TABLE I

Fractional atomic coordinates for triglycine calcium bromide

Atom	x	y	z
Br (1)	−0·2556	0·1778	0·3556
Br (2)	0·2722	0·2056	0·3750
Br (3)	0·2278	0·4222	0·2444
Br (4)	−0·2444	0·4611	0·2416
Ca (1)	0·1750	0·2361	0·0111
Ca (2)	0·3278	0 0139	0·1028
O (11)	0·177	0·139	0·121
O (21)	0·025	0·258	0·110
C (11)	0·083	0·194	0·142
C (21)	0·045	0·183	0·215
N (11)	−0·058	0·269	0·253
O (12)	0·322	0·110	−0·002
O (22)	0·472	−0·011	0·000
C (12)	0·411	0 056	−0·028
C (22)	0·456	0·069	−0·100
N (12)	0·533	−0·011	−0·131
O (13)	0·069	0·383	0·000
O (23)	−0·128	0·443	0·052
C (13)	0·011	0·433	0·044
C (23)	0·097	0·494	0·092
N (13)	0·260	0·488	0·076
O (14)	0·369	0·311	0·061
O (24)	0·571	0·376	0·108
C (14)	0·508	0·322	0·069
C (24)	0·596	0·263	0 020
N (14)	0·760	0·258	0·034
O (15)	−0·198	0·064	−0·056
O (25)	−0·042	0·158	−0·028
C (15)	−0·069	0·094	−0·064
C (25)	0·039	0·047	−0·111
N (15)	−0·037	−0·035	−0·139
O (16)	0·708	0·192	0·167
O (26)	0·528	0·094	0·133
C (16)	0·583	0·156	0·167
C (26)	0·467	0·206	0·211
N (16)	0·525	0·291	0·242

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POTASSIUM BROMATE OXIDATION OF ARYL METHYL SULPHIDES

NUMEROUS oxidizing agents[1,2] have been used for the transformation of dialkyl, diaryl and alkyl aryl sulphides to sulphoxides. The products are usually contaminated with the sulphides and/or the corresponding sulphones. Good yields of sulphoxides are reported in oxidations using potassium periodate[2], t-butyl hypochlorite[3], N-halosuccinimides[4] and iodobenzene dichloride[4a], but a low temperature is required for the reaction.

We have now observed that the reaction between aryl methyl sulphides and potassium bromate in 3 : 1 mole ratio at room temperature yields sulphoxides in high yield and purity. The sulphoxides have been characterised by elemental analysis, boiling and/or melting point and mixed melting point (Table I). Their IR and UV absorption spectra are identical with those of the authentic samples obtained by chromic acid[5] oxidation of the sulphides. A very strong S=O stretch absorption occurs in the 1035–1025 cm^{-1} region and the UV absorption maximum occurs around 238 nm in ethanol for these sulphoxides. These values agree with those reported in the literature[6,7].

The reaction in 1 : 1 mole ratio at 100° C leads to the formation of sulphones in 60–70% yield, which are characterised by melting points and mixed melting points with authentic samples (Table II). This study demonstrates a convenient method to obtain sulphoxides in high yield and purity.

Experimental

1. *Aryl methyl sulphoxides* : *General method.*— To a solution of aryl methyl sulphide (0·051 mole) in glacial acetic acid (25 ml) was added Analar potassium bromate (0·017 mole) dissolved in minimum amount of water, in small portions with shaking and cooling under the tap. The mixture was strongly coloured. If any turbidity developed more glacial acetic acid was added to make it homogeneous and then it was allowed to stand for an hour. It was poured into 200 ml of water and neutralised with sodium carbonate. The organic layer was extracted with chloroform and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the liquid distilled under vaccum.

In the case of p-bromophenylmethyl sulphide the sulphoxide separated as soon as the addition of potassium bromate was completed. It was collected on a filter and crystallisation from aqueous ethanol afforded colourless plates.

2. *Aryl methyl sulphones* : *General method.*— Potassium bromate (0·03 mole) dissolved in the minimum quantity of hot water was added to a hot

TABLE I

Characterization data for sulphoxides Ar–SO–CH₃

Ar	Yield, %	B.P./mm, (M.P.), °C Found	Literature	Reference	S=O (ν cm⁻¹)*
C_6H_5	80	118–20/5	144/15	8	1030
$p\text{-}CH_3C_6H_4$	86	138–40/12 (42)	113–4/2 (42–43)	8	1030
$o\text{-}CH_3C_6H_4$	85	138–9/9·5	..	..	1032
$p\text{-}ClC_6H_4$	86	135–6/5 (48)	135–6/5 (47–48)	8	1028
$p\text{-}BrC_6H_4$	95	(87)	(86–87)	9	1033**
$p\text{-}CH_3OC_6H_4$	75	152–3/5	153–4/5	8	1035
$o\text{-}CH_3OC_6H_4$	77	148–50/5	..	..	1025

*IR spectra were recorded on Perkin-Elmer 257 (neat).
**IR spectra in KBr pellet.

TABLE II

$Ar\text{-}SO_2\text{-}CH_3$

Ar	Yield, %	M.P., °C Found	Litera- ture	Refer- ence
C_6H_5	60	88	88	1
$p\text{-}CH_3C_6H_4$	65	88–89	89	11
$p\text{-}ClC_6H_4$	62	96	96	12
$p\text{-}BrC_6H_4$	70	99	99–100	9

solution of the aryl methyl sulphide (0·03 mole) in glacial acetic acid (25 ml), kept on a water-bath and allowed to stand for an hour. It was cooled, poured into crushed ice, stirred and the pricipitated sulphone was collected on a filter and recrystallised from suitable solvents.

Kinetics of oxidation to sulphoxide are under investigation.

We wish to thank Professor N. Arumugam, Head of the Department of Chemistry, for his help and encouragement. Financial support from the Madurai University (PR. A) is gratefully acknowledged.

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CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL ON Mg Al₂₋ₓFeₓO₄

THE catalytic properties of transition metal ions (Ni, Cr) in the environment of a diamagnetic matrix ($MgAl_2O_4$) has attracted a lot of attention in recent years[1,2]. Reports on the catalytic activity of the system $Mg\,Al_{2-x}Fe_xO_4$, are not available although this system shows interesting variation in the electrical and magnetic properties as x varies from 0 to 2[3,4]. This system is also interesting structurally, as while $MgAl_2O_4$ is a normal spinel,