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TWENTY-FIVE YEARS OF DIMETHYLSULFOXONIUM METHYLIDE (COREY'S REAGENT)

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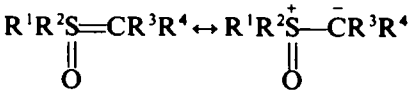
1. INTRODUCTION

Sulfoxonium ylides:



are a class of organic compounds that have been extensively studied in the chemical literature. In particular dimethylsulfoxonium methylide ($R^1 = R^2 = Me$, $R^3 = R^4 = H$) has proved to be a versatile nucleophilic agent capable of reacting with a wide variety of different systems.[1-13]

Some aspects of the chemistry of sulfoxonium ylides have already been reviewed.[14-20] This review is concerned with a comprehensive survey of the preparative possibilities of dimethylsulfoxonium methylide (Corey's reagent). The time period covered is January 1974 to December 1985.

2. SYNTHESIS OF DIMETHYLSULFOXONIUM METHYLIDE

In 1962 Corey and Chaykovsky synthesized dimethylsulfoxonium methylide (DMSY) by the reaction of trimethylsulfoxonium chloride or iodide with sodium hydride (under nitrogen) in dry dimethyl sulfoxide[21]

$$Me_3\overset{+}{S}(O)X^- \xrightarrow{NaH} Me_2\overset{+}{S}(O)\overset{-}{C}H_2 + NaX + H_2. \quad (1)$$

The details of this classical procedure exemplified by trimethylsulfoxonium iodide or chloride were reported by Corey and Chaykovsky in 1965.[22] The ylide can also be obtained in tetrahydrofuran or dioxane solution from trimethylsulfoxonium chloride and NaH. The chloride has sufficient solubility in THF and dioxane to interact with the insoluble sodium hydride. Furthermore, the sodium chloride produced is insoluble and can be removed by filtration.

The solutions of the DMSY in THF are stable for several months if kept in an inert atmosphere (dry nitrogen or argon) at 0°C. Concentration of the ylide is easily determined by titration with standard acid in water. At room temperature, decomposition of DMSY becomes appreciable after about a week.

Lately, a series of sulfoxonium salts have been used for the synthesis of different types of sulfoxonium ylides: dialkylsulfoxonium ethylides,[23] dialkylamino(aryl)sulfoxonium methylides,[24,25] dialkylamino(alkyl)sulfoxonium methylides,[26,27] dialkylamino(alkyl)sulfoxonium ethylides,[26] dialkylamino(aryl)sulfoxonium ethylides,[25,28] dialkylamino(aryl)sulfoxonium cyclopropylides,[28,29] dialkylamino(aryl)sulfoxonium propylides,[28] etc.[30,31]

3. CHEMICAL PROPERTIES OF DMSY

3.1. *Alkylation*

DMSY reacts with different alkylating agents (diazomethane,[32] iodoethane,[33] dimethyl sulfate[33]) to form complex mixtures of products. The reaction of C-acylated stable sulfoxonium ylides with iodomethane produces substituted carbonyl compounds with elimination of DMSO.[32]

Treatment of certain substituted sulfoxonium ylides with such alkylating agents as methyl iodide or trialkyloxonium fluoroborate produces the C-alkylated,[28] S-alkylated[34] and O-alkylated[35] sulfoxonium salts.

The alkylation of the phosphorylated sulfoxonium methylide **1** by methyl iodide leads to the P-containing sulfoxonium salt **2**, but the reaction with the P-alkoxylated phosphorylated sulfoxonium ylide **3** with iodoethane or methyl iodide is accompanied by the alkyl halogen-ethyl-phosphinyl)dimethylsulfoxonium methylide **4**.[36]

$$\underset{\mathbf{1}}{Me_2\overset{+}{S}(O)\overset{-}{C}H{-}P(Et)_2} + MeI \longrightarrow \underset{\mathbf{2}}{Me_2S(O)CH\overset{+}{P}(Me)(Et)_2\,I^-} \quad (2)$$

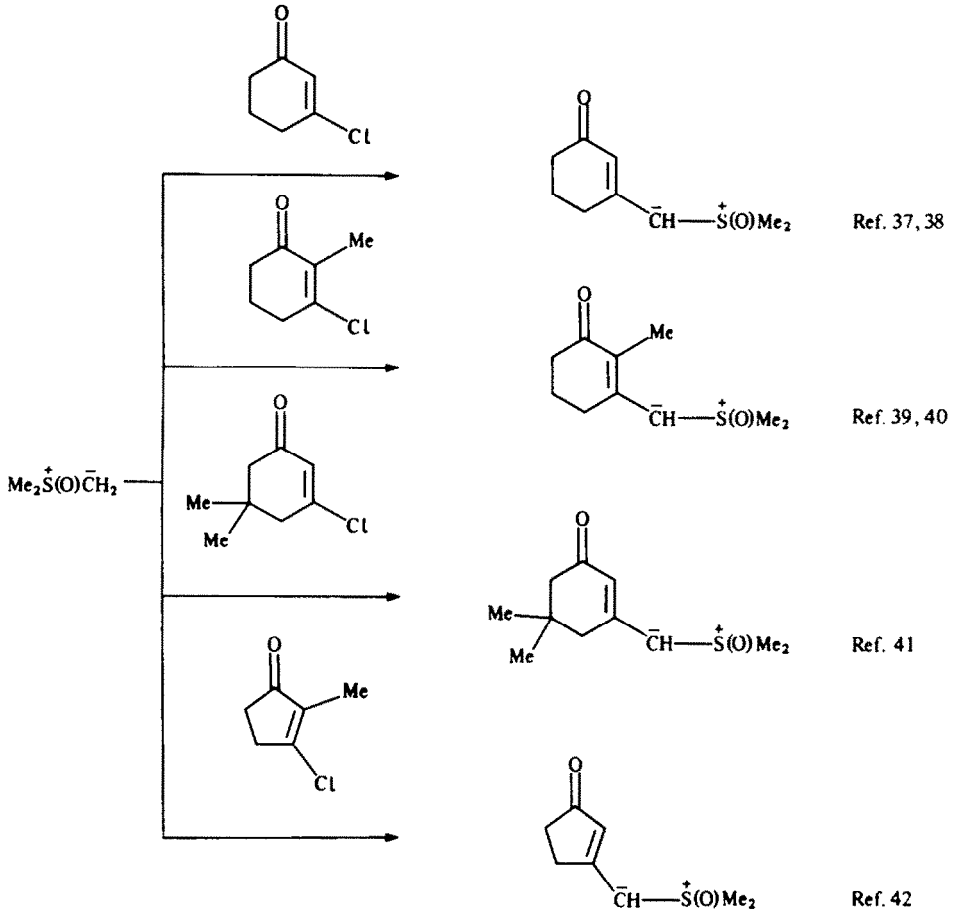
$$\underset{\mathbf{3}}{Me_2\overset{+}{S}(O)\overset{-}{C}H{-}P(OEt)_2} + AlkHlg \xrightarrow[-EtHlg]{} \underset{\mathbf{4}}{Me_2\overset{+}{S}(O)\overset{-}{C}H{-}\overset{\overset{O}{\|}}{P}(Alk)(OEt)} \quad (3)$$

Alk = Me, Et.

3.2. *Substitution reactions of dimethylsulfoxonium methylide with chloro-containing compounds*

It was shown that DMSY reacts with 3-chlorocyclohex-2-enone,[37,38] 3-chloro-2-methyl-2-cyclo-

hexene-1-one,[39,40] 3-chloro-5,5-dimethylcyclohex-2-enone,[41] 3-chloro-2-methyl-2-cyclopenten-1-one,[42] etc. to form the corresponding sulfoxonium ylides according to eqn (4).



(4)

Treatment of the imidoyl chlorides,[43] 2-chloropyrimidine,[43,44] 4-chloropyrimidine,[44] 2-chloro-4,6-dimethylpyrimidine,[45] 3-chlorobenzothiazole 1,1-dioxide,[43] etc. with DMSY results in the formation of sulfoxonium ylides as shown in eqn (5).

3.3. *Acyl-substituted ylides*

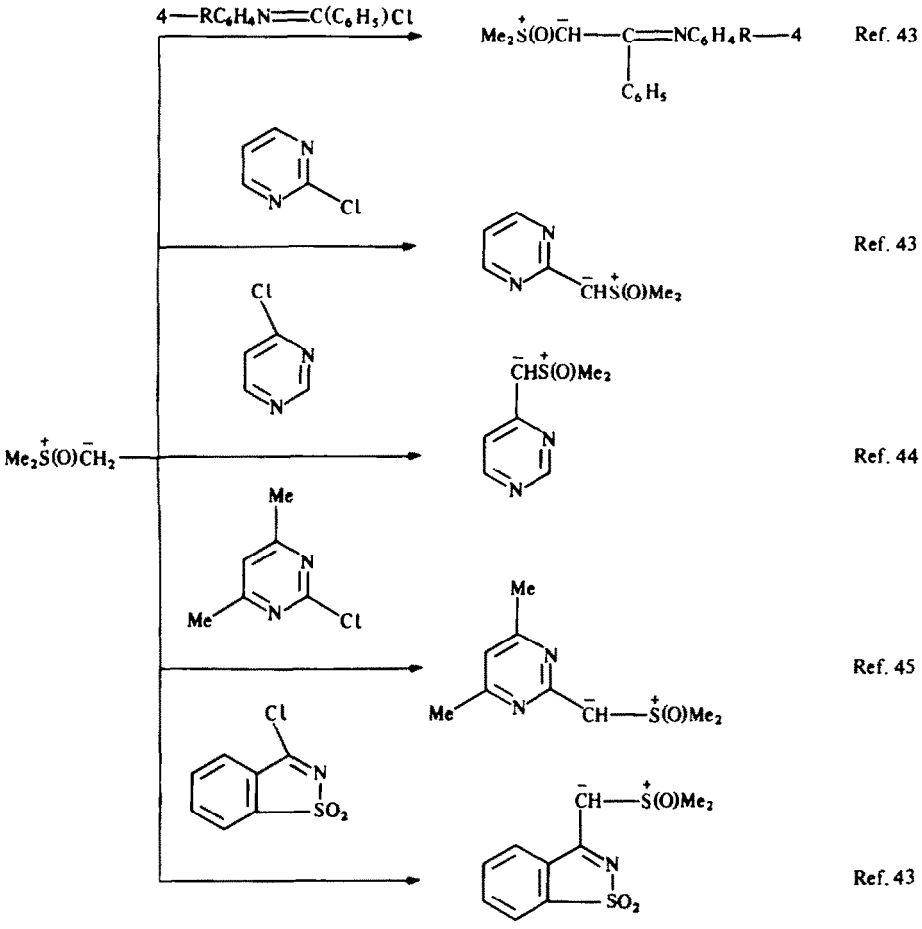
Reactions of the sulfoxonium methylides with such acylating reagents as alkyl chloroformate,[46] acid chlorides,[24,35,45,47-54] acid anhydrides,[32,35,37,45,55] diphenylketen,[48,56,57] phenyl esters of cyclohexenyl (or cyclopentenyl) carboxylic acid,[51] methyl benzoate,[58] phenyl isocyanate,[24,32,37,47,56,57,59,60] etc. are widely used for preparation of the acylated stable ylides as shown in eqn (6).

Reaction of phosphonylsulfoxonium ylides with acetic anhydride or equimolar amounts of phenyl isocyanate gives normal C-acylated ylides.[62]

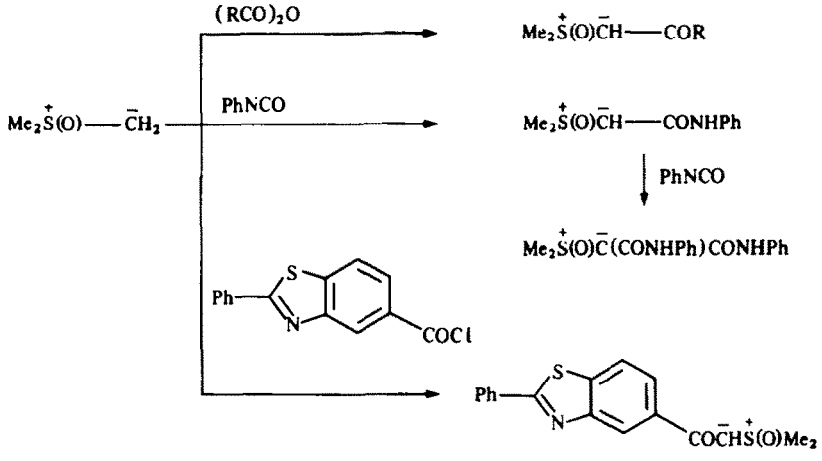
It was shown that (3-oxocyclohex-1-enyl)-substituted ylides **5** reacted with benzoic anhydride to form the C-acylated ylide, but treatment of **5** with benzoyl chloride affords the O-acylated product (products **6** and **7**).[63]

Many acylated sulfoxonium ylides may be converted to other products[32,44,57,61,64-66] with elimination of DMSO. For this purpose Raney Ni,[32,37,45,57,59,63,67] Zn in acid acid,[68] photochemical[51,53,54,69,70] and thermal[35] decomposition of certain acylated ylides are mainly used, as shown in eqn (8).

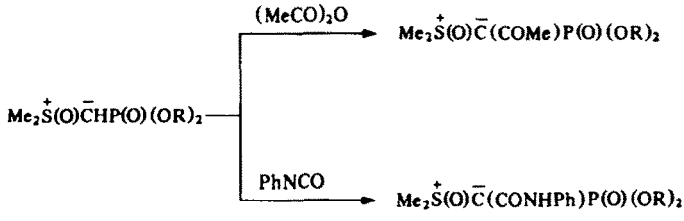
Thermal decomposition of methyl(dimethylamino)acylsulfoxonium ylides in the presence of copper sulfate produces cyclic compounds **8** with elimination of dimethylamine.[35]


4—RC6H4N=C(C6H5)Cl
Me2S(O)CH—C=NC6H4R—4
C6H5
Ref. 43
Cl
N
N
CHS(O)Me2
Ref. 43
Me2S(O)CH2
CHS(O)Me2
Ref. 44
Me
Me
Cl
Me
CH—S(O)Me2
Ref. 45
SO2
CH—S(O)Me2
Ref. 43

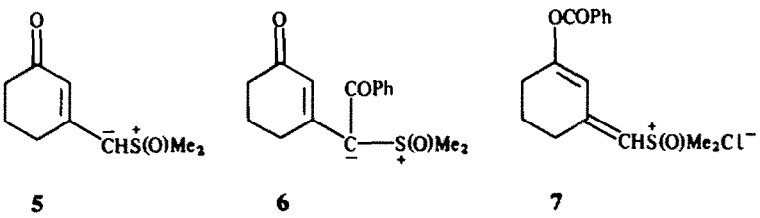
(5)


(RCO)2O
Me2S(O)—CH2
PhNCO
Me2S(O)CH—COR
Me2S(O)CH—CONHPh
PhNCO
Me2S(O)C(CONHPh)CONHPh
Ph
COCl
Ph
COCHS(O)Me2

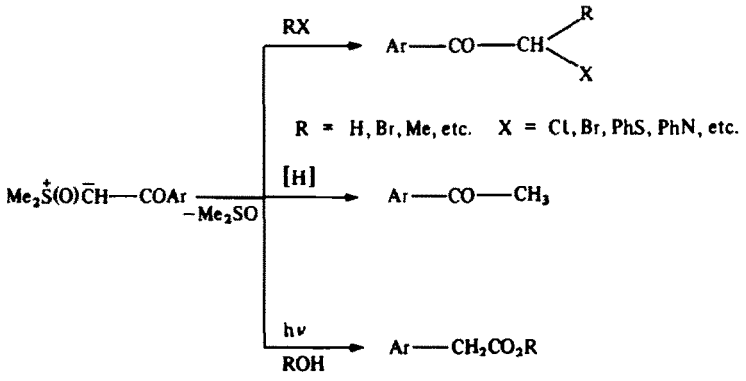
(6)


(MeCO)2O
Me2S(O)C(COMe)P(O)(OR)2
Me2S(O)CHP(O)(OR)2
PhNCO
Me2S(O)C(CONHPh)P(O)(OR)2

(7)



5 6 7



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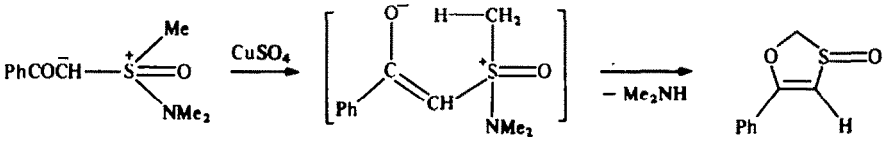
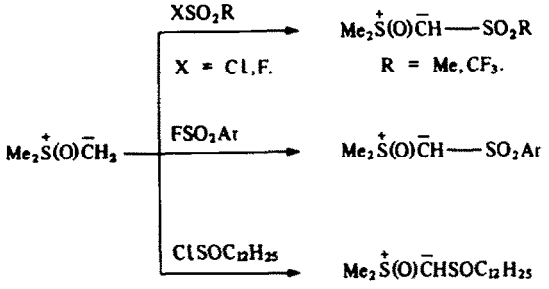


8

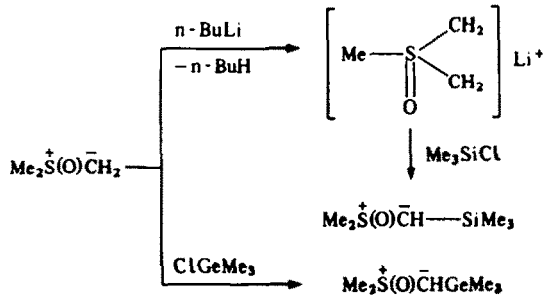
(9)

3.4. *Reactions with organo-element acid halides*

The interaction of sulfoxonium methylides with organoelement acid halides gives the corresponding C-substituted ylides. For this purpose methanesulfonyl chloride,[71,72] trifluoromethanesulfonyl fluoride,[73] arenesulfonyl fluorides,[71,74] dodecanesulfinyl chloride,[75] chlorotrimethylsilane,[76,77] chlorotrimethylgermane and trimethyltin chloride[76,77] are mainly used as shown in equations (10), (11) and (12).



(10)



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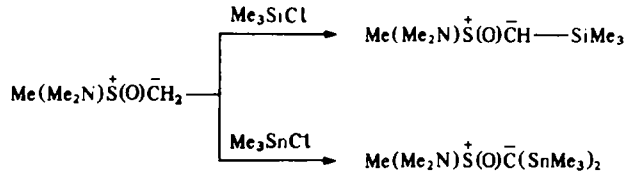
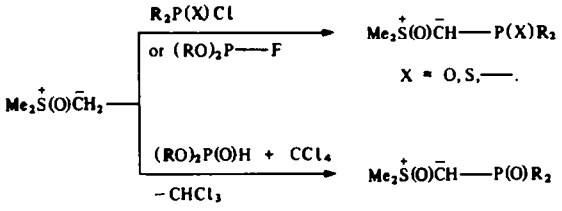


(12)

It was shown that the reaction of DMSY or Li-DMSY with halides of phosphorus acids in THF at −30°C to −20°C gave P(V)- and P(III)-containing sulfoxonium ylides in 60–87% yields.[78,79] Interaction of diethyl phosphite and carbon tetrachloride with DMSY produced the phosphonylsulfoxonium ylide[80] (13) (scheme Atherton–Todd reaction[81]).



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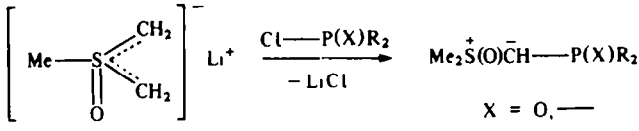
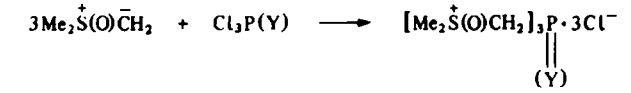


(14)

The P-substituted sulfoxonium ylides prepared from DMSY and phosphorochloridate derivatives are listed in Table 1.

The interaction between DMSY and phorophorus oxychloride, phosphorus trichloride, etc., however, leads to the corresponding P-substituted sulfoxonium salts.[36]



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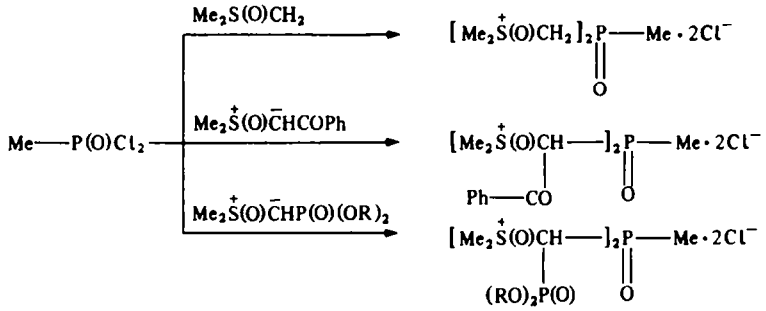
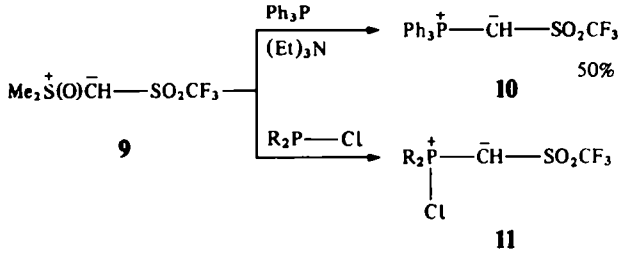


(16)

Table 1. P-substituted sulfoxonium ylides $Me_2S(O)CHP(X)R_2$[78–80]

R	X	Yield (%)	B.p. [°C (mm)]	M.p. (°C)
OEt	O	71	127–128 (0.03)	57–58
OPr-n	O	75	141–142 (0.03)	—
OPh	O	78	—	104–105
piperidino	O	68	—	110–111
OPh	S	70	—	82.5
OEt	—	58	97–98 (0.025)	—
Et	—	73	72–73 (0.03)	—
OPh	—	87	—	82–83
Ph	—	70	—	105.5–106.5

Sulfoxonium methylides react with phosphorus dichlorides to produce analogous products.[82] Sulfoxonium ylide **9**, stabilized with a trifluoromethane-sulfonyl group reacts with triphenylphosphine in the presence of triethylamine giving the corresponding P-ylide **10**.[73] Similar treatment of **9** with chlorodiethylphosphine or chlorodiphenylphosphine gives the chlorocontaining P-ylide stabilized with a CF_3SO_2 group.[73]



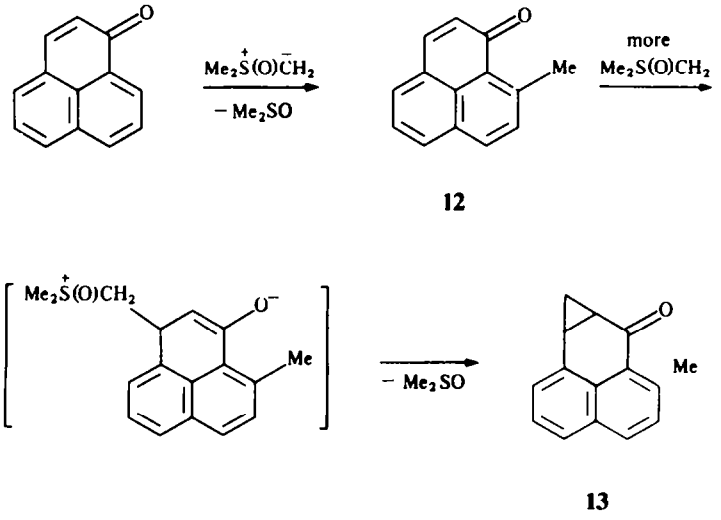
(17)

3.5. *Ylide methylation*

It was shown that DMSY reacted with certain organic compounds to form methylation products.[83-93]

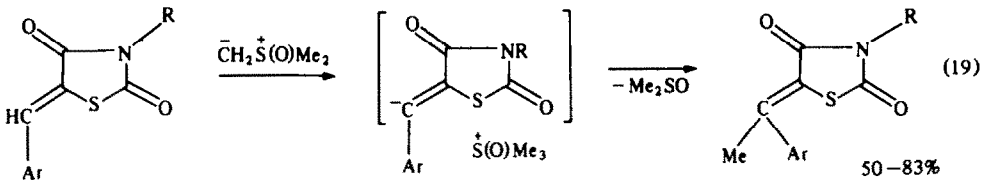
3.5.1. C-*methylation*. When nitrobenzene and DMSY were allowed to react at room temperature, a mixture of *o*- and *p*-nitrotoluene (35% yield) was isolated.[83] The ratio of *ortho* to *para* isomers in the products was about 10–15 : 1 and thus a strong tendency for the *ortho* isomer was revealed. The reaction of 1-nitronaphthalene with DMSY produced 1-nitro-2-methylnaphthalene (12%) along with some resinous material. Treatment of 9-nitroanthracene of *m*-dinitrobenzene with the methylide led to resinous or tarlike materials only. However, the methylation reaction was successfully extended to chloronitrobenzenes, nitrotoluenes and nitroanisoles, with the results summarized in Table 2.[83] Interesting observations evolve from the study of these substituted nitrobenzenes: methylation is directed toward the position *ortho* to the nitro function in preference to *para*, and with *meta*-substituted nitrobenzenes methylation proceeds primarily to the more hindered *ortho* position (C-2) rather than the other *ortho* position (C-6). These features provide a unique character of the reaction which may be used in preparation of highly substituted nitroaromatic compounds.[83]

DMSY reacts with phenalenone to form 9-methylphenalenone **12**, which further gives 9-methyl-2,3-homophenalenone **13**.[84,85]



(18)

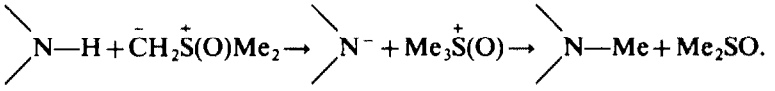
3.5.2. N-*methylation*. Certain organic compounds which contain N–H bonds react with DMSY giving the corresponding N-methylation products.[87-91] The proton of the N-atom was transferred



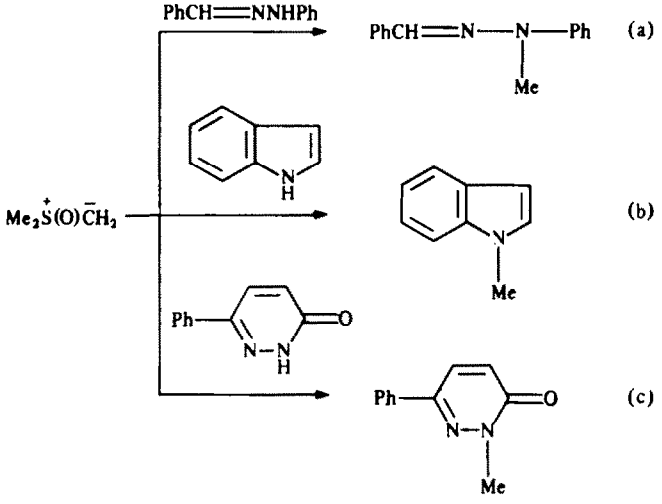
(19)

14 (R = Me, Ph . Ar = (un) substituted phenyl). 15

to DMSY to regenerate the trimethylsulfoxonium salt, which then methylated the amide ion:



Some examples are shown in eqns (20a),[87] (20b)[90] and (20c).[90]



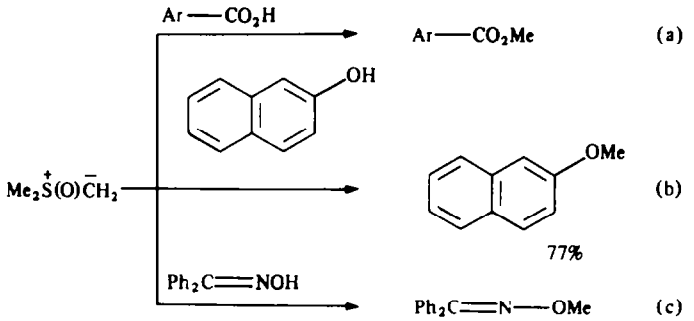
(20)

3.5.3. O-*methylation*. Treatment of such weak acids as phenols, carboxylic acids and oximes, with DMSY leads to O-methylation products, as shown in eqns 21a, 21b[87] and 21c.[92]

3.5.4. S-*methylation*. S-methylation products are easily prepared from DMSY and N-phenylisorhodanine,[86] certain thioketones, dithiocarboxylic esters,[93] etc. [eqns (22) and (23)].

Table 2. Reaction of DMSY with some aromatic nitro compounds[83]

Aromatic substrate	Methylation products (% yield)
1-Nitronaphthalene	2-Methyl-1-nitronaphthalene (12)
o-$ClC_6H_4NO_2$	3-Cl-2-$NO_2C_6H_3CH_3$ (24)
m-$ClC_6H_4NO_2$	2-Cl-6-$NO_2C_6H_3CH_3$ (14) + 4-Cl-2-$NO_2C_6H_3CH_3$ + 2-Cl-4-$NO_2C_6H_3CH_3$ (3, 6)
p-$ClC_6H_4NO_2$	3-Cl-6-$NO_2C_6H_3CH_3$ (25) + 5-Cl-1,3-$(CH_3)_2$-2-$NO_2C_6H_2$ (13)
o-$NO_2C_6H_4CH_3$	1,3-$(CH_3)_2$-2-$NO_2C_6H_3$ (16) + 1,3-$(CH_3)_2$-4-$NO_2C_6H_2$ (2)
m-$NO_2C_6H_4CH_3$	1,2-$(CH_3)_2$-3-$NO_2C_6H_3$ (15) + 1,4-$(CH_3)_2$-2-$NO_2C_6H_3$ (6) + 1,2-$(CH_3)_2$-4-$NO_2C_6H_3$ (2)
p-$NO_2C_6H_4CH_3$	Unidentified amorphous solids
m-$NO_2C_6H_4OCH_3$	2-CH_3O-6-$NO_2C_6H_3CH_3$ (24)
p-$NO_2C_6H_4OCH_3$	5-CH_3O-2-$NO_2C_6H_3CH_3$ (17)



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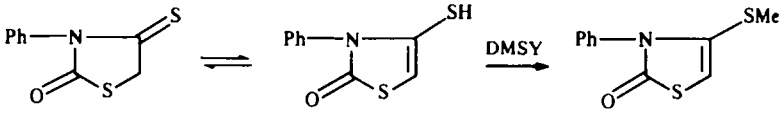

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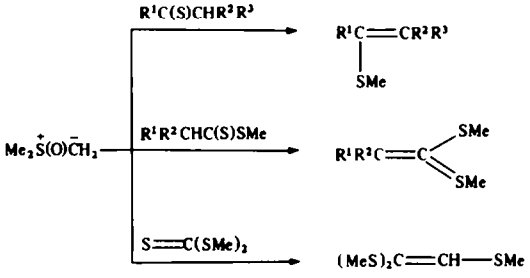


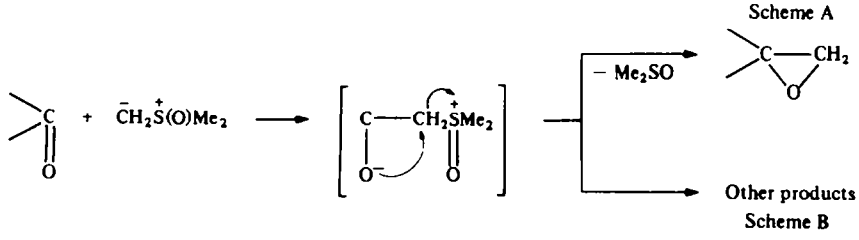
(23)

3.6. *Reactions with multiple bonds*

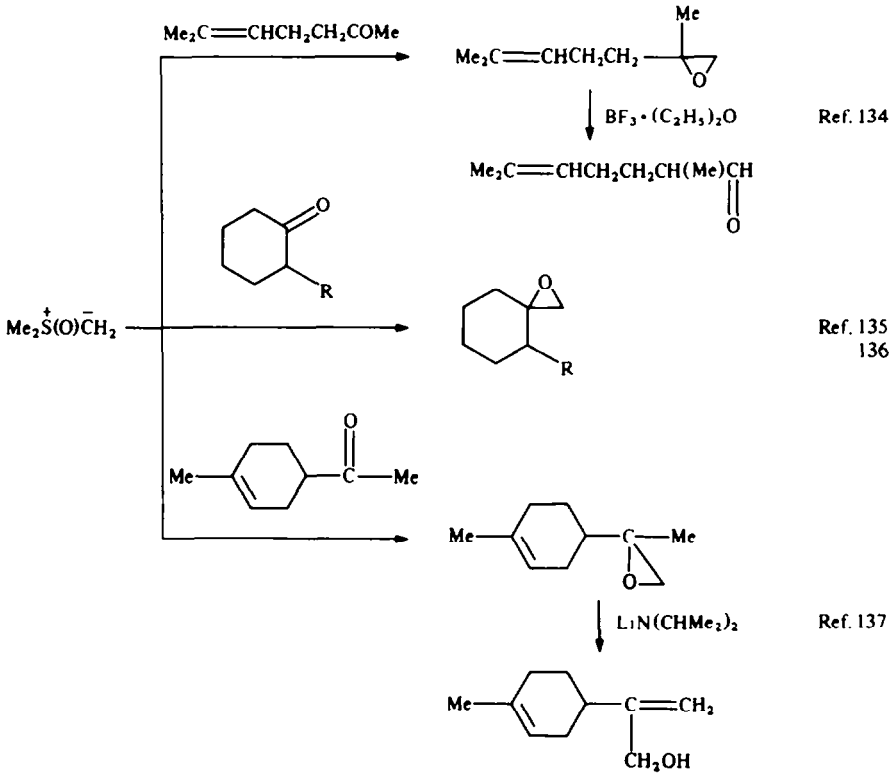
Dimethylsulfoxonium methylide reacts with a large variety of unsaturated systems containing multiple bonds (C=O, C=C, C=S, N=O, N=N, C=C, C=N etc.).[94-109] In these reactions the ylide behaves as a nucleophile in the initial reaction step and then subsequent stages involve the loss of dimethyl sulfoxide and product formation (or product formation without the loss of DMSO). In some cases mixtures of products are obtained. Examples of such reactions are given below.

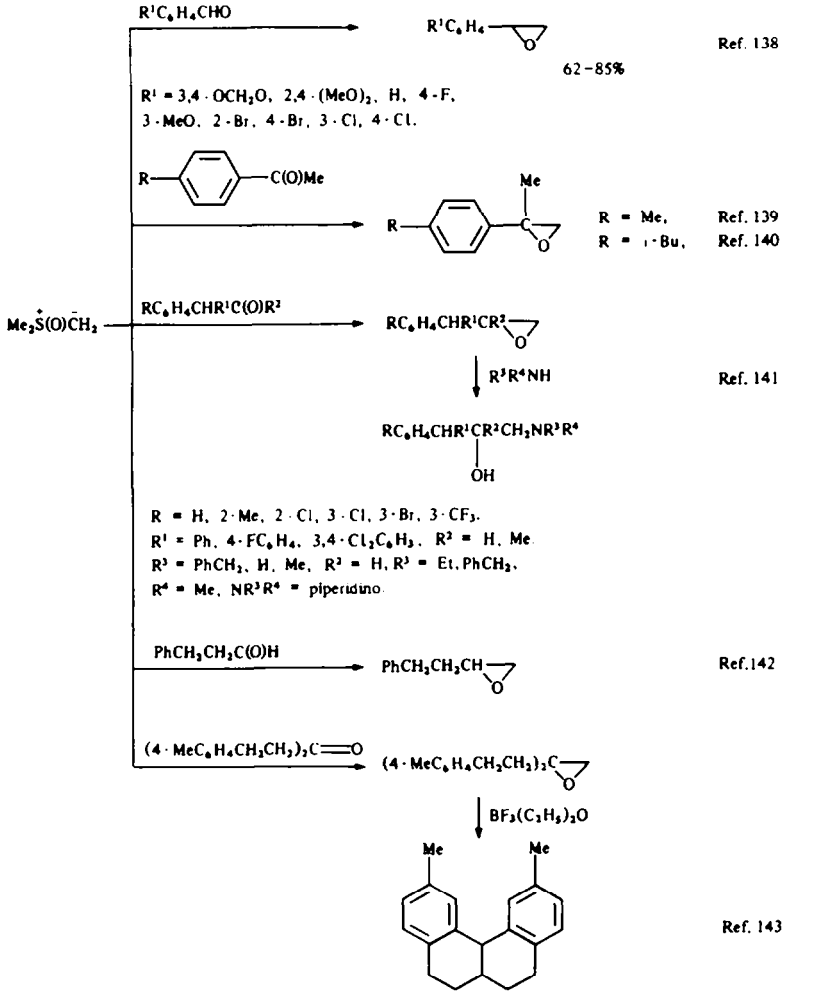
3.6.1. *Reactions with* C=O *group.* Interaction of sulfur ylides with the carbonyl group of aldehydes and ketones is described in many reports.[21,22,24,25,27-30,47,105,110-133]

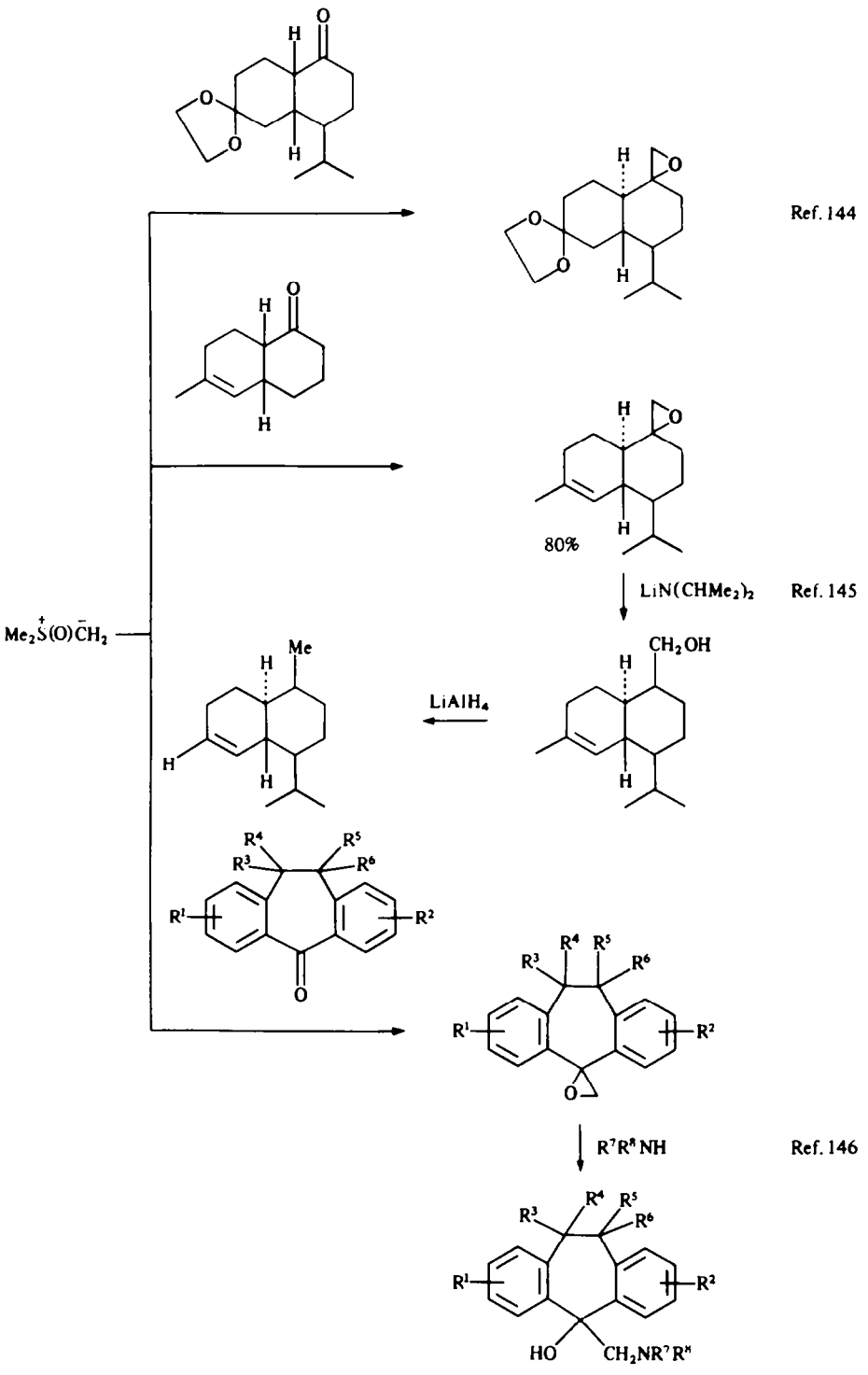
In general, reaction of DMSY with the C=O group leads either to a 3-membered ring or to other reaction products:



One of the most striking properties of DMSY is its reactivity towards carbonyl compounds resulting in the formation of epoxides (Scheme A). Corey's method for the conversation of ketones into epoxides with DMSY finds widespread use in organic synthesis. For this purpose different carbonyl compounds are used, as shown in eqn (24).[134-136]


Me2C=CHCH2CH2COMe
Me2C=CHCH2CH2
Me
O
BF3·(C2H5)2O
Ref. 134
Me2C=CHCH2CH2CH(Me)CH
O
Me2S(O)CH2
R
Ref. 135
136
Me
C
Me
LiN(CHMe2)2
Ref. 137
CH2OH


R1C6H4CHO
R1C6H4
Ref. 138
62–85%
R1 = 3,4-OCH2O, 2,4-(MeO)2, H, 4-F,
3-MeO, 2-Br, 4-Br, 3-Cl, 4-Cl.
R
C(O)Me
Me
R = Me, Ref. 139
R = t-Bu, Ref. 140
Me2S(O)CH2
RC6H4CHR1C(O)R2
RC6H4CHR1CR2
R3R4NH
Ref. 141
RC6H4CHR1CR2CH2NR3R4
OH
R = H, 2-Me, 2-Cl, 3-Cl, 3-Br, 3-CF3.
R1 = Ph, 4-FC6H4, 3,4-Cl2C6H3. R2 = H, Me.
R3 = PhCH2, H, Me, R2 = H, R3 = Et, PhCH2.
R4 = Me, NR3R4 = piperidino.
PhCH2CH2C(O)H
PhCH2CH2CH
Ref.142
(4-MeC6H4CH2CH2)2C=O
(4-MeC6H4CH2CH2)2C
BF3(C2H5)2O
Me
Me
Ref. 143

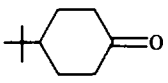


(24)

Analogous reactions of dimethylsulfoxonium methylide with tetrahydrofluorenone derivatives,[147] with methoxyacetophenones,[148-150] dimethoxyacetophenones,[151,152] biphenylyl *tert*-butyl ketone,[153] tetralone,[154,155] fluorenone,[155], benzophenones,[156] chlorophenyl, fluorophenyl ketone,[157] pyridinecarboxaldehydes,[158] dihydromethoxynaphthalenones,[159] deoxytetrulose derivatives or deoxyhexulose,[160] (pentodialdopyranosyl)cytisine,[161] cytidine aldehyde derivatives,[162] oxocycloadenosine derivatives,[163] formylpyridodioxin,[164] etc.[165,166] have been described.

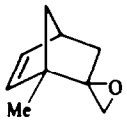
The stereochemistry of the addition of S-ylides to ketones is of considerable interest. The reaction of DMSY with 4-*t*-butylcyclohexanone is stereospecific and produces (*Z*)-oxirane,[22] the reduction

Table 3.

Substrate	S-ylide	(*E*)-oxirane (%)	(*Z*)-oxirane (%)	Ref.
	$Me_2\overset{+}{S}(O)\bar{C}H_2$	—	100	22
	$Me_2\overset{+}{S}\text{-}\bar{C}H_2$	83	17	22
	$PhS(O)\bar{C}H_2$ | $\overset{+}{N}Me_2$	—	100	24

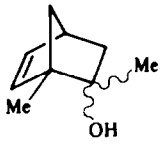
of which affords *trans*-4-*t*-butyl-1-methylcyclohexanol free of the *cis*-isomer. Transfer of methylene from other S-ylides to 4-*t*-butylcyclohexanone is also stereospecific as shown in Table 3.[22,24]

(−)-1-Methyl-5-norbornen-2-one (isolated from the racemic mixture via reduction, esterification, and recrystallization of the brucine salt) reacts with DMSY to give a 73 : 27 mixture of the oxiranes **16** and **17**, which on reduction with lithium aluminium hydride gives 1,2-dimethyl-5-norbornen-2-ols **18** (*exo*- and *endo*-OH, respectively).[125]



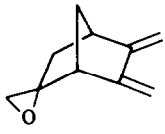
16

17



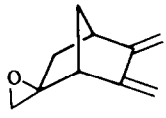
18

When dimethylenebicycloheptanone is treated with DMSY the new dienes **19** and **20** are obtained, in which the oxocyclic s-*cis*-butadiene group is remotely perturbed by an epoxide function.[167]



19

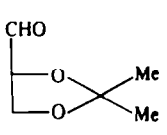
endo-epoxydiene



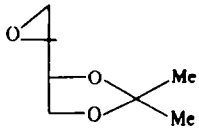
20

exo-isomer

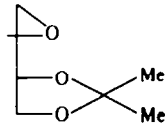
The reaction between the glyceraldehyde **21** and DMSY (or $Me_2S{=}CH_2$) gives two epimeric epoxides **22** and **23** with a slight preference for the latter.[168]



21

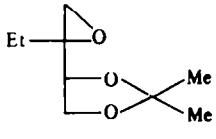


22



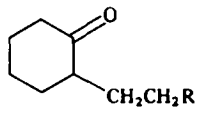
23

It was shown that the reactions of DMSY with dideoxyisopropylidenepentulose gave a mixture of the epoxide **24** and its epimer.[169]

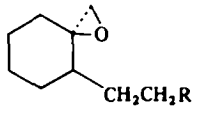


24

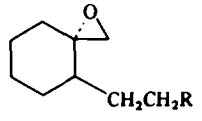
Treatment of cyclohexanones **25** with DMSY gave epoxides **26** and **27** with 26 : 27 ratios of 22–28 (R = cyano) and 11 (for R = Me). For cyclohexanones (R = cyano) the cyano group induces greater stereoselectivity than the methyl group in **25** (R = Me).[170]



25

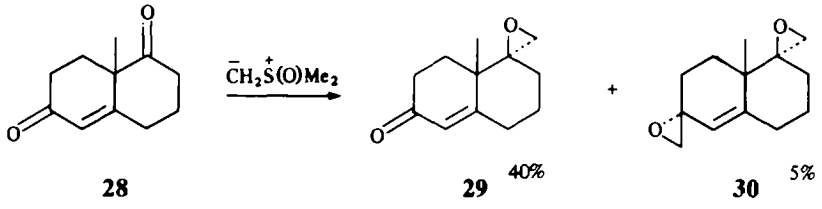


26



27

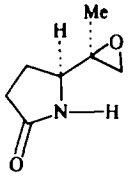
Treatment of bicyclic enedione **28** with DMSY in DMSO at 25°C followed by heating at 60°C gives a mixture of: spiro-1β-oxiranyl-6-oxo-8- α,β-,methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene **29** as a major product and spiro-1β-oxiranyl-6α-oxiranyl-8α,β-methyl-1,2,3,5,6,7,8,8α-octahydronaphthalene **30**.[171]



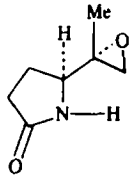
28 **29** 40% **30** 5%

+ liquid product (10%) (25)

Epoxidation of 5-acetyl-pyrrolidin-2-one with DMSY in THF at 20°C for 2 h and then 55°C for 1 h gives a 78 : 22 mixture of epoxides **31** and **32** whereas in the presence of zinc chloride a 23 : 77 mixture of **31** and **32** is obtained.[172]

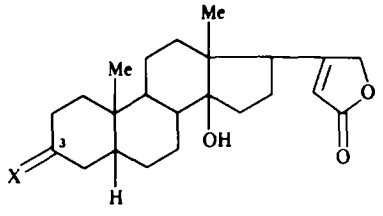


31



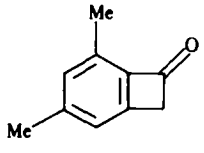
32

Reaction of DMSY with digitoxigenone **33** gives 41% of the corresponding (3S)-epimer **34**.[173]

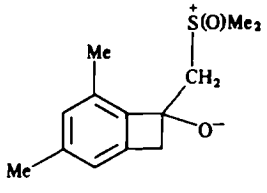


33 X = O
34 X = OCH_2

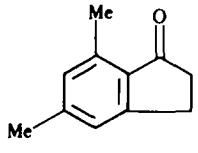
In some cases other products are the favored compounds (Scheme B). For example 4,6-dimethylbenzocyclobuten-1-one **35** with DMSY does not lead to an epoxide, but yields 5,7-dimethylindan-1-one **37** directly via the adduct **36**.[174]



35

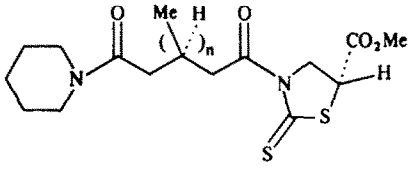


36

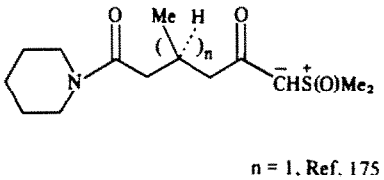


37

N-acylthiazolidinethione derivatives and *meso*-dimethylglutaric acid piperidine thiazolide reacts with DMSY to give **38** and **39**.[175,176]



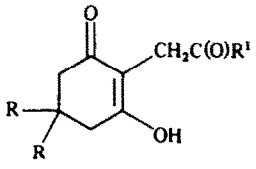
38



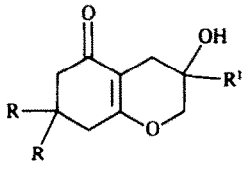
39

n = 1, Ref. 175
n = 2, Ref. 176

Benzopyranones **41** are prepared in 50–74% yields by the cycloaddition of DMSY with cyclohexanediones **40**.[177]



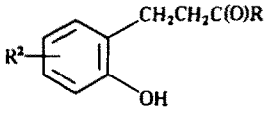
40



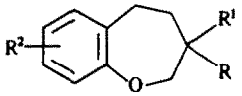
41

R = H, R^1 = Ph, R = R^1 = Me; R = Me, R^1 = Ph

Cycloaddition of DMSY with (hydroxyphenyl)alkanones **42** gives benzoxepin derivatives **43**.[178,179]



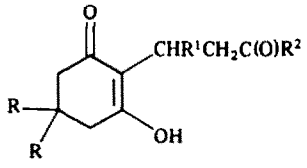
42



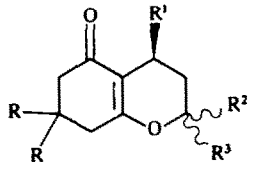
43

R = Me, Et, Me_3C, Ph, p-anisyl; R^1 = H, Ac; R^2 = H, OH, OAc, Me, OMe Ref. 178
R^1 = OH; R = Me, Et, Ph; R^2 = H; R = Me, R^2 = 5-OH; R = Ph, R^2 = 3-MeO Ref. 179

Benzopyranones **45** are also prepared in 45–92% yields by treating **44** with DMSY.[180]



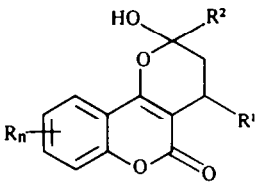
44



45

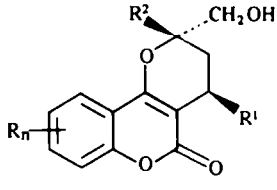
R = H, R^1 = H, Ph, R^2 = Me, R^3 = CH_2OH; R = Me, R^1 = H,
R^2 = Me, Ph, R^3 = CH_2OH; R = R^2 = Me, R^1 = Ph, R^3 = CH_2OH

The Michael adducts **46** of 4-hydroxycoumarins and , - unsaturated ketones react with 2–3 mol excess DMSY in DMSO or THF in 4–20 h giving the angular compounds 3,4-dihydro-2*H*,5*H*-pyrano 3,2-c 1 benzopyran-5-ones **47** (prevailing diastereoisomer shown). Minor amounts of the linear pyranobenzopyranones **48** are also obtained.[181]

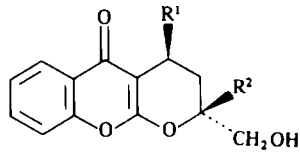


46

R_n = H; 8,10-Me_2; R^1 = R^2 = Me; R^1 = Ph, R^2 = Me. R_n = H, R^1 = Me, Ph; R^2 = Ph



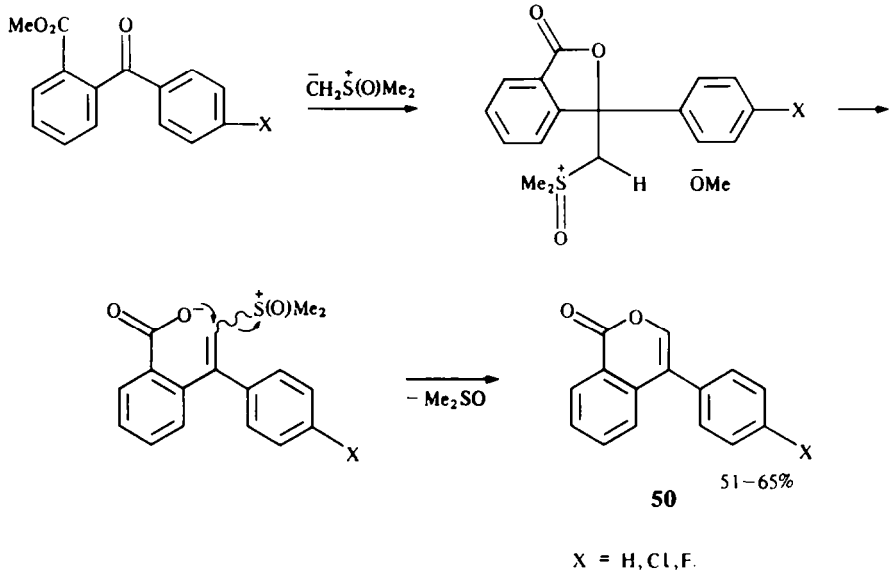
47



48

R^1 = R^2 = Me, Ph
R^1 = Ph, R^2 = Me

Treatment of 2-benzoylbenzoates **49** with DMSY does not lead to epoxides but to 4-phenylisocoumarins **50** via the steps shown in eqn (26).[182]

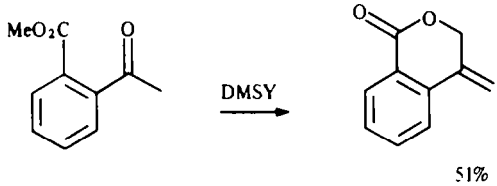


(26)

50

X = H, Cl, F.

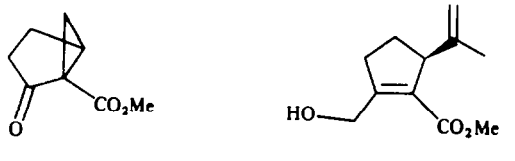
It is interesting that methyl 2-acetylbenzoate gives only 4-methylene-3,4-dihydroisocoumarin **51** under the same reaction conditions.[182]



(27)

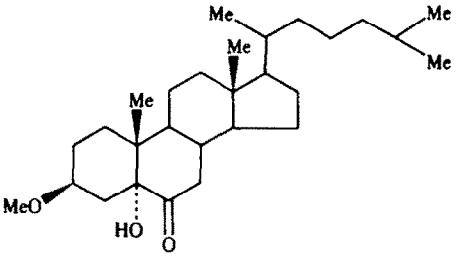
51

Reaction of DMSY with dimethylmethylenebicyclohexanecarboxylate at 55°C for 4 h gives the corresponding hydroxy ester **52**. Evidently this rearrangement does not proceed at the 1,2-addition step.[183]

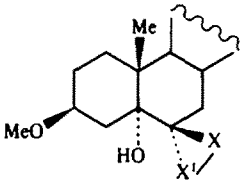


52

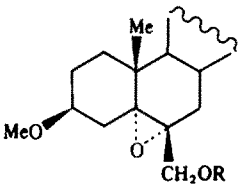
Attempts to prepare **54** by treating the steroidal ketone **53** with DMSY (or $Me_2S{=}CH_2$) led to the rearrangement product **55a** and its ether **55b**.[184]



53

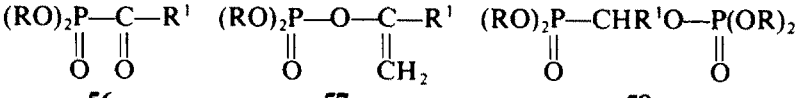


54
$X \neq X^1 = CH_2.O$



55a R = H
55b R = Me

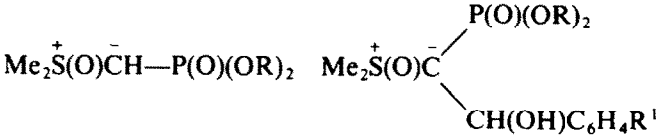
It was shown that acylphosphonates **56** reacted with S-ylides (DMSY or $Me_2S{=}CH_2$) to give enolphosphates **57** and phosphonophosphates **58**. The product ratio of **57** and **58** is determined by the substituent R^1. If R^1 is not an electron-withdrawing substituent, the phosphonophosphate **58** is the sole reaction product.[185]



56 **57** **58**

R = Et, Me; R^1 = Ph,4-MeC_6H_4,2-ClC_6H_4,3-ClC_6H_4,4-ClC_6H_4,Me.

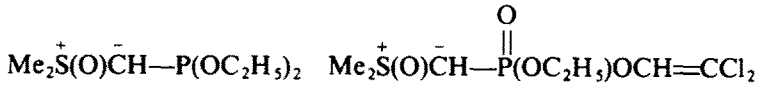
The phosphonylsulfoxonium ylides with benzadehyde or *p*-nitrobenzaldehyde give the corresponding *β*-oxoderivatives **59** instead of epoxides.[62]



59

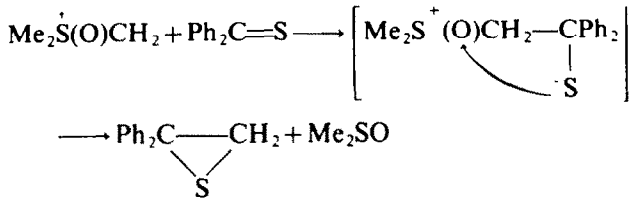
R = Et; R^1 = H, *p*-NO_2.

In contrast, the reaction of the P^{III}-substituted sulfoxonium ylide **60** with chloral gives the rearrangement product **61** (Scheme Perkov reaction).[36]



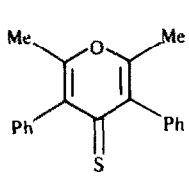
60 **61**

3.6.2. *Reactions with* C=S *double bond.* Several thiocarbonyl derivatives react with DMSY. The behavior of thioketones is of particular interest. It was shown that DMSY with thiobenzophenone gave 1,1-diphenylethylene sulfide.[22,93]

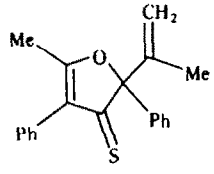


70.7%

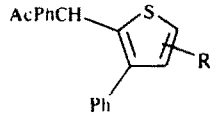
Reaction of 2,6-dimethyl-4-pyran-4-thione **62** with DMSY in DMSO leads to the 5-membered, α,β-unsaturated thione **63** (3%), thienylacetone derivatives **64** (15%, R = 3-Me; 7%, R = 2-Me), a naphtho{2,1-b}-thiophene derivative **65** (trace), and a hemithioacetal **66** (19%).[186] The formation of all the products may be reasonably interpreted as the Michael condensation of DMSY at the C-2 position of the thione **63** which is preferable to reaction with the thiocarbonyl group at the C-4 position.[186]



62

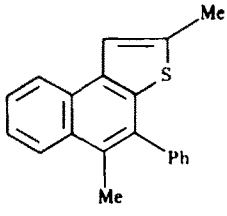


63

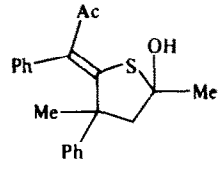


64

R = 3-Me, 2-Me



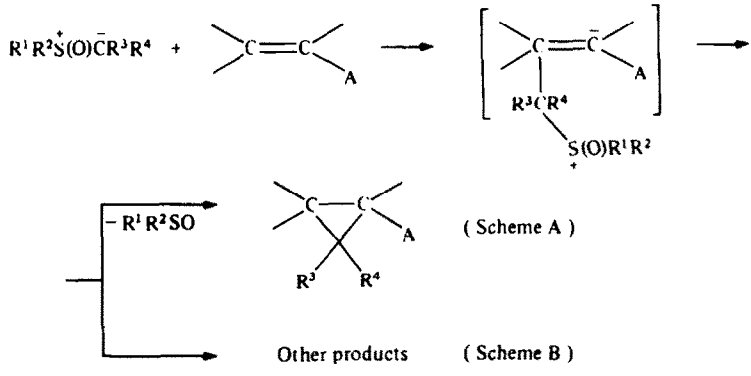
65



66

Interaction of DMSY with certain thioketones leading to the S-methylation products is described in Section 3.5.4.

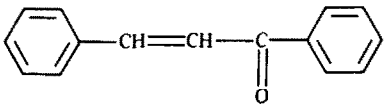
3.6.3. *Reactions with* C=C *double bond.* Reactions of S-ylides with a large variety of electron deficient olefins lead either to cyclopropane derivatives or to other products as shown in the following Scheme.



3.6.3.1. *Reactions with ethylenic ketones.* The interaction of S-ylides with unsaturated carbonyl compounds is described in many reports.[22,28,33,37,67,113,155,187-210]

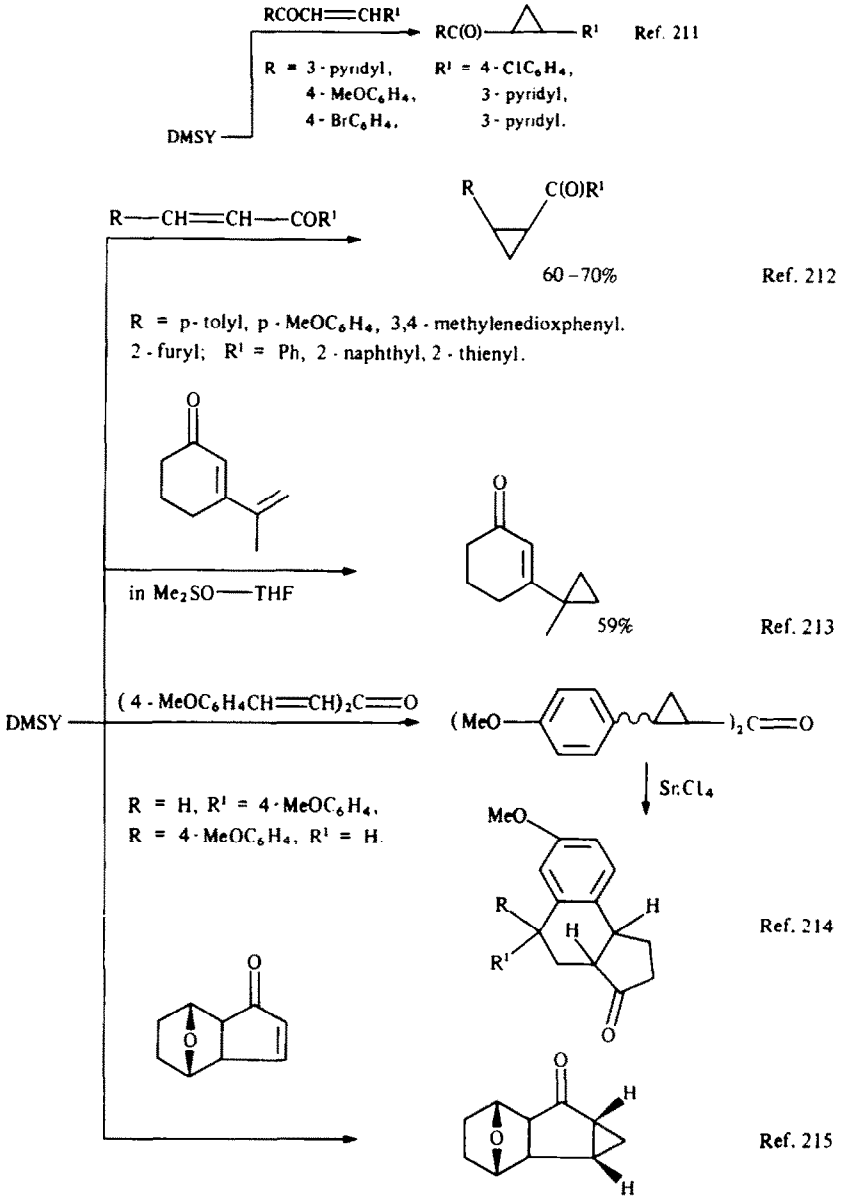
One of the most striking properties of DMSY is its reaction with C=C double bond of certain

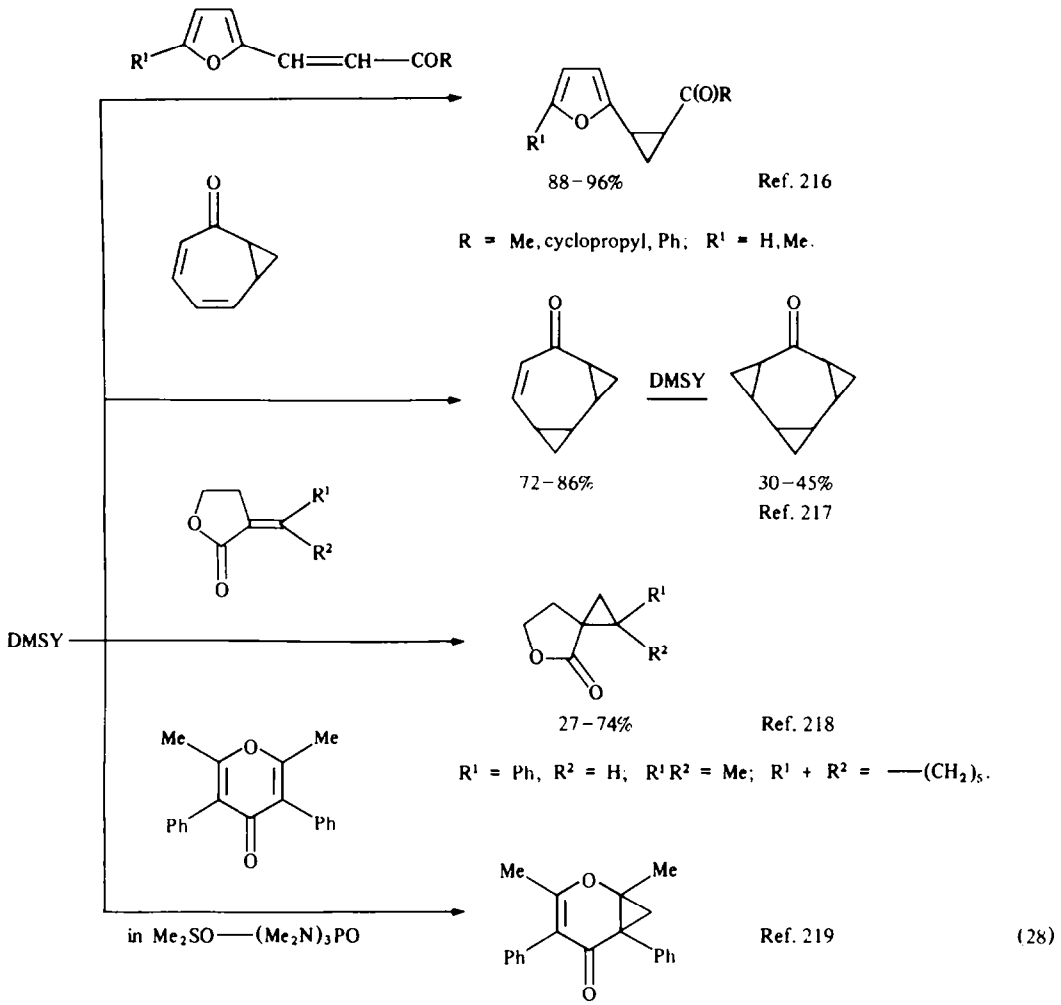
Table 4.

Substrate	S-ylide	Reaction products (%)	Ref.
	$Me_2\overset{+}{S}(O)CH_2$	Cyclopropane (100)	22
	$Me_2\overset{+}{S}-\overset{-}{C}H_2$	Oxirane (100)	22
	$PhS(O)\overset{-}{C}H_2$ | $\overset{+}{N}Me_2$	Cyclopropane (100)	24

ethylenic carbonyl compounds and the formation of the corresponding cyclopropane derivatives in excellent yields (Scheme A).[22,91,190,192,199-204] Regioselectivity of the reactions of some S-ylides as nucleophilic methylene transfer reagents is given in Table 4.

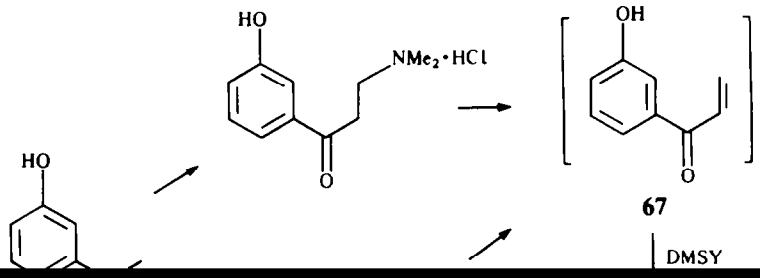
Corey's method for the conversion of α,β-unsaturated systems into cyclopropane derivatives with DMSY has found widespread use in organic synthesis[211-219] (Scheme 28).





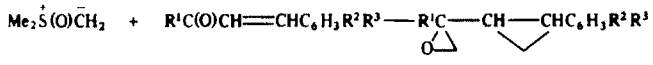
Analogous reactions of DMSY with : acyclic and cyclic α,β-ethylenic ketones,[220,221] cyclohexanol derivatives,[222], benzalacetophenone,[223] *o*-hydroxybenzal ketones,[224] thiatricycloundecatrienones, trimethylcyclohepta[b]thiophen-6-ones, 5,7-dimethylcyclohepta[b]thiophen-6-one,[225] cholest-5,6-dien-3-one,[226] pregnadienone derivatives.[227,228]

The existence of the unstable intermediate enone **67** was proved by trapping experiments with a series of nucleophiles (e.g. DMSY).[229]



It was shown that primary and secondary α-halogencarbonyl compounds of the type RC(O) CHR^{1}X added to a solution of DMSY gave relatively low yields of cyclopropane derivatives.[230-232] The synthesis involved a double participation of the ylide with an overall introduction of two methylene groups into the product.

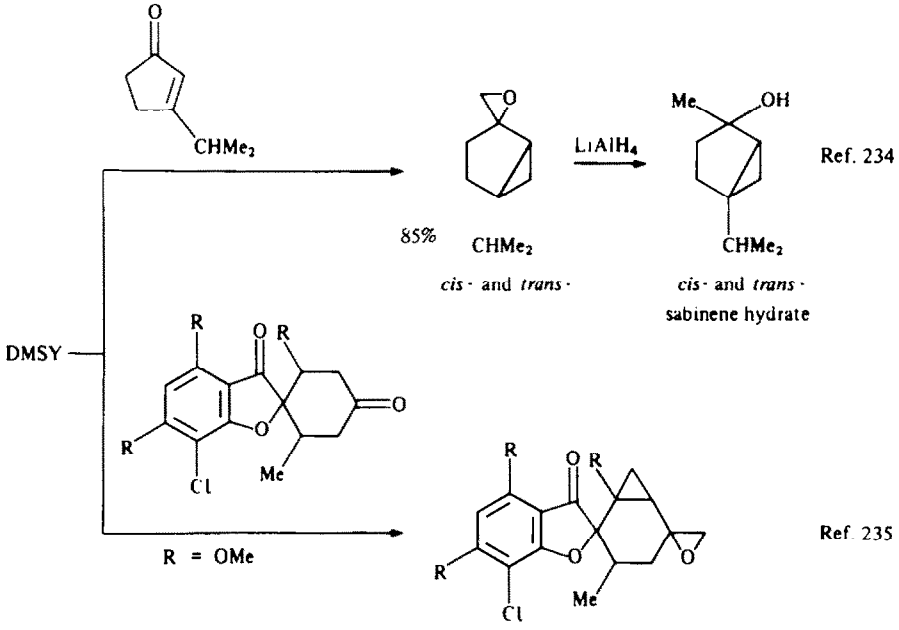
Interaction of DMSY with certain α,β-unsaturated ketones gives the corresponding cyclopropyl epoxides via cyclopropyl ketones.[233-235]



R^1	R^2	R^3
Ph	2-OMe	H
Ph	3,4-OCH_2O	
Ph	4-OMe	H
4-MePh	4-OMe	H

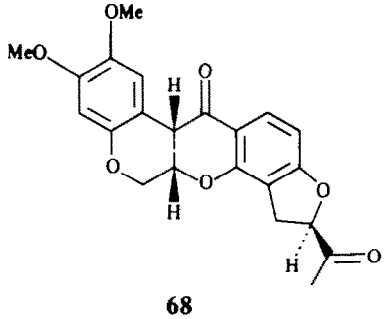
mixture of isomers (30)

Ref. 233

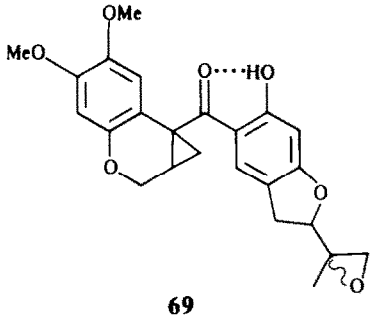


(31)

The cyclopropyl epoxide **69** is prepared by the reaction of DMSY with trienone nor-ketone **68** by rearrangement or corresponding intermediate product.[236,237]

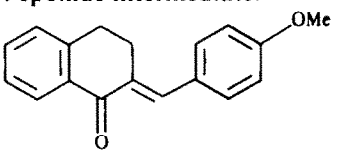


68

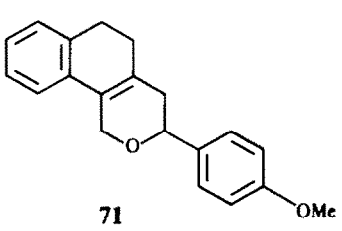


69

Treatment of the arylidene-tetralone **70** with DMSY gives the naphthopyran **71** by rearrangement of a cyclopropyl epoxide intermediate.[238]

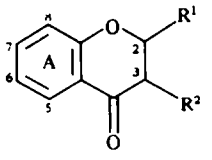


70

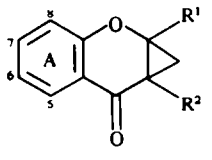


71

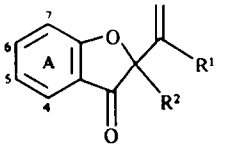
The reaction of benzo-4-pyrones **72** (the 2,3-double bond behaves as an electron deficient structure) with DMSY gives three types of products, 2,3-dihydro-2,3-methanobenzo-4-pyrones **73**, 2-vinylcoumaran-3-ones **74**, and 1-(2-hydroxyaryl)butane-1,4-diones **75**.[205,206]



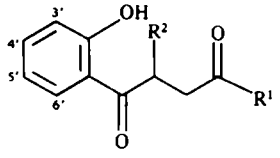
72



73

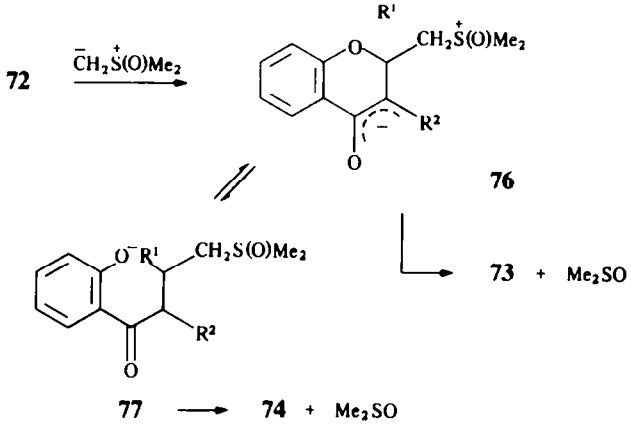


74



75

The yields of each product are summarized in Table 5. This reaction is initiated by nucleophilic attack of the ylide at the 2-position of the pyrone **72**, giving the zwitterion **76**. This zwitterion either cyclises to the cyclopropane **73** with loss of DMSO, or ring-opens by β-elimination giving the zwitterion **77** in which the negative charge is located as a phenoxide anion. Allylic displacement of DMSO in **77** then leads to the vinylcoumaranone **74**. This possible mechanism is summarised in the figure.[206]



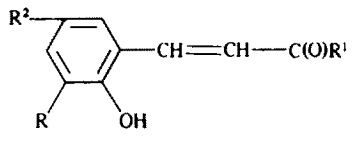
(32)

Table 5. Products of types **73**, **74** and **75** obtained from the reaction of benzo-4-pyrones **72** with DMSY[206]

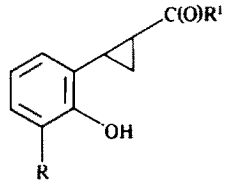
Reactant substituent in **72**				Products % yield		
R^1		R^2	Ring A	**73**	**74**	**75**
H		Ph	7-OH	**80**		
H		2-(OH)C_6H_4	7-OH	**10**		
H		Ph	7-OMe	**58**	**18**	
H		Ph	6-Me	**62**	**5**	
H		Ph	—	**60**	**7**	
H		2-(OMe)C_6H_4	7-OMe	**74**	**4**	
H		2-(OH)C_6H_4	7-OMe		**63**	
H		2-OH-4-(OMe)C_6H_3	7-OMe		**55**	
H		Ph	5-OH-7-OMe	**69**		
Me		Ph	7-OMe	**50**		
Ph		Ph	7-OMe	**72**		
Ph		H	—			**86**
2-(OMe)C_6H_4	**72a**	H	—			**72**
4-(OMe)C_6H_4	**72b**	H	—			**83**
4-(NO_2)C_6H_4	**72c**	H	—	**32**		
H		H	7-OMe	**34**		
Me	**72d**	H	—			**50**
H		Me	H	**72**		
Me		Me	H	**28**		

The formation of butane-1,4-diones **75** from flavones **72a**, **72b**, and **72c** and 2-methylchromone **72d** is not accompanied by the formation of products of type **74**: most likely products **75** result from the hydrolysis of 2,3-dihydro-2,3-methanobenzo-4-pyrones **73** on isolation.[206]

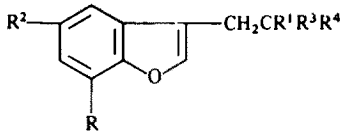
Hydroxybenzal ketones **78** and DMSY yield mixtures of products.[239]



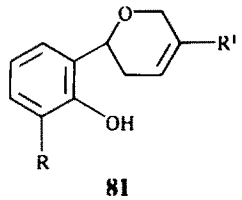
78



79



80

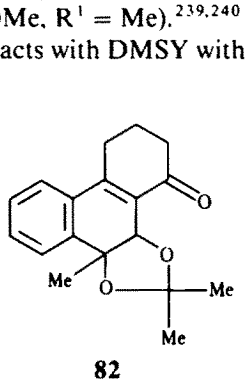


81

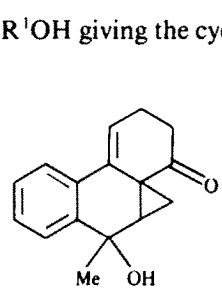
The activated double bond is attacked giving cyclopropanes **79** (R = H, R^1 = Et,CMe_3,Ph,C_6H_4OH-2; R = OMe, R^1 = Me) (8–34%).

78 (R = R^2 = H, R^1 = H,Me) and 1 equivalent DMSY gives only benzofurans **80** [R^3 = OH, R^4 = $CH_2S(O)Me$] (52–72%). DMSY and **78** (R = H, R^1 = Me, R^2 = OH) formed the cyclopropylmethylbenzofuran **80** [R^3R^4 = $CH_2CH(SOMe)$, 61%] as the only product. Other products include **80** [R = R^2 = H, R^1 = CMe_3,Ph,C_6H_4OH-2; R = MeO, R^1 = Me, R^2 = H; R_3R_4 = O; R^3 = OH, R^4 = $CH_2S(O)Me$], **80** [R = R^2 = H, R^1 = Me,Et; R = MeO, R^1 = Me, R^2 = H; R^3R^4 = $CH_2CH(SOMe)$, CH = CR^1CH_2OH] and hydroxyphenyldihydropyrans **81** (R = H, R^1 = Me,Et; R = OMe, R^1 = Me).[239,240]

Compound **82** reacts with DMSY with elimination of R^1OH giving the cyclopropane derivative **83**.[241]

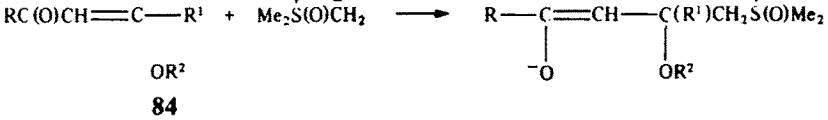


82

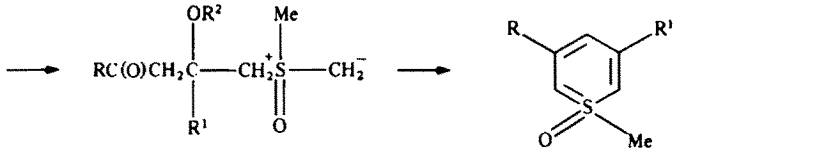


83

The condensation of DMSY with enol ether of β-diketones **84** has been investigated.[242] Initial attack by the ylide at the β-position, followed by the formation of a new ylide by ionization of one of the remaining methyl groups, and finally an intramolecular attack of the new ylide at the CO group, leads to 3,5-disubstituted 1-methylthiabenzene 1-oxides **85**.



84



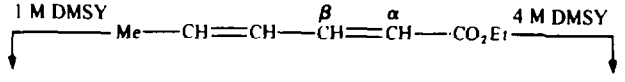
(33)

85

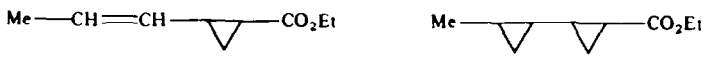
46–68%

It was shown that reaction of stable sulfoxonium allylides with alkoxides gave the thiabenzene 1-oxides derivatives as well.[243]

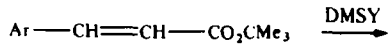
3.6.3.2. *Reactions with unsaturated carboxylic esters.* The reactions between DMSY and α,β-unsaturated carboxylic esters give cyclopropanecarboxylic esters in good yields,[57,244-249] as shown below:



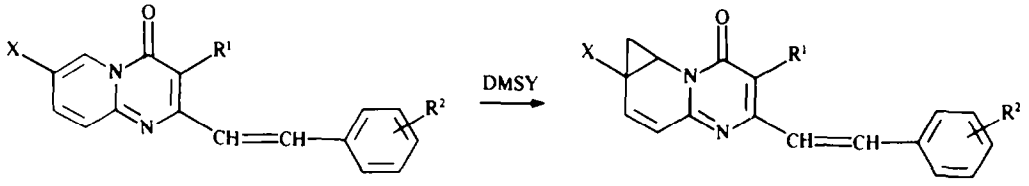
Ref. 245



(34)

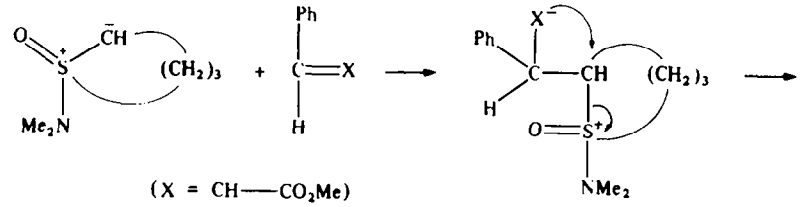


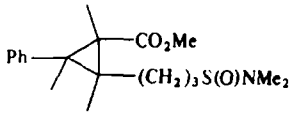
Ref. 247 (35)



X = MeO_2C, R^1 = Et, Pr, R^2 = H, alkyl, alkoxy. Ref 249 (36)

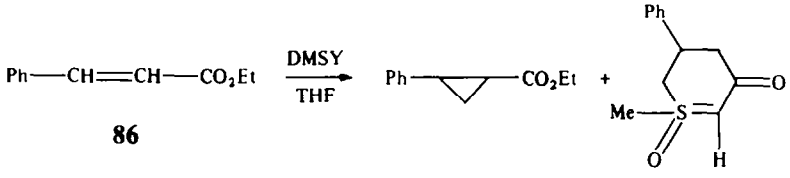
Certain cyclic sulfoxonium ylides react with unsaturated esters giving cyclopropane derivatives containing an S-fragment.[30]



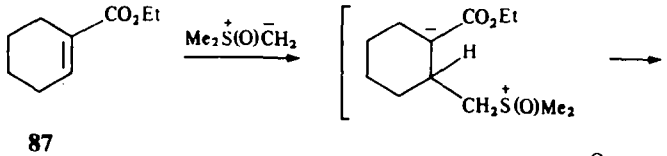


Ref. 30 (37)

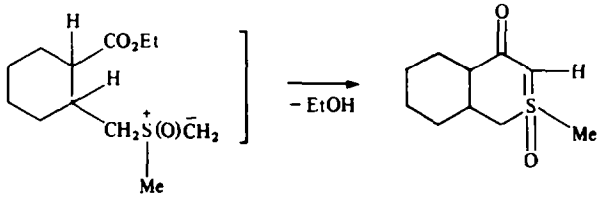
The interaction of DMSY with certain α,β-unsaturated carboxylic esters of the types **86**, **87**, and **88** gives cyclic sulfoxonium ylides:[51,246,250,251]



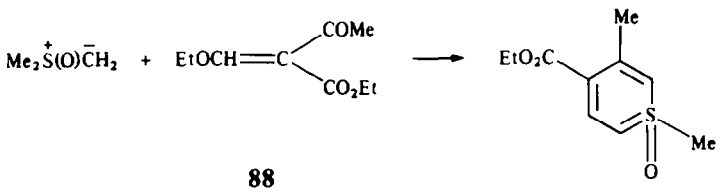
86 Ref. 246 (38)



87



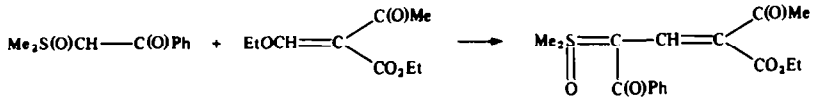
Ref. 51 (39)



88

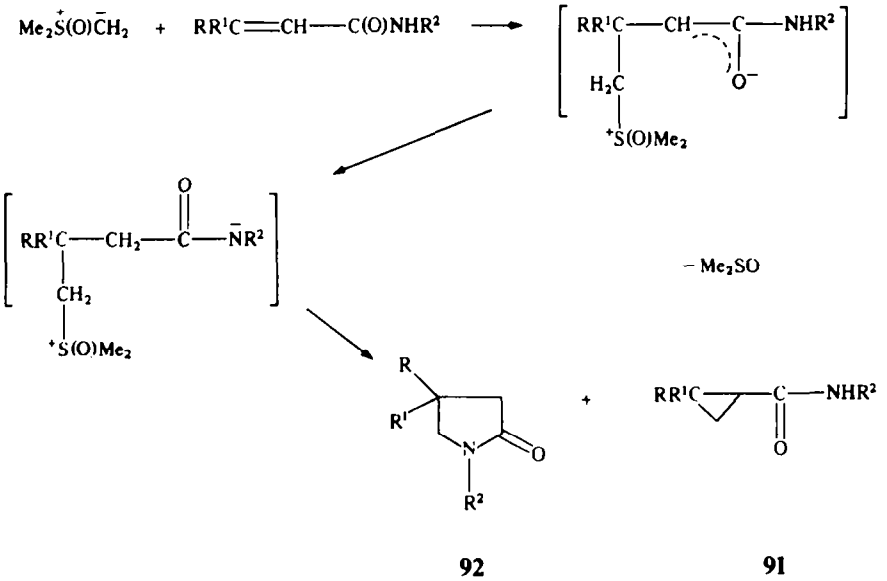
Ref. 250, 251 (40)

On the other hand, the reaction of stable sulfoxonium ylides **89** with 2-acetyl-2-ethoxycarbonyl-1-ethoxyethylene in the presence of triethylamine yields the corresponding sulfoxonium allylides **90**.[252]



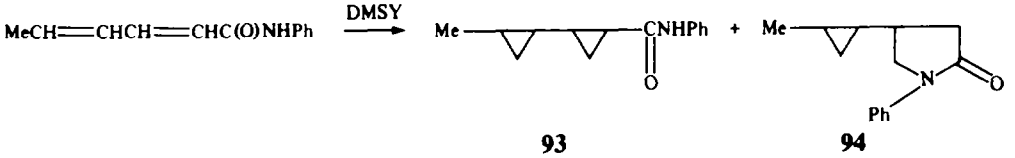
89 **90** Ref. 252 (41)

3.6.3.3. *Reactions with unsaturated amides, imides and relative systems.* DMSY reacts with unsaturated amides giving the corresponding cyclopropanecarboxamides **91**, pyrrolidone derivatives **92** or their mixture, and other products,[33,57,253] as shown below.



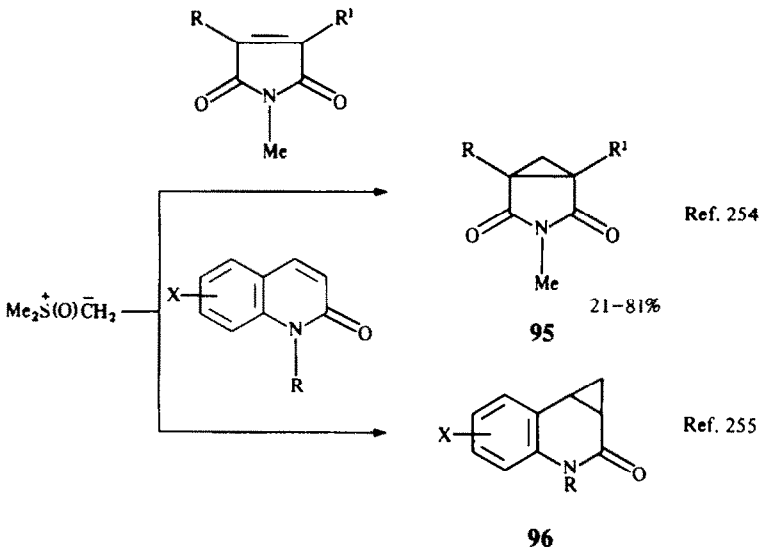
92 **91** (42)

Reaction between sorbamide and DMSY gives the mixture of dicyclopropanecarboxamide **93** and cyclopropylpyrrolidone **94**.[33,253]



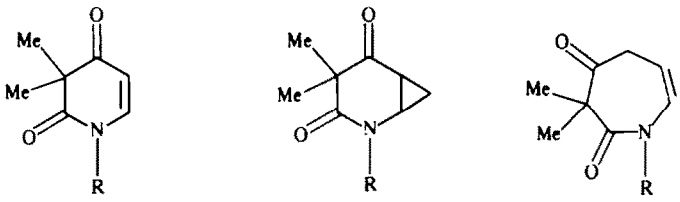
93 **94** (43)

DMSY with *N*-methyl-2-arylmaleimide and *N*-alkyl-2-quinolones gives the corresponding cyclopropane derivatives **95** and **96**.[254,255]



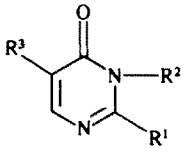
(44)

Reaction of 2,4-dioxo-*N*-alkyl-3,3-dimethyltetrahydropyridine **97** with DMSY gives 2-alkyl-4,4-dimethyl-2-azabicyclo-4,1,0 heptane-3,5-dione **98**. Irradiation of **98** gives 1-alkyl-3,3-dimethyl-1*H*-azepine-2,4-(3*H*,5*H*)-dione **99** with a ring expansion.[256]



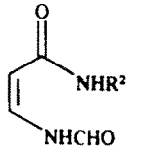
97 **98** **99**

The products obtained from the 4-pyrimidones **100** with DMSY vary with the solvent.[257]



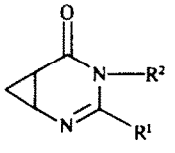
100

	R^1	R^2	R^3
a	H	Me	H
b	H	CH_2Ph	H
c	H	Me	Br
d	H	CH_2Ph	Br
e	Me	Me	H
f	SMe	Me	H
g	SMe	CH_2Ph	H



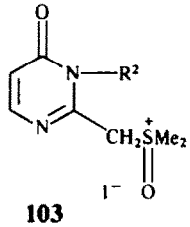
101

a R^2 = Me
b R^2 = CH_2Ph

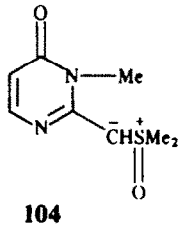


102

	R^1	R^2
a	H	Me
b	H	CH_2Ph
f	SMe	Me



103

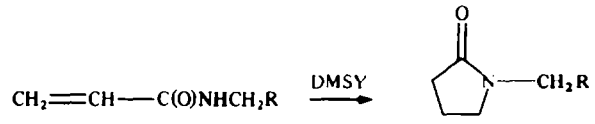


104

In DMSO as the solvent each compound **100a**, **100b** and **100f** gives two products. In the case of **100a** and **100b** the (*Z*)-3-formylaminoacrylamides **101a** and **101b** are the major products. The minor

products are the cyclopropapyrimidones (diazabicycloheptenones) **102a** and **102b** (8% and 7% yields, respectively). In THF solutions, the compound **102b** could be obtained (yield 24%). From pyrimidone **100f** in DMSO the cyclopropapyrimidone **102f** is formed but the major product is the sulfoxonium ylide salt **103**. By using THF as a solvent, the yield of the ylide **104** could be raised (41%).[257]

Pyrrolidinones **106** are prepared by cyclocondensation of DMSY with acrylamides **105** in DMSO for 3 h at room temperature and the 2 h at 50°C.[258]

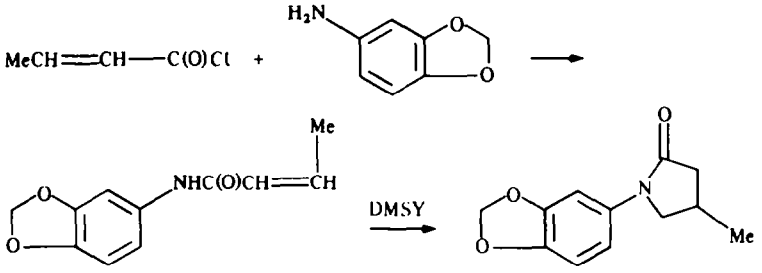


(45)

105 **106**

R = $CONH_2$, CN, CO_2Et

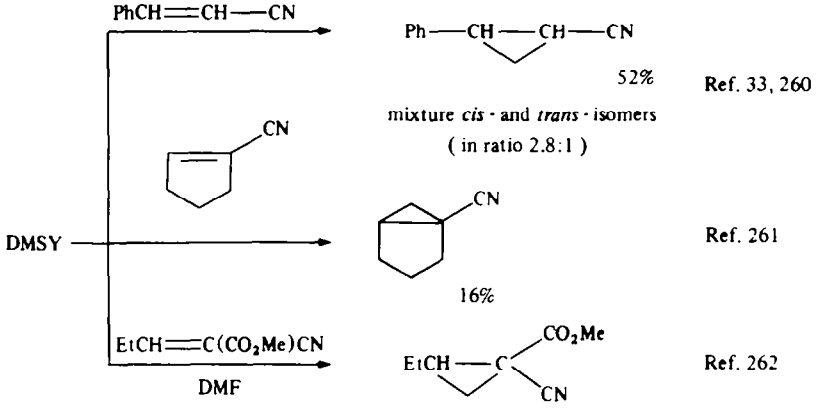
Cyclization of DMSY with *N*-benzodioxolyl(butenamide) **107** gives the corresponding pyrrolidinone **108**. This compound shows mild analgesic activity and has an antiinflammatory action (ED_{50} 120 mg/kg) orally in rats.[259]



(46)

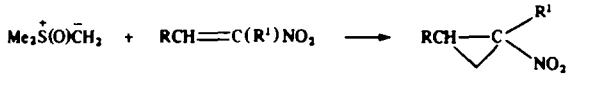
107 **108**

3.6.3.4. *Reactions with unsaturated nitriles, conjugated nitroolefins and vinylsulfones.* α,β-Unsaturated nitriles react with DMSY giving the corresponding cyclopropanecarbonitriles.



(47)

DMSY is an effective reagent for converting conjugated nitroolefins into substituted nitrocyclopropanes.[263] Conversion of 2-nitro-1-alkenes into nitrocyclopropanes is inefficient, however, because of the polymerization of the nitro olefins by DMSY.



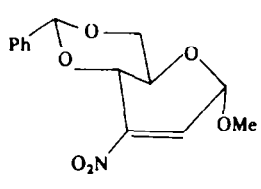
31–44% Ref. 263

(48)

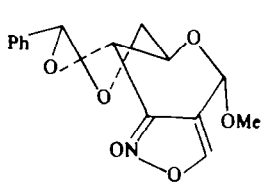
R	R¹	Yield, %
Me	H	31
$MeCH_2$	H	40
$Me(CH_2)_2$	H	43
Me	Me	37
Ph	H	44

The α-nitro-β-substituted cyclopropanes prepared appear to have *trans* stereochemistry.[263]

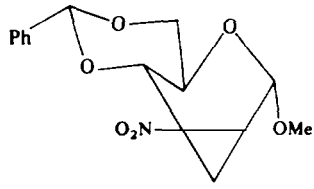
In the reaction of DMSY with the nitro sugar **109**, axial approach predominates over equatorial approach. The axial attack selectively gives the 1,4-addition product **110** whereas equatorial approach yields the 1,2-addition product **111**.[264]



109

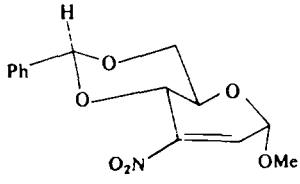


110

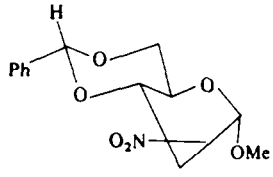


111

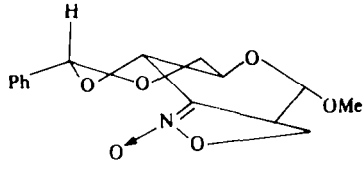
Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside **112** with DMSY in DMSO at room temperature for 1.5 h gives a mixture of methyl (2*R*,3*R*)-4,6-*O*- benzylidene-2,3-dideoxy-2,3-*C*-methylene-3-nitro-α-D-*erythro*-hexopyranoside **113** and (methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hexopyranosido)[3,2-c]isoxazoline *N*-oxide **114** in 1 : 3.5 ratio determined by NMR spectroscopy.[265]



112



113 16.5%

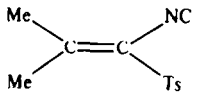


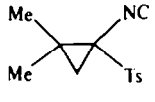
56.2%

114

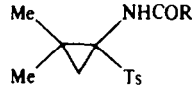
The interaction of DMSY with vinylic sulfones yields the corresponding cyclopropyl sulfones. *cis*-Phenyl ω-styrylsulfone and DMSY in DMSO at room temperature yields *trans*-1-(phenylsulfonyl)-2-phenylcyclopropane (85% yield).[266]

DMSY and 1-tosyl-isobutenylisocyanide gave 2,2-dimethyl-1-isocyano-1-tosylcyclopropane **115** (yield 85%) which with the appropriate benzoyl chloride or HCl yields *N*-acyl derivatives **116**.[267]





115

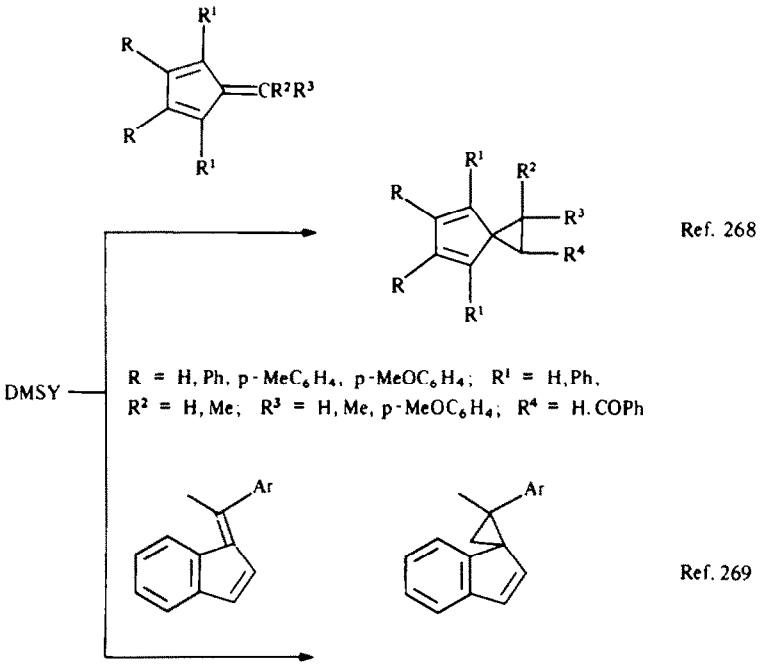


116

R = H, 4—ClC$_6$H$_4$, 3—PhOC$_6$H$_4$

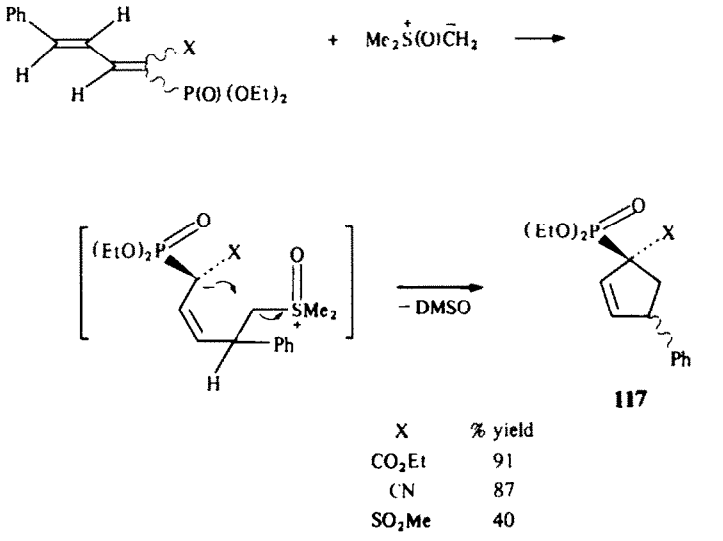
3.6.3.5. *Reactions with other systems.* DMSY reacts with fulvenes and 2-phenyl-5-(phenylmethylene)cyclopentadiene-1,3 giving cyclopropane derivatives.[268,269]

By contrast, treatment of 1,3-butadienylphosphonates with DMSY leads to none of the expected cyclopropanation products but only to diethyl 1-substituted-4-phenyl-2-cyclopenten-1-yl phosphonates **117** in very good yields.[270] This interesting observation could be explained as the Michael addition of the DMSY to the carbon of the butadienylphosphonates. The intermediate betaines,



(49)

that are stabilized by both phosphoryl and electron-withdrawing groups, the eliminate DMSO yielding 2-cyclopentenylphosphonates **117**.



117

X	% yield
CO_2Et	91
CN	87
SO_2Me	40

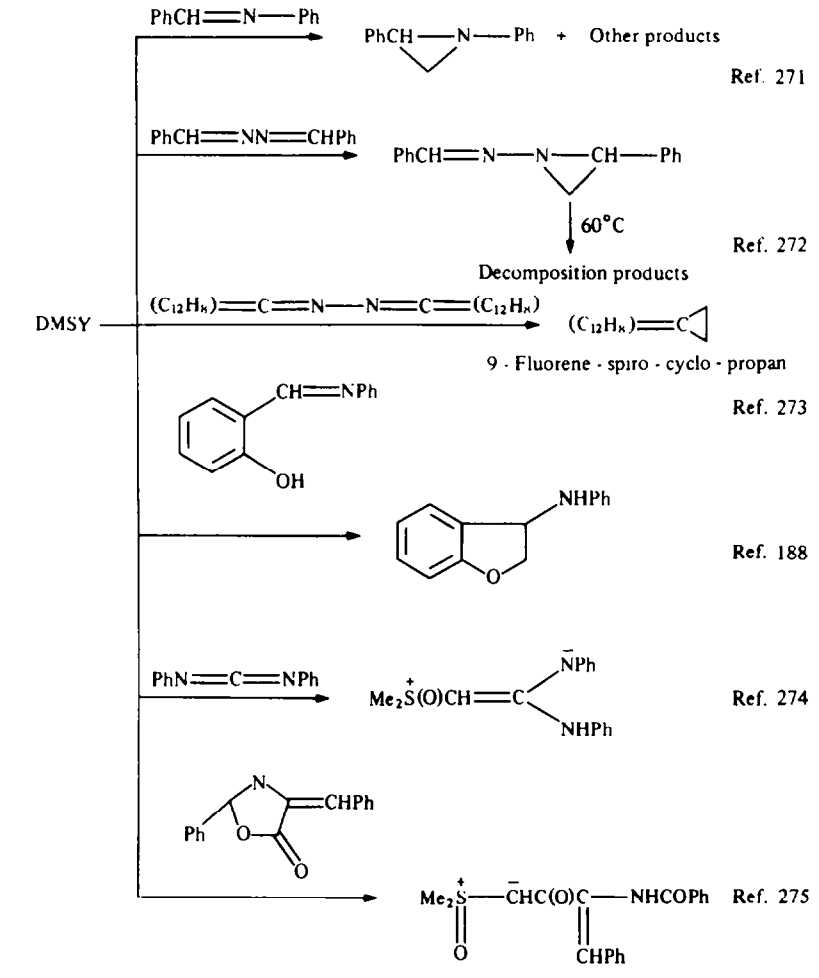
(50)

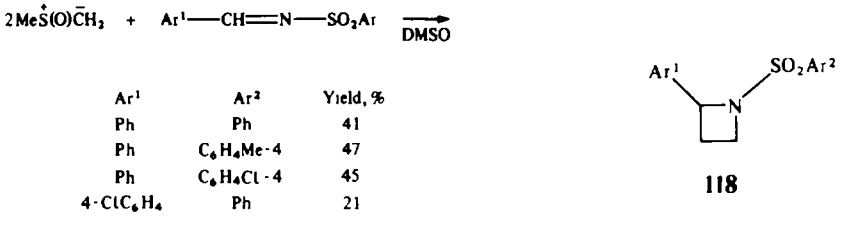
3.6.4. *Reactions with* C=N *double bond.* The interaction of DMSY with the C=N double bond to form the mixture of products is described in several reports.[89,188,271-278] Some examples are shown below.

The reaction of DMSY with *N*-arenesulfonylimines gives 2-aryl-*N*-arenesulfonylazetidines **118**.[277]

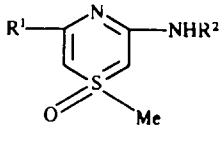
Although modest, the yields of azetidines **118** exceed the yields obtained by other methods. Besides, the given conditions are mild, the procedure is only one-step, and is based on available chemicals. However, the method is limited only to *N*-arenesulfonylazetidines. Thus, when *N*-benzylideneaniline was reacted with DMSY, no 4-membered heterocycle was obtained.[277]

1-Methyl-4-azathiabenzene 1-oxide derivatives **119** can be prepared by cyclocondensation of DMSY with $MeSC(R^1)=NCN$.[278]





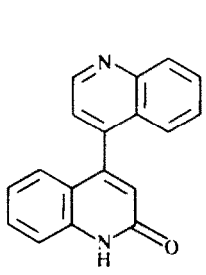
(52)



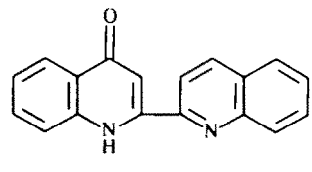
119

R^1 = SMe, OEt; R^2 = H

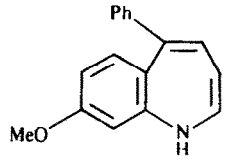
3.6.5. *Reactions with* N=O *and* N=N *double bond.* DMSY reacts with N=O and N=N bond systems to give various products.[33,260,279-281] nitrobenzene yields aniline, nitrobenzene and azobenzene.[33,260] The interaction of quinoline *N*-oxide and 7-methoxy-4-phenylquinoline *N*-oxide with DMSY produces 2,2'-biquinolyl and 2,2'-bis(7-methoxy-4-phenylquinolyl), respectively.[279] The interaction between quinoline *N*-oxide and DMSY in the presence of benzenesulfonyl chloride, yields 2-quinolone and a quinolinylquinolone **120** or **121**. 7-Methoxy-4-phenylquinoline *N*-oxide undergoes ring expansion: 5-phenyl-8-methoxy-1*H*-1-benzazepine **122** and its dimer are produced.[279]



120

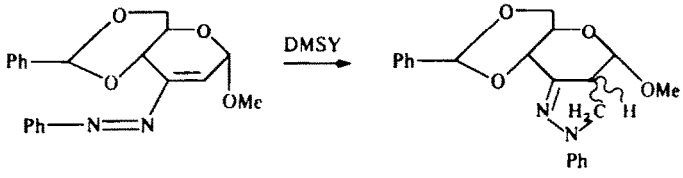


121



122

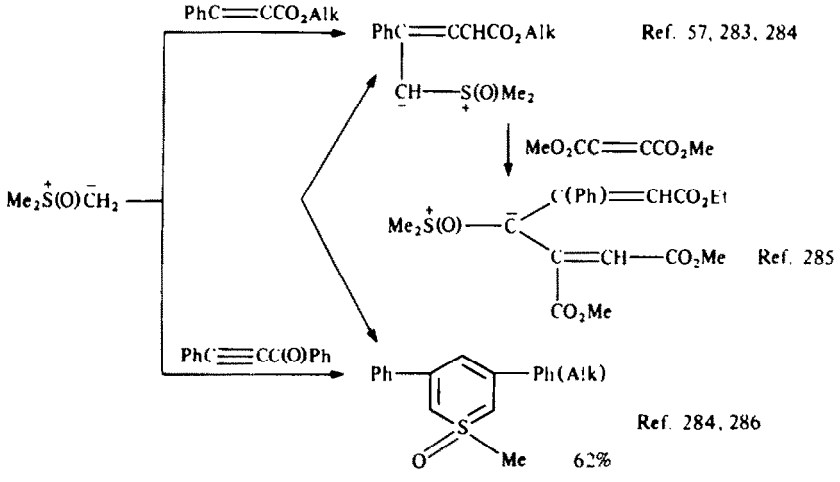
DMSY reacts with N=N bond containing systems to form either heterocyclic compounds[280] or cyclopropyl adducts.[281]



(53)

3.6.6. *Reactions with* C≡C *bond.* The reactions of DMSY with acetylenic compounds was examined in some reports.[57,282-284,286] No evidence is contained in the report[280] for methylene transfer onto the triple bond in the reaction of DMSY with α,β-acetylenic ketones: yields of acetylenic epoxides are only 5–10% and no cyclopropenyl ketones were found in the remaining involatile product.

Reaction of DMSY with alkyl phenylpropiolate gave dimethylsulfoxonium 3-alkoxycarbonyl-2-phenylallylides,[57,283,284] and with certain acetylenic ketones DMSY formed thiabenzene 1-oxide derivatives.[284,286]



(54)

Some substituted sulfoxonium ylides react with certain acetylenic compounds by conjugated addition giving allylic sulfoxonium ylides which then undergo 3,2-sigmatropic rearrangement giving the corresponding sulfoxides **123**.[287,288] At 80°C, **123** readily loses methanesulfinic acid giving dihydropyridines **124**. These reactions go *via* azatriene intermediates.[288]

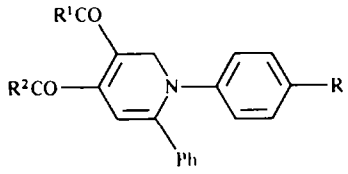
$$Me_2\overset{+}{S}(O)\bar{C}H{-}\underset{\underset{\overset{\|}{N}C_6H_4R\text{-}4}{\|}}{C}{-}Ph + R^1COC{=}CCOR^1 \longrightarrow$$

R = NH, NO_2. R^1 = OMe, PH.

$$4\text{-}RC_6H_4N{=}C(Ph)CH{=}C(COR^1)CH(COR^1)CH_2S(O)Me$$

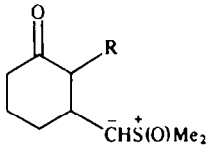
↓

123

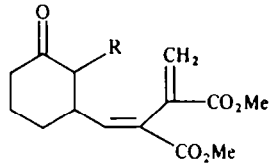


124 (55)

The stable ylides **125** react with dimethyl acetylenedicarboxylate by a similar sequence to give the trienones **126**.[287,288]



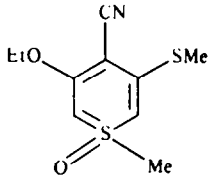
125



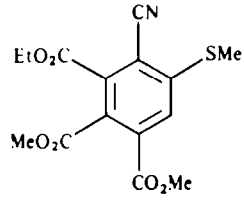
126

R = H, Me.

Finally, it should be noted that the corresponding derivative **128** is formed from 1-methylthiabenzene 1-oxide **127** and dimethyl acetylenedicarboxylate.[289]

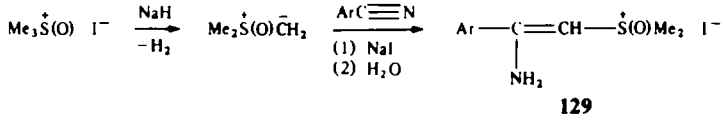


127



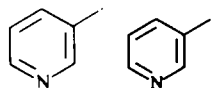
128

3.6.7. *Reactions with* C≡N *bond.* DMSY prepared *in situ* by the method of Corey and Chaykovsky was treated with aromatic nitriles for 48 H at 25°C. Poured onto ice the mixture yielded the corresponding β-aminovinylsulfoxonium salts **129**.[290]



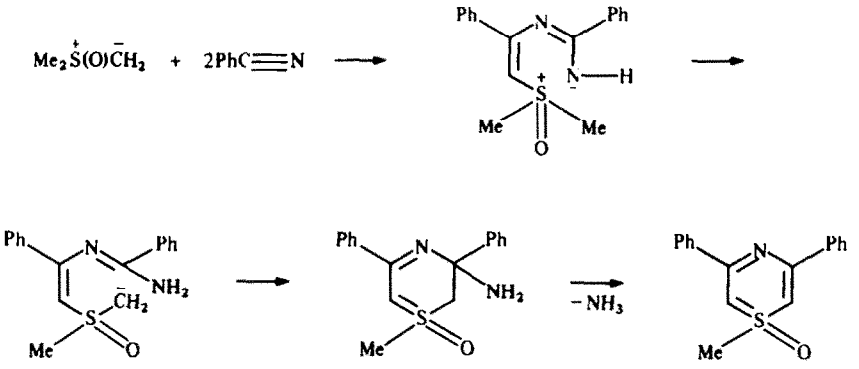
129

Ar	Yield, %
Ph	72
p-ClC_6H_4	77
p-MeC_6H_4	64



73 (56)

A similar procedure with 4-nitrobenzonitrile gave a resinous product.[290] Reaction of DMSY with excess of benzonitrile yields 4-azaanalog of thiobenzene 1-oxide derivative **130**.[89,291]

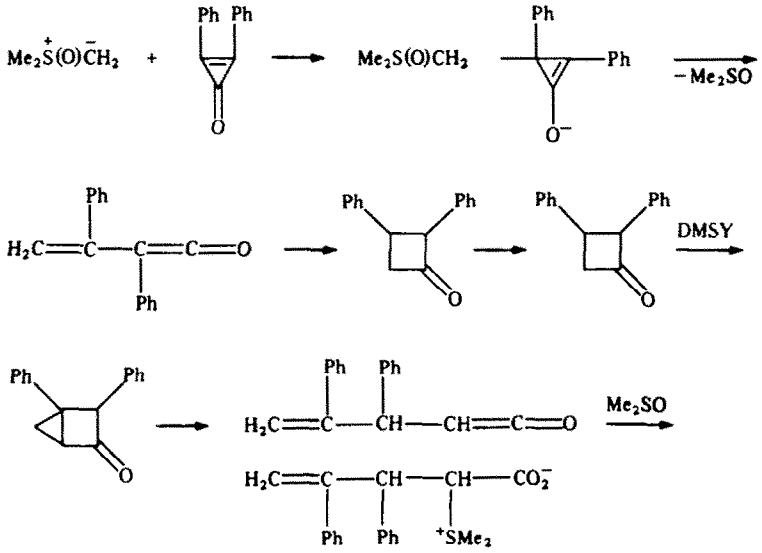


(57)

130

3.7. *Reactions with cyclic systems*

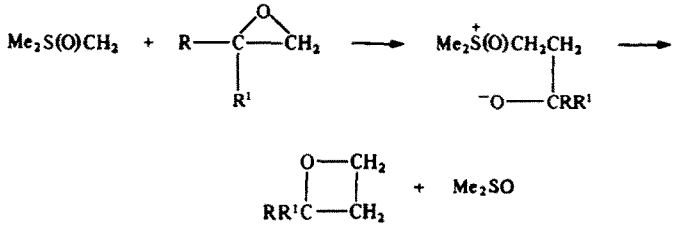
Certain cyclic compounds (diphenylcyclopropenone, epoxides, keto-lactones, aziridines, etc.) react with sulfoxonium ylides.[292-297] For example, reaction of 2 moles of DMSY with diphenylcyclopropenone in DMSO gave the betaine **131** which on heating at 135°C gave 3-pentenoate isomer of **131** and 2,3-diphenyl-2-cyclopentene-1-one. It was shown that the formation of the betaine **131** involved initial conjugate addition of the DMSY to the ketone.[298]



(58)

131

The DMSY is an efficient methylene-transfer reagent in reactions with epoxides, affording the corresponding oxetanes **132** on standing at 50°C for 3 days.[299]



(59)

132

As shown in Table 6, oxetanes are obtained in 83–97% yields.[299]

The use[299] of DMSY as a nucleophilic methylene-transfer reagent to epoxides had advantages over most of the known methods of oxetane synthesis. The reaction conditions are mild and

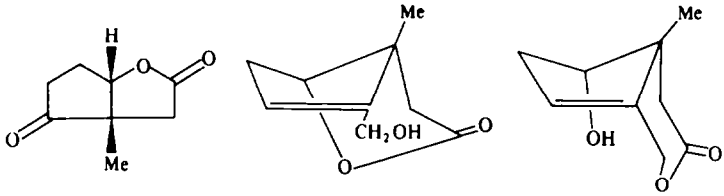
Table 6. Preparation of oxetanes from epoxides[299]

R	R^1	Yield[a] (%)	Yield[b] (%)
H	Ph	65	94
Ph	Ph	55[c]	99
H	*p*-ClC_6H_4	23[c]	88
Me	Ph	24[c]	85
cyclohexanone		81	83

[a] 10 mol. % excess DMSY, reflux 4 h.
[b] 100 mol. % excess DMSY, 50°C, 3 days.
[c] Unreacted epoxide recovered in yields of 25%, 45% and 50%, respectively.

the yields of the products are much higher than in the procedures reported by Deric,[300] Biggs (20–40%),[301] and Welch (46–96%).[302]

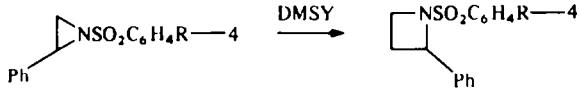
DMSY when treated with (hydroxymethyloxocyclopentyl)acetic acid lactone **133** in DMSO at 10°–room temperature for 4 h yields a 3 : 1 mixture of γ-lactone alcohol **134** and δ-lactone alcohol **135**.[303]



133 **134** **135**

This mixture is equilibrated with 1 N KOH to give a more stable γ-lactone alcohol **134** as the single product (60–65% yield from **133**). The reaction mechanism involves initial formation of spirooxiranes and subsequent rearrangement. It was shown that if alkali hydride is used as a base instead of sodium hydroxide in the preparation of the DMSY then the γ-lactone alcohol **134** can be obtained directly from the ketolactone **133** (yield 60%).[303]

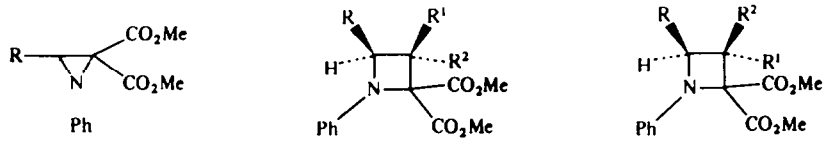
Treatment of the DMSY with (arylsulfonyl)aziridines in an inert atmosphere (ambient temperature, 18–20 h) gives the corresponding azetidines **136** by a methylene insertion process.[304]



(60)

R = H, Me, Cl. (51–72%)

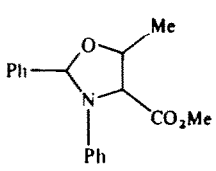
The azetidines **138** and **139** are prepared by reaction of the aziridines **137** with sulfur ylides: $Me_2S(O)CR^1R^2$ or $Me_2SCR^1R^2$.[305]



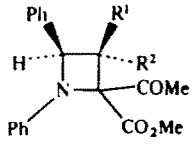
137 **138** **139**

R = Ph, CO_2Me; R^1 = H, Cl; R^2 = H, CO_2Et, COPh, CO_2Me, R^1R^2 = fluorenylidene.

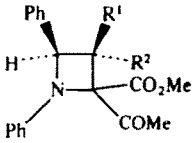
The azetidines **141** and **142** are similarly prepared from S-ylides: $Me_2S(O)CR^1R^2$ or $Me_2SCR^1R^2$ and 4-oxazoline derivative **140**.[305]



140



141

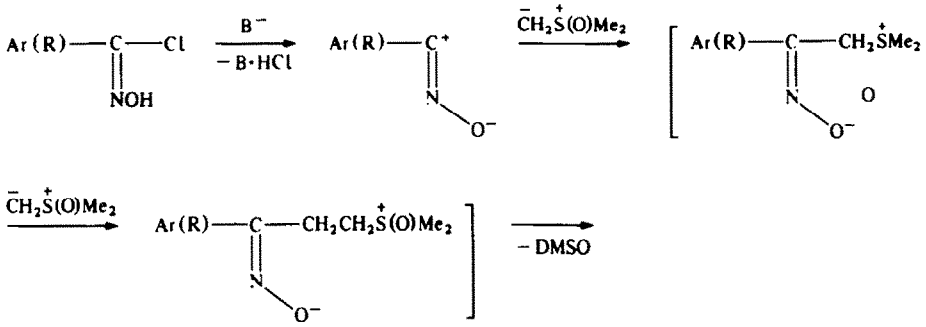


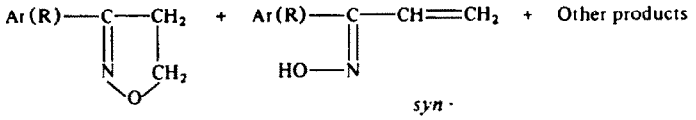
142

R^1 = H, Cl; R^2 = H, CO_2Et, CO_2Me, COPh; R^1R^2 = fluorenylidene.

3.8. *Reactions with* 1,3-*dipolar systems*

1,3-Dipolar compounds (nitrile oxides, nitrile-imines, azides, etc.) are highly reactive systems towards DMSY. Thus, nitrile oxides on treatment with DMSY are converted through two consecutive transfers of methylene groups into 3-aryl(alkyl)-2-isoxazoline **143** by ring closure and to aryl(alkyl)vinyl ketoximes **144** by β-elimination.[306–310]



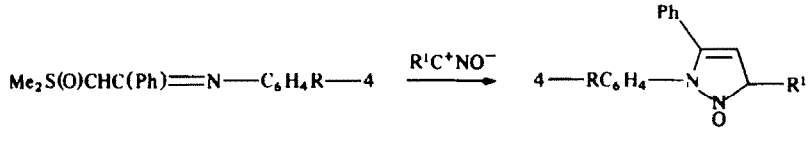


(61)

143 **144**

Ar(R)	**143** yield, %	**144** yield, %	Ref.
Ph	10–12	30	306–310
p-$O_2NC_6H_4$	5	11	310
2,4,6-$Me_3C_6H_2$	–	40	310
tert-Bu	16	41	310

Imidoyl-substituted sulfoxonium ylides react with nitrile oxides giving the corresponding pyrazole oxides (9–75%).[43]

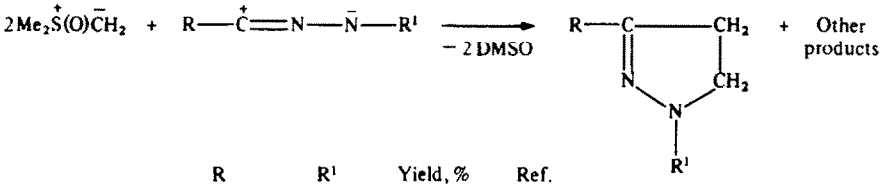


(62)

R = H, NO_2, R^1 = CO_2Et, Ph; R = NO_2, R^1 = COMe

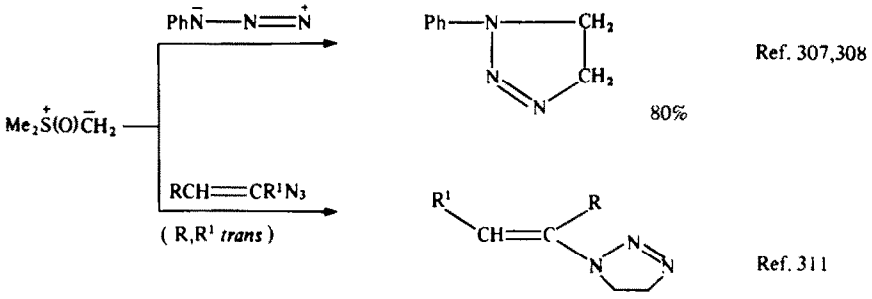
p-Nitrophenylsubstituted ylides with benzonitrile oxide gives 31% of the 2:1 adduct, 4,5-dihydro-4,5-bis-)4-nitrophenyl)-3-phenyl-isoxazole.[43]

The reactions between other 1,3-dipoles and DMSY have been investigated: some examples are shown in eqns (63) and (64).[307-310]



(63)

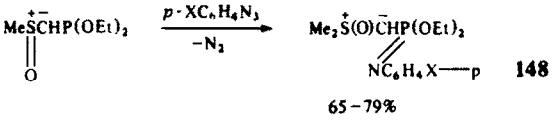
R	R¹	Yield, %	Ref.
Ph	Ph	45	307, 310
CO_2Et	m-$O_2NC_6H_4$	73	310
Ac	Ph	41	310



(64)

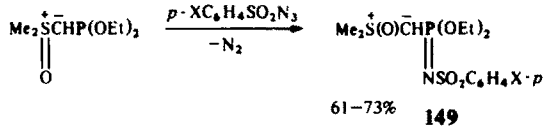
R	R¹	145 Yield, %	146 Yield, %
Ph	Me	95	93
Bu	H	91	93
H	CMe_3	93	94
$(CH_2)_6$		89	91

The reaction of the P(III) containing sulfoxonium ylide **147** with organic azides gives the phosphazo compounds **148** and **149** (Scheme Staudinger reaction).[62,312,313]



(65a)

X = H, Me, MeO, Br



(65b)

X = H, Me, Cl, NO_2.

3.8.1. *Mechanism of Staudinger reaction.*[314-316] The general mechanism of the Staudinger reaction is known. The stability of the intermediate phosphazide **150** determines the kinetic order of the product formation in the Staudinger reaction:

$$R_3P + N_3R^1 \overset{k_1}{\rightleftarrows} R_3PN_3R^1 \xrightarrow{k_2} R_3P{=}NR^1 + N_2. \quad (66)$$

150

The reaction may be either first or second order, depending upon whether the unimolecular decomposition or bimolecular formation of the phosphazide is the rate-determining step.

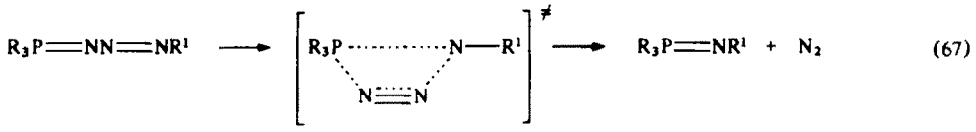
The primary electrophilic attack of an azide molecule on phosphorus in the first step in Scheme

Table 7. ρ-Values of Hammett correlations in the Staudinger reaction (THF)[314]

Phosphorus(III) reagent	Azide	ρ-Values 1st step	2nd step
$(EtO)_2PCHS(O)Me_2$	$XC_6H_4N_3$	0.76	0.61
$(EtO)_3P$	$XC_6H_4N_3$	1.53	0.67
$(EtO)_2PNMe_2$	$XC_6H_4N_3$	0.85	0.67
$(EtO)_2PCH(CO_2Et)_2$	$XC_6H_4N_3$	1.28	0.93
Ph_3P (xylene)	$XC_6H_4N_3$	1.36	—
Ph_3P (benzene)	$XC_6H_4N_3$	1.25	−0.19
$(EtO)_2PCHS(O)Me_2$	$YC_6H_4SO_2N_3$	—	−0.12
$(EtO)_2PCH(CO_2Et)_2$	$YC_6H_4SO_2N_3$	0.46	−0.16

(66) is accelerated by acceptor groups of the azide and donor groups of the trivalent P compound.[314] This is expressed in terms of the Hammett correlation parameters in Table 7.

The phosphazide decomposes giving the corresponding phosphazo compound by an intramolecular mechanism via the 4-membered cyclic transition state **151**.



(67)

151

The effect of groups at phosphorus upon the rate of formation and decomposition of the phosphazide is inverse[315] as the nucleophilic function of the phosphorus centre changes into an electrophilic one along reaction coordinate. The sign of the Hammett parameter ρ for the second step of the Staudinger reaction also alters with the azide component (Table 7). This is probably due to the nonconcerted character of the bond redistribution in the transition state **151**.[317]

σ,ρ-Analysis of substituent effects upon the rates of imination in terms of inductive, mesomeric and steric increments has revealed some unexpected features of the Staudinger reaction.[318] This study was mainly performed with phenyl azide. The first imination step is controlled only by the inductive properties of the group attached to the p atom and the corresponding $\log k_1$ values that are linearly related to the sums of σ_I parameters of the substituents.[314]

The unique inductive control of the first step in the Staudinger reaction is used to evaluate the polar properties of various groups R at phosphorus, according to the linear equation (68):

$$\log k_1 = 2.274 - 5.656 \Sigma \sigma_I \quad (68)$$

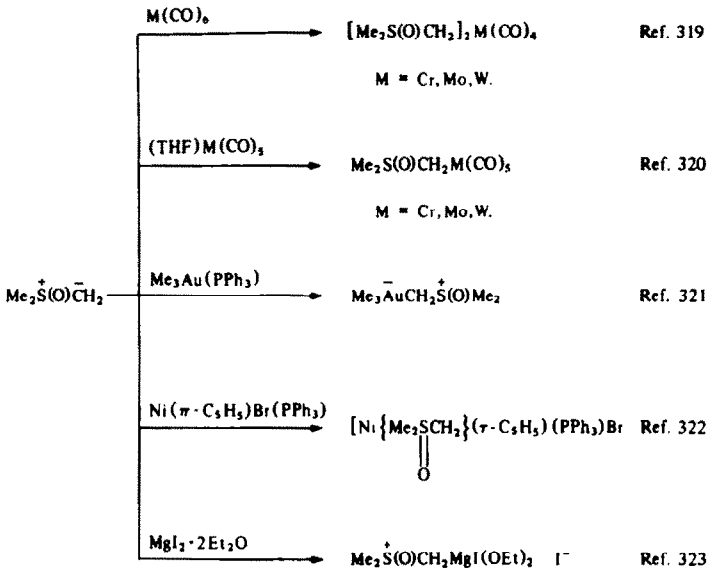
$$(r = 0.996,\ s = 0.08)$$

with known experimental constants k_1 for the imination of model compounds, $(EtO)_2P$-R, by phenyl azide under standard conditions (THF, 20°C) (Table 8).[314]

The dependence of the phosphazide decomposition rate on the properties of substituents at phosphorus is more complicated. Their inductive, mesomeric and steric characteristics commensurably contribute to the reactivity of a phosphorus reagent as it follows from the 3-parameter representation of $\log k_2$.[318] The total donative character of electronic effects (inductive and mesomeric) stabilizes the phosphazide and reduces its decomposition rate. The introduction of donor groups on phosphorus results in a shift of the limiting act from the first to the second step and a change in the kinetic order of the reaction. The steric screening of phosphorus causes the analogous stabilization of phosphazides. The steric requirements in the transition state **151** are more rigorous in the transition state associated with the primary electrophilic addition of the azide.[314]

3.9. *Dimethylsulfoxonium methylide as a ligand in metal complexes*

DMSY reacts with certain metal-containing compounds to form the corresponding metal complexes.[319-325] For these purposes, metal carbonyls,[319,320] gold complex,[321] bromo(cyclopentadienyl)(triphenylphosphine) nickel,[322] magnesium iodide,[323] etc. are mainly used, as shown in eqn (69).



(69)

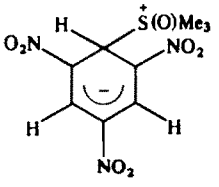
In the literature, the following sulfoxonium methylide metal complexes are described:

$ME_2S(O)CHSiMe_2Fe(CO)_2(C_5H_5\text{-}\pi)$ Ref. 326

$Me_2S(O)CHSiMe_2SiMe_2Fe(CO)_2(C_5H_5\text{-}\pi)$ Ref. 327

$Me_2S(O)CHFe(CO)(CO)_2(C_5H_5\text{-}\pi)$. Ref. 328

It was shown that DMSY reacted with trinitrobenzene to give a zwitterionic Meisenheimer σ complex **152**.[329,330]



λmax 495 nm

152

(identified by UV spectra)

Table 8. Rate constants for the first step of the reaction between $(EtO)_2PR$ and phenyl azide (THF, 20°C) and σ_1 parameters of radicals R[318]

Radicals	$k_1 \times 10^3\ M^{-1}\ s^{-1}$	σ_1[a]
—CHS(O)Me$_2$	253.0	−0.03
—N(Pr-i)CH$_2$CO$_2$Et	28.8	0.14
—CH$_2$CO$_2$Et	11.1	0.21
—OC$_6$H$_{11}$-cyclo	5.68	0.26
—OAd-2	5.11	0.27
—OAd-1	2.93	0.31
—N(Ph)N=CMe$_2$	2.50	0.32
—CH(CO$_2$Et)$_2$	1.59	0.36
—OC(Me)=CHCl	0.43	0.46
—OC(Me)=CHAc	0.28	0.49
—OC$_6$H$_4$CN-p	0.25	0.50
—OC(CN)=CHMe	0.25	0.50

[a] Calculated according to the equation:

$$\Sigma\sigma_1 = 0.405 + 0.176 \log k_1.$$

3.10. *Spectral properties and stabilization*[331]

In the IR spectra of sulfoxonium ylides, the appearance of the competition of electron-acceptor substituents for the excess negative charge of the carbanionic centre was observed.[331] The nature of the electron transition in the UV spectra of the ylides stabilized by the participation of the CO group is discussed[331] from the point of view of the intramolecular charge transfer. The effect of an onium fragment on the character of the delocalization of electron density was examined. Intramolecular interactions with participation of P containing sulfoxonium ylides in model complexes with a H bond and with lanthanide-shift reagent for which the selected ylides are ambidentate ligands were studied.[331]

4. CONCLUSIONS

To date, some hundred articles and patents have been published which cover the synthesis of different organic compounds via dimethylsulfoxonium methylide (Corey's reagent). Using this versatile nucleophilic agent one can prepare most epoxides and cyclopropane derivatives having different substituents as well as other important products.[332-345]

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