ADDITION REACTIONS OF 8-ARYLIMINOTROPONES WITH CARBON DISULFIDE TO GIVE THIAZOLIDINE-2-THIONE AND 4-THIAZOLINE-2-THIONE DERIVATIVES

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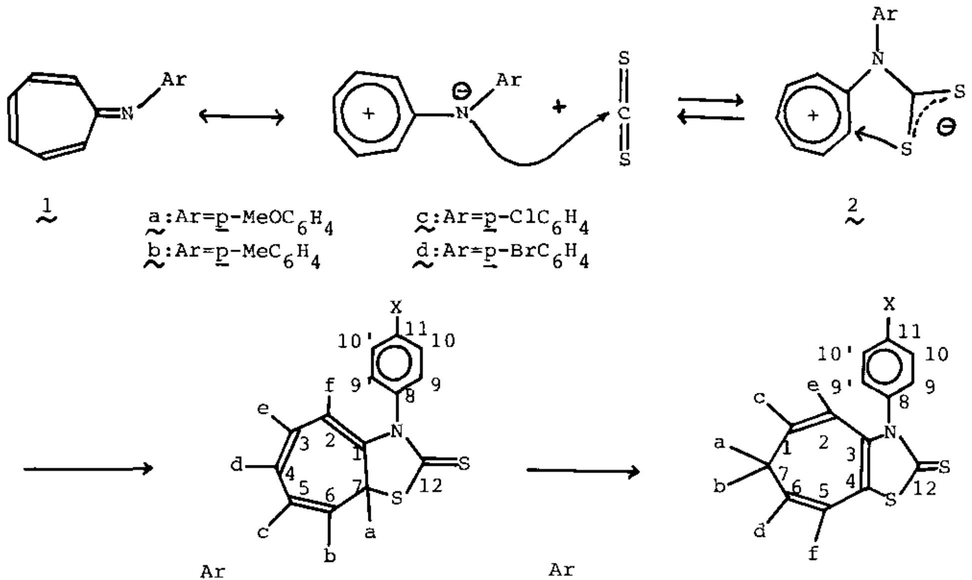
Abstract —— [8π + 2π]-Type cycloaddition reactions of 8-aryliminotropones with carbon disulfide proceeded quantitatively to afford thiazolidine-2-thione derivatives, which turned to 4-thiazoline-2-thione derivatives *via* 1,5-hydrogen shift upon further heating.

Troponoid compounds such as tropone, thiotropone, or iminotropone derivatives are well known to be nonbenzenoid aromatic compounds because of contributions of 6π-electron aromatic structures.[1] However, in spite of their aromaticities, tropones proceed thermal cycloaddition reactions through [4+2] and/or [8+2] manner with many kinds of olefins containing cumulenes such as allenes or ketenes.[2] However, not so much investigations seem to have been progressed concerning thiotropones and iminotropones. One of the reasons for these situations may be attributed to their difficult availability.[3]

As a series of our investigations on the addition reactions of troponoid compounds,[4] we studied reactions of 8-aryliminotropones[5] with carbon disulfide to obtain thiazolidine-2-thione and 4-thiazoline-2-thione derivatives, quantitatively. The results of these reactions will be reported here.

A solution of *p*-methoxyphenyliminotropone (**1a**) in carbon disulfide was heated at 60 °C for 24 h in an autoclave to afford thiazolidine-2-thione derivative (**3a**) quantitatively. Similar reactions using *p*-methyl- (**1b**), *p*-chloro- (**1c**), and *p*-bromophenyliminotropone (**1d**) also gave the corresponding products (**3b**-**d**) in 100, 94, and 100% yields, respectively. Upon heating in carbon disulfide at 120 °C for 24 h, **3a** turned to 4-thiazoline-2-thione derivative (**4a**) in 97% yield. All the other thiazolidine derivatives (**3b**-**3d**) also afforded 90-100% yields of the corresponding thiazoline derivatives (**4b**-**4d**), respectively.



1

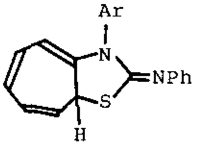
a:Ar=p-MeOC$_6$H$_4$
b:Ar=p-MeC$_6$H$_4$

c:Ar=p-ClC$_6$H$_4$
d:Ar=p-BrC$_6$H$_4$

2

3

4



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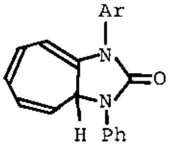

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The structures of 3 were deduced on the basis of their spectral properties as follows. The molecular ion peaks in their mass spectra showed that 3 were 1:1 adducts between 1 and carbon disulfide. ^{1}H Nmr[6] and ^{13}C nmr[7] spectra indicated the existences of phenyl and 1,7-disubstituted tropilidene moieties. Ir spectra showed strong absorptions at ca. 1500 and 1290 cm^{-1}, which were characteristic for thioamide groups.[8] The location of the methine proton (H_a) at the 5-position of the thiazolidine-2-thione moiety was deduced by the ^{1}H nmr chemical shift of H_a, which was close to that of the analogous compound (5) rather than 6.[6a]

The structures of 4 were deduced also on the basis of their spectral properties. The assignment of the each protons on the tropilidene moiety was carried out using NMDR and NOE measurement in ^{1}H nmr spectra. Irradiation on the phenyl groups of 4a-d caused 6-15% enhancements of the signal of proton H_e, but the signal of H_f showed no change. This fact showed that the phenyl groups are located to close to H_e but not to H_f, supporting the assignment of the protons on the tropilidene moieties shown in the figure.

The reaction is considered to proceed through nucleophilic attack of the nitrogen atom of 1 to the carbon atom of carbon disulfide[9] to afford an intermediate (2), which then cyclizes to give 3. 1,5-Hydrogen shift in 3[10] can give 4.

Molecular orbital calculations on 1 using MNDO and MINDO/3 methods showed existences of relatively large charge separations between the carbon and the nitrogen atoms of C=N bonds resulting in appearance of dipole momentum.[11] This high electron density on the nitrogen atom is considered to be responsible for the initial attack of the nitrogen atom to carbon disulfide.

Table 1. Values of Net Atomic Charges on C=N Bonds of 1a~d Calculated by MNDO and MINDO/3 Methods.

Ar	MNDO		MINDO/3	
	N	C	N	C
p-MeOC$_6$H$_4$ (1a)	-0.2613	+0.1446	-0.2273	+0.2111
p-MeC$_6$H$_4$ (1b)	-0.2618	+0.1430	-0.2299	+0.2165
p-ClC$_6$H$_4$ (1c)	-0.2694	+0.1530	-0.2352	+0.2206
p-BrC$_6$H$_4$ (1d)	-0.2694	+0.1518	-	-

EXPERIMENTAL

Melting points were measured on Yanagimoto Micro Melting Point Apparatus and were not corrected. Nmr spectra were recorded with a Varian XL 200 spectrometer. Ir, and uv were measured with a JASCO FT/IR 5300 and a Hitachi 220A spectrophotometers, respectively. Mass spectra were measured with a Hitachi M 2000S spectrometer.

Reaction of 1 with Carbon Disulfide. A solution of 1 (3.0-5.1 mmol) in carbon disulfide (20 ml) was heated at 60°C for 24 h in an autoclave. After evapolation of the excess carbon disulfide the residual oil was separated with column chromatography on silica gel to give 3.

3a: Colorless oil. 100% yield. Hrms: 287.0431. Calcd for $C_{15}H_{13}NOS_2$: 287.0437. Ms *m/z* (rel intensity): 287 (M^+, 40), 211 (34), 133 (100). Uv (MeOH): 224 nm (log ε, 4.16), 286 (4.02), 343 (3.88). Ir (oil): 1600, 1510, 1290 cm^{-1}. ^1H Nmr ($CDCl_3$) δ ppm: 3.83 (s, 3H, Me), 4.20 (d, H_a), 5.32 (d, H_f), 5.41 (dd, H_b), 6.22 (dd, H_c), 6.38 (dd, H_d), 6.48 (dd, H_e), 6.80-7.36 (m, 4H, phenyl). Coupling constants in Hz: $J_{ab}=4.4$, $J_{bc}=9.4$, $J_{cd}=6.2$, $J_{de}=11.2$, $J_{ef}=6.2$. ^{13}C Nmr ($CDCl_3$) δ ppm: 46.7 (C_7), 55.3 (Me), 104.6 (C_6), 114.8 (C_9 or $C_{9'}$), 115.2 ($C_{9'}$ or C_9), 118.0 (C_5), 126.2 (C_2), 127.2 (C_4), 128.8 (C_8), 129.1 (C_3), 129.5 (C_{10} or $C_{10'}$), 129.8 ($C_{10'}$ or C_{10}), 140.9 (C_1), 159.7 (C_{11}), 198.3 (C_{12}).

3b: Yellow crystals (from ethanol). 100% yield. mp 109-110°C. Hrms: 271.0486. Calcd for $C_{15}H_{13}NS_2$: 271.0488. Ms *m/z* (rel intensity): 271 (M^+, 100), 195 (74), 149 (28). Uv (MeOH): 236 nm (log ε, 4.02), 290 (4.02), 346 (3.88). Ir (KBr):

1600, 1510, 1300 cm^{-1}. ^{1}H Nmr ($CDCl_3$) δ ppm: 2.42 (s, 3H, Me), 4.23 (d, H_a), 5.34 (d, H_f), 5.46 (dd, H_b), 6.25 (dd, H_c), 6.40 (dd, H_d), 6.50 (dd, H_e), 6.95-7.50 (m, 4H, phenyl). Coupling constants in Hz: J_{ab}=5.0, J_{bc}=10.8, J_{cd}=6.5, J_{de}=11.5, J_{ef}=6.3. ^{13}C Nmr ($CDCl_3$) δ ppm: 21.2 (Me), 46.9 (C_7), 104.5 (C_6), 118.1 (C_5), 126.6 (C_2), 127.3 (C_4), 128.2 (C_{10} and $C_{10'}$), 129.1 (C_3), 130.5 (C_9 and $C_{9'}$), 134.8 (C_{11}), 139.3 (C_8), 140.8 (C_1), 198.2 (C_{12}).

3c: Yellow crystals (from ethanol). 94% yield. mp 140-141°C. Hrms: 289.9831. Calcd for $C_{14}H_9NS_2Cl$: 289.9864. Ms *m/z* (rel intensity): 291 (M^+, 100), 215 (93), 180 (35), 137 (54). Uv (MeOH): 237 nm (log ε , 4.03), 289 (4.05), 344 (3.89). Ir (KBr): 1620, 1490, 1290, 1230 cm^{-1}. ^{1}H Nmr ($CDCl_3$) δ ppm: 4.22 (d, H_a), 5.31 (d, H_f), 5.44 (dd, H_b), 6.25 (dd, H_c), 6.42 (dd, H_d), 6.49 (dd, H_e), 7.00-7.70 (m, 4H, phenyl). Coupling constants in Hz: J_{ab}=4.3, J_{bc}=9.5, J_{cd}=5.4, J_{de}=10.8, J_{ef}=4.9. ^{13}C Nmr ($CDCl_3$) δ ppm: 47.0 (C_7), 104.4 (C_6), 118.1 (C_5), 126.7 (C_2), 127.6 (C_4), 129.0 (C_3), 129.4 (C_9 and $C_{9'}$), 130.1 (C_{10} and $C_{10'}$), 135.2 (C_{11}), 135.8 (C_8), 140.2 (C_1), 198.1 (C_{12}).

3d: Yellow crystals (from dichloromethane-ethanol). 100% yield. mp 154-155°C. Hrms: 334.9463. Calcd for $C_{14}H_{10}NS_2Br$: 334.9438. Ms *m/z* (rel intensity): 337 (M^+, 33), 336 (25), 335 (M^+, 29), 261 (100), 259 (97). Uv (MeOH): 236 nm (log ε, 4.19), 289 (4.16), 346 (3.99). Ir (KBr): 3020, 2920, 1620, 1490, 1290 cm^{-1}. ^{1}H Nmr ($CDCl_3$) δ ppm: 4.25 (d, H_a), 5.34 (d, H_f), 5.47 (dd, H_b), 6.38 (dd, H_c), 6.44 (dd, H_d), 6.62 (dd, H_e), 6.90-7.90 (m, 4H, phenyl. Coupling constants in Hz: J_{ab}=4.6, J_{bc}=10.0, J_{cd}=5.4, J_{de}=11.0, J_{ef}=5.4. ^{13}C Nmr ($CDCl_3$) δ ppm: 47.2 (C_7), 104.6 (C_6), 118.4 (C_5), 123.6 (C_{11}), 127.0 (C_2), 127.8 (C_4), 129.2 (C_3), 130.0 (C_9 and $C_{9'}$), 133.4 (C_{10} and $C_{10'}$), 136.8 (C_8), 140.4 (C_1).

Thermal Isomerization of **3**. A solution of **3** (4.2-7.6 mmol) in carbon disulfide (20 ml) was heated at 120°C for 24 h in an autoclave. After evaporation of the excess carbon disulfide the residue was column chromatographed on silica gel to give crystals **4**.

4a: Yellow crystals (from ethyl acetate). 97% yield. mp 156-157°C. Hrms: 287.0417. Calcd for $C_{15}H_{13}NOS_2$: 287.0437. Ms *m/z* (rel intensity): 287 (M^+, 100), 286 (60), 167 (17), 148 (26). Uv (MeOH): 230 nm (log ε , 4.43), 230 339 (4.17). Ir (KBr), 1600, 1510, 1290 cm^{-1}. ^{1}H Nmr ($CDCl_3$) δ ppm: 2.55 (dd, H_a and H_b), 3.88 (s, 3H, Me), 5.32-5.63 (m, H_c and H_d), 5.93 (d, H_e), 6.45 (d, H_f), 7.05-7.35 (m, 4H, phenyl). Coupling constants in Hz: J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.0, J_{ce}=9.2, J_{df}=9.4. ^{13}C Nmr ($CDCl_3$) δ ppm: 27.4 (C_7), 55.6 (Me), 115.1 (C_{10} and

$C_{10'}$), 119.2 (C_1 or C_6), 119.9 (C_6 or C_1), 120.8 (C_2 or C_5), 122.2 (C_5 or C_2), 125.9 (C_4), 129.3 (C_9 and $C_{9'}$), 130.1 (C_8), 141.8 (C_3), 160.1 (C_{11}), 187.9 (C_{12}).

4b: Pale yellow crystals (from ethyl acetate). 99% yield. mp 149-150°C. Hrms: 271.0475. Calcd for $C_{15}H_{13}NS_2$: 271.0488. Ms m/z (rel intensity): 271 (M^+, 100), 270 (95), 149 (23). Uv (MeOH): 218 nm (log ε , 4.40), 337 (4.04). Ir (KBr): 1610, 1490, 1290 cm^{-1}. ^1H Nmr ($CDCl_3$) δ ppm: 2.44 (s, 3H, Me), 2.52 (dd, H_a and H_b), 5.30-5.61 (m, H_c and H_d), 5.89 (d, H_e), 6.43 (d, H_f), 7.10-7.50 (m, 4H, phenyl). Coupling constants in Hz: $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.0$, $J_{ce}=9.2$, $J_{df}=9.4$. ^{13}C Nmr ($CDCl_3$) δ ppm: 21.4 (Me), 27.4 (C_7), 119.2 (C_1 or C_6), 119.9 (C_6 or C_1), 120.9 (C_2 or C_5), 122.3 (C_5 or C_2), 126.0 (C_4), 127.9 (C_9 and $C_{9'}$), 130.6 (C_{10} and $C_{10'}$), 135.0 (C_{11}), 139.7 (C_8), 141.6 (C_3), 187.7 (C_{12}).

4c: Yellow crystals (from benzene). 100% yield. mp 170-171°C. Hrms: 289.9833. Calcd for $C_{14}H_9NS_2Cl$: 289.9863. Ms m/z (rel intensity): 291 (M^+, 100), 290 (98), 212 (25), 180 (24). Uv (MeOH): 225 nm (log ε , 4.59), 341 (4.21). Ir (KBr): 1610, 1510, 1290 cm^{-1}. ^1H Nmr ($CDCl_3$) δ ppm: 2.56 (dd, 2H, H_a and H_b), 5.30-5.68 (m, 2H, H_c and H_d), 5.89 (d, H_e), 6.46 (d, H_f), 7.20-7.60 (m, 4H, phenyl). Coupling constants in Hz: $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.0$, $J_{ce}=9.2$, $J_{df}=9.4$. ^{13}C Nmr ($CDCl_3$)δ ppm: 27.4 (C_7), 118.8 (C_1 or C_6), 119.8 (C_6 or C_1), 121.1 (C_2 or C_5), 122.6 (C_5 or C_2), 126.3 (C_4), 129.7 (C_9 and $C_{9'}$), 130.2 (C_{10} and $C_{10'}$), 135.6 (C_{11}), 135.9 (C_8), 141.1 (C_3), 187.8 ($_{12}$).

4d: Yellow crystals (from benzene). 90% yield. mp 169-170°C. Hrms: 334.9419. Calcd for $C_{14}H_{10}NS_2Br$: 334.9437. Ms m/z (rel intensity): 335 (M^+, 66), 212 (31), 167 (34), 159 (100). Uv (MeOH): 229 nm (log ε , 4.44), 341 (4.13). Ir (KBr): 1610, 1490, 1280 cm^{-1}. ^1H Nmr ($CDCl_3$) δ ppm: 2.53 (dd, 2H, H_a and H_b), 5.30-5.63 (m, 2H, H_c and H_d), 5.83 (d, H_e), 6.43 (d, H_f), 7.15-7.90 (m, 4H, phenyl). Coupling constants in Hz: $J_{ac}=J_{ad}=J_{bc}=J_{bd}=6.0$, $J_{ce}=9.2$, $J_{df}=9.4$. ^{13}C Nmr ($CDCl_3$)δ ppm: 27.4 (C_7), 118.8 (C_1 or C_6), 119.8 (C_6 or C_1), 121.2 (C_2 or C_5), 122.6 (C_5 or C_2), 123.7 (C_{11}), 126.3 (C_4), 130.0 (C_9 and $C_{9'}$), 133.2 (C_{10} and $C_{10'}$), 136.5 (C_8), 141.1 (C_3), 187.7 (C_{12}).

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