18) S. D. Boyd, unpublished work.

(19) A. Dornow and K. Fust, *Chem. Ber.*, **90**, 1769 (1957).

(F) The Reaction of α -Nitrocyclohexyl *p*-Tolyl Sulfone (XVIII) with the Lithium Salt of 2-Nitropropane. Using 25 ml of DMSO, 2.83 g (10 mmol) of the α -nitro sulfone, and 1.43 g (15 mmol) of the 2-nitropropane salt the reaction was carried out as in A, under the lights,¹⁷ for 4 hr. The usual work-up, followed by recrystallization from methanol, gave 1.86 g (85% yield) of the dinitroisopropylcyclohexane, mp 148.5–149.5°, which by vpc is pure.

A duplicate experiment using 2.83 g of the α -nitro sulfone, 1.90 g of salt, 50 ml of DMF, and a reaction time of 16 hr gave 1.75 g (81% yield) of vpc pure dinitroisopropylcyclohexane, mp 148.5–149.5°.

(G) The Reaction of α -Nitrocyclohexyl *p*-Tolyl Sulfone with the Lithium Salt of Nitrocyclohexane. The α -nitro sulfone (5.36 g, 20 mmol), the lithium salt (3.38 g, 25 mmol), and 50 ml of DMSO were employed as in A. After 11 hr in the light, the usual work-up, and one recrystallization from acetone, gave 4.21 g (82% yield) of white 1,1'-dinitrobicyclohexane, mp 218–219° (vpc pure).

(H) The Reaction of α -Nitrocycloheptyl Phenyl Sulfone with the Lithium Salt of Nitrocyclohexane. The reaction was carried out as in A using 2.83 g (10 mmol) of the α -nitro sulfone, 1.69 g (12.5 mmol) of the nitrocyclohexane salt, and 25 ml of DMSO. After 11 hr under the light apparatus, the usual work-up, and two recrystallizations from methanol, there was obtained 2.30 g (85% yield) of the dinitrocycloheptylcyclohexane, mp 171–172°.

Anal. Calcd for C₁₃H₂₂N₂O₄: C, 57.75; H, 8.20; N, 10.36; mol wt, 270. Found: C, 57.75; H, 8.18; N, 10.40; mol wt, 274.

Inhibition Studies. The Reaction of α -Nitroisopropyl Phenyl Sulfone (IV) with the Lithium Salt of 2-Nitropropane. Experiment A was repeated in the presence of 0.084 g (0.5 mmol) of *p*-DNB. After one hr the reaction mixture was worked up as in A and the crude product was chromatographed on acid washed alumina initially using 25% benzene–75% hexane and gradually going to pure benzene for development of the column. In this way 0.221 g (13% yield) of pure 2,3-dimethyl-2,3-dinitrobutane, mp 211–212°, was isolated; it is pure by vpc and its nmr spectrum consists of a singlet at δ 1.74. This was followed by 1.677 g of the starting α -nitro sulfone, mp 112–114°; one recrystallization from 95% ethanol raised the mp to that of the pure α -nitro sulfone (IV), 115–116°, and vpc analysis and the nmr spectrum confirmed its purity, 1.60 g (70% recovery).

Experiment A was repeated again except that this time 0.072 g (0.5 mmol) of di-*tert*-butyl nitroxide was added to the reaction mixture. After 4 hr the reaction mixture was worked up as in A; vpc analysis showed that less than 1% of the expected product (2,3-dimethyl-2,3-dinitrobutane) was present. Recrystallization of the crude from 95% ethanol gave 2.04 g (89% recovery) of pure α -nitroisopropyl phenyl sulfone, mp 116–117°; its purity was confirmed by vpc analysis and by its nmr spectrum.

The Reaction of α -Nitrocyclohexyl Phenyl Sulfone (VII) with the Lithium Salt of 2-Nitropropane. The experiment in the absence of inhibitors employed 90 ml of DMSO, 2.69 g (10 mmol) of the α -nitro sulfone (VII), and 1.90 g (20 mmol) of the lithium salt of 2-nitropropane and was conducted under the light apparatus as described in A. After 1.5 hr the reaction mixture was worked up as in A and the crude product was recrystallized from methanol; 1.85 g (85% yield) of dinitroisopropylcyclohexane (VIII), mp 148.5–149.5°, was obtained. Its purity was confirmed by vpc analysis and by its nmr spectrum.

A duplicate experiment in which 0.084 g (0.5 mmol) of *p*-DNB was present was worked up in the usual way after 1.5 hr. The crude product was chromatographed on acid washed alumina using benzene–hexane mixtures and, then, pure benzene. This gave 0.212 g (10% yield) of the dinitroisopropylcyclohexane (VIII), mp 148.5–149.5° (vpc and nmr pure), and, then, 2.346 g (87% recovery) of the α -nitro sulfone (VII), mp 102–103° (vpc and nmr pure).

Another duplicate experiment was carried out except that this time 0.072 g (0.5 mmol) of di-*tert*-butyl nitroxide was added. After 4.5 hr, on work-up of the reaction mixture in the usual way, vpc analysis showed *ca.* 2% reaction. Recrystallization of the crude product from 95% ethanol gave 2.44 g (91% recovery) of the α -nitro sulfone (VII), mp 102–103°.

The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Lithium Salt of 2-Nitropropane. A set of four reactions was carried out using 1.22 g (5 mmol) of the sulfone (V), 0.95 g (10 mmol) of the lithium salt of 2-nitropropane, and 50 ml of DMSO under the light apparatus. But, instead of removing oxygen with a nitrogen stream, the DMSO solution of the lithium salt was frozen under argon, the system was evacuated to <1 mm pressure, and the flask contents were allowed to thaw while stirring magnetically; argon

was then bled in and the freeze–thaw cycle repeated. Without opening the system the α -nitro sulfone and the nitroaromatic (if any was employed) were added, at room temperature, to the DMSO solution, and the reaction was allowed to proceed, with stirring, for 15 min under argon.

In the absence of any nitroaromatic the reaction is complete (by nmr) and, after recrystallization from 95% ethanol, 0.70 g (80% yield) of 2,3-dimethyl-2,3-dinitrobutane (VI), which is vpc pure and has mp 208–210°, is obtained. In the second experiment 0.615 g (5 mmol) of nitrobenzene was present; nmr examination of the crude product obtained after a 15 min reaction time indicated that 88% reaction had occurred. Chromatography on acid washed alumina using benzene–hexane (1:1) gave 0.096 g (8% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°, and 0.55 g (63% yield) of vpc pure dinitrobutane (VI), mp 208–210°. In the third experiment 0.084 g (0.5 mmol) of *m*-dinitrobenzene was present and, after the usual 15 min reaction period, work-up gave a crude product whose nmr spectrum indicated that only 29% reaction had taken place. Chromatographing on acid washed alumina resulted in the isolation of 0.77 g (59% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°, and 0.13 g (15% yield) of vpc pure dinitrobutane (VI), mp 208–210°. Finally, with 0.042 g (0.25 mmol) of *p*-dinitrobenzene the reaction (by nmr) had gone only 7% in 15 min. The crude product was allowed to stand with 50 ml of *n*-hexane at *ca.* +5° for 3 hr after which the resulting white solid was isolated by filtration and recrystallized from 95% ethanol. This gave 1.01 g (83% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°.

Displacements Employing the Sodium Salt of Diethyl Methylmalonate. (A) Preparation of the Sodium Salt of Diethyl Methylmalonate (XI). Sodium (4.6 g, 0.2 mol) was dissolved in 170 ml of absolute ethanol and then 39 g (0.213 mol) of diethyl methylmalonate was added. Most of the ethanol was then removed *in vacuo*, the residual cake was broken up, 100 ml of dry cyclohexane was added, and the mixture was again subjected to rotary vacuum evaporation. Addition of 100-ml portions of dry cyclohexane, followed by vacuum rotary evaporation, was repeated two more times after which the salt was washed thoroughly with *ca.* 500 ml of dry cyclohexane and then rotated at 1 mm for 1 hr. Finally, the salt was heated at 50° for 5 hr in the rotary evaporator at 1 mm. The resulting white powder had a neutral equivalent 194, 198, theoretical, 196.

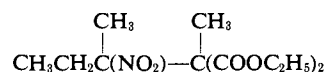
(B) The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of Diethyl Methylmalonate (XI). The sodium salt (4.0 g, 20 mmol) and a magnetic stirring bar are placed in a 200-ml flask which is then swept with nitrogen for 0.5 hr. Then 100 ml of DMSO (through which nitrogen had been passed for 0.5 hr) is added. When the salt has dissolved a solution of 2.43 g (10 mmol) of α -nitroisopropyl *p*-tolyl sulfone in 50 ml of DMSO is added. After 2 hr at room temperature under the light apparatus the reaction mixture is poured into ice–water and ether extracted. The extracts are washed with water, dried, and concentrated under reduced pressure. The excess diethyl methylmalonate is removed by short path distillation at 1 mm (bath temperature 50–60°) for *ca.* 5 hr and the residual pale yellow liquid is chromatographed on acid washed alumina using benzene for elution. This gave 2.14 g (82% yield) of the colorless β -nitromalonic ester XIII; n_D^{20} 1.4492; ir (neat) 5.7, 6.4 μ ; nmr (CCl₄) δ 1.27 (t, 6 H), 1.65 (s, 3 H), 1.78 (s, 6 H), 4.24 (q, 4 H).

Anal. Calcd for C₁₁H₁₅NO₆: C, 50.57; H, 7.33; N, 5.36. Found: C, 50.73; H, 7.25; N, 5.53.

(C) The Reaction of α -Nitrocyclohexyl Phenyl Sulfone (VII) with the Sodium Salt of Diethyl Methylmalonate (XI). Using the same procedure as in B 2.70 g (0.01 mol) of α -nitro sulfone VII, 4.0 g (0.02 mol) of the sodium salt XI, and 150 ml of DMSO were employed. After a 3 hr reaction time, work-up as in B gave 2.62 g (87% yield) of the colorless β -nitromalonic ester XII; n_D^{20} 1.4728; ir (neat) 5.8, 6.5 μ ; nmr (CCl₄) δ 1.28 (t, 6 H), 1.56 (s, 3 H), 1.70–2.8 (m, 10 H), 4.22 (q, 4 H).

Anal. Calcd for C₁₄H₂₃NO₆: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.78; H, 7.89; N, 4.61.

(D) The Reaction of α -Nitro-*sec*-butyl Phenyl Sulfone with the Sodium Salt of Diethyl Methylmalonate (XI). Using 12.2 g (0.05 mol) of α -nitro-*sec*-butyl phenyl sulfone, 20 g (0.1 mol) of XI, and 300 ml of DMSO procedure B was followed. After a 15-hr reaction time (almost certainly much longer than required) the product was worked up in the usual way except that the β -nitromalonic ester



was isolated as a colorless liquid by distillation at 1 mm; bp 136–138°; yield 9.96 g (73%); n_D^{20} 1.4548; ir (neat) 5.9, 6.6 μ .

Anal. Calcd for $C_{12}H_{13}NO_6$: C, 52.35; H, 7.69; N, 5.09. Found: C, 52.57; H, 7.57; N, 5.04.

(E) **Inhibition Studies.** The reaction of eq 15 was studied at room temperature under argon using the freeze-thaw technique (*vide supra*) to remove oxygen from the system. Each experiment of this set employed 1.22 g (5 mmol) of α -nitroisopropyl *p*-tolyl sulfone (V), 2.0 g (10 mmole) of the sodium salt of diethyl methylmalonate (XI), 50 ml of DMSO, and a reaction time of 30 min. Except for the one experiment carried out in the dark, these reactions were conducted under the light apparatus.¹⁷ In every case, work-up involved pouring the reaction mixture into ice-water, extracting with ethyl ether, washing the ether solution with water, and then drying over anhydrous magnesium sulfate. The crude product obtained on removing the ethyl ether was dissolved in a small amount of benzene for vpc analysis and then the benzene was removed and the components of the mixture isolated as described below.

In the absence of inhibitors the reaction was 95% complete after 30 min. The crude product remaining after removal of benzene was treated with *ca.* 30 ml of hexane and the resulting mixture was cooled to *ca.* 5° for 3 hr. The white precipitate (0.065 g, 5% recovery) is vpc pure α -nitro sulfone (V) and has the same mp as the starting α -nitro sulfone (109–110°); *in vacuo* evaporation of the hexane gives a pale yellow liquid consisting of diethyl methylmalonate and the β -nitromalonate XIII. The former is removed by short path distillation at *ca.* 1 mm (bath temperature *ca.* 50°) and the residual yellow liquid is dissolved in hexane and passed through a short column of acid washed alumina. Elution with hexane gives 1.06 g (81% yield) of colorless XIII (n_D^{20} 1.4490) which is vpc pure and has the correct nmr spectrum (see B above).

The second experiment was a duplicate of the first except that it was conducted in the complete absence of light. Vpc analysis revealed that only 63% reaction had taken place; by proceeding as in the first experiment 0.39 g (32% recovery) of vpc pure α -nitro sulfone V (mp 109–110°) was isolated along with 0.68 g (51% yield) of colorless β -nitromalonate ester XIII which is vpc pure and has n_D^{20} 1.4490. (In other experiments the difference between light and dark reactions employing V and XI (*i.e.*, the reaction of eq 15) is also very small; clearly, if there is a light effect it is very small.)

The third experiment differed from the first only in that 0.615 g (5 mmol) of nitrobenzene was present. Vpc analysis indicated that a mere 16% reaction had occurred. The crude product was treated with *ca.* 50 ml of hexane and the mixture was cooled to 5° for 3 hr. The white solid thus obtained on recrystallization from 95% ethanol gave 0.88 g (72% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°. No effort was made to isolate the β -nitromalonate ester XIII.

The fourth experiment differed from the first only in having 0.084 g (0.5 mmol) of *m*-dinitrobenzene present. Vpc analysis revealed that only 4% reaction had occurred; by proceeding as in the third experiment 0.98 g (81% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°, was isolated.

In the fifth experiment 0.042 g (0.25 mmol) of *p*-dinitrobenzene was present. Now vpc showed only 2% reaction and work-up gave 1.02 g (82% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°.

The last experiment was conducted in the presence of 0.036 g (0.25 mol) of di-*tert*-butyl nitroxide. By vpc there was no reaction at all after 30 min and 1.04 g (83%) of vpc pure α -nitro sulfone V, mp 109–110°, was recovered.

Displacements Employing the Sodium Salt of 2-Carbomethoxycyclopentanone. (A) **Preparation of the Sodium Salt of 2-Carbomethoxycyclopentanone (XIV).** A solution of 4.6 g (0.2 mol) of sodium in 150 ml of anhydrous methanol was treated with 30.0 g (0.21 mol) of 2-carbomethoxycyclopentanone and from the resulting solution the salt was isolated by a procedure strictly analogous to that used to make the sodium salt of diethyl methylmalonate (*vide supra*). The white powder so obtained had a neutral equivalent of 162, theoretical, 164.

(B) **The Reaction of α -Nitroisopropyl Phenyl Sulfone (IV) with the Sodium Salt of 2-Carbomethoxycyclopentanone (XIV).** This reaction is carried out in the same way as the reaction of α -nitro sulfone V with sodio diethyl methylmalonate (part B preceding section) using 11.5 g (0.05 mol) of α -nitroisopropyl phenyl sulfone (IV), 16.5 g (0.1 mol) of the sodium salt XIV, 300 ml of DMSO, and a reaction time of 6 hr. The reaction mixture is poured into ice-water and ether extracted. The extracts are washed with water,

dried, and concentrated under reduced pressure. The resulting white solid is recrystallized by dissolving in hexane-benzene at *ca.* 40° and then cooling to –20°; this gives 9.70 g (84% yield) of XV, white crystals: mp 56–57°; ir ($CHCl_3$) 5.75, 5.85, 6.6 μ ; nmr ($CDCl_3$) δ 1.75 (s, 3 H), 1.87 (s, 3 H), 2.0–2.64 (m, 6 H), 3.80 (s, 3 H).

Anal. Calcd for $C_{16}H_{19}NO_6$: C, 52.40; H, 6.60; N, 6.11. Found: C, 52.67; H, 6.41; N, 6.09.

(C) **The Reaction of α -Nitrocyclohexyl Phenyl Sulfone (VII) with the Sodium Salt of 2-Carbomethoxycyclopentanone (XIV).** Using the procedure of part B, 5.4 g (0.02 mol) of α -nitro sulfone VII, 6.6 g (0.04 mol) of sodium salt XIV, and 150 ml of DMSO are allowed to react for 6 hr. The reaction mixture is then poured into ice-water and ether extracted, and the extracts are washed with water. On drying and concentrating under reduced pressure a yellow oil is obtained which when chromatographed on acid washed alumina using benzene-hexane (1:1) gave 4.18 g (77% yield) of a colorless liquid: n_D^{20} 1.5026; vpc pure; ir (neat) 5.75, 5.80, 6.55 μ ; nmr ($CDCl_3$) δ 1.0–2.9 (m, 16 H), 32.75 (s, 3 H).

Anal. Calcd for $C_{13}H_{19}NO_6$: C, 57.98; H, 7.11; N, 5.20. Found: C, 58.11; H, 7.14; N, 5.26.

(D) **Inhibition Studies.** The reaction of α -nitroisopropyl *p*-tolyl sulfone (V) with the sodium salt of 2-carbomethoxycyclopentanone (XIV) was studied at room temperature under argon using the freeze-thaw technique (*vide supra*) to remove oxygen from the system. Each experiment of this set employed 1.22 g (5 mmol) of the α -nitro sulfone, 1.6 g (10 mmol) of the sodium salt, 50 ml of DMSO, a reaction time of 1 hr and was conducted in the light apparatus. The reaction mixture was poured into ice-water and extracted with ether and the ether solution was washed with water and then dried. Removal of the ethyl ether gave a crude product which was dissolved in a little benzene for vpc analysis. Finally, the benzene was removed and the components of the crude product were isolated as described below.

In the absence of inhibitors the reaction is 83% complete after 1 hr. The crude product is added to a solution consisting of 30 ml of ethyl ether and 20 ml of hexane, and the resulting mixture is stirred for 30 min at room temperature. The white solid which remains is isolated by filtration, the mother liquor is cooled to 0° for *ca.* 2.5 hr, and the white precipitate as produced is combined with the white solid. This is vpc pure α -nitro sulfone (V), mp 109–110°, 0.105 g (9% recovery). The residue obtained on evaporating the ether-hexane mother liquor is recrystallized from hexane-benzene whereupon 0.670 g (58% yield) of the nitro keto ester XV is obtained; it is 98% pure (by vpc) and has mp 53–55°. Pure XV melts at 56–57°.

The second experiment duplicates the first except that now 0.615 g (5 mmol) of nitrobenzene is present. Vpc of the crude indicated that the reaction had gone 74% and isolation as in the first experiment gave 0.22 g (18% recovery) of vpc pure α -nitro sulfone (V), mp 109–110°. Once again the nitro keto ester XV obtained was 98% pure (by vpc) and melted 53–55°, yield 0.540 g (47%).

A third experiment duplicated the first except for the presence of 0.084 g (0.5 mmol) of *m*-dinitrobenzene. Vpc examination of the crude showed only 10% reaction. The crude product was stirred into *ca.* 50 ml of hexane and the mixture was then cooled to 5° for *ca.* 3 hr. The white solid is isolated by filtration and recrystallized from 95% ethanol. This gives 0.89 g of pure α -nitro sulfone V (74% recovery), mp 109–110°.

The fourth experiment differed from the first in having 0.036 g (0.25 mmol) of di-*tert*-butyl nitroxide present. Vpc analysis of the crude product showed that no reaction had occurred and 1.06 g (87% recovery) of the pure α -nitro sulfone (V), mp 109–110°.

(E) **The Effect of Light.** A duplicate of the first experiment of the set described in D was carried out but now the experiment was conducted in the dark (flask completely wrapped in four sheets of aluminum foil). Vpc analysis of the crude product showed only 5% reaction and 0.970 g (80% recovery) of the pure α -nitro sulfone V was isolated, mp 109–110°. This, and a number of similar results, leave no doubt that the reaction of α -nitro sulfone V with the sodium salt of 2-carbomethoxycyclopentanone (XIV) is subject to a substantial light effect.

Displacements Employing Sulfinate Salts. (A) **The Reaction of α -Nitroisopropyl Phenyl Sulfone (IV) with Sodium *p*-Toluenesulfinate.** This was carried out by adding 50 ml of HMPA to 5.32 g (30 mmol) of sodium *p*-toluenesulfinate⁶ under nitrogen. Then 1.14 g (5 mmol) of IV in 30 ml of HMPA was added and the resulting solution was stirred (under nitrogen) for 22 hr under the light apparatus.¹⁷ The reaction product was then poured into 200 ml of water and extracted three times with 100-ml portions of ethyl

ether. The ether extracts, after being washed with water, were dried over anhydrous magnesium sulfate and vacuum evaporated. The white solid which remains (0.985 g) melts over the range 85–96° and by vpc analysis is composed of α -nitro sulfone IV (75%) and 25% of α -nitroisopropyl *p*-tolyl sulfone (V).

A duplicate experiment conducted in the dark for 22 hr and worked up as above gave a crude product which, when dissolved in benzene and analyzed by vpc, contained none of the α -nitro sulfone V. On recrystallization from 95% ethanol 1.04 g (91% recovery) of pure starting sulfone IV was obtained, mp 115–116°.

The third experiment was a duplicate of the first except that 0.036 g (0.25 mmol) of di-*tert*-butyl nitroxide was added. The crude product obtained after a 22-hr reaction period and the usual work-up on vpc analysis was found to contain none of the α -nitro sulfone V. On being washed with cold hexane the crude gave 0.992 g (87% recovery) of white crystals which have mp 115–116° and which, by vpc, is the pure starting α -nitro sulfone (IV).

(B) The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with Sodium Benzenesulfinate. This was carried out as described in the first experiment of part A using 4.92 g (30 mmol) of sodium benzenesulfinate,⁶ 1.22 g (5 mmol) of α -nitro sulfone V, and 80 ml of HMPA. After stirring (under nitrogen) for 29 hr under the light apparatus,¹⁷ work-up gave 0.99 g of a white solid which melts from 95 to 102° and which, by vpc analysis, is 88% starting material (V) and 12% α -nitro sulfone IV.

A duplicate experiment conducted in the dark for 29 hr gave a crude product which, by vpc, had none of the α -nitro sulfone IV. Recrystallization from 95% ethanol gave 1.09 g (90% recovery) of pure V, mp 109–110°.

The third experiment was a duplicate of the first except for the presence of 0.036 g (0.25 mmol) of di-*tert*-butyl nitroxide. Here again the crude product, by vpc, contains no IV. On being washed with cold hexane it gives 1.07 g (88% recovery) of pure starting α -nitro sulfone V, mp 109–110°.

Displacement by the Sodium Salt of *p*-Chlorothiophenol. (A) Preparation of the Sodium Salt of *p*-Chlorothiophenol. A solution of 2.3 g (0.1 mol) of sodium in 150 ml of dry methanol (purged of oxygen by bubbling in dry nitrogen) is treated with 15.0 g (0.105 mol) of *p*-chlorothiophenol. Most of the methanol is then removed *in vacuo* and to the resulting slurry *ca.* 100 ml of dry cyclohexane is added. Most of the cyclohexane is removed *in vacuo*, a second portion of dry cyclohexane (*ca.* 100 ml) is added, and the evaporation is repeated. The addition and removal of cyclohexane is repeated a third time, the resulting white solid is washed with a little dry cyclohexane, and, then, the white solid is heated at 50° for 24 hr on a rotary evaporator at 1 mm. The white powder so obtained has a neutral equivalent of 166, theoretical, 166.5.

(B) The Reaction of α -Nitroisopropyl *p*-Tolyl Sulfone (V) with the Sodium Salt of *p*-Chlorothiophenol. A solution of the sodium salt of *p*-chlorothiophenol (0.835 g, 5 mmol) in 50 ml of DMSO is treated with 1.22 g (5 mmol) of α -nitro sulfone V under argon after prior degassing of the system by the freeze–thaw procedure (see above). The reaction is conducted under the light apparatus¹⁷ for 2 hr at room temperature after which the solution is poured into ice–water and extracted with ethyl ether. The ether extracts are washed with cold water and dried. By nmr, the white solid obtained

on removing the ether *in vacuo* consists of *ca.* 5% of V, *ca.* 5% of *p,p'*-dichlorodiphenyl disulfide, and *ca.* 1% of 2,3-dinitro-2,3-dimethylbutane, the remainder being the α -nitro sulfide (XVII). The white solid is stirred with *ca.* 50 ml of *n*-hexane for 30 min at 25°, the resulting suspension is filtered, and the filtrate is evaporated to dryness to give the crude α -nitro sulfide (XVII). This after one recrystallization from hexane, gives 0.68 g (59% yield) of XVII, mp 81–82°. Analytically pure α -nitro sulfide (XVII) melts at 82–83°.¹² This product and the analytical sample have identical nmr and ir spectra: nmr (CDCl₃) δ 1.83 (s, 6 H), 7.37 (s, 4 H); ir (CHCl₃) 6.5 μ .

A duplicate experiment carried out in the dark gave no reaction in 2 hr (by nmr) and 0.93 g of the α -nitro sulfone (V), mp 109–110°, was recovered.

(C) Mechanistic Studies. A set of four reactions was carried out using 0.42 g (2.5 mmol) of the sodium salt of *p*-chlorothiophenol, 0.61 g (2.5 mmol) of α -nitro sulfone V, 30 ml of DMSO, and a reaction time of 6 min. All four experiments were conducted under argon after degassing by the freeze–thaw technique (*vide supra*). Except for the one experiment carried out in the dark, these reactions were conducted under the light apparatus.¹⁷ In every case work-up involved pouring the reaction mixture into ice–water, ether extracting, washing the ether extracts with water, and drying; removal of the ether under reduced pressure gave the crude product.

In the absence of inhibitors the reaction is 54% complete (nmr) after 6 min. The crude product is stirred with 30 ml of *n*-hexane for 30 min at 25° and the white solid which remains is isolated by filtration; the 0.205 g thus obtained has mp 107–109° and is pure starting α -nitro sulfone V (34% recovery). The *n*-hexane filtrate is evaporated to dryness and the resulting white solid is recrystallized from *n*-hexane; this gave 0.250 g (43% yield) of α -nitro sulfide (XVII), mp 76–79°, which, by nmr, is 95% pure.

The second experiment differed from the first only in that 0.042 g (0.25 mmol) of *m*-DNB was present. Nmr analysis showed that the reaction had only gone 13%; by purifying the crude as in the first experiment 0.37 g (61% recovery) of pure α -nitro sulfone V, mp 107–109°, was isolated. The α -nitro sulfide (XVII) was not obtained in pure form.

The third experiment also duplicated the first except that 0.018 g (0.125 mmol) of di-*tert*-butyl nitroxide was present. Nmr analysis of the crude product revealed that no reaction whatsoever had occurred and on purifying the crude product by stirring with cold *n*-hexane 0.49 g (80% recovery) of α -nitro sulfone V, mp 107–109°, was achieved.

The fourth experiment is a repetition of the first except that it was conducted in total darkness. By nmr analysis of the crude it was found that no reaction took place; on treating the crude product with *n*-hexane 0.50 g of α -nitro sulfone V, mp 108–109°, was obtained (82% recovery).

Acknowledgment. We thank the National Science Foundation and Eli Lilly and Co. for generous support. This paper was written while the senior author was a visiting professor in the Organic Chemistry Department of the Swiss Federal Institute of Technology, Zürich.