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Halo-heterocyclization of *trans*-5-phenyl-3-cinnamylsulfanyl[1,2,4]triazine into [1,3]thiazino[3,2-*b*][1,2,4]triazin-9-ium systems

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trans-3-Cinnamylsulfanyl-5-phenyl-1,2,4-triazine **2**. To a solution of 5-phenyl[1,2,4]-triazine-3-thione (0.189 g, 1 mmol) in acetone (10 ml), triethylamine (2 ml) and cinnamyl chloride (0.14 ml, 1 mmol) were added. The reaction mixture was stirred for 12 h, the precipitate formed was filtered off. The solvent was distilled from the filtrate, the residue was treated with water and extracted with dichloromethane. Yield 90%, m.p. 79–80 °C. ¹H NMR (CDCl₃) δ: 4.18 (dd, 2H, SCH₂, ³*J* 7.2, ⁴*J* 1.1 Hz), 6.44 (dt, 1H, -CH=, ³*J* 15.7, ⁴*J* 7.2 Hz), 6.76 (d, 1H, =CHPh, ³*J* 15.7 Hz), 7.23–7.39 (m, 5H, Ph-3'), 7.56–7.65 (m, 3H, Ph-5), 8.17–8.20 (m, 2H, Ph-5), 9.41 (s, 1H, H-6). ¹³C NMR (CDCl₃) δ: 33.36 (C-1'), 124.00 (C-3'), 126.45 ((*o*-Ph)-5), 127.72 ((*p*-Ph)-3'), 127.78 ((*o*-Ph)-3'), 128.59 ((*m*-Ph)-3'), 129.42 ((*p*-Ph)-5), 132.76 ((*m*-Ph)-5), 133.15 ((*i*-Ph)-5), 133.78 (C-2'), 136.60 ((*i*-Ph)-3'), 142.16 (C-5), 154.79 (C-6), 173.00 (C-3). Found (%): C, 70.53 %; H, 4.68 %. Calculated for C₁₈H₁₅N₃S (%): C, 70.79 %; H, 4.95 %.

(7*r*,8*t*)-7-Bromo-3,8-diphenyl-7,8-dihydro-6*H*-[1,3]thiazino[3,2-*b*][1,2,4]triazin-9-ium bromide **4**. To a stirred and ice-cooled solution of cinnamyl sulfide **2** (95 mg, 0.31 mmol) in dichloromethane (10 ml), solution of bromine (0.03 ml, 0.62 mmol) in dichloromethane (5 ml) was added dropwise. The mixture was left to stand at room temperature for 24 h. The produced orange yellow crystals were filtered off and dried. Yield 0.126 g (87 %), m.p. 121–122 °C. ¹H NMR (DMSO-*d*₆) δ: 3.65 (dd, 1H, SCH₂, ²*J* 14.7, ³*J* 2.8 Hz), 3.85–3.90 (m, 1H, SCH₂), 5.73–5.77 (m., 1H, CHBr), 6.60 (d, 1H, CHPh, ³*J* 2.8 Hz), 7.44–7.49 (m, 5H, Ph-8), 7.75–7.79 (m, 2H, *m*-H_{Ph-3}), 7.91–7.94 (m., 1H, *p*-H_{Ph-3}), 8.56–8.58 (m, 2H, *o*-H_{Ph-3}), 10.11 (s, 1H, H-2). ¹³C NMR (DMSO-*d*₆) δ: 33.08 (SCH₂), 42.67 (CHBr), 75.40 (CHPh), 126.83 ((*p*-Ph)-8), 129.23 ((*o*-Ph)-3), 129.52 ((*o*-Ph)-8), 129.92 ((*p*-Ph)-3), 130.51 ((*m*-Ph)-8), 130.96 ((*m*-Ph)-3), 135.70 ((*ipso*-Ph)-3), 136.71 ((*ipso*-Ph)-8), 144.53 (C-2), 159.87 (C-3), 168.66 (C-4a). Found (%): C, 46.26 %; H, 3.05 %. Calculated for C₁₈H₁₅Br₂N₃S (%): C, 46.47 %; H, 3.25 %.

(7*r*,8*t*)-7-Iodo-3,8-diphenyl-7,8-dihydro-6*H*-[1,3]thiazino[3,2-*b*][1,2,4]triazin-9-ium triiodide **5**. To a solution of iodine (0.452 g, 1.78 mmol) in dichloromethane (15 ml), cinnamyl sulfide **2** (0.271 g, 0.89 mmol) in dichloromethane (10 ml) was added. The reaction mixture was left to stand at room temperature for 72 h. The produced precipitate was filtered and dried. Yield

0.491 g (68 %), m.p. 143-144 °C. ¹H NMR (acetone-d₆) δ: 3.96-4.00 (m, 2H, SCH₂), 5.74 (m, 1H, CHI), 6.66 (d, 1H, CHPh, ³J 4.3 Hz), 7.51-7.58 (m, 5H, Ph-8), 7.80-7.84 (m, 2H, *m*-H_{Ph-3}), 7.96-8.00 (m, 1H, *p*-H_{Ph-3}), 8.63-8.65 (m, 2H, *o*-H_{Ph-3}), 10.02 (s, 1H, H-2). ¹³C NMR (acetone-d₆) δ: 17.3 (CHI), 35.86 (SCH₂), 78.96 (CHPh), 127.82 (*p*-Ph-8), 129.54 (*o*-Ph-3), 130.53 (*o*-Ph-8), 130.81 (*p*-Ph-3), 131.14 (*m*-Ph-8), 132.02 (*m*-Ph-3), 135.74 (*ipso*-Ph-3), 136.51 (*ipso*-Ph-8), 144.70 (C-2), 161.23 (C-3), 170.56 (C-4a). Found (%): C, 26.38 %; H, 1.65 %. Calculated for C₁₈H₁₅I₄N₃S (%): C, 26.59 %; H, 1.86 %.

Main crystallographic data and results of structure refinement for (7*r*,8*t*)-7-bromo-3,8-diphenyl-7,8-dihydro-6*H*-[1,3]thiazino[3,2-*b*][1,2,4]triazin-9-ium bromide 4

Table S1 Crystal data and structure refinement

Identification code	1089_0ma_a
Empirical formula	C ₁₈ H ₁₅ N ₃ SBr ₂
Formula weight	465.21
Temperature/K	293.15
Crystal system	monoclinic
Space group	C2/c
a/Å	25.220(19)
b/Å	11.062(10)
c/Å	18.552(14)
α/°	90.00
β/°	134.79(2)
γ/°	90.00
Volume/Å ³	3673(5)
Z	8
ρ _{calc} /g cm ⁻³	1.683
μ/mm ⁻¹	4.532
F(000)	1840.0
Crystal size/mm ³	0.2 × 0.15 × 0.07
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.1 to 46.36
Index ranges	-27 ≤ h ≤ 27, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	16655
Independent reflections	2385 [R _{int} = 0.0333, R _{sigma} = 0.0179]
Data/restraints/parameters	2385/0/217
Goodness-of-fit on F ²	1.045
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0437, wR ₂ = 0.0999
Final R indexes [all data]	R ₁ = 0.0561, wR ₂ = 0.1075
Largest diff. peak/hole / e Å ⁻³	1.31/-1.51

Table S2 Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br2	C2	1.896(6)	C14	C15	1.375(12)
S1	C6	1.713(6)	C13	C12	1.332(9)
S1	C1	1.835(6)	C3	C2	1.514(8)
C11	C12	1.378(8)	C5	C21	1.486(8)
C11	C3	1.475(7)	C5	C4	1.427(8)
C11	C16	1.392(9)	C21	C26	1.390(9)
N2	N1	1.354(7)	C21	C22	1.390(9)
N2	C3	1.496(7)	C26	C25	1.388(10)
N2	C6	1.343(7)	C25	C24	1.350(11)
N3	C6	1.360(7)	C24	C23	1.352(12)
N3	C5	1.316(7)	C2	C1	1.523(9)
N1	C4	1.305(8)	C22	C23	1.391(9)
C14	C13	1.382(11)	C16	C15	1.335(10)

Table S3 Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	S1	C1	102.3(3)	N3	C5	C21	117.6(5)
C12	C11	C3	115.8(5)	N3	C5	C4	118.7(5)
C12	C11	C16	121.7(5)	C4	C5	C21	123.6(6)
C16	C11	C3	122.4(5)	C26	C21	C5	120.8(6)
N1	N2	C3	113.3(4)	C22	C21	C5	119.1(6)
C6	N2	N1	122.0(5)	C22	C21	C26	120.0(6)
C6	N2	C3	124.6(5)	C25	C26	C21	118.1(7)
C5	N3	C6	118.0(5)	C24	C25	C26	121.8(8)
C4	N1	N2	116.1(5)	C25	C24	C23	120.4(7)
C15	C14	C13	121.6(7)	C3	C2	Br2	110.6(4)
C12	C13	C14	120.8(7)	C3	C2	C1	110.9(5)
C13	C12	C11	117.7(6)	C1	C2	Br2	112.5(4)
C11	C3	N2	107.4(4)	C2	C1	S1	114.8(4)
C11	C3	C2	112.3(5)	N1	C4	C5	123.3(6)
N2	C3	C2	111.9(4)	C21	C22	C23	119.5(7)
N2	C6	S1	126.0(4)	C24	C23	C22	120.2(8)
N2	C6	N3	121.8(5)	C15	C16	C11	119.9(7)
N3	C6	S1	112.2(4)	C16	C15	C14	118.2(8)