Reaction of Tropone Hydrazones with Heterocumulenes such as Isocyanate, Ketene, and Sulfene

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Tropone benzoyl- and tosylhydrazones underwent the [8+2] cycloaddition reaction with isocyanates to afford the cyclohepta[*d*]imidazolin-2-one derivatives. This means that these hydrazones behaved as 8-amino-8-azaheptafulvenes. Also, the tropone hydrazones reacted with phenylketene and phenylsulfene in more complicated manners.

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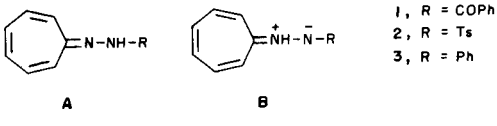
Hydrazones have been prepared mainly for the purpose of the identification or purification of carbonyl compounds. However, the potentiality as a synthetic tool for the heterocyclic compounds has rapidly developed, since the reaction of benzaldehyde hydrazone as 1,3-dipole was reported by George and his co-workers [1].

In the continuation of our studies on the reaction of 8-functionalized 8-azaheptafulvene [2], our attention was focused on the reaction of tropone hydrazones, which could be regarded as 8-substituted amino-8-azaheptafulvenes (**A**) or tautomeric azomethine imines (**B**).

In this paper the reactions of tropone hydrazones with heterocumulenes such as isocyanate, ketene, and sulfene are described.



A B

Results and Discussion.

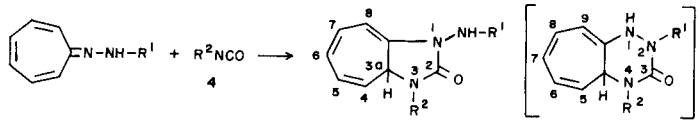
The reaction of tropone benzoylhydrazone (**1**) with phenyl isocyanate (**4a**) at room temperature in dry chloroform gave the (1:1) adduct **5a** as a sole product in 86% yield. In the ir spectrum of **5a** the characteristic carbonyl absorption bands at 1760 and 1660 cm^{-1} were assignable to those of the five-membered ureido and carbamoyl moieties, respectively. Also, in its pmr spectrum the signal pattens of the protons on the seven-membered ring (δ 4.4-6.6 ppm) were closely similar to those of the [8 + 2] cycloadducts [3] from 8-aryl-8-azaheptafulvenes and **4a**. From the analytical and spectral data, the structure of **5a** was deduced to be 1-benzamido-1,2,3,3a-tetrahydro-2-oxo-3-phenylcyclohept[*d*]imidazole, the [8 + 2] cycloadduct from **1** and **4a**.

The reactions of **1** with *p*-chlorophenyl (**4b**) and tosyl isocyanate (**4c**) gave the corresponding [8 + 2] cycloadducts **5b** and **5c**, respectively. Similarly, the reactions of tropone tosylhydrazone (**2**) with **4a** and **4c** afforded the same type of adducts **6a** and **6c**. These results are summarized in Table 1.

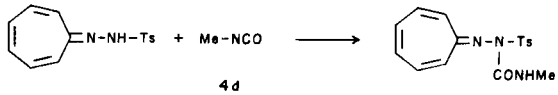
This means that these tropone hydrazones behave as 8-substituted 8-amino-8-azaheptafulvenes (**A**) toward isocyanates. On the other hand, methyl isocyanate (**4d**) did not react with **1** or **2** at room temperature, but only the heating of **2** with **4d** in chloroform under reflux gave tropone *N*-(methylcarbamoyl)tosylhydrazone (**7**) in 61% yield.

Table 1

Reactions of Tropone Hydrazones **1** and **2** with Isocyanates **4**



Compound	R^1	R^2	Yield %
5a	COPh	Ph	86
5b	COPh	*p*-chlorophenyl	98
5c	COPh	Ts	100
6a	Ts	Ph	57
6c	Ts	Ts	96



2 7

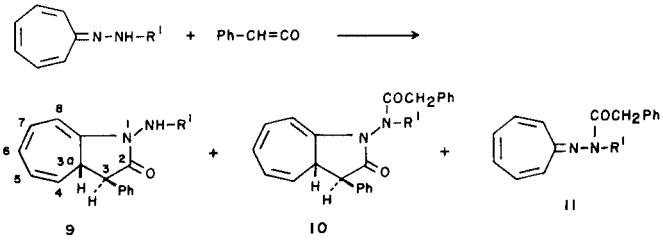
Furthermore, the reactions of the tropone hydrazones with other heterocumulenes such as ketene and sulfene were investigated. It turned out that they were more complicated than those with isocyanates. For example, the reaction of hydrazone **1** with phenylketene (**8**), generated from phenacetyl chloride and triethylamine *in situ*, at room temperature in THF gave the (1:1) adduct **9a** and the (1:2) adduct **10a** in 25 and 5% yields, respectively. The ir spectrum of **9a** shows two carbonyl absorption bands at 1720 and 1675 cm^{-1} as well as the absorption band at 3200 cm^{-1} assigned to amino group. On the other hand, in the ir spectrum of **10a** three carbonyl stretching vibrations at 1755, 1730 and 1705 cm^{-1} were observed, but the adsorption band assignable to amino group was not detected. Also, in the pmr spectra of **9a** and **10a** the signal patterns of the protons on seven-membered ring (δ 4-7 ppm) were

closely similar to those of 1,2,3,3a-tetrahydro-2-oxo-3-phenyl-1-azaazulene [3], the cycloadduct from 8-phenyl-8-azaheptafulvene and phenylketene (**8**). Therefore, the structures of **9a** and **10a** were confirmed as 1-benzamido-1,2,3,3a-tetrahydro-2-oxo-3-phenyl-1-azaazulene and 1,2,3,3a-tetrahydro-2-oxo-1-phenacetylbenzamido-3-phenyl-1-azaazulene, respectively.

Tropone tosylhydrazone (**2**) reacted with ketene **8** to give the (1:1) adduct, tropone phenacetyltosylhydrazone (**11**), and the (1:2) adduct, 1,2,3,3a-tetrahydro-2-oxo-1-phenacetylbenzamido-3-phenyl-1-azaazulene (**10b**). Also, tropone phenylhydrazone (**3**) reacted with ketene **8** to afford the corresponding [8 + 2] cycloadduct **9c** in 25% yield. These results are shown in Table 2.

Table 2

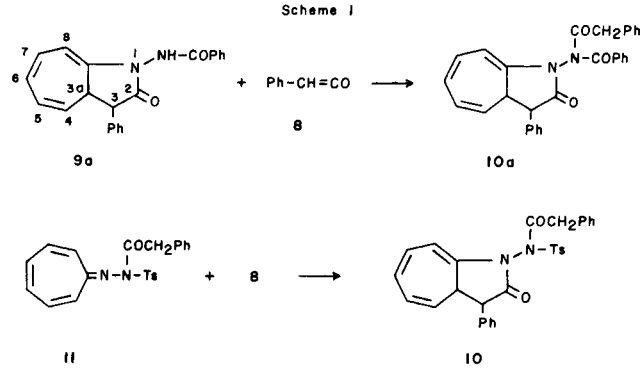
Reactions of **1**, **2** and **3** with Phenylketene (**8**)



Run	R'	Yield 9	10	11
1	COPh	25	5	—
2	Ts	—	33	13
3	Ph	25	—	—

Herein, the (1:2) adduct **10a** or **10b** was obtained by the reaction of the isolated (1:1) adduct **9a** or **11** with ketene **8** and, thus, the [8 + 2] cycloadduct **9a** or the *N*-phenacetylated product **11** was the initially formed product in each case (Scheme 1).

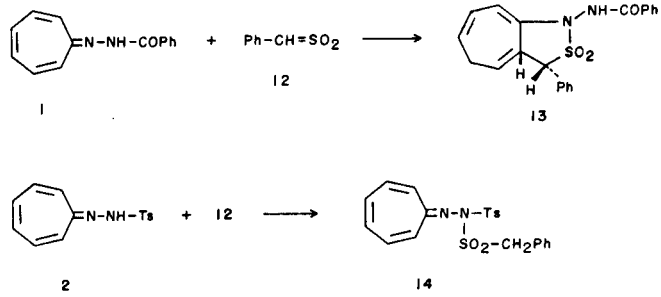
Scheme 1



The configurations between the vicinal methine protons at 3- and 3a-positions in 1-azaazulene derivatives **9** and **10** were deduced to be *trans*, because the coupling constants (J_{3-3a}) and the chemical shifts for the olefin proton at 4-position were consistent with those of the cycloadducts from 8-aryl-8-azaheptafulvenes and phenylketene (**8**) [4].

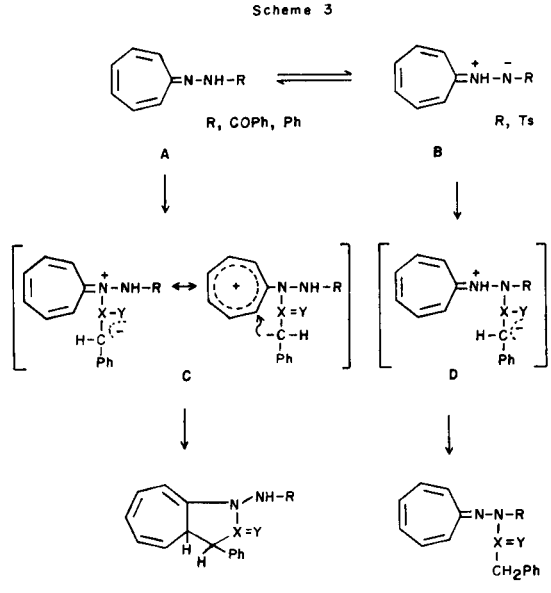
The reaction of hydrazone **1** with phenylsulfene (**12**), generated from benzenemethanesulfonyl chloride and triethylamine *in situ*, gave the [8 + 2] cycloadduct, 1-benzamido-3,3a-dihydro-3-phenyl-1*H*-cyclohepta[*c*]isothiazole 2,2-dioxide (**13**), in 48% yield. The configuration of the protons at 3- and 3a-positions was concluded to be *cis* comparing with that in 1-aryl homolog [5]. Hydrazone **2** reacted with sulfene **12** to afford the *N*-sulfonylated product, tropone benzenemethanesulfonyltosylhydrazone (**14**), in 62% yield. The reaction of tropone phenylhydrazone (**3**) with sulfene **12** gave only a mixture of troublesome products.

Scheme 2



The above results show that the electrophilic attack of isocyanates takes place on the imino-nitrogen atom in the tropone hydrazones (**1-3**) to give the betaine intermediate (**C**), which cyclizes to the cyclohepta[*d*]imidazole derivatives. The attack of ketene or sulfene does also on the imino-nitrogen atom in **1** or **3**. However, the initial attack site of ketene and sulfene toward tropone tosylhydrazone (**2**) changes to amino-nitrogen atom to afford *N*-phenacetylated and *N*-sulfonylated products, respectively, *via* the intermedaite (**D**).

Scheme 3



As this point, we suggested the existence of the equilibrium between 8-amino-8-azaheptafulvene (**A**) and tautomeric azomethine imine (**B**). Herein, the equilibrium would lean toward **B** in tropone tosylhydrazone (**2**) because of the high acidicity of the amino hydrogen atom (Scheme 3).

As other factors controlling the regioselectivity of the nucleophilic addition of heterocumulene, the reactivity of heterocumulene, the existence of a retro-reaction of intermediate **C** or **D** to the starting materials, and the effect of the substituent at 8-position of 8-azaheptafulvene are possible. However, the rational explanation for these respects is not attained so far.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were measured on a Nippon Bunko IRA-1 spectrometer as potassium bromide pellets. The pmr spectra were obtained at 100 MHz using a Nippon Denshi JEOL JNM-MH-100 spectrometer with tetramethylsilane as an internal standard in deuteriochloroform unless otherwise stated. Mass spectra were determined with JEOL JMS-D mass spectrometer equipped a direct inlet system and at an ionization energy of 75 eV.

Preparation of Tropone Benzoyl- (**1**), Tosyl- (**2**), and Phenylhydrazone (**3**).

Although some preparations of tropone hydrazones were reported, the yields were not always satisfactory. Thus, we prepared these hydrazones in an improved method; in the suspension of tropone and the corresponding hydrazine in methanol hydrogen chloride was introduced for ten minutes, then the solution was stirred for one day. After concentrating the methanol solution, the residue was poured into water and extracted with benzene. The aqueous layer was made basic with sodium hydrogencarbonate and extacted with dichloromethane. The organic layer was collected, dried, and evaporated in a reduced pressure to give a residue, which was purified with short column chromatography (silica gel-ethyl acetate) to afford the hydrazone.

Tropone Benzoylhydrazone (**1**).

This compound was obtained in a yield of 69%, mp 137-138° (lit [6] mp 135-136°).

Tropone Tosylhydrazone (**2**).

This compound was obtained in a yield of 83%, mp 144-145° (lit [7] mp 144-145°).

Tropone phenylhydrazone (**3**).

This compound was obtained in a yield of 84%, mp 78-81° (lit [8] mp 89-90°).

General Procedure for the Reactions of Tropone Hydrazones (**1-3**) and Isocyanates (**4**).

When a solution of tropone benzoylhydrazone (**1**) (0.52 g, 2.4 mmoles) and phenyl isocyanate (**4a**) (0.28 g, 2.4 mmoles) in dry chloroform (15 ml) was stirred for three hours at room temperature, the chloroform was removed *in vacuo* to give a residue. The residue was treated with column chromatography (silica gel-chloroform) to give 0.68 g (86%) of **5a**.

1-Benzamido-1,2,3,3a-tetrahydro-2-oxo-3-phenylcyclohept[*d*]imidazole (**5a**).

This compound was obtained as colorless prisms (isopropyl alcohol), mp 187-189° dec; ir: ν NH 3200, ν CO 1760, 1660 cm^{-1}; pmr: δ 4.41 (br d, 1H, 3a-H, J = 3.0 Hz), 4.86 (dd, 1H, 4-H, J = 3.0, 9.5 Hz), 5.63 (d, 1H, 8-H, J = 6.3 Hz), 6.0-6.6 (m, 3H, 5-, 6-, and 7-H), 7.1-7.8 (m, 10H, phenyl potons), 9.71 ppm (br s, 1H, NH); ms: (m/e) 343 (M^+), 224 (M^+-PhNCO), 119 ($PhNCO^+$), 105, 77.

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.13; H, 5.03; N, 12.18.

1-Benzamido-3-(*p*-chlorophenyl)-1,2,3,3a-tetrahydro-2-oxocyclohept[*d*]-imidazole (**5b**).

This compound was obtained as colorless needles (ethanol), mp 187-188°; ir: ν NH 3200, ν CO 1750, 1655 cm^{-1}; pmr: δ 4.46 (br d, 1H, 3a-H, J = 3.3 Hz), 4.92 (dd, 1H, 4-H, J = 3.3, 10.5 Hz), 5.75 (d, 1H, 8-H, J = 6.6 Hz), 6.1-6.7 (m, 3H, 5-, 6-, and 7-H), 7.3-8.0 (m, 9H, phenyl potons), 9.61 ppm (br s, 1H, NH); ms: (m/e) 379, 377 (M^+), 274, 272 (M^+-COPh), 119 ($PhNCO^+$), 105, 77.

Anal. Calcd. for $C_{21}H_{16}ClN_3O_2$: C, 66.75; H, 4.27; N, 11.12. Found: C, 66.63; H, 4.30; N, 11.34.

1-Benzamido-1,2,3,3a-tetrahydro-2-oxo-3-tosylcyclohept[*d*]imidazole (**5c**).

This compound was obtained as colorless crystals (benzene), mp 189-191°; ir: ν NH 3310, ν CO 1770, 1655 ν SO_2 1355, 1170 cm^{-1}; pmr: δ 2.44 (s, 3H, $-CH_3$), 4.66 (br d, 1H, 3a-H, J = 2.5 Hz), 5.41 (dd, 1H, 4-H, J = 2.5, 12.6 Hz), 5.65 (d, 1H, 8-H, J = 5.7 Hz), 6.26 (dd, 1H, 7-H, J = 5.7, 14.6 Hz), 6.4-6.6 (m, 2H, 5-H and 6-H), 7.3-8.1 (m, 9H, phenyl protons), 8.95 ppm (br s, 1H, NH).

Anal. Calcd. for $C_{22}H_{19}N_3O_4S$: C, 62.69; H, 4.54; N, 9.96. Found: C, 62.93; H, 4.59; N, 10.22.

1,2,3,3a-Tetrahydro-2-oxo-3-phenyl-1-tosylamidocyclohept[*d*]imidazole (**6a**).

This compound was obtained as colorless prisms (isopropyl alcohol), mp 171-172°; ir: ν NH 3310, ν CO 1725, ν SO_2 1380, 1160 cm^{-1}; pmr: δ 2.38 (s, 3H, $-CH_3$), 4.38 (br d, 1H, 3a-H, J = 3.5 Hz), 4.84 (dd, 1H, 4-H, J = 3.5, 9.9 Hz), 6.1-6.6 (m, 4H, 5-, 6-, 7-, and 8-H), 7.0-7.4 and 7.7 pm (m, total 10H, phenyl protons and NH); ms: (m/e) 393 (M^+), 238 (M^+-Ts), 155 (Ts^+), 119 ($PhNCO^+$), 77.

Anal. Calcd. for $C_{21}H_{19}N_3O_3S$: C, 64.11; H, 4.87; N, 10.68. Found: C, 64.03; H, 4.88; N, 10.65.

1,2,3,3a-Tetrahydro-2-oxo-3-tosyl-1-tosylaminocyclohept[*d*]imidazole (**6c**).

This compound was obtained as colorless needles (benzene), mp 170-172°; ir: ν NH 3270, ν CO 1760, ν SO_2 1380, 1170 cm^{-1}; pmr: δ 2.39, 2.48 (2s, each 3H, $-CH_3$), 4.71 (d, 1H, 3a-H, J = 3.0 Hz), 5.3-6.6 (m, 5H, 4-, 5-, 6-, 7-, and 8-H), 7.2-8.0 ppm, (m, 9H, phenyl protons and NH).

Anal. Calcd. for $C_{22}H_{21}N_3O_5S_2$: C, 56.03; H, 4.48; N, 8.91. Found: C, 56.18; H, 4.52; N, 9.18.

Reaction of Tropone Tosylhydrazone (**2**) with Methyl Isocyanate (**4d**).

When a solution of the hydrazone **2** (0.55 g, 2 mmoles) and methyl isocyanate (0.11 g, 2 mmoles) in dry chloroform (20 ml) was heated under reflux for sixteen hours, 0.40 g (61%) of a yellow oil **7** was obtained after the usual working-up.

Tropone *N*-Methylcarbamoyl-*N*-tosylhydrazone (**7**).

This compound had ir (neat): ν NH 3380, ν CO 1700, ν SO_2 1355, 1170 cm^{-1}; pmr: δ 2.34, 2.67 (2s, each 3H, $-CH_3$), 6.15 (m, 1H, NH), 6.6-8.0 ppm (m, 10H, olefinic and phenyl protons); ms: (m/e) 331 (M^+), 273 (M^+-MeNCO).

Anal. Calcd. for $C_{16}H_{17}N_3O_3S$: C, 58.00; H, 5.17; N, 12.68. Found: C, 37.65; H, 4.88; N, 12.75.

General Procedure for the Reaction of Tropone Hydrazones (**1-3**) with Phenylketene (**8**).

All these reactions were carried out under nitrogen atmosphere. To a stirred and cooled (0°) solution of tropone benzoylhydrazone (**11**) (1.12 g, 5 mmoles) and triethylamine (0.61 g, 6 mmoles) in dry THF (15 ml), the same solution (5 ml) of phenacetyl chloride (0.77 g, 6 mmoles) was added drop by drop for ten minutes and the reaction mixture was allowed to stand at the temperature for additional thirty minutes. After being warmed to room temperature gradually, the mixture was stirred overnight. The resultant triethylamine hydrochloride was filtered and the filtrate

was evaporated *in vacuo* to give an oily residue. The residue was treated with column chromatography (silica gel-chloroform) to give **9a** and **10a** in 25 and 9% yield, respectively.

1-Benzamido-1,2,3,3a-tetrahydro-2-oxo-3-phenyl-1-azaazulene (**9a**).

This compound was obtained as colorless needles (isopropyl alcohol), mp 179-180°; ir: ν NH 3200, ν CO 1725, 1675 cm^{-1}; pmr: δ 3.12 (br, 1H, 3a-H), 3.86 (br d, 1H, 3-H, J = 5.7 Hz), 5.24 (dd, 1H, 4-H, J = 3.0, 9.0 Hz), 5.44 (d, 1H, 8-H, J = 6.3 Hz), 6.1-6.5 (m, 3H, 5-, 6-, and 7-H), 7.2-7.9 (m, 10H, phenyl protons), 9.3 ppm (br s, 1H, NH); ms: (m/e) 342 (M^+), 224 (M^+-PhCHCO), 119 ($PhNCO^+$), 105, 77.

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.16; H, 5.28; N, 8.35.

1,2,3,3a-Tetrahydro-2-oxo-1-phenylacetylbenzamido-3-phenyl-1-azaazulene (**10a**).

This compound was obtained as colorless prisms (isopropyl alcohol), mp 158-159°; ir: ν CO 1755, 1730, 1705 cm^{-1}; pmr: δ 2.86 (br, 1H, 3a-H), 3.82 (br d, 1H, 3-H, J = 5.4 Hz), 4.15, 4.37 (2d, each, 1H, $-CH_2-$, J = 15.3 Hz), 5.25 (dd, 1H, 4-H, J = 3.2, 9.6 Hz), 5.44 (d, 1H, 8-H, J = 6.3 Hz), 6.0-6.7 (m, 3H, 5-, 6-, and 7-H), 7.1-7.7 ppm (m, 15H, phenyl protons); ms: (m/e) 460 (M^+), 341 (M^+-$PhCH_2CO$), 224 (hydrazone 1^+), 119 ($PhNCO^+$), 105, 77.

Anal. Calcd. for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 5,97. Found: C, 78.23; H, 5.25; N, 6.38.

1,2,3,3a-Tetrahydro-2-oxo-1-(*N*-phenacetyltosylamido)-3-phenyl-1-azaazulene (**10b**).

This compound was obtained as colorless needles (benzene-hexane), mp 104.5-196°; ir: ν CO 1760, 1375, 1170 cm^{-1}; pmr: δ 2.41 (s, 3H, $-CH_3$), 3.28 (br, 1H, 3a-H), 3.69 (s, 2H, $-CH_2-$), 4.11 (br d, 1H, 3-H, J = 5.7 Hz), 5.42 (dd, 1H, 4-H, J = 4.1, 12.0 Hz), 5.80 (d, 1H, 8-H, J = 4.7 Hz), 6.2-6.6 (m, 3H, 5-, 6-, and 7-H), 7.0-7.6, 8.0 ppm (m, total 14H, phenyl protons); ms: (m/e) 510 (M^+), 392 (M^+-PhCHCO), 335 (M^+-Ts), 155 (Ts^+), 91.

Anal. Calcd. for $C_{30}H_{26}N_2O_4$: C, 70.57; H, 5.13; N, 5.49. Found: C, 70.83; H, 5.18; N, 5.48.

Tropone Phenacetyltosylhydrazone (**11**).

This compound was obtained as colorless prisms (isopropyl alcohol), mp 173-174.5°; ir: ν CO 1710, ν SO_2 1360, 1160 cm^{-1}; pmr: δ 2.46 (s, 3H, $-CH_3$), 3.65 (s, 2H, $-CH_2-$), 6.3-7.4, 8.0 ppm (m, total 15H, olefinic and phenyl protons); ms: (m/e) 392 (M^+), 274 (M^+-PhCHCO), 155 (Ts^+), 119, 91.

Anal. Calcd. for $C_{22}H_{20}N_2O_3S$: C, 67.33; H, 5.14; N, 7.14. Found: C, 67.56; H, 5.20; N, 7.28.

1-Anilino-1,2,3,3a-tetrahydro-2-oxo-3-phenyl-1-azazulene (**9c**).

This compound was obtained as colorless prisms (isopropyl alcohol), mp 167-168° dec; ir: ν NH 3240, ν CO 1715 cm^{-1}; pmr: δ 3.13 (br, 1H, 3a-H), 3.83 (br d, 1H, 3-H, J = 5.9 Hz), 5.20 (dd, 1H, 4-H, J = 4.0, 8.7 Hz), 5.76 (d, 1H, 8-H, J = 6.3 Hz), 6.0-6.4 (m, 3H, 5-, 6-, and 7-H), 6.6-7.3 ppm (m, 10H, phenyl protons); ms: (m/e) 314 (M^+), 222 (M^+-PhNH), 196 (hydrazone 3^+), 77.

Anal. Calcd. for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.39; H, 5.76; N, 9.00.

General Procedure for the Reaction of Tropone Hydrazones (**1-3**) with Phenylsulfene (**12**).

To a cooled (−60°) solution of tropone benzoylhydrazone (**1**) (0.22 g, 1 mmole) and triethylamine (0.21 g, 2.1 mmoles) in dry THF (10 ml) benzenemethanesulfonyl chloride (0.4 g, 2.1 mmoles) in the same solvent (5 ml) was added dropwise for 30 minutes and stirred for an additional hour at the same temperature. After being warmed to room temperature, the reaction mixture was allowed to stand overnight. The resultant triethylamine hydrochloride was removed by filtration and the filtrate was evaporated *in vacuo* to give an oily resiude. The residue was purified with column chromatography (silica gel-chloroform) to afford 0.18 g (48%) of **13**.

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.13; H, 5.03; N, 12.18.

1-Benzamido-3,3a-dihydro-3-phenyl-1*H*-cyclohept[*c*]isothiazole 2,2-Dioxide(**13**).

This compound was obtained as colorless prisms (benzene-hexane), mp 181-182° dec; ir: ν NH 3170, ν CO 1655, ν SO_2 1330, 1150 cm^{-1}; pmr: δ 3.28 (br, 1H, 3a-H), 4.5-5.2 (m, 2H, 3-H and 4-H), 5.74 (d, 1H, 8-H, J = 7.2 Hz), 6.1-6.6 (m, 3H, 5-, 6-, and 7-H), 7.4, 7.9 (m, total 9H, phenyl protons), 8.43 ppm (s, 1H, NH); ms: (m/e) 378 (M^+), 314 (M^+-SO_2), 209 (M^+-SO_2-COPh), 105, 77.

Anal. Calcd. for $C_{21}H_{18}N_2O_3S$: C, 66.65; H, 4.79; N, 7.40. Found: C, 66.81; H, 4.78; N, 7.45.

Tropone Benzenemethanesulfonyltosylhydrazone (**14**).

This compound was obtained as yellow prisms (ethanol), mp 151° dec; ir: ν SO_2 1360, 1160 cm^{-1}; pmr: δ 2.44 (s, 3H, $-CH_3$), 4.63 (s, 2H, $-CH_2-$), 6.4-7.6, 8.2 ppm (m, total 15H, olefinic and phenyl protons).

Anal. Calcd. for $C_{21}H_{20}N_4O_2$: C, 58.87; H, 4.71; N, 6.54. Found: C, 58.77; H, 4.75; N, 6.84.

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