# The Wittig-type Reaction of O=C-, C=C-, and N=C-Substituted Methylenetriphenylphosphoranes with *N*-Sulfinyl-*p*-toluenesulfonamide. An Intramolecular 1,3-Dipolar Cyclization of Imidoyl-conjugated Thione *S*-Imides

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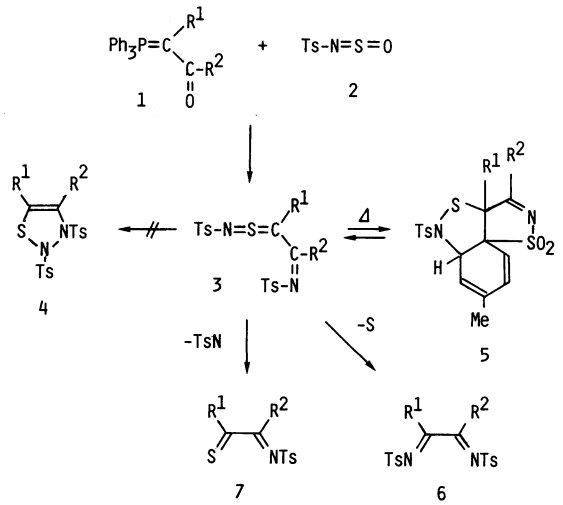
The Wittig-type reactions of *N*-sulfinyl-*p*-toluenesulfonamide with (1) O=C-, (2) C=C-, and (3) N=C-conjugated phosphorus ylides were investigated. In the reaction with (1), *N*-sulfinyl-*p*-toluenesulfonamide reacted at both the ylide and the carbonyl moiety to form TsN=C-conjugated thione *S*-imide, which underwent intramolecular 1,3-dipolar cycloaddition of the CSN group with the aromatic C=C bond of the tosyl group giving a structurally unique spiro-fused tricyclic adduct. The structure of the adduct was determined by means of X-ray diffraction. In the reactions with (2) and (3), 1-azadiene and sulfobetaines were obtained instead of the expected conjugated thione *S*-imides.

We recently reported the first synthesis of α,β-unsaturated (conjugated) thione *S*-imides by the reaction of 3-aminopropene-1-thiones with chloramine salts.[1] The imides showed an interesting chemical property namely that they cyclize reversibly to thiazoline compounds depending on the solvent.

In view of continued interest in conjugated thiocumulenes, we have attempted the synthesis of O=C-, C=C-, and N=C-conjugated thione *S*-imides by the Wittig-type reaction of *N*-sulfinylamines with the corresponding phosphorus ylides. This method is conceivable because of our previous successful preparation of fluorenethione *S*-tosylimides by this Wittig-type reaction.[2]

In the previous paper[2] we reported that (benzoylphenylmethylene)triphenylphosphorane **1a** reacted with *N*-sulfinyl-*p*-toluenesulfonamide (**2**) to form the imidoyl-conjugated thione *S*-tosylimide **3a**, which subsequently underwent an intramolecular 1,5-dipolar cyclization giving a 1,2,3-thiadiazoline compound **4a**. However, reinvestigation of the reaction products in a series of the reactions applying $^{13}C$ NMR and X-ray diffraction analysis reveals that we were previously misled by the spectral features. This paper deals with new and unexpected results including a revised structure (**5**).




| | $R^1$ | $R^2$ |
|---|---|---|
| a | Ph | Ph |
| b | Ph | p-$MeC_6H_4$ |
| c | Ph | p-$MeOC_6H_4$ |
| d | Ph | p-$ClC_6H_4$ |
| e | p-$MeC_6H_4$ | Ph |
| f | p-$MeC_6H_4$ | p-$MeC_6H_4$ |
| g | p-$MeOC_6H_4$ | Ph |
| h | p-$MeOC_6H_4$ | p-$MeC_6H_4$ |

Scheme 1.

TABLE 1. REACTION OF (ACYLARYLMETHYLENE)TRIPHENYLPHOSPHORANES (**1**) WITH *N*-SULFINYL-*p*-TOLUENESULFONAMIDE (**2**)

| | $R^1$ | $R^2$ | Reaction time/h | Yield/% **5** | Yield/% **6** | Mp, $\theta_m$/°C **5** | Mp, $\theta_m$/°C **6** |
|---|---|---|---|---|---|---|---|
| **a** | Ph | Ph | 16 | 40 | 12 | 186—187 | 200—201 |
| **b** | Ph | *p*-$MeC_6H_4$ | 16 | 42 | 9 | 189—190 | 195—196 |
| **c** | Ph | *p*-$MeOC_6H_4$ | 18 | 57 | 6 | 193—194 | 196—197 |
| **d** | Ph | *p*-$ClC_6H_4$ | 9 | 34 | 16 | 184—185 | 70—72 |
| **e** | *p*-$MeC_6H_4$ | Ph | 14 | 28 | 7 | 193—194 | 196—197 |
| **f** | *p*-$MeC_6H_4$ | *p*-$MeC_6H_4$ | 12 | 21 | 6 | 189—192 | 220—223 |
| **g** | *p*-$MeOC_6H_4$ | Ph | 20 | 20 | 13 | 170—171 | 196—197 |
| **h** | *p*-$MeOC_6H_4$ | *p*-$MeC_6H_4$ | 17 | 25 | 9 | 166—167 | 178—179 |

TABLE 2. MASS SPECTRAL FRAGMENTATION PATTERNS OF **3** AND **5** (*m/z*)/%

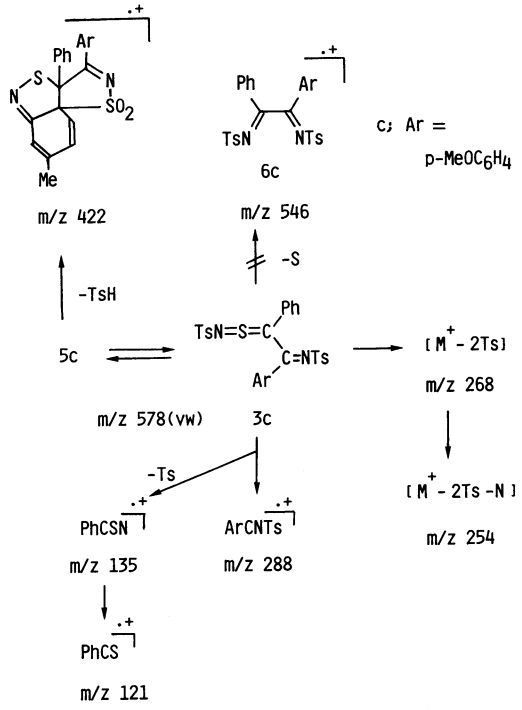
| | **3b** | **3c** | **5a** | **5b** | **5c** |
|---|---|---|---|---|---|
| $M^+$ | 562(0) | 578(vw) | 548(vw) | 562(vw) | 578(0) |
| $M^+-TsH$ | 406(5) | 422(7) | 392(4) | 406(vw) | 422(3) |
| $R^2CNTs^+$ | 272(11) | 288(7) | 258(9) | 272(5) | 288(6) |
| $M^+-2Ts$ | 252(15) | 268(29) | 238(15) | 252(11) | 268(24) |
| $M^+-2Ts-N$ | 238(vw) | 254(29) | 224(9) | 238(9) | 254(30) |
| $R^1CSN^+$ | 135(21) | 135(23) | 135(23) | 135(18) | 135(27) |
| $R^1CS^+$ | 121(76) | 121(52) | 121(9) | 121(62) | 121(10) |
| | **5d** | **5e** | **5f** | **5g** | **5h** |
| $M^+$ | 582(0) | 562(vw) | 576(vw) | 578(0) | 592(0) |
| $M^+-Ts$ | 426(vw) | 406(5) | 420(3) | 422(23) | 436(22) |
| $R^2CNTs^+$ | 292(2) | 258(7) | 272(3) | 258(vw) | 272(vw) |
| $M^+-2Ts$ | 272(vw) | 252(18) | 266(18) | 268(41) | 282(46) |
| $M^+-2Ts-N$ | 258(5) | 238(9) | 252(4) | 254(10) | 268(4) |
| $R^1CSN^+$ | 135(25) | 149(13) | 149(31) | 165(21) | 165(64) |
| $R^1CS^+$ | 121(10) | 135(77) | 135(16) | 151(69) | 151(19) |

vw: very weak $Tol^+$ 91(100%) in all cases.

## Results and Discussion

In refluxing benzene (acylarylmethylene)triphenylphosphoranes **1** reacted with *N*-sulfinyl-*p*-toluenesulfonamide (**2**) at the both functional sites, namely the ylide and the acyl moietiy, yielding compounds **5**—**7** (Scheme 1, Table 1).[3] The structures of **5a**, **b**, and **5d**—**h** were confirmed by comparisons of the spectroscopic data (IR, MS, $^1H$, and $^{13}C$NMR) with those of **5c**, of which the structure was proved by means of the X-ray diffraction analysis (*vide infra*). The reaction mixture was colored orange at the first stage of the reaction, and ultimately turned greenish blue.[4] Although the orange substances are rather labile, they could be isolated in the case of the reactions of **1b**, **c** when performed at room temperature or below, and were identified as the N=C-conjugated thione *S*-imides **3b**, **c** on the basis of the spectral analyses and the reactions described below (Scheme 3).

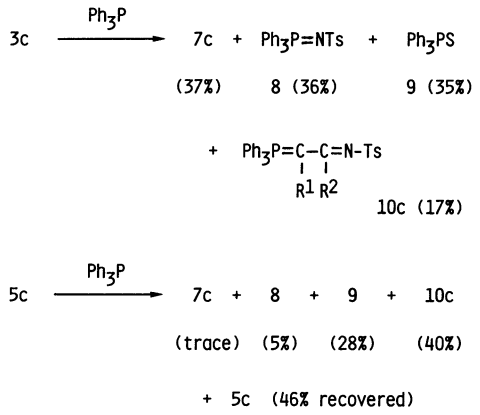
The thione *S*-imides **3b**,**c** exhibited characteristic absorption bands of $\nu$CSN at 990 $cm^{-1}$ and of $\nu$C=NTs at 1550 $cm^{-1}$ in the IR spectra. In the mass spectra of **3** and **5**, almost the same fragmentation patterns were observed (Table 2). This indicates the reversible transformation between **3** and **5**, *e.g.* for **3c** and **5c**, as shown in Scheme 2. Although molecular ion peaks and their desulfurized fragment peaks $\mathbf{6}^{\cdot+}$ were hardly detected (E.I. at 70 eV), the peaks [$M^+$ −TsH] are very indicative of these unique cycloadducts **5**, because facile elimination of TsH can be envisaged from **5** rather than from **3**. The $^1H$ NMR spectra of **3b**, **c** were in good agreement with the proposed structures. The assignments are given in Experimental Section. The geometrical isomerism of **3**, if present, about the bent CSN and C=NTs moieties was not determined. The geometrical rigidity is probably lost to a considerable extent by contribution of a 1,5-dipolar structure due to the conjugation. In the




Scheme 2.

$^{13}C$NMR spectra of **3b**,**c**, the cumulene and imine carbons resonated at a low field of $\delta$=167.2 and 176.3 for **3b**, and 166.3 and 176.6 for **3c**, respectively.

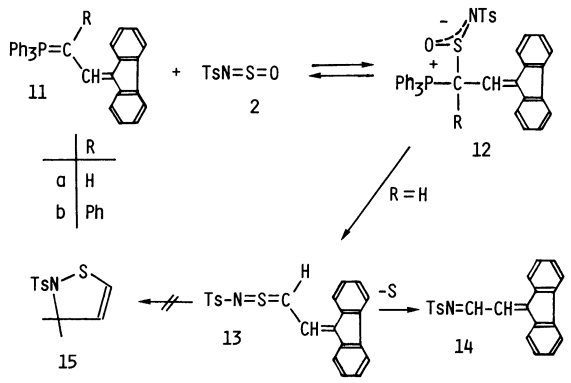
As expected, heating of the isolated imides **3b**, **c** in benzene gave **5b**, **c** and **6b**, **c** along with small amounts of **7b**, **c**. Interestingly, heating (>~110 °C) of **5c** in xylene gave reversion to **3c**, suggesting the existence of equilibrium between **3** and **5** at a higher temperature. This retro-cyclization is also observed during the reactions of **3c** and **5c** with triphenylphosphine; the reactions of both **3c** and **5c** with triphenylphosphine produced **7c**, **8**, **9**, and **10c** (Scheme 3). There is no doubt that in both reactions the products (**7**—**10**) are formed from **3c** by nucleophilic attack of triphenylphosphine at the CSN moiety. It should be



Scheme 3.

noted that the reaction of **3c** was facile even at low temperature (5—8 °C) while that of **5c** took place only at higher temperature (>~70 °C) which is required for the retro-cyclization to **3c**.

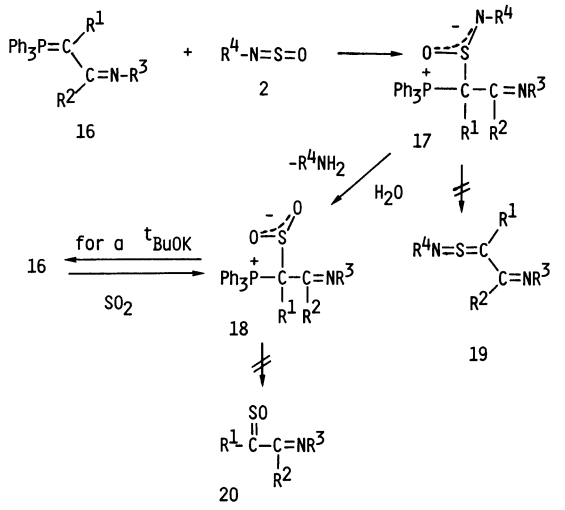
The reaction of C=C-conjugated phosphorus ylide **11a** with **2** yielded a 1-azadiene **14**, which might be formed from the conjugated thione *S*-imide **13** by sulfur extrusion *via* a thiaziridine ring[5] (Scheme 4).



Scheme 4.

Neither **13** nor its 1,5-dipolar cyclization product (**15**) was obtained. On the other hand, the reaction of **11b** with **2** stopped at the stage of the betaine **12** under the same reaction conditions, but an isolation of **12** failed.

Treatment of **16** having a N=C in conjugation with the ylide function with **2** formed a hygroscopic betaine **17** which was ultimately hydrolyzed to give a betaine of sulfur dioxide, **18** (Scheme 5). Treatment of the betaine **18a** with potassium *t*-butoxide led to reconversion to the starting ylide (**16a**). The betaine **18** was also obtained by bubbling sulfur dioxide into a solution of the ylide **16** (Table 3). From the betaines **17** and **18** the corresponding conjugated thione *S*-



Scheme 5.

imides **19** and *S*-oxide **20**,[6] respectively, could not be obtained.

The present results of these Wittig-type reactions reveal that this methodology is promising to prepare conjugated thione *S*-imides, although a limited number of substituents leads a completion of the reaction and stabilizes these conjugated thione *S*-imides sufficiently.

*Structure Determination of* **5**.

*4,5-Diaryl-10-methyl-7-tosyl-2,6-dithia-3,7-diazatricyclo-[6.4.0.0$^{1,5}$]dodeca-3,9,11-triene 2,2-Dioxides* (**5**). In the $^{13}$C NMR spectra of **5**, single-frequency off-resonance decoupling (SFORD) measurements showed signals of the tertiary and two quaternary carbons assigned to the carbons at C(8), C(5), and C(1), respectively (Table 4). This unambiguously excludes the structure **4**. In the $^{1}$H NMR spectra H(8), H(9), $CH_3$(10), H(11), and H(12) protons exhibited plural couplings similar to those of 2-methyl-1,3-cyclohexadiene bicyclo compounds.[7] The assignments of the signals are compiled in Table 5.

*X-Ray Diffraction.* X-Ray diffraction data were collected on a Rigaku AFC automated four-circle diffractometer. The crystal data, details of experimental conditions, and the structure analysis procedures are listed in Table 6. Atomic parameters are given in Table 7. The atomic scattering factors and *f'*, *f''* values were taken from International Tables for X-Ray Crystallograpy.[8] The calculations were carried out on a FACOM M-380 computer using the UNICS-III[9] and ORTEP[10] programs. A stereoscopic drawing of the molecule is shown in Fig. 1, and the selected

TABLE 3. REACTION OF YLIDE **16** WITH **2** AND SULFUR DIOXIDE

| 2, 16—20 | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Reagent | Yield/% **18a** | **18b** |
|---|---|---|---|---|---|---|---|
| **a** | H | Ph | Ph | Ph | **2a** | 53 | 48 |
| **b** | Ph | $PhCH_2$ | Mes | Ts | **2b** | 54 | 9 |
| | | | | | $SO_2$ | 93 | 61 |

Table 4. $^{13}C$ NMR spectral data of **5** ($\delta$, TMS, $CDCl_3$)[a]

| 5 | C(1) | C(4) | C(5) | C(8) | $CH_3$(10) | $CH_3$(Ts) |
|---|---|---|---|---|---|---|
| **a** | 86.20 | 175.57 | b) | 68.56 | 21.05 | 21.64 |
| **b** | 86.16 | 175.57 | b) | 68.56 | 21.10 | 21.73 |
| **c** | 86.20 | 163.93 | 77.19 | 68.61 | 21.10 | 21.73 |
| **d** | 86.30 | 174.74 | 75.87 | 68.61 | 21.10 | 21.69 |
| **f** | 86.06 | 175.82 | 75.58 | 68.46 | 21.05 | 21.69 |
| **g** | 85.91 | 175.87 | 75.58 | 68.42 | 21.10 | 21.64 |
| **h** | 85.86 | 175.87 | 75.43 | 68.37 | 21.10 | 21.69 |

a) **5e** is sparingly soluble in $CDCl_3$ or DMSO-$d_6$. b) Superimposed on the peak of the solvent ($CDCl_3$).

Table 5. $^1H$ NMR spectral data of **5** ($\delta$, TMS, $CDCl_3$)[a]

| 5 | H(8) | H(9) | H(11) | H(12) | $CH_3$(10) | $CH_3$(Ts) | Ar-H | Others |
|---|---|---|---|---|---|---|---|---|
| **a** | 5.60 br,m | 6.25 br,m | 5.89(dd) $J_9$=1.0 $J_{12}$=8 | 4.92(d) $J_{11}$=8 | 1.85(dd) $J_7$=1.5 $J_8$=1.5 | 2.40(s) | 6.6—7.7 (m) | — |
| **b** | 5.52 br,m | 6.18 br,m | 5.84(dd) $J_9$=1.0 $J_{12}$=11 | 4.87(d) $J_{11}$=11 | 1.85(dd) $J_7$=1.5 $J_8$=1.5 | 2.40(s) | 6.6—7.6 (m) | 2.36(s) ($CH_3$) |
| **c** | 5.54 br,m | 6.18 br,m | 5.84(dd) $J_9$=1.0 $J_{12}$=10 | 4.86(d) $J_{11}$=10 | 1.86(dd) $J_7$=1.5 $J_8$=1.5 | 2.42(s) | 6.6—7.7 (m) | 3.84(s) ($OCH_3$) |
| **d** | 5.49 br,m | 6.20 br,m | 5.86(dd) $J_9$=1.0 $J_{12}$=10 | 4.88(d) $J_{11}$=10 | 1.86(dd) $J_7$=1.5 $J_8$=1.5 | 2.42(s) | 6.7—7.6 (m) | — |
| **f** | 5.52 br,m | 6.32 br,m | 5.83(dd) $J_9$=1.5 $J_{12}$=10 | 4.88(d) $J_{11}$=10 | 1.86(dd) $J_7$=1.5 $J_8$=1.5 | 2.40(s) | 6.5—7.6 (m) | 2.28(s) 2.36(s) ($2CH_3$) |
| **g** | 5.54 br,m | 6.18 br,m | 5.87(dd) $J_9$=1.0 $J_{12}$=10 | 4.90(d) $J_{11}$=10 | 1.87(dd) $J_7$=1.5 $J_8$=1.5 | 2.41(s) | 6.6—7.6 (m) | 3.76(s) ($OCH_3$) |
| **h** | 5.52 br,m | 6.16 br,m | 5.86(dd) $J_9$=1.0 $J_{12}$=10 | 4.88(d) $J_{11}$=10 | 1.86(dd) $J_7$=1.5 $J_8$=1.5 | 2.40(s) | 6.7—7.7 (m) | 2.38(s) 3.74(s) ($CH_3$,$OCH_3$) |

a) **5e** is sparingly soluble in $CDCl_3$ or DMSO-$d_6$.

bond lengths and angles are given in Figs. 2 and 3. The reaction of **3** to **5** occurs through the bond formation between C(1) and C(3), and N(2) and C(4), which results the three fused rings system A, B, C. The torsion angles within these rings are shown in Fig. 4. The isothiazolidine ring B is considerably deformed. The distance C(1)-C(3), 1.587 Å, is longer than the ordinary single bond distance 1.54 Å. The six-membered ring C takes half chair form. The dihedral angles among the mean planes A, B, C are 74.8(1), 71.6(1), and 80.9(1)° for A-B, B-C, and C-A, respectively.

Complete $F_o$—$F_c$ data, hydrogen atomic parameters and anisotropic thermal parameters are deposited as Document No. 8549 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*

## Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard ($^1H$; at 100 MHz, $^{13}C$; at 25.05 MHz). Mass spectra were recorded on a Hitachi double focusing mass spectrometer RMU-7M, operating at an ioninzing potential of 70 eV. Elemental analyses were performed using a Yanaco Model MT-3 CHN corder.

*N*-Sulfinylamines (**2**),[11] the conjugated ylides **1**,[12] **11a**,[13] **16**[14] were prepared by the methods reported in the literature. Ylide **11b** was newly synthesized by the modified method.[13]

***11b***: Deep red cubes, mp 197—198 °C. IR(KBr) 1540 and 1440 $cm^{-1}$. MS *m/z* 528 (2%, $M^+$). Found: C, 88.70; H, 5.51%. Calcd for $C_{39}H_{29}P$: C,88.61; H, 5.53%.

*[A] General Procedure for the Reaction of (Acylarylmethylene) triphenylphosphorane (1) with N-Sulfinyl-p-toluenesulfonamide (2).* A solution of **2** (6.6 mmol) in dry benzene (10 $cm^3$) was added dropwise to a benzene solution (50 $cm^3$) of **1** (3.0 mmol) with stirring at room temperature, and then the reaction mixture was heated under reflux for 9—20h until the orange color of **3** disappeared. Removal of the solvent and column chromatography (silica gel, benzene) of the residue gave **5** and **6** (Table 1). When **5** was contaminated with a small amount of blue **7**, the crude **5** was washed with diethyl ether-hexane and recrystallized from chloroform-hexane to give analytically pure **5** as colorless crystals.

*4,5-Diaryl-10-methyl-7-tosyl-2,6-dithia-3,7-diazatricyclo[6.4.0.0$^{1,5}$]-dodeca-3,9,11-triene 2,2-Dioxide (5).* ***5a***: IR(KBr) 1555 (C=N), 1345, 1165 ($SO_2$) $cm^{-1}$. Found: C, 61.38; H, 4.17; N,

Table 6. Crystal data, details of experimental conditions and structure analysis procedures for X-ray diffraction of **5c**

| | |
|---|---|
| **Crystal Data** | |
| Formula | $C_{29}H_{26}N_2O_5S_3$ |
| Crystal color | Colorless |
| shape | Prismatic |
| size(mm) | 0.34×0.34×0.31 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| Unit cell dimensions $a$(Å) | 13.268(3) |
| $b$(Å) | 19.738(2) |
| $c$(Å) | 10.245(2) |
| Unit cell volume $U$(Å$^3$) | 2683(1) |
| $Z$ | 4 |
| $\mu$(mm$^{-1}$) | 0.306 |
| $F$(000) | 1208 |
| **Experimental**[a] | |
| Radiation and wavelength λ(Å) | Mo $K\alpha$, 0.71073(graphite monochromatized) |
| Scan speed $\omega$ (deg/min) | 4 |
| Max. $2\theta$(deg) | 55 |
| Range of $hkl$ | $h$=0—17, $k$=0—25, $l$=0—13 |
| Temperature of measurement(K) | 296 |
| Criterion for observed reflections | $\|F_o\|>3\sigma(\|F_o\|)$ |
| No. of unique reflections | 2674 |
| **Structure analysis** | |
| Method | The direct method using MULTAN78[15] |
| Method of refinement | The block-diagonal least-squares |
| Magnitudes in LS refinement | $\|F\|$ |
| Weight | Unit weight for all reflections |
| Temperature factors | Anisotropic temperature factors for all non-hydrogen atoms |
| No. of refined parameters | 457 |
| Method of locating and refining H-atoms | Difference Fourier syntheses |
| Final values of $R$ | 0.034 |
| $R\omega$ | 0.034 |
| $S$ | 0.047 |
| Ratio of max. LS shift to error | 0.39(H-atom) |
| Max. and min. height in final diff. Fourier (eÅ$^{-3}$) | 0.23, −0.20 |

a) Deterioration correction was made but not for absorption.

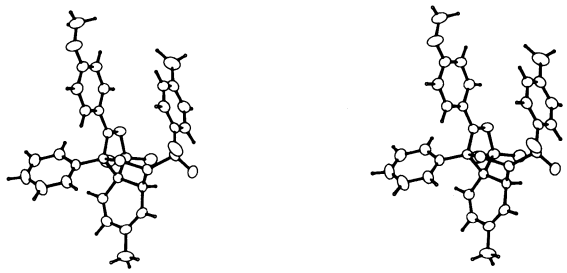


Fig. 1. Stereoscopic view of **5c**.

Table 7. Atomic parameters

Positional parameters are multiplied by $10^5$. Thermal parameters are given by the equivalent temperature factors.

| Atom | $X$ | $Y$ | $Z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| S(1) | 31220(6) | 13524(5) | 55971 (9) | 2.6 |
| S(2) | 2951(6) | 20066(5) | 61583 (9) | 2.4 |
| S(3) | 5188(7) | 8977(5) | 80654 (9) | 3.1 |
| O(1) | 38610(19) | 15233(15) | 46422(29) | 3.8 |
| O(2) | 32409(20) | 7361(13) | 63179(30) | 3.7 |
| O(3) | 18311(23) | 48006(14) | 92159(31) | 4.4 |
| O(4) | 6093(26) | 1817(14) | 79153(29) | 4.6 |
| O(5) | −3652(20) | 11965(18) | 86088(27) | 4.5 |
| N(1) | 30449(21) | 19996(15) | 66282(28) | 2.6 |
| N(2) | 5912(23) | 11971(15) | 65606(28) | 2.6 |
| C(1) | 18426(24) | 14073(17) | 48777(32) | 2.1 |
| C(2) | 22828(24) | 23781(17) | 63792(33) | 2.1 |
| C(3) | 15213(23) | 21440(17) | 53390(33) | 2.1 |
| C(4) | 11477(24) | 8615(17) | 54998(33) | 2.2 |
| C(5) | 4139(26) | 5431(16) | 45605(38) | 2.6 |
| C(6) | 5332(28) | 5493(17) | 32778(37) | 2.8 |
| C(7) | 13794(30) | 9260(20) | 27264(35) | 3.0 |
| C(8) | 19670(28) | 13257(19) | 34246(34) | 2.7 |
| C(9) | 21609(23) | 30213(17) | 71014(33) | 2.2 |
| C(10) | 28771(26) | 31907(18) | 80359(38) | 2.7 |
| C(11) | 28025(27) | 37808(18) | 87691(37) | 2.9 |
| C(12) | 19915(29) | 42129(18) | 85585(37) | 2.9 |
| C(13) | 12723(27) | 40565(19) | 76182(40) | 3.0 |
| C(14) | 13477(26) | 34678(17) | 69031(37) | 2.6 |
| C(15) | 26027(40) | 50324(24) | 100957(49) | 4.4 |
| C(16) | 14373(25) | 26463(17) | 42021(33) | 2.2 |
| C(17) | 5652(27) | 27041(19) | 34687(36) | 2.8 |
| C(18) | 5229(30) | 31426(22) | 24213(39) | 3.6 |
| C(19) | 13552(34) | 35237(21) | 20885(40) | 3.7 |
| C(20) | 22272(32) | 34671(20) | 28066(41) | 3.5 |
| C(21) | 22685(26) | 30317(20) | 38618(38) | 2.9 |
| C(22) | 15527(26) | 11914(18) | 89754(34) | 2.5 |
| C(23) | 15071(29) | 18265(19) | 95604(38) | 3.1 |
| C(24) | 23388(32) | 20593(19) | 102303(37) | 3.2 |
| C(25) | 32041(30) | 16718(20) | 103492(37) | 3.1 |
| C(26) | 32181(30) | 10284(20) | 97786(39) | 3.3 |
| C(27) | 24022(30) | 7845(19) | 90855(38) | 3.1 |
| C(28) | 40950(33) | 19467(30) | 110968(49) | 5.3 |
| C(29) | −1553(31) | 1966(24) | 23457(46) | 4.1 |

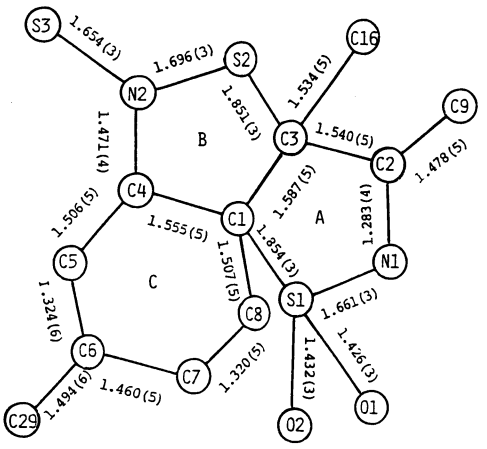
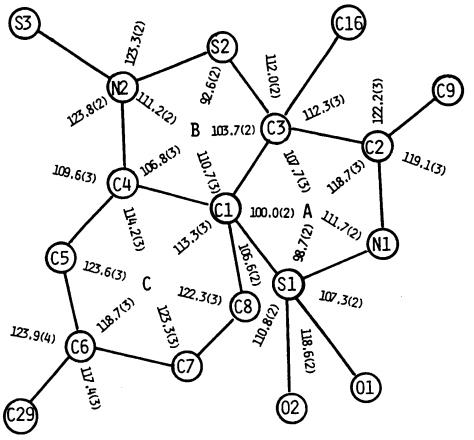



Fig. 2. Selected bond lengths ($l$/Å) within tricyclic system A,B, and C.




| | |
|---|---|
| S1-C1-C4 | 109.9(2) |
| C3-C1-C8 | 114.9(3) |
| O1-S1-C1 | 110.1(2) |
| O2-S1-N1 | 109.4(2) |
| S2-C3-C2 | 107.9(2) |
| C1-C3-C16 | 112.7(3) |

Fig. 3. Selected bond angles ($\phi$/°) within tricyclic system A,B, and C.

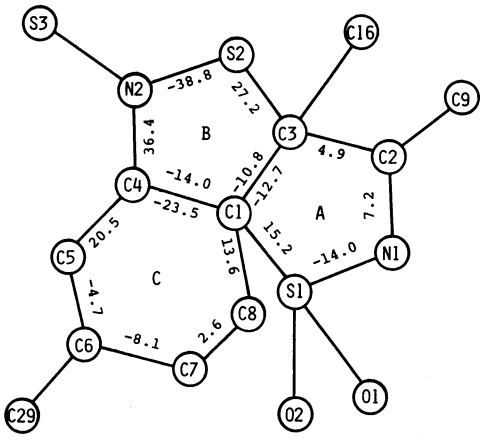



Fig. 4. Torsion angles ($\theta$°).

5.12; S, 17.31%. Calcd for $C_{28}H_{24}N_2O_4S_3$: C, 61.29; H, 4.41; N, 5.11; S, 17.53%.

***5b***: IR(KBr) 1550 (C=N), 1350, and 1160 ($SO_2$) $cm^{-1}$. Found: C, 61.96; H, 4.70; N, 4.91; S, 17.06%. Calcd for $C_{29}H_{26}N_2O_4S_3$: C, 61.90; H, 4.66; N, 4.98; S, 17.09%.

***5c***: IR(KBr) 1550 (C=N), 1350, and 1165 ($SO_2$) $cm^{-1}$. Found: C, 60.21; H, 4.50; N, 4.81; S, 16.92%. Calcd for $C_{29}H_{26}N_2O_5S_3$: C, 60.19; H, 4.53, N, 4.84; S, 16.62%.

***5d***: IR(KBr) 1550 (C=N), 1350, and 1160 ($SO_2$) $cm^{-1}$. Found: C, 57.70; H, 4.01; N, 4.79%. Calcd for $C_{28}H_{23}N_2O_4S_3Cl$: C, 57.67; H, 3.98; N, 4.80%.

***5e***: IR(KBr) 1560 (C=N), 1345, and 1160 ($SO_2$) $cm^{-1}$. Found: C, 62.01; H, 4.65; N, 4.99%. Calcd for $C_{29}H_{26}N_2O_4S_3$: C, 61.90; H, 4.66; N, 4.98%.

***5f***: IR(KBr) 1550 (C=N), 1340, and 1160 ($SO_2$) $cm^{-1}$. Found: C, 62.50; H, 4.88; N, 4.85%. Calcd for $C_{30}H_{28}N_2O_4S_3$: C, 62.48;H, 4.89; N, 4.86%.

***5g***: IR(KBr) 1560 (C=N), 1350, and 1160 ($SO_2$) $cm^{-1}$. Found: C, 60.20; H, 4.51; N, 4.84%. Calcd for $C_{29}H_{26}N_2O_5S_3$: C, 60.19;H, 4.53;N, 4.84%.

***5h***: IR(KBr) 1550 (C=N), 1340, and 1165 ($SO_2$) $cm^{-1}$. Found: C, 60.81;H, 4.77; N, 4.73%. Calcd for $C_{30}H_{28}N_2O_5S_3$: C, 60.79; H, 4.76; N, 4.73%.

*1,2-Diaryl-N,N′-ditosyl-1,2-ethanediimine (**6**).* ***6a***: IR (KBr) 1560 $cm^{-1}$ (C=N). $^1H$ NMR ($CDCl_3$) $\delta$=2.38 (s, 6H, $2CH_3$(Ts)), 7.19—7.85 (m, 18H, Ar-H). $^{13}C$ NMR ($CDCl_3$) $\delta$=172.75 (C=N), 21.64 ($CH_3$(Ts)). MS (70eV) *m/z* 516 (vw, $M^+$), 258 (20%, PhC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

***6b, e***: IR(KBr) 1590 and 1560 $cm^{-1}$ (C=N). $^1H$ NMR $\delta$= 2.35 (s, 3H, $CH_3$), 2.38 (s, 6H, $2CH_3$(Ts)), 7.10—7.90 (m, 17H, Ar-H). $^{13}C$ NMR $\delta$=172.94, 172.51 (C=N), 21.83 ($CH_3$), 21.64 ($CH_3$(Ts)). MS *m/z* 530 (vw, $M^+$) 272 (17, *p*-TolC=NTs$^{\cdot+}$), 258 (6, PhC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

***6c, g***: IR(KBr) 1590 and 1555 $cm^{-1}$ (C=N). $^1H$ NMR $\delta$= 2.43 (s, 6H, $2CH_3$(Ts)), 3.83 (s, 3H, $OCH_3$), 6.8—8.0 (m, 17H, Ar-H). $^{13}C$ NMR $\delta$=173.04, 171.53 (C=N), 55.60 ($OCH_3$), 21.64 ($CH_3$(Ts)). MS *m/z* 546 (vw, $M^+$), 288 (27, *p*-$CH_3OC_6H_4$C=NTs$^{\cdot+}$), 258 (4, PhC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

***6d***: IR(KBr) 1585 and 1555 $cm^{-1}$ (C=N). $^1H$ NMR 2.42 (s, 6H, $2CH_3$ (Ts)), 7.2—7.9 (m, 17H, Ar-H). $^{13}C$ NMR 172.16, 171.48 (C=N), 21.64 (s, 6H, $2CH_3$(Ts)). MS *m/z* 550 (vw, $M^+$), 292 (5, *p*-$ClC_6H_4$C=NTs$^{\cdot+}$), 258 (11, PhC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

***6f***: IR(KBr) 1550 $cm^{-1}$ (C=N). $^1H$ NMR 2.36 (s, 6H, $2CH_3$), 2.40 (s, 6H, $2CH_3$(Ts)), 7.10—7.88 (m, 16H, Ar-H). $^{13}C$ NMR 172.70 (C=N), 21.83($CH_3$), 21.64 ($CH_3$(Ts)). MS *m/z* 544 (vw, $M^+$), 272 (18, *p*-TolC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

***6h***: IR(KBr) 1585 and 1550 $cm^{-1}$ (C=N). $^1H$ NMR 2.34 (s, $CH_3$), 2.37 (s, 6H, $2CH_3$(Ts)), 3.76 (s, 3H, $OCH_3$), 6.66—7.90 (m, 16H, Ar-H). $^{13}C$ NMR 172.79, 171.73 (C=N), 55.55 ($OCH_3$), 21.74 ($CH_3$), 21.59 ($CH_3$(Ts)). MS *m/z* 560 (vw, $M^+$), 288 (22, *p*-$CH_3OC$=NTs$^{\cdot+}$), 272 (8, *p*-TolC=NTs$^{\cdot+}$), 91 (100, *p*-Tol$^{\cdot+}$).

*1-Phenyl-2-(p-methoxyphenyl)-2-tosylimino-1-ethanethione (**7c**)*: Blue oil, IR(neat) 1535 (C=N), 1315, and 1150 ($SO_2$) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) 2.35 (s, 3H, $CH_3$(Ts)), 3.70 (s, 3H, $OCH_3$), 6.7—8.0 (m, 12H, Ar-H). $^{13}C$ NMR ($CDCl_3$) 235.52 (C=S), 175.94 (C=N), 55.49 ($OCH_3$), 21.50 ($CH_3$(Ts)). MS *m/z* 409 (2%, $M^+$), 288 (3, $M^+$—PhCS), 254 (56, $M^+$—Ts), 121 (100, PhCS$^{\cdot+}$).

*1-p-Tolyl-2-phenyl-2-tosylimino-1-ethanethione (**7e**)*: Blue oil, IR (neat) 1560 (C=N), 1330 and 1160 ($SO_2$) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) 2.35 (s, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$(Ts)), 7.1—7.9 (m, 13H, Ar-H). $^{13}C$ NMR ($CDCl_3$) 233.35 (C=S), 176.18 (C=N), 21.96 (s, $CH_3$), 21.55 (s, $CH_3$(Ts)). MS *m/z* 393 (3, $M^+$), 238 (10, $M^+$—Ts), 135 (100, *p*-TolCS$^{\cdot+}$).

[*B*] *Isolation of 1,2-Diaryl-2-tosylimino-1-ethanethione S-Tosylimides **3b, c**.* To a solution of **2** (3.0mmol) in benzene (50 $cm^3$) was added dropwise a solution of **1** (6.6 mmol) in benzene (10 $cm^3$) with stirring at 10—15 °C. The reaction mixture was stirred for 5—10h at room temperature until the materials were consumed (TLC). Evaporation of the solvent without heating and column chromatography (silica gel, 1/50 ethyl acetate/benzene) of the residue gave **3** as orange-red oil in 70—79% yields. The isolated thione *S*-imides **3b,c** (2mmol) were heated at reflux in 50 $cm^3$ of benzene for 16—18h. The work-up as described in the procedure A gave **5b** (40% yield) and **6b** (5% yield) or **5c** (40%) and **6c** (2%) along with **7b,c** (trace).

**3b**: IR($CHCl_3$) 1550 (C=N), and 990 (CSN) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$=2.37 (s, 6H, $2CH_3$), 2.42 (s, 3H, $CH_3$), 7.06—7.86 (m, 17H, Ar-H). $^{13}C$ NMR ($CDCl_3$) $\delta$=176.28 (C=N), 167.22 (CSN), 146.26—125.06, 21.74, 21.54, and 21.35 ($CH_3$).

**3c**: IR(KBr) 1550 (C=N), and 990 (CSN) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$=2.30 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$), 3.74 (s, 3H, $OCH_3$), 6.62—7.78 (m, 17H, Ar-H). $^{13}C$ NMR ($CDCl_3$) $\delta$= 176.60 (C=N), 166.27 (CSN), 165.15—114.66, 55.60 ($OCH_3$), 21.49 ($CH_3$), 21.25 ($CH_3$).

[*C*] *Thermolysis of 5c.* When the adduct **5c** (1.6 mmol) was heated at 112 °C in xylene (75 $cm^3$)–benzene (35 $cm^3$), orange-colored **3c** appeared and was identified by TLC. After heating for 28 h, the usual work-up and column chromatography of the reaction mixture gave **6c** (19% yield), **7c** (2% yield) and an unidentified colorless oil.

[*D*] *Reaction of 3c with Triphenylphosphine.* To a benzene solution (40 $cm^3$) of **3c** (2.0 mmol) was added a benzene solution (10 $cm^3$) of triphenylphosphine (2.1 mmol) in a cold bath. After stirring at room temperature for 12 h, removal of the solvent and column chromatography (silica gel, benzene→ethyl acetate) of the residue gave 0.3 g of **7c** (37% yield), 0.31 g of **8** (36%), 0.20 g of **9** (35%), and 0.22 g of **10c** (17%).

***10c***: Colorless crystals, mp 248—251 °C. IR(KBr) 1610, 1440, 1390, 1140, and 1090 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$=2.21 (s, 3H, $CH_3$(Ts)), 3.62 (s, 3H, $OCH_3$), 6.5—7.6 (m, 28H, Ar-H). $^{13}C$ NMR ($CDCl_3$) $\delta$=171.36 (d, $J_{C-P}$=7.3 Hz, C=N), 82.48 (d, $J_{C-P}$=101.3 Hz, C=P), 54.87 ($OCH_3$), 21.20 ($CH_3$(Ts)). MS *m/z* 639 (9, $M^+$), 484 (34, $M^+$—Ts), 262 (4, $PPh_3$), 222 (100, $M^+$—Ts–$PPh_3$).

[*E*] *Reaction of 5c with Triphenylphosphine.* To a solution of **5c** (1.2 mmol) in chloroform (5 $cm^3$) was added a benzene solution (35 $cm^3$) of an equimolar amount of triphenylphosphine. The reaction mixture was heated at reflux for 22 h. After cooling to room temperature, the precipitate (partial **5c**) was filtered. The work-up of the filtrate in the same manner as described in the procedure D gave **7c** (trace), **8** (5%), **9** (28%), **10c** (40%), *p*-toluenesulfonamide, and 46% (total)-recovered **5c**.

[*F*] *Reaction of C=C-conjugated Ylides 11 with N-Sulfinyl-p-toluenesulfonamide (2).* To a partial suspension of **11b** (1.24 g, 2.74 mmol) in benzene (30 $cm^3$) was added a benzene solution (20 $cm^3$) of **2** (0.71 g, 3.3 mmol) at temperatures of 10—15 °C. The resulted reaction mixture was warmed for 10 min until the solution turned clear. The solvent was evaporated and the residue was recrystallized from dichloromethane–diethyl ether to give **14** in a 45% yield.

**14**: Yellow needles, mp 204—205 °C. IR(KBr) 1600 and 1560 (C=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$=2.44 (s, 3H, $CH_3$(Ts)), 7.06 (d, *J*=10 Hz, 1H, =CH–), 7.12—7.96 (m, 12H, Ar-H), 9.68 (d, *J*=10 Hz, 1H, –CH=N–). MS *m/z* 359 (4, $M^+$), 204 (100, $M^+$—Ts), 91 (24, $Tol^+$). Found: C, 73.55; H, 4.81; N, 3.92%. Calcd for $C_{22}H_{17}O_2NS$: C, 73.51; H, 4.77; N, 3.90%.

[*G*] *Reaction of N=C-conjugated Ylides 16 with N-Sulfinylamines (2) and Sulfur Dioxide.* To a benzene solution (25 $cm^3$) of **16** (4.55 mmol) was added dropwise a benzene solution (10 $cm^3$) of **2** (4.51 mmol) at temperatures of about 10 °C. The orange suspension turned to a clear solution. The reaction mixture was very hygroscopic. On standing in the air it hydrolyzes to form white crystals **18**, which were filtered off and washed with benzene.

**18a**: White needles, mp 133—135 °C (dec). IR(KBr) 1570 (C=N), 1440 (P-C), and 1260 ($SO_2$) $cm^{-1}$. MS *m/z* 455 (58, $M^+$—$SO_2$), 378 (12, $M^+$—$SO_2$–Ph), 262 (100, $Ph_3P$).

**18b**: White needles, mp 252—254 °C. IR(KBr) 1660 (C=N), 1445 (P-C), and 1265 ($SO_2$) $cm^{-1}$. MS *m/z* 587 (36, $M^+$—$SO_2$), 496 (100, $M^+$—$SO_2$–$CH_2Ph$), 262 (30, $Ph_3P$). Dry sulfur dioxide gas was bubbled into a benzene solution (20 $cm^3$) of **16** (2.0 mmol). After 2h orange suspension turned to a white suspension. The precipitate was collected by filtration to give **18a**, **b**, which were identical with the products obtained above.

[*H*] *Conversion of 18a to 16a by Base.* A suspended mixture of **18a** (0.52 g, 1.0 mmol) and potassium *t*-butoxide (0.62 g, 2.0 mmol) in benzene (20 $cm^3$) was stirred for 3 h. Removal of the solvent and extraction of the residue by chloroform gave **16a** in an 89% yield (recrystallized from chloroform–petroleum ether).

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