Tetrahedron Vol. 42, No. 9, pp. 2563 to 2570, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

COMPETITION BETWEEN ADDITION AND REDOX PROCESSES IN REACTIONS OF NITROARENES WITH LITHIUM-DITHIANES

Giuseppe Bartoli,* Renato Dalpozzo, Loris Grossi, Paolo E. Todesco

Istituto Chimica Organica, Università, V.le Risorgimento 4,
40136 Bologna, Italy

(*Received in UK* 3 *March* 1986)

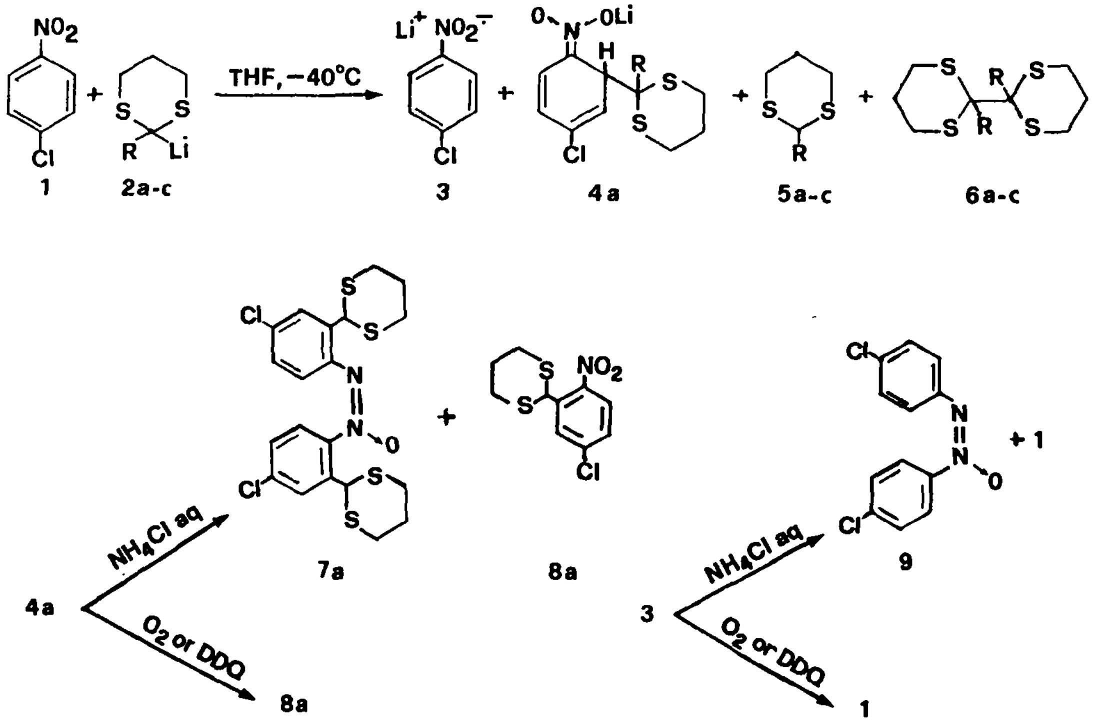
Abstract. The reaction of 2-lithio-1,3-dithianes with nitroarenes gives 2-(or 4-)[(1,3-dithian)-2'-yl]cyclohexa-3,5(or 2,5-)-diene-1-nitronate compounds (conjugate-addition products), free nitroarene radical anions (redox products), 1,3-dithianes and 2,2'-bis-(1,3-dithianes). The conjugate-addition and redox products were converted in the respective nitroaromatic compounds by oxidation in situ with O_2 or DDQ. The ratio between addition and redox products increases with decrease of temperature. 2-H-2-Lithio-1,3-dithiane can give both 1,4- and 1,6-addition products, while 2-methyl- and 2-phenyl derivatives give only 1,6-addition products. A mechanism involving an s.e.t. from lithium dithianes to nitroarenes followed by various decay routes is suggested for the two radical species.

The introduction of a masked carbonylic function into an activated aromatic ring by using 1,3-dithiane-anions represents an important goal in organic chemistry; however, this synthetic strategy has shown serious unresolved problems.[1] Lithium-dithianes are reported to give addition to 2-bromopyridine, but redox on mono- and dinitro-halobenzenes.[2] Recently, mechanistic investigations on factors affecting reaction product distribution has led to correct some erroneous opinions on the action of carbanions toward strong electron-acceptor substrates.[3] A significant example is represented by the conjugate-addition of alkyl Grignard reagents to mononitroarenic systems, recently discovered.[4] These remarks led us to investigate on the possibility to observe conjugate-addition also in the reaction of lithium dithianes with mononitroarenes.

At variance with previous reports, the reaction of 4-chloronitrobenzene (**1**) with 2-lithio-1,3-dithiane (**2a**), in THF at -40°C, gives large amounts of 1,4-addition product (**4a**), together with free 4-chloronitrobenzene radical anion (**3**), 1,3-dithiane (**5a**) and 2,2'-bis-(1,3-dithiane) (**6a**) (see Scheme I).

The decomposition of the reaction mixture with NH_4Cl allowed to isolate the following compounds: 1-chloro-3-[(1,3-dithian)-2'-yl]-4-nitrobenzene (**8a**; 19.5% yields) and its correspondent azoxy compound **7a** (18.5%) (i.e. the disproportionation products of the unstable nitronate adduct **4a**);[4] the starting nitroarene **1** (26.5%) and its correspondent azoxy derivative **9** (18.5%) (i.e. the disproportionation products of the radical anion **3**);[5] 1,3-dithiane (19%) and bis-dithiane **6a** (20%). The global yields accounted for the 80% and the 70% of the reactants **1** and **2a** respectively.

Scheme I



a; R=H; b; R=Me; c; R=Ph

The adduct **4a** and the radical anion 3 can be converted into the corresponding aromatic nitroderivatives **8a** and 1 respectively, by bubbling oxygen in the reaction mixture. Selective oxidation without affecting the sulphur atoms of dithiane moiety, can be also carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), but this alternative method seems to be less efficient.

The formation of radical anion 3 in the reaction mixture was confirmed by ESR spectroscopy.[6] Its amount was estimated to account for the 35% of the starting material 1, which is slightly below the quantity of 4-chloronitrobenzene recovered after O_2 quenching. This difference might suggest the occurence of a competitive metallation process of lithium-dithiane at the 2-position of 4-chloronitrobenzene[7] or, alternatively, a partial disproportionation of the radical anion in THF.[5a] The former hypothesis was ruled out by deuterium labelling experiments (see experimental section), but nothing can be confirmed about the latter one, owing to the large experimental errors affecting the quantitative measurements of the radical anion concentration. However, the almost constant concentration of radical anion 3, analyzed over a large period of time for measurements carried out at different temperatures, seems to exclude the disproportionation process to a large extent.

Reaction product distribution is strongly influenced by temperature. As temperature decreases, the efficiency of lithium-dithiane to give conjugate-addition increases to the detriment of redox process (see Table 1).

Table 1. - Efficiency in conjugate addition of 2-lithium-1,3-dithiane with 1-chloro-4-nitrobenzene at various temperature.[a]

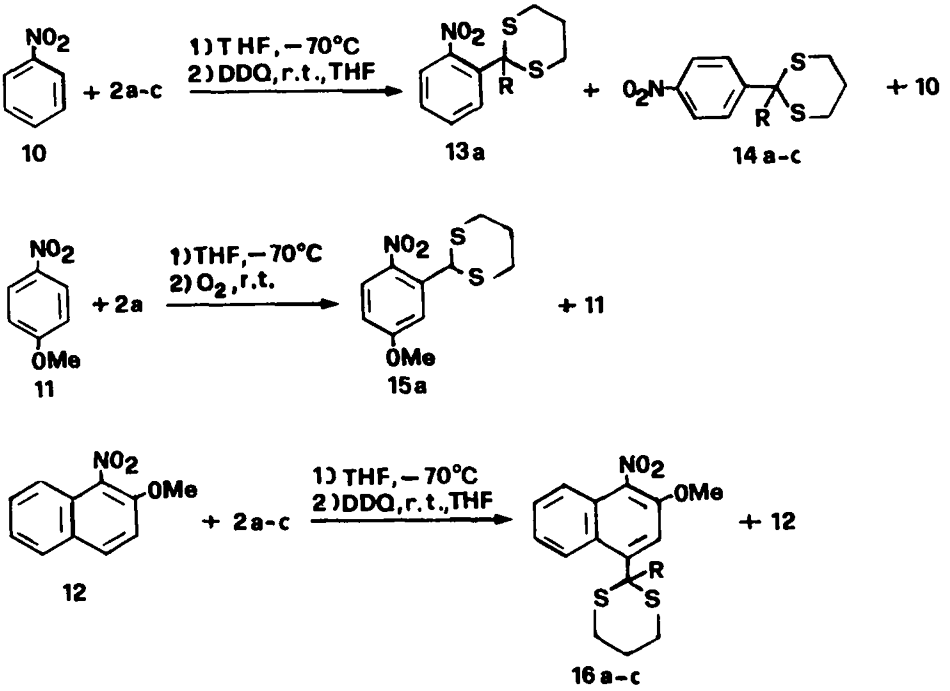
Temperature (°C)	Recovered products[b] 1(%)	4(%)	Percentage of 9 detected by ESR in the reaction mixture
- 5	67	13	52
-40	41	39	35
-70	21	48	18

[a] Reactions carried out at the desired temperature for 10 minutes and then treated with oxygen at room temperature.

[b] Yields of isolated products.

In order to give some generality to the above results, reaction between 4-chloronitrobenzene and other lithium dithianes [2-methyl (**2b**) and 2-phenyl (**2c**)] as well as between lithium dithianes **2a-c** and various nitroarenes, such as nitrobenzene (**10**), 4-nitroanisole (**11**) and 2-methoxy-1-nitronaphthalene (**12**) (see Scheme II), were carried out at -70°C in THF.

Scheme II



In every experiment, the relative amounts between addition and redox processes were determined by oxidative quenching methods. The obtained results are summarized in table 2.

The following points must be outlined:

i) the 2H-lithium dithiane **2a** can give both 1,4- and 1,6-addition; the 2-methyl and 2-phenyl derivatives **2b-c** are able to give only 1,6-addition.

ii) In all cases, including 4-chloronitrobenzene system, no products arising from nucleophilic replacement of the hetero-substituent, such as chlorine and methoxy groups, were observed. These findings indicate that the reaction follows the same regioselectivity rules established for reaction with alkyl Grignard reagents:[5b] i.e. the preferred attack at unsubstituted positions, when the irreversible formation of a carbon-carbon bond is involved in a nucleophilic attack to an aromatic ring.

iii) Oxygen is a very good oxidizing agent for 1,4-addition products, but it is completely inefficient for 1,6-addition products; in same cases, DDQ is less efficient than oxygen for the 1,4-products, but it is able to oxidize the 1,6-products.

Table 2. Competition between conjugate-addition and redox process in the reaction of some nitroarenes with various lithium-dithianes, in THF at -70°C.

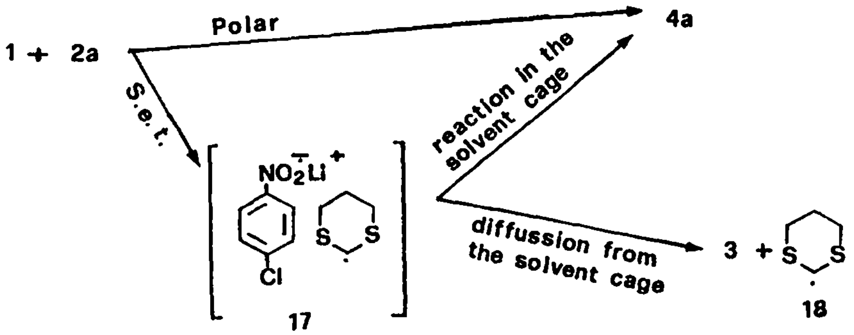
Nitroarene	Lithium-dithiane	Quenching	Product and Yield 1,4-addition (%)	Product and Yield 1,6-addition (%)	Yield (%) of Recovered Starting Material
1	**2b**	O_2[a]	**8b** (0)	-	78
1	**2c**	O_2[a]	**8c** (0)	-	93
10	**2a**	O_2[a]	**13a** (41)	**14a** (0)	26
10	**2a**	DDQ[b]	**13a** (39)	**14a** (29)	27
10	**2b**	DDQ[b]	**13b** (0)	**14b** (54)	43
10	**2c**	DDQ[b]	**13c** (0)	**14c** (18)	75
11	**2a**	O_2[a]	**15a** (41)	-	34
12	**2a**	DDQ[b]	-	**16a** (51)	39
12	**2b**	DDQ[b]	-	**16b** (55)	37
12	**2c**	DDQ[b]	-	**16c** (40)	35

[a] By bubbling O_2 in the reaction mixture. [b] By adding a THF solution of DDQ (1.4 eq) into the reaction mixture.

A straightforward interpretation of the present results is not possible, because it is related to the vexed question whether the addition product is originated from a single-electron-transfer (s.e.t.) or a polar pathway.

In scheme III, a general mechanistic picture is illustrated for the reaction of 4-chloronitrobenzene (**1**) with 2-lithio-1,3-dithiane (**2a**).

Scheme III



A) $3 + 18 \xrightarrow{\text{non-geminate recombination}} 4a$

B) $18 + 18 \longrightarrow 6a$

C) $18 + \text{SolvH} \longrightarrow 5a$

A 4-chloronitrobenzene anion dithian-2-yl radical pair is formed from an s.e.t. interaction between the nitroarene and the organolithium compound. Its geminate recombination gives the nitronate adduct **4a**.[8] Alternatively the two radical species can diffuse from the solvent cage, to give the free radicals 3 and 18. The dithianyl radical 18 can follow three different reaction pathways: it can react, in a non-geminate recombination, with a free nitroarene radical anion to give the adduct **4a** (eq. A); with another molecule of dithianyl radical to give bis-dithiane **6a** (eq. B); or with the solvent to give the dithiane **5a**. On the other hand, the adduct **4a** may arise from a polar attack of the dithianyl anion on the 4-chloronitrobenzene.

Cage reactions are expected to be favoured at low temperatures, since the diffusion coefficient decreases with decreasing temperature.[3a,9] In a fashion of an s.e.t. mechanism, the adduct **4a** and the radical anion 3 are typical in-cage and out-of-cage products respectively. The positive effect of low reaction temperatures on addition-product yields to the detriment of redox process is a strong support for an s.e.t. pathway. Further supporting evidence is provided by the influence of the substituent at the 2-position of lithium dithiane on reaction product distribution. If we assume a polar character for addition reaction and an s.e.t. for redox process, the dramatic enhancement of the redox compound 3 in the reaction of 4-chloronitrobenzene with substituted dithiane anions **2b-c** must be ascribed to their greater ability to promote s.e.t. reaction than the unsubstituted **2a**.[10] However, the yield sequences **2b** > **2a** > 2c and **2b** ≥ **2a** > 2c observed for 1,6-addition products, in nitrobenzene and 2-methoxy-1-nitronaphthalene system respectively, seems to be completely in disagreement with this interpretation.

If we assume an s.e.t. pathway for the whole of the reaction, the inefficiency of **2b** and 2c to give 1,4-addition product can be explained in terms of steric hindrance of the derived radical to collapse at **ortho**-position of a nitroarene radical anion. In other words, in a system having only an **ortho** reactive position, such as 4-chloronitrobenzene, the steric repulsion of bulky 2-methyl or 2-phenyl-1,3-dithian-2-yl radical with the oxygen atoms of the nitro-group of the radical anion delays the geminate recombination. Therefore, the geminate partners can dissociate and diffuse in the solvent.

The probability of an efficient collision between two radical species in singlet state, when they return into the solvent cage is less than that shown when the same radicals are directly generated in the solvent cage by an s.e.t. process. In fact, in the former situation, the radical pair is formed with random geometries and it may be expected to undergo many collisions before finding a favourable one.[8] In the latter situation, because of the electron transfer from the dithianyl radical to the nitro group, the two species are generated close to the reaction centre with a favourable geometry. Thus, if all the radical pairs escape a geminate recombination and diffuse in the reaction medium, there is a very low probability that nitroarene radical anion can scavenge the dithianyl radicals. In fact, the rate of decay of a dithianyl radical **via** dimerization or hydrogen abstraction (see eq. B and C, scheme III) can be estimated to occur close to diffusion-controlled rate.[11] Therefore, a large amount of dithianyl radical will have an independent decay, although cross-coupling (eq. A, scheme III) is statistically favoured by the absence of an independent decay of radical anion.

In a system having only a **para** reactive position, such as 2-methoxy-1-nitronaphthalene, the bulky dithianyl radicals, which migrate from the region in which they are formed to the poor-hindered **para** position, can easily collapse at this position. The ratio between radical pairs which give the addition product and those which escape geminate recombination is essentially determined by the relative stability of the dithianyl radicals, as reflected by the yield sequence reported in table 2.

Finally, on the basis of the π-spin density distribution,[12] one may expect that the **ortho** and **para** positions of a nitrobenzene radical anion have comparable chances to be attacked by a non-hindered alkyl radical. Data reported in table 2 for the reaction of nitrobenzene with the less hindered lithium dithiane **2a**, show, in fact, that the 1,4:1,6-addition product ratio (39:29) is fairly in agreement with the value (2:1) predicted by statistical factors. In the reaction with the more hindered lithium-dithianes **2b–c**, the steric repulsions at the **ortho**-position favour the collapsing of the derived radicals at the **para**-carbon.

To sum up, the assumption that addition products arise substantially from in-cage reactions, and redox processes from out-of-cage reactions, can be a convincing approach to interpretate the interaction between strong bases and high electrophilic substrates, on the basis of a unifying mechanism. Furthermore, this interpretation is in good agreement with the existence of a polar-s.e.t. mechanistic spectrum, as recently proposed in the electron shift theory.[13]

At this point in time, the reaction, at -70°C, seems interesting for synthetic purposes, for the absence of alternative methods.

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian XL-100 instrument. Carbon and Proton shifts are given from Me_4Si in $CDCl_3$ solutions. E.s.r. spectra were recorded with a Varian E-104 spectrometer, and mass spectra with a Jeol JMS-D100 mass spectrometer.

Materials: THF was purified as previously described.[3a] The commercial nitrobenzene (**10**); 4-nitro anisole (**11**), 1,3-dithiane (**5a**) 2-methyl-1,3-dithiane (**5b**), 4-chloronitrobenzene (**1**) were recrystallized or re-distilled before use. 1-Nitro-2-methoxy naphthalene (**12**)[14] and 2-phenyl-1,3-dithiane (**5c**)[15] were prepared and purified by reported methods. The commercial n-butyl lithium was titred by Bergbreiter's method[16] before every experiment.

Reaction of nitroarenes 1, 10, 11 and 12 with lithium-dithianes 2a–c. General procedure.

A solution of a nitroarene (10 mmol) in 20 ml of THF was added dropwise, under stirring and nitrogen atmosphere, at the appropriate temperature, to 15 ml of a THF solution of a lithium-dithiane (12 mmol), prepared from n-butyl lithium and the corresponding 1,3-dithiane according to Corey and Seebach's method.[17] After ten minutes the reaction mixture was quenched with one of the following methods:

Method A. A saturated, oxygen-free, aqueous solution of NH_4Cl was added dropwise at the reaction mixture, at room temperature. The reaction was stirred for 4 hours and then extracted with diethyl ether, dried over Na_2SO_4, evaporated under reduced pressure and submitted to a flash-chromatographic separation on a silica-gel column.

Method B. Dry oxygen was bubbled into the stirred reaction mixture, for 10 minutes, at room temperature. The reaction mixture was extracted with diethyl ether, dried over Na_2SO_4, evaporated under reduced pressure and submitted to a flash-chromatographic separation on a silica-gel column.

Method C. 15 ml of a THF solution of DDQ (13 mmol) was added dropwise to the stirred reaction mixture. The reaction was allowed to warm at room temperature, stirred for a hour, diluted with diethyl ether. The mixture was filtered, and the filtrate was evaporated under reduced pressure and submitted to a flash-chromatographic purification on a silica-gel column.

Reaction of 4-chloronitrobenzene (1) and 2-lithio-1,3-dithiane (2a) at -40°C.

Reactions carried out as above described were quenched with methods A, B or C, giving the following elution order and product amount after elution with light petroleum (b.p. 40-60°): diethyl ether 98:2.

Method A. 4,4'-Dichloroazoxybenzene (**9**, 0.41 g); 4-chloronitrobenzene (**1**, 0,42 g); 1,3-dithiane (**5a**, 0.50 g); 1-chloro-3-[(1,3-dithian)-2'-yl]-4-nitrobenzene (**8a**, 0.54 g); 2,2'-bis-(1,3-dithiane) (**6a**, 0.45 g); 4,4'-dichloro-2,2'-bis-[(1,3-dithian)-2"-yl]-azoxybenzene (**7a**, 0.93 g). Products **1** and **5a** were identified by comparison with authentic samples; products **9**[18] and **6a**[19] by comparing their physical data with the literature.
Physical data for products **8a** and **7a** follow:

8a: mp 109-11°C; ^{1}H-NMR, δ ($CDCl_3$); 1.67-2.32 (m,2H,$-CH_2-$); 2.60-3.10 (m,4H,$-CH_2S-$); 5.85 (s,1H,CH); 7.33 (dd,1H,H-6; $J_{2,6}$=2 Hz, $J_{5,6}$=9 Hz); 7.79 (d,1H,H-5); 7.82 (d,1H,H-2); ^{13}C-NMR, ppm ($CDCl_3$), 24.82 ($-CH_2-$); 32.05 ($-CH_2S-$); 45.34 (-CH-); 126.23, 129.16, 130.85, 135.51 and 140.01 (arom); m/e 275-77 ($M^{\cdot +}$) 258-60, 200, 106; (Found: C, 43.6; H, 3.6; N, 5.0; S, 23.1; Cl, 12.9%, $C_{10}H_{10}ClNO_2S_2$ requires C, 43.56; H, 3.65; N, 5.08; S, 23.25; Cl, 12.86%).

7a: mp 100°C dec; ^{1}H-NMR, δ ($CDCl_3$) 1.66-2.20 ($m,4H,-CH_2-$); 2.52-3.33 ($m,8H,-CH_2S-$); 5.67 and 5.92 (s,1H+1H,-CH-); 7.20-7.88 and 8.53-8.77 (m,5H+1H,arom); ^{13}C-NMR, ppm ($CDCl_3$), 24.79 and 24.98 ($-CH_2-$); 31.88 and 31.97 ($-CH_2-S-$); 44.99 and 45.07 (-CH-); 123.38, 125.57, 128.53, 129.17, 129.45, 130.24, 134.01, 135.96, 136.96, 138.47 and 138.90 (arom) (Found: C, 47.9; H, 4.1; N, 5.5; S, 25.3; Cl, 14.0%; $C_{20}H_{20}Cl_2N_2OS_4$ requires C, 47.71; H, 4.00; N, 5.56; S, 25.47; Cl, 14.08%).

Method B. 1 (0.65 g); **5a** (0.42 g); **8a** (1.08 g); **6a** (0.60 g).

Method C. 1 (0.50 g); **8a** (0.73 g).

Temperature effect on the reaction between 1 and 2a.

The reaction carried out at -5°C and -70°C and quenched with method B gave the following amounts of starting material 1 and 1,4 addition product **8a** respectively: 1 (1.06 g) and **8a** (0.46 g); 1 (0.33 g) and **8a** (1.32 g).

Reaction of 1 with 2-methyl (2b) and 2-phenyl-2-lithio-1,3-dithiane (2c) at -70°C.

In the title reaction, carried out as above described and quenched with method B, we were able to isolate only large amount of starting material 1 (1.23 g for the reaction with **2b**; 1.46 g, 2c).

Reaction of nitrobenzene (10) with lithium-dithianes (2a-c) at -70°C.

Reactions of 10 and **2a** carried out as above described were quenched with methods B or C, giving the following elution order and product amounts after elution with light petroleum (b.p. 40-60°): diethyl ether 95:5.

Method C. Starting material (10, 0.33 g); 2-[(1,3-dithian)-2'-yl]-nitrobenzene (**13a** 0.94 g); 4-|(1,3-dithian)-2'-yl|-nitrobenzene (**14a**; 0.70 g). Physical data for compounds **13a** and **14a** follow:

13a: mp 117-9°C; ^{1}H-NMR δ ($CDCl_3$); 1.70-2.40 ($m,2H,-CH_2-$); 2.63-3.43 ($m,4H,-SCH_2-$); 5.83 (s, 1H,-SCHS-); 7.30-8.00 (m,3H,arom). (Found: C, 49.9; H, 4.6; N, 5.8; S, 23.4%; $C_{10}H_{11}NO_2S_2$ requires: C, 49.79; H, 4.60; N, 5.81; S, 23.53%).

14a: mp 124-6°C; ^{1}H-NMR δ ($CDCl_3$) 1.83-2.33 ($m,2H,-CH_2-$); 2.60-3.33 ($m,4H,-SCH_2-$); 5.30 (s,1H, $-SCH_2S-$); 7.60-7.93 and 8.20-8.48 (A_2B_2 syst., J=9.0 Hz, 4H,arom). (Found: C, 49.7; H, 4.6; N, 5.8; S, 23.6%: $C_{10}H_{11}NO_2S_2$ requires: C, 49.79; H, 4.60; N, 5.81; S, 23.53%).

Method B. 10 (0.32 g); **13a** (0.99 g); no amount, even in traces, of **14a** was isolated by this method.

The reaction of 10 with **2b** followed by decomposition of the reaction mixture according to method C gave the following products: starting material (10; 0.53 g); 4-[(2-methyl-1,3-dithian)-2'-yl]-nitrobenzene (**14b**, 1.38 g).

Under the same procedure, reaction of 10 with **2c** gave the following products: starting material (10; 0.92 g); 4-[(2-phenyl-1,3-dithian)-2'-yl]-nitrobenzene (**14c**; 0.57 g). Physical data for compounds **14b** and **14c** follow:

14b: mp 119-21°C; ^{1}H-NMR δ ($CDCl_3$) 1.67-2.13 ($m,2H,-CH_2-$); 1.77 ($s,1H,CH_3$); 2.47-3.07 (m,4H, $-SCH_2-$); 7.93-8.30 (m,A_2B_2 syst,4H,arom). (Found: C, 51.8; H, 5.1; N, 5.4; S, 25.2%; $C_{11}H_{13}NO_2S_2$ requires C, 51.76; H, 5.13; N, 5.49; S, 25.08%).

14c: mp 117-9°C; ^{1}H-NMR δ ($CDCl_3$) 1.77-2.23 ($m,2H,-CH_2-$); 2.57-2.95 ($m,4H,-SCH_2-$); 7.17-8.33 (m,9H,arom). (Found: C, 60.4; H, 4.8; N, 4.5; S, 20.2%; $C_{16}H_{15}NO_2S_2$ requires C, 60.56; H, 4.77; N, 4.41; S, 20.17%).

Reaction of 4-nitroanisole (11) and 2a at -70°C.

The reaction carried out as above described was quenched with method B, giving, after elution with light petroleum (b.p. 40-60°): diethyl ether 80:20, the following products: starting material (11, 0.52 g); 3-[(1,3-dithian)-2'-yl]-4-nitroanisole (**15a**; 1.11 g).

Physical data for compound **15a** follow: mp 98-100°C; ^{1}H-NMR δ ($CDCl_3$) 1.83-2.42 ($m,2H,-CH_2-$); 2.66-3.47 ($m,4H,-SCH_2-$); 3.90 ($s,3H,OCH_3$); 6.10 (s,1H,-SCHS-); 6.90 (dd,1H,H6, $J_{2,6}$=2.5 Hz; $J_{5,6}$=9.0 Hz); 7.36 (d,1H,H2); 8.03 (d,1H,H5). (Found: C, 48.8; H, 4.8; N, 5.2; S, 23.6%; $C_{11}H_{13}NO_3S_2$ requires C, 48.71; H, 4.83; N, 5.16; S, 23.60%).

Reaction of 2-methoxy-1-nitronaphthalene (12) with lithium dithianes 2a-c at -70°C.

The reaction of 12 with **2a** carried out as above described was quenched with method C giving the following products after elution with light petroleum (b.p. 40-60): diethyl ether 75:25 : starting material (12, 0.79 g); 4-[(1,3-dithian)-2'-yl)]-2-methoxy-1-nitronaphthalene (**16a**, 1.64 g). Under the same experimental procedure the reaction with **2b** and **2c** gave the following products respectively: starting material (12, 0.75 g); 4-[(2-methyl-1,3-dithian)-2'-yl]-2-methoxy-1-nitronaphthalene (**16b**, 1.84 g); starting material (12, 0.71 g); 4-[(2-phenyl-1,3-dithian)-2]-methoxy-1-nitronaphthalene (**16c**, 1.59 g).

Physical data for unknown compounds **16a,b,c** follow:

16a: mp 137-9°C; ^{1}H-NMR δ (CDCl$_3$): 2.00-2.40 (m,2H,-CH$_2$-); 2.85-3.32 (m,4H,-CH$_2$S-); 4.09 (s,3H, OCH$_3$); 5.93 (s,1H,-SCHS-); 7.48-7.82 and 8.18-8.40 (m,4H+1H,arom). (Found: C, 56.0; H, 4.8; N, 4.3; S, 20.0%; $C_{15}H_{15}NO_3S_2$ requires C, 56.07; H, 4.71; N, 4.36; S, 19.92%).

16b: mp 185-7°C; ^{1}H-NMR δ(CDCl$_3$); 1.87-2.30 (m,2H,-CH$_2$-); 2.20 (s,3H,CH$_3$); 2.70-3.05 (m,4H, -SCH$_2$-); 4.03 (s,3H,OCH$_3$); 7.23-7.73 and 9.07-9.33 (m,3H+1H,arom); 8.22 (s,1H,H5). (Found: C, 57.4; H, 5.1; N, 4.2; S, 19.0%; $C_{16}H_{17}NO_3S_2$ requires C, 57.31; H, 5.11; N, 4.18; S, 19.09%).

16c: mp 220-2°C; ^{1}H-NMR δ(CDCl$_3$): 1.88-2.33 (m,2H,-CH$_2$-); 2.70-3.12 (m,4H,-SCH$_2$-); 4.10 (s,3H, OMe); 7.00-7.90 and 8.03-8.40 (m,8H+2H,arom). (Found: C, 63.6; H, 4.9; N, 3.5; S, 16.0%; $C_{21}H_{19}NO_3S_2$ requires C, 63.47; H, 4.82; N, 3.53; S, 16.10%).

E.s.r. experiments: Qualitative analysis: A sample was prepared, under nitrogen atmosphere, by filling some drops of the reaction mixture between 4-chloronitrobenzene and 2-lithio-1,3-dithiane in a U-tube and then subjected to vacuum by the freeze-thaw technique. This apparatus allowed us to obtain the best conditions to record a well resolved spectrum of the 4-chloronitrobenzene radical anion **3**, characterized by the h.f.s. constants[6] a_N=10.78, a_{2H}=3.55, a_{2H}=1.25 gauss. Quantitative measurements: A weighted amount of the two reactants was introduced, under nitrogen atmosphere, into a U-tube, each in their separate chamber. The sealed sample-tube was placed in a cold-bath, for ten minute durations, the reactants mixed, and then introduced in a precooled cavity of the EPR spectrometer; all these operations were performed, for the selected temperatures (Table 1), under thermostatic conditions. Absolute radical **3** concentrations were determined by double integration followed by calibration against a solution containing a known concentration of the diphenylpicrylhydrazyl free radical.

Deuterium labelling experiments. A reaction of 4-chloronitrobenzene with 2-lithio-1,3-dithiane carried out at -40°C as above described was quenched with an oxygen-free solution of 5% CH$_3$COOD in D$_2$O. The reaction mixture was extracted with CH$_2$Cl$_2$ the organic layer was washed with a saturated aqueous solution of NaHCO$_3$ and then dried with Na$_2$SO$_4$, evaporated under reduced pressure and submitted to a chromatographic separation on a silica-gel column (light petroleum (b.p. 60-40°): diethyl ether 98:2 as eluant). The same products were obtained and in similar yields, as from method A. No deuterium incorporation was revealed by NMR-analysis except for a 10% in the 1,3-dithiane.

REFERENCES AND NOTES

1. B.T. Groebel, D. Seebach, Synthesis, 357 (1977).
2. W. Baarschers, T.L. Loh, Tetrahedron Lett., 3483, (1971).
3. a. G. Bartoli, M. Bosco, G. Cantagalli, R. Dalpozzo, F. Ciminale, J.Chem.Soc., Perkin Trans. II, 773, (1985); b. E.C. Ashby, J.R. Bowers Jr., J.Am.Chem.Soc., **103**, 2242 (1981).
4. G. Bartoli, Acc.Chem.Res., **17**, 109 (1984).
5. a. D. Behar, P. Neta, J.Phys.Chem., **85**, 690 (1981); b. G. Bartoli, M. Bosco, A. Melandri, A.C. Boicelli, J.Org.Chem., **44**, 2087 (1979).
6. K. Nakamura, Bull.Chem.Soc. Japan, **40**, 1 (1967).
7. G. Kobrich, P. Buck, Angew.Chem.Int.Ed.Eng., **5**, 1044 (1966).
8. J.F. Garst, C.D. Smith, J.Am.Chem.Soc., **98**, 1526 (1976).
9. D.C. Nonhebel, J.M. Tedder, J.C. Walton, "Radicals", ed. Cambridge University Press, Cambridge, 1979.
10. This assumption can be made on the basis of the following argument: electron transfer from carbanions is expected to be facilitated by low oxidation potential and high stability of the derived radicals. 2-Methyl-2-lithio-1,3-dithiane is more basic than 2-H-derivative and, as a consequence, the oxidation potential for the former is lower, and gives a slightly more stable radical. The 2-phenyl derivative is less basic, but the derived radical is much more stable. See also E. Juaristi, B. Gordillo, D.M. Aparicio, Tetrahedron Lett., **26**, 1927 (1985).
11. C. Gaza, B.C. Gilbert, J.Chem.Soc., Perkin Trans. II, 763 (1979).
12. W.M. Gulick Jr., J.Am.Chem.Soc., **94**, 29 (1972).
13. A. Pross, Acc.Chem.Res., **18**, 212 (1985).
14. E. Baltazzi, C.R. Hebd.Seances Acad.Sci., **230**, 2207 (1950).
15. D. Seebach, B.W. Erickson, G. Singh, J.Org.Chem., **31**, 4303 (1966).
16. D.E. Bergbreiter, E. Pendergrass, J.Org.Chem., **46**, 219 (1981).
17. E.J. Corey, D. Seebach, J.Org.Chem., **40**, 231 (1976).
18. a. Beil., **16**, II, 315; b. H. Suhr, Chem.Ber., **96**, 1720 (1963).
19. D.R. Williams, D.L. Coffen, P.E. Garret, R.N. Schwartz, J.Chem.Soc.(B), 1132 (1968).