states: B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **99**, 3214 (1977).

(6) A referee has pointed out that there is, of course, no reason to expect dielectric constants to correlate with UV transition energies. Thus F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc. B*, 460 (1971), report that solvent effects on chemical and physical properties, including UV transition energies, are poorly correlated by d or functions of d, and there are few, if any, indications in the literature that absorption maxima (in the absence of H bonding) are linear with d or the $(d-1)/(d+2)$ function.

(7) E.g., (a) G. S. Hammond and F. J. Modic, *J. Am. Chem. Soc.*, **75**, 1385 (1953); (b) K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 189; (c) M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

(8) The difference between the two net interaction energies ($\Delta H_{solute-solvent}$) is equal to the enthalpy of solvent transfer ($\delta\Delta H_{DMF\rightarrow MeOH}$) less the difference between the two solvent cavity formation energies ($\Delta H_{solvent-solvent}$), or

$$\delta\Delta H_{DMF\rightarrow MeOH} = \Delta H_{solute-MeOH} - \Delta H_{solute-DMF} + \Delta H_{MeOH-MeOH} - \Delta H_{DMF-DMF}$$

(9) In the case of the two anisoles, hydrogen bonding to the methoxyl oxygen might also make a significant contribution. See, however, the cogent argument of Kamlet (ref 7c) dismissing this possibility for the case of 4-nitroanisole. The 4-nitroacetophenone, on the other hand, undoubtedly has significant carbonyl group–solvent interaction contributions which complicate matters.

(10) R. Fuchs and R. F. Rodewald, *J. Am. Chem. Soc.*, **95**, 5897 (1973).

(11) P. P. Saluja, T. M. Young, R. F. Rodewald, F. H. Fuchs, D. Kohli, and R. Fuchs, *J. Am. Chem. Soc.*, **99**, 2949 (1977).

(12) This observation is in agreement with the findings of M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977), who found that DMF is a more polar solvent (has a larger π^* value) than methanol.

(13) L. C. Allen, *J. Am. Chem. Soc.*, **97**, 6921 (1975).

(14) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962).

Replacement of the Nitro Group by Hydrogen[1]

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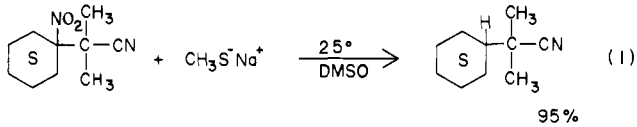
Abstract: The reaction of an aliphatic nitro compound with the sodium salt of methanethiol can occur with clean replacement of the nitro group by hydrogen. This is so despite the existence of a competitive process—replacement of nitro by thiomethyl. Evidence in support of the view that both transformations are electron transfer processes is presented and a radical anion–free radical chain mechanism is proposed. The factors which control the course of reaction of a nitro compound and the sodium salt of methanethiol are described and a simple rationale is presented.

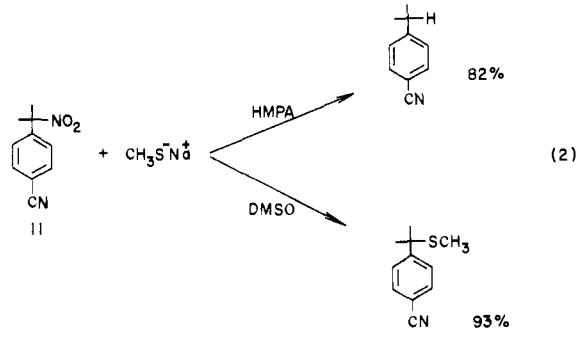
Until 1954 a synthetically useful method for the preparation of tertiary nitroparaffins did not exist. Since that time a number of reactions have been discovered which give excellent yields of pure aliphatic and alicyclic tertiary nitro compounds;[2-11] these reactions employ mild conditions and most of them are carbon-carbon bond forming processes. It is noteworthy that they give rise to highly branched compounds—many of them virtually unobtainable by other means—and that they are capable of providing tertiary nitro compounds in which other functional groups are present, e.g., cyano, keto, and ester.

With such a wide variety of unusual structures readily available it is apparent that any process which results in the replacement of a nitro group by other atoms or groups of atoms has considerable value. In this paper we describe a new reaction—the replacement of a nitro group by hydrogen. This occurs at room temperature when the nitro compound is treated with the sodium salt of methyl mercaptan. Equation 1 is illustrative and Table I summarizes our results; it should be emphasized that yields refer to pure, isolated products.



(1)

Although matters are easily arranged so that the handsome yields of Table I are readily achieved, this is so despite the existence of a competitive process—the replacement of a nitro group by the thiomethyl group. Indeed, in certain systems replacement by thiomethyl can be made overriding simply by the proper choice of solvent. An example is shown in eq 2. The "proper" choice of solvent depends on the structure of the nitro compound and in order to facilitate discussion of this, and related matters, we shall consider tertiary nitro compounds as falling into three groups.



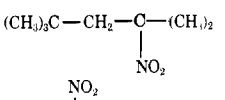
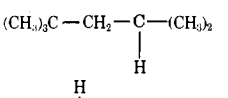
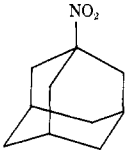
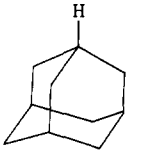
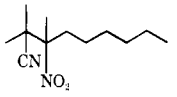
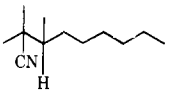
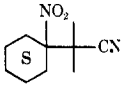
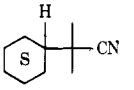
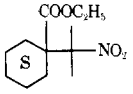
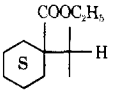
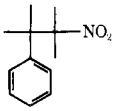
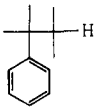
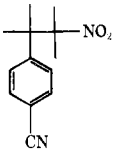
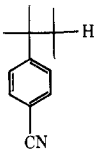
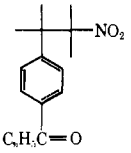
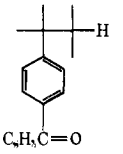
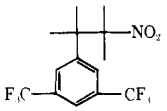
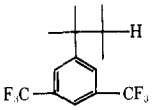
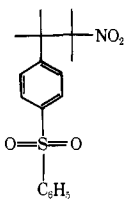
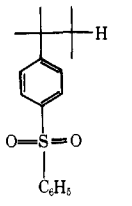
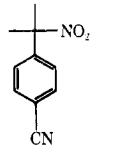
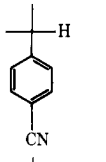
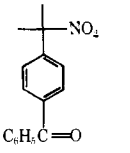
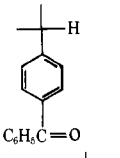
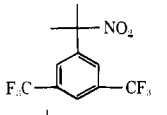
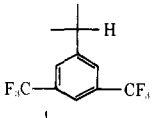
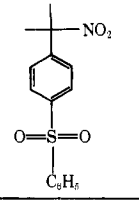
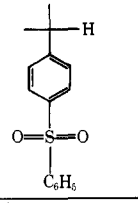
(2)

The first group consists of compounds **1–6** (Table I); except for **6** they are all purely aliphatic or alicyclic systems. (It is of interest that **6** is the only β-arylated nitro compound which falls into this group; note will be taken of this in the accompanying paper.) The common characteristic of compounds **1–6** is that on treatment with the sodium salt of methyl mercaptan the nitro group is replaced by hydrogen—regardless of the solvent employed. In no instance is a detectable amount of the methyl thioether produced. (Here, and indeed with the other two groups as well, the solvent has a large influence on rate; in all cases studied the reaction of a nitro compound with the sodium salt of methyl mercaptan is much faster in hexamethylphosphoramide (HMPA) than in dimethylformamide (DMF) or in dimethyl sulfoxide (Me_2SO).)

Compounds **7–10** comprise the second group which, it will be noted, consists of β-arylated nitroparaffins. Here, as with the preceding group, the reaction with sodium thiomethoxide in DMF results in replacement of the nitro group by hydrogen; the yields are excellent and, once again, the methyl thioether cannot be detected. However, in contrast to what is observed with the first group, when the reaction is conducted in HMPA substantial amounts of the thioether are produced, e.g., as in

0002-7863/79/1501-0647$01.00/0

Table I. Replacement of the Nitro Group by Hydrogen at 25 °C[a]

compd no.	nitro compd	solvent	reaction time, h	product	yield, %[b]
1		HMPA	46		55
2		HMPA	42[c]		71
3		Me_2SO	17		92
4		Me_2SO	3		95
5		Me_2SO	24		83
6		HMPA	8		94
7		DMF	15		91
8		DMF	18		76
9		DMF	20		84
10		DMF	8		83
11		HMPA	16[d]		82
12		HMPA	12[d]		80
13		HMPA	16[d]		77
14		HMPA	10[e]		80

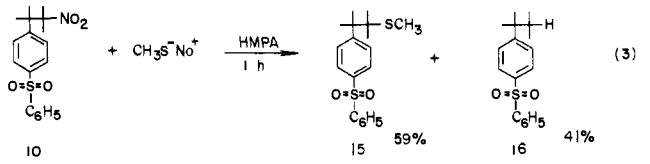
[a] All reactions were carried out with exposure to two two 20-W ordinary fluorescent lights unless otherwise noted. [b] Pure, isolated product. [c] At 100 °C. [d] In total darkness. [e] Room light.

Table II. Solvent and Substituent Effects in the Reaction of β-Arylated Nitro Compounds with the Sodium Salt of Methyl Mercaptan[a]

compd no.[b]	solvent	product[c] R-H	product[c] R-SCH$_3$
7	DMF	96 (91)	0
7	HMPA	68 (64)	32 (22)
8	DMF	86 (76)	0
8	HMPA	4	96 (87)
9	DMF	98 (84)	0
9	HMPA	53 (45)	47 (37)
10	DMF	92 (83)	0
10	HMPA	41 (23)	59 (45)
6	DMF	100 (80)	0
6	HMPA	100 (94)	0

[a] All reaction conducted at room temperature with exposure to two 20-W ordinary fluorescent lights. [b] Cf. Table I. [c] NMR yields; yields of isolated, pure products in parentheses.

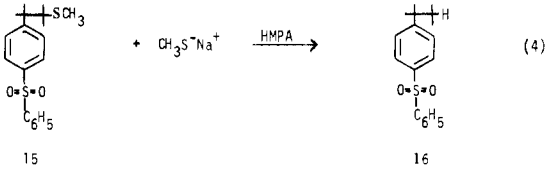
the reaction of eq 3. Indeed, in the case of nitro compound **8**



10 15 16 (3)

the yield of thioether is almost quantitative (Table II). It is clear from the data of Table II that the reaction of β-arylated nitro compounds with the sodium salt of methyl mercaptan is subject to major solvent and substituent effects,[13]

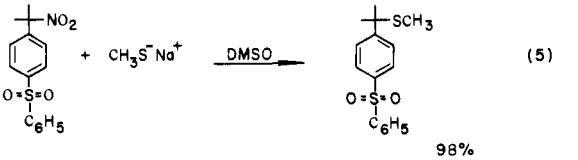
The possibility that the mixtures of products obtained from nitro compounds **7–10** may derive from further reaction of the initially produced thioether, e.g., as shown in eq 4, was rejected



15 16 (4)

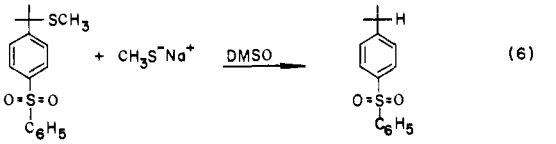
because a thioether such as **15** is stable under the conditions employed. Thus, while the reaction of eq 3 requires 1 h to go to completion, repetition of this experiment using a 24-h reaction time does not change the yields of **15** and **16.** Also, if thioether **15** is treated with the sodium salt of methyl mercaptan in HMPA for 48 h most of the thioether is recovered along with a 5% yield of the reduction product **16.** Thus, although the reaction of eq 4 does occur, its rate is far too slow to account for what is observed when nitro compound **10** is treated with the sodium salt of methyl mercaptan, i.e., to account for the process of eq 3. In the same way it was shown that the mixture obtained on treating nitro compound **7** with the sodium salt of methyl mercaptan in HMPA does not arise from a process analogous to that of eq 4. It was also established that β-arylated thiomethyl ethers such as **15** are stable to the sodium salt of methyl mercaptan in DMF solution. Clearly the reactions of β-arylated nitro compounds **7–10** (Table II) are kinetically controlled processes.

α-Nitrocumenes **11–14** comprise the third group of compounds. Their response to the sodium salt of methyl mercaptan is distinctly different from that of the other groups. In Me_2SO, or in DMF, the methyl thioether is formed first and it then is slowly converted to the cumene. Indeed, replacement of the thiomethyl group by hydrogen is sufficiently slow that excellent yields of methyl thioethers are readily obtained. The reaction of eq 2 provides one example, that of eq 5 another. The reaction



(5)

of eq 5 is complete in 15 min, at which time the sole product is the thiomethyl ether; if the reaction mixture is not worked up at this point, conversion to the cumene, i.e., the reaction of eq 6, is detected after 2 h (ca. 2%), and after 2 days 20% of the thioether is reduced to cumene.



(6)

The situation in HMPA parallels that in Me_2SO (or DMF) except that now both processes are greatly speeded up and the initially produced thioether is rather rapidly transformed into the cumene. As a consequence, unless the reaction in HMPA is run for a very short time (1 min or so) or for a relatively long time (ca. 8 h) mixtures of thioether and cumene are produced. In other words, in the α-nitrocumene series the kinetically controlled process in Me_2SO, DMF, or HMPA is formation of the methyl thioether, and subsequent replacement of the thiomethyl group by hydrogen is comparatively slow.

Mechanism of the Replacement of Nitro by Hydrogen. The mechanism by which a nitro group is replaced by hydrogen appears to be

$$R_3CNO_2 + CH_3S^- \rightarrow R_3CNO_2^- \cdot + CH_3S \cdot \quad (7)$$

$$R_3CNO_2^- \cdot \rightarrow R_3C \cdot + NO_2^- \quad (8)$$

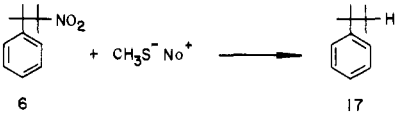
$$R_3C \cdot + H_3CS^- \rightarrow R_3CH + H_2\dot{C}S^- \quad (9)$$

$$H_2\dot{C}S^- + R_3CNO_2 \rightarrow H_2C{=}S + R_3CNO_2^- \cdot \quad (10)$$

The first two steps (eq 7 and 8) are fully consistent with what is known about electron transfer reactions of aliphatic nitro compounds.[11] The last two (eq 9 and 10), which provided the initiative for this work, were suggested by the studies of Bunnett, Boyle, and Wamser[12] on the free-radical chemistry of methoxide ion.

A number of observations support the proposed radical anion–free radical chain mechanism. Thus, although the reaction of eq 1 is complete in 3 h, and gives a 95% yield of the pure product, when it is repeated with 10 mol % of di-*tert*-butyl nitroxide present 97% of the nitro compound is recovered. At the 10 mol % level *m*-dinitrobenzene also acts as an inhibitor; after 3 h only about 10% of the nitro compound reacts. Indeed, even nitrobenzene (50 mol %) inhibits the reaction of eq 1; in 3 h it proceeds only 8%.

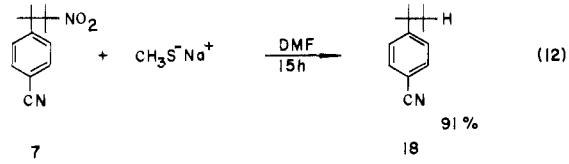
The reaction of eq 11, like that of eq 1, involves a member



6 17 (11)

of the first group of nitro compounds. (These, it will be recalled, undergo replacement of the nitro group by hydrogen—regardless of the solvent employed.) In DMF, 85% of compound **6** reacts in 24 h and the reduction product **17** is isolated in 74% yield. In contrast, when 20 mol % of di-*tert*-butyl nitroxide is present there is no detectable reaction after 24 h and 99% of the nitro compound is recovered. The reaction of eq 11 in HMPA is also completely inhibited by 20 mol % of di-*tert*-butyl nitroxide.

Another reaction studied in regard to the matter of mechanism is that of eq 12; in DMF it gives a 91% yield of pure **18**



7 18 (12)

in 15 h. But when 20 mol % of di-*tert*-butyl nitroxide is added no reaction whatsoever occurs and 94% of the nitro compound is recovered. As befits a member of the second group of nitro compounds (vide supra), in HMPA the reaction of **7** with the salt of methanethiol produces a mixture of **18** and the thiomethyl ether (cf. Table II); this reaction is also completely inhibited by 20 mol % of di-*tert*-butyl nitroxide.

As shown in eq 2, the reaction of *p*-cyano-α-nitrocumene (**11**) with the sodium salt of methyl mercaptan proceeds cleanly to the thioether, or to the reduction product, depending on the solvent. In Me_2SO the transformation is complete in 4 h but in the presence of 20 mol % of di-*tert*-butyl nitroxide no reaction occurs. In HMPA the α-nitrocumene **11** is completely consumed in 0.5 h but here again 20 mol % of the nitroxide exerts a powerful inhibitory effect and 93% of the α-nitrocumene is recovered.[14]

Di-*tert*-butyl nitroxide is a free-radical scavenger,[15] *m*-dinitrobenzene and nitrobenzene are recognized as diagnostics for radical anions,[11,16] and, clearly, the reactions of tertiary nitro compounds with the sodium salt of methyl mercaptan are chain processes. The mechanism of eq 7–10 provides a simple basis for understanding the foregoing facts and is consistent with what is known about aliphatic nitro systems,[8,11,17]

Most of the reactions of tertiary nitro compounds with the sodium salt of methyl mercaptan will take place in the dark at a measurable rate but they are unambiguously accelerated by light. Illumination by diffuse daylight or ceiling lights will do but usually a "light bank" consisting of two 20-W ordinary fluorescent lights is employed. Thus, when conducted under the "light bank" the reaction of eq 1 is over in 3 h whereas a duplicate experiment carried out in total darkness proceeds only 4% to completion.

The reactions of β-arylated tertiary nitro compounds (**6–10**) are also speeded up by light. For example, compound **6** is completely reduced after 8-h exposure to the "light bank" (Table I), whereas in the dark there is no detectable reaction.[18]

The effect of light on the reaction of α-nitrocumenes, while less dramatic, is, nonetheless, real. Thus, *p*-benzenesulfonyl-α-nitrocumene (**14**) is completely destroyed by the sodium salt of methyl mercaptan after exposure to the "light bank" for 1 min; in the dark only 53% of this α-nitrocumene reacts in 1 min. It is a fortunate circumstance that α-nitrocumenes react readily in the dark with the sodium salt of methyl mercaptan for, as shown in Table I, with three of these compounds replacement of the nitro group by hydrogen is effected in the dark and in the fourth case this transformation is achieved with room light. This shunning of the "light bank" is not a capricious act but, rather, derives from the observation that with α-nitrocumenes reactions conducted under the "light bank" produce small amounts of olefins, and products derived from the olefins, whereas in the dark, and in diffuse light, olefin formation does not occur (see Experimental Section).

Radical anion substitution processes are frequently accelerated by light.[11] Consequently, the fact that the reactions of tertiary nitro compounds with the sodium salt of methyl mercaptan are speeded up by light is consonant with the electron transfer mechanism of eq 7–10.

Mechanism of Thioether Formation. The proposed mechanism provides a simple basis for understanding how an aliphatic nitro group is replaced by hydrogen, i.e., for rationalizing the reactions of the first group of nitro compounds (**1–6**). But it says nothing about the formation of methyl thioethers nor does it provide any insight regarding the various perplexing facts associated with the chemistry of nitro compounds of the second and third groups.

Actually, the mechanism of eq 7–10 is a useful starting point for considering the questions associated with thioether formation. According to eq 9 a carbon free radical abstracts a hydrogen atom from the methyl mercaptide ion—a process reasonably regarded as essentially irreversible. One can, however, envision an alternate outcome for the encounter of a carbon free radical with the methyl mercaptide ion—collapse to form a radical anion (eq 13). This would be expected to be followed by electron transfer, the step of eq 14. It is, then, easy to imagine that thiomethyl ether formation is also a radical anion–free radical chain process (eq 7, 8, 13, 14).

$$R_3C\cdot + H_3CS^- \rightarrow R_3C\dot{S}CH_3 \quad (13)$$

$$R_3CNO_2 + R_3C\dot{S}CH_3 \rightarrow R_3CNO_2^{-}\cdot + R_3CSCH_3 \quad (14)$$

While this proposal has the merit of simplicity and directness it does not provide a basis for dealing in a meaningful way with the question: why do the radicals formed from nitro compounds **1–6** only abstract hydrogen from the methyl mercaptide ion while those of the second group (**7–10**), to a greater or lesser extent, also form thioethers? In particular, there is no obvious reason why the unsubstituted radical **19** is so sharply differ-

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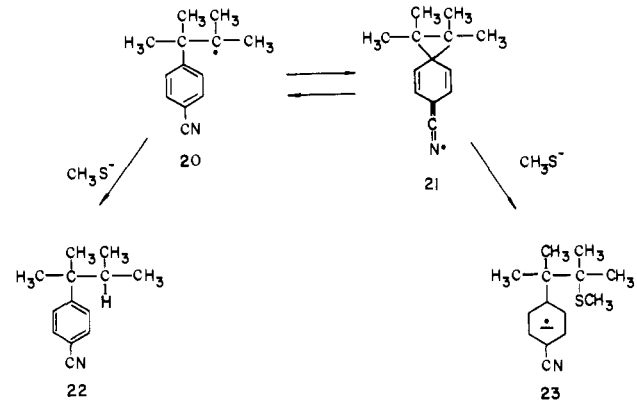
entiated from the β-arylated radicals derived from nitro compounds **7–10.**

We propose that the substituted β-aryl radicals derived from compounds **7–10** differ from the other radicals in that they readily cyclize to spiranes, e.g., **20** → **21,** and that thioethers are formed from these spiranes.[19] Thioether formation is presumed to arise from a nucleophilic displacement by the methyl mercaptide ion on one of the carbon atoms of the spirane ring, part of the driving force being the formation of a relatively stable radical anion, e.g., **23.** It is reasonable to as-



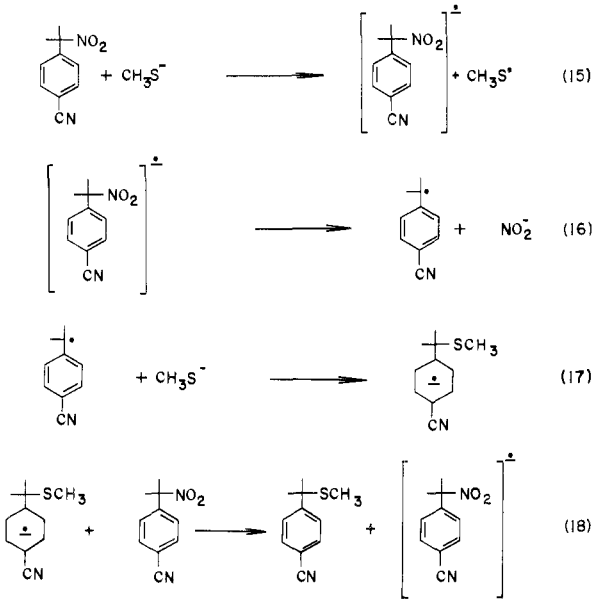
sume that a radical anion such as **23** will readily transfer one electron to the starting nitro compound with the overall result that a nitro group is replaced by thiomethyl via a radical anion–free radical chain mechanism. And, of course, the reaction of the open-chain radical, **20,** with the methyl mercaptide ion is but another example of the general process described by eq 9; it not only results in replacement of nitro by hydrogen but, also, since it produces the $\dot{C}H_2S^-$ radical anion, enables the chain to continue. We see then that both of the reactions exhibited by nitro compounds of the second group (**7–10**) are readily accommodated within the framework of radical anion–free radical substitution processes. The underlying assumptions necessary for this accommodation are dis-

cussed in more detail in the sequel, and in the accompanying paper.[20]

Solvent Effect. As noted in Table II, the solvent has a large influence on the reaction course when nitro compounds **7–10** are treated with the sodium salt of methyl mercaptan. In DMF the sole result is replacement of nitro by hydrogen whereas in HMPA replacement by hydrogen and by thiomethyl both occur. The mechanism proposed for replacement by thiomethyl provides an insight into the ability of HMPA to foster thioether formation; this mechanism invokes the idea that a spirane radical such as **21** undergoes a nucleophilic displacement by the methyl mercaptide ion to give the radical anion **23.** The available data leave little room for doubting that nucleophilic displacement reactions (S_N2) are much faster in HMPA than in DMF or in Me_2SO.[21,22] Thus, in HMPA the nucleophilic displacement process enjoys an advantage over the hydrogen abstraction reaction by which **20** is converted to **22,** and this advantage is greatly diminished in DMF or in Me_2SO.

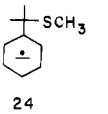
Formation of Cumylic Thiomethyl Ethers and Their Conversion to Cumenes. The third group is composed of α-nitrocumenes **11–14.** With these compounds, irrespective of solvent, the methyl thioether is first produced and then, by the continued action of the sodium salt of methyl mercaptan, this is converted to the cumene (vide supra). The formation of the methyl thioether presumably derives from a sequence such as is shown for *p*-cyano-α-nitrocumene (eq 15–18).

Chain initiation (eq 15) may be looked upon as an example



of the general reaction of eq 7 or, alternately, the odd electron of the radical anion may largely be delocalized in the *p*-cyanophenyl portion of the system. In either event, there is ample precedent for the second step (eq 16).[11] The third step, collapse of the *p*-cyanocumyl radical with a methyl mercaptide ion to give the radical anion (eq 17), rather than hydrogen abstraction, is rationalized on two grounds. First it is assumed that a *p*-cyanocumyl radical is enough less reactive than a simple alkyl radical that it has difficulty abstracting hydrogen from the methyl mercaptide ion. And, indeed, as we shall see below, even the unsubstituted cumyl radical derived from α-nitrocumene, if it is able to abstract hydrogen from methyl mercaptide ion, does so only with difficulty. Apparently, cumyl radicals are so well stabilized that it is not easy for them to abstract a hydrogen atom from methyl mercaptide ions.

The second assumption is that the radical anion produced in eq 17 is of lower energy than the sulfur radical anion of eq 13 which has its odd electron localized on sulfur. It is significant that the unsubstituted cumyl radical when exposed to methyl mercaptide ion gives very little cumyl methyl sulfide (vide infra); apparently neither the sulfur radical anion corresponding to that of eq 13 nor the unsubstituted radical anion **24** forms easily. The last step of this sequence (eq 18) produces



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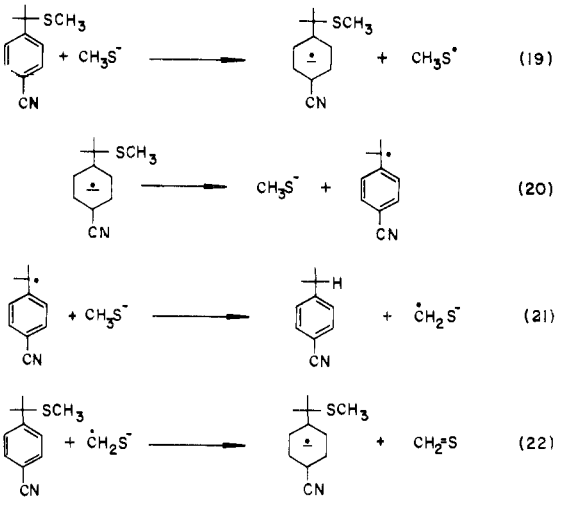
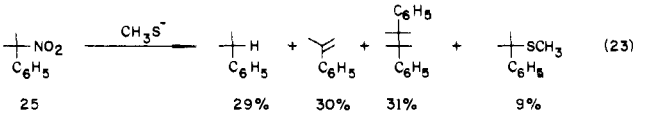
the methyl thioether and regenerates the chain carrying radical anion of *p*-cyano-α-nitrocumene. Thus, with α-nitrocumenes **11–14** the kinetically controlled formation of thioethers is a consequence of the difficulty which cumyl radicals have abstracting a hydrogen atom from the methyl mercaptide ion and, also, of the relatively low energy of the radical anions produced by the collapse of these cumyl radicals with mercaptide ions (eq 17).

The relatively low energy of a radical anion such as that of eq 17 not only brings about rapid formation of thiomethyl ethers but also facilitates their destruction. It will be recalled that cumylic thiomethyl ethers derived from α-nitrocumenes **11–14** are reduced to cumenes by the sodium salt of methyl mercaptan; that transformation is easily understood on the basis of eq 19–22.



It will be noted that the reaction of eq 20 is simply the reverse of the process shown by eq 17. Thus we deal with a rapid, but reversible, combination of the cumylic radical with mercaptide ion followed by the slower, but irreversible, hydrogen abstraction process of eq 21. The concomitantly formed $\dot{C}H_2S^-$ radical anion propagates the chain as shown in eq 22. Thus, while α-nitrocumenes **11–14** follow a pattern all their own, their reactions with the sodium salt of methyl mercaptan can be rendered intelligible on the basis of rather small, and quite reasonable, variations of the mechanisms used to rationalize the chemistry of the first two groups of tertiary nitro compounds.[23]

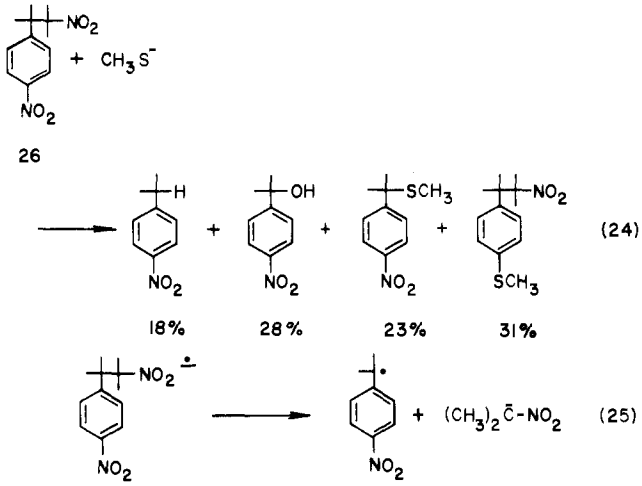
Special Cases. α-Nitrocumene (**25**) differs from the substituted α-nitrocumenes (**11–14**), both as regards products and rate (eq 23). It will be seen that very little thioether is formed,



the major products being derived from dimerization and disproportionation of cumyl radicals. (The essentially identical yields of cumene and α-methylstyrene are taken to mean that little, if any, cumene arises by hydrogen abstraction from the methyl mercaptide ion.) The substantial yield of bicumyl also testifies to the reluctance of a cumyl radical to enter into re-

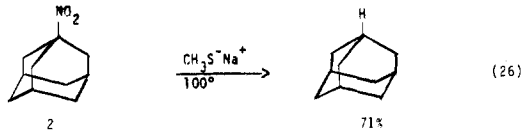
action with methyl mercaptide ion—either by hydrogen abstraction or by combination to form a radical anion. This preference of cumyl radicals for disproportionation and dimerization makes it easy to understand why the reaction of α-nitrocumene is very much slower than that of the other α-nitrocumenes.[24]

Among the β-arylated nitro compounds there is also a special case—the *p*-nitro substituted compound **26.** Although its reaction with the sodium salt of methyl mercaptan has only been explored in a preliminary way, there is no question but that the result is unusual. In HMPA this compound is consumed after 1 h and a complex set of products is produced (eq 24). The first three apparently derive from the fragmentation process of eq 25, which doubtless is facilitated by the relatively



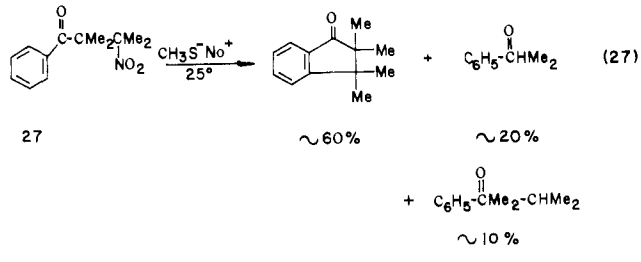
high stability of the *p*-nitrocumyl radical. The fourth compound of eq 24 arises from a hitherto unobserved reaction—displacement of the aromatic nitro group by the methyl mercaptide ion.[25]

1-Nitroadamantane (**2**) is unique in that it fails to react with the sodium salt of methyl mercaptan at room temperature, even after 3 days. However, at 100 °C the reaction of eq 26



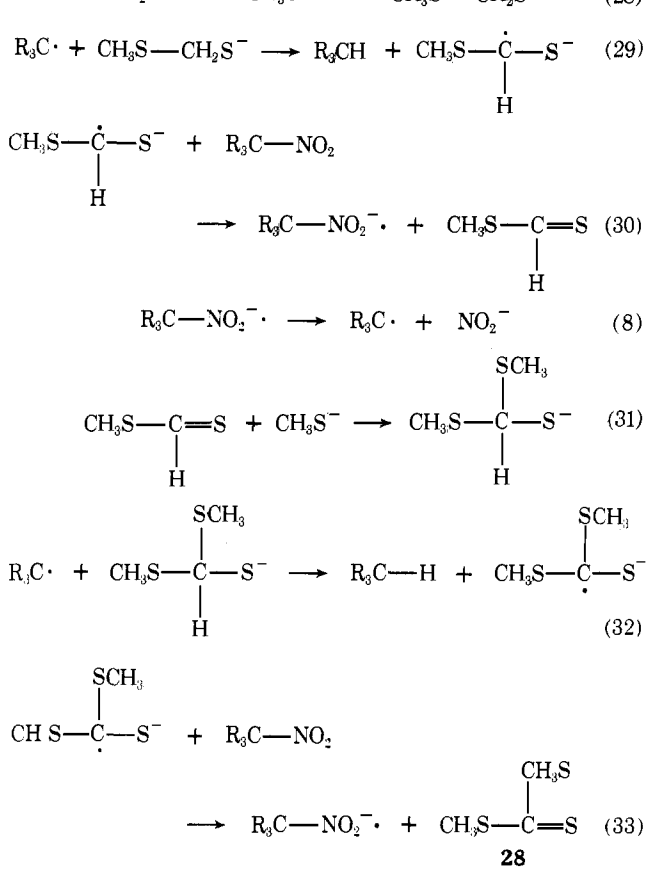
proceeds to completion in 41 h and a 71% yield of adamantane is isolated.[26]

The reaction of a single γ-arylated tertiary nitro compound (**27**) with the sodium salt of methyl mercaptan was examined in rather a preliminary way. As shown in eq 27 cyclization to



the indanone is the major process along with lesser amounts of fragmentation and reduction (cf. Experimental Section).

Primary and Secondary Nitro Compounds. How primary and secondary nitro compounds behave on treatment with the sodium salt of methyl mercaptan is an obvious question for which a definitive answer is not yet available. Preliminary studies reveal that secondary nitro compounds are less reactive than



tertiary nitro compounds and that they do not seem to react cleanly.

The Fate of the Methyl Mercaptide Ion. Finally, a word needs to be said about the fate of the methyl mercaptide ion. This, according to the proposed mechanism, is oxidized to thioformaldehyde (eq 10). But neither thioformaldehyde nor its trimer trithiane is detected. Instead, dimethyl trithiocarbonate (**28**) is produced. The usual workup procedure does not lend itself to the isolation of **28** but in one instance, the reaction of eq 1,[27] dimethyl trithiocarbonate was isolated and characterized. This result is readily explained by a straightforward extension of the radical anion–free radical mechanism of eq 7–10. It is easy to believe that the conversion of thioformaldehyde to dimethyl trithiocarbonate is very rapid indeed.

Experimental Section

Caution: HMPA should be handled with great care since it has recently been found to cause cancer in laboratory animals.[41]

Sodium thiomethoxide is prepared as follows. Under N_2 9.20 g (0.40 mol) of sodium is added to 350 mL of freshly distilled 2-propanol. The mixture is refluxed until the reaction is complete (ca. 5 h) after which heating is discontinued; the flask is promptly fitted with a dry ice condenser and 25 g (0.52 mol) of methyl mercaptan is passed in. 2-Propanol is then removed under reduced pressure at 30–35 °C. When the solution becomes viscous ca. 250 mL of cyclohexane is added and the solvents are removed under reduced pressure. Two additional 250-mL portions of cyclohexane are added and the azeotroping repeated. The resulting white solid is subjected to a vacuum of ca. 1 mm for 0.5 h (rotary evaporator) and then the free-flowing white powder is transferred to a sintered glass funnel (protected by a N_2 blanket), and washed with a total of 500 mL of anhydrous ethyl ether. The solid, still moist with ether, is transferred to a round-bottom flask which is evacuated to ca. 1 mm and heated at 55–60 °C for ca. 15 h (rotary evaporator). The product, a finely divided, free-flowing white powder, is stored under N_2. It has a neut equiv of 71 (calcd, 70). Presumably, replacement of nitro by hydrogen would also occur with salt prepared in situ, but this has not yet been tried.

2-Cyano-2-nitropropane was first prepared in these laboratories

by W. M. Weaver as follows. To a stirred solution at room temperature of urea (19 g), sodium nitrite (14.2 g, 0.21 mol), and 200 mL of DMF was added 2-bromo-2-cyanopropane (20.4 g, 0.137 mol). After 10 days the solution was poured onto 1 L of ice-water and extracted with diethyl ether. The organic extracts were washed with water, dried over anhydrous $MgSO_4$, and then concentrated by distillation through a short column. Distillation at 14 mm and 71–80 °C gave 7.2 g (47% yield) of 2-cyano-2-nitropropane, mp 35.5–36 °C.

Anal. Calcd for $C_4H_6N_2O_2$: C, 42.1; H, 5.30; N, 24.6. Found: C, 42.40; H, 5.53; N, 24.28.

2-(Nitrocyclohexyl)isobutyronitrile (4).[8] A. Preparation. β-Nitronitrile **4** was obtained by treating a solution of the lithium salt of nitrocyclohexane[30] (24.4 g, 180 mmol) in 500 mL of Me_2SO with 2-cyano-2-nitropropane (13.32 g, 120 mmol) for 10 h under N_2 in the light bank.[28] The resulting solution was poured into water and extracted with benzene. The organic phase was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo to yield 27.8 g of a light yellow solid. This, on recrystallization from hexane, gave 20.52 g (87% yield) of a colorless solid: mp 108–109 °C; NMR ($CDCl_3$) δ 1.42 (s, 6 H), 1.0–2.0 (m, 8 H), 2.5–2.9 (m, 2 H); IR (CCl_4) cm^{-1} 2247 (C≡N), 1550 (NO_2).

Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.19; H, 8.21; N, 14.28; mol wt, 196. Found: C, 61.33; H, 8.06; N, 14.07; mol wt, 195.

B. Reaction with Sodium Thiomethoxide. This procedure is representative of the reactions of tertiary nitro compounds with sodium thiomethoxide. The center neck of a 200-mL three-neck flask was fitted with a gas inlet adapter. Each of the other two necks was fitted with an addition tube so constructed that its contents may be emptied into the flask without opening the system, merely by rotating around the joint.[2] One of the addition tubes was charged with compound **4** (0.392 g, 2 mmol) and the other contained sodium thiomethoxide (0.420 g, 6 mmol); a magnetic stirring bar and 20 mL of Me_2SO were placed in the flask. The system was purged of air by evacuating and then bleeding in N_2; this purge was repeated three times.

The flask was placed in the light bank[28] and the sodium thiomethoxide was added. After the salt had dissolved, **4** was added and the solution allowed to stir for 3 h at room temperature. The solution was then poured into water and extracted with diethyl ether and pentane. The organic phase was washed with water and dried over anhydrous $MgSO_4$, and then the solvent was removed by distillation through a short column. A small amount of silica gel was added to the resulting oil and the mixture was placed on top of a silica gel column. Elution with hexane removed low-boiling impurities; further elution with hexane–ether (9:1) followed by removal of solvents by distillation through a short column and finally Kugelrohr distillation at 1 mm and 70 °C gave 0.287 g (95% yield) of VPC- and TLC-pure 2-cyano-2-cyclohexylpropane as a colorless oil: NMR ($CDCl_3$) δ 1.30 (s, 6 H), 1.05–2.1 (m, 11 H); IR (neat) cm^{-1} 2242 (C≡N).

Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.63; H, 11.47; N, 9.40.

C. Dark Reaction. This experiment was a duplicate of the preceding one except that it was conducted in a dark room and the reaction system was completely wrapped in aluminum foil. By VPC analysis 96% of the reaction product was **4** and 4% was 2-cyano-2-cyclohexylpropane. Chromatography on silica gel using hexane–ether (9:1) as eluent gave 0.358 g (91% recovery) of pure **4**, mp 108–109 °C.

D. Di-*tert*-butyl Nitroxide. This experiment was a duplicate of B except that now a four-neck flask containing three addition tubes[2] was employed. The third addition tube contained di-*tert*-butyl nitroxide (0.029 g, 0.20 mmol). By VPC analysis 98% of the reaction product was **4** and 2% was 2-cyano-2-cyclohexylpropane. Chromatography on silica gel using hexane–ether (19:1) gave 0.380 g (97% recovery) of pure **4**, mp 108–109 °C.

E. *m*-Dinitrobenzene. This experiment was a duplicate of the preceding experiment except that *m*-dinitrobenzene (0.027 g, 0.20 mmol) was placed in the third addition tube. By VPC analysis 88% of the reaction product was **4** and 12% was 2-cyano-2-cyclohexylpropane. Chromatography on silica gel using hexane–ether (19:1) gave 0.297 g (76% recovery) of pure **4**, mp 108–109 °C.

F. Nitrobenzene. This experiment was a duplicate of D except that nitrobenzene (0.123 g, 1 mmol) was placed in the third addition tube. By VPC analysis 92% of the reaction mixture was the starting material (**4**) and 8% was 2-cyano-2-cyclohexylpropane. Chromatography on silica gel using hexane–ether (19:1) followed by Kugelrohr distillation at 70 °C and 0.005 mm gave 0.262 g (67% recovery) of pure **4**, mp 108–109 °C.

G. Isolation of Dimethyl Trithiocarbonate (28). The reaction of sodium thiomethoxide (3.50 g, 50 mmol) with the β-nitronitrile **4** (4.90 g, 25 mmol) in 100 mL of HMPA was conducted under N_2 in the light bank[28] for 1.5 h. After the usual workup using pentane for extraction, the solvent was removed by distillation through a short column. By VPC analysis the product consists of 2-cyano-2-cyclohexylpropane contaminated with a small amount of olefin and a low-boiling unknown. Chromatography on Florisil with pentane as eluent followed by removal of solvent in vacuo at 25 °C gave a VPC-pure sample of dimethyl trithiocarbonate. The IR (neat) and NMR ($CDCl_3$) are exact matches with Sadtler IR (20911) and NMR (2883). Exact mass: calcd for $C_3H_6S_3$, 137.963; found, 137.961.

The usual workup procedure did not lend itself to the isolation of this low-boiling liquid; however, in many instances it could be detected by its characteristic unpleasant odor, its intense yellow color, and as a singlet at δ 2.77 in the NMR spectra of the crude reaction products.

***tert*-Nitrooctane[3c] (1).** Sodium thiomethoxide (21.0 g, 300 mmol), *tert*-nitrooctane (**1**, 15.9 g, 100 mmol), 300 mL of HMPA, a N_2 atmosphere, the light bank,[28] and a reaction time of 54 h were employed. The resulting solution was held at 1 mm and the volatile material was collected in a dry ice trap. The 10.1 g thus obtained, by VPC analysis, consisted of 89% isooctane and 11% of two low-boiling olefins. It was filtered through a small amount of silica gel–10% $AgNO_3$ using pentane as the eluent. The filtrate was stirred over 96% sulfuric acid for 6 h, and then was poured onto ice, washed with water, dried, and distilled through a short column to yield 6.3 g (55% yield), bp 92–94 °C. This colorless liquid was pure isooctane as shown by VPC and NMR.

2-Cyano-2,3-dimethyl-3-nitrononane (3). A. Preparation. This was accomplished as follows. 2-Nitrooctane[29] (4.80 g, 0.030 mol) was treated under N_2 in the light bank[28] with 0.028 mol of lithium methoxide (prepared in situ from 0.194 g of lithium and 40 mL of methanol).[30] Concentration in vacuo yielded a light yellow, granular solid which was treated in situ with 2-cyano-2-nitropropane (3.84 g, 0.0336 mol) dissolved in 100 mL of Me_2SO.[8] After 6 h, the reaction mixture was worked up in the usual way using ether and hexane for extraction. The 6.31 g of liquid obtained on removing the solvents was chromatographed on silica gel using hexane–ether (49:1 to 4:1) as eluent. Removal of solvent, followed by Kugelrohr distillation at 80 °C and 0.006 mm, gave 5.10 g (80% yield) of 2-cyano-2,3-dimethylnonane as a colorless oil: NMR ($CDCl_3$) δ 0.65–1.05 (m, 3 H), 1.10–1.50 (m, 8 H), 1.41 (s, 3 H), 1.44 (s, 3 H), 1.60 (s, 3 H), and 1.5–2.8 (m, 2 H); IR (neat) cm^{-1} 2250 (C≡N), 1545 and 1355 (NO_2).

Anal. Calcd for $C_{12}H_{22}N_2O_2$: C, 63.69; H, 9.80; N, 12.38. Found: C, 63.91; H, 10.02; N, 12.26.

B. Reaction with Sodium Thiomethoxide. The cyanonitro compound **3** (1.13 g, 5 mmol), sodium thiomethoxide (1.050 g, 15 mmol), 50 mL of Me_2SO, the light bank, a N_2 atmosphere, and a reaction time of 17 h were employed. After an ether workup, the solvent was removed by distillation through a short column. Chromatography on silica gel using hexane as eluent removed low-boiling impurities; further elution with hexane–ether (9:1) yielded TLC-pure product. Concentration by distillation through a short column, followed by a Kugelrohr distillation at 80 °C and 1 mm, gave 0.831 g (92% yield) of pure 2-cyano-2,3-dimethylnonane as a colorless oil: NMR ($CDCl_3$) δ 0.80–1.15 (m, 6 H); 1.15–1.75 (m, 17 H); IR (neat) cm^{-1} 2242 (C≡N).

Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.30; H, 12.97; N, 7.50.

Ethyl 1-(2-Nitroisopropyl)cyclohexanecarboxylate (5). A. Preparation. Compound **5** was prepared by treating the lithium salt of 2-nitropropane[30] (3.80 g, 20 mmol) dissolved in 50 mL of Me_2SO with ethyl 1-nitrocyclohexanecarboxylate (2.08 g, 10.3 mmol) for 47 h under N_2 in the light bank.[8,31] A benzene–ether workup yielded 2.91 g of a white solid which, after chromatography on silica gel using hexane and hexane–benzene (19:1 to 1:3), gave 2.37 g (94% yield) of a colorless solid, mp 50–53 °C. This was sublimed twice: mp 51.5–53 °C; NMR ($CDCl_3$) δ 1.29 (t, 3 H), 1.61 (s, 6 H), 4.19 (q, 2 H), 1.1–2.4 (m, 10 H); IR (CCl_4) cm^{-1} 1736 (C=O), 1548 (NO_2).

Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.23; H, 8.70; N, 5.76; mol wt, 243. Found: C, 59.07; H, 8.75; N, 5.85; mol wt, 242.

B. Reaction with Sodium Thiomethoxide. Sodium thiomethoxide (0.420 g, 6 mmol), the β-nitro ester **5** (0.486 g, 2 mmol), 20 mL of Me_2SO, a N_2 atmosphere, the light bank, and a reaction time of 24

h were employed. After an ether–pentane workup and removal of solvent, the residue was chromatographed on silica gel using hexane as the initial eluent and, then, hexane–ether (19:1). Solvents were removed by distillation through a short column and the residue was Kugelrohr distilled at 1 mm and 80 °C. This gave 0.328 g (83% yield) of pure ethyl 1-isopropylcyclohexanecarboxylate as a colorless oil: NMR ($CDCl_3$) δ 0.87 (d, 6 H), 1.26 (t, 3 H), 1.00–2.35 (m, 11 H), 4.16 (q, 2 H); IR (neat) cm^{-1} 1715 (C=O).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.66; H, 11.33.

2,3-Dimethyl-2-phenyl-3-nitrobutane (6).[2] A. Reaction with Sodium Thiomethoxide in DMF. Sodium thiomethoxide (0.420 g, 6 mmol), compound **6** (0.414 g, 2 mmol), 20 mL of DMF, the freeze–pump–thaw (FPT) degassing procedure,[2] and a reaction time of 24 h in the light bank[28] were employed. After a pentane workup, chromatography through silica gel–1% $AgNO_3$ using pentane as the eluent, and, finally, Kugelrohr distillation at 60 °C and 1 mm there was obtained 0.258 g (80% yield) of VPC-pure 2,3-dimethyl-2-phenylbutane as a colorless oil: NMR ($CDCl_3$) δ 0.75 (d, 6 H), 1.22 (s, 6 H), 1.92 (septet, 1 H), 7.0–7.4 (m, 5 H).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol wt, 162. Found: C, 88.74; H, 11.42; mol wt, 160.5.

A parallel experiment, on VPC analysis of the crude, was only 85% complete. (Reaction times are not exactly reproducible as one might expect for a chain reaction.)

B. Reaction in DMF—Dark. This experiment was a duplicate of A except that it was conducted in a dark room and the reaction system was completely wrapped in aluminum foil. A pentane workup yielded 0.403 g (97% recovery) of pure **6**, mp 61–62 °C.

C. Reaction of DMF–Di-*tert*-butyl Nitroxide. This experiment was a duplicate of A except that di-*tert*-butyl nitroxide (0.058 g, 0.4 mmol) was added. After a pentane workup, chromatograpy on silica gel using pentane as the eluent gave 0.411 g (99% recovery) of pure **6**, mp 61–62 °C.

D. Reaction in Me_2SO. This experiment was a duplicate of A except that Me_2SO was the solvent. After a pentane workup, the crude product was found, by VPC analysis, to consist of 2,3-dimethyl-2-phenylbutane (36%) and compound **6** (64%). Chromatography on silica gel–1% $AgNO_3$ using pentane as the eluent and, finally, Kugelrohr distillation at 60 °C and 1 mm gave 0.058 g (18% yield) of VPC-pure 2,3-dimethyl-2-phenylbutane. Further elution with pentane–ether (9:1) gave 0.210 g (51% recovery) of the pure starting nitro compound **6**, mp 61–62 °C.

E. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that HMPA was the solvent and the reaction time was 8 h. After a pentane workup, VPC analysis revealed that the reaction was complete. Kugelrohr distillation at 60 °C and 1 mm gave 0.304 g (94% yield) of VPC- and NMR-pure 2,3-dimethyl-2-phenylbutane.

F. Reaction in HMPA—Light Effect. Two experiments, duplicates of E except for a 5-h reaction time, were carried out, one in the light bank,[28] the other in the dark room with the reaction system completely wrapped in aluminum foil. After a pentane workup VPC analysis revealed that the crude product of the light reaction was 87% 2,3-dimethyl-2-phenylbutane and 13% compound **6**; the dark reaction product was 100% **6**. Chromatography of the crude from the dark reaction on silica gel–1% $AgNO_3$ using pentane–ether (9:1) as eluent gave 0.398 g (96% recovery) of pure **6**, mp 61–62 °C. Chromatography of the crude product from the light reaction on silica gel–1% $AgNO_3$ using pentane as eluent, followed by Kugelrohr distillation at 60 °C and 1 mm, gave 0.189 g (59% yield) of VPC- and NMR-pure 2,3-dimethyl-2-phenylbutane. Further elution with pentane–ether (9:1) followed by two sublimations at 1 mm and 50 °C gave 0.041 g (10% recovery) of the pure starting compound (**6**), mp 61–62 °C.

G. Reaction in HMPA—Di-*tert*-butyl Nitroxide Effect. Experiment E was duplicated except that a 3.5-h reaction time was used. A parallel experiment was carried out in which di-*tert*-butyl nitroxide (0.058 g, 0.4 mmol) was present. By VPC analysis the crude product from the control experiment consisted of 2,3-dimethyl-2-phenylbutane (62%) and compound 6 (38%). Chromatography on silica gel with pentane as eluent followed by Kugelrohr distillation at 50 °C and 1 mm gave 0.181 g (56% yield) of VPC- and NMR-pure 2,3-dimethyl-2-phenylbutane. Further elution with pentane–ether (9:1) gave 0.155 g (37% recovery) of pure starting material (**6**), mp 61–62 °C. The crude product from the nitroxide-inhibited experiment by VPC only consisted of starting material and, on chromatographing, 0.405 g (98% recovery) of compound **6**, mp 61–62 °C, was isolated.

2,3-Dimethyl-2-(*p*-cyanophenyl)-3-nitrobutane (7).[2] A. Reaction with Sodium Thiomethoxide in DMF. Sodium thiomethoxide (0.420 g, 6 mmol), compound **7** (0.464 g, 2 mmol), 20 mL of DMF, freeze–pump–thaw (FPT) degassing,[2] and a reaction time of 15 h in the light bank[28] were employed. Benzene workup yielded 0,377 g of crude which, by VPC analysis, was 96% 2,3-dimethyl-2-(*p*-cyanophenyl)-butane and 4% olefin. It was subjected to overnight treatment with 0.4 g of $KMnO_4$, 1.2 g of $MgSO_4 \cdot nH_2O$, 20 mL of acetone, and 4 mL of H_2O at 25 °C. The resulting mixture was poured into saturated aqueous $NaHSO_3$, extracted with benzene, dried, and concentrated in vacuo. Filtration through silica gel using benzene as the eluent, followed by Kugelrohr distillation at 70 °C and 1 mm, gave 0.340 g (91% yield) of pure 2,3-dimethyl-2-(*p*-cyanophenyl)butane as a colorless oil: NMR ($CDCl_3$) δ 0.77 (d, 6 H), 1.26 (s, 6 H), 1.90 (septet, 1 H), 7.25–7.75 (m, 4 H); IR (neat) cm^{-1} 2240 (C≡N).

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.16; H, 9.30; N, 7.56.

B. Reaction in DMF—Dark. This experiment was a duplicate of A except that it was conducted in a dark room and the reaction system was completely wrapped in aluminum foil. A benzene workup yielded 0.455 g of crude which NMR analysis revealed was 98% starting material (**7**) and 2% 2,3-dimethyl-2-(*p*-cyanophenyl)butane. Chromatography on silica gel using benzene–hexane (1:1) as eluent removed the minor component. Further elution with benzene–ether (4:1) gave 0.444 g (96% recovery) of pure starting nitro compound **7**, mp 166–167 °C.

C. Reaction in DMF–Di-*tert*-butyl Nitroxide. This reaction was a duplicate of A except that di-*tert*-butyl nitroxide (0.058 g, 0.4 mmol) was added. The crude product obtained on benzene workup by NMR was pure starting nitro compound (**7**), Chromatography through silica gel gave 0.438 g (94% recovery) of pure starting material (**7**), mp 166–167 °C.

D. Reaction with Sodium Thiomethoxide in Me_2SO. This experiment was a duplicate of A except that Me_2SO was the solvent, the reaction time was 18 h, and the reaction was run on half the scale of A (0.232 g, 1 mmol, of **7**). Benzene workup yielded 0.215 g of crude which by NMR analysis was 35% starting nitro compound **7**, 61% 2,3-dimethyl-2-(*p*-cyanophenyl)butane, and 4% olefin. Clearly, the reaction is distinctly slower in Me_2SO than in DMF.

E. Reaction with Sodium Thiomethoxide in HMPA. Two experiments, duplicates of A except that the solvent was HMPA and the reaction times were 1 and 24 h, were carried out. Benzene workup of the 1-h experiment yielded 0.405 g of crude which, by NMR analysis, was 68% 2,3-dimethyl-2-(*p*-cyanophenyl)butane, 32% 2,3-dimethyl-2-(*p*-cyanophenyl)-3-thiomethoxybutane, and a trace of *p*-cyanocumene. Chromatography through silica gel using benzene–hexane (3:2) followed by Kugelrohr distillation gave 0.240 g (64% yield) of 2,3-dimethyl-2-(*p*-cyanophenyl)butane which by VPC was contaminated with 3% *p*-cyanocumene. Further elution with benzene–ether (99:1 to 9:1) followed by Kugelrohr distillation at 1 mm and 120 °C and finally recrystallization from hexane gave 0.100 g, mp 85–86 °C (22% yield), of pure 2,3-dimethyl-2-(*p*-cyanophenyl)-3-thiomethoxybutane: NMR ($CDCl_3$) δ 1.22 (s, 6 H), 1.50 (s, 6 H), 1.76 (s, 3 H), 7.55 (s, 4 H); IR (KBr) cm^{-1} 2230 (C≡N).

Anal. Calcd for $C_{14}H_{19}SN$: C, 72.07; H, 8.21; S, 13.72; N, 6.00. Found: C, 71.99; H, 8.21; S, 13.60; N, 5.90.

Benzene workup of the 24-h experiment yielded 0.400 g of crude which, by NMR analysis, was 56% 2,3-dimethyl-2-(*p*-cyanophenyl)butane, 44% thioether, and a trace of *p*-cyanocumene. Isolation as in the 1-h experiment gave 0.206 g (55% yield) of 2,3-dimethyl-2-(*p*-cyanophenyl)butane which by VPC analysis was contaminated with 6% *p*-cyanocumene and 0.157 g (34% yield) of pure 2,3-dimethyl-2-(*p*-cyanophenyl)-3-thiomethoxybutane, mp 85–86 °C. Thus, within the experimental error, the 1-h and the 24-h experiments gave the same yields of products in which the nitro group was replaced by hydrogen and by thiomethoxy. It is also of interest that a small, but real, amount of fragmentation occurs.

F. Dark Reaction—HMPA. This experiment was a duplicate of E except that it was conducted in a dark room and the reaction system was completely wrapped in aluminum foil. Benzene workup yielded 0.435 g of crude which, by NMR analysis, was 49% starting material (**7**), 33% 2,3-dimethyl-2-(*p*-cyanophenyl)butane, and 18% 2,3-dimethyl-2-(*p*-cyanophenyl)-3-thiomethoxybutane. Chromatography on silica gel using benzene–hexane (1:1) followed by Kugelrohr distillation at 1 mm and 70 °C gave 0.111 g (30% yield) of 2,3-dimethyl-2-(*p*-cyanophenyl)butane contaminated with ca. 3% *p*-cyanocumene. Further elution, first with benzene and then with ben-

zene–ether (19:1), gave a mixture of the starting nitro compound (**7**) and the thiomethyl ether. This mixture was dissolved in 20 mL of absolute ethanol and to this was added 10 mL of saturated ethanolic mercuric chloride solution. After the solution had stood overnight at 0 °C precipitation did not occur and, therefore, the ethanol was removed in vacuo and the residue was stirred with 100 mL of benzene–ether (9:1) for 15 min at 25 °C. The resulting solution was decanted from insoluble material and concentrated to dryness. The residue was treated with saturated aqueous sodium sulfide for 12 h and then extracted with benzene. The benzene phase was washed with water, dried, and then concentrated to dryness. This gave 0.263 g of impure starting nitro compound **7** which, after two recrystallizations from methanol, yielded 0.122 g (26% recovery) of pure **7**, mp 165.5–166.5 °C.

The material which did not dissolve in 100 mL of benzene–ether (9:1) was extracted with 100 mL of ether, the ether phase was isolated by decantation, the solvent was removed, and the residue was treated with saturated aqueous sodium sulfide for 12 h. The resulting mixture was extracted with benzene, the benzene extracts were washed with water and dried, and then the benzene was removed. This gave 0.017 g of NMR-pure 2,3-dimethyl-2-(*p*-cyanophenyl)-3-thiomethoxybutane (4% yield).

G. Reaction in HMPA–Di-*tert*-butyl Nitroxide. This reaction was a duplicate of E except that di-*tert*-butyl nitroxide (0.058 g, 0.4 mmol) was included. Benzene workup gave NMR-pure starting nitro compound **7**. Chromatography on silica gel using benzene–hexane (1:4 to 4:1) removed trace impurities and further elution with benzene–ether (19:1) yielded 0.445 g (96% recovery) of pure **7**, mp 166–167 °C.

2,3-Dimethyl-2-(*p*-benzoylphenyl)-3-nitrobutane (8).[2] A. Reaction with Sodium Thiomethoxide in DMF. Sodium thiomethoxide (0.420 g, 6 mmol), compound **8** (0.622 g, 2 mmol), 20 mL of DMF, FPT degassing,[2] and a reaction time of 18 h in the light bank[28] were employed. Benzene workup yielded 0.538 g of crude product which, by NMR analysis, was 86% 2,3-dimethyl-2-(*p*-benzoylphenyl)butane, 8% olefin, and 5% unknown. Treatment with $KMnO_4$ in acetone (vide supra) followed by filtration of a benzene solution through silica gel gave 0.404 g (76% yield) of 2,3-dimethyl-2-(*p*-benzoylphenyl)butane as a colorless solid: mp 68–69 °C; NMR ($CDCl_3$) δ 0.77 (d, 6 H), 1.27 (s, 6 H), 1.88 (septet, 1 H), 7.2–7.9 (m, 9 H); IR (KBr) cm^{-1} 1655 (C=O).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.67; H, 8.12.

B. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that the solvent was HMPA and the reaction time was 0.25 h. Benzene workup yielded 0.666 g of crude which, by NMR analysis, was 96% methyl thioether and 4% 2,3-dimethyl-2-(*p*-benzoylphenyl)butane. Chromatography on silica gel using hexane–benzene mixtures eluted trace impurities and then elution with benzene–ether (19:1) eluted 0.016 g of NMR-pure 2,3-dimethyl-2-(*p*-benzoylphenyl)butane. Further elution gave 0.545 g (87% yield) of 2,3-dimethyl-2-(*p*-benzoylphenyl)-3-thiomethoxybutane as a colorless oil: NMR ($CDCl_3$) δ 1.25 (s, 6 H), 1.53 (s, 6 H), 1.75 (s, 3 H), 7.3–7.9 (m, 9 H); IR (neat) cm^{-1} 1660 (C=O).

Anal. Calcd for $C_{20}H_{24}SO$: C, 76.89; H, 7.74; S, 10.24. Found: C, 77.08; H, 7.53; S, 10.33.

2,3-Dimethyl-2-[3′,5′-bis(trifluoromethyl)phenyl]-3-nitrobutane (9).[2] A. Reaction with Sodium Thiomethoxide in DMF. Sodium thiomethoxide (0.420 g, 6 mmol), compound **9** (0.686 g, 2 mmol), 20 mL of DMF, freeze–pump–thaw degassing,[2] and a reaction time of 20 h in the light bank[28] were employed. A pentane workup, treatment with $KMnO_4$ in acetone (vide supra), and finally Kugelrohr distillation gave 0.500 g (84% yield) of VPC-pure 2,3-dimethyl-2-[3′,5′-bis(trifluoromethyl)phenyl]butane as a colorless oil: NMR ($CDCl_3$) δ 0.78 (d, 6 H), 1.32 (s, 6 H), 1.94 (septet, 1 H), 7.65–7.95 (m, 3 H).

Anal. Calcd for $C_{14}H_{16}F_6$: C, 56.38; H, 5.41; F, 38.21; mol wt, 298.3. Found: C, 56.48; H, 5.50; F, 38.12; mol wt, 299.1.

B. Reaction with Sodium Thiomethoxide in HMPA. This experiment is a duplicate of A except that the solvent was HMPA and the reaction time was 2 h. Pentane workup yielded 0.614 g of crude product which, by VPC analysis, was 53% 2,3-dimethyl-2-[3′,5′-bis(trifluoromethyl)phenyl]butane and 45% thioether. Chromatography on silica gel using pentane as eluent followed by Kugelrohr distillation gave 0.268 g (45%) of VPC-pure 2,3-dimethyl-2-[3′,5′-bis(trifluoromethyl)phenyl]butane. Further elution with benzene–hexane mixtures followed by Kugelrohr distillation gave 0.257 g (37% yield) of 2,3-dimethyl-2-[3′,5′-bis(trifluoromethyl)phenyl]-3-thiomethoxybutane: NMR ($CDCl_3$) δ 1.25 (s, 6 H), 1.58 (s, 6 H), 1.74 (s, 3 H), 7.77 (s, 1 H), 7.97 (s, 2 H).

Anal. Calcd for $C_{15}H_{18}F_6S$: C, 52.31; H, 5.27; F, 33.10; S, 9.31; mol wt, 344.4. Found: C, 52.50; H, 5.37; F, 33.00; S, 9.21; mol wt, 345.2.

2,3-Dimethyl-2-(*p*-benzenesulfonylphenyl)-3-nitrobutane (10).[2] A. Reaction with Sodium Thiomethoxide in DMF. Sodium thiomethoxide (1.050 g, 15 mmol), compound **10** (1.73 g, 5 mmol), 50 mL of DMF, freeze–pump–thaw degassing,[2] and a reaction time of 8 h in the light bank[28] were employed. Benzene workup yielded 1.76 g of crude which by NMR analysis was 92% 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane and 8% olefin. Treatment with $KMnO_4$ in acetone (vide supra), chromatography on silica gel using benzene–ether (19:1) as eluent, and finally recrystallization from hexane gave 1.22 g (83% yield) of 2,3-dimethyl-2-(p-benzenesulfonylphenyl)butane as a colorless solid: mp 79.5–80.5 °C; NMR ($CDCl_3$) δ 0.73 (d, 6 H), 1.20 (s, 6 H), 1.90 (septet, 1 H), 7.20–7.65 (m, 5 H), 7.75–8.05 (m, 4 H).

Anal. Calcd for $C_{18}H_{22}SO_2$: C, 71.50; H, 7.33; S, 10.58. Found: C, 71.50; H, 7.34; S, 10.41.

B. Reaction with Sodium Thiomethoxide in Me_2SO. This experiment was a duplicate of A except that Me_2SO was the solvent, the reaction time was 6 h, and the reaction was run on one-fifth the scale (1 mmol of **10**). By NMR analysis, the reaction mixture was 82% **10** and 18% 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane. Clearly this reaction is slower in Me_2SO than in DMF.

C. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that HMPA was the solvent, the reaction time was 1 h, and the reaction was run on one-fifth the scale (1 mmol of **10**). A benzene workup gave 0.360 g of crude product which, by NMR analysis, was 41% 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane and 59% thioether. The mixture was dissolved in 6 mL of absolute ethanol and treated with 10 mL of saturated ethanolic $HgCl_2$ for 24 h at 3 °C. The resulting precipitate was isolated by filtration and then was stirred overnight with a saturated aqueous Na_2S solution. The organic material was isolated by extraction with benzene, washed with H_2O, and dried and the solvent was removed. This gave 0.155 g (45% yield) of 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)-3-thiomethoxybutane as a colorless solid: mp 131.5–132.5 °C; NMR ($CDCl_3$) δ 1.20 (s, 6 H), 1.48 (s, 6 H), 1.69 (s, 3 H), 7.25–8.05 (m, 9 H).

Anal. Calcd for $C_{19}H_{24}S_2O_2$: C, 65.50; H, 6.94; S, 18.37. Found: C, 65.67; H, 6.98; S, 18.14.

The ethanolic filtrate remaining from the $HgCl_2$ treatment of the crude product was poured into water and extracted with benzene. After the solution was washed with water and dried and the benzene was removed, the residue was treated with $KMnO_4$ in acetone (vide supra). After recrystallization from methanol–water 0,069 g (23% yield) of pure 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane, mp 79.5–80.5 °C, was obtained.

A duplicate experiment, except for a reaction time of 24 h, was carried out. A benzene workup yielded 0.385 g of crude which, by NMR analysis, was 45% 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane and 55% thioether. Isolation as before gave 0.153 g (44% yield) of pure 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)-3-thiomethoxybutane, mp 131.5–132.5 °C, and 0.054 g (18% yield) of pure 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane, mp 79.5–80.5 °C. The virtually identical results obtained in the 1-h and in the 24-h experiments show that conversion of the thiomethyl ether to 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane does not occur at a significant rate under the reaction conditions.

***p*-Cyano-α-nitrocumene (11).[10] A. Reaction with Sodium Thiomethoxide in Me_2SO.** Sodium thiomethoxide (2.10 g, 30 mmol), *p*-cyano-α-nitrocumene (**11**, 1.90 g, 10 mmol), 30 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 2 h were employed. Benzene workup and recrystallization of the crude product from pentane gave 1.76 g (93% yield) of *p*-cyano-α-thiomethoxycumene: mp 44–44.5 °C; NMR ($CDCl_3$) δ 1.70 (s, 6 H), 1.77 (s, 3 H), 7.67 (s, 4 H); IR (KBr) cm^{-1} 2230 (C≡N).

Anal. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.85; N, 7.32; S, 16.73. Found: C, 69.16; H, 6.84; N, 7.42; S, 16.89.

B. Di-*tert*-butyl Nitroxide Effect in Me_2SO. Sodium thiomethoxide (0.420 g, 6 mmol), compound **11** (0.380 g, 2 mmol), 20 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 4 h were employed. A duplicate experiment, except for the inclusion of di-*tert*-butyl nitroxide (0.058 g, 0.4 mmol), was also carried out. Benzene workup of the control experiment, followed by Kugelrohr

distillation at 50 °C and 1 mm, gave 0.335 g (88% yield) of *p*-cyano-α-thiomethoxycumene, mp 44–44.5 °C. The crude product from the nitroxide-inhibited reaction by NMR analysis contained only starting material and chromatography on silica gel using benzene–ether (19:1) gave 0.356 g (94% recovery) of pure **11**, mp 60.5–61.5 °C.

C. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that the solvent was HMPA and that the reaction was run for 16 h in the dark. The usual workup followed by chromatography on silica gel–1% $AgNO_3$ using benzene–ether (49:1) as the eluent gave 1.189 g (82% yield) of *p*-cyanocumene as a colorless oil: n^{20}_D 1.5196 (lit.[32] n^{20}_D 1.5194); NMR ($CDCl_3$) δ 1.22 (d, 6 H), 2.93 (septet, 1 H), 7.2–7.7 (m, 4 H); IR (neat) cm^{-1} 2240 (C≡N).

D. Di-*tert*-butyl Nitroxide Effect in HMPA. An experiment which duplicated B, except that the solvent was HMPA and the reaction time was 0.5 h, was carried out. A parallel experiment was also performed except that now 0.058 g (0.4 mmol) of di-*tert*-butyl nitroxide was present. Workup of the first experiment gave a crude product which by NMR analysis was 58% *p*-cyano-α-thiomethoxycumene, 34% *p*-cyanocumene, and 8% *p*-cyano-α-methylstyrene. This material (0.364 g) was chromatographed on silica gel using a 3:2 hexane–benzene mixture as eluent. The first fractions (0.077 g) consisted of *p*-cyanocumene and *p*-cyano-α-methylstyrene; this material was subjected to the $KMnO_4$–acetone treatment (vide supra) and then Kugelrohr distilled. In this way 0.043 g (15% yield) of NMR-pure *p*-cyanocumene was isolated.

Continued elution using hexane–benzene (2:3) followed by Kugelrohr distillation at 90 °C and 1 mm gave 0.156 g (41% yield) of pure *p*-cyano-α-thiomethoxycumene, mp 44–44.5 °C. Benzene workup of the nitroxide-inhibited reaction gave 0.392 g of crude product which, by NMR analysis, was 93% starting material (**11**) and 7% *p*-cyano-α-thiomethoxycumene. Chromatography on silica gel–1% $AgNO_3$ using hexane–benzene (4:1 to 1:4) removed trace impurities. Further elution with benzene gave 0.352 g (93% recovery) of pure *p*-cyano-α-nitrocumene (**11**), mp 60.5–61.5 °C.

***p*-Benzoyl-α-nitrocumene (12).[10] A. Reaction with Sodium Thiomethoxide in Me_2SO.** Sodium thiomethoxide (2.10 g, 30 mmol), the nitro ketone **12** (2.69 g, 10 mmol), 30 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 1 h were employed. Benzene workup followed by chromatography on silica gel using benzene–ether (9:1) gave 2.46 g (91% yield) of pure *p*-benzoyl-α-thiomethoxycumene as a colorless oil: NMR ($CDCl_3$) δ 1.70 (s, 6 H), 1.78 (s, 3 H), 7.3–8.0 (m, 9 H); IR (neat) cm^{-1} 1655 (C=O).

Anal. Calcd for $C_{17}H_{18}SO$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.37; H, 6.75; S, 11.63.

B. Reaction with Sodium Thiomethoxide in HMPA. This reaction is a duplicate of A except that the solvent was HMPA and the reaction time was 12 h in the dark. Benzene workup, followed by chromatography on silica gel–1% $AgNO_3$ using ether–benzene (1:99) as the eluent, gave 1.80 g (80% yield) of pure *p*-benzoylcumene as a colorless oil: NMR ($CDCl_3$) δ 1.27 (d, 6 H), 2.96 (septet, 1 H), 7.2–8.0 (m, 9 H);[33] IR (neat) cm^{-1} 1655 (C=O).

3,5-Bis(trifluoromethyl)-α-nitrocumene (13).[10] A. Reaction with Sodium Thiomethoxide in Me_2SO. Sodium thiomethoxide (0.630 g, 9 mmol), compound **13** (0.903 g, 3 mmol), 30 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 2 h were employed. Pentane workup followed by Kugelrohr distillation at 50 °C and 1 mm gave 0.876 g (97% yield) of pure 3,5-bis(trifluoromethyl)-α-thiomethoxycumene: NMR ($CDCl_3$) δ 1.73 (s, 6 H), 1.78 (s, 3 H), 7.75 (s, 1 H), 8.07 (s, 2 H).

Anal. Calcd for $C_{12}H_{12}F_6S$: C, 47.68; H, 4.00; F, 37.71; S, 10.61. Found: C, 47.73; H, 4.29; F, 37.44; S, 10.69.

B. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that HMPA was the solvent and the reaction was conducted for 16 h in the dark. Following a pentane workup, the pentane was removed by distillation through a short column, Kugelrohr distillation of the residue at room temperature and 1 mm gave 0.594 g (77% yield) of VPC-pure 3,5-bis(trifluoromethyl)cumene as a colorless oil. The NMR spectrum (CCl_4) duplicates that of an authentic sample: δ 1.32 (d, 6 H), 3.06 (septet, 1 H), 7.66 (s, 3 H).[34]

***p*-Benzenesulfonyl-α-nitrocumene (14).[10] A. Reaction with Sodium Thiomethoxide in Me_2SO.** Sodium thiomethoxide (2,10 g, 30 mmol), the nitrosulfone **14** (3.05 g, 10 mmol), 30 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 0.25 h were employed. Benzene workup followed by recrystallization from hexane–benzene gave 2.98 g (98% yield) of pure *p*-benzenesulfonyl-α-thiomethoxycumene: mp 94.5–95 °C; NMR ($CDCl_3$) δ 1.66 (s, 6 H), 1.73 (s, 3 H), 7.4–8.2 (m, 9 H).

Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.74; H, 5.92; S, 20.88. Found: C, 62.77; H, 5.91; S, 20.89.

B. Product Stability in Me_2SO. Two experiments, duplicates of A except that one-tenth the scale (0.305 g, 1 mmol, of **14**) was employed and that the reaction times were 2 h and 24 h, were carried out. By NMR analysis of the crude products the 2- and 24-h reactions gave *p*-benzenesulfonyl-α-thiomethoxycumene contaminated with 2 and 20%, respectively, of *p*-benzenesulfonylcumene. Thus, replacement of thiomethoxy by hydrogen occurs at a slow but measurable rate in Me_2SO.

C. Reaction with Sodium Thiomethoxide in HMPA. This experiment was a duplicate of A except that the solvent was HMPA, the reaction time was 10 h, and it was conducted in room light. Benzene workup followed by chromatography on silica gel–1% $AgNO_3$ using benzene–ether (17:3) gave 2.00 g (80% yield) of pure *p*-benzenesulfonylcumene: mp 98.5–99.5 °C (lit.[35] mp 97.5–98.5 °C); NMR ($CDCl_3$) δ 1.15 (d, 6 H), 2.90 (m, 1 H), 7.20–7.60 (m, 5 H), 7.78–8.15 (m, 4 H).

D. Light Effect in HMPA. Sodium thiomethoxide (0.105 g, 1.5 mmol), nitrosulfone **14** (0.153 g, 0.5 mmol), 5 mL of HMPA, a nitrogen atmosphere, the light bank,[28] and a reaction time of 1 min were employed. A duplicate experiment, on twice the scale (0.306 g, 1 mmol, of **14**), was conducted in a dark room with the reaction system completely wrapped in aluminum foil. Benzene workup of the solution produced by the light reaction gave 0.154 g of crude which by NMR analysis, was 96% *p*-benzenesulfonyl-α-thiomethoxycumene and 4% *p*-benzenesulfonylcumene; the crude product from the dark reaction weighed 0.286 g and by NMR analysis it was 47% starting nitrosulfone **14** and 52% *p*-benzenesulfonyl-α-thiomethoxycumene. Thus there is an unambiguous light effect on this reaction. Also noteworthy is the fact that the nitrosulfone is completely consumed in less than 1 min; and, finally, it is also of interest that even with such a short reaction time a discernible amount of replacement of nitro by hydrogen is observed. Whether this last product derives directly from the nitrosulfone or is mainly produced from the thioether cannot be stated at present.

2,3-Dimethyl-2-(*p*-benzenesulfonylphenyl)-3-thiomethoxybutane (15). A. Stability in DMF. Sodium thiomethoxide (0.174 g, 0.5 mmol), thioether **15** (0.105 g, 1.5 mmol), 5 mL of DMF, a N_2 atmosphere, the light bank,[28] and a reaction time of 48 h were employed. Benzene workup yielded 0.151 g (87% recovery) of crude which has the NMR spectrum and the melting point of the pure starting thioether **15**. Thus little, if any, reaction occurred in 48 h.

B. Stability in HMPA. This experiment was a duplicate of A except that HMPA was the solvent and the reaction was run on twice the scale (0.348 g, 1 mmol, of **15**). Benzene workup yielded 0.281 g of crude which, by NMR analysis, was 95% starting thioether **15** and 5% 2,3-dimethyl-2-(*p*-benzenesulfonylphenyl)butane. Thus, even in HMPA the thioether is only very slowly reduced by the thiomethoxide ion.

α-Nitrocumene (25).[2] Sodium thiomethoxide (0.420 g, 6 mmol), α-nitrocumene (0.330 g, 2 mmol), 20 mL of HMPA, a nitrogen atmosphere, the light bank,[28] and a reaction time of 30 h were employed. An ether–pentane workup gave 0.223 g of crude product which by NMR analysis was 29% cumene, 30% α-methylstyrene, 39% bicumyl, and 9% α-thiomethoxycumene.

2,3-Dimethyl-2-(*p*-nitrophenyl)-3-nitrobutane (26).[36] A. Reaction with Sodium Thiomethoxide. Sodium thiomethoxide (0.420 g, 6 mmol), compound **26** (0.504 g, 2 mmol), 20 mL of HMPA, freeze–pump–thaw degassing, and a reaction time of 0.25 h were employed. A parallel experiment was allowed to run for 1 h, Benzene workup of the 0.25-h experiment gave 0.477 g of crude material which, by NMR analysis, was 68% starting material and 32% 2,3-dimethyl-2-(*p*-thiomethoxyphenyl)-3-nitrobutane. Similar workup of the 1-h experiment gave 0.394 g of crude material which, by NMR analysis, was 31% 2,3-dimethyl-2-(*p*-thiomethoxyphenyl)-3-nitrobutane, 18% *p*-nitrocumene, 28% *p*-nitrocumyl alcohol, and 23% *p*-nitro-α-thiomethoxycumene.

B. Effect of Light. Two experiments, duplicates of A, were run for 0.25 h, one in the light bank[28] and the other in a dark room with the reaction system wrapped in aluminum foil. Benzene workup of the light reaction yielded 0.468 g of crude which, by NMR analysis, consisted of starting material (77%) and 2,3-dimethyl-2-(*p*-thiomethoxyphenyl)-3-nitrobutane. Workup of the dark reaction gave 0.495 g which, by NMR analysis, consisted of starting material (73%)

and 27% 2,3-dimethyl-2-(*p*-thiomethoxyphenyl)-3-nitrobutane. The two reaction products were combined and chromatographed on silica gel using benzene–hexane mixtures as eluent. The initial fractions contained 0.212 g of a solid, mp 81–83 °C, which after Kugelrohr distillation at 120 °C and 1 mm and two recrystallizations from hexane yielded 0.147 g (16% yield) of pure 2,3-dimethyl-2-(*p*-thiomethoxyphenyl)-3-nitrobutane: mp 86–87 °C; NMR ($CDCl_3$) δ 1.48 (s, 6 H), 1.50 (s, 6 H), 2.47 (s, 3 H), 7.24 (s, 4 H); IR (KBr) cm^{-1} 1515 and 1340 (NO_2).

Anal. Calcd for $C_{13}H_{19}SNO_2$: C, 61.64; H, 7.56; N, 5.53; S, 12.63; mol wt, 253. Found: C, 61.84; H, 7.43; N, 5.47; S, 12.60; mol wt, 254.

1-Nitroadamantane (2).[37] Sodium thiomethoxide (0.420 g, 6 mmol), 1-nitroadamantane (0.362 g, 2 mmol), 20 mL of HMPA, a nitrogen atmosphere, the light bank,[28] a reaction time of 42 h, and a temperature of 100 °C were employed. A pentane workup yielded 0.268 g, which was chromatographed on silica gel using pentane as the eluent and was then Kugelrohr sublimed. This gave 0.178 g (71% yield) of a white, crystalline material which by NMR, IR, and VPC is pure adamantane.

A duplicate experiment except that the reaction time was 3 days and the temperature was ca. 30 °C was also carried out. Workup yielded 0.301 g of crude material which, by VPC analysis, was starting material contaminated with less than 1% adamantane.

α-Nitroisobutyrophenone[38] was prepared by treating a Me_2SO solution (50 mL) of sodium nitrite (3.80 g, 54.8 mmol) with a solution of α-bromoisobutyrophenone (11.35 g, 50 mmol) in 25 mL of Me_2SO under a N_2 atmosphere. After 3 h a benzene–ether workup gave 9.53 g of an oil. Chromatography on silica gel using hexane–benzene mixtures gave 8.54 g (89% yield) of pure α-nitroisobutyrophenone as a colorless oil: bp 67 °C (1 mm); NMR (CCl_4) δ 1.88 (s, 6 H), 7.48 (m, 3 H), 7.75 (m, 2 H); IR (neat) cm^{-1} 1701 (C=O), 1550 and 1344 (NO_2).

Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.25; H, 5.83; N, 7.18.

2,2,3-Trimethyl-3-nitrobutyrophenone (27). A. Preparation.[39] The lithium salt of 2-nitropropane[30] (1.90 g, 20 mmol), α-nitroisobutyrophenone (1.95 g, 10 mmol), a nitrogen atmosphere, room light, and a reaction time of 5 h were employed. A benzene–ether workup, followed by three recrystallizations from hexane, yielded 1.55 g (66% yield) of pure 2,2,3-trimethyl-3-nitrobutyrophenone: mp 55–56 °C; NMR (CCl_4) δ 1.34 (s, 6 H), 1.72 (s, 6 H), 7.37 (s, 5 H).

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95; mol wt, 235. Found: C, 66.65; H, 7.45; N, 6.20; mol wt, 237.

B. Reaction with Sodium Thiomethoxide. Sodium thiomethoxide (0.210 g, 3 mmol), compound **27** (0.235 g, 1 mmol), 10 mL of Me_2SO, a nitrogen atmosphere, the light bank,[28] and a reaction time of 2 h were employed. A pentane–ether workup gave 0.165 g of material which, by NMR analysis, was 63% 2,2,3,3-tetramethylindanone, 24% isobutyrophenone, and 13% of a compound whose NMR suggests that it may be 2,2,3-trimethylbutyrophenone.

Pure 2,2,3,3-tetramethylindanone was isolated during a study which preceded the present investigation.[40] Compound **27** (3.92 g, 14 mmol), sodium thiophenoxide (4.62 g, 35 mmol), 70 mL of DMF, 70 mL of triethylamine, a nitrogen atmosphere, illumination by a sunlamp, and a reaction time of 23 h were employed. A pentane workup, followed by removal of the solvent by distillation through a short column, gave 1.33 g which, by VPC analysis, was 25% isobutyrophenone and 75% of a higher boiling material. Preparative VPC (on a 15% SE-30 column) gave 0.31 g (15% yield) of isobutyrophenone (identified by IR and NMR) and 0.94 g (36% yield) of 2,2,3,3-tetramethylindanone as a colorless oil: bp 137–138 °C (9 mm); NMR (CCl_4) δ 1.02 (s, 6 H), 1.20 (s, 6 H), 7.20–7.77 (m, 4 H); IR (CCl_4) cm^{-1} 1718 (C=O).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.66; H, 8.66.

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References and Notes

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(13) The reactions of compounds **7** and **10** with $CH_3S^-Na^+$ were also carried out in Me_2SO. In both instances the results paralleled those obtained in DMF, i.e., the nitro group is replaced by hydrogen and none of the methyl thioether can be detected. Also, in these two cases the reaction in Me_2SO was distinctly slower than in DMF.
(14) At 0.5 h the product of the uninhibited reaction in HMPA is a mixture consisting principally of the methyl thioether (58%) and *p*-cyanocumene (34%). After some hours (cf. Experimental Section) all of the thioether is converted into *p*-cyanocumene as shown in eq. 2. In the nitroxide-inhibited reaction ca. 5% of the methyl thioether is present after 0.5 h but no *p*-cyanocumene is detected.
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(19) With **20**, and also with the *p*-benzoylated and the *p*-sulfonated radicals, it is easy to see that spirane formation is facilitated by delocalization of the odd electron. It is less obvious why two trifluoromethyl groups serve to favor spirane formation but it appears that this is indeed the case.
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(23) The reactions of methyl thioethers with the sodium salt of methyl mercaptan will be described for their own sake in a subsequent paper.
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(25) Nitrobenzenes substituted by electron-withdrawing groups readily undergo nucleophilic displacement of the nitro group (ref 10). To the best of our knowledge, however, this is the first example of the replacement of an aromatic nitro group by methyl mercaptide ion in a nitrobenzene which does not have an electron-withdrawing group on the ring.
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