Substitution and Elimination Reactions *via* One Electron Transfer Process. A New Olefin Synthesis from β-Nitro Sulfones[1]

Noboru Ono,* Rui Tamura, Tamon Nakatsuka, Jun-ichi Hayami,[2] and Aritsune Kaji

Department of Chemistry, Faculty of Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

(Received April 15, 1980)

gem-Bromonitro compounds or *gem*-dinitro compounds couple with carbanions derived from α-cyano sulfones or α-carbonyl sulfones to give β-nitro sulfones. The nitro and sulfonyl groups are eliminated from the coupling products on treatment with reductive one electron transfer reagents to give α,β-unsaturated carbonyl compounds or nitriles.

Reductive elimination of nitro groups from the vicinal dinitro compounds is a useful procedure for olefin synthesis, where olefins are obtained in good yields by the action of mild reducing agents such as sodium sulfide,[3] tin(II) chloride,[4] or calcium amalgam.[5] If one of the nitro groups can be replaced by a sulfonyl group in this type of elimination, synthetic utility must increase to give a wide variety of olefins from β-nitro sulfones.

In this paper we wish to report the preparation of β-nitro sulfones by the reaction of *gem*-bromonitro compounds(**1**) or *gem*-dinitro compounds(**2**) with α-sulfonyl carbanions followed by the conversion of β-nitro sulfones to olefins.

Results and Discussion

Preparation of β-Nitro Sulfones. The reaction of *gem*-bromonitro compounds(**1**) or *gem*-dinitro compounds(**2**) with α-sulfonyl carbanions was carried out in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide(DMSO) as shown in Eq. 1. Carbanions sta-

$$\underset{\substack{|\\ NO_2}}{R^1R^2C}\text{-X} + ArSO_2\text{-}\bar{C}(Y)R^3M^+ \longrightarrow \underset{\substack{|\\ NO_2}}{R^1R^2C}\text{—}\underset{\substack{|\\ SO_2Ar}}{C}(Y)R^3 \quad (1)$$

1 X=Br; **2** X=NO_2; **4**

Y=CN, $-\overset{\overset{O}{\|}}{C}-$; Ar=*p*-Tolyl or phenyl; M=Na, K

bilized by the sulfonyl and cyano groups or by the sulfonyl and carbonyl groups react with **1** or **2** to give the cross coupling products(**4**), but carbanions stabilized by one sulfonyl group or by the sulfonyl and nitro groups do not react with **1** or **2** at all. Results are summarized in Table 1.

Compounds **1** or **2** undergo a variety of reactions with carbanions. The following three types of reactions have been reported; 1) cross coupling reaction *via* a radical chain process, 2) cross coupling reaction *via* a radical non-chain process, 3) oxidative dimerization of carbanions.[6] Carbanions which undergo type 1 reaction are those derived from nitroalkanes, malonate esters, malonitriles, β-keto nitriles, cyanoacetates, β-keto esters, and β-diketones.[7]

It is clear that the coupling reaction of Eq. 1 proceeds *via* a radical chain process, since it is completely inhibited by the presence of 10 mol% of di-*t*-butylnitroxide. Thus, carbanions derived from α-cyano sulfones and α-carbonyl sulfones undergo type 1 reaction. A chain sequence of this type of reaction can be expressed as follows.

$$R\text{-}X + C^- \longrightarrow R\text{-}X^{\cdot-} + C\cdot$$
$$R\text{-}X^{\cdot-} \longrightarrow R\cdot + X^- \qquad X=\text{leaving groups}$$
$$R\cdot + C^- \longrightarrow R\text{-}C^{\cdot-} \qquad C^-=\text{carbanions}$$
$$R\text{-}C^{\cdot-} + R\text{-}X \longrightarrow R\text{-}C + R\text{-}X^{\cdot-}$$

It should be emphasized that the coupling reaction using α-sulfonyl carbanions involves anion radical intermediates from which a sulfonyl group can be eliminated.[8] Actually, α,β-unsaturated nitriles are formed in about 10% yield during the preparation of **4c**, **4d**, **4f**, or **4g**. This lowers the yield of the coupling products, however, this finding has an important bearing in a sense of organic synthesis.

Potassium is used as a counter cation of carbanions to prepare **4j**, **4l**, and **4m**. The reactions using sodium as a counter cation proceed very slowly. For example, it takes about 30 h to complete the reaction to prepare **4l** when sodium is a counter cation. Not much attention has been paid to counter cations of carbanions in nucleophilic substitution reaction *via* a radical chain process. Although sodium salts of carbanions have often been used, potassium salts seem to be much more reactive than sodium salts and are generally the reagent of choice.[9]

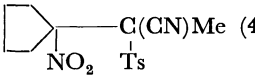
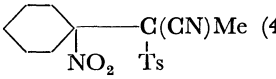
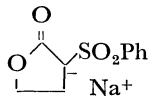
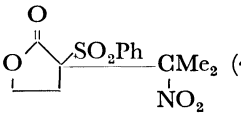
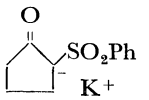
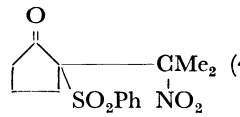
All attempts to bring about a coupling reaction of a carbanion stabilized by one sulfonyl group with **1** or **2** have failed. Starting materials were recovered unchanged (see Table 1). Simple β-nitro sulfones, the requisite starting materials to get non-functionalized olefins, have not been available by this S_{RN} route. Carbanions stabilized by one nitro group react with **1** or **2** very rapidly to afford the coupling products in good yields,[3] but highly stabilized carbanions such as those stabilized by the nitro and sulfonyl or by the nitro and carbonyl groups do not react with **1** or **2**. A possible explanation is that these highly stabilized anion is not a good electron donor to the S_{RN} acceptor.[10] Thus elimination from the vicinal dinitro compounds cannot be applied to the preparation of olefins substituted by electron-withdrawing groups at the sp^2 center.

Conversion of β-Nitro Sulfones to Olefins It is expected that the nitro and sulfonyl groups are eliminated from β-nitro sulfones on treatment with reductive one electron transfer reagents. In fact, **4a** is converted to olefin(**5a**) on treatment with various one electron transfer reagents as shown in Table 2 (Eq. 2). Inter-

$$\mathbf{4a} \longrightarrow \underset{(\mathbf{5a})}{Me_2C{=}C(CN)Me} \quad (2)$$

estingly, such a weak reducing agent as sodium

Table 1. Preparation of β-nitro sulfones (4)

Nitro compound	Carbanion	Solvent	Temp °C	Time h	Products	Yield[a] %
$Me_2C(Br)NO_2$ (**1a**)	$MeC^-(CN)Ts\ Na^+$ (**3a**)[b]	DMF	0	1.5	$Me_2C(NO_2)-C(CN)Me(Ts)$ (**4a**)	73
$Et(Me)C(NO_2)_2$ (**2b**)	**3a**	DMF	0	5	$Et(Me)C(NO_2)-C(CN)Me(Ts)$ (**4b**)	63
	**3a**	DMF	0	2	 (**4c**)	45[c]
	**3a**	DMF	0	3	 (**4d**)	40[c]
$Me_2C(NO_2)_2$ (**2a**)	$EtC^-(CN)Ts\ Na^+$	DMF	−20	5	$Me_2C(NO_2)-C(CN)Et(Ts)$ (**4e**)	65
2a	$n\text{-}C_4H_9C^-(CN)Ts\ Na^+$	DMF	−20	5	$Me_2C(NO_2)-C(CN)n\text{-}C_4H_9(Ts)$ (**4f**)	45[c]
2a	$n\text{-}C_8H_{17}C^-(CN)Ts\ Na^+$	DMF	−20	5	$Me_2C(NO_2)-C(CN)n\text{-}C_8H_{17}(Ts)$ (**4g**)	48[c]
2a	$MeC^-(CO_2Et)Ts\ Na^+$	DMF	25	3	$Me_2C(NO_2)-C(CO_2Et)Me(Ts)$ (**4h**)	80
2b	$MeC^-(CO_2Et)Ts\ Na^+$	DMSO	25	5	$Et(Me)C(NO_2)-C(CO_2Et)Me(Ts)$ (**4i**)	70
2a	$EtC^-(CO_2Et)Ts\ K^+$	DMSO	25	10	$Me_2C(NO_2)-C(CO_2Et)Et(Ts)$ (**4j**)	59
2a		DMSO	25	5	 (**4k**)	62
2a	$MeC^-(CMe)Ts\ K^+$ (C=O)	DMSO	25	5	$Me_2C(NO_2)-C(Ts)(CMe)Me$ (C=O) (**4l**)	49[d]
2a		DMSO	25	10	 (**4m**)	54[d]
2a	$EtC^-(NO_2)Ts\ Na^+$	DMSO	25	24	No reaction	
2a	$Me_2C^-Ts\ Na^+$	DMSO	25	5	No reaction	

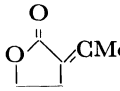
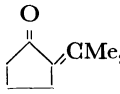
a) Pure isolated yield. b) Ts=*p*-CH_3-$C_6H_4SO_2$-. c) α,β-Unsaturated nitrile is obtained in about 10% yield. d) The reaction is carried out under irradiation of 150W tungsten lamp.

Table 2. Conversion of **4a** to **5a** under various conditions

Reducing reagent	Solvent	Light	Temp °C	Time h	Yield of **5a**[a] /%
$Na_2S\cdot 9H_2O$	DMF	20W[b]	25	3	92
$Na_2S\cdot 9H_2O$	DMF	dark	25	3	90
PhSNa	DMF	150W[c]	25	3	70
PhSNa	DMF	dark	25	3	5
$Me_2C(NO_2)^-Li^+$	DMF	150W	25	3	53
$Me_2C(NO_2)^-Li^+$	DMF	dark	25	3	2
Na	HMPA[d]		0	0.25	70
$Na_2S_2O_4$	HMPA	20W	25	168	50

a) Yields were determined by GLPC. b) Fluorescent lamp. c) Tungsten lamp. d) Hexamethylphosphoric triamide.

Table 3. Conversion of β-nitrosulfones(**4**) to olefins(**5**) on treatment with sodium sulfide

4	5	Yield[a]/%
4a	$Me_2C{=}C(CN)Me$ (**5a**)	69
4b	$Et(Me)C{=}C(CN)Me$ (**5b**)	62
4c	 (**5c**)	70
4d	 (**5d**)	70
4e	$Me_2C{=}C(CN)Et$ (**5e**)	62
4f	$Me_2C{=}C(CN)n\text{-}C_4H_9$ (**5f**)	71
4g	$Me_2C{=}C(CN)n\text{-}C_8H_{17}$ (**5g**)	74
4h	$Me_2C{=}C(CO_2Et)Me$ (**5h**)	79
4i	$Et(Me)C{=}C(CO_2Et)Me$ (**5i**)	60
4j	$Me_2C{=}C(CO_2Et)Et$ (**5j**)	59
4k	 (**5k**)	62
4l	$Me_2C{=}C(\overset{\overset{O}{\|}}{C}Me)Me$ (**5l**)	48[b]
4m	 (**5m**)	65

a) Pure isolated products. b) Besides **5l**, α,β-unsaturated sulfone (**6**) was obtained in 15% yield.

benzenethiolate or the lithium salt of 2-nitropropane can induce the elimination of Eq. 2, when the reaction mixture is irradiated by a 150 W tungsten lamp. Among various reducing agents, sodium sulfide is the best one to prepare olefins in its availability, effectiveness and in the mildness of the reaction conditions. β-Nitro sulfones(**4**) listed in Table 1 are converted to olefins (**5**) on treatment with sodium sulfide in DMF at room temperature (Eq. 3). Results are summarized

$$\mathbf{4} + Na_2S \longrightarrow \underset{(\mathbf{5})}{R^1R^2C{=}C(Y)R^3} + NaNO_2 + S + ArSO_2Na \quad (3)$$

$Y = CN, -\overset{\overset{O}{\|}}{C}-$

in Table 3. The reaction proceeds very rapidly as shown in Fig. 1. The yield in the table refers to pure and isolated products. The reaction proceeds smoothly to give **5** in good yields, for example, the yield of **5a** or **5f** determined by GLPC using an internal standard is 92 and 97%, respectively. On treatment with sodium sulfide, elimination from **4h**, **4i**, or **4j** proceeds faster than hydrolysis of an ester function of these compounds. Thus, α,β-unsaturated carboxylates are obtained in good yields on treatment with **4h**, **4i**, or **4j** with sodium sulfide.

But the reaction of **4l** with sodium sulfide gives the mixture of **5l** and α,β-unsaturated sulfone(**6**) (Eq. 4).

$$\mathbf{4l} + Na_2S \longrightarrow \mathbf{5l} + \underset{(\mathbf{6})}{Me_2C{=}C(SO_2Ar)Me} \quad (4)$$

Compound **6** is formed by elimination of the nitro and acetyl groups from **4l**. This may proceed *via* one electron transfer process.[11]

It is recommended to carry out the coupling reaction

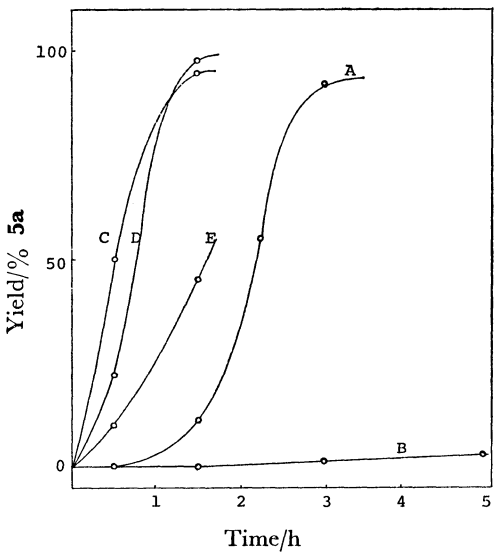


Fig. 1. Effects of di-*t*-butylnitroxide and nitro aromatics on the reaction of Eq 3. A: None, B: di-*t*-butylnitroxide (5 mol%), C: *m*-DNB (10 mol%), D: *p*-DNB (10 mol%), E: nitrobenzene (10 mol%).

Table 4. Synthesis of α,β-unsaturated nitriles by one-pot procedure

R^1	R^2	X	R^3	Products[a] (Yield/%)
CH_3	CH_3	NO_2	C_2H_5	**5e** (74)[b]
CH_3	CH_3	NO_2	$n\text{-}C_8H_{17}$	**5g** (77)[b]
$-(CH_2)_5-$		Br	CH_3	**5d** (71)[c]
CH_3	$n\text{-}C_5H_{11}$	NO_2	CH_3	**5n** (68)[c]
CH_3	$n\text{-}C_5H_{11}$	NO_2	$n\text{-}C_8H_{17}$	**5o** (62)[c]

a) $R^1R^2C{=}C(CN)R^3$. b) Yields were determined by GLPC. c) Pure isolated products.

of carbanions with **1** or **2** and the subsequent elimination by one-pot procedure to prepare α,β-unsaturated nitriles, for some amounts of olefins are already formed while the coupling reaction proceeds. Thus, α,β-unsaturated nitriles are obtained in good yields by the one-pot procedure shown in Eq. 5. Results are summarized in Table 4.

$$\mathbf{1}\text{ or }\mathbf{2} + \underset{CN}{R^3\bar{C}}\text{-}SO_2Ar\ Na^+ \xrightarrow[3\,h]{-20\text{ or }0^\circ C} \xrightarrow[3\,h]{rt} \underset{Na_2S}{R^1R^2C{=}C(CN)R^3} \quad (5)$$

The elimination of the nitro and sulfonyl groups from β-nitro sulfones is not a simple ionic process. This is clear from the data in Fig. 1, where the effect of di-*t*-butylnitroxide or nitro aromatics on the reaction of Eq. 3 is summarized. Five mol% of di-*t*-butylnitroxide inhibits this reaction completely, this fact suggests that the present elimination reaction proceeds by a free radical chain mechanism. As shown in Fig. 1, the reaction is strongly affected by nitrobenzene, *m*-dinitrobenzene (*m*-DNB), and *p*-dinitrobenzene(*p*-DNB). These nitro aromatic compounds generally retard the substitution reaction *via* one electron transfer

processes, but the present reaction is accelerated by these π-acids. These facts, and observations of other aliphatic nitro system,[3,7] suggest that the elimination reaction is initiated by the formation of anion radical of β-nitro sulfone, from which sulfinate ion and nitrogen dioxide can be split off (Eq. 6).[12]

$$\mathbf{4} \longrightarrow \underset{\mathbf{4}^{\cdot-}}{\underset{NO_2^{\cdot-}}{>}\!\!-\!\!\underset{SO_2Ar}{<}} \longrightarrow >C{=}C< + NO_2\cdot + ArSO_2^- \qquad (6)$$

The unique olefin synthesis reported herein provides a potentially useful alternative to the classical methods using carbonyl compounds and carbanions. An important feature of the present procedure is that both the coupling and the elimination steps proceed *via* radical chain mechanism involving one electron transfer process to give highly hindered olefins under mild conditions.

Experimental

Solvents were purified by distillation. The IR spectra were recorded with a Hitachi 215 spectrophotometer. The ^{1}H-NMR spectra were recorded using a JEOL PE-100 spectrometer with TMS as an internal standard. GLPC analyses were performed with a Varian Aerograph 920 using a column containing Silicone DC-550 (20%, 1 m). The following compounds were prepared by the standard procedure; *gem*-bromonitro compounds,[13] *gem*-dinitro compounds,[14] α-cyanoalkyl sulfones.[15] Other sulfones were prepared by the reaction of the corresponding bromides with sodium *p*-toluenesulfinate or sodium benzenesulfinate in DMF. All reactions for the preparation of β-nitro sulfones (**4**) and olefins (**5**) were performed under a nitrogen atmosphere.

Preparation of β-Nitro Sulfones (4). Preparation of 4a as a Typical Procedure: Sodium hydride (44 mmol, 50% mineral oil dispersion) was placed in a 300 ml flask which was fitted with a rubber septum through which reagents can be introduced by a syringe. After sodium hydride was washed with hexane to remove mineral oil, the flask was placed under nitrogen and 50 ml of DMF was introduced *via* a syringe. A solution of 2-tosylpropionitrile (8.4 g, 40 mmol) in 50 ml of DMF was added dropwise to sodium hydride and the mixture was stirred until the evolution of hydrogen ceased. Then the DMF solution of the carbanion was cooled to 0 °C and to this solution was added 2-bromo-2-nitropropane (8.1 g, 40 mmol) in 30 ml of DMF. The resulting solution was stirred at 0 °C for 1.5 h. Working up by dilution with water, benzene extraction, followed by aqueous washing of the benzene layer, drying over anhydrous magnesium sulfate, and concentration gave a solid material. The crude material was recrystallized from ethanol to give **4a** (8.6 g, 73% yield). Other β-nitro sulfones were prepared by the similar procedure, but **4g** and **4i** were purified by column chromatography on silica gel using benzene as an eluent. Compound **4b** consisted of two diastereomers (A and B). They were separated by column chromatography on silica gel using benzene as an eluent. The ratio of A to B was unity. For the preparation of **4j**, **4k**, and **4m**, t-C_4H_9OK was used as a base instead of NaH. Reaction conditions are summarized in Table 1 and physical data of **4** are summarized in Table 5.

Inhibition Study. The reaction of the sodium salt of 2-tosylpropionitrile with 2-bromo-2-nitropropane was carried out at 0 °C. Each experiment consists of the sodium salt of the nitrile (6 mmol) and the nitro compound (7 mmol) in 15 ml of DMF and a reaction time of 1 h. Working up was carried out in the usual way. In the absence of di-*t*-butylnitroxide the crude product was subjected to column chromatography on silica gel using benzene as an eluent to give **4a** (1.0 g, 68% yield). In the presence of di-*t*-butylnitroxide (0.086 g, 0.6 mmol) **4a** was not detected on TLC. The crude product was subjected to column chromatography to give 2-tosylpropionitrile (0.85 g, 70% recovery).

Conversion of 4a to 5a under Various Conditions. Compound **4a** (1 mmol) was treated with various reducing reagents (3 mmol) under conditions listed in Table 2. After the period listed in the table, diethyl malonate (1 mmol) which is an internal standard was added. Then the reaction mixture was worked up in the usual manner and the organic materials were analyzed by GLPC. Yield of **5a** was determined from calibration curve which was made from pure **5a** and diethyl malonate. Results are summarized in Table 2.

Conversion of β-Nitro Sulfones (4) to Olefins (5) by Sodium Sulfide. General Procedure: A mixture of **4** (15 mmol) and $Na_2S{\cdot}9H_2O$ (5.0 g, 18 mmol) in 30 ml of DMF was stirred at room temperature for 3 h, then 150 ml of water was added and the mixture was extracted with diethyl ether three times. The extract was washed with water, dried over magnesium sulfate, and concentrated. Distillation gave **5**. The following olefins were prepared by this procedure.

Physical Properties: **5a**: Bp 60 °C/35 Torr. (1 Torr=133.32 Pa, lit,[16] 155—157 °C). ^{1}H-NMR (CCl_4); δ 2.04 (3H, s), 1.82 (6H, s). IR (neat); 2215 cm^{-1} (CN), 1640 cm^{-1} (C=C). MS (20 eV), *m/e* (rel intensity), 95 (M^+, 100), 80(41), 68 (50).

5b: Bp 82 °C/40 Torr (lit,[17] 64 °C/17 Torr). ^{1}H-NMR (CCl_4); δ 2.44 (1H, q, J=7.5 Hz), 2.23 (1H, q, J=7.5 Hz), 2.07 (1.5H, s), 1.88 (3H, s), 1.84 (1.5H, s), 1.12 (1.5H, t, J=7.5 Hz), 1.06 (1.5H, t, J=7.5 Hz). IR (neat); 2215 cm^{-1} (CN), 1640 cm^{-1} (C=C). MS (20 eV), *m/e* (rel intensity), 109 (M^+, 14), 94(16), 67(14), 43(100).

5c: Bp 112.5 °C/32 Torr (lit,[18] 131/63 Torr). ^{1}H-NMR (CCl_4); δ 2.72—2.42 (2H, m), 2.42—2.16 (2H, m), 1.80 (3H, s), 2.0—1.6 (4H, m). IR (neat); 2215 cm^{-1} (CN), 1640 cm^{-1} (C=C). MS (20 eV), *m/e* (rel intensity), 121 (M^+, 34), 106(13), 67(80), 43(100).

5d: Bp 110 °C/15 Torr (lit,[19] 103 °C/13 Torr). ^{1}H-NMR (CCl_4); δ 2.6—2.4 (2H, m), 2.4—2.2 (2H, m), 1.87 (3H, s), 1.8—1.4 (6H, m). IR (neat); 2205 cm^{-1}(CN), 1627 cm^{-1}(C=C). MS (20 eV), *m/e* (rel intensity), 135 (M^+, 46), 120(20), 81(74), 68(100).

5e: Bp 92 °C/25 Torr. ^{1}H-NMR (CCl_4); δ 2.24 (2H, q, J=7.1 Hz), 2.07 (3H, s), 1.86 (3H, s), 1.13 (3H, t, J=7.1 Hz). IR (neat); 2210 cm^{-1}(CN), 1635 cm^{-1}(C=C). MS (20 eV), *m/e* (rel intensity), 109 (M^+, 12), 94(20), 67(12), 43(100).

5f: Bp 95 °C/25 Torr. ^{1}H-NMR (CCl_4); δ 2.19 (2H, m), 2.08 (3H, s), 1.85 (3H, s), 1.6—1.2 (4H, m), 0.97 (3H, t, J=7.1 Hz). IR (neat); 2210 cm^{-1} (CN), 1635 cm^{-1}(C=C). MS (20 eV), *m/e* (rel intensity), 137 (M^+, 25), 122(17), 96(18), 69(100).

5g: Bp 93.5 °C/0.6 Torr. ^{1}H-NMR (CCl_4); δ 2.17 (2H, m), 2.06 (3H, s), 1.84 (3H, s), 1.1—1.6 (12H, m), 0.89 (3H, t, J=7.5 Hz). IR (neat); 2210 cm^{-1}(CN), 1635 cm^{-1}(C=C). MS (20 eV), *m/e* (rel intensity), 193 (M^+, 51), 178(62), 164(80), 136(100).

5h: Bp 106 °C/100 Torr (lit,[20] 99 °C/81.5 Torr). ^{1}H-NMR (CCl_4); δ 4.10 (2H, q, J=7.0 Hz), 2.00 (3H, s), 1.77 (6H, s), 1.28 (3H, t, J=7.0 Hz). IR (neat); 1700 cm^{-1} (C=O), 1620 cm^{-1}(C=C). MS (20 eV), *m/e* 135 (M^+).

5i: Bp 95 °C/38 Torr (lit,[21] 67—72 °C/14 Torr). ^{1}H-

Table 5. Physical data of β-nitro sulfones (4)

4	Mp/°C	^{1}H-NMR: δ(CDCl$_3$, J)	IR ν̄/cm^{-1}	Found (%) (Calcd %) C	H	N	Molecular formula
4a	118.5—119.5	7.95(2H, d, 7.5 Hz), 7.40(2H, d. 7.5 Hz), 2.48(3H, s), 2.14(3H, s), 1.98(3H, s), 1.68(3H, s)	1555 1330 1160	52.52 (52.69	5.55 5.44	9.42 9.45)	$C_{13}H_{16}N_2O_4S$
4b	A 144—144.5	7.86(2H, d, 7.5 Hz), 7.40(2H, d, 7.5 Hz), 2.72(2H, q, 7.5 Hz), 2.48(3H, s), 1.92 (3H, s), 1.64(3H, s), 0.92(3H, t, 7.5 Hz)	1555 1330 1150	54.46 (54.18	5.98 5.85	8.72 9.03)	$C_{14}H_{18}N_2O_4S$
	B 129—130	7.86(2H, d, 7.5 Hz), 7.40(2H, d, 7.5 Hz), 2.48(3H, s), 2.10(2H, q, 7.5 Hz), 1.97 (3H, s), 1.81(3H, s), 0.93(3H, t, 7.5 Hz)	1555 1350 1150	53.97	5.94	9.00	
4c	121—121.5	7.91(2H, d, 7.5 Hz), 7.45(2H, d, 7.5 Hz), 2.5—2.9(4H, m), 2.52(3H, s), 1.84(3H, s), 1.0—1.9(4H, m)	1555 1335 1160	55.64 (55.89	5.25 5.36	8.40 8.69)	$C_{15}H_{18}N_2O_4S$
4d	161.5—162	7.87(2H, d, 7.5 Hz), 7.40(2H, d, 7.5 Hz), 2.3—2.8(4H, m), 2.49(3H, s), 1.63(3H, s), 1.4—1.8(6H, m)	1555 1325	57.03 (57.13	6.13 6.00	8.30 8.33)	$C_{16}H_{20}N_2O_4S$
4e	84—85	7.94(2H, d, 7.5 Hz), 7.46(2H, d, 7.5 Hz), 2.50(3H, s), 2.12(3H, s), 2.02(2H, q, 7.5 Hz), 1.96(3H, s), 0.88(3H, t, 7.5 Hz)	1550 1325 1145	54.19 (54.18	5.54 5.85	8.91 9.03)	$C_{14}H_{18}N_2O_4S$
4f	77.5—78.5	7.82(2H, d, 7.5 Hz), 7.38(2H, d, 7.5 Hz), 2.49(3H, s), 2.08(3H, s), 1.92(3H, s), 1.9—2.1(2H, m), 0.9—1.4(7H, m)	1555 1325 1145	56.98 (56.79	6.64 6.55	8.26 8.28)	$C_{16}H_{22}N_2O_4S$
4g	liquid	7.82(2H, d, 7.5 Hz), 7.36(2H, d, 7.5 Hz), 2.48(3H, s), 2.07(3H, s), 1.97(3H, s), 1.9—2.1(2H, m), 1.11(12H, m), 0.87(3H, m)	1565 1315 1160	60.51 (60.89	7.84 7.67	7.36 7.10)	$C_{20}H_{33}N_2O_4S$
4h	58—59	7.60(2H, d, 7.5 Hz), 7.24(2H, d, 7.5 Hz), 4.00(2H, q, 7.0 Hz), 2.46(3H, s), 2.24 (3H, s), 1.92(3H, s), 1.60(3H, s), 1.16 (3H, t, 7.0 Hz)	1740 1550 1160	52.30 (52.49	6.38 6.10	3.84 4.08)	$C_{15}H_{21}NO_6S$
4i	liquid	7.73(2H, d, 7.5 Hz), 7.31(2H, d, 7.5 Hz), 3.98(2H, m), 2.71(1H, q, 7.0 Hz), 2.48 (3H, s), 2.34(1H, q, 7.0 Hz), 2.20(1.5H, s), 1.90(1.5H, s), 1.71(1.5H, s), 1.50(1.5H, s), 1.04(6H, m)	1730 1540 1150	53.87 (53.77	6.63 6.49	3.95 3.92)	$C_{16}H_{23}NO_6S$
4j	83—84	7.70(2H, d, 7.5 Hz), 7.34(2H, d, 7.5 Hz), 4.16(2H, m), 2.45(3H, s), 2.40—2.10(2H, m), 2.21(3H, s), 2.03(3H, s), 1.25(3H, t, 7.0 Hz), 0.95(3H, t, 7.5 Hz)	1730 1550 1160	53.89 (53.77	6.60 6.49	3.99 3.92)	$C_{16}H_{23}NO_6S$
4k	133—134	7.89(2H, m), 7.60(3H, m), 4.06(1H, m), 3.65(1H, m), 3.22(1H, m), 2.45(1H, m), 2.00(3H, s), 1.98(3H, s)	1750 1545 1140	50.02 (49.83	4.98 4.83	4.33 4.47)	$C_{13}H_{15}NO_6S$
4l	139—140	7.65(2H, d, 7.5 Hz), 7.53(2H, d, 7.5 Hz), 2.45(3H, s), 2.07(3H, s), 1.98(3H, s), 1.96(3H, s), 1.80(3H, s)	1715 1540 1135	53.56 (53.66	6.19 6.11	4.52 4.47)	$C_{14}H_{19}NO_5S$
4m	76—77	7.89(2H, m), 7.60(3H, m), 2.2(2H, m), 2.00(3H, s), 1.82(3H, s), 1.6—2.0(4H, m)	1720 1545 1145	53.89 (54.01	5.38 5.50	4.32 4.50)	$C_{14}H_{17}NO_5S$

NMR (CCl_4); δ 4.14 (2H, q, J=7.0 Hz), 2.29 (2H, q, J=7.0 Hz), 1.94 (3H, s), 1.80 (3H, s), 1.28 (3H, t, J=7.0 Hz), 0.97 (3H, t, J=7.0 Hz). IR (neat); 1700 cm^{-1} (C=O), 1620 cm^{-1} (C=C). MS (20 eV), *m/e* 156 (M^+).

5j: Bp 54 °C/9 Torr (lit,[22] 67 °C/13 Torr). ^{1}H-NMR (CCl_4); δ 4.07 (2H, q, J=7.2 Hz), 2.25 (2H, q, J=7.2 Hz), 1.92 (3H, s), 1.78 (3H, s), 1.26 (3H, t, J=7.2 Hz), 0.95 (3H, t, J=7.2 Hz). IR (neat); 1700 cm^{-1} (C=O), 1630 cm^{-1} (C=C).

5k: Bp 109 °C/12 Torr (lit,[23] 71—73 °C/0.9 Torr). ^{1}H-

NMR (CCl_4); δ 4.20 (2H, t, J=7.5 Hz), 3.0—2.7 (2H, m), 2.21 (3H, t, J=1.5 Hz), 1.88 (3H, s). IR (neat); 1740 cm^{-1} (C=O), 1665 cm^{-1} (C=C).

5l: Bp 57 °C/49 Torr (lit,[24] 145—148 °C). ^{1}H-NMR (CCl_4); δ 2.10 (3H, s), 1.81 (6H, s), 1.73 (3H, s). IR (neat); 1690 cm^{-1} (C=O), 1610 cm^{-1} (C=C).

5m; Bp 80—82 °C/11 Torr (lit,[25] 78—79 °C/10 Torr). ^{1}H-NMR (CCl_4); δ 2.50 (2H, m), 1.9—2.1 (4H, m), 2.15 (3H, t, J=1.5 Hz), 1.80 (3H, s). IR (neat); 1700 cm^{-1} (C=O), 1610 cm^{-1} (C=C). MS (20 eV), *m/e* (rel intensity), 124 (M^+, 100), 108 (48), 96 (19), 82 (21).

Preparation of Olefins (5) by One-pot Procedure. Preparation of **5o** is described here as a typical procedure. To the 20 ml of the DMF solution of the sodium salt of 2-tosyldecanenitrile (20 mmol) which had been prepared as mentioned in the preparation of **4** was added 2,2-dinitroheptane (1.1 g, 6 mmol) in 5 ml of DMF at −20 °C, and the resulting solution was stirred at −20 °C for 3 h. Then $Na_2S\cdot 9H_2O$ (2.4 g, 9 mmol) was added to this solution. The reaction mixture was stirred at room temperature for additional 3 h. After the usual work up, the crude product was distilled to give **5o** (0.93 g, 62% yield). Bp 144.5 °C/1 Torr. ^{1}H-NMR (CCl_4); δ 2.35 (2H, t, J=7.5 Hz), 2.14 (2H, t, J=7.5 Hz), 2.02 (1.5H, s), 1.79 (1.5H, s), 1.30 (18H, m), 0.90 (6H, m). The NMR spectra show that **5o** consists of the equal amount of *E* and *Z* isomer. IR (neat); 2210 cm^{-1} (CN), 1630 cm^{-1} (C=C). MS (20 eV), *m/e* (rel intensity), 249 (M^+, 53), 234 (33), 220 (53), 206 (100), 192 (60). Found: C, 81.81; H, 12.82; N, 5.42%. Calcd for $C_{17}H_{31}N$: C, 81.86; H, 12.53; N, 5.62%. Similarly, **5n** was prepared in 68% yield. Bp 108 °C/21 Torr. ^{1}H-NMR (CCl_4); δ 2.36 (1.3H, t, J=7.5 Hz), 2.14 (0.7H, t, J=7.5 Hz), 2.02 (1H, s), 1.86 (3H, s), 1.80 (3H, s), 1.34 (6H, m), 0.92 (3H, t, J=7.5 Hz). IR (neat); 2210 cm^{-1} (CN), 1630 cm^{-1}(C=C). MS (20 eV), *m/e* (rel intensity), 151 (M^+, 38), 136 (15), 95 (85), 82 (100).

Elimination from 4l by Sodium Sulfide. The reaction of **4l** with sodium sulfide was carried out in the same way as described in a general procedure. A volatile product (**5l**) was distilled and the residue was subjected to a column chromatography to give **6** in 15% yield. Mp 60.5—61.5 °C. ^{1}H-NMR ($CDCl_3$); 7.72 (2H, d, J=7.5 Hz), 7.28 (2H, d, J=7.5 Hz), 2.42 (3H, s), 2.22 (3H, m), 1.89 (3H, m), 1.88 (3H, s). IR (Nujol); 1610 cm^{-1} (C=C). Found: C, 64.44; H, 7.12%. Calcd for $C_{12}H_{16}SO_2$: C, 64.25; H, 7.19%.

Reaction of 4a with Sodium Sulfide in the Presence of Di-t-butylnitroxide or Aromatic Nitro Compounds. The reaction of **4a** (0.888 g, 3 mmol) with sidium sulfide (2.16 g, 9 mmol) in 30 ml of DMF was carried out at room temperature in the presence of various additives, *i.e.*, A: none, B: di-*t*-butylnitroxide (0.022 g, 0.15 mmol), C: *m*-DNB (0.05 g, 0.3 mmol), D: *p*-DNB (0.05 g, 0.3 mmol), E: nitrobenzene (0.037 g, 0.3 mmol). The yield of **5a** was determined by GLPC, and the results are summarized in Fig. 1.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No 447020) from the Ministry of Education, Science and Culture.

References

1) For a preliminary communication on portion of this work, see, N. Ono, R. Tamura, J. Hayami, and A. Kaji, *Tetrahedron Lett.*, **1978**, 763.

2) Present address, Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University.

3) N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *J. Am. Chem. Soc.*, **93**, 4316 (1971).

4) K. Fukunaga and M. Kimura, *Bull. Chem. Soc. Jpn.*, **52**, 1107 (1979).

5) N. Kornblum and L. Cheng, *J. Org. Chem.*, **42**, 2944 (1977).

6) G. A. Russell, M. Jawdosiuk, and M. Makosza, *J. Am. Chem. Soc.*, **101**, 2355 (1979).

7) G. A. Russell, R. K. Norris, and E. J. Panek, *J. Am. Chem. Soc.*, **93**, 5839 (1971); N. Ono, H. Eto, R. Tamura, J. Hayami, and A. Kaji, *Chem. Lett.*, **1976**, 757; N. Ono, R. Tamura, J. Hayami, and A. Kaji, *Chem. Lett.*, **1977**, 189; Review: N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).

8) The sulfone group is eliminated as a sulfinate ion from anion radicals of α-nitro sulfones: N. Kornblum, S. D. Boyd, and N. Ono, *J. Am. Chem. Soc.*, **96**, 2580 (1974). So the behaviour of anion radicals of β-nitro sulfones is of interest.

9) We have found that the potassium salts of β-diketones or β-keto esters are also more reactive to **1** or **2** than the corresponding sodium salts. This finding has enabled one to prepare new coupling products of carbanions with **1** or **2** which are difficult to prepare using the sodium salts.

10) Reactivity of carbanions to **1** or **2** is an interesting problem, but complexities of chain sequence preclude a detailed discussion about this. The reaction of free radicals with carbanions to form anion radicals consists of the following equilibrium. $R\cdot + C^- \rightleftharpoons R^- + C\cdot \rightleftharpoons R\text{-}C^{\cdot}$ It is noteworthy that the chain reaction proceeds when the stability of R^- and C^- is close.

11) R. Tamura, T. Nakatsuka, N. Ono, and A. Kaji, *Chem. Lett.*, **1980**, 281, where the nitro and acetyl groups are eliminated from β-acetyl nitro compounds *via* one electron transfer processes.

12) A number of chain sequences can be envisioned, but we cannot specify the mechanism at the time being. Nitrogen dioxide may be involved in a chain sequence.

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

14) R. B. Kaplan and H. Shecter, *J. Am. Chem. Soc.*, **83**, 3535 (1961).

15) N. Ono, R. Tamura, R. Tanikaga, and A. Kaji, *Synthesis*, **1977**, 690.

16) B. T. Brooks, U. S. Patent 2364422 (1944); *Chem. Abstr.*, **1945**, 3545.

17) E. M. Osman and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 881 (1944).

18) S. F. Birch and G. A. R. Kon, *J. Chem. Soc.*, **123**, 2440 (1923).

19) A. Kandiah and R. P. Linstead, *J. Chem. Soc.*, **1929**, 2139.

20) R. C. Huston and G. L. Goerner, *J. Am. Chem. Soc.*, **68**, 2504 (1946).

21) G. A. R. Kon and K. S. Nargund, *J. Chem. Soc.*, **1932**, 2461.

22) R. C. Huston, G. L. Goerner, and H. H. György, *J. Am. Chem. Soc.*, **70**, 389 (1948).

23) K. Tanaka, H. Uneme, N. Yamagishi, N. Ono, and A. Kaji, *Chem. Lett.*, **1978**, 653.

24) P. G. Stevens, *J. Am. Chem. Soc.*, **56**, 450 (1934).

25) G. A. R. Kon and J. H. Nutland, *J. Chem. Soc.*, **1926**, 3101.