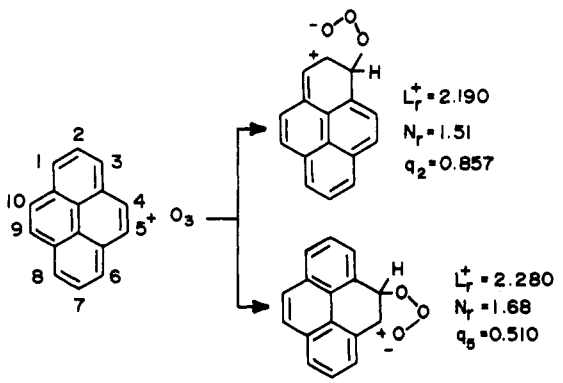
Scheme III



ucts. Steric or electronic factors which militate against cyclization will favor the reverse reaction; this reversal will then lead to other σ-complexes that can cyclize more readily, thus resulting in formation of products not consistent with attack by ozone at the "most favorable" atom. This is diagramatically represented for pyrene in Scheme III. Both the HMO atom localization and PMO reactivity number parameters slightly favor attack at position 1 relative to position 4. Subsequent 1,2,3-trioxolane formation would occur via bonding between the negatively charged terminal oxygen and an accessible positively charged carbon. When initial ozone attack is at position 4, position 5 maintains a large amount of positive charge (low charge density, q) and cyclization would be expected to be rapid. However, if the initial attack occurs at position 1, position 2 has less positive character, cyclization would be slower, and more reversal could occur. Thus the observed products found would be those expected from attack at the C_4–C_5 bond.

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Registry No. Benzene, 71-43-2; triphenylene, 817-59-4; naphthalene, 91-20-3; phenanthrene, 85-01-8; chrysene, 218-01-9; pyrene, 129-00-0; 1,2-benzanthracene, 56-55-3; perylene, 198-55-0; anthracene, 120-12-7.

Substitution Reactions of Nitrothiophenes. 6. Disparate Mechanisms for Substitution Reactions at Neopentyl Carbons Bearing 4- and 5-Nitrothienyl Groups[1,2]

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The reaction of the (5-nitro-2-thienyl)- and (4-nitro-2-thienyl)neopentyl chlorides (**9** and **10**) with *p*-toluenesulfinate, azide, and *p*-toluenethiolate ions proceeds smoothly and in high yield (70–95%) under mild conditions (20 °C, Me_2SO) to give the sulfones **14** and **15**, the azides **16** and **17**, and the sulfides **18** and **19**, respectively. The mechanisms of these substitutions are quite different, however. The substitutions in the 5-nitro series take place by the $S_{RN}1$ mechanism, whereas those in the 4-nitro series take place by the ionic S_N(AEAE) process, which involves initial attack of a nucleophile at the 5-position of the thiophene ring.

Nucleophilic substitution at a neopentylic carbon is a notoriously difficult process and is strongly sterically hindered under conditions which favor the S_N2 mechanism.[3] We have found that the benzylic substrate **1**, under

$ArCH(X)Bu^t$

	Ar	X
1	Ph	Cl
2	p-$O_2NC_6H_4$	Cl
3	p-$O_2NC_6H_4$	PhS
6	m-$O_2NC_6H_4$	Cl
7	p-$O_2NC_6H_4$	p-$MeC_6H_4SO_2$
8	m-$O_2NC_6H_4$	p-$MeC_6H_4SO_2$

S_N2 conditions, e.g., sodium benzenethiolate in Me_2SO, is extremely resistant to nucleophilic attack.[4] The *p*-nitrobenzylic analogue **2**, on the other hand, reacts very smoothly and gives a near quantitative yield of the sulfide **3**. Both **1** and **2** are sterically hindered because the benzylic carbon is also part of a neopentyl group. In similar fashion the lithium salt **4** of 2-nitropropane readily reacts

Scheme I

$$ArCR^1R^2X + A^- \longrightarrow [ArCR^1R^2X]^{-\cdot} + A^\cdot \quad (1)$$

$$[ArCR^1R^2X]^{-\cdot} \longrightarrow Ar\dot{C}R^1R^2 + X^- \quad (2)$$

$$Ar\dot{C}R^1R^2 + A^- \longrightarrow [ArCR^1R^2A]^{-\cdot} \quad (3)$$

$$[ArCR^1R^2A]^{-\cdot} + ArCR^1R^2X \longrightarrow ArCR^1R^2A + [ArCR^1R^2X]^{-\cdot} \quad (4)$$

$Li^+ {}^-CMe_2NO_2$ (**4**) $\qquad$ p-$O_2NC_6H_4COBu^t$ (**5**)

with **2** to give the ketone **5**, whereas the chloride **1** is completely unreactive.[5] The substitution reactions of **2** have been shown[4,5] to be examples of the $S_{RN}1$ reaction,[6] which, for benzylic substrates, is given in Scheme I. More

(1) (a) Supported by Grants C73-15098 and C79-15554 from The Australian Research Grants Scheme. (b) Abstracted, in part, from the Ph.D. Thesis of Peter J. Newcombe, The University of Sydney, Sept 1980. (c) For the previous paper in this series see ref 2.
(2) Newcombe, P. J.; Norris, R. K. *Aust. J. Chem.* **1982**, *35*, 973.
(3) March, J. "Advanced Organic Chemistry: Reactions, Mechanism and Structure", 2nd ed; McGraw-Hill: New York, 1977; pp 315–317.
(4) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1979**, *32*, 1487.
(5) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1976**, *29*, 2621.
(6) For reviews see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. Norris, R. K. In "The Chemistry of Functional Groups"; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1983; Supplement D, Chapter 16. Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

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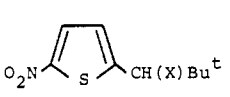
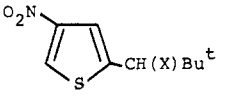
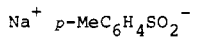
recently we have found that the *m*-nitro neopentyl chloride **6** also undergoes substitution by the $S_{RN}1$ mechanism but under more vigorous conditions and much more slowly than the *p*-nitro compound **2**.[7] For example, the sulfone **7** is formed in 86% yield in 2 h from the chloride **2** (Me_2SO at 50 °C)[4] whereas the sulfone **8** is formed in only 24% yield after 7 days from chloride **6** [in the more effective solvent, $(Me_2N)_3PO$, at 50 °C].[7]

As part of our studies of the reactions of nitrothiophenes and particularly of 4- and 5-nitrothenylic derivatives with nucleophiles[2,8,9] we undertook the preparation of the chlorides **9** and **10** and a study of their reactions with





	X		X
9	Cl	**10**	Cl
14	*p*-$MeC_6H_4SO_2$	**15**	*p*-$MeC_6H_4SO_2$
16	N_3	**17**	N_3
18	*p*-MeC_6H_4S	**19**	*p*-MeC_6H_4S
29	OH		



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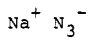

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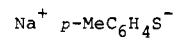

13

nucleophiles. The results of these reactions constitute this report.

Reaction of the Neopentyl Nitrothenylic Chlorides 9 and 10 with Nucleophiles. The yields of products from the treatment of the chlorides **9** and **10** with sodium *p*-toluenesulfinate (**11**), sodium azide (**12**), and sodium *p*-toluenethiolate (**13**), under a variety of conditions, are given in Table I. The products were the sulfones **14** and **15**, the azides **16** and **17**, and the sulfides **18** and **19** in the 5- and 4-nitro series, respectively, and were formed in yields in excess of 70%.

It is clear from the data in Table I that the substitution reactions on the 5-nitro chloride **9** are taking place by the $S_{RN}1$ mechanism, i.e., it is behaving as an analogue of the benzylic chloride **2** for which $S_{RN}1$ processes have been clearly demonstrated.[4,5] For example, the formation of the sulfone **14** from **9** is catalyzed by light (compare entries 1 and 2) and completely inhibited by oxygen (compare entries 2 and 3) and di-*tert*-butyl nitroxide (compare entries 1 and 4). Similar effects, although not as pronounced, were observed in the conversion of chloride **9** into the azide **16** (entries 6–9). In marked contrast the reactions of the chloride **10** with toluenesulfinate and azide ions (entries 5 and 10) were completely unaffected by oxygen, di-*tert*-butyl nitroxide, and/or irradiation by white light (Table I, entries 5 and 10). The reactions of chlorides **9** and **10** with the thiolate **13** were extremely fast, and inhibition studies were not performed.

The similar yields and times taken for reactions of the chlorides **9** and **10** with the salt **11** (entries 1 and 5) are also in marked contrast with the large difference in both yields and reaction times for reaction of the corresponding nitrobenzylic compounds **2**[4] and **6**[7] with the same salt (see above). This lack of rate difference and the absence of

Table I. Yields of Substitution Products from the Reaction of Nucleophiles with 4- and 5-Nitro-α-*tert*-butylthenyl Chlorides (9 and 10)[a]

entry	substrate[a]	salt	time, h	products, % yield
1	**9**	**11**[b]	0.5	**14** (90-95)
2	**9**	**11**[b]	**11**[c]	**14** (90)
3	**9**	**11**[b]	**12**[c,d]	*e*
4	**9**	**11**[b]	0.5[f]	*e*
5	**10**	**11**[b]	0.5[g]	**15** (85-95)
6	**9**	**12**[h]	0.5	**16** (70)[i]
7	**9**	**12**[h]	0.5[c]	**16** (34)[j]
8	**9**	**12**[h]	0.5[c,d]	**16** (5)[k]
9	**9**	**12**[h]	0.5[f]	**16** (42)[l]
10	**10**	**12**[h]	6-24[g]	**17** (78-81)
11	**9**	**13**[m,n]	0.08	**18** (74)
12	**10**	**13**[m]	0.08	**19** (78)
13	**10**	**4**[o]	1.2[g]	**26** (ca. 80)[p]
14	**9**	**4**[o]	1.1	**28** (56); **29** (10)
15	**9**	**4**[o]	1.1[c,d,q]	**28** (42); **29** (5); **30** (7)
16	**9**	**4**[o]	2.5[c,d]	**28** (53); **29** (6); **30** (7)

[a] All reactions were carried out in Me_2SO at 20 °C, unde under nitrogen, and with sunlamp irradiation (see Experimental Section) unless otherwise stated. Substrate concentration was 0.08 M except for entries 13-16 where 0.25 M solutions were used. [b] 0.25 M. [c] In the dark. [d] Under O_2. [e] Unchanged starting material was recovered (80-95%). [f] Solution was also 0.08 M in di-*tert*-butyl nitroxide. [g] Reaction time and yield were unaffected by oxygen, lack of irradiation, or by the presence of di-*tert*-butyl nitroxide. [h] 0.17 M. [i-l] **9** was recovered in 7%, 34%, 71% and 13% yield, respectively. [m] 0.125 M. [n] In Me_2NCHO. [o] 0.5 M. [p] Including derived products, see ref 2. [q] **9** (21%) was also recovered.

catalytic and inhibition effects clearly rule out the $S_{RN}1$ mechanism for the substitution reaction of **10**. The similarity in rate of reaction of **9** and **10** also would rule out a nonchain electron-transfer process, similar to that proposed for *m*-nitrocumyl substrates.[10,11] Both a nonchain and an $S_{RN}1$ reaction of **10** will be slower than the corresponding reactions of **9**, since it is known that the rates of dissociation of radical anions from *m*-nitrobenzylic chlorides are much slower than those of the *p*-nitro analogues.[12]

The ionic, S_N1 and S_N2 processes can also be excluded as possible mechanisms for the substitution reactions of chloride **9**. An S_N2 process is ruled out on general steric grounds, e.g., the failure of the benzylic analogue **1** to undergo S_N2 reactions.[4] Further, more direct evidence is available in this work. When the $S_{RN}1$ reaction of the 5-nitro chloride **9** with the salt **11** is inhibited (Table I, entry 3), no substitution (<2%) takes place after 12 h. The 4-nitro chloride **10**, under the same reaction conditions (Table I, entry 5—see footnote *g*), has reacted completely in 0.5 h. The rate difference for these two reactions is approximately 1000-fold. The S_N2 reactivities of the chlorides **9** and **10** will be similar, since *p*- and *m*-nitrobenzylic halides differ in reaction rates by only a factor of 2–3, and with anionic nucleophiles the para isomer (here **9**) normally reacts marginally *faster* than the *m*-nitro compound (here **10**).[13] The large observed rate difference clearly rules out an S_N2 mechanism for substitution re-

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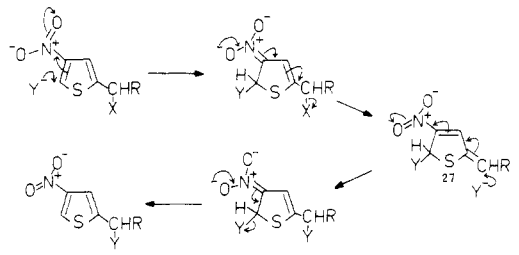
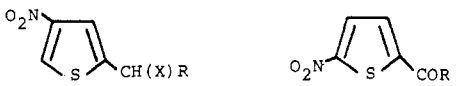
(8) Newcombe, P. J.; Norris, R. K. *Aust. J. Chem.* **1979**, *32*, 2647.
(9) Newcombe, P. J.; Norris, R. K. *Aust. J. Chem.* **1981**, *34*, 1879.
(10) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6219.
(11) Kornblum, N.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Snow, D. H.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6221.
(12) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1980**, *102*, 4798.
(13) Stephan, E. *Bull. Soc. Chim. Fr.* **1977**, 779 and references therein.

Scheme II



actions of **10**. An S_N1 process is also discounted since both the chlorides **9** and **10** are recovered in high yield after reflux in methanol (see Experimental Section), conditions which should favor S_N1 reactions.

We have reported previously[8] that the 4-nitrothenylic derivatives (**20** and **21**) undergo facile, high-yielding re-

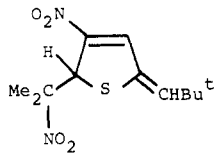


	R	X
20	H	Cl
21	Me	Cl
22	H	CMe_2NO_2
23	Me	CMe_2NO_2
24	H	OAc
25	Me	OAc

28 R = Bu^t

30 R = H

actions with the salt **4**, which are not inhibited by oxygen, and that the C-alkylation products (**22** and **23**) are formed. Since the S_N2 reactions of *aci*-nitronate ions with benzylic halides normally give O-alkylation products[14] and since the acetates **24** and **25** also reacted with equal facility, $S_{RN}1$, S_N1, and S_N2 processes were all excluded.[8] The mechanism proposed to account for these observations is given in generalized form in Scheme II, and has subsequently been termed the S_N(AEAE) reaction.[9] The recent isolation[2] of compound **26** and products derived from it, when the



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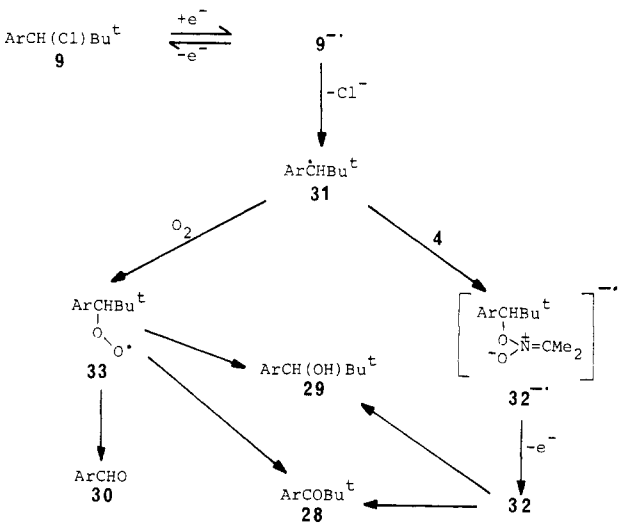
chloride **10** is treated with the salt **4** (see Table I, entry 13), lends overwhelming support to this mechanism. Compound **26** corresponds to the intermediate **27** in the S_N(AEAE) process (Scheme II). It is now proposed that the chloride **10** reacts with the salts **11**–**13** by this S_N(AEAE) mechanism. The observation made previously[2] that the compound **26** on treatment with the salt **11** gives the sulfone **15** and the further observation (see Experimental Section) that **26** gives the azide **17** on treatment with the salt **12** lend strong independent support for this proposed mechanism. The intermediates **27** (Scheme II Y = N_3, *p*-$MeC_6H_4SO_2$, or *p*-MeC_6H_4S, and R = *t*-Bu) could not be detected in the reaction of **10** with the salts **11**, **12**, and **13**. Presumably the latter two steps in Scheme II, when Y^- is *not* the 2-nitro-2-propanide ion, are faster than the initial addition and elimination steps which lead to **27**.

Finally, by way of contrast with the corresponding reactions of chloride **10** with the salt **4**, the reactions of

Scheme III[a]



[a] Ar = 5-nitro-2-thienyl.

chloride **9** with **4** gave the ketone **28** and the neopentyl alcohol **29** under a nitrogen atmosphere (Table I, entry 14) and, at a reduced reaction rate, gave the same two products and the aldehyde **30** under oxygen (Table I, entries 15 and 16). The formation of these products is rationalized in Scheme III. The radical **31** formed by dissociation of the radical ion $9^{-\cdot}$ can be trapped by the salt **4** with sterically induced O-alkylation[4,5,15] to give the radical anion of the nitronic ester **32** and/or is trapped by oxygen to give the peroxy radical **33**. These intermediates lead to the observed products by the usual pathways[15] as summarized in Scheme III.

It is apparent that the analogous chlorides **9** and **10** react with the salts **11**, **12**, and **13** to give analogous substitution products under similar conditions and for similar reaction times but by the quite different $S_{RN}1$ and S_N(AEAE) mechanisms.

Experimental Section

The general experimental procedures and descriptions of instrumentation are the same as previously stated.[2,9] **Preparation of 2-(1′-Chloro-2′,2′-dimethylpropyl)-5-nitrothiophene (9) and 2-(1′-Chloro-2′,2′-dimethylpropyl)-4-nitrothiophene (10).** 2,2-Dimethyl-1-(2′-thienyl)-1-propanone was nitrated as previously described[2] and the 4- and 5-nitro isomers were separated by HPLC (2% ethyl acetate/98% light petroleum; Waters Associates PrepLC/System 500) to give 2,2-dimethyl-1-(4′-nitro-2′-thienyl)-1-propanone and 2,2-dimethyl-1-(5′-nitro-2′-thienyl)-1-propanone (**28**). The former ketone was reduced and the resulting alcohol chlorinated as previously described,[2] to give the chloride **10**. The ketone **28** was reduced in an analogous fashion[2] and the product was recrystallized from ether/cyclohexane to give a near quantitative yield of **2,2-dimethyl-1-(5′-nitro-2′-thienyl)-1-propanol (29)**: mp 69–70 °C; ^{1}H NMR δ 1.00 (s, 9 H, *t*-Bu), 2.49 (br d, 1 H, OH, J = 3.4 Hz), 4.63 (br d, 1 H, H 1, J = 3.4 Hz), 6.86 (dd, 1 H, H 3′, $J_{3',4'}$ = 4.14 Hz, $J_{1,3'}$ = 0.80 Hz), 7.78 (dd, 1 H, H 4′, $J_{3',4'}$ = 4.14 Hz, $J_{1,4'}$ = 0.26 Hz); IR ($CHCl_3$) 3535, 3105, 1500, 1430, 1360, 1020, 820, 740 cm^{-1}; UV (MeOH) 212 nm (ϵ 5.3 × 10^3), 321 (1.08 × 10^4); mass spectrum, *m/e* 215 (M^+, 0.6%), 200 (1), 159 (100), 142 (53), 112 (27), 84 (9), 58 (11), 57 (95).

Anal. Calcd for $C_9H_{13}NO_3S$: C, 50.21; H, 6.09; N, 6.51; S, 14.90. Found: C, 50.33; H, 6.09; N, 6.36; S, 14.9.

The alcohol **29** was chlorinated by addition of a solution in pyridine to thionyl chloride in the usual fashion.[8] Purification by PLC (25% ethyl acetate/75% light petroleum on silica gel) gave the chloride **9**, a pale oil in 85–95% yield: bp (Kugelrohr)

(14) Hass, H. B.; Bender, M. L. *J. Am. Chem. Soc.* **1949**, *71*, 1767.

(15) Norris, R. K.; Randles, D. *J. Org. Chem.* **1982**, *47*, 1047; *Aust. J. Chem.* **1982**, *35*, 1621.

150 °C/0.2 mmHg; ^{1}H NMR δ 1.12 (s, 9 H, *t*-Bu), 4.90 (d, 1 H, H 1′, $J_{1',3}$ = 0.61 Hz), 6.98 (dd, 1 H, H 3, $J_{1',3}$ = 0.61 Hz, $J_{3,4}$ = 4.25 Hz), 7.78 (d, 1 H, H 4, $J_{3,4}$ = 4.25 Hz); IR (liquid film) 3100, 1500, 1430, 1365, 820 cm^{-1}; UV (MeOH) 316 nm (ε 9 × 10^3); mass spectrum, *m/e* 235 (M$^+$ + 2, 0.2%), 233 (0.5), 220 (1.5), 218 (5), 179 (22), 177 (61), 168 (7), 160 (6), 96 (8), 57 (100), 45 (7), 41 (32).

Anal. Calcd for $C_9H_{12}ClNO_2S$: C, 46.25; H, 5.18; Cl, 15.17; N, 5.99; S, 13.72. Found: C, 46.47; H, 5.38; Cl, 15.8; N, 6.02; S, 14.2.

Reactions of Chlorides 9 and 10 with Nucleophiles. General Procedure. These reactions were carried out under the conditions specified in Table I using apparatus and workup procedures (including PLC) described previously.[2,9,15] Where samples of starting materials **9** and **10**, the alcohol **29**, or the ketone **28** were isolated from reaction mixtures, they were shown to be identical with the samples prepared above. The following compounds were isolated in the yields stated in the appropriate entries in Table I.

2,2-Dimethyl-1-(5′-nitro-2′-thienyl)propyl *p*-tolyl sulfone (14) (entry 1): mp 146–147.5 °C (methanol); ^{1}H NMR[16] δ 1.22 (s, 9 H, *t*-Bu), 1.91 (s, 3 H, Me), 3.86 (d, 1 H, ArC*H*, $J_{1,3'}$ = 0.49 Hz), 6.44 (dd, 1 H, H 3′, $J_{1,3'}$ = 0.49, $J_{3',4'}$ = 4.23 Hz), 7.17 (d, 1 H, H 4′, $J_{3',4'}$ = 4.23 Hz), AA′XX′ pattern 6.71 (m, 2 H), 7.33 (m, 2 H), J_{AX} + $J_{AX'}$ = 8.1 Hz; IR ($CHCl_3$) 3025, 1510, 1430, 1365, 1340, 1160, 1095, 820 cm^{-1}; UV (MeOH) 221 nm (ε 1.6 × 10^4), 298 (3.7 × 10^3); mass spectrum, *m/e* 353 (M$^+$, 2%), 198 (100), 156 (20), 142 (14), 91 (15).

Anal. Calcd for $C_{16}H_{19}NO_4S_2$: C, 54.37; H, 5.42; N, 3.96; S, 18.14. Found: C, 54.38: H, 5.52; N, 3.94; S, 17.9.

2,2-Dimethyl-1-(4′-nitro-2′-thienyl)propyl *p*-tolyl sulfone (15) (entry 5): white needles, mp 152–153 °C (lit.[2] mp 152–153.5 °C).

2-(1′-Azido-2′,2′-dimethylpropyl)-5-nitrothiophene (16) (entry 6): a pale oil, which decomposed on heating or exposure to light; ^{1}H NMR δ 1.00 (s, 9 H, *t*-Bu), 4.41 (d, 1 H, H 1′, $J_{1',3}$ = 0.6 Hz), 6.86 (dd, 1 H, H 3, $J_{1',3}$ = 0.6 Hz, $J_{3,4}$ = 4.1 Hz), 7.75 (d, 1 H, H 4, $J_{3,4}$ = 4.1 Hz); IR (liquid film) 3100, 2105, 1505, 1440, 1390 cm^{-1}; UV (EtOH) 324 nm (ε 8.4 × 10^3); mass spectrum, *m/e* 212 (M$^+$ − N_2, 1%), 156 (20), 139 (12), 57 (100), 41 (52); high-resolution mass spectrum calcd for $C_9H_{12}N_4O_2S$ − N_2, 212.0619; found, M$^+$ − N_2, 212.0621.

2-(1′-Azido-2′,2′-dimethylpropyl)-4-nitrothiophene (17) (entry 10): an oil; ^{1}H NMR δ 1.00 (s, 9 H, *t*-Bu), 4.48 (m, 1 H, H 1′), 7.52 (dd, 1 H, H 3, $J_{1',3}$ = 0.7 Hz, $J_{3,5}$ = 1.6 Hz), 8.26 (dd, 1 H, H 5, $J_{1',5}$ = 0.5 Hz, $J_{3,5}$ = 1.6 Hz); IR (liquid film) 3110, 2104, 1540, 1520, 1460, 1390 cm^{-1}; UV (EtOH) 228 nm (ε 1.21 × 10^4), 272 (7.5 × 10^3); mass spectrum, *m/e* 156 (M$^+$ − *t*-Bu − N_2, 7%), 109 (3), 82 (10), 57 (100), 41 (40).

Anal. Calcd for $C_9H_{12}N_4O_2S$: C, 45.00; H, 5.03; N, 23.32. Found: C, 45.48; H, 5.24; N, 23.09.

2,2-Dimethyl-1-(5′-nitro-2′-thienyl)propyl *p*-tolyl sulfide (18) (entry 11): an oil; ^{1}H NMR δ 1.17 (s, 9 H, *t*-Bu); 2.27 (s, 3 H, Me), 4.02 (d, 1 H, ArC**H**, $J_{1,3'}$ = 0.5 Hz), 6.69 (dd, 1 H, H 3′, $J_{1,3'}$ = 0.5 Hz, $J_{3',4'}$ = 4.3 Hz), 7.64 (d, 1 H, H 4′, $J_{3',4'}$ = 4.3 Hz), AA′XX′ pattern 6.92 (m, 2 H), 7.10 (m, 2 H, J_{AX} + $J_{AX'}$ = 8.4 Hz); IR (liquid film) 3090, 1530, 1490, 1385, 825, 741 cm^{-1}; UV (EtOH) 220 nm (ε 1.09 × 10^4), 245 (7.7 × 10^3), 326 (7.2 × 10^3); mass spectrum, *m/e* 321 (M$^+$, 21%), 275 (42), 265 (33), 248 (22), 198 (100), 177 (10), 156 (40), 142 (30), 124 (60), 91 (44), 77 (20), 69 (23), 57 (73), 41 (49).

Anal. Calcd for $C_{16}H_{19}NO_2S_2$: C, 59.78; H, 5.96, N, 4.36. Found: C, 59.46; H, 6.12; N, 4.52.

2,2-Dimethyl-1-(4′-nitro-2′-thienyl)propyl *p*-tolyl sulfide (19) (entry 12): an oil; ^{1}H NMR δ 1.16 (s, 9 H, *t*-Bu), 2.24 (s, 3 H, Me), 4.07 (m, 1 H, ArC*H*), AA′XX′ pattern 6.92 (m, 2 H), 7.10 (m, 2 H, J_{AX} + $J_{AX'}$ = 8.35 Hz), 7.25 (dd, 1 H, H 3′, $J_{1,5'}$ = 0.3 Hz, $J_{3',5'}$ = 0.8 Hz), 8.07 (dd, 1 H, H 5′, $J_{1,3'}$ = 0.1 Hz, $J_{3',5'}$ = 0.8 Hz); IR (liquid film) 3110, 1540, 1510, 1491, 1380, 824, 800, 736 cm^{-1}; UV (EtOH) 223 nm (ε 1.71 × 10^4); mass spectrum, *m/e* 321 (M$^+$, 18%), 265 (18), 248 (13), 198 (100), 156 (50), 142 (38), 124 (52), 91 (49), 77 (19), 69 (20), 57 (47), 41 (45).

Anal. Calcd for $C_{16}H_{19}NO_2S_2$: C, 59.78; H, 5.96; N, 4.36. Found: C, 59.85; H, 6.06; N, 4.71.

5-Nitro-2-thiophenecarboxaldehyde (30) (entries 15 and 16): mp 69–71 °C (lit.[17] mp 73–74 °C). **Reaction of Compound 26 with Sodium Azide 12.** Reaction of the nitro diene **26**[2] (100 mg, 0.35 mmol) with sodium azide (**12**) (150 mg, 2.3 mmol) in Me_2SO (6.0 mL) at 20 °C in the dark for 5 min gave, after workup and purification by PLC, the azide **17** (44 mg, 53%), identical with the sample prepared above (TLC and ^{1}H NMR).

Attempted Methanolyses of Chlorides 9 and 10. The chloride **9** or **10** (100 mg) was heated under reflux in methanol (10.0 mL) for 1 h. Workup gave the unchanged chlorides **9** or **10** in near quantitative recovery.

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(16) Spectrum was recorded in toluene-d_7 at 100 °C to sharpen the aromatic signals which were broadened at lower temperatures by DNMR phenomena resulting from slow rotation about the 2′ to α C–C bond.

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