λ_{max} 343 nm (ϵ 6250); ^{1}H NMR (CD_3SOCD_3) δ 3.82 (q, 1 H, J = 4.8 Hz, H-4), 4.15 (s, 2 H, CH_2Ph), 4.52 (dd, 1 H, J = 3.0, 4.8 Hz, ArC*H*(OH)), 4.65 (dd, 1 H, J = 4.8, 9.8 Hz, H-5), 5.60 (d, 1 H, J = 3.0 Hz, exchanged with D_2O, OH), 5.83 (br d, 1 H, J = 9.8 Hz, H-6), 6.57-7.80 (m, 12 H, H-2, NH_2, C_6H_4, Ph); ^{13}C NMR (CD_3SOCD_3) δ 40.7, 56.0, 75.1, 100.7, 101.8, 109.1, 119.2, 126.7, 127.1, 128.3, 130.1, 130.7, 138.0, 138.5, 149.0, 170.2; MS, *m/e* (relative intensity) 345 (1, M^+), 327 (1), 213 (33), 131 (26), 130 (40), 123 (11), 122 (16), 105 (14), 102 (16), 91 (100).

Photosensitized Reaction of 1f. A 150-mL methanolic solution of **1f** (0.72 g, 6.8 mmol), BNAH (3.31 g, 15.5 mmol), and the sensitizer (30 mg, 0.04 mmol) was irradiated for 15 h, evaporated, and then chromatographed on basic alumina as described above to give BNAH (0.5 g), diastereomeric mixtures of **4f** (2.0 g, 85%), and **5** (< 20 mg). The diastereoisomers of **4f** were separated by repeated column chromatography. A pure sample of the *RR* + *SS* isomer was thus obtained whereas the *RS* + *SR* isomer could not be made free from contamination of small amounts of others.

(*RR*)- + (*SS*)-**4f**: mp 171.5-172.5 °C dec ($CHCl_3$-MeOH); IR (KBr) ν_{max} 3270, 3115, 1669, 1640, 1554 cm^{-1}; UV (MeOH) λ_{max} 342 nm (ϵ 4750); ^{1}H NMR (CD_3SOCD_3) δ 3.70 (dd, 1 H, J = 3.2, 5.8 Hz, H-4), 4.23 (s, 2 H, CH_2Ph), 4.43 (dd, 1 H, J = 2.2, 5.8 Hz, ArC*H*(OH)), 4.47 (dd, 1 H, J = 3.2, 6.0 Hz, H-5), 6.01 (dd, 1 H, J = 2.2, 6.0 Hz, H-6), 6.06 (br s, exchanged with D_2O, OH), 6.78-7.50 (m, 13 H, H-6, NH_2, 2 × Ph); ^{13}C NMR (CD_3SOCD_3) δ 40.9, 56.0, 76.9, 101.6, 126.2, 126.8, 127.1, 128.4, 130.5, 138.1, 139.2, 143.3, 170.9; MS, *m/e* (relative intensity) 320 (0.5, M^+), 302 (2, M - H_2O), 213 (57), 123 (5), 106 (5, PhCHO), 105 (4), 91 (100). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.74. Found: C, 74.70; H, 6.21; N, 8.77.

(*RS*)- + (*SR*)-**4f**: mp 162-163 °C dec ($CHCl_3$-MeOH); IR (KBr) ν_{max} 3460, 3340, 3170, 1665, 1635, 1560 cm^{-1}; UV (MeOH) λ_{max} 342 nm (ϵ 6170); ^{1}H NMR (CD_3SOCD_3) δ 3.62 (q, 1 H, J = 5.6 Hz, H-4), 4.23 (s, 2 H, CH_2Ph), 4.38 (dd, 1 H, J = 5.6, 7.8 Hz, H-5), 4.45 (dd, 1 H, J = 3.8, 5.6 Hz, ArC*H*(OH)), 5.64 (d, 1 H, J = 3.8 Hz, exchanged with D_2O, OH), 5.99 (br d, 1 H, J = 7.8 Hz, H-6), 6.74-7.60 (m, 13 H, H-2, NH_2, 2 × Ph); ^{13}C NMR (CD_3SOCD_3) δ 40.4, 56.0, 77.1, 101.6, 102.7, 126.7, 127.1, 127.5, 128.5, 129.7, 138.3, 143.1, 170.7; MS, *m/e* (relative intensity) 320 (0.5, M^+), 302 (1), 213 (33), 123 (6), 106 (5), 105 (7), 91 (100).

Thermal Reactions. Each 3-mL methanolic solution containing **1a-f** (50 mM) and BNAH (0.2 M) in a Pyrex tube was bubbled with a gentle stream of Ar for 15 min and then heated at 60 ± 0.5 °C in a dark room. All the experimental procedures were performed in the dark in order to avoid exposure of reaction solutions to scattering light. The progress of the reactions was followed by both VPC and HPLC.

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Supplementary Material Available: X-ray crystallographic data including positional parameters, temperature factors, bond distances and angles, torsional angles, weighted least-squares planes, and an ORTEP drawing for (*RR*)- + (*SS*)-**4e** and (*RR*)- + (*SS*)-**4f** (32 pages). Ordering information is given on any current masthead page.

$S_{RN}1$ Reactions in Nitrofuran Derivatives[1]

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The reaction of the sterically hindered neopentylic chloride 2-(1′-chloro-2′,2′-dimethylpropyl)-5-nitrofuran (1) with *p*-toluenesulfinate, azide, and *p*-toluenethiolate ions and the salts derived from 2-methylmalononitrile and 2-nitropropane proceed by the $S_{RN}1$ mechanism. The operation of this mechanism is confirmed by the inhibitory effect of oxygen, di-*tert*-butyl nitroxide, and galvinoxyl and the catalytic effect of irradiation by white light. Methoxide and thiocyanate ions do not bring about substitution on 1, and this and other evidence confirms that substitution is not occurring by either the S_N1 or S_N2 mechanisms.

Nucleophilic substitution at the benzylic carbon in *p*- and *m*-nitrobenzylic substrates has been demonstrated to occur, in many cases, by the $S_{RN}1$ mechanism[2] which is given in Scheme I. Our particular interest in this reaction

Scheme I

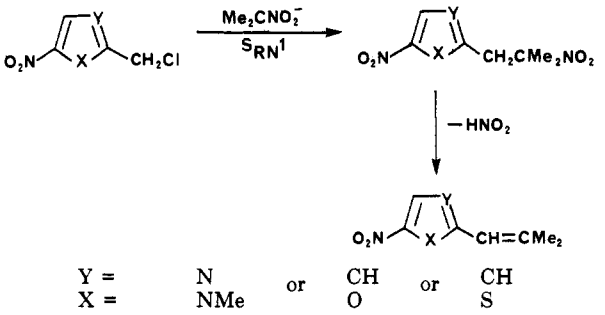
$$ArCR^1R^2X + Y^- \rightarrow [ArCR^1R^2X]^{\bullet -} + Y^{\bullet}$$

$$[ArCR^1R^2X]^{\bullet -} \rightarrow Ar\dot{C}R^1R^2 + X^-$$

$$Ar\dot{C}R^1R^2 + Y^- \rightarrow [ArCR^1R^2Y]^{\bullet -}$$

$$[ArCR^1R^2Y]^{\bullet -} + [ArCR^1R^2X] \rightarrow ArCR^1R^2Y + [ArCR^1R^2X]^{\bullet -}$$

Scheme II



Y =	N	or	CH	or	CH
X =	NMe		O		S

has been in the reactivity of systems which are neopentylic (Scheme I, Ar = *p*- or *m*-$O_2NC_6H_4$, R^1 = *t*-Bu).[3,4] We have shown that substitution by the $S_{RN}1$ mechanism at neopentyl positions also takes place with nitro heteroaromatic

(1) (a) This research was supported by grants from the Australian Research Grants Scheme (to R.K.N.). (b) Part of this work has been abstracted from the Ph.D. Thesis of Peter J. Newcombe, The University of Sydney, September 1980.

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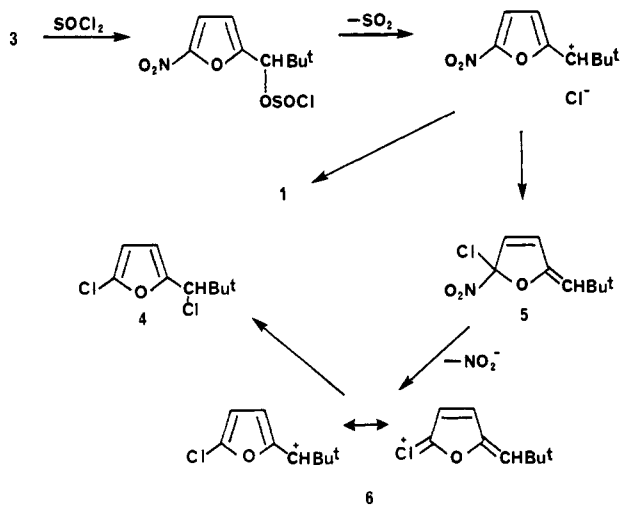
0022-3263/87/1952-2796$01.50/0

Scheme III



compounds, such as nitrothiophene derivatives (Scheme I, Ar = 5-nitro-2-thienyl, R^1 = *t*-Bu, R^2 = H).[5] Substitution proceeding by the $S_{RN}1$ mechanism, at benzylic carbons which are attached to heteroaromatic systems, has not been as widely studied as in the benzene series. Reactions with derivatives of pyridines,[6] nitrothiophenes,[7] nitroimidazoles,[8] and nitrofurans[9] have been reported, but the benzylic carbons in the substrates used were not neopentylic, and the nucleophiles used in the latter systems[7-9] were restricted to the anions of secondary nitroalkanes. In the reactions of primary and secondary benzyl halides in the nitrothiophene system, we found that the first-formed *C*-alkylates eliminated nitrous acid under the reaction conditions, to give vinylated nitrothiophenes,[7] behavior which was found subsequently in the nitroimidazole[8] and nitrofuran[9] systems (Scheme II).

The recent report[9] of the $S_{RN}1$ reaction of 5-nitrofurfuryl halides was limited to reactions with the sodium salt of 2-nitropropane,[10] since Bowman and his co-workers had shown earlier that substitution reactions with other nucleophiles were proceeding by the S_N2 mechanism.[11] We have prepared the neopentyl chloride **1**, which incorporates the 5-nitrofuryl moiety, and have undertaken a study of its reactions with a range of nucleophiles. It was expected, in similar fashion to thienyl neopentyl substrates, that S_N2 reactions would be prevented by the *α-tert*-butyl group.[5,12]

Results and Discussion

Preparation of Chloride 1. Reduction of the ketone **2**[13] proceeded in good yield to give the alcohol **3**. Treatment of this alcohol with thionyl chloride gave a near-quantitative yield of an inseparable mixture of the required chloride **1** and an unstable chloride, which was identified by ^1H NMR and MS as the 5-chloro chloride **4** (see Experimental Section). A possible mechanism for formation of the chlorides **1** and **4** is given in Scheme III and is based on the mechanism proposed for "abnormal" substitution reactions in the reaction of furfuryl chlorides with cyanide ion.[14] Presumably, the driving force for the loss of nitrite ion from the intermediate **5** is the greater stability of 5-chloro cation **6**, over the corresponding 5-nitro cation. On chromatography the chloride **4** decomposed and the chloride **1** could be obtained free of impurities.

Table I. Reaction of 2-(1′-Chloro-2′,2′-dimethylpropyl)-5-nitrofuran (1) with Nucleophiles[a]

entry	salt	time, h	products (% yield[b])
1	**7**	1.5	**15** (>95)
2	**7**	69[c]	**15** (*94*)
3	**7**	65[c,d]	**1** (*80*); **3** (*7*)
4	**7**	1.5[e]	**1** (94); **15** (<4)
5	**8**	0.5	**1** (9); **16** (86)
6	**8**	0.75	**16** (>95)
7	**8**	0.9	**16** (>95, *83*)
8	**8**	0.75[d]	**1** (77); **16** (6)
9	**8**	0.75[e]	**1** (93); **16** (7)
10	**8**	0.75[f]	**1** (89); **16** (11)
11	**9**[g,h]	0.08	**17** (>95, *82*)
12	**10**[i]	0.5	**1** (17–30); **18** (7–12)
13	**10**[j]	0.67	**1** (9)
14	**10**[h,i]	1.33	**1** (*33*); **18** (*20*)
15	**10**[h,j]	1.83	*k*
16	**10**[h,i]	2.0	**1** (22); **18** (28)
17	**10**[h,i]	5.5	**1** (11); **18** (25)
18	**10**[h,i]	5.5[d]	**2** (50)
19	**10**[h,i]	5.5[e]	**1** (68); **18** (16)
20	**10**[h,i]	3.0[l]	**18** (49, *35*)
21	**11**	1.0	**1** (>95)
22	**12**[h,i,m]	1.5	*k*
23	**13**[n]	4.0	**1** (11); **2** (12); **3** (5); **19** (40)
24	**13**[n]	7.0[c,d]	**1** (29); **2** (21); **3** (9); **19** (10)
25	**14**[h]	5.5	**1** (81)
26	**14**[h]	5.5[d]	**1** (46); **2** (28)
27	*o*	3.0	**1** (76)

[a] All reactions were performed on the substrate **1** (0.08 M) with the appropriate salt (0.25 M) in dimethyl sulfoxide at 20 °C under nitrogen with irradiation by a sunlamp, unless otherwise stated. [b] Yields were estimated by ^1H NMR spectroscopy with 2,4,6-trinitrotoluene as an internal standard; isolated yields are given in italics. [c] In the dark. [d] Under O_2. [e] In the presence of di-*tert*-butyl nitroxide (0.008 M). [f] In the presence of galvinoxyl (0.008 M). [g] 0.125 M. [h] In dimethylformamide. [i] 0.16 M. [j] 0.75 M. [k] No detectable products. [l] In the presence of 2-methylmalononitrile (0.16 M). [m] The same result was obtained in the presence of diethyl 2-methylmalonate (0.16 M). [n] 0.5 M with **1** (0.25 M). [o] In methanol at reflux.

Reaction of Chloride 1 with Nucleophiles. The yields of products from the reaction of the chloride **1** with the salts **7**–**14** in either dimethyl sulfoxide or dimethylformamide at 20 °C are given in Table I. Excellent yields of the sulfone **15** (entries 1 and 2), the azide **16** (entries 6 and 7), and the sulfide **17** (entry 11) were obtained. The preparation of the malononitrile derivative **18** from reaction of **1** with the salt **10** was less successful. It was apparent that **18** was unstable under the reaction conditions, and it was found that even solid, isolated **18** decomposed rapidly at room temperature (see Experimental Section). Very poor material balances were obtained in dimethyl sulfoxide, particularly with higher concentrations of the

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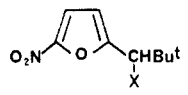
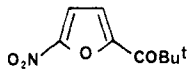


	X
1	Cl
3	OH
15	p-$MeC_6H_4SO_2$
16	N_3
17	p-MeC_6H_4S
18	$Me(NC)_2C$
20	MeO

7	Na^+ p-$MeC_6H_4SO_2^-$
8	Na^+ N_3^-
9	Na^+ p-$MeC_6H_4S^-$
10	Na^+ $Me(NC)_2C^-$
11	K^+ NCS^-
12	Na^+ $Me(EtO_2C)_2C^-$
13	Li^+ $Me_2CNO_2^-$
14	Na^+ MeO^-



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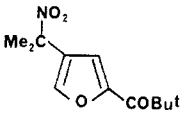

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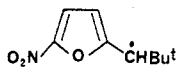
salt **10** (entries 12 and 13). In dimethylformamide (entries 14–17), similar results were obtained, but 20–25% yields of **18** could be obtained. It has been suggested that decomposition of 5-nitrofurfuryl derivatives might occur through formation of an α-carbanion leading to ring-opening of the furan ring,[9] and so the reaction of the chloride **1** with the salt **10** was carried out in the presence of the conjugate acid, 2-methylmalononitrile. A significant increase in yield was observed (compare entry 20 with entries 14–17). Potassium thiocyanate (**11**) did not give any substitution products with **1** (entry 21), and the use of the malonic ester salt **12** gave only destruction of starting material (entry 22). The lithium salt of 2-nitropropane (**13**) reacted with **1** to give the ketone **2**, the alcohol **3**, and the 2,4-disubstituted furan derivative **19**, whose formation from the ketone **2** has been reported recently.[15] No detectable amount of proucts arising from C-alkylation of the *aci*-nitronic salt **13** could be detected. Reaction with sodium methoxide in dimethylformamide (entry 25) or reflux with methanol (entry 27) failed to produce the methyl ether **20**.

The substitution reactions of chloride **1** are taking place by the $S_{RN}1$ mechanism (Scheme I, Ar = 2-nitrofuryl, R^1 = *t*-Bu, R^2 = H, X = Cl), since the usual catalytic and inhibitory effects found when this mechanism is operating were observed. The catalytic effect of white-light irradiation is apparent, for example, in the reactions of **1** with *p*-toluenesulfinate ion (compare entries 1 and 2) and with the anion from 2-methylmalononitrile (compare entries 17 and 19). The inhibitory effect of di-*tert*-butyl nitroxide (compare entries 1 and 4, and 6 and 9) and galvinoxyl (compare entries 6 and 10) on the reactions of **1** with salts **7** and **8** is also clear. The effect of oxygen varies with the salt being used. In the reaction with the sulfinic salt **7** the formation of the sulfone **15** was stopped completely, and small amounts of the alcohol **3**, presumably arising from oxygenation of the radical intermediate **21**, were isolated (entry 3). With azide ion, oxygen markedly retards the formation of the azide **16** (compare entries 6 and 8). Oxygen completely prevents formation of the dinitrile **18** (compare entries 17 and 18), and the ketone **2** is formed in moderate yield. In a separate experiment it was shown that treatment of the dinitrile **18** (0.05 M) with the salt **10** (0.10 M) under oxygen gave only small amounts of recovered **18** and none (<2%) of the ketone **2**. This rules out formation of the ketone **2** from oxidation of the dinitrile **18**. It is possible that the ketone **2** might be being formed by oxygenation of the α-carbanion **22**.[16] To test



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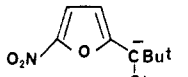

22

this possibility, the chloride **1** was treated with the otherwise unreactive salt **14** (see entry 25). Some conversion to **2** did take place under oxygen (entry 26). Since methoxide ion and the anion from 2-methylmalononitrile have different basicities in dimethylformamide, no great significance should probably be placed on the different rates of production and yields of the ketone **2** (compare entries 18 and 26), and all that can be stated is that **2** arises from both or either of the species **21** and **22**. The effect of oxygen on the reaction of **1** with the lithium salt **13** is somewhat obscured by the secondary ionic reaction in which the ketone **2** is converted into the cine-substitution product **19**.[15] It is clear, however, that oxygen retards the overall conversion of **1** into products (compare entries 23 and 24).

Finally, other mechanisms for the substitution of chloride in **1** by nucleophiles are inconsistent both with the data in Table I and with the established reactivity patterns of neopentyl substrates. The sterically unlikely S_N2 mechanism is further discounted by the failure of the normally potent nucleophiles, methoxide, and thiocyanate (see entries 21 and 25) to participate in substitution reactions with **1**. Substitution by the S_N1 mechanism is precluded by the failure of **1** to undergo solvolysis under more vigorous conditions which are also more amenable to operation of the S_N1 processes (see entry 27). In addition, similar reactivity toward azide and thiocyanate ions is exhibited by neopentyl substrates, which have been demonstrated to undergo substitution by the S_N1 mechanism, in the thiophene series.[12] This behavior is not shown by compound **1** (compare entries 7 and 21).

Experimental Section

Melting points were determined thermoelectrically on a Reichert hot stage melting point apparatus and are uncorrected. ^1H NMR spectra were determined on a Varian Associates EM-390 or a Bruker WM-400 spectrometer on ca. 10% w/v solutions in $CDCl_3$. The ^{13}C NMR spectrum was recorded on a JEOL FX-60Q spectrometer on ca. 30% w/v solutions in $CDCl_3$ and is proton-coupled. Both ^{13}C and ^1H chemical shifts are quoted in ppm downfield of internal $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer, and ultraviolet spectra were recorded on Perkin-Elmer 402 and Hitachi 150-20 spectrophotometers. Mass spectra were recorded on an A.E.I. MS-902 spectrometer at 70 eV. Analyses were carried out at the Australian Microanalytical Service, Melbourne. Thin-layer chromatography (TLC) was performed on Merck Kieselgel $HF_{254+366}$ (type 60). Flash chromatography[17] was performed on Merck silica gel 60 (230–240 mesh). Light petroleum refers to the fraction of bp 65–70 °C. Reactions were worked up by dilution with water followed by threefold extraction with ether, washing of the ether layer with water and brine, drying ($MgSO_4$), and removal of the ether under reduced pressure to give the crude product.

Preparation of 2,2-Dimethyl-1-(5′-nitro-2′-furyl)-1-propanol (3) and 2-(1′-Chloro-2′,2′-dimethylpropyl)-5-nitrofuran (1). Powdered sodium borohydride (0.12 g, 3.2 mmol) was added to a solution of the ketone **2**[13] (1.2 g, 6.0 mmol) in absolute ethanol (30 mL), and the mixture was stirred for 25–30 min at ca. 25 °C. Water was added, and the resulting solution was worked up with ether in the usual manner. The crude product was

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(16) The formation and oxidation by oxygen of α-carbanions in 5-nitrothienyl analogues of **1** has been suggested in our earlier work.[7]

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purified by column chromatography on silica gel with 25% ethyl acetate/75% light petroleum as eluent to give **3**: an oil; 0.11 g (87%); ^{1}H NMR δ 0.99 (s, 9 H, *t*-Bu), 2.84 (br s, 1 H, OH), 4.46 (br t, 1 H, H1, $J_{1,3'}$ = 0.72 Hz, $J_{1,4'}$ = 0.55), 6.52 (dd, 1 H, H3', $J_{1,3'}$ = 0.72 Hz, $J_{3',4'}$ = 3.74 Hz), 7.30 (dd, 1 H, H4', $J_{1,4'}$ = 0.55 Hz, $J_{3',4'}$ = 3.74 Hz); IR (liquid film) 3500 (br), 1530, 1495, 1375, 1255, 1025, 815 cm^{-1}; UV (MeOH) 274 nm (ϵ 1.24 × 10^4); mass spectrum, *m/z* (relative intensity) 200 (M^+ + 1, 2), 199 (M^+, 1), 143 (100), 126 (57), 113 (15), 96 (13), 68 (15), 57 (71), 43 (12), 41 (38), 39 (16), 29 (30).

Anal. Calcd for $C_9H_{13}NO_4$: C, 54.3; H, 6.6; N, 7.0. Found: C, 54.2; H, 6.7; N, 7.1.

The alcohol **3** (0.64 g, 3.2 mmol) was chlorinated by addition of excess thionyl chloride (3.0 mL, 4.8 g) with stirring at 0–5 °C over 30 min. The reaction mixture was then stirred for an additional hour at 20 °C, followed by refluxing for an additional hour. The reaction mixture was worked up in the usual manner to give the crude product, which was shown by ^{1}H NMR to be a 3:2 mixture of the required 5-nitro chloride **1** and the 5-chloro chloride **4** in 89% combined yield. Although the chloride **4** decomposed on attempted chromatography, the following data for **4** was obtained from the mixture: ^{1}H NMR δ 1.08 (s, 9 H, *t*-Bu), 4.62 (br t, 1 H, H1', $J_{1',3}$ = 0.3 Hz, $J_{1',4}$ = 0.35 Hz), 6.12 (dd, 1 H, H3, $J_{1',3}$ = 0.3 Hz, $J_{3,4}$ = 3.35 Hz), 6.30 (dd, 1 H, H4, $J_{1',4}$ = 0.35 Hz, $J_{3,4}$ = 3.35 Hz);high-resolution mass spectrum calcd for $C_9H_{12}O^{35}Cl_2$ 206.0265, found $C_9H_{12}O^{35}Cl_2$ 206.0265. Subjection of the mixture to column chromatography (25% dichloromethane/75% light petroleum on silica gel) gave the 5-nitro chloride **1**: an oil, 0.28 g (40%); bp (Kugelrohr) 145 °C (0.15 mmHg); ^{1}H NMR δ 1.14 (s, 9 H, *t*-Bu), 4.69 (m, 1 H, H1'), 6.57 (dd, 1 H, H3, $J_{1',3}$ = 0.47 Hz, $J_{3,4}$ = 3.70 Hz), 7.28 (dd, 1 H, H4, $J_{1',4}$ = 0.39 Hz, $J_{3,4}$ = 3.70 Hz); IR (liquid film) 1535, 1500, 1375, 1250, 1030, 820 cm^{-1}; UV (MeOH) 276 nm (ϵ 7.6 × 10^3); mass spectrum, *m/z* (relative intensity) 219 (M^+ + 2, 0.1), 217 (M^+, 0.6), 202 (6), 182 (2), 161 (68), 152 (4), 144 (3), 137 (2), 82 (6), 57 (100), 41 (12).

Anal. Calcd for $C_9H_{12}ClNO_3$: C, 49.7; H, 5.6; Cl, 16.3; N, 6.4. Found: C, 50.0; H, 5.7; Cl, 16.2; N, 6.7.

Reactions of Chloride 1 with Nucleophiles. General Procedure. These reactions were carried out under the conditions specified in Table I by using apparatus and workup procedures (including PLC) described previously.[5] The sodium salts **9**, **10**, **12**, and **14** were prepared in situ by reaction of the appropriate conjugate acid with sodium hydride, followed by filtration from the excess of sodium hydride. The following compounds were isolated in the yields stated in the appropriate entries in Table I.

2,2-Dimethyl-1-(5'-nitro-2'-furyl)propyl *p*-tolyl sulfone (15) (entries 1 and 2): white needles, mp 123–124 °C (methanol); ^{1}H NMR (deuteriotoluene at 100 °C) δ 1.12 (s, 9 H, *t*-Bu), 1.95 (s, 3 H, Me), 3.93 (br t, 1 H, ArCH), 6.20 (dd, 1 H, H3', $J_{1,3'}$ = 0.33 Hz, $J_{3',4'}$ = 3.68 Hz), 6.56 (dd, 1 H, H4', $J_{1,4'}$ = 0.50, $J_{3',4'}$ = 3.68 Hz), [AA'XX' pattern] 6.68 (m, 2 H), 7.32 (m, 2 H, J_{AX} + $J_{AX'}$ = 8.1 Hz); IR ($CHCl_3$) 1530, 1490, 1375, 1345, 1160, 815 cm^{-1}; UV (MeOH) 225 (sh, ϵ 1.42 × 10^4), 307 nm (7.7 × 10^3); mass spectrum, *m/z* (relative intensity) 337 (M^+, 1), 182 (100), 140 (22), 126 (9), 93 (26), 91 (31), 82 (17), 79 (12), 77 (10), 65 (19), 57 (10), 43 (12), 41 (20), 39 (13).

Anal. Calcd for $C_{16}H_{19}NO_5S$: C, 57.0; H, 5.7; N, 4.2. Found: C, 56.9; H, 5.7; N, 4.0.

2-(1'-Azido-2',2'-dimethylpropyl)-5-nitrofuran (16) (entry 7): a pale yellow oil; ^{1}H NMR δ 1.01 (s, 9 H, *t*-Bu), 4.36 (br t, 1 H, H1'), 6.56 (dd, 1 H, H3, $J_{1',3}$ = 0.5 Hz, $J_{3,4}$ = 3.7 Hz), 7.32 (dd, 1 H, H4, $J_{1',4}$ = 0.4 Hz, $J_{3,4}$ = 3.7 Hz); IR (liquid film) 2099, 1581, 1522, 1492, 1388, 1243, 1015 cm^{-1}; UV (EtOH) 312 nm (ϵ 1.11 × 10^4); mass spectrum, *m/z* (relative intensity) 182 (M^+ – N_3, 0.8), 181 (1), 168 (5), 140 (9), 123 (3), 108 (3), 93 (15), 91 (11), 57 (100), 43 (3), 41 (1); high-resolution mass spectrum calcd for $C_9H_{12}N_4O_3$ – N_3 182.0813, found M^+ – N_3 182.0817.

Anal. Calcd for $C_9H_{12}N_4O_3$: C, 48.2; H, 5.4; N, 25.0. Found: C, 48.4; H, 5.8; N, 24.9.

2,2-Dimethyl-1-(5'-nitro-2'-furyl)propyl *p*-tolyl sulfide (17) (entry 11): a thick yellow oil; ^{1}H NMR δ 1.15 (s, 9 H, *t*-Bu), 2.28 (s, 3 H, Me), 3.95 (t, 1 H, ArCH), 6.36 (dd, 1 H, H3', $J_{1,3'}$ = 0.43 Hz, $J_{3',4'}$ = 3.70 Hz), 7.18 (dd, 1 H, H4', $J_{1,4'}$ = 0.45, $J_{3',4'}$ = 3.70 Hz), [AA'XX' pattern] 7.03 (m, 2 H), 7.16 (m, 2 H, J_{AX} + $J_{AX'}$ = 8.0 Hz); IR (liquid film) 1486, 1351, 1241, 1016, 801 cm^{-1}; UV (EtOH) 222 (sh, ϵ 1.39 × 10^4), 326 nm (8.57 × 10^3); mass spectrum, *m/z* (relative intensity) 305 (M^+ 35), 259 (100), 249 (40), 232 (36), 217 (11), 182 (60), 140 (31), 124 (86), 107 (13), 91 (61), 82 (34), 79 (55), 65 (19), 57 (48).

Anal. Calcd for $C_{16}H_{19}NO_3S$: C, 62.9; H, 6.3; N, 4.6. Found: C, 62.8; H, 6.2; N, 4.6.

Oxidation of the sulfide **17** with *m*-chloroperbenzoic acid in dichloromethane at room temperature gave sulfone **15** identical with the sample isolated from reactions of **1** with **7**.

2-[2',2'-Dimethyl-1'-(5''-nitro-2''-furyl)propyl]-2-methylmalononitrile (18) (entry 20): mp 117–119 °C (light petroleum), which decomposed on exposure to light and on standing at room temperature; ^{1}H NMR δ 1.27 (s, 9 H, *t*-Bu), 1.77 (s, 3 H, Me), 3.20 (m, 1 H, H1'), 6.73 (br d, 1 H, H3'', $J_{1',3''} \leq$ 0.15 Hz, $J_{3'',4''}$ = 3.75 Hz), 7.33 (dd, 1 H, H4'', $J_{1',4''}$ = 0.45 Hz, $J_{3'',4''}$ = 3.75 Hz); IR ($CHCl_3$) 1591, 1491, 1356, 1021 cm^{-1}; UV (EtOH) 293 nm (ϵ 6.21 × 10^3); mass spectrum, *m/z* (relative intensity) 261 (M^+, 0.1), 246 (0.3), 205 (16), 178 (9), 167 (12), 93 (26), 79 (4), 65 (2), 57 (100), 51 (42), 41 (20); high-resolution mass spectrum (the molecular ion at *m/z* 261 was too weak to measure accurately) calcd for $C_{13}H_{15}N_3O_3$ – C_4H_8 205.0487, found, M^+ – C_4H_8 (isobutylene) 205.0487.

Reactions of Chloride 1 with the Lithium Salt 13 (Entries 23 and 24). The crude product from these reactions was separated by column chromatography (10–25% ethyl acetate/light petroleum) to give unchanged **1**, alcohol **3**, and ketone **2** (each identical with authentic samples) and **2,2-dimethyl-1-[4'-(1''-methyl-1''-nitroethyl)-2'-furyl]-1-propanone 19**: white prisms, mp 89–90 °C (cyclohexane); ^{1}H NMR δ 1.34 (s, 9 H, *t*-Bu), 1.96 (s, 6 H, Me_2CNO_2), 7.29 (d, 1 H, H3', $J_{3',5'}$ = 1.03 Hz), 7.65 (d, 1 H, H5', $J_{3',5'}$ = 1.03 Hz); ^{13}C NMR (coupled spectrum) δ 26.7 (qm, Me_2 and Me_3, $^1J_{C,H}$ = 130 Hz), 43.1 (decet, C2, ^2J = 4 Hz), 84.0 (septet, CMe_2NO_2, ^2J = 4 Hz), 116.5 (dd, C3', ^1J = 178 Hz, $^3J_{C,H5'}$ = 6 Hz), 128.5 (m, C4'), 142.5 (dd, C5', ^1J = 203, $^3J_{C,H3'}$ = 7 Hz), 153.2 (d, C2', $^2J_{C,H3'}$ = 6 Hz), 194.7 (m, C1); IR ($CHCl_3$) 1665, 1545, 900 cm^{-1}; UV (MeOH) 267 nm (ϵ 1.26 × 10^4); mass spectrum, *m/z* (relative intensity) 193 (M^+ – NO_2, 100), 136 (10), 135 (11), 108 (11), 79 (11), 57 (94), 41 (40).

Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.2; H, 7.2; N, 5.9. Found: C, 60.4; H, 7.3; N, 5.7.

Reaction of Compound 18 with the Sodium Salt 10. Reaction of compound **18** (26 mg, 0.1 mmol) with sodium salt **10** (16 mg, 0.2 mmol) in dimethylformamide (2.0 mL) at 20 °C, under oxygen, and with sunlamp irradiation for 5.5 h gave a poor recovery of unchanged chloride **1** (<20%) and no trace of the ketone **2**.

Methanolyses of Chloride 1 (Entry 27). The chloride **1** (35 mg, 0.16 mmol) was heated under reflux in methanol (2.0 mL) for 3 h. Workup gave the unchanged chloride **1**.

Registry No. **1**, 108344-54-3; **2**, 23222-86-8; **3**, 108344-55-4; **4**, 108344-56-5; **7**, 824-79-3; **8**, 26628-22-8; **9**, 10486-08-5; **10**, 81709-97-9; **11**, 333-20-0; **12**, 18424-77-6; **13**, 3958-63-2; **15**, 108344-57-6; **16**, 108344-58-7; **17**, 108344-59-8; **18**, 108344-60-1; **19**, 101384-07-0; O_2, 7782-44-7; di-*tert*-butyl nitroxide, 2406-25-9; galvinoxyl, 2370-18-5; 2-methylmalononitrile, 3696-36-4.