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A Simple Strategy for Styryl Sulfonyl Ethynylogues and 1,4-Diarylbut-1-en-3-ynes

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Abstract : A general and simple strategy for 2-arylethenyl-2′-arylethynyl sulfones (**9**) and 1,4-diarylbut-1-en-3-ynes (**10**) has been developed by the lability of carbon-heteroatom bond in heterocycles, 1,2,3-selenadiazole (**3**) as the basis.
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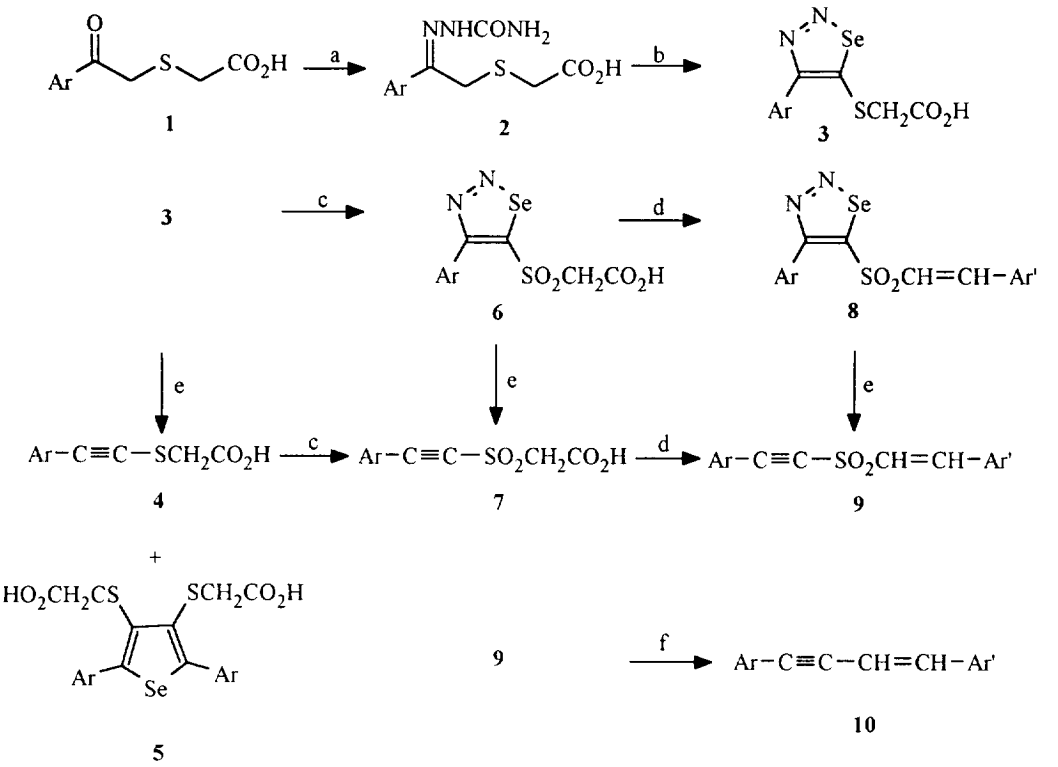
The bis olefinic sulfones are valuable tools in organic synthesis and have received considerable attention in recent times.[1] In contrast to different methods developed for Z,Z-and E,E-bis (styryl)sulfides/ sulfones,[2] less attention was focused on E,Z-bis(styryl) sulfones. Infact, the latter were reported earlier from our laboratories by the Knoevenagel condensation of Z-styrylsulfonylacetic acid with araldehydes.[3] Our sustained interest in this field led us to develop a simple and an elegant methodology for a new class of compounds, enyne sulfones through a facile route. Literature search shows not only the compounds involving alkene - alkyne moieties but also chalcone ethynylogues are relatively less.[4] One such method involves the palladium coupling reaction of vinyl halides with terminal alkynes and alkynyl metals. Moreover, the carbonyl activated enyne systems have also been obtained by the direct condensation of phenylacetylene with a stoichiometric amount of triethylamine and dichlorobis(triphenylphosphine) palladium and copper iodide as a catalyst.[4e] However, there have been no reports to date about styryl sulfonyl ethynylogues. Apart from this, while there have been evidences on copper and palladium - assisted substitution reactions for the synthesis of enyne systems, the lability of carbon-heteroatom bonds in heterocycles becomes a different method.

The synthetic scheme is based on the reactivity of 1,2,3-selenadiazolyl ring which on pyrolysis affords alkynes as major products.[5] This paves the way for the synthesis of 2-arylethenyl-2′-arylethynyl sulfones. To achieve the target species, phenacyl sulfanylacetic acid[6] (**1**) has been chosen in which the α-keto methylene group is exploited for developing selenadiazole ring.[7] The former on reaction with semicarbazide hydrochloride gave **2** which on oxidative cyclization with SeO_2 results 4-aryl-1,2,3-selenadiazolyl-5-sulfanylacetic acid (**3**). The reactivity of **3** is investigated. The pyrolysis with copper powder at 200°C was found to result 2-arylethynylsulfanylacetic acid (**4**) as a major product (58%) and a dimerized product, 2,5-diarylselenophene-3,4-bis(sulfanylacetic acid) (**5**) as a minor one (18%). In contrast to this, the oxidized product of **3** (**6**), under similar conditions afforded 2-arylethenylsulfonylacetic acid only (**7**). The latter was also obtained by the oxidation of **4** in cold conditions with 30% H_2O_2 in AcOH. On the other hand, the styryl sulfonyl ethynylogues, *E*-2-arylethenyl-2′-arylethynyl sulfones **9** have been obtained by three different routes: a) Knoevenagel condensation of 7 with araldehydes in the presence of a base, $C_6H_5CH_2NH_2$; b)

by the same reaction with **4** followed by oxidation with 30% H_2O_2 in AcOH; c) similar reaction of **6** with araldehydes in the presence of a base, $C_6H_5CH_2NH_2$ gave 4-aryl-1,2,3-selenadiazolyl-5-styrylsulfones (**8**) which on pyrolysis led to **9** in quantitative yields. These enyne sulfones **9** are novel compounds



Scheme: (a) $NH_2NHCONH_2HCl$, CH_3COONa, MeOH (b) SeO_2, AcOH (c) H_2O_2, AcOH
(d) Ar'CHO, $C_6H_5CH_2NH_2$, AcOH (e) Cu Powder, CH_2Cl_2, Δ (f) $(Ph_3P)_3RuCl_2$, C_6H_6, Δ

and the method adopted is a new and a general one. Desulfonylation of the former in the presence of dichlorotris(triphenylphosphine) ruthenium results an enyne system, *E*-1,4-diarylbut-1-en-3-ynes (**10**).[2d] Until now only a limited number of reports are available for the synthesis of **10**.[8] The method described in the present instance is yet another facile route. However, some Z-isomers were also reported by the palladium catalysed cross-coupling of organic halides with organotin compounds in the presence of norbornadiene followed by the pyrolysis.[9] Indeed, the **9** and **10** are valuable synthons in a number of organic reactions and a study related to them is under progress. The physical data of all the compounds are compiled in Tables 1 & 2.

In conclusion we have developed a different strategy not only for enyne systems but also for *E*-styryl sulfonyl ethynylogues, where the reactivity of heterocyclic ring forms the basis for such methodology. The efficient synthesis of *E*-2-arylethenyl-2′-arylethynyl sulfones (**9**) and *E*-1,4-diarylbut-1-en-3-ynes (**10**) established the versatility of present methodology.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra (KBr-disc) were recorded on a Beckman IR-18 spectrophotometer. NMR spectra were recorded in $CDCl_3$/DMSO-d_6 using 90 MHz on a varian EM-360 spectrophotometer using TMS as a standard. Elemental analyses were obtained from the University of Poona, Pune, India.

The starting material phenacylsulfanylacetic acid (1) was prepared by the same procedure described in the preceding paper.[6]

Semicarbazone of Phenacylsulfanylacetic acids (2): General Procedure: A mixture of 1.2 mmol of semicarbazide hydrochloride, 1.0 mmol of **1** and 1.0 mmol of sodium acetate in 25 ml of alcohol was refluxed for 3 hr and poured onto crushed ice. The semicarbazone separated was purified by recrystallization. 2a: (Found: C, 49.24; H, 4.95; N, 15.60. $C_{11}H_{13}N_3O_3S$ requires C, 49.43; H, 4.90; N, 15.72%); ν_{max} (KBr)/cm^{-1} 3450 (OH), 3350 (NHCO), 3200 ($CONH_2$), 1720 (COOH), 1690 ($CONH_2$), 1460 (C=N); δ_H (90 MHz; $CDCl_3$) 3.30 (s, 2H, SCH_2), 3.90 (s, 2H, CH_2CO_2H), 6.42 (s, 2H, $CONH_2$), 7.20-7.42 (m, 5H, ArCH), 9.51 (s, 1H, COOH). 2b: (Found: C, 51.45; H, 5.49; N, 14.76. $C_{12}H_{15}N_3O_3S$ requires C, 51.23; H, 5.37; N, 14.94%); ν_{max} (KBr)/cm^{-1} 3452 (OH), 3344 (NHCO), 3208 ($CONH_2$), 1720 (COOH), 1685 ($CONH_2$), 1460 (C=N); δ_H (90 MHz; $CDCl_3$) 2.21 (s, 3H, CH_3), 3.38 (s, 2H, SCH_2), 3.93 (s, 2H, CH_2CO_2H), 6.34 (s, 2H, $CONH_2$) 7.16-7.38 (m, 4H, ArCH), 9.48 (s, 1H, COOH). 2c: (Found: C, 50.35; H, 5.35; N, 13.62. $C_{13}H_{17}N_3O_4S$ requires C, 50.15; H, 5.50; N, 13.50%); ν_{max} (KBr)/cm^{-1} 3448 (OH), 3350 (NHCO), 3200 ($CONH_2$), 1716 (COOH), 1684 ($CONH_2$), 1465 (C=N); δ_H (90 MHz; $CDCl_3$) 1.18 (t, 3H, OCH_2CH_3), 3.36 (s, 2H, SCH_2), 3.85 (s, 2H, CH_2CO_2H), 3.95-4.03 (q, 2H, OCH_2CH_3), 6.32 (s, 2H, $CONH_2$) 7.23-7.45 (m, 4H, ArCH), 9.56 (s, 1H, COOH). 2d: (Found: C, 43.83; H, 4.09; N, 13.82. $C_{11}H_{12}ClN_3O_3S$ requires C, 43.78; H, 4.01; N, 13.93%); ν_{max} (KBr)/cm^{-1} 3450 (OH), 3345 (NHCO), 3205 ($CONH_2$), 1725 (COOH), 1688 ($CONH_2$), 1462 (C=N); δ_H (90 MHz; $CDCl_3$) 3.35 (s, 2H, SCH_2), 3.94 (s, 2H, CH_2CO_2H), 6.38 (s, 2H, $CONH_2$), 7.15-7.38 (m, 4H, ArCH), 9.49 (s, 1H, COOH). 2e: (Found: C, 38.04; H, 3.44; N, 12.17. $C_{11}H_{12}BrN_3O_3S$ requires C, 38.16; H, 3.49; N, 12.14%); ν_{max} (KBr)/cm^{-1} 3445 (OH), 3348 (NHCO), 3210 ($CONH_2$), 1718 (COOH), 1690 ($CONH_2$), 1458 (C=N); δ_H (90 MHz; $CDCl_3$), 3.36 (s, 2H, SCH_2), 3.93 (s, 2H, CH_2CO_2H), 6.41 (s, 2H, $CONH_2$), 7.26-7.48 (m, 4H, ArCH), 9.51 (s, 1H, COOH). 2f: (Found: C, 42.17; H, 3.94; N, 18.12. $C_{11}H_{12}N_4O_5S$ requires C, 42.31; H, 3.87; N, 17.94%); ν_{max} (KBr)/cm^{-1} 3452 (OH), 3355 (NHCO), 3208 ($CONH_2$), 1724 (COOH), 1690 ($CONH_2$), 1455 (C=N); δ_H (90 MHz; $CDCl_3$), 3.35 (s, 2H, SCH_2), 3.94 (s, 2H, CH_2CO_2H), 6.44 (s, 2H, $CONH_2$), 7.24-7.50 (m, 4H, ArCH), 9.48 (s, 1H, COOH).

4-Aryl-1,2,3-selenadiazolyl-5-sulfanylacetic acids (3): General Procedure: To a warm solution of **2** (1.0 mmol) in glacial acetic acid (10 ml), powdered SeO_2 (1.0 mmol) was added slowly while stirring. The selenium deposited on cooling was removed and the filtrate poured onto crushed ice. The solid obtained was purified by column chromatography. 3a: (Found: C, 40.24; H, 2.67; N, 9.47. $C_{10}H_8N_2O_2SSe$ requires C, 40.14; H, 2.70; N, 9.36%); ν_{max} (KBr)/cm^{-1} 3676 (OH), 1701 (COOH), 1434 (N=N); δ_H (90 MHz; $CDCl_3$) 3.90 (s, 2H, CH_2CO_2H), 7.32 - 7.55 (m, 5H, ArCH), 9.50 (s, 1H, COOH). 3b: (Found: C, 42.32; H, 3.24; N, 8.82. $C_{11}H_{10}N_2O_2SSe$ requires C, 42.18; H, 3.22; N, 8.94%); ν_{max} (KBr)/cm^{-1} 3605 (OH), 1712 (COOH), 1430 (N=N); δ_H (90 MHz; $CDCl_3$) 2.24 (s, 3H, CH_3), 3.86 (s, 2H, CH_2CO_2H), 7.29 - 7.54 (m, 4H, ArCH), 9.47 (s, 1H, COOH). 3c: (Found: C, 41.74; H, 3.60; N, 8.00. $C_{12}H_{12}N_2O_3SSe$ requires C, 41.99; H, 3.52; N, 8.16%); ν_{max} (KBr)/cm^{-1} 3595 (OH), 1705 (COOH), 1435 (N=N); δ_H (90 MHz; $CDCl_3$) 1.21 (t, 3H, OCH_2CH_3), 3.85 (s, 2H, CH_2CO_2H), 3.96-4.04 (q, 2H, OCH_2CH_3), 7.20-7.45

(m, 4H, ArCH), 9.48 (s, 1H, COOH). 3d: (Found: C, 36.18; H, 2.07; N, 8.52. $C_{10}H_7ClN_2O_2SSe$ requires C, 36.00; H, 2.11; N, 8.40%); ν_{max} (KBr)/cm^{-1} 3602 (OH), 1720 (COOH), 1442 (N=N); δ_H (90 MHz; $CDCl_3$) 3.88 (s, 2H, CH_2CO_2H), 7.35-7.57 (m, 4H, ArCH), 9.52 (s, 1H, COOH). 3e: (Found: C, 31.92; H, 1.89; N, 7.28. $C_{10}H_7BrN_2O_2SSe$ requires C, 31.77; H, 1.87; N, 7.41%); ν_{max} (KBr)/cm^{-1} 3587 (OH), 1718 (COOH), 1442 (N=N); δ_H (90 MHz; $CDCl_3$) 3.86 (s, 2H, CH_2CO_2H), 7.40-7.58 (m, 4H, ArCH), 9.52 (s, 1H, COOH). 3f: (Found: C, 34.72; H, 2.00; N, 12.12. $C_{10}H_7N_3O_4SSe$ requires C, 34.89; H, 2.05; N, 12.21%); ν_{max} (KBr)/cm^{-1} 3590 (OH), 1710 (COOH), 1437 (N=N); δ_H (90 MHz; $CDCl_3$) 3.88 (s, 2H, CH_2CO_2H), 7.38-7.54 (m, 4H, ArCH), 9.50 (s, 1H, COOH).

Pyrolysis of 3: General Procedure: A solution of 1.0 mmol of **3** and 750 mg of copper powder in CH_2Cl_2 was slowly heated to evaporate the solvent in such a way that the solid material covered the walls of the flask. The pyrolysis was carried out under nitrogen atmosphere at 180-200°C in an oil bath for 15 min. Later 15 ml of CCl_4 was added to the contents and chromatographed on silicagel to get pure (a) 2-arylethynylsulfanylacetic acids (**4**). 4a: (Found: C, 62.60; H, 4.28. $C_{10}H_8O_2S$ requires C, 62.48; H, 4.19%); ν_{max} (KBr)/cm^{-1} 3411 (OH), 2149 (C≡C), 1719 (COOH); δ_H (90 MHz; $CDCl_3$) 3.90 (s, 2H, CH_2CO_2H), 7.25-7.47 (m, 5H, ArCH), 9.51 (s, 1H, COOH). 4b: (Found: C, 63.89; H, 5.03. $C_{11}H_{10}O_2S$ requires C, 64.05; H, 4.89%); ν_{max} (KBr)/cm^{-1} 3415 (OH), 2200 (C≡C), 1722 (COOH); δ_H (90 MHz; $CDCl_3$) 2.20 (s, 3H, CH_3), 3.91 (s, 2H, CH_2CO_2H), 7.20-7.44 (m, 4H, ArCH), 9.50 (s, 1H, COOH). 4c: (Found: C, 61.14; H, 5.19. $C_{12}H_{12}O_3S$ requires C, 61.00; H, 5.12%); ν_{max} (KBr)/cm^{-1} 3430 (OH), 2168 (C≡C), 1720 (COOH); δ_H (90 MHz; $CDCl_3$) 1.19 (t, 3H, OCH_2CH_3), 3.88 (s, 2H, CH_2CO_2H), 3.95-4.02 (q, 2H, OCH_2CH_3), 7.18-7.37 (m, 4H, ArCH), 9.52 (s, 1H, COOH). 4d: (Found: C, 53.08; H, 3.07. $C_{10}H_7ClO_2S$ requires C, 52.99; H, 3.11%); ν_{max} (KBr)/cm^{-1} 3520 (OH), 2198 (C≡C), 1718 (COOH); δ_H (90 MHz; $CDCl_3$) 3.89 (s, 2H, CH_2CO_2H), 7.24-7.45 (m, 4H, ArCH), 9.54 (s, 1H, COOH). 4e: (Found: C, 44.22; H, 2.55. $C_{10}H_7BrO_2S$ requires C, 44.30; H, 2.60%); ν_{max} (KBr)/cm^{-1} 3532 (OH), 2200 (C≡C), 1721 (COOH); δ_H (90 MHz; $CDCl_3$) 3.92 (s, 2H, CH_2CO_2H), 7.30-7.54 (m, 4H, ArCH), 9.53 (s, 1H, COOH). 4f: (Found: C, 50.75; H, 2.98. $C_{10}H_7NO_4S$ requires C, 50.63; H, 2.97%); ν_{max} (KBr)/cm^{-1} 3518 (OH), 2210 (C≡C), 1725 (COOH); δ_H (90 MHz; $CDCl_3$) 3.92 (s, 2H, CH_2CO_2H), 7.28-7.55 (m, 4H, ArCH), 9.54 (s, 1H, COOH). (b) 2,5-diarylselenophene-3,4-bis (sulfanylacetic acid) (**5**). 5a: ν_{max} (KBr)/cm^{-1} 3450 (OH), 1715 (COOH); δ_H (90 MHz; $CDCl_3$) 4.02 (s, 4H, SCH_2CO_2H), 7.02-7.45 (m, 10H, ArCH), 9.50 (s, 2H, COOH).

4-Aryl-1,2,3-selenadiazolyl-5-sulfonylacetic acids (6): General Procedure: To a solution of **3** (1.0 mmol) in 100 ml of glacial acetic acid 120 ml of 30% H_2O_2 was added. The reaction mixture was kept aside at room temperature for 30-36 hr and poured into ice-cold water. The solid separated was filtered, dried ($MgSO_4$) and column chromatographed to get pure **6**. 6a: (Found: C, 36.15; H, 2.48; N, 8.34. $C_{10}H_8N_2O_4SSe$ requires C, 36.26; H, 2.43; N, 8.46%); ν_{max} (KBr)/cm^{-1} 3415 (OH), 1695 (COOH), 1430 (N=N), 1310, 1140 (SO_2); δ_H (90 MHz; DMSO) 4.10 (s, 2H, CH_2CO_2H), 7.04-7.27 (m, 5H, ArCH), 9.42 (s, 1H, COOH). 6b: (Found: C, 38.20; H, 2.81; N, 8.19. $C_{11}H_{10}N_2O_4SSe$ requires C, 38.27; H, 2.92; N, 8.11%); ν_{max} (KBr)/cm^{-1} 3425 (OH), 1698 (COOH), 1432 (N=N), 1315, 1135 (SO_2); δ_H (90 MHz; DMSO) 2.18 (s, 3H, CH_3), 4.04 (s, 2H, CH_2CO_2H), 7.01-7.26 (m, 4H, ArCH), 9.41 (s, 1H, COOH). 6c: (Found: C, 38.52; H, 3.25; N, 7.52. $C_{12}H_{12}N_2O_5SSe$ requires C, 38.41; H, 3.22; N, 7.46%); ν_{max} (KBr)/cm^{-1} 3450 (OH), 1700 (COOH), 1434 (N=N), 1320, 1145 (SO_2); δ_H (90 MHz; DMSO) 1.20 (t, 3H, OCH_2CH_3), 3.89-4.02 (q, 2H, OCH_2CH_3), 4.05 (s, 2H, CH_2CO_2H), 6.98-7.30 (m, 4H, ArCH), 9.45 (s, 1H, COOH). 6d: (Found: C, 33.00; H, 1.97; N, 7.60. $C_{10}H_7ClN_2O_4SSe$ requires C, 32.85; H, 1.93;

N, 7.66%); ν_{max} (KBr)/cm^{-1} 3495 (OH), 1702 (COOH), 1440 (N=N), 1315, 1140 (SO_2); δ_H (90 MHz; DMSO) 4.10 (s, 2H, CH_2CO_2H), 7.05-7.32 (m, 4H, ArCH), 9.52 (s, 1H, COOH). 6e: (Found: C, 29.38; H, 1.65; N, 6.66. $C_{10}H_7BrN_2O_4SSe$ requires C, 29.29; H, 1.72; N, 6.83%); ν_{max} (KBr)/cm^{-1} 3512 (OH), 1710 (COOH), 1442 (N=N), 1325, 1120 (SO_2); δ_H (90 MHz; DMSO) 4.08 (s, 2H, CH_2CO_2H), 7.12-7.34 (m, 4H, ArCH), 9.50 (s, 1H, COOH). 6f: (Found: C, 32.04; H, 1.91; N, 11.00. $C_{10}H_7N_3O_6SSe$ requires C, 31.93; H, 1.88; N, 11.17%); ν_{max} (KBr)/cm^{-1} 3510 (OH), 1715 (COOH), 1436 (N=N), 1320, 1115 (SO_2); δ_H (90 MHz; DMSO) 4.12 (s, 2H, CH_2CO_2H), 7.02-7.35 (m, 4H, ArCH), 9.51 (s, 1H, COOH).

Pyrolysis of 6: General Procedure: It was done following the same procedure as for **3**. The TLC indicates the formation of only one product, thus the possibility of a dimerized product has been ruled out. Instead, only a pure 2-arylethynylsulfonylacetic acids (7) was obtained. 7a: (Found: C, 53.72; H, 3.72. $C_{10}H_8O_4S$ requires C, 53.56; H, 3.60%); ν_{max} (KBr)/cm^{-1} 3410 (OH), 2200 (C≡C), 1700 (COOH), 1315, 1145 (SO_2); δ_H (90 MHz; $CDCl_3$) 4.20 (s, 2H, CH_2CO_2H), 6.98-7.25 (m, 5H, ArCH), 9.81 (s, 1H, COOH). 7b: (Found: C, 55.25; H, 4.25. $C_{11}H_{10}O_4S$ requires C, 55.45; H, 4.23%); ν_{max} (KBr)/cm^{-1} 3408 (OH), 2210 (C≡C), 1704 (COOH), 1315, 1125 (SO_2); δ_H (90 MHz; $CDCl_3$) 2.22 (s, 3H, CH_3), 4.15 (s, 2H, CH_2CO_2H), 6.94-7.27 (m, 4H, ArCH), 9.75 (s, 1H, COOH). 7c: (Found: C, 54.00; H, 4.54. $C_{12}H_{12}O_5S$ requires C, 53.72; H, 4.51%); ν_{max} (KBr)/cm^{-1} 3450 (OH), 2194 (C≡C), 1700 (COOH), 1320, 1125 (SO_2); δ_H (90 MHz; $CDCl_3$) 1.94 (t, 3H, OCH_2CH_3), 3.85-4.00 (q, 2H, OCH_2CH_3), 4.12 (s, 2H, CH_2CO_2H), 6.85-7.10 (m, 4H, ArCH), 9.68 (s, 1H, COOH). 7d: (Found: C, 46.31; H, 2.66. $C_{10}H_7ClO_4S$ requires C, 46.43; H, 2.73%); ν_{max} (KBr)/cm^{-1} 3495 (OH), 2205 (C≡C), 1705 (COOH), 1325, 1140 (SO_2); δ_H (90 MHz; $CDCl_3$) 4.14 (s, 2H, CH_2CO_2H), 7.10-7.35 (m, 4H, ArCH), 9.79 (s, 1H, COOH). 7e: (Found: C, 39.48; H, 2.37. $C_{10}H_7BrO_4S$ requires C, 39.62; H, 2.33%); ν_{max} (KBr)/cm^{-1} 3490 (OH), 2210 (C≡C), 1704 (COOH), 1315, 1125 (SO_2); δ_H (90 MHz; $CDCl_3$) 4.22 (s, 2H, CH_2CO_2H), 7.02-7.34 (m, 4H, ArCH), 9.62 (s, 1H, COOH). 7f: (Found: C, 44.72; H, 2.50. $C_{10}H_7NO_6S$ requires C, 44.61; H, 2.62%); ν_{max} (KBr)/cm^{-1} 3500 (OH), 2208 (C≡C), 1705 (COOH), 1310, 1145 (SO_2); δ_H (90 MHz; $CDCl_3$) 4.18 (s, 2H, CH_2CO_2H), 7.12-7.40 (m, 4H, ArCH), 9.65 (s, 1H, COOH).

4-Aryl-1,2,3-selenadiazolyl-5-styrylsulfones (8): General Procedure: To a solution of 1.0 mmol of **6** in 10 ml of glacial acetic acid, 1.0 mmol of araldehyde and a catalytic amount of benzylamine was added and refluxed for 3-4 hr. The cooled reaction mixture was diluted with ether. The solid if any separated was filtered. The ethereal layer was washed successively with $NaHCO_3$, $NaHSO_3$, dilute HCl and finally with water. The solvent was removed under rotary evaporator to get **8** which was purified by column chromatography. 8a: (Found: C, 51.12; H, 3.35; N, 7.65. $C_{16}H_{12}N_2O_2SSe$ requires C, 51.21; H, 3.22; N, 7.46%); ν_{max} (KBr)/cm^{-1} 1620 (C=C), 1428 (N=N), 1300, 1135 (SO_2); δ_H (90 MHz; DMSO) 6.70 (d, 1H, J=16.2 Hz, -SO_2-CH=CH-Ar), 7.02-7.45 (m, 11H, ArCH, -SO_2-CH=CH-Ar). 8b: (Found: C, 52.20; H, 3.50; N, 7.12. $C_{17}H_{14}N_2O_2SSe$ requires C, 52.45; H, 3.62; N, 7.20%); ν_{max} (KBr)/cm^{-1} 1618 (C=C), 1432 (N=N), 1310, 1135 (SO_2); δ_H (90 MHz, DMSO) 2.25 (s, 3H, CH_3), 6.64 (d, 1H, J=16.0 Hz, -SO_2-CH=CH-Ar), 6.95-7.42 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 8c: (Found: C, 46.78; H, 2.75; N, 6.70. $C_{16}H_{11}ClN_2O_2SSe$ requires C, 46.90; H, 2.71; N, 6.84%); ν_{max} (KBr)/cm^{-1} 1625 (C=C), 1438 (N=N), 1320, 1145 (SO_2); δ_H (90 MHz; DMSO) 6.72 (d, 1H, J=16.0 Hz, -SO_2-CH=CH-Ar), 6.98-7.45 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 8d: (Found: C, 52.32; H, 3.60; N, 7.34. $C_{17}H_{14}N_2O_2SSe$ requires C, 52.45; H, 3.62; N, 7.20%); ν_{max} (KBr)/cm^{-1} 1624 (C=C), 1440 (N=N), 1315, 1140 (SO_2); δ_H (90 MHz; DMSO) 2.18 (s, 3H, CH_3), 6.68 (d, 1H, J=16.1 Hz, -SO_2-CH=CH-Ar), 7.05-7.42 (m, 10H, ArCH, -SO_2-CH=CH-

Ar). 8e: (Found: C, 48.14; H, 3.14; N, 6.65. $C_{17}H_{13}ClN_2O_2SSe$ requires C, 48.18; H, 3.09; N, 6.61%). 8f: (Found: C, 51.40; H, 4.00; N, 6.74. $C_{18}H_{16}N_2O_3SSe$ requires C, 51.55; H, 3.85; N, 6.68%); ν_{max} (KBr)/cm^{-1} 1623 (C=C), 1442 (N=N), 1325, 1135 (SO_2); δ_H (90 MHz; DMSO) 1.22 (t, 3H, OCH_2CH_3), 3.89-4.00 (q, 2H, OCH_2CH_3), 6.65 (d, 1H, J=16.0 Hz, -SO_2-CH=CH-Ar), 7.05-7.42 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 8g: (Found: C, 46.99; H, 2.72; N, 6.75. $C_{16}H_{11}ClN_2O_2SSe$ requires C, 46.90; H, 2.70; N, 6.84%); ν_{max} (KBr)/cm^{-1} 1625 (C=C), 1438 (N=N), 1330, 1125 (SO_2); δ_H (90 MHz; DMSO) 6.75 (d, 1H, J=16.2 Hz, -SO_2-CH=CH-Ar), 7.08-7.40 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 8h: (Found: C, 43.46; H, 2.28; N, 6.20. $C_{16}H_{10}Cl_2N_2O_2SSe$ requires C, 43.26; H, 2.27; N, 6.31%). 8i: (Found: C, 42.19; H, 2.49; N, 6.05. $C_{16}H_{11}BrN_2O_2SSe$ requires C, 42.31; H, 2.44; N, 6.17%); ν_{max} (KBr)/cm^{-1} 1605 (C=C), 1435 (N=N), 1320, 1140 (SO_2); δ_H (90 MHz; DMSO) 6.71 (d, 1H, J=16.1 Hz, -SO_2-CH=CH-Ar), 7.02-7.43 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 8j: (Found: C, 45.75; H, 2.70; N, 9.72. $C_{16}H_{11}N_3O_4SSe$ requires C, 45.72; H, 2.64; N, 10.00%); ν_{max} (KBr)/cm^{-1} 1620 (C=C), 1445 (N=N), 1330, 1140 (SO_2); δ_H (90 MHz; DMSO) 6.69 (d, 1H, J=16.0 Hz, -SO_2-CH=CH-Ar), 6.98-7.45 (m, 10H, ArCH, -SO_2-CH=CH-Ar).

2-Arylethenyl-2'-arylethynyl sulfones (9): General Procedure: Pyrolysis of **8** was carried out in a similar way as that of **3** to get **9**. The latter was also obtained from **7** by Knoevenagel condensation as per the procedure given for the preparation of **8**. 9a: (Found: C, 71.80; H, 4.60. $C_{16}H_{12}O_2S$ requires C, 71.62; H, 4.51%); ν_{max} (KBr)/cm^{-1} 2180 (C≡C), 1620 (C=C), 1325, 1140 (SO_2); δ_H (90 MHz; $CDCl_3$) 6.91 (d, 1H, J=16.4 Hz, -SO_2-CH=CH-Ar), 7.09-7.40 (m, 11H, ArCH, -SO_2-CH=CH-Ar). 9b: (Found: C, 72.15; H, 5.02. $C_{17}H_{14}O_2S$ requires C, 72.31; H, 5.00%); ν_{max} (KBr)/cm^{-1} 2182 (C≡C), 1620 (C=C), 1320, 1135 (SO_2); δ_H (90 MHz; $CDCl_3$) 2.19 (s, 3H, CH_3), 6.82 (d, 1H, J=16.2 Hz, -SO_2-CH=CH-Ar), 6.98-7.38 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9c: (Found: C, 63.55; H, 3.59. $C_{16}H_{11}ClO_2S$ requires C, 63.47; H, 3.66%); ν_{max} (KBr)/cm^{-1} 2202 (C≡C), 1608 (C=C), 1320, 1135 (SO_2); δ_H (90 MHz; $CDCl_3$) 6.93 (d, 1H, J=16.3 Hz, -SO_2-CH=CH-Ar), 7.09-7.43 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9d: (Found: C, 72.47; H, 5.05. $C_{17}H_{14}O_2S$ requires C, 72.31; H, 5.00%); ν_{max} (KBr)/cm^{-1} 2185 (C≡C), 1600 (C=C), 1335, 1140 (SO_2); δ_H (90 MHz; $CDCl_3$), 2.20 (s, 3H, CH_3), 6.85 (d, 1H, J=16.2 Hz, -SO_2-CH=CH-Ar), 7.00-7.35 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9e: (Found: C, 64.55; H, 4.08. $C_{17}H_{13}ClO_2S$ requires C, 64.45; H, 4.14%). 9f: (Found: C, 69.00; H, 5.10. $C_{18}H_{16}O_3S$ requires C, 69.21; H, 5.16%); ν_{max} (KBr)/cm^{-1} 2180 (C≡C), 1624 (C=C), 1315, 1145 (SO_2); δ_H (90 MHz; $CDCl_3$) 1.20 (t, 3H, OCH_2CH_3), 3.96-4.02 (q, 2H, OCH_2CH_3), 6.85 (d, 1H, J=16.4 Hz, -SO_2-CH=CH-Ar), 6.95-7.40 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9g: (Found: C, 63.55; H, 3.72. $C_{16}H_{11}ClO_2S$ requires C, 63.47; H, 3.66%); ν_{max} (KBr)/cm^{-1} 2200 (C≡C), 1625 (C=C), 1320, 1140 (SO_2); δ_H (90 MHz; $CDCl_3$) 6.95 (d, 1H, J=16.3 Hz, -SO_2-CH=CH-Ar), 7.05-7.42 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9h: (Found: C, 56.82; H, 2.92. $C_{16}H_{10}Cl_2O_2S$ requires C, 56.99; H, 2.99%). 9i: (Found: C, 55.21; H, 3.14. $C_{16}H_{11}BrO_2S$ requires C, 55.35; H, 3.19%); ν_{max} (KBr)/cm^{-1} 2198 (C≡C), 1620 (C=C), 1325, 1120 (SO_2); δ_H (90 MHz; $CDCl_3$) 6.93 (d, 1H, J=16.2 Hz, -SO_2-CH=CH-Ar), 7.00-7.41 (m, 10H, ArCH, -SO_2-CH=CH-Ar). 9j: (Found: C, 61.45; H, 3.48. $C_{16}H_{11}NO_4S$ requires C, 61.33; H, 3.54%); ν_{max} (KBr)/cm^{-1} 2202 (C≡C), 1625 (C=C), 1320, 1145 (SO_2); δ_H (90 MHz; $CDCl_3$) 6.96 (d, 1H, J=16.4 Hz, -SO_2-CH=CH-Ar), 7.03-7.42(m, 10H, ArCH, -SO_2-CH=CH-Ar).

1,4-Diarylbut-1-en-3-ynes (10): General Procedure: A mixture of 1.0 mmol of **9**, 0.1 mmol of dichlorotris (triphenylphosphine)ruthenium in dry benzene was refluxed for 24 hr in an oil bath while passing HCl gas. After cooling, the catalyst was filtered off. The solvent was removed under reduced pressure. The product obtained was purified by recrystallization. 10a: mp: 86-87 (Lit.87[8c], 94-95[8d]), (Found: C, 93.92;

Table 1. Physical data of the compounds 2-7

Compound	Ar	M.P. °C	Yield (%)
2a	C_6H_5	202-203	72
2b	4-$CH_3C_6H_4$	206-207.5	74
2c	4-$OC_2H_5C_6H_4$	198-199	68
2d	4-ClC_6H_4	204-205	76
2e	4-BrC_6H_4	214-215.5	70
2f	4-$NO_2C_6H_4$	212-213	66
3a	C_6H_5	136-137	62
3b	4-$CH_3C_6H_4$	120-121	60
3c	4-$OC_2H_5C_6H_4$	128-129	58
3d	4-ClC_6H_4	138-139	72
3e	4-BrC_6H_4	148-149	64
3f	4-$NO_2C_6H_4$	158-159.5	60
4a	C_6H_5	78-79	58
4b	4-$CH_3C_6H_4$	90-91	55
4c	4-$OC_2H_5C_6H_4$	69-70	52
4d	4-ClC_6H_4	101-102	50
4e	4-BrC_6H_4	105-106	54
4f	4-$NO_2C_6H_4$	113-114	55
6a	C_6H_5	167-168	84
6b	4-$CH_3C_6H_4$	159-160	78
6c	4-$OC_2H_5C_6H_4$	164-165	80
6d	4-ClC_6H_4	175-176	85
6e	4-BrC_6H_4	184-185	82
6f	4-$NO_2C_6H_4$	193-194.5	84
7a	C_6H_5	112-113	72
7b	4-$CH_3C_6H_4$	132-133	70
7c	4-$OC_2H_5C_6H_4$	126-127	74
7d	4-ClC_6H_4	144-145	68
7e	4-BrC_6H_4	148-149	71
7f	4-$NO_2C_6H_4$	152-153	66

Table 2. Physical data of the compounds 8-10

Compound	Ar	Ar′	M.P. °C	Yield (%)
8a	C_6H_5	C_6H_5	62-63	73
8b	C_6H_5	4-$CH_3C_6H_4$	129-130	68
8c	C_6H_5	4-ClC_6H_4	99-100	74
8d	4-$CH_3C_6H_4$	C_6H_5	107-108	62
8e	4-$CH_3C_6H_4$	4-ClC_6H_4	124-125	66
8f	4-$OC_2H_5C_6H_4$	C_6H_5	94-95	70
8g	4-ClC_6H_4	C_6H_5	89-90	67
8h	4-ClC_6H_4	4-ClC_6H_4	134-135	75
8i	4-BrC_6H_4	C_6H_5	93-94	72
8j	4-$NO_2C_6H_4$	C_6H_5	112-113	64
9a	C_6H_5	C_6H_5	68-69	70
9b	C_6H_5	4-$CH_3C_6H_4$	74-75	73
9c	C_6H_5	4-ClC_6H_4	82-83	76
9d	4-$CH_3C_6H_4$	C_6H_5	72-73	68
9e	4-$CH_3C_6H_4$	4-ClC_6H_4	91-92	66
9f	4-$OC_2H_5C_6H_4$	C_6H_5	67-68	69
9g	4-ClC_6H_4	C_6H_5	80-81	74
9h	4-ClC_6H_4	4-ClC_6H_4	96-97	78
9i	4-BrC_6H_4	C_6H_5	95-96	62
9j	4-$NO_2C_6H_4$	C_6H_5	102-103	60
10a	C_6H_5	C_6H_5	86-87	62
10b	C_6H_5	4-$CH_3C_6H_4$	92-93	60
10c	C_6H_5	4-ClC_6H_4	89-90	63
10d	4-$CH_3C_6H_4$	C_6H_5	75-76	65
10e	4-$CH_3C_6H_4$	4-ClC_6H_4	97-98	62
10f	4-$OC_2H_5C_6H_4$	C_6H_5	82-83	60
10g	4-ClC_6H_4	C_6H_5	88-89	69
10h	4-ClC_6H_4	4-ClC_6H_4	105-106	68
10i	4-BrC_6H_4	C_6H_5	113-114	67
10j	4-$NO_2C_6H_4$	C_6H_5	108-109	64

H, 5.72. $C_{16}H_{12}$ requires C, 94.08; H, 5.91%); ν_{max} (KBr)/cm^{-1} 2180 (C≡C), 1605 (C=C); δ_H (90 MHz, $CDCl_3$) 6.21 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 6.82 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 7.02-7.34 (m, 10H, ArCH). 10b: (Found: C, 93.26; H, 6.31. $C_{17}H_{14}$ requires C, 93.54; H, 6.46%); ν_{max} (KBr)/cm^{-1} 2195 (C≡C), 1600 (C=C); δ_H (90 MHz; $CDCl_3$) 2.18 (s, 3H, CH_3), 6.18 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 6.84 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 6.99-7.38 (m, 9H, ArCH). 10c: (Found: C, 80.30; H, 4.75. $C_{16}H_{11}Cl$ requires C, 80.50; H, 4.64%); ν_{max} (KBr)/cm^{-1} 2204 (C≡C), 1605 (C=C); δ_H (90 MHz; $CDCl_3$) 6.27 (d, 1H, J=16.3 Hz, Ar-C≡C-CH=CH-Ar), 6.94 (d, 1H, J=16.3 Hz, Ar-C≡C-CH=CH-Ar), 7.04-7.35 (m, 9H, ArCH). 10d: (Found: C, 93.69; H, 6.60. $C_{17}H_{14}$ requires C, 93.54; H, 6.46%); ν_{max} (KBr)/cm^{-1} 2200 (C≡C), 1612 (C=C); δ_H (90 MHz; $CDCl_3$) 2.19 (s, 3H, CH_3), 6.22 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 6.89 (d, 1H, J=16.2 Hz, Ar-C≡C-CH=CH-Ar), 6.97-7.42 (m, 9H, ArCH). 10e: (Found: C, 80.92; H, 5.00. $C_{17}H_{13}Cl$ requires C, 80.79; H, 5.18%). 10f: (Found: C, 86.94; H, 6.32. $C_{18}H_{16}O$ requires C, 87.06; H, 6.49%); ν_{max} (KBr)/cm^{-1} 2194 (C≡C), 1605 (C=C); δ_H (90 MHz; $CDCl_3$) 1.21 (t, 3H, OCH_2CH_3), 3.98-4.03 (q, 2H, OCH_2CH_3) 6.20 (d, 1H, J=16.0 Hz, Ar-C≡C-CH=CH-Ar), 6.85 (d, 1H, J=16.0 Hz, Ar-C≡C-CH=CH-Ar), 6.96-7.38 (m, 9H, ArCH). 10g: (Found: C, 80.62; H, 4.72. $C_{16}H_{11}Cl$ requires C, 80.50; H, 4.64%); ν_{max} (KBr)/cm^{-1} 2192 (C≡C), 1604 (C=C); δ_H (90 MHz; $CDCl_3$) 6.24 (d, 1H, J=16.4 Hz, Ar-C≡C-CH=CH-Ar), 6.85 (d, 1H, J=16.4 Hz, Ar-C≡C-CH=CH-Ar), 7.00-7.38 (m, 9H, ArCH). 10h: (Found: C, 70.20; H, 3.72. $C_{16}H_{10}Cl_2$ requires C, 70.35; H, 3.69%). 10i: (Found: C, 67.70; H, 3.90. $C_{16}H_{11}Br$ requires C, 67.87; H, 3.92%); ν_{max} (KBr)/cm^{-1} 2200 (C≡C), 1602 (C=C); δ_H (90 MHz; $CDCl_3$) 6.25 (d, 1H, J=16.3 Hz, Ar-C≡C-CH=CH-Ar), 6.82 (d, 1H, J=16.3 Hz, Ar-C≡C-CH=CH-Ar), 7.05-7.40 (m, 9H, ArCH). 10j: (Found: C, 76.92; H, 4.52. $C_{16}H_{11}NO_2$ requires C, 77.10; H, 4.45%); ν_{max} (KBr)/cm^{-1} 2195 (C≡C), 1600 (C=C); δ_H (90 MHz; $CDCl_3$) 6.22 (d, 1H, J=16.4 Hz, Ar-C≡C-CH=CH-Ar), 6.86 (d, 1H, J=16.4 Hz, Ar-C≡C-CH=CH-Ar), 7.02-7.45 (m, 9H, ArCH).

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REFERENCES

1. (a) Yamamura, H.; Kleffel, D.; Blount, J.F.; Hunkler, D.; Jodaro, L.J.; Otto, H.H. *Liebigs Ann. Chem.* **1984,** *5*, 1013; (b) Bhaskar Reddy, D.; Reddy, S.; Padmavathi, V.; Ramana Reddy, M.V. *Sulfur Lett.* **1990**, *11*, 281; (c) Bhaskar Reddy, D.; Padmavathi, V.; Reddy, S.; Ramana Reddy, M.V. *ibid,* **1991,** *13*, 123; (d) Bhaskar Reddy, D.; Padmavathi, V.; Seenaiah, B.; Padmaja, A. *Heteroatom Chem.* **1993,** *4*, 55.
2. (a) Baliah, V.; Anantapadmanabhan, S. *Indian J. Chem.* **1971,** *9*, 1167; (b) Yamamura, H.; Otto, H.H. *Arch. Pharm.* **1978,** *311*, 762; (c) Takikawa, Y.; Shimida, K.; Matsumoto, H.; Tanabe, H.; Takizawa, S. *Chem. Lett.* **1983,** 1351; (d) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985,** *50*, 5045; (e) Ramana Reddy, M.V.; Manjubhashini, A.B.; Reddy, S.; Ramana Reddy, P.V.; Bhaskar Reddy, D. *Syn. Commun.* **1991,** *21*, 1589.
3. (a) Ramana Reddy, M.V.; Reddy, S. *Synthesis*, **1984,** 322; (b) Ramana Reddy, M.V.; Reddy, S.; Bhaskar Reddy, D.; Padmavathi, V. *Syn. Commun.* **1989,** *19*, 1101.
4. (a) Nightingale,D.; Wadsworth, F.T. *J. Am. Chem. Soc.* **1945,** *67*, 416; (b) Nightingale, D.; Wadsworth, F.T. *ibid,* **1947**, *69*, 1181; (c) Sladkov, A.M.; Golding, I.R. *Khim. Atsetilena Tr. Vses,*

Konf 3rd Ed, Petrov, A.A. Nauka, Moscow, USSR (1968); (d) Rampazzo, L.; Inesri,A.; Zeppa, A. *J. Electroanal. Chem.* **1977,** *76,* 175; (e) Tohda, Y.; Sonogashira, K.; Hagihara, N. *Synthesis,* **1977,** 777.

5. (a) Lalezari, I.; Shafiee, A.; Yalpani, M. *Angew. Chem.* **1970,** *82,* 484; (b) Lalezari, I.; Shafiee, A.; Yalpani, M. *Angew Chem. Int. Ed. Engl.* **1970,** *9,* 464; (c) Meier, H.; Peterson, H.; Kolshorn, H. *Chem. Ber,* **1980,** *113,* 2398; (d) Gleiter, R.; Kartz, D.; Schafer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991,** *113,* 9258.
6. Bhaskar Reddy, D.; Muralidhar Reddy, M.; Ramana Reddy, P.V. *Indian J. Chem.* **1993,** *32B,* 1018.
7. Lalezari, I.; Shafiee, A. *Tetrahedron Lett.* **1969,** *58,* 5105.
8. (a) Hatnaka, Y.; Hiyama, T. *J. Org. Chem.* **1988,** *53,* 918; (b) Daddoub, M.J.; Daddoub, V.B.; Comasseto, J.V. *Tetrahedron Lett.* **1992,** *33,* 2261; (c) Masayuki, H.; Yuzuru, M.; Akira, A. *Bull. Chem. Soc. Jpn.,* **1983,** *56,* 2855; (d) Trofimov, B.A.; Sobenina, L.N.; Petrova, O.V.; Mikhaleva, A.I. *Dokl. Akad. Nauk.* **1993,** *328,* 61.
9. Masanori, K.; Tomoyuki, K.; Hiroshi, O.; Toshihiko, M. *Bull. Chem. Soc. Jpn.,* **1993,** *66,* 3522.

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