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GEOMETRICAL ISOMERISM IN UNSATURATED SULPHIDE-SULPHONES AND DISULPHONES—I

SYNTHESIS OF *CIS* (Z) AND *TRANS* (*E*)-1,2-*BIS*(*p*-TOLYLSULPHONYL)STILBENES

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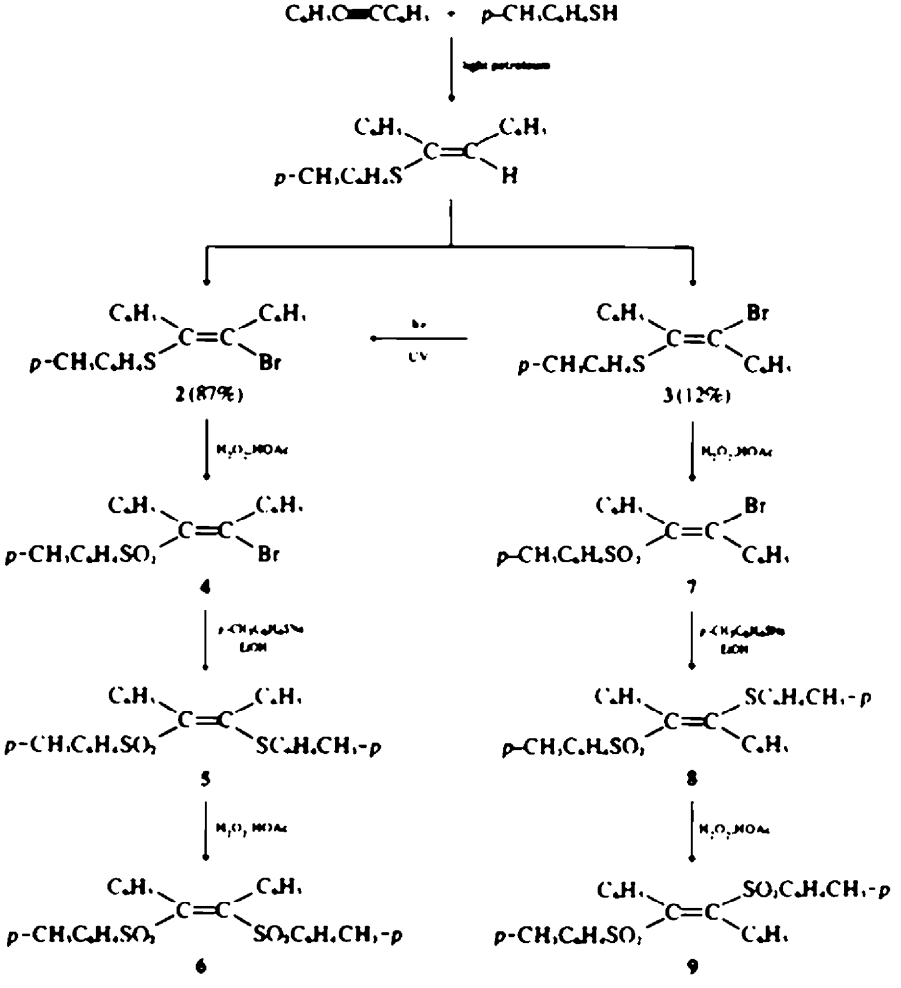
Abstract—The synthesis of (*Z*) and (*E*) 1,2-bis(*p*-tolylsulphonyl)stilbenes are described and their UV and IR spectra are recorded. The geometrical configurations of these isomers have been established through stereospecific syntheses.

The synthesis and structural studies of 1,2-bis(arylthio)ethylenes and their corresponding unsaturated disulphones are of recent origin. Bis(organosulphonyl)ethylenes,[1] vinylene sulphonyl compounds[2] (*cis* and *trans*) and bis(arylthio)ethylenes[3] have been reported as effective fungicides to protect seed. One of the most convenient and common procedures adopted for the preparation of 1,2-bis(alkyl or arylthio)ethylenes and their sulphones was by the nucleophilic displacement of halogens with thiols from tetrachloroethylene,[4-6] dich-



loroethylenes,[9-12] vinylidine halides[11] and vinyl halides.[11,13-15] The present paper describes the preparation of *cis* (*Z*)-1,2-bis(*p*-tolylsulphonyl)stilbene and its corresponding *trans* (*E*) isomer. The *trans* isomer has been synthesized stereospecifically by four different methods.

1-*p*-Tolylthiostilbene (1) prepared by treating tolan with *p*-thiocresol proved to be identical with the *cis* isomer reported[16] earlier by dehydrochlorination of erythro-2-*p*-thiocresoxy-1,2-diphenyl-1-chloroethane. Bromination of the *cis* isomer 1, resulted with the formation of two monobromo substituted isomers 2 and 3 with the elimination of HBr. The isomer 2 formed in major proportion (87%) and the isomer 3 constituted only 12% of the total product formed. Benati *et al.*[17] carried out a similar reaction with *cis*-1-*p*-bromophenylthiostilbene and reported the formation of the bromosubstituted *cis* isomer as a major product of the reaction and the *trans* bromosubstituted isomer in very low yields.

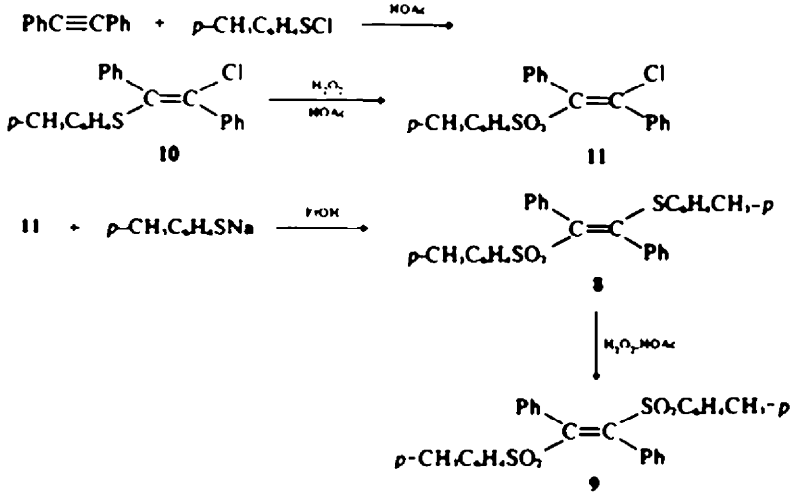
Our studies confirmed that the compound 2 is a *cis* isomer. On irradiation of 3 with UV light in benzene solution for 18 hr resulted with the formation (32%) of a compound which was found to be identical with 2. The m.p. was same (141-142°) and there was no depression in the mixed m.p. on admixture with 2 and both the compounds gave identical IR spectra.

The above studies also confirm 3 as a *trans* isomer and on oxidation of this compound lead to the formation of 7, which on treatment with sodium *p*-toluenethiolate gave (*E*)-1-*p*-tolylthio-2-*p*'-tolylsulphonylstilbene (8). Oxidation of 8 gave the *trans* isomer, (*E*)-1,2-bis(*p*-tolylsulphonyl)stilbene (9).

(*Z*)-1-Bromo-2-*p*-tolylthiostilbene (2) whose configuration has been established as *cis* isomer, was oxidised to give (*Z*)-1-bromo-2-*p*-tolylsulphonylstilbene (4). (*Z*)-1-*p*-Tolylthio-2-*p*'-tolylsulphonylstilbene (5) was obtained by the nucleophilic displacement of bromine from 4 with the retention of configuration.[17,18,19] Compound 5, on oxidation under mild conditions gave the *cis* isomer (*Z*)-1,2-bis(*p*-tolylsulphonyl)stilbene (6).

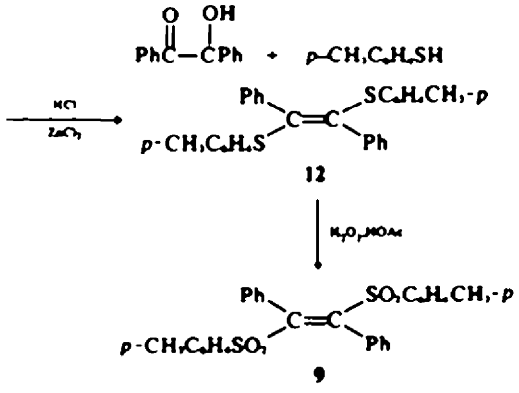
The *trans* isomer 9, has been synthesized by another three methods.

Method 1



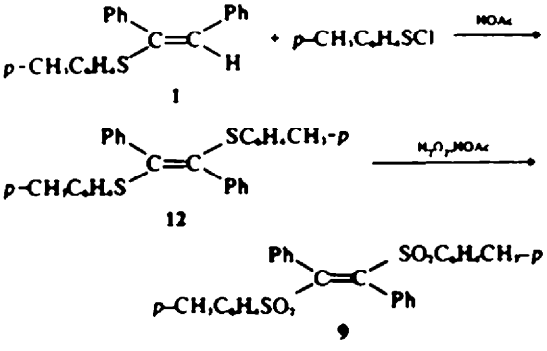
The compounds 10 and 11 were reported by Nunno *et al.*[20] and claimed to be *trans* isomers.[21,22] Therefore, the compounds 8 and 9 should also possess the *trans* (*E*) configurations.

Method 2



Schönberg and Mustafa[23] prepared 12 and the corresponding *p*-bromosubstituted compound has been reported by Benati *et al.*[17] and showed it to possess the *trans* (*E*) configuration. Hence, the unsaturated disulphone 9 should also be a *trans* isomer.

Method 3



(*E*)-1-*p*-Tolylthiostilbene (1) on treatment with *p*-toluenesulphenyl chloride gave a compound which was found to be identical with 12 reported in method 2. This was oxidised to yield (*E*)-1,2-bis(*p*-tolylsulphonyl)stilbene (9). Preparation by all the four different routes yielded the same *trans* (*E*) isomer

(*E*)-1-*p*-Tolylthio-2-*p'*-tolylsulphonylstilbene (8) was converted into its corresponding *cis* isomer 5 by irradiation with a trace of bromine or iodine. Similarly (*Z*)-1,2-bis(*p*-tolylsulphonyl)stilbene (6) isomerized into its *trans* form 9 by heating it to its m.p.

A series of *cis* and *trans* unsaturated sulphide-sulphones and their corresponding disulphones are under preparation and their spectral characteristics will be discussed in the next communication.

EXPERIMENTAL

All m.ps were determined on a Mel-Temp apparatus and are uncorrected. The elemental analyses were performed by Dr. R. D. MacDonald, Australian Microanalytical Service. UV absorption measurements were determined in 95 per cent EtOH with a Beckman Model DU-2 UV Spectrophotometer and IR spectra were recorded on a Beckman IR-18 IR Spectrophotometer and a Perkin-Elmer IR Spectrophotometer Model 700 as KBr pellets and in nujol mulls.

Diphenylacetylene[10] (m.p. 60–61°) and *p*-toluenesulphenyl chloride[11] (b.p. 82–84°/4 mm) were prepared as described.

(*E*)-1-*p*-*Tolylthiostilbene* (1). Diphenylacetylene (17.8 g, 100 mmole) in warm light petroleum (200 ml) was treated with *p*-thiocresol (12.4 g, 100 mmole) and the mixture was boiled for 5 min and was left overnight at room temp. The soln was washed successively with 2 per cent NaOH and water and dried over $CaCl_2$. The residue left after evaporation of the solvent was subjected to distillation under reduced pressure. The distillate collected at 114–117°/3 mm, yielded 4.3 g of unreacted diphenylacetylene and the residue amounted to 21.9 g (72.5%) of light brown viscous oil. This oil was solidified on treatment with MeOH and melted at 75–77°. Recrystallization from 95 per cent EtOH twice yielded colourless crystals, m.p. 82–83° (Lit.[6] m.p. 83–84°) (Found: C, 83.34; H, 6.01. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00%).

Bromination of (*E*)-1-*p*-*tolylthiostilbene*. To a solution of 1 (4.54 g, 15 mmole) in glacial AcOH (150 ml) at room temp., Br_2 (2.4 g, 15 mmole) in glacial AcOH (40 ml) was added dropwise with stirring. During addition decolourization was observed with immediate precipitation. The addition took about 25 min and the stirring was continued for an additional 60 min. The solid 2 separated was filtered and recrystallized from AcOH, yielding 5.0 g (87.4%), m.p. 137–140°.

The mother liquor from the above reaction on concentration under flash evaporation and dilution with water gave 700 mg (12%) of 3.

(*Z*)-1-*Bromo*-2-*p*-*tolylthiostilbene* (2). The solid material 2 obtained on bromination of 1 as a major product was further purified by repeated recrystallizations from glacial AcOH, to yield fine pale yellow crystals, m.p. 141–142° (Found: C, 66.36; H, 4.69. Calcd for $C_{21}H_{17}BrS$: C, 66.14; H, 4.49%). λ_{max}^{EtOH} 323 nm (ε 6,237), 270 (14,850), 228 (25,660), 203 (43,780). ν_{max}^{Nujol} 692, 710, 759, 804, 828, 843, 908, 935, 960, 980, 1011, 1028, 1070, 1091 (m) (S-aryl), 1175, 1184, 1208, 1252, 1274, 1303, 1374, 1440, 1455, 1484, 1567, 1594 and 1620 cm^{-1} (w) (C=C).

(*E*)-1-*Bromo*-2-*p*-*tolylthiostilbene* (3). The material obtained from the mother liquor by the action of bromine on 1 was purified by repeated recrystallizations from 95 per cent EtOH, colourless long needles, m.p. 105–106° (Found: C, 66.34; H, 4.61. Calcd for $C_{21}H_{17}BrS$: C, 66.14; H, 4.49%). λ_{max}^{EtOH} 255 nm (ε 14,120), 204 (40,510). ν_{max}^{Nujol} 660, 707, 753, 780, 810, 843, 860, 914, 950, 1000, 1030, 1075 (m) (S-aryl), 1105, 1177, 1180, 1208, 1240, 1278, 1302, 1377, 1442, 1458, 1486, 1578, 1585, 1620 (C=C), 1880 and 1945 cm^{-1}.

Isomerization of (*E*)-1-*bromo*-2-*p*-*tolylthiostilbene* (3) *to* (*Z*)-1-*bromo*-2-*p*-*tolylthiostilbene* (2). A soln of 3 (1.0 g) in benzene (500 ml) was irradiated with UV light for 18 hr. The residue obtained on evaporation of the solvent was subjected to fractional crystallizations from AcOH. Pale yellow needles (320 mg, 32%) obtained, did not depress the mixed m.p. on admixture with 2. The UV and IR spectra of both the compounds were found to be identical.

(*Z*)-1-*Bromo*-2-*p*-*tolylsulphonylstilbene* (4). To a soln of 2 (2.5 g) in warm glacial AcOH (50 ml) was added 30 per cent H_2O_2 (9 ml). The soln was refluxed for 1 hr and allowed to stand overnight. Crystals separated were filtered (2.5 g, 93.7%) and recrystallization from AcOH thrice gave colourless needles, m.p. 154–155° (Found: C, 61.15; H, 4.25. Calcd for $C_{21}H_{17}BrO_2S$: C, 61.02; H, 4.15%). λ_{max}^{EtOH} 239 nm (ε 19,430), 203 (46,570). ν_{max}^{Nujol} 614, 640, 675, 695, 762, 800, 820, 832, 922, 962, 1003, 1032, 1088 (s) (S-aryl), 1154 (s) (SO_2), 1189, 1216, 1242, 1256, 1310, 1326 (s) (SO_2), 1385, 1408, 1448, 1490, 1584, 1598, 2310, 2329, 3030 and 3070 cm^{-1}.

(*Z*)-1-*p*-*Tolylthio*-2-*p*-*tolylsulphonylstilbene* (5). A soln of *p*-thiocresol (372 mg, 3 mmole) and Na (69 mg, 3 mg atom) in abs. EtOH (5 ml) was added at once to a hot soln of 4 (1.329 g, 3 mmole) in abs. EtOH (25 ml). The mixture was refluxed for 1 hr, cooled and worked up the product to yield 1.27 g (92.7%) of light, yellow material. Three recrystallizations from aqueous AcOH gave colourless crystals, m.p. 158–159° (Found: C, 73.84; H, 5.47. Calcd for $C_{28}H_{24}O_2S_2$: C, 73.65; H, 5.30%). λ_{max}^{EtOH} 293 nm (ε 11,950), 203 (56,140). ν_{max}^{Nujol} 628, 678, 694, 735, 767, 796, 848, 1016, 1078 (s) (S-aryl), 1143 (s) (SO_2), 1182, 1241, 1292, 1301 (s) (SO_2), 1400, 1445, 1495, 1540 (m) (C=C), 1580, 1598 and 3020 cm^{-1}.

(*Z*)-1,2-*Bis*(*p*-*tolylsulphonyl*)*stilbene* (6). Into a soln of 5 (300 mg) in warm glacial AcOH (25 ml) was added 30 per cent H_2O_2 (3 ml) and the soln was boiled gently for 1 min. The mixture was allowed to stand for 1 hr and then poured over crushed ice. The product separated was filtered to yield 260 mg (81%) of 6, m.p. 176–178°. Recrystallization from 95 per cent EtOH thrice gave colourless needles, m.p. 185–185° (Found: C, 68.57; H, 5.20. Calcd for $C_{28}H_{24}O_4S_2$: C, 68.83; H, 4.95%). λ_{max}^{EtOH} 244 nm (ε 22,160), 226 (25,830), 202 (54,530). ν_{max}^{Nujol} 648, 683, 694, 763, 811, 1087 (m) (S-aryl), 1125, 1154 (s) (SO_2), 1190, 1317 (s) (SO_2), 1408, 1453, 1495 and 1602 cm^{-1}.

When the oxidation was carried out under vigorous refluxing conditions, it resulted with the isomerization of the *cis* product to its *trans* isomer. M.p. and mixed m.p. were the same as that of the *trans* isomer 9, m.p. 276–277°.

(*E*)-1-*Bromo*-2-*p*-*tolylsulphonylstilbene* (7). To a soln of 3 (1 g) in glacial AcOH (40 ml) was added 30 per cent H_2O_2 (7 ml). Refluxed for 1 hr and poured over crushed ice (250 g). The solid separated was filtered and recrystallized from 95 per cent EtOH, to yield 920 mg (84.9%) of colourless needles, m.p. 157–158° (Found: C, 61.31; H, 4.13. Calcd for $C_{21}H_{17}BrO_2S$: C, 61.02; H, 4.15%). λ_{max}^{EtOH} 235 nm (ε 20,140), 203 (46,740). ν_{max}^{Nujol} 633, 676, 787, 910, 956, 1087 (m) (S-aryl), 1150 (s) (SO_2), 1186, 1237, 1309, 1326 (s) (SO_2), 1401, 1449, 1495, 1600 and 1636 cm^{-1} (C=C).

(*E*)-1-*p*-*Tolylthio*-2-*p'*-*tolylsulphonylstilbene* (8). A soln of 7 (620 mg, 1.5 mmole) in hot abs. EtOH (25 ml) was treated with a soln of *p*-thiocresol (186 mg, 1.5 mmole) in an ethanolic soln of NaOEt prepared from Na (35.5 mg, 1.5 mg atom) and abs. EtOH (5 ml). The mixture was refluxed for 6 hr, cooled and the light yellow product (500 mg, 73%) separated was filtered. Recrystallization twice from aqueous EtOH gave colourless needles, m.p. 190–191° (Found: C, 73.52; H, 5.33. Calcd for $C_{28}H_{24}O_2S_2$: C, 73.65; H, 5.30%). λ_{max}^{EtOH} 289 nm (ε 13,810), 268 (12,800), 203 (52,590). ν_{max}^{Nujol} 638, 672, 697, 732, 754, 812, 851, 914, 926, 976, 1003, 1021, 1035, 1077, 1092 (m) (S-aryl), 1110, 1150 (s) (SO_2), 1186, 1202,

1239, 1299, 1310, 1323 (s) (SO_2), 1408, 1452, 1496, 1583, 1607, 2920 and 3060 cm^{-1}.

(*E*)-1,2-*Bis*(*p-tolylsulphonyl*)*stilbene* (**9**). To a warm soln of **8** (300 mg) in glacial AcOH (25 ml) was added 30 per cent H_2O_2 (4 ml) and the soln was refluxed for 1 hr. A colourless product started separating during the process and the mixture was cooled and filtered. Recrystallization twice from AcOH yielded 210 mg (65.4%) of colourless needles, m.p. 276–277° (Found: C, 68.93; H, 5.24. Calcd for $C_{28}H_{24}O_4S_2$: C, 68.83; H, 4.95%); λ_{max}^{EtOH} 244 nm (*ε* 22,210), 227 (27,750), 202 (50,890); ν_{max}^{KBr} 649, 701, 792, 801, 817, 847, 936, 1022, 1035, 1087 (m) (S-aryl), 1155 (s) (SO_2), 1189, 1229, 1300, 1332 (s) (SO_2), 1408, 1451, 1499, 1603, 1717, 2920 and 3047 cm^{-1}.

Stereospecific syntheses of (*E*)-1,2-*bis*(*p-tolylsulphonyl*)*stilbene by three different methods*

Method 1. (a) (*E*)-1-*Chloro*-2-*p-tolylthiostilbene* (**10**). To a soln of diphenylacetylene (35.6 g, 200 mmole) in glacial AcOH (Analytical Grade, 500 ml) was added *p*-toluenesulphenyl chloride (28.9 g, 200 mmole) and refluxed for 12 hr. AcOH was removed *in vacuo* and the viscous residue was treated with isopropanol (50 ml). The solid product separated was filtered and washed with small quantities of isopropanol. The compound on recrystallization from AcOH yielded 52 g (77.2%) of colourless plates. Two more crystallizations from AcOH afforded an analytical sample, m.p. 89–90° (Lit.[20] m.p. 91°).

(b) (*E*)-1-*Chloro*-2-*p-tolylsulphonylstilbene* (**11**). Compound **10** (25 g) was oxidised with H_2O_2 (75 ml) in glacial AcOH (200 ml). The product on recrystallization from 95 per cent EtOH gave 29.5 g (85.7%) of fine colourless needles, m.p. 142–143° (Lit.[20] m.p. 140°).

(c) (*E*)-1-*p-Tolylthio*-2-*p'-tolylsulphonylstilbene* (**8**). To a soln of NaOEt prepared from (230 mg, 10 mg atom) of Na and abs. EtOH (25 ml) was added *p*-thiocresol (1.2 g, 10 mmole) and **9** (3.69 g, 10 mmole) dissolved in abs. EtOH (85 ml). The soln was refluxed for 8 hr, cooled and the product separated was filtered. Recrystallization from 95 per cent EtOH yielded 3.74 g (81.9%) of colourless crystals, m.p. 190–191°.

This compound has been proved to be identical with that of **8**, reported earlier by the condensation of **7** with sodium *p*-toluenethiolate.

(d) (*E*)-1,2-*Bis*(*p-tolylsulphonyl*)*stilbene* (**9**). About 300 mg of **8** was oxidised with H_2O_2 (4 ml) in glacial AcOH (25 ml). The product 210 mg (65.4%) was recrystallized from AcOH, colourless needles, m.p. 276–277°.

Method 2. (a) (*E*)-1,2-*Bis*(*p-tolylthio*)*stilbene* (**12**). This compound was prepared according to the procedure of Schönberg and Mustafa[21]. The product on recrystallization from benzene gave fine colourless plates of (*E*)-1,2-bis(*p*-tolylthio)stilbene, m.p. 180–181° (Lit.[21] m.p. 170°) (Found: C, 79.14; H, 5.93. Calcd for $C_{28}H_{24}S_2$: C, 79.20; H, 5.70); λ_{max}^{EtOH} 263 nm (*ε* 15,420), 227 (28,370), 204, (52,290); ν_{max}^{KBr} 700, 746, 800, 812, 852, 860, 924, 1020, 1035, 1080, 1092 (m) (S-aryl), 1105, 1160, 1180, 1210, 1300, 1376, 1395, 1442, 1458, 1489, 1568, 1590 and 1634 cm^{-1} (C=C).

(b) (*E*)-1,2-*Bis*(*p-tolylsulphonyl*)*stilbene* (**9**). Into a soln of **12** (300 mg) in hot glacial AcOH (20 ml) was added 30 per cent H_2O_2 (6 ml) and the soln was refluxed for 1 hr. The crystals separated on cooling were filtered. Recrystallization from AcOH yielded (210 mg, 57.8%) colourless crystals, m.p. 276–277°.

Method 3. (a) *Reaction of p-toluenesulphenyl chloride with* **1**. To a soln of **1** (3.025 g, 10 mmole) in glacial AcOH (150 ml) was added *p*-toluenesulphenyl chloride (1.585 g, 10 mmole) and refluxed for 14 hr. The solvent was removed *in vacuo* and the residue on cooling deposited 3.7 g (87.1%) of **12**. Recrystallization from benzene gave colourless plates, m.p. 181–182°. The m.p. of this compound was not depressed on admixture with **12**, prepared earlier by method 2(a).

(b) *Oxidation of* **12** *to* **9**. The procedure followed was identical with method 2(b) described earlier. The compound obtained was recrystallized from AcOH, colourless needles, m.p. 276–277°. There was no depression in mixed m.ps with the compounds **9**, obtained through the three other methods.

Isomerization of **8** *to* **5**. A sample (1 g) of **8** (m.p. 190–191°) was dissolved in 35 ml of glacial AcOH containing a trace of Br_2 and exposed to sun light for 24 hr. The solvent was evaporated and the resulting material was recrystallized from aqueous AcOH. A second recrystallization from aqueous AcOH gave a product (0.4 g, 40%) which did not depress the m.p. (158–159°) of an authentic sample of **5**.

Isomerization of **6** *to* **9**. About 200 mg of **6** (m.p. 184–185°) was heated to 190°. It melted and then solidified. Heating was continued for 5 min and cooled. On recrystallization from AcOH gave 120 mg of a product which did not depress the m.p. (276–277°) of an authentic sample of **9**.

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