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REACTION OF SULPHOXIMIDES WITH DIAZOMALONATE IN THE PRESENCE OF Cu-SALT

A NEW SYNTHESIS AND STEREOCHEMISTRY OF OPTICALLY ACTIVE OXOSULPHONIUM YLIDES[1]

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Abstract—Sulphoximides (Ia-Ie) were found to react with dimethyl diazomalonate (DDM) in the presence of a catalytic amount of Cu-salts affording the corresponding oxosulphonium ylides in moderate yields. The reaction did not proceed at all under irradiation of UV light. (−)-Methylphenyloxosulphonium bis(methoxycarbonyl)-methylide ((−)-IIb) was obtained from (+)-(S)-methylphenylsulphoximide ((+)-(S)-Ib) together with (−)-(S)-methyl phenyl sulphoxide ((−)-(S)-IIIb) by this reaction. Hydrolysis of (−)-IIb gave (+)-methylphenyloxosulphonium methoxycarbonylmethylide ((+)-IIf) which was converted to (−)-(S)-IIIb upon treatment with dibenzoylethylene. Stereochemical cycle starting from (+)-(S)-Ib to (−)-(S)-IIIb was established and the absolute configurations of both ylides, (−)-IIb and (+)-IIf were assigned as (R)-configuration. The stereochemical courses, namely from (+)-(S)-Ib or (−)-(S)-IIIb to (−)-(R)-IIb or (+)-(R)-IIf to (−)-(S)-IIIb were determined as retention processes. The optical purities of the oxosulphonium ylides obtained from both reactions, (+)-(S)-Ib → (−)-(R)-IIb and (−)-(S)-IIIb → (−)-(R)-IIb, were almost equal. These results indicate that the mechanism of the reaction of sulphoximides with carbenes (or carbenoids) involves the initial formation of the sulphoxides which react subsequently with carbenes to afford the final products.

Recently, sulphoximides were found to have larger pKa values than those of the corresponding sulphones or sulphoxides, suggesting that sulphoximides are more polar and basic than sulphones or sulphoxides.[2] We found recently that when dimethylsulphoximide (DMSOI) was used as solvent, the rates of S_N2 reactions of alkyl halides were markedly enhanced as compared to those protic solvents as methanol or water and were nearly equal or comparable to those in such polar aprotic solvents as dimethyl sulphoxide or sulpholane.[3] This large rate enhancement of the S_N2 reactions in DMSOI suggests that the nucleophiles such as cyanide and azide are remarkably activated by strong solvation of the counter cations by sulphoximido group like in such polar aprotic solvents as dimethyl sulphoxide and dimethylformamide.

In the course of the studies on the chemistry of sulphoximides, we found that chloroform decomposed violently when it was treated with potassium hydroxide in the presence of DMSOI. When the decomposition was carried out in the presence of cyclohexene, 7,7-dichlorobicyclo[4.1.0]heptane was obtained only in 5% yield with a concomitant decomposition of DMSOI. This observation suggests that dichlorocarbene is generated and consumed by a competing reaction with DMSOI during the reaction thus lowering the yield of the carbene-olefin adduct. Therefore in order to clarify the nature of the reaction of sulphoximides with carbenes (or carbenoids), a few typical sulphoximides (Ia–Ic)[2] were treated with dimethyl diazomalonate (DDM) in the presence of a catalytic amount of Cu-salts. There was no reaction under irradiation of UV light incidentally, however in the thermal reactions, the NH group of sulphoximides was eventually displaced by dimethyl malonate group affording the corresponding oxosulphonium ylides as the major products.

Although preparations of optically active sulphoxides, sulphimides and sulphoximides were reported[4] and topological treatment of these compounds was documented by Cram *et al.*,[4] preparation of optically active oxosulphonium ylides has never appeared in the literature. This paper describes the reactions of sulphoximides with diazomalonate in the presence of Cu-salts and the syntheses and the stereochemistry of optically active oxosulphonium ylides, (−)-(R)-IIb and (+)-(R)-IIf along with the most likely mechanism of this new substitution reaction on the chiral S atom.

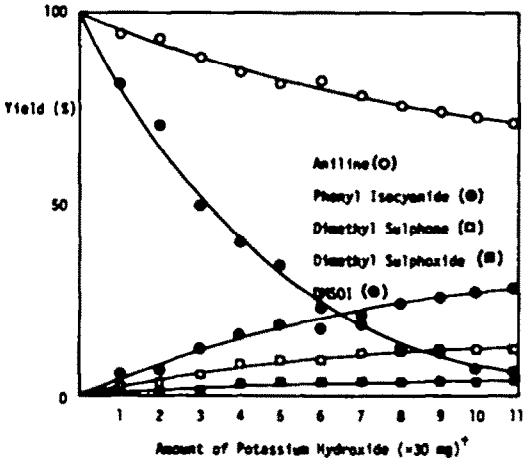
RESULTS AND DISCUSSION

Reaction of dimethylsulphoximide with dichlorocarbene. DMSOI was treated with dichlorocarbene, generated by intermittent additions of powdered potassium hydroxide into chloroform at room temperature. As soon as potassium hydroxide was added a violent reaction took place and finished within a few minutes giving a disagreeable odor. The products analyzed by gas chromatography were found to be dimethyl sulphone (10%) and dimethyl sulphoxide (6%) at 90% conversion of DMSOI, respectively. As the amount of DMSOI which can be followed by gas chromatography decreased, the yields of both dimethyl sulphone and dimethyl sulphoxide increased gradually. However, the combined yields of these two compounds did not exceed more than 20% at 100% decomposition of DMSOI. The rest of the products were not identified.

Ethylene which can be produced in a similar reaction of dimethyl sulphone and carbon tetrachloride in the presence of potassium hydroxide via the Ramberg–Bäcklund reaction,[5] was not observed in the present experiment.

In order to assess the rough reactivity of DMSOI toward dichlorocarbene, the reaction of the sulphoximide

with dichlorocarbene was carried out in the presence of aniline since aniline is more basic than sulphoximide and dichlorocarbene is expected to react preferentially with aniline to yield phenyl isocyanide† without any serious decomposition of sulphoximide.[6] The results shown in Fig. 2, however indicate that even in the presence of aniline, dimethyl sulphone and dimethyl sulphoxide were formed in nearly the same yields as in the reaction without aniline by the decomposition of DMSOI, though phenyl isocyanide was formed in a substantial yield (30%).



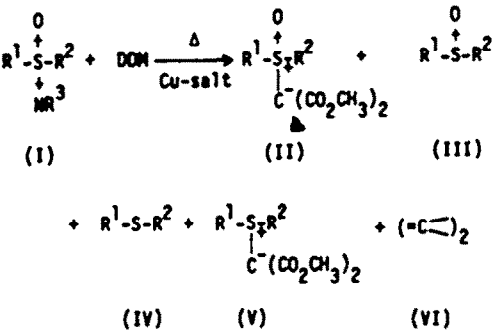
†The yields of the products were determined at various concentrations (1-11) of potassium hydroxide added.

Fig. 1. The reaction of dimethylsulphoximide (DMSOI) with dichlorocarbene in the presence of aniline at room temperature.

Apparently, the presence of aniline did not change the rate of decrease of DMSOI. The decomposition of DMSOI with dichlorocarbene proceeded very readily when carbon tetrachloride was employed as the carbene source instead of chloroform. The reaction of DMSOI with dichlorocarbene generated from carbon tetrachloride was comparatively mild as compared to the reaction with that generated from chloroform at room temperature. However, the rate of decrease of DMSOI appeared to be faster than that of the formation of phenyl isocyanide. These facts suggest that DMSOI is more reactive toward dichlorocarbene than such a primary amine as aniline, though the basicity of aniline (pK_a 4.70) is larger than DMSOI (pK_a 3.24).

Reaction of sulphoximides with dimethyl diazomalonate (DDM). In order to examine the general nature of the reactions of sulphoximides with carbenes, a few sulphoximides (Ia–Ie) were prepared and treated with DDM in refluxing benzene in the presence of a catalytic amount of Cu-salts. Then, the products were separated by column chromatography and identified by their spectroscopic and elemental analyses. The products and their yields are summarized in Scheme 1 and Table 1.

The products isolated in the reactions are oxosulphonium ylides (II), the major products, sulphoxides



Scheme 1.

(III), sulphides (IV), sulphonium ylides (V) and dimer of DDM (VI). Recently, a few oxosulphonium ylides were prepared both by photolysis and by thermolysis of DDM in the presence of the corresponding sulphoxides.[7] However, photolysis of a mixture of diphenylsulphoximide (Ic) and DDM in benzene with high pressure Hg lamp did not proceed at all and the sulphoximide was recovered nearly quantitatively, implying that the free carbene is not the key intermediate but the Cu-carbenoid is the key intermediate for the thermolysis with sulphoximides. Meanwhile, the color of the solution changed to deep green and the solution turned to homogeneous (methylphenylsulphoximide (Ib) and cuprous chloride) at the initial stage of the reaction while in the case of DMSOI or Ib with cupric sulphate, blue crystalline precipitates were formed.

An adduct formed between Ib and cupric sulphate‡ was isolated and analyzed spectrometrically.[8] IR absorption of the adduct (Ib-$CuSO_4$) due to the sulphoximido group shifted toward somewhat higher wave numbers (1020, 1040, 1100, 1150, 1170 cm^{-1}) than those of the original sulphoximide (1010, 1030, 1100, 1120, 1140 cm^{-1}). However, the NH group absorption band became somewhat broad, centered at 3200 cm^{-1}, as compared with a sharp band appeared at 3250 cm^{-1} of the original sulphoximide.[2] The UV absorption maxima of the same adduct appeared at 217 nm with log ϵ 3.87 (abs MeOH) which showed an almost similar absorption with that of the original sulphoximide (λ_{max} 216 log ϵ 3.83 abs MeOH). The UV spectrum suggests that the bond between the sulphoximide and cupric sulphate is weak and dissociates very readily into the original sulphoximide and cupric sulphate in abs methanol. The spectroscopic and elemental analyses, however, undoubtedly indicate the formation of an 1:1 adduct between the sulphoximide and Cu-salt. In order to see the fate of the N atom of the sulphoximide, a few N-substituted sulphoximides (Id, Ie) were prepared and treated with DDM. Unfortunately, no product containing N-benzyl group could be isolated with N-benzylmethylphenylsulphoximide (Id). However, with N-phenyldimethylsulphoximide (Ie)[9] and DDM, aniline and methyl dihydroxymalonate[10] were obtained in moderate yields together with the corresponding oxosulphonium (35%) and sulphonium (10%) ylides. Furthermore, when the reaction mixture was developed with tlc soon after the reaction completed, an unstable product having a R_f value of 0.45 on chromatography was obtained. This product was separated carefully and analyzed by mass spectrometer as shown in Table 2.

Thus this unstable product was confirmed to be the corresponding Shiff's base having the structure as

†The reaction of dichlorocarbene with primary amines was known as a general method to prepare the corresponding isocyanides.

‡Recently, the complexes between sulphimides and Pd or Pt salts were reported.

Table 1. The reaction of sulphoximides (Ia–Ie) with DDM. The reaction conditions and the yields of the products

Sulphoximide (I)			Cu-salt	Solv.	Time	(II)	(III)	(IV)	(V)	(VI)
R^1	R^2	R^3								
(Ia) CH_3	CH_3	H	CuCl	neat	1 min	16	–	–	–	–
CH_3	CH_3	H	$CuSO_4$	C_6H_6	12 hr	53	–	–	trace	–
(Ib) CH_3	C_6H_5	H	CuCl	C_6H_6	6.5 hr	25	11	1.5	–	13
CH_3	C_6H_5	H	$CuSO_4$	C_6H_6	20 hr	39	16	2.4	12	12
(Ic) C_6H_5	C_6H_5	H	$CuSO_4$	neat	12 hr	60	19	5.8	–	16
(Id) CH_3	C_6H_5	$CH_2C_6H_5$	$CuSO_4$	C_6H_6	24 hr	14	–	–	18	–
(Ie) CH_3	CH_3	C_6H_5†	$CuSO_4$	C_6H_6	7 hr	35	–	–	10	5.3

†In this reaction, aniline and methyl dihydroxymalonate were obtained in 10 and 16% yields, respectively.

Table 2. Mass spectrum of $C_6H_5N{=}C(CO_2CH_3)_2$

m/e		Relative Intensity (20 eV)
221	Parent	0.633
162	P-59 $[C_6H_5N{=}CCO_2CH_3]^+$	0.993
118	P-103$[C_6H_5N{=}C{-}CH_3]^+$	0.497
93	P-128$[C_6H_5NH_2]^+$	0.748
77	P-144$[C_6H_5]^+$	1.000
59	P-162$[CO_2CH_3]^+$	0.221

$C_6H_5N{=}C(CO_2CH_3)_2$, suggesting that aniline and methyl dihydroxymalonate are derived from this Shiff's base during the isolation process. These observations seem to indicate rather clearly that DDM attacks initially the nitrogen atom of the sulphoximide.

Stereochemical cycle involving optically active oxosulphonium ylides. In order to explore the stereochemistry of formation of the oxosulphonium ylides, we prepared (+)-(S)-methylphenylsulphoximide ((+)-(S)-Ib), $[\alpha]_D^{25} = +36.0°$ (*c* 2.594 acetone), o.p. 98.7%, according to the known method[11,12] and treated it under the similar reaction condition as described above. Then, (−)-methylphenyloxosulphonium bis(methoxycarbonyl)methylide ((−)-IIb), $[\alpha]_D^{25} = -46.0°$ (*c* 2.080 acetone) was separated carefully in order to avoid further fractionation of the product. Oxosulphonium ylide (−)-IIb, $[\alpha]_D^{25} = -37.2°$ (*c* 0.904 acetone), was also prepared in the reaction of (−)-(S)-methyl phenyl sulphoxide ((−)-(S)-IIIb), $[\alpha]_D^{25} = -119.2°$ (*c* 2.660 acetone), o.p. 80.0%,[44,13] and DDM. The optical rotation of (−)-IIb was increased by several repeated recrystallizations of the partially racemized compound, $[\alpha]_D^{25} = -37.2°$, from ether-hexane and eventually reached the constant value of $[\alpha]_D^{25} = -49.9°$ (*c* 1.616 acetone). If we assume this value to be 100% optically pure, the optical purity obtained by this reaction, namely (+)-(S)-Ib → (−)-IIb is around 93%. Sulphoximide (+)-(S)-Ib was initially confirmed nearly 100% optically pure by means of nuclear magnetic resonance spectrum with tris-[3-(trifluoromethylhydroxymethylene)-d-camphorate]europium(III) shift reagent. Meanwhile, sulphoxide (−)-(S)-IIIb, upon reaction with DDM, afforded (−)-IIb which had also an optical purity of more than 93% without further treatment. In order to determine the absolute configuration of oxosulphonium ylide (−)-IIb and the stereochemical courses of the reactions of both routes, (+)-(S)-Ib → (−)-IIb and (−)-(S)-IIIb → (−)-IIb, oxosulphonium ylide (−)-IIb, $[\alpha]_D^{25} = -47.8°$ (*c* 1.710 acetone), o.p. 95.8%, was hydrolyzed at first by potassium hydroxide in methanol to (+)-methylphenyloxosulphonium methoxycarbonylmethylide ((+)-IIf), $[\alpha]_D^{25} = +94.7°$ (*c* 1.126 acetone) in 35% yield, since (−)-IIb was so stable that it was quite difficult to degrade (−)-IIb directly to the sulphoxide having a known configuration. Oxosulphonium ylide (+)-IIf, thus obtained, is less stable and hence was found to react with dibenzoylethylene affording (−)-(S)-IIIb (79%), $[\alpha]_D^{25} = -139.1°$ (*c* 0.574 acetone), o.p. 93.4%, and (+)-methyl 2,3-dibenzoylcyclopropanecarboxylate (53%), $[\alpha]_D^{25} = +11.4°$ (*c* 0.844 acetone).[14a] Therefore, the stereochemical reaction cycle between (−)-(S)-IIIb, (−)-IIb and (+)-IIf was examined starting from the sulphoxide. The results are illustrated in Fig. 2.

In this stereochemical cycle, the route (−)-IIb → (+)-IIf should be a retention process since the route (−)-IIb → (+)-IIf involves neither the direct bond formation nor the cleavage at the chiral center. The route (+)-IIf → (−)-(S)-IIIb should also be another retention process, since the similar reaction of optically active (amino)oxosul-

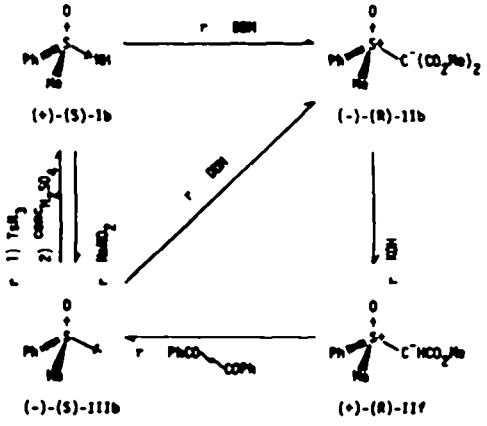


Fig. 2.

phonium ylide† with olefin afforded the sulphinamide with retention of configuration around the chiral S atom.[12]

The experimental results indicate clearly that the sulphoxide obtained finally by this reaction cycle retains 97.5% optical purity with (S)-configuration. Therefore, the absolute configurations of both oxosulphonium ylides, (−)-IIb and (+)-IIf, can be assigned as (R)-configuration. Consequently, both routes to afford (−)-IIb, namely the route (+)-(S)-Ib→(−)-(R)-IIb and (−)-(S)-IIIb→(−)-(R)-IIb are considered to proceed via retention of the configurations around the S atom.

Mechanism of the reaction of sulphoximides with dimethyl diazomalonate (DDM). Both the sulphoximides, Ib and Ic, when they were treated with DDM, afforded the corresponding sulphoxides (IIIb and IIIc) in moderate yields together with other products, such as II, IV, V and VI. Meanwhile, when excess Ib was treated with DDM, the apparent reaction rate increased and the product obtained in a comparatively fair yield was only IIIb. When Ie was treated with DDM similarly, the products obtained were aniline and methyl dihydroxymalonate which are the hydrolyzed products of the corresponding Shiff's base. Furthermore, when both (+)-(S)-Ib and (−)-(S)-IIIb were treated with DDM, (−)-(R)-IIb obtained had almost the same optical purities in both reactions, i.e. (+)-(S)-Ib→(−)-(R)-IIb and (−)-(S)-IIIb→(−)-(R)-IIb. The detailed product analyses and stereochemical results seem to suggest the following mechanism of the reactions of sulphoximides with carbenes as shown in Fig. 3.

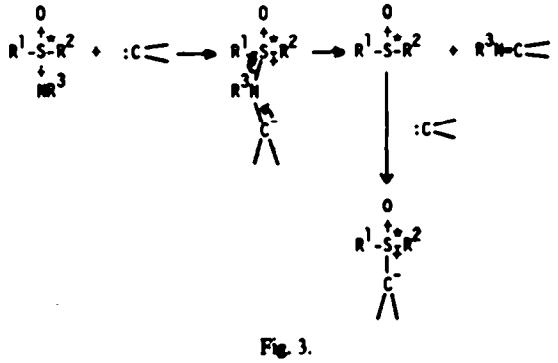


Fig. 3.

Namely, the N atom of sulphoximido group would be attacked initially by the carbene to form the corresponding intermediate (betaine) which then readily decomposes to the sulphoxide and the imine. Finally the subsequent reaction of the sulphoxide formed by the above procedure and DDM gives the oxosulphonium ylide and the other products. The formation of the oxosulphonium ylide in the reaction of the sulphoximide with DDM proceeded faster than that in the reaction of the corresponding sulphoxide with DDM‡ due mainly to the formation of the adduct between the sulphoximide and Cu-salt which may induce the facile decomposition of DDM. The formation of the complex between the adduct and DDM, might cause a partial racemization of the oxosulphonium ylide resulted from the sulphoxide since thermal racemization of the sulphoxide proceeded faster in the presence of sulphoximide and Cu-salt than in the absence of sulphoximide.§ However, the reaction of sulphoximide with carbene is a useful synthetic method of optically active oxosulphonium ylide since the synthesis of optically active sulphoximide does not involve any difficult procedure.

EXPERIMENTAL

General. Chemicals were of reagent grade unless otherwise specified. All m.p. are uncorrected. IR spectra were taken on a HITACHI 215 spectrometer. NMR spectra were obtained with a HITACHI R-24 or HITACHI Perkin-Elmer R-20 spectrometer on dilute solns in $CDCl_3$ using TMS as the internal standard. Optical rotations were taken at 25° with a Yanako OR-50D spectropolarimeter in a 0.5 dm, jacketed cell. UV spectra were recorded on a JASCO UVIDEC-1 spectrophotometer in 1 cm quartz cells in abs. MeOH. Mass spectra were taken with a HITACHI RMU-6MG mass spectrometer. Yanako Model G 80 (FID) was used for gas chromatography using N_2 as a carrier gas. Silica gel for column chromatography was either Wako or Merk chromatographic grade; for tlc Merk DC-Plastikfolien Kieselgel 60 F 254 with fluorescent indicator was used. Development was followed with UV light or by coloring using iodine.

Reaction of dimethylsulphoximide (DMSOI) with dichlorocarbene. To a stirred soln of 1 ml $CHCl_3$ dissolved DMSOI (240 mg, 2.58 mmol) was periodically added powdered KOH (30 mg, 0.54 mmol) at room temp. The reaction took place violently and the color of the soln changed to dark brown immediately producing a disagreeable odor. After the reaction, the products were analyzed by gas chromatography by comparing their glc behavior with those of the authentic samples and their yields were determined using diphenylmethane as the internal standard when KOH was added. Column used was 2 m stainless tube (3 mm i.e.) packing 5% polyethylene glycol 20M (mesh 60–80) on chromosorb W. Oven temp. was 155° and the pressure of carrier gas was 30 ml min^{-1}. The products obtained were dimethyl sulphone (10%), dimethyl sulphoxide (6%) and recovered DMSOI (10%).

Reaction of dimethylsulphoximide (DMSOI) with dichlorocarbene in the presence of aniline. To a stirred soln of 1 ml $CHCl_3$ containing DMSOI (235 mg, 2.53 mmol) and aniline (201 mg, 2.16 mmol) was added powdered KOH (30 mg, 0.54 mmol) at room temp. The reaction took place with some vigor except for the formation of phenyl isocyanide. The products and their yields were determined by glc similarly, and the results are shown in Fig. 2.

Reaction of sulphoximides (Ia–Ic) with dimethyl diazomalonate (DDM). A typical experiment of Ib with DDM was carried out in a following way: a mixture of Ib (0.594 g, 3.83 mmol) and DDM (0.653 g, 4.13 mmol) was refluxed in the presence of cuprous chloride (10 mg, 0.101 mmol) in dry benzene for 6.5 hr. When cuprous chloride was added to a mixture, the color of the soln changed to deep green and after a while, to dark brown upon refluxing the soln continuously. After the reaction, the mixture was added to $CHCl_3$ and cuprous chloride was filtered off. Then removal of the solvent left a dark brown oil, which was chromatographed through silica gel by eluting with $CHCl_3$. A mixture of the sulphoxide and the oxosulphonium ylide obtained were further chromatographed through silica gel by eluting with EtOAc since they could not be separated with $CHCl_3$ as the eluent. The products obtained were identified by comparing their

†C. R. Johnson *et al.* reported the preparation of optically active (amino)oxosulphonium ylide but did not isolate it.

‡The apparent rate of the reaction of methylphenylsulphoximide with DDM proceeded *ca.* seven times faster than that of the corresponding sulphoxide when they were treated *in situ*.

§When the reaction of (+)-(S)-Ib with DDM to afford (−)-(R)-IIb was repeated several times to check the reproducibility of the reaction, the optical purity of (−)-(R)-IIb obtained was found to change from 60 to 94% depending upon the reaction conditions employed. The optical purity of (−)-(S)-IIIb obtained by the process starting from (−)-(R)-IIb via (+)-(R)-IIf was found to be 97.5% and hence the partial racemization is considered to arise mainly via the route, (+)-(S)-Ib→(−)-(R)-IIb, however, good control of the reaction conditions can avoid the partial racemization of the products.

m.ps and spectroscopic data with those reported earlier[7] and by elemental analyses. Compound IIb was obtained in white crystalline form of m.p. 108–109°. IR (KBr) 1625, 1690 cm^{-1} (C=O). NMR (δ) 3.57 (s, 6H, OCH_3), 3.70 (s, 3H, SCH_3), 7.54–8.04 (m, 5H, Ar-H). Mass; 270 (M^+). (Found: 53.41; H, 5.16. Calc. for $C_{12}H_{14}O_5S$: C, 53.32; H, 5.22%). The other sulphoximides (Ia–Ic) were treated similarly. The products and their yields are summarized in Table 1.

Adduct of methylphenylsulphoximide (Id) *with cupric sulphate.* Excess Ib was dissolved in dry benzene and stirred under N_2. To the soln was added anhyd. $CuSO_4$ and the soln was refluxed for 7.5 hr. Then blue crystalline ppts were filtered off and washed three times with hot benzene. The adduct was obtained quantitatively, m.p. 153–155° (dec). IR (KBr) 3200 cm^{-1} (NH). UV; λ_{max} 217 nm log ϵ 3.87 (abs. MeOH). (Found: C, 27.07; H, 3.13; N, 4.19. Calc. for $C_{12}H_{11}NO_5SCu$: C, 26.70; H, 2.88; N, 4.44%).

N-*Benzylmethylphenylsulphoximide* (Id). To a soln of Ib (2.3 g 14.8 mmol) in 25 ml dry dimethoxyethane under dry N_2 was added 1.5 equiv of NaH (1.1 g 22.8 mmol). The resulting suspension was stirred for 3 hr by mechanical stirring and 1.5 equiv of benzyl bromide (3.8 g 22.2 mmol) was added dropwise. The resulting mixture was stirred at room temp. for 36 hr under dry N_2 and then quenched with 50 ml water. After removal of the solvent, the aqueous layer was extracted three times with 50 ml $CHCl_3$. The combined $CHCl_3$ layer was washed with water, dried over $MgSO_4$. The solvent was evaporated and the resulted residue was chromatographed through silica gel by eluting with $CHCl_3$. The product purified by vacuum distillation (Kugelrohr) was obtained in 19% yield as a pale yellow oil: b.p. 180° (5 mmHg). NMR (δ) 3.06 (s, 3H, SCH_3), 4.00 (ABq, 2H, J = 14 Hz, CH_2), 7.00–7.90 (m, 10H, Ar-H). Mass; 245 (M^+). (Found: C, 68.23; H, 5.94; N, 5.50. Calc. for $C_{14}H_{15}NOS$: C, 68.53; H, 6.16; N, 5.70%).

Reaction of N-*benzylmethylphenylsulphoximide* (Id) *with dimethyl diazomalonate* (*DDM*). A mixture of Id (291 mg 1.19 mmol) and DDM (235 mg 1.49 mmol) was stirred and refluxed in 1 ml dry benzene for 24 hr in the presence of $CuSO_4$. Then benzene was added and the benzene soln was filtered to remove off $CuSO_4$. Removal of the solvent left a dark brown oil, which was chromatographed through silica gel using EtOAc as eluent. The products obtained were identified by comparing their spectroscopic data with those of the authentic samples. Id was recovered in 36% yield. The results are shown in Table 1.

Reaction of N-*phenyldimethylsulphoximide* (Ie) *with dimethyl diazomalonate* (*DDM*). A mixture of Ie (210 mg 1.24 mmol), prepared by Swern's method[9] and DDM (217 mg 1.37 mmol) was stirred and refluxed in 0.5 ml dry benzene for 7 hr in the presence of $CuSO_4$. Then benzene was added and the benzene soln was filtered to remove off $CuSO_4$. The resulting mixture was washed several times with water and the organic layers were analyzed by gas chromatography. Aniline was obtained in 10% yield and the other products were also chromatographed as in the previous cases. The aqueous layer was concentrated by vacuum distillation (Kugelrohr) and extracted three times with $CHCl_3$. The combined $CHCl_3$ layer was dried over Na_2SO_4. Evaporation of the solvent gave methyl dihydroxymalonate (16%) together with the oxosulphonium ylides. Methyl dihydroxymalonate was identified by comparing its NMR spectrum with that of the authentic sample.[10] The other products were identified by comparing their m.ps and spectroscopic data with those of the authentic samples. Ie was recovered in 49% yield. The results are shown in Table 1.

(−) - (*R*) - *Methylphenyloxosulphonium bis(methoxycarbonyl)methylide* ((−)-(*R*)-IIb) *from* (+)-(*S*)-*Methylphenylsulphoximide* ((+)-(*S*)-Ib). Treatment of (+)-(S)-Ib,[11,12] $[\alpha]_D^{25}$ = +36.0° (*c* 2.594 acetone), o.p. 98.7%, with DDM was carried out by the same procedure for the racemate and the products were obtained in the same yields. The reaction was carried out six times under a few different conditions and their optical rotations are shown in Table 3.

Constant values of both m.p. and the optical rotation of (−)-(R)-IIb were obtained by several repeated recrystallizations of the crude compound from ether-hexane: m.p. 145–146°, $[\alpha]_D^{25}$ = −49.9° (*c* 1.616 acetone).

(−) - (*R*) - *Methylphenyloxosulphonium bis(methoxycarbonyl) methylide* ((−)-(*R*)-IIb) *from* (−)-(*S*)-*methylphenyl sulfoxide* ((−)-(*S*)-IIIb). A mixture of (−)-(S)-IIIb,[4d,13] $[\alpha]_D^{25}$ = −119.2° (*c* 2.660 acetone), o.p. 80.0%, (565 mg, 4.06 mmol) obtained by diazotization of (+)-(S)-Ib and DDM (596 mg, 3.77 mmol) was heated at 80° for 12 hr in the presence of $CuSO_4$ (23 mg, 1.44 mmol). The resulting mixture was directly chromatographed through silica gel using $CHCl_3$ as eluent. Separation of the recovered sulphoxide and the oxosulphonium ylide was carried out further by chromatography through silica gel with EtOAc as eluent. The products obtained were identified by comparing their spectroscopic data with those of the authentic samples. The results were the following: (−)-(R)-IIb (21%), $[\alpha]_D^{25}$ = −37.2° (*c* 0.904 acetone), o.p. 74.5%, recovered (−)-(S)-IIIb (32%), IVb (3%), Vb (21%) and VI (2.7%).

Hydrolysis of (−)-(*R*)-*methylphenyloxosulphonium bis-(methoxycarbonyl)methylide* ((−)-(*R*)-IIb) *to* (+)-(*R*)-*methylphenyloxosulphonium methoxycarbonylmethylide* ((+)-(*R*)-IIf). A mixture of (−)-(R)-IIb, $[\alpha]_D^{25}$ = −47.8° (*c* 1.710 acetone), o.p. 95.8%, (260 mg, 0.96 mmol) and KOH (243 mg, 4.34 mmol) in 2 ml abs. MeOH was refluxed for 1.5 hr. To a mixture was added 10 ml water and then MeOH was evaporated. The aqueous layer was acidified by adding 10 ml 2N HCl saturated with NaCl and washed three times each with 15 ml $CHCl_3$. The aqueous layer was made slightly alkaline with K_2CO_3 and extracted five times with 50 ml $CHCl_3$. The combined $CHCl_3$ layer was dried over Na_2SO_4. Then $CHCl_3$ was distilled off. The product was obtained in white crystals having $[\alpha]_D^{25}$ = +94.7° (*c* 1.126 acetone) in 35% yield. The optical rotation of (+)-(R)-IIf reached the constant value of $[\alpha]_D^{25}$ = +105.1° (*c* 0.274 acetone), m.p. 109–110° upon several repeated recrystallizations of the crude compound from ether-hexane. The racemate has m.p. 119–120°. IR (KBr) 1635 cm^{-1} (C=O). NMR (δ) 3.45 (s, 3H, OCH_3), 3.53 (s, 3H, SCH_3), 4.05 (broad s, 1H, CH), 7.65–8.00 (m, 5H, Ar-H). Mass: M^+ + 1, 213 (C.I.). (Found: C, 56.66; H, 5.62. Calc. for $C_{10}H_{12}O_5S$: C, 56.58; H, 5.69%).

Table 3. Optical rotations and optical purities of ylide ((−)-(R)-IIb) and sulphoxide ((−)-(S)-IIIb) for the route from sulphoximide ((+)-(S)-Ib) to ylide ((−)-(R)-IIb)

	React. Time	(−)-(R)-IIb		(−)-(S)-IIIb	
1	7 h	$[\alpha]_D^{25}$=-46.9° (c 0.904)	o.p. 94.0	$[\alpha]_D^{25}$=-144.8° (c 0.268)	o.p. 97.2
2	7 h	$[\alpha]_D^{25}$=-46.0° (c 2.080)	o.p. 92.2	–	
3	8 h	$[\alpha]_D^{25}$=-43.5° (c 1.792)	o.p. 87.2	$[\alpha]_D^{25}$=-135.4° (c 0.164)	o.p. 90.9
4	20 h	$[\alpha]_D^{25}$=-34.5° (c 2.180)	o.p. 69.1	–	
5	20 h	$[\alpha]_D^{25}$=-34.4° (c 2.198)	o.p. 68.9	$[\alpha]_D^{25}$=-122.1° (c 1.074)	o.p. 81.9
6	20 h	$[\alpha]_D^{25}$=-29.8° (c 1.816)	o.p. 59.7	$[\alpha]_D^{25}$=-130.3° (c 0.402)	o.p. 87.4

†All optical rotations were taken in acetone. Optical purities were shown as %.

Conversion of (+) - (R) - methylphenyloxosulphonium methoxycarbonylmethylide ((+)-(*R*)-IIf) *to (−)-(S)-methyl phenyl sulphoxide* ((−)-(*S*)-IIIb). A mixture of (+)-(R)- IIf (55 mg, 0.26 mmol), $[\alpha]_D^{25} = +94.7°$ (*c* 1.126 acetone) and dibenzoylethylene (67.4 mg, 0.29 mmol) in 1 ml dry THF was refluxed for 10 hr. After removal of the solvent, the resulting mixture was chromatographed through silica gel with benzene as eluent. The products obtained were (+)-methyl 2,3-dibenzoylcyclopropanecarboxylate (53%), $[\alpha]_D^{25} = +11.4°$ (*c* 0.844 acetone) which was identified by comparing its NMR spectrum with that cited in the literature[14a] and (−)-(S)-IIIb (79.1%), $[\alpha]_D^{25} = -139.1°$ (*c* 0.574 acetone), o.p. 93.4%, respectively.

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