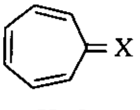
FORMATIONS OF AZAZULANONES AND DIHYDROAZAZULANONES VIA REACTIONS OF TROPONIMINES WITH HETEROCUMULENES

Kazuaki Ito, Yasushi Hara, Reiji Sakakibara, and Katsuhiro Saito*

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-Cho,
Showa-ku Nagoya 466 Japan

Abstract——Reactions of troponimines with carbon disulfide, phenyl isocyanate, tosyl isocyanate, or diphenylketene afforded dihydroazazulanone and azazulanone derivatives through [8+2]-type cycloadducts. Reaction with dimethyl acetylenedicarboxylate gave a dihydroazazulene derivative and a quinoline derivative.

Although the chemistries of tropone (**1**)[1] and troponthione (**2**)[2] attracted attention of chemists and were investigated in detail, surprisingly few studies have so far been made the researches on the chemistry of troponimines (**3**).[3] This may be because **3** have been regarded to be a mere analogue of **1** or **2**, and its chemical natures could be deduced easily from those of **1** or **2**. However, considering the differences of reactivities between **1** and **2** the study on **3** seems to be worth developing. We investigated the reactions of **3** with heterocumulenes to afford dihydroazazulanones, azazulanones and azulenes. Here the results will be reported.

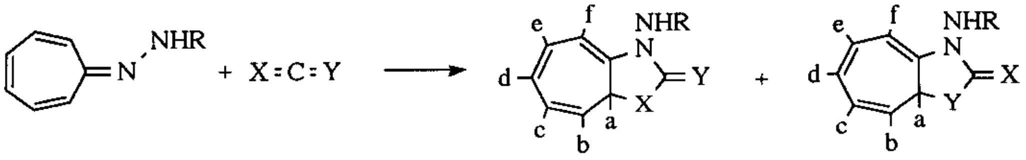


1: X=O
2: X=S
3: X=NR

The reaction of tropone phenylhydrazone (**3a**) with carbon disulfide (**4a**) afforded a 1:1 adduct (**5a**) quantitatively. An analogous reaction of **3a** with phenyl isocyanate (**4b**), tosyl isocyanate (**4c**), diphenylketene (**4d**) also gave the corresponding 1:1 adducts (**5b**,**5c**, and **5d**) in almost quantitatively yields, respectively. The similar reactions using tropone tosylhydrazone (**3b**) with heterocumulenes (**4a**-**4d**) produced the corresponding adducts (**5e**, **5f**, **5g**, and **5h**) in considerable yields, respectively. On the other hand, the reaction of **3b** with phenyl isothiocyanate (**4e**) gave **5i** and **6i** in 38 and 61% yields, respectively. Upon standing in benzene at room temperature, **5i** changed quantitatively to **6i**.

The reaction of *N*-methoxytroponimine (**3c**) with chlorophenyl- (**7a**) and dichloroketenes (**7b**) gave azazulanone derivatives (**8a**) and (**8b**) in 90 and 62% yields, respectively. Reaction of **3c** with chloroketene (**7c**) afforded **9** in 36% yield. The reaction of **3c** with **4e** afforded a cycloheptatriene derivative (**10** or **10'**) in 32% yield. Oxidation of **10** or **10'** using manganese oxide gave a ketimine derivative (**11**) in 82% yield. The reaction of **3c** with **4b** gave a cycloheptatriene derivative (**12**) and a 1,3-diazazulanone derivatives (**14**) in 27 and 43% yields, respectively. The thermal reaction of **12** afforded **13**, **14**, and a recovery of **12** in 15, 5, and 80% yields, respectively. In contrast, the similar reaction of **12** in the presence of *p*-chloranil gave **14** in 87% yield. The reaction of **3c** with **4c** afforded **16** in 60% yield. When a limited quantity of **4c** was used, a [8+2]-type adduct (**15**) could be detected in ^{1}H-nmr spectrum.[4] Reaction of **3c** with dimethyl acetylenedicarboxylate (**17**) afforded a dihydroazazulene derivative (**18** or **18'**) and a quinoline derivative (**19**) in 12 and 5% yields, respectively. Subsequent oxidation of **18** or **18'** afforded an azazulene derivative (**20**) in 91% yield. These reaction conditions and product yields were summarized in Table 1.

The structures of **5** and **6** were deduced as follows. The molecular ion peaks in mass spectra demonstrated that the products were all 1:1 adducts between the hydrazone and heterocumulenes. Analyses of their ^{1}H-nmr spectra and comparisons of the spectra to those of the analogous compounds showed that the products contained 1,7-disubstituted cycloheptatriene moieties. The chemical shifts of the methine protons (H_a) of **5a**, **5e**, and **5i** (the neighboring atom of H_a on the heterocyclic moieties are sulfur atom), **5b**, **5c**, **5f**, **5g**, and **6i** (those are nitrogen atom), and **5d** and **5h**(those are carbon atom) should be expected to be



3

a: R=Ph
b: R=Ts

4

a: X=Y=S
b: X=NPh, Y=O
c: X=NTs, Y=O
d: X=CPh$_2$, Y=O
e: X=S, Y=NPh

5

a: R=Ph, X=Y=S
b: R=Ph, X=NPh, Y=O
c: R=Ph, X=NTs, Y=O
d: R=Ph, X=CPh$_2$, Y=O

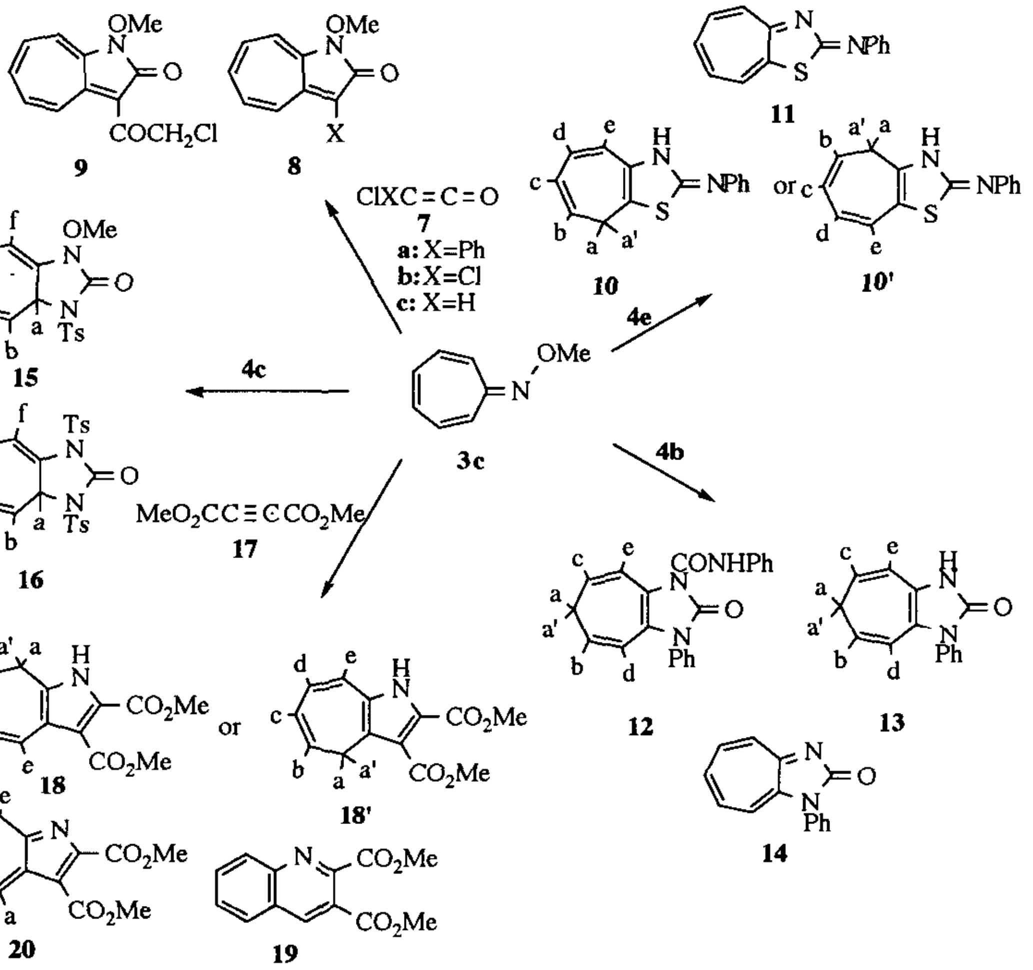
6

e: R=Ts, X=Y=S
f: R=Ts, X=NPh, Y=O
g: R=Ts, X=NTs, Y=O
h: R=Ts, X=CPh$_2$, Y=O
i: R=Ts, X=S, Y=NPh

Table 1. Reaction Conditions and Products Yields

Tropon-imine	Hetero-cumulene	Tempera-ture[°C]	Time [hour]	Solvent	Products Yield(%)
3a	**4a**	60[1]	13	-	**5a** (99)
3a	**4b**	60	0.25	benzene	**5b** (99)
3a	**4c**	r. t.	0.5	benzene	**5c** (99)
3a	**4d**	r. t.	20	ether	**5d** (69)
3b	**4a**	60[1]	48	-	**5e** (99)
3b	**4b**	60	2	benzene	**5f** (97)
3b	**4c**	r. t.	0.5	benzene	**5g** (99)
3b	**4d**	r. t.	20	ether	**5h** (86)
3b	**4e**	60	4	benzene	**5i** (38) **6i** (61)
3c	**7a**	r. t.	24	CH$_2$Cl$_2$	**8a** (90)
3c	**7b**	r. t.	2	CH$_2$Cl$_2$	**8b** (62)
3c	**7c**	r. t.	24	CH$_2$Cl$_2$	**9** (36)
3c	**4e**	reflux	5	toluene	**10** (32)
3c	**4b**	reflux	34	toluene	**12** (27) **14** (43)
3c	**4c**	0	0.5	benzene	**16** (60)
3c	**17**	70	24	benzene	**18** (12) **19** (5)
Oxidation of **10**		r. t.	1	CH$_2$Cl$_2$	**11** (82)
Thermal Reaction of **12**		reflux	48	toluene	**13** (15) **14** (5)[2]
Thermal Reaction of **12**[3]		reflux	2	toluene	**14** (87)
Oxidation of **18**		r. t.	1	CH$_2$Cl$_2$	**20** (91)

1) in an autoclave. 2) 80% of **12** was recovered. 3) in the presence of *p*-chloranil



about 4.20, 4.45, and 3.60 ppm, respectively, referring to the analogous compounds.[3] The observed values of **5a** (4.20), **5e** (3.98), **5i** (3.95), **5b** (4.50), **5c** (4.58), **5f** (4.47), **5g** (4.57), **6i** (4.72), **5d** (3.66), and **5h** (3.57) were in good agreement with expected values. Ir spectra showed that **5b**, **5c**, **5d**, **5f**, **5g**, and **5h** had carbonyl groups (1720-1740 cm^{-1}), **5a**, **5f**, and **6i** had thiocarbonyl groups (1290-1330cm^{-1}), and **5i** had an imino group (1620 cm^{-1}).[3a]

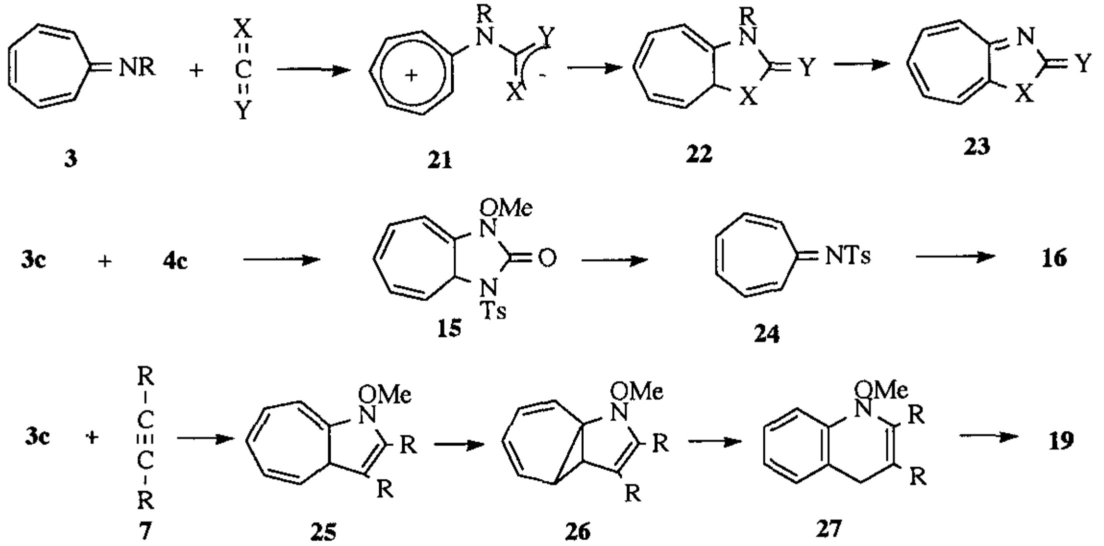
The structures of the products from **3c** were also deduced as follows. Molecular ion peaks of **10**, **13**, and **18** *in mass spectra demonstrated that these products were derived from the addition reactions of* **3c** *with the* heterocumulenes followed by the eliminations of methoxy groups. The existences of 1,2- (**10** and **18**) or 3,4-disubstituted cycloheptatriene moieties (**12** and **13**) were showed by the coupling constant values and the spin split pattern of the protons on cyclohepatriene moieties in ^{1}H-nmr spectra.[3b] In the ir spectra, the characteristic absorptions of an imino group (**10**: 1597 cm^{-1}) and carbonyl groups (**12**: 1736, **13**: 1740, **18**: 1732 cm^{-1}) were observed.

The structures of azazulanone derivatives (**8**, **9**, **11**, and **14**) and the azazulene derivative (**20**) were deduced on the basis of their spectral properties. λ_{max} Values in the uv spectra of these compounds (**8a**: 424, **8b**: 418, **9**: 412, **11**: 414, **14**:390, **20**:455 nm) were in good agreement with those of the analogous compounds.[3b,5] The ir spectra indicated the existences of the carbonyl groups (**8a**: 1680, **8b**:1694, **9**: 1682, **14**:1667, **20**:1736 cm^{-1}) and an imino group (**11**:1601 cm^{-1}). The dihydroazazulanone derivative (**16**) and the quinoline derivative (**19**) were confirmed by coincidence of their spectral properties to those of the authentic samples.[6]

The reactions of **3a** and **3b** are considered to proceed through [8+2] cycloadditions, where the electron-rich nitrogen atoms of the troponimine attacked the electron poor central carbon atoms of the heterocumulenes to form ionic intermediates (**21**), which then cyclized to [8+2] cycloaddcuts (**22**). The reactions of **3c** are also considered to be initiated by the similar stepwise process to give the adducts of the type (**22**). An elimination of the methoxy group in **22** formed **10** and **13**, which were then oxidized to the corresponding azulanone derivatives of type **23** (**11** and **14**).

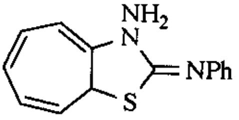
The reaction of **3c** with **4c** is thought to give the initital adduct (**15**), which then eliminated methoxy isocyanate to give **24**. The [8+2] cycloaddition of **24** with **4c** could form **16**.

The quinoline derivatives (**19**) is considered to be produced from the [8+2] cycloadduct (**25**), which cyclized to a norcaradiene-type intermediate (**26**). The subsequent ring enlargement to **27** followed by an elimination of methanol afforded the final product (**19**).[7]

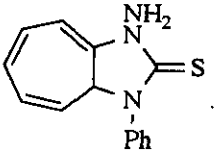


These cycloaddition reactions are considered to proceed through a zwitter ionic intermediate (**21**), which has two anion centers (X and Y). The selectivity of these nucleophiles was explained by HSAB theory.[8] Tropylium ion is a soft acid and so preferred to react with softer base, therefore, a nitrogen atom in **4b** and **4c**, a carbon atom in **4d**, and a sulfur atom in **4e** were selected as the suitable nucleophiles.

In order to clarify the isomerization process of **5i** to **6i**, their thermodynamic stabilities were evaluated by PM3 MO calculations using model compounds of **5j** and **6j**. The calculation showed that **6j** (heat of formation; 156 kcal/mol) was more stable than **5j** (165 kcal/mol), suggesting the formation of the initial product (**5i**) was kinetically controlled and that of **6i** thermodynamically controlled.



5j



6j

EXPERIMENTAL

Melting points were uncorrected. Nmr spectra were measured in deuterio chloroform solution with a Varian XL-200 spectrometer. Ir and uv spectra were measured with JASCO FT/IR-5300 and Hitachi 220A spectrophotometers, respectively. Mass spectra were measured with Hitachi M-2000S spectrometer. Only typical experiments are mentioned.

Reaction of Tropone Phenylhydrazone (3a) with Carbon Disulfide (4a). A solution of **3a** (230 mg, 1.2 mmol) in **4a** (20 ml, 330 mmol) was heated at 60°C for 13 h in an autoclave. Removal of excess **4a** afforded crystals of **5a** (0.32 g, 99%)

5a: pale yellow crystals. mp 130-131°C (benzene). Ms m/z (rel intensity): 272 (M^+, 49), 196 (100). Uv (MeOH): 353 nm (log ε , 4.02) 287 (4.19). Ir (KBr): 3200, 1600, 1290 cm^{-1}. ^{1}H-Nmr δ : 4.20 (d, H_a), 5.39 (dd, H_b), 6.12 (d, H_c), 6.28 (dd, H_d), 6.44 (dd, H_e), 6.62 (dd, H_f), 6.70-7.40 (m, 5H, Ph). Coupling constants in Hz; J_{ab}=4.0, J_{bc}=9.2, J_{cd}=6.4, J_{de}=11.4, J_{ef}=5.8. ^{13}C-Nmr δ : 43.2, 104.6, 114.6, 117.6, 122.6, 127.1, 127.7, 129.2, 129.3, 135.2, 144.0. Anal. Calcd for $C_{14}H_{12}N_2S_2$: C, 61.73; H, 4.44. Found: C, 61.79; H, 4.41.

Reaction of Tropone Phenylhydrazone (3a) with Phenyl Isocyanate (4b). A solution of **3a** (0.23 g, 1.2 mmol) and **4b** (0.38 g, 3.2 mmol) in benzene (5.0 ml) was heated at 60°C for 15 min under a nitrogen stream. After evaporation of the solvent the residual colorless oil was purified with thin layer chromatography on silica gel using hexane-ethyl acetate 1:2 as a developing solvent to give a colorless oil **5b** (370 mg, 99%, R_f= 0.59).

5b: colorless oil. Ms m/z (rel intensity): 315 (M^+, 33), 210 (40), 182 (100). Uv (MeOH): 320 nm (log ε , 3.56), 244 (4.25). Ir (oil): 3250, 3000, 1720, 1600 cm^{-1}. ^{1}H-Nmr δ : 4.50 (d, H_a), 4.96 (dd, H_b), 5.82 (dd, H_c), 6.24 (d, H_d), 6.38 (dd, H_e), 6.62 (dd, H_f), 6.70-7.70 (m, 10H, Ph). Coupling constants in Hz: J_{ab}=3.0, J_{bc}=9.2, J_{cd}=6.6, J_{de}=11.2, J_{ef}=6.0. ^{13}C-Nmr δ : 55.3, 94.9, 113.3, 115.7, 118.3, 121.5, 123.6, 124.1, 125.7, 129.0, 129.1, 129.2, 131.7, 137.3, 145.7. Anal. Calcd for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43. Found: C, 76.00; H, 5.46.

5c: colorless crystals. mp 152-154°C (ethyl acetate). Ms m/z (rel intensity): 393 (M^+, 1), 278 (14), 220 (100). Ir (KBr): 3350, 1760, 1720, 1350, 1170 cm^{-1}. ^{1}H-Nmr δ : 2.45 (s, 3H, Me), 4.58 (br s, H_a), 5.52 (m, H_b), 5.84 (br s, H_c), 6.12 (br s, H_d), 6.40 (m, 2H, H_e and H_f), 7.05-8.05 (m, 9H, aromatic protons). ^{13}C-Nmr δ : 21.6, 56.7, 97.2, 118.6, 125.0, 126.6, 127.0, 128.0, 128.4, 129.5, 129.7, 129.9, 130.1, 130.3, 145.1. Anal. Calcd for $C_{21}H_{19}N_3O_3S$: C, 64.11; H, 4.87. Found: C, 64.01 ; H, 4.69.

5d: colorless oil. Hrms m/z: 390.1716. Calcd for $C_{27}H_{22}N_2O$: 390.1730. Ms m/z (rel intensity): 390 (M^+,12), 194 (100), 165 (97). Ir (oil) : 1730, 1650, 1500 cm^{-1}. ^{1}H-Nmr δ : 3.66 (d, H_a), 4.57 (dd, H_b), 5.92 (d, H_f), 6.02 (dd, H_e), 6.57-7.60 (m, 17H, H_c, H_d, aromatic protons). Coupling constants in Hz; J_{ab}=4.8, J_{bc}=9.8, J_{cd}=6.6, J_{de}=10.2, J_{ef}=6.3. ^{13}C-Nmr δ : 46.0, 98.2, 113.6, 120.1, 121.8, 125.9, 126.2, 127.2, 127.9, 128.6, 129.2, 129.3, 129.5, 133.6, 142.9, 145.5, 174.2.

5e: pale yellow crystals. mp 130-132°C (benzene). Ms m/z (rel intensity): 350 (M^+, 10),163 (100). Uv (MeOH): 352 nm (log ε , 4.03) 289 (4.21). Ir (KBr): 3180, 1350, 1290, 1160 cm^{-1}. ^{1}H-Nmr δ : 2.39 (s, 3H, Me), 3.98 (br s, H_a), 5.30 (br s, H_b), 6.05-6.80 (m, 4H, H_c, H_d, H_e, and H_f), 7.10-7.80 (m, 4H, aromatic protons). ^{13}C-Nmr δ : 21.7, 42.8, 105.4, 117.4, 128.2, 128.8, 129.7, 145.7. Anal. Calcd for $C_{15}H_{14}N_2O_2S_3$: C, 51.41; H, 4.03. Found: C, 51.61; H, 3.87.

5f: colorless crystals. mp 159-160°C (benzene). Ms m/z (rel intensity): 393 (M^+, 40), 238 (100), 180 (27). Uv (MeOH): 317 nm (log ε , 3.42), 250 (4.23). Ir (KBr): 3100, 2900, 1700, 1640, 1160 cm^{-1}. ^{1}H-Nmr δ : 2.42 (s, 3H, Me), 4.47 (br s, H_a), 4.92 (br s, H_b), 6.00-6.80 (m, 4H, H_c, H_d, H_e, and H_f), 7.10-7.90 (m, 9H, aromatic protons). ^{13}C-Nmr δ : 21.6, 55.6, 97.1, 115.7, 118.8, 124.1, 125.8, 128.4, 129.0, 129.1, 129.6, 136.6, 145.0. Anal. Calcd for $C_{21}H_{19}N_3O_3S$: C, 64.11;H, 4.87. Found: C, 64.12; H, 4.85.

5g: colorless crystals. mp 173-175°C (ethyl acetate). Uv (MeOH): 310 nm (log ε , 3.59). Ir (KBr): 1760, 1660, 1360, 1150 cm^{-1}. ^{1}H-Nmr δ : 2.45 (s, 3H, Me), 2.48 (s, 3H, Me), 4.57 (br s, H_a), 5.35 (br s, H_b), 6.20-6.62 (m, 4H, H_c, H_d, H_e, and H_f), 7.16-7.85 (m, 8H, aromatic protons). ^{13}C-Nmr δ : 21.8, 56.7, 98.7, 118.0, 125.3, 126.7, 126.9, 128.0, 128.3, 129.7, 129.8, 145.0. Anal. Calcd for $C_{22}H_{21}N_3O_5S_2$: C, 56.15; H, 4.20. Found: C, 56.04; H, 4.49.

5h: colorless oil. Hrms m/z: 468.1499. Calcd for $C_{28}H_{24}N_2O_3S$: 468.1506. Ms m/z (rel intensity): 468 (M^+, 4), 167 (100). Uv (MeOH): 289 nm (log ε , 3.80). Ir (oil): 1740, 1650, 1490 cm^{-1}. ^{1}H-Nmr δ : 2.38 (s, 3H, Me), 3.57 (d, H_a), 4.56 (dd, H_b), 6.15 (m, 2H, H_e and H_f), 6.59 (dd, H_d), 6.70-7.90 (m, 15H, H_c and aromatic protons). Coupling constants in Hz; J_{ab}=5.0, J_{bc}=9.6, $J_{c\,d}$=6.8, $J_{d\,e}$=11.2, $J_{e\,f}$=5.8. ^{13}C-Nmr δ : 21.7, 46.2, 57.8, 98.8, 119.5, 126.4, 127.2, 127.3, 127.9, 128.1, 128.2, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 129.6, 139.3, 142.2, 145.5, 172.0.

5i: pale yellow oil. Hrms m/z: 409.0908. Calcd for $C_{21}H_{19}N_3O_2S_2$: 409.0918. Ms m/z (rel intensity): 409 (M^+, 46), 395 (58), 254 (100). Uv (MeOH): 325 nm (log ε , 3.83), 266 (3.89). Ir (KBr): 3200, 2900, 1620, 1160 cm^{-1}. ^{1}H-Nmr δ : 2.40 (s, 3H, Me), 3.95 (br s, H_a), 5.15 (br s, H_b), 6.00-6.90 (m, 4H, H_c, H_d, H_e, and H_f), 7.00-8.00 (m, 9H, aromatic protons). ^{13}C-Nmr δ : 21.4, 42.2, 110.3, 119.4, 120.8, 124.2, 125.4, 127.3, 128.7, 128.9, 129.3, 129.4, 144.9, 147.4.

6i: pale yellow crystals. mp 194-195°C (benzene). Ms m/z (rel intensity) :409 (M^+, 41), 254 (100). Uv (MeOH): 334 nm (log ε , 3.76), 276 (4.13). Ir (KBr): 3200, 1440, 1170 cm^{-1}. ^{1}H-Nmr δ : 2.45 (s, 3H, Me), 4.72 (br s, H_a), 4.87 (br s, H_b), 6.10-6.42 (m, 4H, H_c, H_d, H_e, and H_f), 7.20-7.90 (m, 9H, aromatic protons), 8.00 (br s, NH). ^{13}C-Nmr δ : 21.8, 61.4, 98.6, 113.8, 124.9, 125.9, 127.5, 128.2, 129.2, 129.5, 129.7, 137.2, 145.4. Anal. Calcd for $C_{21}H_{19}N_3O_2S_2$: C, 61.59; H, 4.68. Found: C, 61.47; H, 4.60.

*Reaction of N-Methoxytroponimine (**3c**) with Chlorophenylketene (**7a**).* To a solution of **3c** (135 mg, 1.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (1.5 ml) was slowly added a solution of chlorophenylacethyl chloride (570 mg, 3.0 mmol) in dichloromethane (1.0 ml) at room temperature. After the addition was completed, the mixture was stirred at room temperature for 24 h and then poured into water, extracted with dichloromethane, and the organic layer was dried over sodium salfate. After removal of the solvent the residue was separated with column chromatography on silica gel to give red crystals of **8a** (91 mg, 90%, hexane-ethyl acetate 65 : 35 as an eluent).

8a: orange crystals. mp 128-130°C (ethyl acetate). Ms m/z (rel intensity): 251 (M^+, 100), 178 (50), 165 (52). Uv (MeOH): 424 nm (log ε , 3.75), 288 (4.22). Ir (KBr): 1680, 1583 cm^{-1}. ^{1}H-Nmr δ : 4.18 (s, 3H, OMe), 6.90-7.90 (m, 10H, olefinic protons). ^{13}C-Nmr δ : 65.1, 110.4, 127.6, 127.8, 128.6, 129.0, 130.1, 131.0, 131.6, 135.6, 139.0. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21. Found: C, 76.46; H, 5.20.

8b: yellow crystals. mp 120-121°C (ethyl acetate). Ms m/z (rel intensity): 209 (M^+, 100), 179 (41), 150 (90). Uv (MeOH): 418 nm (log ε , 3.84), 273 (4.46). Ir (KBr): 1694, 1593 cm^{-1}. ^{1}H-Nmr δ : 4.12 (s, 3H, OMe), 6.92-7.65 (m, 5H, olefinic protons). ^{13}C-Nmr δ : 65.4, 103.1, 111.3, 126.5, 130.3, 131.2, 132.1, 135.0, 138.0. Anal. Calcd for $C_{10}H_8NO_2Cl$: C, 57.30; H, 3.85. Found: C, 57.20; H, 3.80.

9: yellow crystals. mp 190-192°C (ethyl acetate). Hrms m/z: 253.0337. Calcd for $C_{12}H_{10}NO_3Cl$: 253.0319. Ms m/z (rel intensity): 253 (M^+, 15), 202 (100), Uv (MeOH): 436 nm (log ε , 3.84). Ir (KBr): 1682, 1651, 1607 cm^{-1}. ^{1}H-Nmr δ : 4.20 (s, 3H, Me), 4.95 (s, 2H, CH_2), 7.50-7.85 (m, 4H, H_a, H_b, H_c, and H_d), 9.54 (d, H_e, J_{de}=11.0 Hz). ^{13}C-Nmr δ : 49.7, 65.3, 116.8, 132.8, 134.3, 136.3, 138.7.

10: pale yellow crystals. mp 126-128°C (benzene). Ms m/z (rel intensity): 240 (M^+, 100), 137 (85). Uv (MeOH): 343 nm (log ε , 4.22), 293 (3.90), 273 (3.90). Ir (KBr): 1597, 1568, 1520, 1424 cm^{-1}. ^{1}H-Nmr δ : 4.15 (d, 2H, H_a and $H_{a'}$), 5.49 (dt, H_b), 6.14 (dd, H_c), 6.38 (dd, H_d), 6.69 (d, H_e), 7.02-7.42 (m, 5H, aromatic protons). Coupling constants in Hz; J_{ab}=$J_{a'b}$=6.9, J_{bc}=10.1, J_{cd}=5.7, J_{de}=11.5. ^{13}C-Nmr δ : 29.6, 118.9, 119.0, 121.4, 121.9, 123.5, 126.7, 127.3, 129.6, 140.3, 143.4, 167.1. Anal. Calcd for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03. Found: C, 70.00; H, 5.01.

12: corless crystals. mp 129-131°C (ethyl acetate). Hrms m/z: 343.0340. Calcd for $C_{21}H_{17}N_3O_2$: 3430320. Ms m/z (rel intensity): 343 (M^+, 1), 224 (88), 119 (100). Uv (MeOH): 291 nm (log ε , 3.84), 242 (4.33). Ir (KBr): 1736, 1601, 1561 cm^{-1}. ^{1}H-Nmr δ : 2.41 (2H, t, H_a and $H_{a'}$), 5.22 (dt, H_b), 5.34 (dt, H_c), 6.05 (d, H_d), 6.92 -7.59 (m, 11H, H_e and Aromatic protons). Coupling constants in Hz; J_{ab}=$J_{a'b}$=J_{ac}=$J_{a'c}$= 6.0, J_{bd}= 9.2, J_{ce}= 9.4. ^{13}C-Nmr δ : 25.8, 114.1, 115.9, 120.3, 123.5, 124.4, 125.6, 126.5, 127.3, 127.4, 128.5, 129.1, 129.6, 133.6, 137.4, 148.8, 151.6.

14: pale yellow crystals. mp 137-139°C (methanol). Ms m/z (rel intensity): 222 (M^+, 67), 119 (100). Uv (MeOH): 390 nm (log ε , 3.68). Ir (KBr): 1667, 1591, 1562, 1392 cm^{-1}. ^{1}H-Nmr : 6.90-8.05 (m, 10H, olefinic and aromatic protons). ^{13}C-Nmr δ : 115.0, 127.4, 129.1, 129.8, 129.9, 131.8, 133.5, 136.1, 139.1, 149.7, 164.9, 165.7. Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54. Found: C, 75.65, H, 4.54.

Thermal reaction of ***12***. A solution of **12** (66 mg, 0.19 mmol) in toluene (4.0 ml) was refluxed for 48 h and then separated with thin layer chromatography on silica gel using methanol-ethyl acetate 1:4 as a developing solvent to give a colorless oil **13** (R_f=0.82, 6 mg, 15%), recovered **12** (R_f= 0.94, 53 mg, 80%), and **14** (R_f=0.41, 2mg, 5%).

13: colorless oil. Hrms m/z: 224.0958. Calcd for $C_{14}H_{12}N_2O$: 224.0949. Ms m/z (rel intensity): 224 (M^+, 24), 149 (12), 119 (100). Uv (MeOH): 299 nm (log ε , 3.77), 241 (4.29). Ir (oil): 1740, 1601, 1560 cm^{-1}. ^{1}H-Nmr δ : 2.41 (t, 2H, H_a and $H_{a'}$), 5.07 (dt, H_b), 5.18 (dt, H_c), 6.08 (d, H_d), 6.35 (d, H_e), 7.18-7.57 (m, 5H, aromatic protons). Coupling constants in Hz; J_{ab}=$J_{a'b}$=J_{ac}=$J_{a'c}$= 6.0, J_{bd}= 9.0, J_{ce}= 9.1.

Thermal Reaction of ***12*** *in the Presence of p-Chloranil.* A mixture of **12** (90 mg, 0.26 mmol) and *p*-chloranil (100 mg, 0.41 mmol) in toluene (3.0 ml) was refluxed for 2 h and then separated with thin layer chromatograophy on silica gel using ethyl acetate-methanol 4:1 as a developing solvent to give **14** (50 mg, 87%).

18: colorless oil. Hrms m/z: 247.0859. Calcd for $C_{13}H_{13}NO_4$: 247.0844. Ms m/z (rel intensity): 247 (M^+, 68), 215 (100), 157 (77). Ir (oil): 1732, 1693, 1589 cm^{-1}. ^{1}H-Nmr δ : 3.21 (d, 2H, H_a and $H_{a'}$), 3.84 (s, 3H, Me), 3.85 (s, 3H, Me), 5.48 (dt, H_b), 6.04 (dd, H_c), 6.23 (dd, H_d), 6.93 (d, H_e), 9.23 (br s, NH). Coupling constants in Hz; $J_{ab}=J_{a'b}=6.7$, $J_{bc}=11.3$, $J_{cd}=6.5$, $J_{de}=11.4$.

Oxidation of ***10***. To a solution of **10** (86 mg, 0.36 mmol) in dichloromethane (5.0 ml) was added manganeses oxide (900 mg, 7.6 mmol) and the mixture was stirred at room temerature for 1 h. After filtration the solvent was removed to give crystals of **11** (70 mg, 82%).

11: red yellow crystals. mp 138-140°C (dichloromethane-ethyl acetate 1:1). Ms m/z (rel intensity): 238 (M^+, 100), 135 (52). Uv (MeOH): 414 nm (log ε , 4.17), 265 (4.48). Ir (KBr): 1601, 1580, 1444 cm^{-1}. ^{1}H-Nmr δ : 6.90-7.65 (m, 10H, olefinic and aromatic protons). ^{13}C-Nmr δ : 120.4, 126.7, 129.6, 130.9, 133.0, 133.8, 138.2, 151.2, 156.9, 172.7. Anal. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23. Found: C, 70.50; H, 4.20.

20: yellow crystals. mp 151-153°C (ethyl acetate). Ms m/z (rel intensity): 245 (M^+, 58), 214 (86), 129 (100). Uv (MeOH): 455 nm (log ε , 3.03), 316 (3.88), 281 (4.67), 215 (4.34). Ir (KBr): 1736, 1709 cm^{-1}. ^{1}H-Nmr δ : 3.98 (s, 3H, Me), 4.07 (s, 3H, Me), 8.01 (dd, H_b), 8.04 (dd, H_d), 8.19 (dd, H_c), 8.95 (d, H_e), 9.69 (d, H_a). Coupling constants in Hz; $J_{ab}=10.2$, $J_{bc}=9.4$, $J_{cd}=10.5$, $J_{de}=9.7$. Anal. Calcd for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52. Found: C, 63.70; H, 4.55.

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4. ^{1}H-Nmr spectrum of **15** was as follows: ^{1}H-nmr δ : 2.38 (s, 3H, Me), 3.88 (s, 3H, OMe), 4.41 (br s, H_a), 5.30 (br s, H_b), 5.58-6.53 (m, 4H, H_c, H_d, H_e, and H_f), 7.10-8.20 (m, 4H, aromatic protons). Compound (**15**) could not be isolated, since it easily decomposed under the reaction conditions and during the purification process.
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