[8 + 2]-TYPE CYCLOADDITION REACTIONS OF *N*-ARYL-2,4,6-CYCLOHEPTATRIENE-1-IMINES AND 2,4,6-CYCLOHEPTATRIENE-1-THIONE WITH *p*-TOLUENESULFONYL ISOCYANATE: FORMATION OF 1,3-DIAZAAZULANONES

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Abstract ——— Reactions of *N*-aryl-2,4,6-cycloheptatriene-1-imines and 2,4,6-cycloheptatriene-1-thione with *p*-toluenesulfonyl isocyanate gave [8+2]-type cycloadducts in good yields. Eliminations of tosyl groups and dehydrogenations of the adducts afforded 1,3-diazaazulanones.

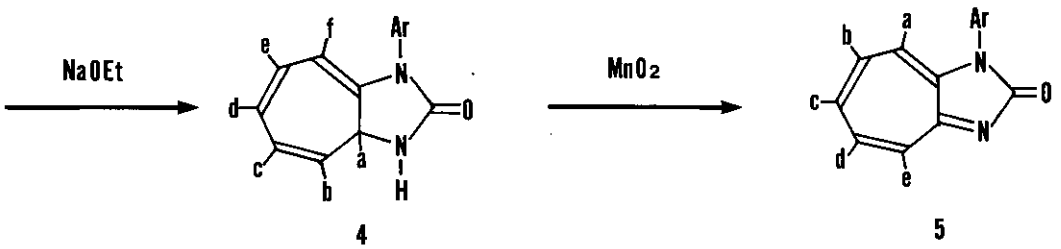
Diazaazulanones and related compounds have attracted much attention from the viewpoint of not only their characteristic chemical and physical natures but also their pharmacological activities.[1] Fukuda reported that 1-(2-dimethylaminoethyl)-1,3-diazaazulanone selectively inhibited DNA synthesis in rats.[2] Nishiwaki documented on the synthesis of 1,3-diazaazulanone-1-ribonucleosides, which were expected to have biological activities.[3]

2,4,6-Cycloheptatriene-1-ones and 2,4,6-cycloheptatriene-1-imines possess large dipolar momenta due to the contributions of polarized aromatic structures. As a consequence, the external hetero atoms of these compounds have negative charges and are expected to undergo nucleophilic reactions.[4] Previously, we employed this nucleophilicity of 2,4,6-cycloheptatriene-1-imines in the synthesis of thiazolidine-2-thiones and azaazulanones through the addition reactions of 2,4,6-cycloheptariene-1-imines and carbon disulfide or chloroketenes.[5] 2,4,6-Cycloheptatriene-1-thione also has a dipole momentum, but the degree of a contribution of the ionic structure is considered to be not so large as those of 2,4,6-cycloheptatriene-1-ones or 2,4,6-cycloheptatriene-1-imines.[6] The concerted pathway on the cycloaddition reactions of 2,4,6-cycloheptatriene-1-thione with chloroketene well explains the difference of the nucleophilicities of the external hetero atoms of these troponoid compounds.[7] The reactivities of 2,4,6-cycloheptatriene-1-thione have not been studied enough, and more detailed studies are desired.[8]

As a series of studies on cycloaddition reactions of troponoid compounds,[9] we investigated the reactions of *N*-aryl-2,4,6-cycloheptatriene-1-imines (1) and 2,4,6-cycloheptatriene-1-thione (6) with sulfonyl isocyanate (2) to give [8+2]-type cycloadducts (3), which were derived to 1,3-diazaazulanones (5). Here the results will be reported.

1 2 3

a: Ar=C_6H_4(p-OMe), c: Ar=C_6H_4(p-Cl),
b: Ar=C_6H_4(p-Me), d: Ar=C_6H_4(p-Br)



4 5

6 7

A mixture of *N*-*p*-methoxyphenyl-2,4,6-cycloheptatriene-1-imine (1a) and *p*-toluenesulfonyl isocyanate (2) was stirred at room temperature for 15 min under a nitrogen stream to afford [8+2]-type cycloadduct (3a) in 98 % yield. Similar reactions using *N*-*p*-tolyl- (1b), *N*-*p*-chlorophenyl- (1c), and *N*-*p*-bromophenyl-2,4,6-cycloheptatriene-1-imines (1d) afforded the corresponding adducts (3b-d) in 98 % yields, respectively. Eliminations of tosyl groups and dehydrogenations of 3 afforded 1,3-diazaazulanones (5a-d) in 35-61 % yields. The intermediacy of 4 was confirmed by the isolation of 4c in 42% yield.

The similar reaction using 2,4,6-cycloheptatriene-1-thione (6) afforded the corresponding [8+2]-type cycloadduct (7) in 85 % yield. However, reactions of 6 with phenyl isocyanate, phenyl isothiocyanate, and carbon disulfide under various reaction conditions led to com-

plex mixture. The elimination of tosyl group of 7 did not proceed and 7 went back to 6 in the presence of sodium ethoxide.

The structures of the products (3, 4c, 5, and 7) were deduced on the basis of their spectral properties and confirmed by comparison of these spectral properties to those of the analogous compounds.[10,11]

Molecular orbital calculations[5,6] showed that the electrons on the seven membered rings of 1 and 6 were withdrawn toward the external hetero atoms, resulting in the large dipole moment. The calculation also showed that the central carbon atom of isocyanate (2) had a large positive charges (+0.444) due to the introduction of the tosyl group.[12] Therefore, it is likely that the reactions of 1 and 6 with highly polar cumulene (2) proceed through the ionic pathway rather than the concerted one.

EXPERIMENTAL

Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and were not corrected. Nmr spectra were measured with Hitachi R-90 or Varian XL-200 spectrometers. Ir and uv spectra were measured with Jasco FT/IR-5300 and Hitachi 220A spectrophotometers, respectively. Mass spectra were taken on a Hitachi M-2000S sepctrometer. Wakogel C-200 and Wakogel B-5 F were used for column and thin-layer chromatography, respectively.

General Procedure of the Addition Reactions of N-Aryl-2,4,6-cycloheptatriene-1-imines (1) with p-Toluenesulfonyl Isocyanate(2). To a solution of 1 (3.0 mmol) in dichloromethane (5 ml) was slowly added 2 (0.60 g, 3.0 mmol) at room temperature under an N_2. After the addition was completed, the mixture was stirred at room temperature for 15 min. Evaporation of the solvent gave colorless crystals of the adduct (3).

3a: Colorless crystals (from ethyl acetate). mp 173-174 °C. Hrms: m/z 408.1161. Calcd for $C_{22}H_{20}N_2O_4S$: m/z 408.1153. Ms m/z (rel intensity): 408 (M^+, 22), 253 (100), 237 (13), 211 (100), 197 (94). Uv (MeOH): 225 nm (log ε, 4.38), 267 (3.45), 312 (3.61). Ir (KBr): 1745, 1645, 1520, 1305, 1165 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.45 (s, 3H, Me), 3.80 (s, 3H, OMe), 4.68 (d, H_a), 5.40 (d, H_f), 5.49 (dd, H_b), 6.21 (dd, H_c), 6.29-6.50 (m, 2H, H_d and H_e), 6.90-8.20 (m, 8H, aryl protons). Coupling constants in Hz; J_{ab}= 2.8, J_{bc}= 9.9, J_{cd}= 5.4, J_{ef}=5.4. ^{13}C Nmr ($CDCl_3$) δ 21.7, 55.5, 57.7, 97.4, 114.8, 118.4, 125.0, 128.2, 128.3, 128.6, 129.8, 130.0, 131.9, 135.8, 145.3, 152.0, 159.5.

3b: Colorless crystals (from ethyl acetate). mp 189-190 °C. Hrms: m/z 392.1185. Calcd for $C_{22}H_{20}N_2O_3S$: m/z 392.1178. Ms m/z (rel intensity): 392 (M^+, 13), 237 (42), 197 (100), 195 (100). Uv (MeOH): 227 nm (log ε, 4.38), 254 (3.88), 307 (3.75). Ir (KBr): 1745, 1645, 1515, 1300, 1170 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.36 (s, 3H, Me), 2.46 (s, 3H, Me), 4.68 (d, H_a), 5.46 (d, H_f), 5.50 (dd, H_b), 6.22 (dd, H_c), 6.37 (dd, H_d), 6.46 (dd, H_e), 7.10-8.14 (m, 8H, aryl protons). Coupling constants in Hz; J_{ab}=3.2, J_{bc}=9.4, J_{cd}=5.5, J_{de}=10.3, J_{ef}=5.3. ^{13}C Nmr ($CDCl_3$) δ 21.2, 21.7, 57.7, 97.5, 118.4, 125.0, 126.0, 128.3, 128.6, 129.8, 130.2, 130.5, 131.6,

135.7, 145.3, 151.8.

3c: Colorless crystals (from ethyl acetate). mp 193–194 °C. Hrms: m/z 412.0653. Calcd for $C_{21}H_{17}N_2O_3SCl$: m/z 412.0647. Ms m/z (rel intensity): 414 (M^+, 13), 412 (M^+, 32), 259 (91), 257 (100), 217 (82), 215 (100). Uv (MeOH): 220 nm (log ε, 4.65), 265 (3.88), 274 (sh. 3.86), 309 (3.79). Ir (KBr): 1750, 1645, 1495, 1310, 1180 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.46 (s, 3H, Me), 4.67 (d, H_a), 5.47 (d, H_f), 5.5 (dd, H_b), 6.24 (dd, H_c), 6.42 (dd, H_d), 6.48 (dd, H_e), 7.20–8.12 (m, 8H, aryl protons). Coupling constants in Hz; J_{ab}=3.1, J_{bc}=9.4, J_{cd}=5.3, J_{de}=10.7, J_{ef}=5.2. ^{13}C Nmr ($CDCl_3$) δ 22.8, 58.8, 98.8, 119.5, 126.2, 127.6, 129.1, 129.5, 129.6, 130.8, 130.9, 131.8, 132.8, 135.3, 136.7, 146.6, 152.6.

3d: Colorless crystals (from ethyl acetate). mp 191–192 °C. Hrms: m/z 458.0096. Calcd for $C_{21}H_{17}N_2O_3SBr$: m/z 458.0122. Ms m/z (rel intensity): 458 (M^+, 12), 456 (M^+, 12), 303 (95), 301 (100), 261 (65), 259 (66). Uv (MeOH): 224 nm (log ε, 4.41), 277 (sh. 3.61), 313 (3.69). Ir (KBr): 1760, 1640, 1530, 1305, 1160 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.46 (s, 3H, Me), 4.66 (d, H_a), 5.39–5.60 (m, 2H, H_b and H_f), 6.26 (dd, H_c), 6.32–6.54 (m, 2H, H_d and H_e), 7.10–8.20 (m, 8H, aryl protons). Coupling constants in Hz; J_{ab}= 3.0, J_{bc}= 10.0, J_{cd}= 4.1. ^{13}C Nmr ($CDCl_3$) δ 21.7, 57.7, 97.7, 118.4, 122.3, 125.1, 126.5, 128.3, 128.4, 128.5, 129.9, 130.6, 132.3, 132.8, 135.6, 145.5, 151.5.

General Procedure of the Preparation of 1,3-Diazaazulanones (5). To a solution of 1 (3.0 mmol) in dichloromethane (5 ml) was slowly added 2 (0.60 g, 3.0 mmol) at room temperature under an N_2. After the addition was completed, the mixture was stirred at room temperature for 15 min. To the reaction mixture was added a solution of sodium ethoxide (0.81 g, 12.0 mmol) in ethanol (10 ml) and the mixture was stirred for 2 h. The solvent was removed by rotary evaporator to give a white residual oil, which was redissolved with dichloromethane (20 ml), washed with water, and dried over anhydrous sodium sulfate. After filtration manganese oxide (0.96 g, 11.0 mmol) was added to the filtrate and the mixture was stirred at room temperature for 4 h. Filtration of the reaction mixture gave brown filtrate, which was separated with column chromatography on silica gel to give the corresponding 1,3-diazaazulanone (5).

5a: Light yellow crystals (from ethanol-dichloromethane). 41% yield. mp 215–216 °C. Hrms: m/z 252.0868. Calcd for $C_{15}H_{12}N_2O_2$: m/z 252.0897. Ms m/z (rel intensity): 252 (M^+, 100), 237 (27), 221 (3), 149 (5). Uv (MeOH): 229 nm (log ε, 4.48), 250 (4.70), 304 (3.98), 345 (4.03), 382 (sh. 3.92), 391 (3.87). Ir (KBr): 1700, 1590, 1530, 1440 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 3.88 (s, 3H, Me), 7.10 (m, 2H, aryl protons), 7.30 (d, H_a), 7.35 (m, 2H, aryl protons), 7.46 (dd, H_c), 7.63 (dd, H_b), 7.88 (dd, H_d), 8.10 (d, H_e). Coupling constants in Hz; J_{ab}=9.4, J_{bc}=10.5, J_{cd}=7.4, J_{de}=10.9. ^{13}C Nmr ($CDCl_3$) δ 55.6, 114.9, 115.1, 125.9, 128.6, 129.6, 131.6, 136.0, 138.9, 150.1, 160.0, 165.2, 165.6.

5b: Light yellow crystals (from ethanol-dichloromethane). 61% yield. mp 195–196 °C. Hrms: m/z 236.0923. Calcd for $C_{15}H_{12}N_2O_2$: 236.0948. Ms m/z (rel intensity): 236 (M^+, 100), 221

(27), 185 (64), 119 (97). Uv (MeOH): 251 nm (log ε, 4.39), 347 (3.92), 382 (sh. 3.79), 391 (sh. 3.74). Ir (KBr): 1700, 1600, 1530, 1480, 1450 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.46 (s, 3H, Me), 7.30 (d, H_a), 7.36 (m, 4H, aryl protons), 7.46 (dd, H_c), 7.62 (dd, H_b), 7.87 (dd, H_d), 8.14 (d, H_e). Coupling constants in Hz; J_{ab}=9.6, J_{bc}=10.2, J_{cd}=7.9, J_{de}=10.9. ^{13}C Nmr ($CDCl_3$) δ 21.3, 114.9, 127.2, 129.7, 130.5, 131.5, 135.9, 138.9, 139.3, 145.0, 165.0, 165.7.

5c: Light yellow crystals (from ethanol–dichloromethane). 35% yield. mp 213–215 °C. Hrms: m/z 221.0715. Calcd for $C_{14}H_9N_2O$: m/z 221.0713. Ms m/z (rel intensity): 258 (M^+, 18), 256 (M^+, 51), 236 (31), 221 (18), 119 (100). Uv (MeOH): 217 nm (log ε, 4.33), 252 (4.45), 346 (3.98), 378 (sh. 3.90), 390 (sh. 3.83). Ir (KBr): 1700, 1600, 1530, 1500, 1450 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 7.31 (d, H_a), 7.40 (m, 2H, aryl protons), 7.48 (dd, H_c), 7.58 (m, 2H, aryl protons), 7.63 (dd, H_b), 7.88 (dd, H_d), 8.13 (d, H_e). Coupling constants in Hz; J_{ab}=9.5, J_{bc}=10.3, J_{cd}=7.2, J_{de}= 10.9. ^{13}C Nmr ($CDCl_3$) δ 114.9, 128.7, 130.0, 130.1, 132.1, 135.1, 136.1, 139.3, 149.4, 164.6, 165.8.

5d: Light yellow crystals (from ethanol–dichloromethane). 41% yield. mp 233–234 °C. Hrms: m/z 302.0150. Calcd for $C_{14}H_9N_2OBr$: m/z 302.0184. Ms m/z (rel intensity): 302 (M^+, 98), 300 (M^+, 100), 221 (32), 192 (9), 157 (10). Uv (MeOH): 222 nm (log ε, 4.40), 251 (4.54), 346 (4.02), 379 (sh. 3.91), 390 (sh. 3.83). Ir (KBr): 1700, 1600, 1530, 1490, 1450 cm^{-1}. ^1H Nmr($CDCl_3$) δ 7.31 (d, H_a), 7.35 (m, 2H, aryl protons), 7.48 (dd, H_c), 7.65 (dd, H_b), 7.75 (m, 2H, aryl protons), 7.90 (dd, H_d), 8.13 (d, H_e). Coupling constants in Hz; J_{ab}= 9.2, J_{bc}=10.6, J_{cd}= 7.6, J_{de}=11.0. ^{13}C Nmr ($CDCl_3$) δ 114.8, 129.0, 129.2, 130.0, 132.0, 132.5, 133.1, 136.0, 139.2, 149.3, 164.5, 165.9.

Addition Reaction of 2,4,6-Cycloheptatriene-1-thione (6) with p-Toluenesulfonyl Isocyanate (2). To a solution of 6 (2.4 g, 20 mmol) in dichloromethane (200 ml) was slowly added 2 (1.1 g, 5.6 mmol) at room temperature under an N_2. After the addition was completed, the mixture was stirred at room temperature for 1 h. The solvent was evaporated to give a red oily residue, which was separated with column chromatography on silica gel to give 7 (1.5g, 85% yield, hexane–ethyl acetate 6:4).

7: Light yellow crystals (from dichloromethane–hexane). mp 128–129 °C. Hrms: m/z 259.0674. Calcd for $C_{14}H_{13}NO_2S$: m/z 259.0666. Ms m/z (rel intensity): 319 (M^+, 16), 259 (31), 197 (63), 155 (100). Uv (MeOH): 220nm (log ε, 4.41), 234 (sh. 4.23), 270 (sh. 3.58), 276 (sh. 3.54), 301 (3.55). Ir (KBr): 1750, 1650, 1510, 1305, 1250, 1165 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 2.48 (s, 3H, Me), 4.65 (dm, H_a), 5.47 (dd, H_b), 6.15 (dm, H_f), 6.26 (ddm, H_c), 6.58–6.75 (m, 2H, H_d and H_e), 7.40–8.10 (m, 4H, aryl protons). Coupling constants in Hz; J_{ab}=4.4, J_{bc}=9.7, J_{cd}=3.0, J_{ef}= 4.8. ^{13}C Nmr ($CDCl_3$) δ 21.8, 63.8, 116.6, 120.3, 121.9, 124.1, 128.7, 129.7, 129.8, 130.1, 135.0, 146.0, 167.5.

Formation of 4c. To a solution of 3c (220 mg, 0.53 mmol) in dichloromethane (10 ml) was added a solution of sodium ethoxide (340 mg, 5.3 mmol) in ethanol (15 ml) and the mixture was stirred at room temperature for 2 h. The usual workup of the reaction mixture gave

4c (60 mg, 42% yield).

4c: Colorless oil. Hrms: m/z 260.0500. Calcd for $C_{14}H_{11}N_2OCl$: m/z 260.0529. Ms m/z (rel intensity): 260 (M^+, 31), 258 (M^+, 100), 257 (85), 223 (17), 199 (46), 184 (96). Uv (MeOH): 215 nm (log ε, 4.47), 255 (3.92), 322 (3.81). Ir (KBr): 1720, 1640, 1540, 1490, 1440 cm^{-1}. ^1H Nmr ($CDCl_3$) δ 4.18 (bs, H_a), 5.18 (d, H_b), 5.48 (d, H_f), 6.12(dd, H_c), 6.27 (dd, H_d), 6.45 (dd, H_e), 7.26-7.56 (m, 4H, aryl protons). Coupling constants in Hz; J_{bc}=9.9, J_{cd}=6.6, J_{de}=11.5, J_{ef}=6.6. ^{13}C Nmr ($CDCl_3$) δ 54.7, 97.3, 119.3, 125.8, 126.2, 129.2, 130.3, 130.8, 134.6, 137.0, 149.2, 159.6.

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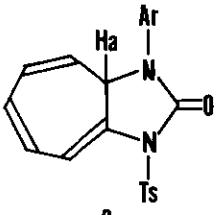
11. The structures of the products were deduced as follows. ^{1}H Nmr and ^{13}C nmr spectra of 3 and 4c indicated the existences of aryl and 1,7-disubstituted 2,4,6-cycloheptatriene moieties.[10] In the ir spectra of 3 and 4c, the existences of carbonyl groups were shown by the strong characteristic absorption bands at ca. 1750 cm^{-1} (3) and 1720 cm^{-1} (4c), respectively.[10] The molecular ion peaks in the mass spectra of 3 demonstrated that 3 were 1:1 adducts between 1 and 2. The molecular ion peak of 4c indicated that 4c was derived from the elimination of the tosyl group of 3c. The signal of the methine proton (H_a) of 4c in the ^{1}H nmr spectrum appeared at a high field (4.18 ppm) comparing to that of 3c (4.67 ppm) because of the absence of the tosyl group. The structures of 5 were identified as follows. Uv spectra showed characteristic absorption patterns as 1,3-diazaazulanones with maximum absorptions or shoulders at *ca.* 250, 345, 380, and 390 nm.[1,2] In the ir spectra, the characteristic absorptions for the carbonyl groups of 1,3-diazaazulanone ring were clearly observed at ca. 1700 cm^{-1}.[1,2] The assignment of the protons on the seven-membered rings was decided by the use of the double resonance technique in ^{1}H nmr spectra. The chemical shifts of the signals of H_a in ^{1}H nmr spectra were influenced by the aryl groups, suggesting that H_a and the ary groups were located closely each other, thus supporting the structures of 5 shown in the figure. The structure of 7 was decided as follows. The molecular ion peak in mass spectrum of 7 demonstrated that the product was derived from 1:1 adduct between 2 and 6. In the ir spectrum, the absorption of carbonyl group was observed at 1750 cm^{-1}. ^{1}H Nmr and ^{13}C nmr spectra showed a good resemblance to those of 3 and were compatible to the structure shown in the figure.

Alternative structures (8, 9, and 10), though mechanistically questionable, for these products (3, 4c, and 7) can be rejected by the fact that the chemical shifts of the signals of H_a of 8, 9, and 10 in the ^{1}H nmr spectra should be expected to be about 4.45–4.48, 4.45–4.48, and 4.20–4.25 ppm, respectively, refering to the analogous compounds.[5,10] The observed chemical shifts of H_a of 3 (4.67–4.68 ppm), 4c (4.18 ppm), and

7 (4.65 ppm) are different from these expected values, supporting the structures of 3, 4c, and 7 shown in the figure.



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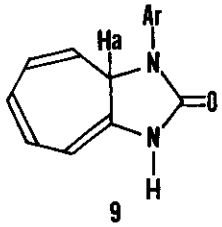

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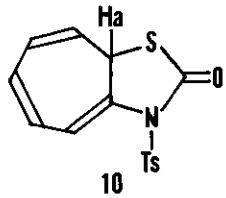

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12. Calculations were carried out at the Computer Center of the Institute for Molecular Sience, using MOPAC program.

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