Enhanced Reactivities in Substitution and Elimination Reactions in Dimethyl Sulphoximide [1]

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The dielectric constants of dimethyl sulphoximide (DMSOI), tetramethylene sulphoximide (TMSOI), and dimethyl *N*-methylsulphoximide (*N*-MeDMSOI) were measured. The sulphoximides were tested as solvents for typical nucleophilic substitutions (S_N2) and base-catalysed $E2$ reactions. The rates for several S_N2 reactions and the activation parameters of the typical S_N2 reaction between butyl bromide and sodium azide in DMSOI revealed that it behaves almost like a polar aprotic solvent despite the presence of the protic NH group. In a mixed solvent of DMSOI and MeOH, the rates of a few S_N2 reactions were enhanced more than those in dimethyl sulphoxide–MeOH or dimethylformamide–MeOH. The rate enhancements of S_N2 reactions in various mixed solvents appeared to be related to their pK_a values. While the rate of the $E2$ reaction of 1-methylheptyl bromide with sodium methoxide or potassium t-butoxide in DMSOI is substantially higher (240 times) than that in methanol or t-butyl alcohol, the orientation of olefin formation in elimination from 2-substituted octanes in sulphoximides is similar to that in MeO⁻–MeOH. Solvolyses of some alkyl tosylates and halides in DMSOI afforded the corresponding dimethyl *N*-alkyl sulphoximides in moderate yields. These results indicate that the sulphoximides belong to a new type of solvent which is protic in origin but also behaves almost like a characteristic polar aprotic solvent.

For the last two decades, bimolecular organic reactions with nucleophiles in polar aprotic solvents have received considerable attention due to the remarkable rate enhancement observed with such solvents as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), hexamethylphosphoramide (HMPA), *N*-methylpyrrolidone, etc.[2,3] Each of these polar aprotic solvents appears to support ' naked ' anions which are extremely powerful nucleophiles.[2] For example, the relative rates of the reaction between methyl iodide and chloride ion in MeOH and DMF are 1 and 7.4 × 10⁶,[4] while the methoxide ion-catalysed racemization of 2-methyl-3-phenylpropiononitrile in MeOH is accelerated by nearly 10⁹-fold on changing the solvent from MeOH to DMSO.[5]

In our studies on sulphoximides, we found that sulphoximido-group is quite basic, *i.e.* the pK_a value is much larger than those of the corresponding sulphone and sulphoxide groups.[6] One example of the markedly different behaviour of sulphoximides from that of the corresponding sulphones is that the lower alkyl sulphoximides such as dimethyl sulphoximide (DMSOI) or tetramethylene sulphoximide (TMSOI) can dissolve many inorganic salts in substantial quantities like most polar aprotic solvents and are freely soluble both in polar solvents such as water and alcohols and in nonpolar solvents such as benzene and dioxan. We found recently that in the presence of a small amount of DMSOI in chloroform, hydroxide ion is activated by the strong solvation of Na⁺ ion by DMSOI and attacks chloroform to generate dichlorocarbene.[7] We also found that the rates of S_N2 reactions of alkyl halides were substantially enhanced in DMSOI. These observations suggest that sulphoximides may be used as polar rate-enhancing solvents, somewhat similar to DMSO or DMF despite their protic nature. Thus, in order to exploit new and useful applications for sulphoximides, a few alkyl sulphoximides were prepared and tested as solvents. This paper describes the unprecedented solvent properties of the sulphoximides for a few typical nucleophilic reactions as well as for $E2$ reactions and also a new method of preparing dimethyl *N*-alkylsulphoximides by treating DMSOI with the corresponding alkyl tosylates or halides.

RESULTS AND DISCUSSION

Physical Properties of Sulphoximides.—A few sulphoximides, *i.e.* DMSOI, TMSOI, dimethyl *N*-methylsulphoximide (*N*-MeDMSOI), prepared by conventional methods,[6] are found to be freely soluble in water or other organic solvents. They were also found to dissolve most common inorganic salts to a considerable extent upon heating above their m.p.s. The dielectric constants of the sulphoximides were measured by the usual two-terminal method and their values (Table 1)

TABLE 1

Physical properties of sulphoximides

B.p. (°C)/p (mmHg)	DMSOI	TMSOI	*N*-MeDMSOI
	100/5 ᵃ	140/7	80/5
$d_{25}°$	1.1819 ᵇ	1.2453	1.1236
ε	16—22 ᶜ	37 ᵈ	24 ᵉ
pK_a	3.24 ᶠ		

ᵃ M.p. 52—53 °C.[6] ᵇ At 65 °C. ᶜ At 26—27 °C. ᵈ At 27 °C. ᵉ At 23 °C. ᶠ Ref. 9.

indicate clearly that they are highly polar. Unfortunately, the dielectric constant of DMSOI could not be determined accurately because of its hygroscopic nature; however it is estimated to be in the range 16—22. The dielectric constant of TMSOI is larger than that of HMPA and comparable with that of DMF.[8] B.p.s, densities, and pK_a values [9] are also listed in Table 1.

The solubilities of common inorganic salts in a few typical solvents and DMSOI are summarized in Table 2.

Inspection of Table 2 revealed that DMSOI can dissolve many inorganic salts, in a manner similar to DMF, indicating that DMSOI is a polar solvent like DMF.

Solvent Effects of DMSOI in S_N2 *Reactions.*—The typical S_N2 reaction between butyl bromide and sodium azide was carried out in DMSOI and the activation parameters of the reactions were determined. As shown in

TABLE 2

Solubilities of inorganic salts (g per 100 ml)

Salt	MeOH$_{25°}$ [a]	Acetone$_{25°}$ [a]	DMF$_{25°}$ [a]	DMSOI$_{65°}$	DMSO$_{25°}$ [b]
KSCN	soluble	20.75	18.2	15	
NaN$_3$	1	$<10^{-2}$		2	
KI	17.4	2.93	>25.0	27	
KCl	0.53	8.7×10^{-4}	<0.05	<1	
AgNO$_3$				4	130

[a] Ref. 4. [b] ' Dimethyl Sulphoxide Technical Bulletin,' Crown Zellerbach Co., 1963 or 1966 edns.

Table 3, the rate constant k_2 calculated by the second-order kinetic equation is $1.44 \pm 0.11 \times 10^{-1}$ l mol^{-1} s^{-1} at 60 °C. The activation parameters are E_a 18.56 kcal mol^{-1} and $\Delta S^{\ddagger}$ -8.90 cal mol^{-1} K^{-1} (r 0.999). The product obtained in quantitative yield was found to be butyl azide.

Since DMSOI is also a nucleophile bearing an imido-group, the Menshutkin type reaction between DMSOI and butyl bromide proceeds concurrently with the normal S_N2 reaction with sodium azide. However, the rate of the reaction calculated by the pseudo-first-order kinetic equation was found to be negligibly small (k_1 $5.39 \pm 0.31 \times 10^{-4}$ s^{-1} at 60 °C) and hence can be omitted in the kinetic calculation.

Delpuech had reported a kinetic study of the S_N2 reaction between butyl bromide and sodium azide in a few common solvents [10] and the results are listed in Table 3 together with our result in DMSOI. This typical S_N2 reaction is accelerated markedly in DMSOI,

withdrawing sulphoximido NH group which is protic, and yet quite nucleophilic, like phosphoramides.

One drawback of DMSOI is that it is a solid at room temperature (m.p. 52—53 °C) and it is difficult to dissolve inorganic salts at room temperature. Therefore, a mixed solvent system of DMSOI and MeOH was used for the S_N2 reactions and the effect was compared with that of DMSO–MeOH or DMF–MeOH. The results obtained are summarized in Table 4.

Inspection of the data in Table 4 reveals clearly that the rate of the reaction between butyl bromide and sodium azide is accelerated more in DMSOI–MeOH than in DMF–MeOH. Similarly, the S_N2 reaction between benzyl chloride and potassium cyanide was carried out in the same mixed solvents. Here again, the Menshutkin-type reaction with the solvent was negligible and the

TABLE 3

Reaction of BuBr with NaN$_3$ in various solvents

Solvent [a]	$k_{60°}$/l mol^{-1}s^{-1})	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
(CH$_2$)$_4$SO$_2$	4.95×10^{-2}	15.36	-17.3
DMF	4.39×10^{-1}	16.45	-13.0
DMSO	2.29×10^{-1}	16.91	-12.9
DMSOI [b]	$1.44 \pm 0.11 \times 10^{-1}$ [c]	18.5 ± 2.2	-9 ± 6
MeOH	3.70×10^{-4}	21.18	-12.8
H$_2$O	2.59×10^{-3}	21.41	-8.28

[a] Rate constants and activation parameters were calculated from the results cited in ref. 10. [b] Present study. [c] $k_{65°}$ $2.15 \pm 0.15 \times 10^{-1}$, $k_{70°}$ $3.26 \pm 0.21 \times 10^{-1}$ l mol^{-1} s^{-1}.

product obtained quantitatively was found to be benzyl cyanide. The results shown in Table 4 reveal that the rate was enhanced markedly in DMSOI–MeOH compared with that in pure MeOH. Once again, DMSOI showed the largest rate acceleration among mixed solvent systems with MeOH for compositions of

TABLE 4

Rate constants for the S_N2 reactions BuBr + NaN$_3$ ⟶ BuN$_3$ + NaBr (I) and PhCH$_2$Cl + KCN ⟶ PhCH$_2$CN + KCl (II) in mixed solvents with MeOH

			$k_{60°}$ l mol^{-1} s^{-1}		
Wt % MeOH	100	80	50	30	0
(I) MeOH	3.70×10^{-4} *				
DMSOI		$7.27 \pm 0.27 \times 10^{-4}$	$2.09 \pm 0.12 \times 10^{-3}$	$5.96 \pm 0.15 \times 10^{-3}$	$1.44 \pm 0.11 \times 10^{-3}$
DMSO		$6.93 \pm 0.15 \times 10^{-4}$	$2.55 \pm 0.05 \times 10^{-3}$	$7.40 \pm 0.25 \times 10^{-3}$	2.29×10^{-1} *
DMF		$6.32 \pm 0.27 \times 10^{-4}$	$1.78 \pm 0.08 \times 10^{-3}$	$4.92 \pm 0.37 \times 10^{-3}$	4.39×10^{-1} *
(II) MeOH	$1.79 \pm 0.08 \times 10^{-4}$				
DMSOI			$1.19 \pm 0.05 \times 10^{-3}$	$3.62 \pm 0.09 \times 10^{-3}$	
DMSO			$7.99 \pm 0.37 \times 10^{-4}$	$2.17 \pm 0.02 \times 10^{-3}$	
DMF			$5.04 \pm 0.03 \times 10^{-4}$	$1.39 \pm 0.07 \times 10^{-3}$	

* Calculated from the results cited in ref. 10.

DMSO, or sulpholan compared with such protic solvents as MeOH or H$_2$O. The activation parameters of the S_N2 reaction in DMSOI fall in the range between those in common polar aprotic solvents and those in protic solvents. According to Delpuech, the activation energy of this reaction is usually <17 kcal mol^{-1} in polar aprotic solvents, while in protic solvents it is generally >20 kcal mol^{-1}.[10] This means that DMSOI has dual properties, *i.e.* it is a protic solvent and yet behaves like a polar aprotic solvent. Indeed, DMSOI has a strong electron-

50 and 30% DMSOI. The large rate enhancement in DMSOI–MeOH may be due to the basic nature of the sulphoximido-group. The pK_a values of DMF,[8] DMSO,[8] and DMSOI [9] are -0.01, 1.4, and 3.24, respectively. In MeOH, the nucleophile is considered to be solvated strongly by hydrogen bonding with MeOH. However, the addition of DMSOI, DMSO, or DMF diminishes the solvation of the nucleophile by MeOH (by breaking hydrogen bonding with the solvent) and this would be more effective for solvents with higher pK_a

values.[11] This is why the largest rate enhancement was observed in DMSOI–MeOH. When the amount of MeOH was small, the mixed solvent behaves almost like an aprotic solvent, thus resulting in a large rate acceleration of the S_N2 reactions.[11]

Mode of E2 Reactions in DMSOI.—The E2 reaction of 1-methylheptyl bromide or tosylate with either sodium

stantial in the potassium t-butoxide–DMSOI system (Table 6). This is mainly due to the poor solubility of sodium methoxide in DMSOI but not to the formation of substitution products. In the potassium t-butoxide–sulphoximide systems, except in N-MeDMSOI, the actual base should be the corresponding sulphoximido-anion formed by proton removal from imido-group by a strong

TABLE 5

Elimination of 1-methylheptyl bromide

1-Methylheptyl bromide + OR⁻ ⟶ oct-1-ene + *trans*-oct-2-ene + *cis*-oct-2-ene + Br⁻

Base–solvent	Temp (°C)	Time (min)	Total octene [a] yield (%)	Oct-1-ene	*trans*-Oct-2-ene	*cis*-Oct-2-ene	Oct-2-ene : oct-1-ene	*trans* : *cis*
MeONa–MeOH [b]	69.6			24.2	58.3	17.5	3.1	3.3
Bu^tOK–Bu^tOH [b]	69.6			82.8	9.6	7.6	0.21	1.26
Bu^tOK–DMSO [b]	30.0			50.4	41.7	7.9	0.98	5.3
MeONa–DMSOI	60.0	1440	30.3	22.8	58.7	18.5	3.4	3.2
Bu^tOK–DMSOI	60.0	1080	92.7	27.0	57.0	16.0	2.7	3.6
Bu^tOK–TMSOI	60.0	1080	90.2	11.0	69.3	19.7	8.1	3.5
Bu^tOK–N-MeDMSOI	60.0	1080	82.0	16.1	68.0	15.9	5.2	4.3

[a] The difference between the total olefin yield and 100% represents unchanged starting materials. [b] Ref. 12.

methoxide or potassium t-butoxide was accelerated substantially in DMSOI compared with MeOH or t-butyl alcohol. The products obtained were the corresponding olefins in both reactions. The rate constants k_2 were calculated by the second-order kinetic equation and found to be $4.48 \pm 0.31 \times 10^{-3}$ (DMSOI), and $1.87 \pm 0.07 \times 10^{-5}$ l mol⁻¹ s⁻¹ (t-butyl alcohol), respectively. The rate of this E2 reaction in DMSOI was 240 times larger than that in t-butyl alcohol.

Interesting results were observed in the orientation of

base, *i.e.* potassium t-butoxide (in sodium methoxide–sulphoximide methoxide ion is presumed to behave as the base) since, when these sulphoximides were treated with excess of methyl iodide, the corresponding N-methyl-sulphoximides were actually obtained, *e.g.* in the potassium t-butoxide–DMSOI system (see Experimental section).

In the E2 reaction of 1-methylheptyl bromide with potassium t-butoxide in DMSOI, the isomer ratios of the resulting olefins, *i.e.* oct-2-ene : oct-1-ene and *trans*-oct-

TABLE 6

Elimination of 1-methylheptyl tosylate

1-Methylheptyl tosylate + OR⁻ ⟶ oct-1-ene + *trans*-oct-2-ene + *cis*-oct-2-ene + OTs⁻

Base–solvent	Temp (°C)	Time (min)	Total octene [a] yield (%)	Oct-1-ene	*trans*-Oct-2-ene	*cis*-Oct-2-ene	Oct-2-ene : oct-1-ene	*trans* : *cis*
MeONa–DMSOI	60.0	1080	27.3	11.4	52.7	35.9	7.9	1.5
Bu^tOK–DMSOI	60.0	1020	67.9	43.4	35.4	21.2	1.3	1.7
Bu^tOK–TMSOI	60.0	1020	24.0	25.0	52.1	22.9	3.0	2.2
Bu^tOK–N-MeDMSOI	60.0	1020	17.3	29.7	51.4	18.9	2.4	2.6
DMSOI	95.0	1080	22.5 [b]	8.9	56.9	34.2	10.4	1.7

[a] The difference between the total olefin yield and 100% represents unchanged starting material. [b] Dimethyl N-(1-methylheptyl)-sulphoximide was obtained in 54.4% yield.

the olefins formed in these sulphoximides. The base-solvent systems employed were sodium methoxide or potassium t-butoxide–sulphoximide and the experiment was carried out according to the method reported by Bunnett *et al.*[12] Olefin isomerization was not observed under our present experimental conditions when a blank experiment was conducted using Bartsch's special experimental technique.[13]

The products obtained in the E2 reactions of 1-methylheptyl bromide and tosylate were oct-1-ene, *trans*-oct-2-ene, and *cis*-oct-2-ene. The reaction conditions, yields, and ratios of the stereoisomers obtained are summarized in Tables 5 and 6.

The yields of the products were rather poor in the reaction between 1-methylheptyl bromide or tosylate and sodium methoxide in DMSOI (Table 5), but sub-

2-ene : *cis*-oct-2-ene, were found to be identical with those observed in the E2 reactions in sodium methoxide–MeOH. It is interesting to compare these results with those of the E2 reaction of 1-methylpentyl tosylate in sodium methoxide–MeOH reported earlier.[14]

The higher *trans* : *cis* ratios obtained in N-MeDMSOI as well as DMSO or DMF is due to the polar aprotic nature of N-MeDMSOI in contrast to DMSOI and TMSOI. The E2 reaction of 2-substituted alkane in polar aprotic solvents generally affords the alkenes of higher *trans* : *cis* ratio.[14] An unusually high oct-2-ene : oct-1-ene ratio (8.1) was observed in the case of 1-methylheptyl bromide in potassium t-butoxide–TMSOI system. Perhaps the relatively high dielectric constant (37), polarizability, and somewhat high acidity of the imido-proton compared with other sulphoximides may be responsible for

the facile dissociation of bromide ion, eventually shifting the transition state to the E1-like paenecarbonium side, thus resulting in the predominant formation of the Saytzeff elimination products.

Direct Reaction between Alkyl Tosylates and Halide with DMSOI.—When 1-methylheptyl tosylate was treated with DMSOI, the corresponding N-substituted product, dimethyl N-(1-methylheptyl)sulphoximide, was formed in 54.4% yield together with the olefins in a total yield of 22.5%. The products obtained were identified by

tetramethylene sulphoximide (TMSOI) were prepared by the procedure reported earlier.[6] TMSOI was prepared in the following manner: to a mixture of tetramethylene sulphoxide (22 g, 0.21 mol) and sodium azide (56 g, 0.86 mol) in dry $CHCl_3$ (150 ml), stirred mechanically and cooled in an ice–water bath, was added dropwise and with care concentrated H_2SO_4 (56 ml). After addition was complete, the mixture was gradually warmed to 50—55 °C and maintained at this temperature for 60 h. After the mixture cooled, ice–water was added. The organic layer was separated and the solvent evaporated to give unchanged

TABLE 7

Yields, b.p.s, and n.m.r. spectra of dimethyl N-alkylsulphoximides

Alkyl	Yield (%)	B.p. (°C)/p(mmHg)	Chemical shift [d]
Octyl	83	115/8	0.68—1.87 (17 H, m, C_8H_{17}), 2.98 (6 H, s, SCH_3)
Benzyl	58	128/11	2.95 (6 H, s, SCH_3), 4.24 (2 H, s, CH_2), 7.26 (5 H, m, ArH)
2-Phenylethyl	72	126/8	2.83 (6 H, s, SCH_3), 3.05—3.45 (4 H, m, CH_2CH2), 7.15 (5 H, s, ArH)
1-Methylheptyl [a]	54	98/4	0.60—1.70 (17 H, m, C_8H_{17}), 2.97 (6 H, s, SCH_3)
Cyclohexyl [b]	38	100/8	0.85—2.03 (11 H, m, C_6H_{11}), 3.00 (6 H, s, SCH_3)
1-Adamantyl	91	133.5—134.5 [c]	1.55—2.20 (15 H, m, $C_{10}H_{15}$), 3.00 (6 H, s, SCH_3)

[a] Octene was obtained in 22.5% yield.   [b] Cyclohexene was obtained in 46.5% yield.   [c] M.p.   [d] In $CDCl_3$ at 35 °C.

spectroscopic and elemental analyses. The isolation of [N-(1-methylheptyl)amino]oxosulphonium tosylate suggests that this substitution proceeds *via* a Menshutkin-type S_N2 reaction. When 1-iodoadamantane [15] was treated similarly in DMSOI, dimethyl N-(1-adamantyl)-sulphoximide was obtained in 91% yield suggesting that the S_N1-type reaction is also enhanced in DMSOI.

Similarly, several alkyl tosylates [16] were treated in DMSOI and the results obtained are summarized in Table 7. In the reaction of cyclohexyl tosylate with DMSOI, the formation of cyclohexene reduced the yield of the N-substitution product.

Recently, a convenient method of preparing dimethyl N-arylsulphoximides was reported by Swern and his co-workers; [17] however no general procedure for preparing various N-alkyl-substituted sulphoximides has been reported previously. This reaction of various alkyl tosylates and halides with DMSOI constitutes a syntheses of the corresponding N-alkyl-substituted dimethyl sulphoximides.

EXPERIMENTAL

General.—Chemicals used were of reagent grade unless otherwise specified. M.p.s and b.p.s were uncorrected. I.r. spectra were taken on a Hitachi 215 spectrometer. N.m.r. spectra were obtained with a Hitachi R-24 or Hitachi–Perkin-Elmer R-20 spectrometer for dilute solutions in deuteriochloroform using tetramethylsilane as internal standard. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. A Yanako model G 80 (FID) or a Hitachi 163 gas chromatograph were used for g.l.c. with nitrogen or helium as carrier gas. Dielectric constants were taken with a Meguro Denpa Soki MQ-160 B instrument using a 1 MHz alternating current. Silica gel used for column chromatography was of either Wako or Merck chromatographic grade; for t.l.c. Merck DC-Plastik-folien Kieselgel 60 F 254 with a fluorescent indicator was used.

Sulphoximides.—Dimethyl sulphoximide (DMSOI) and

starting materials. The aqueous layer was made slightly basic with $NaHCO_3$ and was extracted several times with CH_2Cl_2 (50 ml). The combined organic layers were dried ($MgSO_4$) and after removal of the solvent, the product was purified by distillation *in vacuo*. TMSOI (14.6 g, 0.12 mol, 58%) was obtained as a transparent liquid, b.p. 140° at 7 mmHg, $v_{max.}$ (NaCl) 3 250 (NH), 1 200, and 1 040 cm^{-1} (O=S=N), δ 2.27 (4 H, m, CH_2), 2.72 (1 H, s, NH), and 3.14 (4 H, m, SCH_2), m/e 119 (M^+) (Found: C, 39.9; H, 7.4; N, 11.5. C_4H_9NOS requires C, 40.3; H, 7.6; N, 11.75%).

Dimethyl N-methylsulphoximide (N-MeDMSOI) was prepared in the following manner: potassium t-butoxide (25 g, 0.22 mol) was added to DMSOI (50 g, 0.54 mol) with stirring and heated at 90 °C for 12 h. After the mixture was returned to room temperature, excess CH_3I (41.2 g, 0.29 mol) was added with cooling in an ice–water bath. Potassium iodide was filtered off after the addition of CH_2Cl_2 (200 ml). Removal of the solvent under reduced pressure afforded a mixture of DMSOI, unchanged starting material, and N-MeDMSOI. The mixture was separated by column chromatography with silica gel using $CHCl_3$ a · eluant, and N-MeDMSOI (11.7 g, 0.11 mol, 49%) wa: obtained as a transparent liquid upon purification under a reduced pressure of nitrogen, b.p. 82° at 5 mmHg, $v_{max.}$ (NaCl) 1 110, 1 150, and 1 235 cm^{-1} (O=S=N), δ 2.79 (3 H, s, NCH_3) and 2.98 (6 H, s, SCH_3), m/e 107 (M^+) (Found: C, 33.4; H, 8.3; N, 12.8. C_3H_9NOS requires C, 33.6; H, 8.5; N, 13.1%).

Densities, Solution Properties, and Dielectric Constants of Sulphoximides.—The densities of sulphoximides and the solubilities of inorganic salts in DMSOI were measured at the desired temperature. The results obtained are summarized in Table 1.

The dielectric constants of the sulphoximides were measured at room temperature.[18] The value of DMSOI was measured for a range of applied pressure of 400 kg cm^{-2} to 10^{-3} Torr at 26—27 °C for 16 h. The value obtained, ε 18.9 ± 3.0, was derived from the calculation according to Bottch's equation.[19] The value of TMSOI at 27 °C was 37.2 and that of N-MeDMSOI at 23 °C was 24.0.

Kinetics.—The kinetic procedure for the reaction between butyl bromide and sodium azide in DMSOI is as follows: to

a hermetically sealed solution of sodium azide (4.0×10^{-4} mol) in DMSOI (3.6×10^{-2} mol) at 60 ± 0.025 °C was added butyl bromide (3.7×10^{-4} mol) and toluene (2.3×10^{-4} mol) as the internal standard. At intervals, 0.2 ml of the solution was taken out and immediately quenched into cold 1N-HCl (0.5 ml). After addition of benzene (ca. 20 μl), the mixture was shaken vigorously for a while. The benzene layer was then separated and 2 μl of the benzene solution injected directly into a gas chromatograph. The column was a 2.5-m stainless-steel tube (3 mm i.d.), packed with 15% squalane (60—80 mesh) on Chromosorb W, the oven temperature was 65 °C, and the pressure of carrier gas was 25 ml min^{-1}. The rate constants for the reaction were calculated by the second-order kinetic equation, where the change in concentration of butyl bromide was calculated from the relative peak areas of butyl bromide and toluene. The activation parameters were calculated from the rate constants obtained at three different temperatures by the Arrhenius equation. The results obtained are listed in Table 3.

Rate constants for the reaction between butyl bromide and DMSOI were also derived by an identical procedure except for the absence of NaN$_3$. Rate constants, obtained from the pseudo-first-order kinetic equation, are $k_{60°}$ $5.39 \pm 0.31 \times 10^{-4}$ and $k_{70°}$ $9.90 \pm 0.48 \times 10^{-4}$ s^{-1}.

The kinetic procedures for the reaction between butyl bromide and sodium azide in mixed solvents of DMSOI, DMSO, and DMF with MeOH were as follows. To a solution of sodium azide (6.1×10^{-4} mol) in mixed solvent (5 ml) was added butyl bromide (5.8×10^{-4} mol) and toluene (3.3×10^{-4} mol) as internal standard at room temperature. The solution (0.3 ml) was taken into a 1 ml ampoule by a 1 ml syringe. Several ampoules were then immersed in an incubator at 60 ± 0.025 °C and removed at intervals. The solution was quenched with cold water (0.5 ml). After addition of benzene (ca. 20 μl), the ampoule was shaken vigorously for a while. The benzene layer was then separated immediately and 2 μl of the solution was injected directly into a gas chromatograph. The results are summarized in Table 4.

Rate constants of the reaction between benzyl chloride and potassium cyanide in mixed solvents of DMSOI, DMSO, and DMF with MeOH were obtained similarly. Benzyl chloride (6.6×10^{-4} mol) and bromobenzene (3.7×10^{-4} mol) as internal standard were added to a solution of potassium cyanide (7.9×10^{-4} mol) in mixed solvent (5 ml) and the mixture was kept at room temperature. Then solution (0.3 ml) was taken in a 1 ml ampoule by a 1 ml syringe, and further treated as above. The chromatography column used was a 2-m stainless-steel tube (3 mm i.d.), packed with 10% silicone G.E. SE-30 (60—80 mesh) on Chromosorb, the oven temperature was 88 °C, and the pressure of carrier gas was 10 ml min^{-1}. The rate constants were obtained by using the second-order kinetic equation, where the change in concentration of benzyl chloride was calculated from the relative peak areas of bromobenzene. The results are summarized in Table 4.

Rates of the reaction between 1-methylheptyl bromide with potassium t-butoxide in DMSOI and in t-butyl alcohol were followed in the manner described for the kinetic procedure for the S_N2 reaction in DMSOI. The internal standard added was mesitylene, the temperature of the thermostatted bath was maintained at 60 ± 0.025 °C, and the column was a 2-m stainless-steel tube (3 mm i.d.) packed with 10% silicone G.E. SE-30 (60—80 mesh) on

Chromosorb W, oven temperature 100 °C, pressure of carrier gas 16 ml min^{-1}. The rate constants were obtained using the second-order kinetic equation, k_2 $4.48 \pm 0.31 \times 10^{-3}$ in DMSOI and $1.87 \pm 0.07 \times 10^{-5}$ l mol^{-1} s^{-1} in t-butyl alcohol.

Elimination of 1-Methylheptyl Bromide or Tosylate.—To an ampoule (10 ml) containing a solution of 1-methylheptyl bromide or tosylate (1.1×10^{-3} mol) in the sulphoximide (3.0×10^{-2} mol) was added sodium methoxide or potassium t-butoxide (2.0×10^{-3} mol) at room temperature. The ampoule was then immersed in an oil-bath and maintained at the desired temperature for the desired time. After cooling, the products were extracted carefully with hexane (1 ml) and analysed by g.l.c. using toluene as internal standard by comparing their g.l.c. behaviour with that of authentic samples. The column used was a 2-m stainless-steel tube (3 mm i.d.), packed with 10% silicone G.E. SE-30 (60—80 mesh) on Chromosorb W, oven temperature 39.5 °C, pressure of carrier gas 27 ml min^{-1}. The results are summarized in Tables 5 and 6.

Solvolyses of Alkyl Tosylates and Halides in Dimethyl Sulphoximide (DMSOI).—An alkyl tosylate or halide (2.5×10^{-3} mol) was added to DMSOI (1.9×10^{-2} mol) in an ampoule (10 ml) at room temperature. The ampoule was then heated at 95 °C for 20 h. After cooling the mixture with dry ice–MeOH, the solution was quenched with H$_2$O (5 ml) and extracted with CHCl$_3$ (5 ml). The aqueous layer was made slightly alkaline with Na$_2$CO$_3$ in order to neutralize the corresponding (N-alkylamino)-oxosulphonium tosylate or halide. In the reaction between 1-iodo-adamatane and DMSOI, dimethyl N-(1-adamantyl)sulphoximide was obtained immediately as a crystalline solid when H$_2$O was added to the reaction mixture. The combined organic layers were dried (MgSO$_4$) and removal of the solvent afforded the corresponding dimethyl N-alkyl-sulphoximide.

The products were purified by recrystallization or distillation by Kugelrohr apparatus under reduced pressure. Their yields, m.p.s or b.p.s, and n.m.r. spectra are summarized in Table 7. Oct-1- and -2-enes were obtained in 22.5% total yield and small amount of [N-(1-*methyl-heptyl*)*amino*]*oxosulphonium tosylate* was also obtained in the reaction of 1-methylheptyl tosylate with DMSOI, needles (from CH$_2$Cl$_2$–ether), m.p. 107—108 °C, $\nu_{max.}$ (KBr) 1 010, 1 035, 1 120, 1 175, 1 225, and 1 250 cm^{-1}, δ 0.60—1.80 (17 H, m, C$_8$H$_{17}$), 2.35 (3 H, s, ArCH$_3$), 3.80 (6 H, s, SCH$_3$), and 7.00—7.80 (4 H, ABq, Ar) (Found: C, 54.3; H, 8.3; N, 4.05. C$_{17}$H$_{31}$NO$_4$S$_2$ requires C, 54.1; H, 8.3; N, 3.7%).

Dimethyl N-*octylsulphoximide* forms hygroscopic crystals, m.p. 37—39 °C, $\nu_{max.}$ (NaCl) 1 120 and 1 220 cm^{-1} (O=S=N), *m/e* 205 (M^+) (Found: C, 58.1; H, 11.2; N, 6.7. C$_{10}$H$_{23}$NOS requires C, 58.5; H, 11.3; N, 6.8%).

Dimethyl N-*benzylsulphoximide* forms hygroscopic crystals, m.p. 56—57 °C, $\nu_{max.}$ (NaCl) 1 125, 1 215 (O=S=N), and 3 020 cm^{-1} (C$_6$H$_5$) (Found: C, 58.8; H, 7.0; N, 7.6. C$_9$H$_{13}$NOS requires C, 59.0; H, 7.15; N, 7.6%).

Dimethyl N-(2-*phenylethyl*)*sulphoximide* is a hygroscopic pale yellow oil, $\nu_{max.}$ (NaCl) 1 135, 1 230 (O=S=N), and 3 020 cm^{-1} (C$_6$H$_5$), *m/e* 106 {[CH$_3$S(O)(NCH$_2$)CH$_2$]$^+$, 100%}, 91 ([C$_6$H$_5$CH$_2$]$^+$, 9.4), 78{[CH$_3$S(O)CH$_3$]$^+$, 19.7}, and 77([C$_6$H$_5$]$^+$, 3.5) Found: C, 60.6; H, 7.7; N, 7.35. C$_{10}$H$_{15}$NO$_3$ requires C, 60.9; H, 7.7; N, 7.1%).

Dimethyl N-(1-*methylheptyl*)*sulphoximide* is a hygroscopic liquid, $\nu_{max.}$ (NaCl) 1 135 and 1 235 cm^{-1} (O=S=N), *m/e* 205

(M^+) (Found: C, 58.2; H, 11.4; N, 6.7. $C_{10}H_{23}NOS$ requires C, 58.5; H, 11.3; N, 6.8%).

Dimethyl N-cyclohexylsulphoximide forms hygroscopic crystals, m.p. 46—48 °C, $\nu_{max.}$ (KBr) 1 120 and 1 220 cm^{-1} (O=S=N), m/e 175 (M^+) (Found: C, 54.2; H, 9.6; N, 8.1. $C_8H_{16}NOS$ requires C, 54.8; H, 9.8; N, 8.0%).

Dimethyl N-(1-adamantyl)sulphoximide forms crystals upon recrystallization from acetone–hexane, $\nu_{max.}$ (KBr) 1 150 and 1 250 cm^{-1} (O=S=N), m/e 227 (M^+) (Found: C, 63.5; H, 9.3; N, 5.9. $C_{12}H_{21}NOS$ requires C, 63.4; H, 9.3; N, 6.2%).

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