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# Nucleophilic Reactions of N-Unsubstituted Sulfoximines with Activated Acetylenes, Olefins, and Diphenylcyclopropenone

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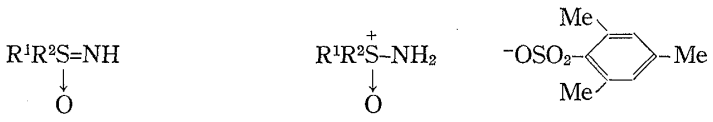
A study of the stereochemical course of the nucleophilic addition of N-unsubstituted sulfoximines **1a**—**e** to dimethyl acetylenedicarboxylate showed that *Z*-adducts were formed as the major products in methanol whereas *E*-adducts were predominantly or almost exclusively obtained in DMSO. The reactions of dimethylsulfoximine (**1a**) with ethyl propiolate and acetylacetylene were complicated by the concomitant isomerization of the adducts under the reaction conditions used. The reaction of **1a** with *trans*-1,2-dibenzoylethylene gave a normal 1 : 1 adduct, while that with tetracyanoethylene gave an addition-elimination product, N-(1,2,2-tricyanovinyl)dimethylsulfoximine. Heating **1a** with diphenylcyclopropenone in refluxing toluene gave N-(3-amino-2,3-diphenylpropenoyl)-dimethylsulfoximine. The mechanisms of these reactions are discussed.

**Keywords**——O-mesitylenesulfonylhydroxylamine; *cis*-addition to acetylenes; *trans*-addition to acetylenes; solvent effect; *cis-trans* isomerization

The imino group of N-unsubstituted sulfoximines **1** is amphoteric, and thus a variety of reactions can take place at the nitrogen atom: acylation and sulfonylation as well as alkylation have been reported.[2] However, little information is available concerning the nucleophilic addition of sulfoximines **1** to multiple bonds.[3,4] The renewed interest in this area of organosulfur chemistry has prompted us to report our observations on the stereochemical course of the nucleophilic addition of **1** to acetylenic compounds, as well as on the reactivity of **1** towards activated olefins and diphenylcyclopropenone. The sulfoximines **1a**—**e** employed in this study were synthesized from the corresponding *S*-aminosulfoxonium mesitylenesulfonates **2a**—**e**, which, in turn, were obtained by the reaction of sulfoxides with *O*-mesitylenesulfonylhydroxylamine (MSH).[5]



**1a**—**e** **2a**—**e**

**a**, $R^1=R^2=Me$; **b**, $R^1=R^2=PhCH_2$; **c**, $R^1=R^2=-(CH_2)_4-$; **d**, $R^1=Me$, $R^2=Ph$; **e**, $R^1=R^2=Ph$

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2) For recent reviews, see *a*) P.D. Kennewell and J.B. Taylor, *Chem. Soc. Rev.*, **4**, 189 (1975); *b*) S.L. Huang and D. Swern, *Phosphorus and Sulfur*, **1**, 309 (1976).
3) Williams and Cram have reported the reaction of methyl-*p*-tolylsulfoximine with 1,3-diphenylpropynone in the presence of sodium hydride, yielding 3,5-diphenyl-2-azathiabenzene 1-oxide directly. [T.R. Williams and D.J. Cram, *J. Org. Chem.*, **38**, 20 (1973)].
4) Michael addition of methylphenylsulfoximine to methyl acrylate in the presence of sodium hydride has been reported. [C.R. Johnson, J.J. Rigdu, M. Haake, D. McCants, Jr., J.E. Keiser, and A. Gertsema, *Tetrahedron Lett.*, **1968**, 3719.
5) *a*) Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, **1972**, 4137; *b*) Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, **1977**, 1.

## Reaction with Activated Acetylenes

Reaction of equimolar amounts of **1a** and dimethyl acetylenedicarboxylate (DAC) (3) in methanol at room temperature afforded a mixture of two isomeric adducts **4a** and **5a** in 92% combined yield and in a ratio of *ca.* 1:5 [as determined by nuclear magnetic resonance (NMR) spectroscopy]. Recrystallization from benzene-petroleum ether gave pure *Z*-adduct **5.** The same reaction in dimethylsulfoxide, however, gave a mixture of **4a** and **5a** in 65% yield and in a ratio of *ca.* 7:1. Recrystallization from benzene gave pure *E*-adduct **4a.** The sulfoximines **1b—e** also reacted with DAC at 70° in methanol or dimethylsulfoxide to give mixtures of **4b—e** and **5b—e.** The product distributions are summarized in Table I.

The stereochemistry of the adducts was readily ascertained by examination of the NMR spectra; the vinylic proton of **5** appears at 0.43—0.80 ppm lower field than that of **4**, because the former is subjected to greater deshielding by the two ester carbonyl groups.[6] We have confirmed that neither **4** nor **5** isomerizes to the other compound under the reaction conditions used.

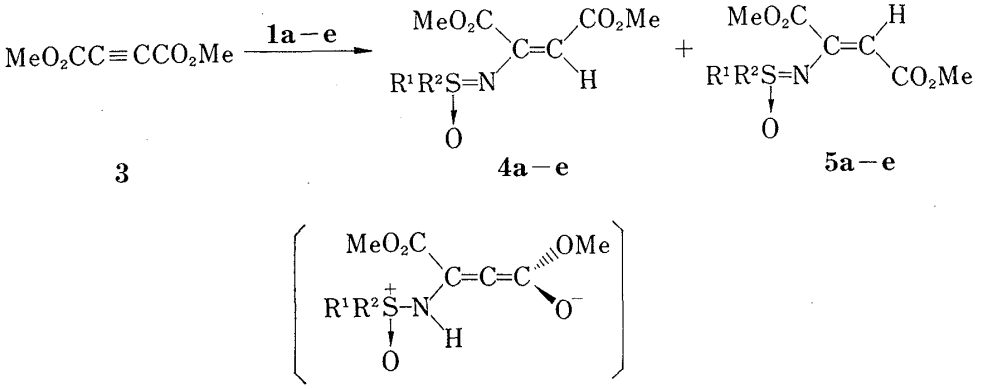



Chart 1

TABLE I. Product Distributions in the Reactions of **1a—e** with DAC[a]

| | $R^1$ | $R^2$ | In methanol | | In DMSO | |
|---|---|---|---|---|---|---|
| | | | Total yield (%) | Ratio (**4:5**) | Total yield (%) | Ratio (**4:5**) |
| **a** | $CH_3$ | $CH_3$ | 92 | 1:5 | 65 | 7:1 |
| **b** | $PhCH_2$ | $PhCH_2$ | 79 | 1:3 | 70 | 10:1 |
| **c** | $-(CH_2)_4-$ | | 80 | 1:4 | 63 | 10:1 |
| **d** | $CH_3$ | Ph | 89 | 1:5 | 80 | 10:1 |
| **e** | Ph | Ph | 78 | 1:4 | 50 | 6:1 |

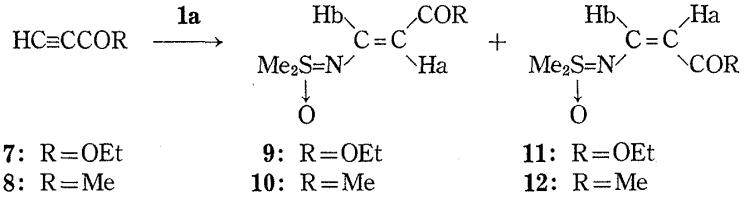
*a*) Product ratios were determined by area measurement of the vinyl proton peaks in the NMR spectra of the total product mixtures.

The stereochemistry of nucleophilic addition of amines to acetylenic esters has been extensively investigated.[6–9] In general, the addition of amines proceeds non-stereoselectively to give the *E* and *Z* adducts in proportions that are highly dependent upon the nature of the solvent used. It has been suggested that in aprotic solvents, internal proton transfer from

6) J.E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965).
7) E. Winterfeldt and H. Preuss, *Angew. Chem.*, **77**, 679 (1965).
8) W.E. Truce and D.G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).
9) *a*) R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, **1967**, 1883; *b*) B. Giese and R. Huisgen, *Tetrahedron Lett.*, **1967**, 1889.

the initially formed dipolar intermediate **6** [$R^1R^2NH$ instead of $R^1R^2\overset{+}{S}(O)NH$] is the sole proton source, resulting in predominant *cis*-addition, while in protic solvents, protonation of the dipolar intermediate by solvent becomes the favored process, leading to predominant *trans*-addition. The stereochemical course of the addition of the sulfoximines **1** to DAC can be rationalized by assuming similar intermediates **6**; the size of the substituents on sulfur seems to have little effect on the stereochemical outcome.

The reactions of **1a** with ethyl propiolate (**7**) and with acetylacetylene (**8**), however, proceeded with concomitant isomerization of the adducts under the reaction conditions used. Refluxing of equimolar amounts of **1a** and **7** in chloroform for 8 hr gave a mixture of two isomeric adducts in 62% yield (the reaction also proceeded at room temperature, but very slowly). The mixture could be separated by preparative thin layer chromatography (TLC) to give pure adducts **9** and **11**. The same reaction in refluxing ethanol for 3 hr gave only **9**. The stereochemical assignment of the adducts **9** and **11** was readily made on the basis of the coupling constants between Ha and Hb (13 and 8 Hz for **9** and **11**, respectively). It was noted that the *Z*-isomer **11** isomerizes to the *E*-isomer **9** in chloroform even at 34° (this process took 48 hr for completion) and the isomerization occurs more rapidly in ethanol (completed within *ca.* 30 hr at 34°). Thus, the proportions of **9** and **11** were dependent on the reaction time and the solvent used.




**7**: R=OEt
**8**: R=Me

**9**: R=OEt
**10**: R=Me

**11**: R=OEt
**12**: R=Me

Chart 2

Only the *E*-isomer **10** was obtained from the reaction of **1a** and **8** in methanol at room temperature, or (more conveniently) at refluxing temperature. The *E*-stereochemistry of **10** was assigned on the basis of the large vicinal coupling constant (13 Hz) for Ha and Hb. When the same reaction was carried out in methanol at 34° and monitored by NMR spectroscopy, the formation of small amounts of the isomeric adduct **12** [$\delta$ 7.17 (d, $J$=8 Hz) for Hb] was seen at the early stage of the reaction but the signal soon disappeared.

The easy isomerization observed with **11** and **12** may reflect the degree of delocalization of the electrons from the imino nitrogen to the carbonyl group; the greater the delocalization (**12**>**11**$\gg$**4** or **5**), the lower the energy barrier for rotation about the carbon-carbon double bond would be expected to be.

**Reactions with Activated Olefins**

We next investigated the reactivity of **1a** towards olefinic compounds. Johnson[4] has noted that the reaction of methylphenylsulfoximine (**1d**) with methyl acrylate takes place in the presence of catalytic amounts of sodium hydride to give N-(carbomethoxyethyl)methylphenylsulfoximine. It was expected that **1a** might react with more electron-deficient olefins in the absence of a catalyst. In fact, **1a** reacted with *trans*-1,2-dibenzoylethylene (**13**) and tetracyanoethylene (**15**).

Refluxing a solution of **1a** and **13** in benzene for 15 hr gave an addition product **14**, which was isolated in 39% yield as an oil after TLC separation. The structure of **14** was deduced on the basis of spectroscopic evidence (see "Experimental"). This reaction was not completed even after prolonged heating and, moreover, *cis*-dibenzoylethylene was detected in the reaction mixture (on TLC). This implies that this reaction is reversible. Indeed, heating a pure sample of **14** in benzene gave *cis*- and *trans*-dibenzoylethylenes (on TLC).

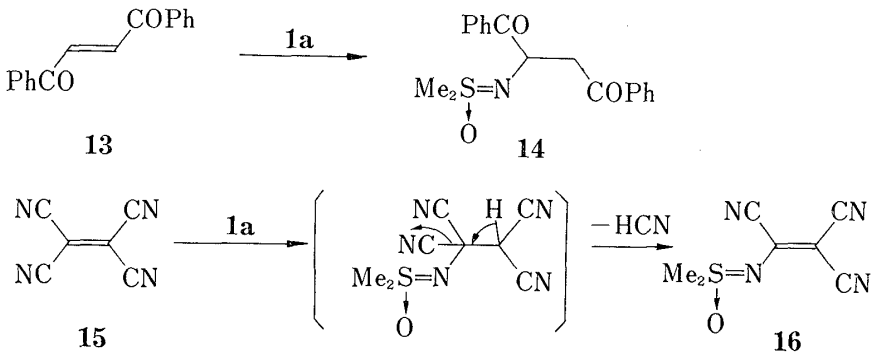


Chart 3

Reaction of **1a** with **15** was found to occur readily in chloroform at room temperature to give the adduct **16** in 78% yield. A possible mechanism involves an addition-elimination process, and a similar reaction has been observed in the reaction of **15** and diphenylsulfilimine.[10]

However, attempts to react **1a** with maleic anhydride, N-methylmaleimide, and phenyl vinyl sulfone were unsuccessful even in refluxing ethanol.

**Reaction with Diphenylcyclopropenone**

The reaction of **1a** with highly electron-deficient diphenylcyclopropenone (DPP) (**17**)[11] in refluxing toluene for 3 hr gave a new sulfoximine **19** in 67% yield. The structure was assigned on the basis of spectral data (see "Experimental").

The formation of **19** probably proceeds *via* the ketene intermediate **18**, which can be attacked by another molecule of **1a**. The possible intermediate **18** could be trapped by heating equimolar amounts of **1a** and DPP in absolute methanol in a sealed tube at 130—140° for 14 hr to give two products, **20** and **21**, in 21 and 20% yields, respectively. Compound **21** was formed probably through direct attack of methanol on DPP at high temperature.

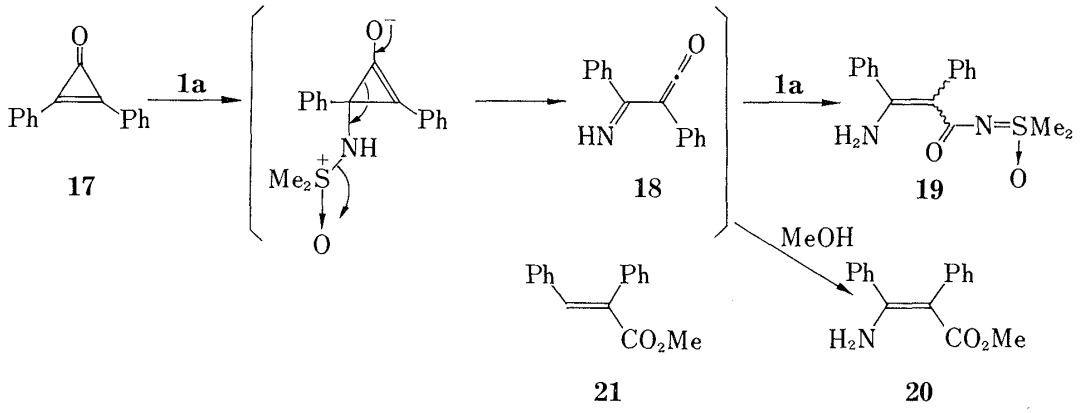


Chart 4

## Experimental[12]

**General Procedure for the Preparation of S-Aminosulfoxonium Mesitylenesulfonates 2a—e**——A mixture of a sulfoxide (2 mmol) and MSH (2 mmol) in methylene chloride (5 ml) was allowed to stand at room tempera-

10) Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi, and M. Ikeda, *J. Org. Chem.*, **38**, 4324 (1973).
11) K.T. Potts and J.S. Baum, *Chem. Rev.*, **74**, 189 (1974).
12) Melting points are uncorrected. NMR spectra were determined with a Hitachi R-20A spectrometer using tetramethylsilane as an internal standard. Infrared (IR) spectra were recorded with a Hitachi EPI-G2 spectrophotometer. Low resolution mass spectra were obtained with a Hitachi RMU-6D instrument with a direct inlet system at 70 eV.

Table II. Preparation of S-Aminosulfoxonium Mesitylenesulfonates **2a—e**

| | $R^1$ | $R^2$ | mp (°C)[a] | Yield (%) | Formula | Analysis (%) Calcd. C | H | N | Found C | H | N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2a** | $CH_3$ | $CH_3$ | 176—178 | 72 | $C_{11}H_{19}NO_4S_2$ | 45.04 | 6.53 | 4.77 | 44.77 | 6.50 | 4.87 |
| **2b** | $PhCH_2$ | $PhCH_2$ | 133—135 | 61 | $C_{23}H_{27}NO_4S_2$ | 61.67 | 5.98 | 3.17 | 62.01 | 6.11 | 3.14 |
| **2c** | $-(CH_2)_4-$ | | 151—153 | 100 | $C_{13}H_{21}NO_4S_2$ | 48.90 | 6.63 | 4.44 | 49.12 | 6.64 | 4.34 |
| **2d** | $CH_3$ | Ph | 207—209 | 93 | $C_{16}H_{21}NO_4S_2$ | 54.08 | 5.96 | 3.94 | 54.16 | 6.07 | 3.92 |
| **2e** | Ph | Ph | 179—182 | 65 | $C_{21}H_{23}NO_4S_2$ | 60.47 | 5.55 | 3.36 | 60.25 | 5.66 | 3.51 |

a) Recrystallized from methylene chloride–pet. ether (bp 30—60°).

ture for 10 min. After addition of petroleum ether, the white precipitate was collected and recrystallized to give **2a—e**. The melting points, yields, and analytical data are summarized in Table II.

**Preparation of Sulfoximines 1a—e**——A solution of **2** in chloroform was passed through a short alumina column and eluted with chloroform. After removal of the solvent by evaporation, the free sulfoximine **1** was obtained in quantitative yield. Dimethylsulfoximine (**1a**) was obtained as a hygroscopic crystalline solid;[13] dibenzylsulfoximine (**1b**) was obtained as white needles, mp 167—168° (from ethanol–water). *Anal.* Calcd. for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71. Found: C, 68.26; H, 6.22; N, 5.49; tetramethylenesulfoximine (**1c**) was obtained as an oil; methylphenylsulfoximine (**1d**) was obtained as an oil;[14] diphenylsulfoximine (**1e**) was obtained as white needles, mp 96—97° (lit.[15] 97—98°).

**General Procedure for *E*- and *Z*-N-(1,2-Dicarbomethoxyvinyl)sulfoximines 4 and 5**——A. In Methanol: A solution of the sulfoximine **1** (1 mmol) and DAC (3) (1 mmol) in methanol (10 ml) was refluxed at 70° until the starting sulfoximine was no longer detectable on TLC (3—7 hr). After removal of the solvent, the crude product was purified either by preparative TLC on alumina (with chloroform as a solvent) followed by recrystallization, or by recrystallization alone. In the case of **1a**, the reaction was carried out at room temperature.

B. In DMSO: A solution of the sulfoximine **1** (1 mmol) and DAC (3) (1 mmol) in DMSO (5 ml) was heated at 70° until the starting sulfoximine disappeared (3—7 hr). The reaction mixture was poured into cold water and extracted with three 20 ml portions of benzene. The benzene extracts were washed with water, then dried ($Na_2SO_4$), and concentrated. The crude product was purified by recrystallization. In the case of **1a**, the reaction was carried out at room temperature. The yields and product distributions are summarized in Table I, and the analytical and physical data are given in Tables III and IV, respectively.

***E*- and *Z*-N-(2-Carbethoxyvinyl)dimethylsulfoximines (9 and 11)**——A. In Chloroform: A solution of **1a** (186 mg, 2 mmol) and **7** (196 mg, 2 mmol) in chloroform (10 ml) was refluxed for 8 hr. The solvent was removed *in vacuo* and the crude material was subjected to preparative TLC on alumina (with ethyl acetate as a solvent) to give two isomeric products.

The *E*-isomer **9** (208 mg) gave mp 87° (from benzene–petroleum ether). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1685, 1605, 1145, and 1025. NMR ($CDCl_3$) $\delta$: 7.70 (d, 1H, $J$=13 Hz, Hb), 5.31 (d, 1H, $J$=13 Hz, Ha), 4.13 (q, 2H, $J$=7 Hz, $C\underline{H}_2CH_3$), 3.15 (s, 6H, $2\times CH_3$), and 1.16 (t, 3H, $J$=7 Hz, $CH_2C\underline{H}_3$). MS *m/e*: 191 ($M^+$). *Anal.* Calcd. for $C_7H_{13}NO_3S$: C, 43.96; H, 6.85; N, 7.32. Found: C, 44.41; H, 6.91; N, 7.35.

The *Z*-isomer **11** (28 mg) gave mp 77—78° (from benzene–petroleum ether). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1690, 1605, 1150, and 1020. NMR ($CDCl_3$) $\delta$: 6.98 (d, 1H, $J$=8 Hz, Hb), 5.02 (d, 1H, $J$=8 Hz, Ha), 4.12 (q, 2H, $J$=7 Hz, $C\underline{H}_2CH_3$), 3.19 (s, 6H, $2\times CH_3$), and 1.29 (t, 3H, $J$=7 Hz, $CH_2C\underline{H}_3$). *Anal.* Calcd. for $C_7H_{13}NO_3S$: C, 43.96; H, 6.85; N, 7.32. Found: C, 43.79; H, 6.85; N, 7.27.

B. In Ethanol: A solution of **1a** (93 mg, 1 mmol) and **7** (98 mg, 1 mmol) in ethanol (5 ml) was refluxed for 3 hr. After removal of the solvent, the crude material was recrystallized from benzene–petroleum ether to give **9** (124 mg, 65%). The NMR spectrum of the crude material showed it to be free from **11**.

**Isomerization of 11 to 9**——A solution of **11** (28 mg) in $CDCl_3$ (0.4 ml) in an NMR tube was kept at 34°, and the reaction was followed by NMR spectroscopy. It took *ca.* 48 hr for complete isomerization of **11** to **9**. When the same experiment was carried out in ethanol, the isomerization was completed within 30 hr.

***E*-N-(2-Acetylvinyl)dimethylsulfoximine (10)**——A solution of **1a** (93 mg, 1 mmol) and **8** (68 mg, 1 mmol) in methanol (5 ml) was refluxed for 2 hr. The solvent was removed *in vacuo* and the crude material was subjected to preparative TLC on alumina (with ethyl acetate as a solvent) to give **10** (84 mg, 52%), mp 113—114° (from benzene). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$; 1658, 1600, and 1570. NMR ($CDCl_3$) $\delta$: 7.75 (d, 1H, $J$=13 Hz, Hb), 5.74 (d, 1H, $J$=13 Hz, Ha), 3.22 (s, 6H, $2\times CH_3$), and 2.16 (s, 3H, $COCH_3$). MS *m/e*: 161 ($M^+$). *Anal.* Calcd. for $C_6H_{11}NO_2S$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.98; H, 6.92; N, 8.76.

13) H.R. Bently and J.K. Whitehead, *J. Chem. Soc.*, **1950**, 2081.
14) C.R. Johnson, M. Haake, and C.W. Schroeck, *J. Am. Chem. Soc.*, **92**, 6594 (1970).
15) F. Misani, T.W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951).

Table III. Preparation of *E*- and *Z*-N-(1,2-Dicarbomethoxyvinyl)sulfoximines **4** and **5**

| | mp (°C) (Recryst'd from) | Formula | Analysis (%) Calcd. C | H | N | Found C | H | N |
|---|---|---|---|---|---|---|---|---|
| **4a** | 95—97 (benzene) | $C_8H_{13}NO_5S$ | 40.84 | 5.54 | 5.95 | 41.14 | 5.58 | 5.90 |
| **5a** | 84—86 (benzene–pet. ether) | $C_8H_{13}NO_5S$ | 40.84 | 5.54 | 5.95 | 40.73 | 5.55 | 6.03 |
| **4b** | 153—155 (benzene) | $C_{20}H_{21}NO_5S$ | 62.00 | 5.46 | 3.62 | 62.24 | 5.36 | 3.61 |
| **5b** | 149—150 (benzene–pet. ether) | $C_{20}H_{21}NO_5S$ | 62.00 | 5.46 | 3.62 | 62.22 | 5.35 | 3.66 |
| **4c** | 100—102 (benzene–pet. ether) | $C_{10}H_{15}NO_5S$ | 45.96 | 5.78 | 5.36 | 46.07 | 5.90 | 5.28 |
| **5c** | 110—112 (AcOEt–pet. ether) | $C_{10}H_{15}NO_5S$ | 45.96 | 5.78 | 5.36 | 46.04 | 5.81 | 5.39 |
| **4d** | 116—118 (benzene–pet. ether) | $C_{13}H_{15}NO_5S$ | 52.52 | 5.08 | 4.71 | 52.49 | 4.94 | 4.79 |
| **5d** | 119—121 (AcOEt–pet. ether) | $C_{13}H_{15}NO_5S$ | 52.52 | 5.08 | 4.71 | 52.68 | 5.03 | 4.74 |
| **4e** | 150—151 (benzene) | $C_{18}H_{17}NO_5S$ | 60.16 | 4.76 | 3.89 | 60.39 | 4.66 | 4.03 |
| **5e** | 104—106 (benzene–pet. ether) | $C_{18}H_{17}NO_5S$ | 60.16 | 4.76 | 3.89 | 60.41 | 4.72 | 3.92 |

Table IV. Physical Data for *E*- and *Z*-N-(1,2-Dicarbomethoxyvinyl)sulfoximines **4** and **5**

| | IR $\nu_{max}^{CHCl_3}$ | | | =C-H | NMR($CDCl_3$) $\delta$ $2\times CO_2CH_3$ | | Others |
|---|---|---|---|---|---|---|---|
| **4a** | 1735 | 1700 | 1595 | 5.48 | 3.63 | 3.82 | 3.22 (s, 6H, $2\times CH_3$) |
| **5a** | 1730 | 1710$^{sh}$ | 1600 | 6.05 | 3.68 | 3.82 | 3.28 (s, 6H, $2\times CH_3$) |
| **4b** | 1730 | 1690 | 1575 | 5.42 | 3.85 | 3.62 | 4.35 (s, 4H, benzylic H)<br>7.4 (s, 10H, arom. H) |
| **5b** | 1740 | 1700 | 1585 | 5.85 | 3.74 | 3.69 | 4.58, 4.37 (ABq, 2H each, $J=13$ Hz, benzylic H)<br>7.3 (s, 10H, arom. H) |
| **4c** | 1730 | 1700 | 1580 | 5.35 | 3.82 | 3.64 | 2.5—2.0, 3.7—3.0 [m, 4H each, $-(CH_2)_4-$] |
| **5c** | 1735 | 1700 | 1590 | 5.92 | 3.80 | 3.67 | 2.5—2.0, 3.6—3.0 [m, 4H each, $-(CH_2)_4-$] |
| **4d** | 1725 | 1695 | 1590 | 5.21 | 3.83 | 3.53 | 3.22 (s, 3H, $CH_3$)<br>8.1—7.4 (m, 5H, arom. H) |
| **5d** | 1735 | 1700 | 1590 | 6.00 | 3.80 | 3.71 | 3.30 (s, 3H, $CH_3$)<br>8.2—7.3 (m, 5H, arom. H) |
| **4e** | 1740 | 1700 | 1590 | 5.35 | 3.88 | 3.55 | 8.1—7.3 (m, 10H, arom. H) |
| **5e** | 1735 | 1710 | 1600 | 6.04 | 3.78 | 3.64 | 8.3—7.3 (m, 10H, arom. H) |

**N-(1,2-Dibenzoylethyl)dimethylsulfoximine (14)**——A solution of **1a** (93 mg, 1 mmol) and **13** (207 mg, 1 mmol) in benzene (5 ml) was refluxed for 15 hr. After removal of the solvent, the oily residue was subjected to preparative TLC on alumina (with chloroform as a solvent) to give **14** (127 mg, 39%, as an oil. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1680. NMR ($CDCl_3$) $\delta$: 8.3—7.2 (m, 10H, aromatic protons), 5.48 (t, 1H, methine proton), 3.2—4.0 (m, 2H, methylene protons), and 2.86, 2.94 (s, 3H each, $2\times CH_3$).

**N-(1,2,2-Tricyanovinyl)dimethylsulfoximine (16)**——A solution of **1a** (186 mg, 2 mmol) and **15** (256 mg, 2 mmol) in chloroform (5 ml) was stirred at room temperature for 1 hr. The precipitated crystals were collected and recrystallized from ethyl acetate to give **1** (300 mg, 78%) as colorless cubes, mp 212—214°. IR $\nu_{max}^{KCl}$ $cm^{-1}$: 2210 and 1500. NMR (DMSO-$d_6$) $\delta$: 3.65 (s, 6H, $2\times CH_3$). *Anal.* Calcd. for $C_7H_6N_4OS$: C, 43.19; H, 3.33; N, 28.78. Found: C, 43.42; H, 3.05; N, 28.52.

**N-(3-Amino-2,3-diphenylpropenoyl)dimethylsulfoximine (19)**——A solution of **1a** (93 mg, 1 mmol) and **17** (206 mg, 1 mmol) in toluene (5 ml) was refluxed for 6 hr. After cooling, the pale yellow crystals were collected and recrystallized from chloroform–petroleum ether to give **19** (200 mg, 67%), mp 185—187°. IR $\nu_{max}^{KCl}$ $cm^{-1}$: 3360, 3260 ($NH_2$), and 1600. NMR ($CDCl_3$) $\delta$: 7.10, 6.98 (s, the region 6.5—7.5 integrating as 12H, falling to 10H upon $D_2O$ exchange), and 3.20 (s, 6H, $2\times CH_3$). MS *m/e*: 314 ($M^+$). *Anal.* Calcd. for $C_{17}H_{18}N_2O_2S$; C, 64.94; H, 5.77; N, 8.91. Found: C, 65.02; H, 5.74; N, 8.75.

**Methyl 3-Amino-2,3-diphenylacrylate (20) and Methyl 2,3-Diphenylacrylate (21)**——A solution of **1a** (93 mg, 1 mmol) and **18** (206 mg, 1 mmol) in absolute methanol (10 ml) was heated at 130—140° in a sealed tube for 14 hr. The solvent was evaporated off *in vacuo* and the crude product was subjected to preparative TLC on silica gel and chloroform–benzene (1 : 1) to give two products **20** (53 mg, 21%), mp 110—112° (Lit.[16] 112—114°), and **21** (45 mg, 20%), mp 73—75° (Lit.[17] 75°).

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