

Synthesis and Reactions of 2-Arylhydrazinotropones. I. Preparation of 2-(2-Arylhydrazino)tropones and the 4-Substituted Derivatives¹⁾

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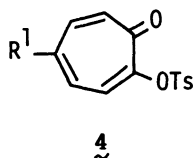
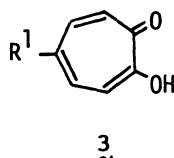
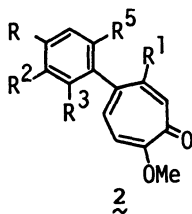
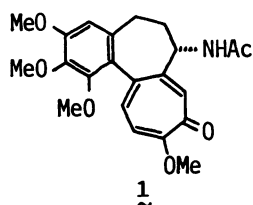
A wide variety of 2-(2-arylhydrazino)tropones were prepared by the reactions of 2-tosyloxytropone with arylhydrazines. The dimeric compounds 6,6'-bis(arylhydrazono)-1,1'-bi(2,4-cycloheptadiene)-7,7'-diones, 2-anilinotropones, and 3-(2-arylhydrazino)tropones were isolated as minor products in some cases. Similarly, starting with 2-tosyloxytropones bearing an isopropyl, isopropenyl, (1-acetamidoethyl), and protected acetyl group at the 5-position, 4-substituted 2-(2-arylhydrazino)tropones were obtained as the major products by the abnormal substitution reaction. These 2-(2-arylhydrazino)tropones are expected to effectively serve as precursors for a convenient synthesis of 5-aryl-substituted tropolones via benzidine-type rearrangement. ¹H NMR (200 or 500-MHz) parameters for these 4-substituted 2-(2-arylhydrazino)tropones are given for their unambiguous structural assignments.

Many hydrazoarenes and 1,2-diarylhydrazines (Ar-NHNHAr') are prepared by reduction of nitro-, azo-, and azoxyarenes.²⁾ As for troponoids,³⁾ several arylhydrazinotropones have been reported to be made by the substitution reaction of 2-methoxy-,⁴⁾ 2-chloro-,^{1a)} and 2-tosyloxytropones^{1b,5)} with arylhydrazines. Meanwhile, it became known that some 2-(2-arylhydrazino)-

tropones exhibited interesting physiological activity but were somewhat unstable towards acid.⁶⁾ We wish to describe in this paper a detailed study on preparation of a wide variety of 2-(2-arylhydrazino)tropones with or without a C-substituent at the 4-position. These compounds are expected to be valuable as the precursors for our attempt to exploit a convenient, general method of preparing B-ring-open colchicine analogues of type 2, by utilizing a novel benzidine type rearrangement of these 2-(2-arylhydrazino)tropones.¹⁾ This is because colchicine itself (1), though possessing highly important biological activity,⁷⁾ is often too toxic clinically and thus various analogues of 1 are drawing an increasing interest from the viewpoint of pharmacological activity.⁸⁾

Results and Discussion

As model compounds for the synthetic study on the B-ring-open analogues of type 2, six kinds of tropolones 3a–f were chosen as the starting materials: namely, those bearing no substituent, an isopropyl, isopropenyl, acetyl, (1-acetamidoethyl), and a protected acetyl group at the 5-position. Among these, 5-(1-acetamidoethyl)- (3e) and 5-(2,5,5-trimethyl-1,3-dioxan-2-yl)tropolone (3f) were newly synthesized from 5-acetyltropolone⁹⁾ (3d) by an application of the three-step procedure^{10,11)} (i.e., by the reaction with hydroxylamine, followed by hydrogenation over Pd–C and then acetylation with acetic anhydride) and by treatment with 2,2-dimethyl-1,3-propanediol in the presence of acid, respectively; the overall yields of these products are given in Table 1. These tropolones were then led to the tosylates 4a–f by the reaction with tosyl chloride in pyridine (see Table 1 for the



3, 4	R ¹
a	H
b	i-Pr
c	isopropenyl
d	Ac
e	-CHMeNHAc
f	

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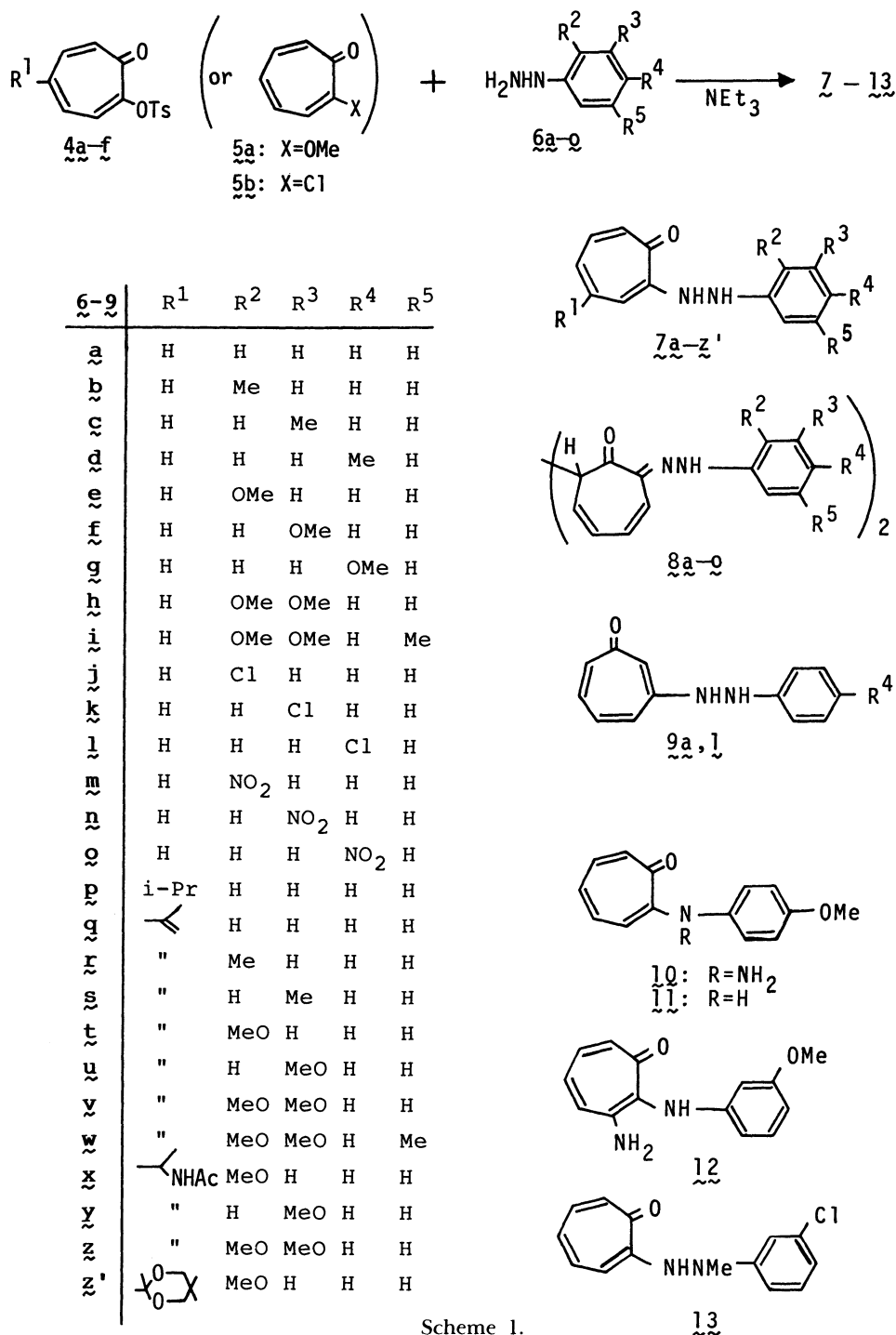
Table 1. Preparation of Tropolones and Tropolone Tosylates

Starting material	Product	
	Yield/%	Yield/%
3a		4a ^{a)} 100
3b		4b ^{b)} 100
3c		4c ^{c)} 97
3d		4d ^{d)} 21
3d	3e 47 ^{e)}	4e ^{g)} 70
3d	3f 70	4f ^{g)} 89

a) Ref. 17. b) Ref. 13. c) Ref. 14. d) Moisture-sensitive at 20°C. e) Overall yield from **3d**. f) From **3e**. g) From **3f**.

yields of **4**).

The tosylates **4** were treated with an excess (2–3 equiv) of various arylhydrazines **6a–o** (hydrochloride) either in refluxing methanol (or ethanol) for 6–24 h or in *N,N*-dimethylformamide (DMF) at 0–25 °C for 3–48 h in the presence of an excess (3–4 equiv) of triethylamine under nitrogen (see Scheme 1). After the usual work-up procedures including chromatographic separation, 27 kinds of 2-(2-arylhydrazino)tropolones **7a–z'** were isolated mostly as the main product in good to moderate yields. Besides **7**, certain amounts of by-products **8a–g, j–o, 9a,l**, and **10–13** were



Scheme 1.

isolated by the additional or unusual reactions of **4a** with some kinds of **6**; for further discussion on these minor products **8**–**13**, see below. The yields of these products are summarized in Table 2. 5-Acetyltropolone tosylate (**2d**), which was rather unstable at room temp, did not afford any of the expected 4-acetyl-2-(2-arylhazino)tropones. Also, the reaction of 2-methoxytropone (**5a**) with some of the arylhydrazines **6** was conducted in refluxing methanol. However, the yields of the products by this combination tend to become lower than those obtained by the reaction starting with tosylate **4a** and the corresponding arylhydrazines, as had also been observed in the case^{1a} with 2-chlorotropone (**5b**) (see Table 2).

Structures of these products were established by spectroscopy [UV, IR, ¹H NMR, MS, and ¹³C NMR (for some compds)] and elemental analysis; their exact data and the rational assignments for the spectral parameters are described in the Experimental section. The unequivocal assignments of the C-substituents of **7p**–**z'** to the 4-position, not 5-position, were based on the careful analysis of the 200 or 500-MHz ¹H NMR data by taking into account the parameters established earlier for similar compounds, such as 4-substituted 2-methoxytropones.¹¹ Characteristic features in the δ

and *J* values for these 4-substituted 2-(2-arylhazino)tropones are summarized in Table 3. These data are obviously of considerable value in precisely determining the positions of substituents even of hitherto unreported polysubstituted troponoids, such as those of type **2**.¹² It should be noticed that the 4-substituted products **7p**–**z'** were smoothly derived by the abnormal (ciné) substitution reactions of 5-substituted tropolone tosylates **4b**–**f** with arylhydrazines at room temperature in a polar aprotic solvent (DMF) as in the case of the reaction of **4b,c** with liquid ammonia.^{13,14}

By taking the parent tosylate **4a** as a representative, model compound, an effort to isolate the minor products **8**–**13** was made for the purpose of mechanistic study on this rather subtle, substitution reactions with primary arylhydrazines.¹⁵ The dimeric structures, 6,6'-bis(arylhazino)-1,1'-bi(2,4-cycloheptadiene)-7,7'-diones, were assigned for **8** primarily on the ground of their elemental analysis, IR, and doubly overlapping NMR signals, although MS gave no molecular ions but two intense fragment peaks presumably assignable to moieties **7** (*m/z* M⁺/2+1) and the corresponding 2-arylazotropones (*m/z* M⁺/2–1) derived from **8** as the result of facile fission by a disproportionation reaction. The dimers **8** are considered to be produced by oxidation of the monomeric arylhazino tropones **7**, since **8a** was obtained in 93% yield by refluxing **7a** in benzene in the presence of benzoyl peroxide.¹⁵

Another type of the minor products obtained in the case of the reaction of **4a** with **6a** and **6l** were 3-(2-arylhazino)tropones **9a** (6% yield) and **9l** (10%), respectively. These products are apparently derived as the result of the abnormal attack of the hydrazino

Table 2. Synthesis of 2-(2-Arylhazino)tropones

Starting material	Product			
	Yield/% ^{a, b}	Yield/%	Yield/%	Yield/%
4a (5a, 5b)	7a 66 (28 ^c , 48 ^d)	8a 3	9a 6	
4a (5a, 5b)	7b 82 (31, 34 ^d)	8b Trace		
4a (5a, 5b)	7c 72 (12, 57 ^d)	8c Trace		
4a (5a)	7d 63 (24)	8d Trace		
4a	7e 56	8e 2		
4a	7f 80	8f Trace	12 29 ^e	
4a	7g 47	8g 8	10 7	
4a		10 10 ^f	11 33 ^f	
4a	7h 22			
4a	7i 31			
4a	7j 64	8j Trace		
4a	7k 80	8k 2	13 3	
4a	7l 80	8l 1	9l 10	
4a	7m 21	8m Trace		
4a (5b)	7n 62 (53 ^d)	8n Trace		
4a	7o 51	8o Trace		
4b	7p 40			
4c	7q 63			
4c	7r 57			
4c	7s 77			
4c	7t 59			
4c	7u 60			
4c	7v 71			
4c	7w 61			
4e	7x 58			
4e	7y 57			
4e	7z 74			
4f	7z' 50			

a, b) Values in parentheses are for starting materials **5a** and **5b**, respectively. c) Ref. 4. d) Ref. 1a. e, f) Values obtained when the free bases **6f** and **6g** were used, respectively.

Table 3. Characteristic Features in the δ and *J* Values (Hz) for 4-Substituted 2-(2-Arylhazino)tropones **7p**–**z'**

Proton	δ	<i>J</i>
NH-2	8.3–8.1	
H-3	7.0–7.3	<i>J</i> _{3,5} ≈ 1.5
R-4	a, b, c, d)	
H-5	6.7–6.95	<i>J</i> _{5,6} = 9.5, <i>J</i> _{5,7} ≈ 1.0
H-6	7.2–7.3	<i>J</i> _{6,7} = 11.5–12.0
H-7	7.05–7.15	
NH-1'	5.6–6.3	
H-2'	6.3–6.8	<i>J</i> _{2',3'} = 8.0–8.5, <i>J</i> _{2',4'} ≈ <i>J</i> _{2',6'} ≈ 2
H-3'	6.9–7.35	<i>J</i> _{3',4'} = 7.5–8.0
H-4'	6.2–6.9	<i>J</i> _{4',5'} = 7.5–8.0, <i>J</i> _{4',6'} = 1.5–2.0
H-5'	6.9–7.25	<i>J</i> _{5',6'} = 7.5–8.0
H-6'	6.3–6.8	

a) For *i*-Pr: δ = 1.66 (6H, d, *J* = 7.0 Hz) and 2.81 (1H, sept).

b) For Isopropenyl: δ = 2.02–2.05 (3H, dd or t, *J* = 1.0–1.5 Hz), 5.09–5.13 (1H, dq or quint, *J* = 1.0–1.5 Hz), and 5.13–5.20 (1H, brs). c) For (1-acetamido)ethyl: δ = 1.3–1.4 (3H, d, *J* = 7.0 Hz) 1.85–1.9 (3H, s), 4.8–4.9 (1H, brq), and 5.7–6.3 (1H, brd, *J* = 6.5 Hz). d) For 2,5,5-trimethyl-1,3-dioxan-2-yl: δ = 0.55 (3H, s), 1.20 (3H, s), 1.47 (3H, s), and 3.19 (4H, brs).

group at C-3 of **4a** as was observed¹⁰ in the case of the initial step of the degradative alkaline hydrolysis of **5b** to salicylaldehyde.

The reaction of **4a** with the hydrochloride of **6g** gave, besides **7g** and **8g** (see Table 2), 2-(*N*-amino-4-methoxyanilino)troponone (**10**) in 7% yield. However, 2-(4-methoxyanilino)troponone (**11**) was mainly obtained (33% yield) besides **10** (10%) when **6g** hydrochloride had been converted to the free base with triethylamine before being treated with **4a**; it was later confirmed that compound **10** was converted into **11** in refluxing methanol in the presence of hydrochloric acid. Similarly, the reaction of free **6f** with **4a** gave 3-amino-2-(3-methoxyanilino)troponone (**12**) in 29% yield. These results indicate that *m*- and *p*-methoxyphenylhydrazines (**6f,g**) tend to afford much more complex products depending upon the reaction conditions, whereas *o*-methoxyphenylhydrazine (**6e**) appears to give no product of the anilino-substituted type.

From the reaction of **4a** with **6k**, 2-[2-(3-chlorophenyl)-2-methylhydrazino]troponone (**13**) was also isolated in 3% yield, the reason for which, however, remains to be clarified.¹⁵

The 2-(2-arylhydrazino)tropones thus conveniently obtained in the present study are considered to be not only of interest from the view point of their potential biological activity but also useful precursors to various 5-aryl-substituted troponoids via benzidine-type rearrangement reaction, which is currently under intensive investigation.¹²

Experimental

Melting points were determined with a Yanagimoto MP-S3 instrument and are uncorrected. All reactions were monitored by TLC (Merck silica gel 60F, 0.25 mm) with appropriate solvent systems (mostly with MeOH-CHCl₃, CHCl₃-AcOEt, ether-benzene, and/or AcOEt-hexane). Preparative TLC and column chromatography were performed with Merck Kiesel Gel 60G and Wako C-200 silica gel, respectively. Yields of **3**, **4**, and **7–13** are given in Tables 1 and 2. The IR spectra were taken with a JASCO A-102 or Hitachi 215 spectrometer in chloroform (unless otherwise stated). The UV spectra were recorded in MeOH with a Hitachi EPS-3T spectrophotometer. The ¹H NMR spectra were measured in CDCl₃ (unless otherwise stated) with a Hitachi R-24 or R-600 (60-MHz), JEOL-FX200 (200-MHz, Kinki University), and/or Varian VXR-500 instrument (500-MHz, the SC-NMR Lab., Okayama University) at 27 °C. Chemical shifts are reported as δ values rel to tetramethylsilane as the internal standard measured at 60-MHz (unless otherwise stated). The assignment of all signals were made by employing a first-order analysis with the aid of decoupling technique and the parameters were confirmed by a computer-assisted simulation analysis. ¹³C NMR spectra were recorded with a JEOL FX-100 (25-MHz, Kyushu Univ.). Mass spectra were taken on a JEOL DX-300 low resolution, or JEOL JMX-HX100 (with a JEOL JMA-DA5000 mass data system) high-resolution instrument and

are given in terms of *m/z* (rel intensity) compared with the base peak.

5-(1-Acetamidoethyl)troponone (3e). A slightly modified procedure of Nozoe et al.^{10,11} for 4-cinnamoyltroponones was applied. Thus, a solution of **3d**⁹ (211 mg, 1.29 mmol) and hydroxylammonium chloride (168 mg, 2.42 mmol) in dry ethanol (7 cm³) was refluxed under argon for 1 h. After cooling, the precipitate was filtered off and washed with cold water to give the oxime of **3d** as a brown powder. This was dissolved in acetic acid (7 cm³) containing concd HCl (0.5 cm³) and then hydrogenated in the presence of 5% Pd on carbon (127 mg). The catalyst was filtered off and washed thoroughly with hot ethanol. The filtrate was evaporated in vacuo. The residue was dissolved in acetic anhydride (3 cm³) and heated at 60 °C for 5 min. The excess acetic anhydride was evaporated in vacuo. The residue was chromatographed in a column of silica gel with CHCl₃, giving 5-(1-acetamidoethyl)-2-acetoxytroponone as an amber oil (160 mg, 50% overall yield from **3d**): ¹H NMR δ =1.40 (3H, d, *J*=7.0 Hz, MeC-5), 1.98 (3H, s, AcN), 2.35 (3H, s, AcO), 4.92 (1H, brqint, *J*=7 Hz, HC-5), and 6.9–7.45 (5H, m, aromatic H, NH).

A mixture of this acetate (160 mg), ethanol (3 cm³), and 1 M KOH (1.5 cm³) (1 M=1 mol·dm⁻³) was stirred under argon overnight at 20 °C. The solvent was evaporated in vacuo. The residue was diluted with cold water, taken to pH 4 with dil HCl at 5 °C, and extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄) and evaporated in vacuo, giving **3e** as a pale yellow syrup: ¹H NMR δ =1.41 (3H, d, *J*=7.0 Hz, MeC-5), 1.98 (3H, s, AcN), 4.93 (1H, brqint, *J*=7 Hz, HC-5), 7.0 (1H, brm, NH), 7.35 (2H, d, *J*=11 Hz, H-3,7), 7.40 (2H, d, *J*=11 Hz, H-4,6), and 7.98 (1H, brm, OH); MS *m/z* 207 (M⁺; 100) and 148 (72).

Found: *m/z* 207.0861. Calcd for C₁₁H₁₃NO₃: M, 207.0895.

5-(2,5,5-Trimethyl-1,3-dioxan-2-yl)troponone (3f). A solution of **3d** (50 mg, 0.31 mmol) and 2,2-dimethyl-1,3-propanediol (40 mg, 0.39 mmol) in dry benzene (3 cm³) containing *p*-toluenesulfonic acid (6 mg) was refluxed for 13 h (using a Dean-Stark apparatus). After cooling, the mixture was diluted with cold water and then extracted with CHCl₃. The combined organic layers were extracted with 2 M NaOH. The aq layer was taken to pH 4 with 3 M HCl and then extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄) and evaporated in vacuo. The residue was chromatographed in a column of silica gel with 1:19 MeOH-CHCl₃ to give **3f** as colorless needles: mp 109–110 °C (from cyclohexane); IR (KBr) 3205 (OH) and 1615 cm⁻¹ (C=O); ¹H NMR δ =0.63 [3H, s, (*Z*)-Me-5'], 1.24 [3H, s, (*E*)-Me-5'], 1.52 (3H, s, Me-2'), 3.39 (4H, brs, 2H-4',6'), 7.37 (2H, d, *J*=11 Hz, H-3,7), 7.66 (2H, d, *J*=11 Hz, H-4,6), and 8.75 (1H, brm, OH); MS *m/z* 250 (M⁺; $\approx$ 0), 235 (100), 167 (21), and 149 (50).

Found: *m/z* 235.0959. Calcd for C₁₃H₁₅O₄: M-CH₃, 235.0970.

General Procedure for the Preparation of 5-Substituted Troponone Tosylates (4a–f). To a cold solution of a 5-substituted troponone **3** (1.00 g) in dry pyridine (2.5 cm³) was added tosyl chloride (1.1–1.2 equiv mol) at 5 °C. The mixture was stirred at 20 °C for 10–16 h (but 20 min for **4d**), and then diluted with cold water. The precipitate was filtered off and washed with cold water to give **4**. The filtrate was concentrated in vacuo and extracted with CH₂Cl₂, giving an additional **4** after chromatographic

purification in a column of silica gel.

2-Tosyloxypopone¹⁷ (4a): Colorless needles; mp 155.5—157 °C lit.¹⁷ 159—159.5 °C).

5-Isopropyl-2-tosyloxypopone¹³ (4b): Colorless needles; mp 120.5—121.5 °C (from benzene-hexane, lit.¹³ 122—123 °C); ¹H NMR δ =1.22 (6H, d, J =7.0 Hz, Me₂C-5), 2.46 (3H, s, Me-4'), 2.85 (1H, sept, J =7 Hz, HC-5), 6.89 (1H, dd, $J_{3,4}$ =9.5, $J_{4,6}$ =1.5 Hz, H-4), 7.17 (1H, d, $J_{6,7}$ =11.0 Hz, H-7), 7.23 (1H, dd, H-6), 7.39 (2H, brd, J =8.5 Hz, H-3',5'), 7.47 (1H, d, H-3), and 7.98 (2H, brd, J =8.5 Hz, H-2',6').

5-Isopropenyl-2-tosyloxypopone¹⁴ (4c): Colorless crystals; mp 125.5—126.5 °C (from benzene-hexane, lit.¹⁴ mp 126—127 °C); ¹H NMR δ =2.10 (3H, brd, J =1.0 Hz, MeC-5), 2.44 (3H, s, Me-4'), 5.29 [1H, brs, (E)-HC=C-5], 5.38 [1H, brs, (Z)-HC=C-5], 7.00 (1H, dd, $J_{3,4}$ =11.0, $J_{4,6}$ =1.5 Hz, H-4), 7.12 (1H, d, $J_{6,7}$ =12.5 Hz, H-7), 7.35 (2H, brd, J =8.5 Hz, H-3',5'), 7.41 (1H, dd, H-6), 7.44 (1H, d, H-3), and 7.92 (2H, brd, J =8.5 Hz, H-2',6').

5-Acetyl-2-tosyloxypopone (4d): Pale yellow prisms; mp 115—115.5 °C (from AcOEt-cyclohexane); ¹H NMR δ =2.47 (3H, brs, Me-4'), 2.61 (3H, s, Ac), 7.19 (1H, d, $J_{6,7}$ =12.5 Hz, H-7), 7.37 (2H, brd, J =8.5 Hz, H-3',5'), 7.55 (1H, brd, $J_{3,4}$ =11.5 Hz, H-3), 7.68 (1H, brdd, $J_{4,6}$ =1.5 Hz, H-4), 7.84 (1H, brdd, H-6), and 7.91 (2H, brd, J =8.5 Hz, H-2',6'); MS m/z 318 (M⁺; $\approx$ 0), 254 (37), 164 (27), 155 (57), 149 (15), 139 (16), 121 (17), 91 (100), 65 (20), and 43 (18). 4d decomposes on setting aside at room temp (or rapidly on silica gel).

Found: m/z 254.0939. Calcd for C₁₆H₁₄O₃: M-SO₂, 254.0943.

5-(1-Acetamidoethyl)-2-tosyloxypopone (4e): A pale yellow syrup; ¹H NMR δ =1.39 (3H, d, J =7.0 Hz, MeC-5), 1.97 (3H, s, AcN), 2.46 (3H, s, Me-4'), 4.82 (1H, brqint, J =7 Hz, HC-5), 6.97 (1H, brm, NH), 6.98 (2H, brd, $J_{3,4}$ $\approx$ $J_{6,7}$ =10.5 Hz, H-3,7), 7.27 (1H, brd, H-4), 7.31 (1H, brd, H-6), 7.35 (2H, brd, J =8.5 Hz, H-3',5'), and 7.98 (2H, brd, J =8.5 Hz, H-2',6'); MS m/z 361 (M⁺; 5.5), 302 (17), 295 (100), 239 (18), 238 (42), and 139 (25).

Found: m/z 361.0957. Calcd for C₁₈H₁₉NO₅S: M, 361.0984.

5-(2,5,5-Trimethyl-1,3-dioxan-2-yl)-2-tosyloxypopone (4f): Colorless crystals (89% yield from 3f); mp 114—116 °C (from EtOH); IR 1632 cm⁻¹ (C=O); ¹H NMR δ =0.67 [3H, s, (Z)-Me-5''], 1.22 (3H, s, (E)-Me-5''), 1.49 (3H, s, Me-2''), 2.48 (3H, s, Me-4'), 3.39 (4H, brs, 2H-4'',6''), 7.28—7.62 (4H, m, aromatic H), 7.37 (2H, brd, J =8 Hz, H-3',5'), and 7.98 (2H, brd, J =8 Hz, H-2',6'); MS m/z 404 (M⁺; $\approx$ 0), 389 (27), 361 (22), 341 (27), 340 (100), 326 (15), 325 (60), 275 (15), 249 (11), 155 (23), 129 (25), 107 (9), 91 (17), and 69 (19).

Found: m/z 389.1049. Calcd for C₂₀H₂₁O₆S: M-CH₃, 389.1059.

General Procedure for the Preparation of 2-(2-Arylhydrazino)tropones (7a—z') (with the Formation of By-products 8—13). **A. Procedure for 7a—o:** A mixture of 4a (1.38 g, 5 mmol) and an arylhydrazine 6 (or its hydrochloride, 10 mmol) in methanol (or ethanol for 6m—o, 150 cm³) was refluxed for 6—24 h under nitrogen in the presence of triethylamine (5 mmol, or 15 mmol when the arylhydrazine hydrochloride was used).

B. Procedure for 7p—z': To a solution of a 5-substituted 2-tosyloxypopone 4 (250 mg) in dry DMF (6 cm³) were successively added, under argon at -20 °C, arylhydrazine hydrochloride 6 (3.0 equiv mol) and triethylamine (4.0 equiv mol, dropwise), followed by stirring at -20 °C for 1 h and

then at 20 °C for 7—20 h.

C. Procedure Using Free 6f,g: Triethylamine (1.01 g, 10 mmol) was added to a suspension of hydrochloride (1.75 g, 10 mmol) of 6 in methanol (150 cm³). To the resulting solution was added 4a (1.38 g, 5 mmol), and the mixture was refluxed for 8 h under nitrogen.

D. Procedure for 7b—d Using 5a as the Starting Material: The same method as A described above was employed except for using 5a (in place of 4a).

When the starting material 4 or 5 almost disappeared (by TLC), the solvent was evaporated in vacuo. The residue was diluted with cold water and extracted with CH₂Cl₂ or CHCl₃. The organic layer was dried (Na₂SO₄) and evaporated in vacuo. The residue (when it was a solid) was recrystallized from an appropriate solvent (see below) to give the corresponding product 7; the filtrate was concentrated in vacuo and the residue was chromatographed on preparative thin-layer plates (with CHCl₃-AcOEt) or in a column of silica gel (with MeOH-CHCl₃ or AcOEt-hexane), giving an additional amount of 7 and other by-products.

2-(2-Phenylhydrazino)troponone^{1a,4} (7a): Yellow prisms (by Procedure A); mp 163—165 °C (from benzene, lit.^{1a,4} 168 °C).

2-[2-(*o*-Tolyl)hydrazino]troponone^{1a} (7b): Brown prisms (by Procedures A and D); mp 90—91 °C (from benzene, lit.^{1a} 90—91 °C).

2-[2-(*m*-Tolyl)hydrazino]troponone^{1a} (7c): Yellow prisms (by Procedures A and D); mp 148 °C (from benzene, lit.^{1a} 147 °C).

2-[2-(*p*-Tolyl)hydrazino]troponone^{1a} (7d): Yellow prisms (by Procedures A and D); mp 162—164 °C (from benzene, lit.^{1a} 158 °C).

2-[2-(2-Methoxyphenyl)hydrazino]troponone (7e): Yellow prisms (by Procedure A); mp 118—119 °C (from benzene); IR 3300 (NH) and 1605 cm⁻¹ (C=O); UV $\lambda_{\max}$ 250 (log ϵ 4.58), 339 (4.12), and 402 nm (4.10); ¹H NMR δ =3.48 (3H, s, MeO-2'), 6.25 (1H, brm, NH-1'), 6.5—7.3 (9H, m, aromatic H), and 8.2 (1H, brm, NH-2); MS m/z 242 (M⁺; 93), 123 (100), 122 (49), and 108 (48).

Found: m/z 242.1045. Calcd for C₁₄H₁₄N₂O₂: M, 242.1055.

2-[2-(3-Methoxyphenyl)hydrazino]troponone (7f): Yellow prisms (by Procedures A and C); mp 148—150 °C (from benzene); IR 3305 (NH) and 1605 cm⁻¹ (C=O); UV $\lambda_{\max}$ 248 (log ϵ 4.50), 339 (4.47), and 406 nm (4.07); ¹H NMR δ =3.71 (3H, s, MeO-3'), 6.15 (1H, brm, NH-1'), 6.3—7.4 (9H, m, aromatic H), and 8.3 (1H, brm, NH-2).

Anal. (C₁₄H₁₄N₂O₂) C, H, N.

2-[2-(4-Methoxyphenyl)hydrazino]troponone (7g): Yellow prisms (by Procedures A and C); mp 137—139 °C (from benzene); IR 3300 (NH) and 1605 cm⁻¹ (C=O); UV $\lambda_{\max}$ 250 (log ϵ 4.51), 339 (4.07), and 405 nm (4.08); ¹H NMR δ =3.71 (3H, s, MeO-4'), 5.7 (1H, brm, NH-1'), 6.5—6.9 (1H, m, H-5), 6.71 (4H, s, H-2',3',5',6'), 6.9—7.4 (4H, m, H-3,4,6,7), and 8.25 (1H, brm, NH-2).

Anal. (C₁₄H₁₄N₂O₂) C, H, N.

2-[2-(2,3-Dimethoxyphenyl)hydrazino]troponone (7h): Yellow prisms (by Procedure A using 6h¹⁸); mp 103—105 °C (from benzene-hexane); IR 3305 (NH) and 1605 cm⁻¹ (C=O); UV $\lambda_{\max}$ 250 (log ϵ 4.49), 339 (4.04), and 405 nm (4.07); ¹H NMR δ =3.83 (3H, s, MeO-3'), 3.90 (3H, s, MeO-2'), 6.25—6.65 (3H, m, H-4',5',6'), 6.35 (1H, brm, NH-1'), 6.7—7.4 (5H, m, aromatic H), and 8.23 (1H, brm, NH-2); MS m/z 272 (M⁺; 100), 153 (92), 153 (31), 138 (57), and 137 (29).

Found: m/z 272.1156. Calcd for C₁₅H₁₆N₂O₃: M, 272.1161.

2-[2-(2,3-Dimethoxy-5-methylphenyl)hydrazino]tropone (7i): Yellow prisms (by Procedure A using **6i**¹⁸); mp 73–75 °C (from benzene–hexane); IR 3305 (NH) and 1605 cm⁻¹ (C=O); UV λ_{max} 250 (log ϵ 4.54), 339 (4.08), and 405 nm (4.11); ¹H NMR δ =2.15 (3H, s, Me-5'), 3.84 (3H, s, MeO-3'), 3.88 (3H, s, MeO-2'), 6.16 (1H, d, J =1.8 Hz, H-4'), 6.28 (1H, d, J =1.8 Hz, H-6'), 6.35 (1H, brm, NH-1'), 6.5–7.5 (5H, m, aromatic H), and 8.2 (1H, brm, NH-2); MS m/z 286 (M⁺; 100), 167 (76), 166 (28), 152 (66), 151 (24), 139 (25), 138 (21), and 123 (21).

Found: m/z 286.1304. Calcd for C₁₆H₁₈N₂O₃: M, 286.1317.

2-[2-(2-Chlorophenyl)hydrazino]tropone (7j): Yellow prisms (by Procedure A); mp 91–93 °C (from benzene); IR 3320 (NH) and 1595 cm⁻¹ (C=O); UV λ_{max} 249 (log ϵ 4.58), 338 (4.12), and 402 nm (4.14); ¹H NMR δ =6.35 (1H, brm, NH-1'), 6.5–7.4 (9H, m, aromatic H), and 8.25 (1H, brm, NH-2); MS m/z 248 (M⁺; 19), 246 (M⁺; 58), 129 (33), and 127 (100).

Found: m/z 246.0561. Calcd for C₁₃H₁₁ClN₂O: M, 246.0566.

2-[2-(3-Chlorophenyl)hydrazino]tropone (7k): Yellow prisms (by Procedure A); mp 159–161 °C (from benzene); IR 3320 (NH) and 1595 cm⁻¹ (C=O); UV λ_{max} 248 (log ϵ 4.38), 338 (3.91), and 403 nm (3.93); ¹H NMR δ =6.25 (1H, brm, NH-1'), 6.5–7.4 (9H, m, aromatic H), and 8.35 (1H, brm, NH-2).

Anal. (C₁₃H₁₁ClN₂O) C, H, N.

2-[2-(4-Chlorophenyl)hydrazino]tropone (7l): Yellow prisms (by Procedure A); mp 118–120 °C (from ethanol–benzene); IR 3300 (NH) and 1595 cm⁻¹ (C=O); UV λ_{max} 251 (log ϵ 4.48), 338 (4.00), and 403 nm (4.02); ¹H NMR δ =5.9 (1H, brm, NH-1'), 6.7–7.4 (5H, m, H-3–7), 6.71 (2H, brd, J =8.5 Hz, H-2',6'), 7.18 (2H, brd, J =8.5 Hz, H-3',5'), and 8.3 (1H, brm, NH-2).

Anal. (C₁₃H₁₁ClN₂O) C, H, N.

2-[2-(2-Nitrophenyl)hydrazino]tropone (7m): Yellow prisms (by Procedure A); mp 178–179 °C (from benzene); IR 3320 (NH) and 1610 cm⁻¹ (C=O); UV λ_{max} 245 (log ϵ 4.57), 327 (4.11), and 405 nm (4.25); ¹H NMR δ =6.5–7.8 (8H, m, aromatic H), 8.23 (1H, m, H-3'), and 9.55 (2H, brm, NH-1,2).

Anal. (C₁₃H₁₁N₃O₃) C, H, N.

2-[2-(3-Nitrophenyl)hydrazino]tropone^{1a} (7n): Yellow prisms (by Procedure A); mp 178–180 °C (from ethanol, lit.^{1a} 180 °C).

2-[2-(4-Nitrophenyl)hydrazino]tropone^{1a} (7o): Yellow prisms (by Procedure A); mp 185 °C decomp (from ethanol, lit.^{1a} 191 °C).

4-Isopropenyl-2-(2-phenylhydrazino)tropone (7p): Pale yellow needles (by Procedure B with phenylhydrazine free base); mp 152.5–153.5 °C (from EtOH); ¹H NMR (200-MHz) δ =1.16 (6H, d, J =7.0 Hz, Me₂C-4), 2.81 (1H, sept, J =7.0 Hz, HC-4), 5.71 (1H, brs, NH-1'), 6.73 (1H, brd, $J_{5,6}$ =9.5 Hz, H-5), 6.82 (2H, brd, $J_{2,3}$ = $J_{5',6'}$ =8.0 Hz, H-2',6'), 6.93 (1H, brt, $J_{3',4'}=J_{4',5'}$ =7.0 Hz, H-4'), 7.11 (1H, d, $J_{6,7}$ =12.0 Hz, H-7), 7.13 (1H, d, $J_{3,5}$ =1.5 Hz, H-3), 7.25 (2H, brdd, H-3',5'), 7.29 (1H, dd, H-6), and 8.31 (1H, brs, NH-2); MS m/z 254 (M⁺; 74), 211 (4), 163 (7), 163 (7), 105 (9), 93 (100), and 77 (30).

Found: m/z 254.1422. Calcd for C₁₆H₁₈N₂O: M, 254.1419.

4-Isopropenyl-2-(2-phenylhydrazino)tropone (7q): Yellow needles (by Procedure B); mp 176–178 °C (from EtOH); ¹H NMR (200-MHz) δ =2.04 (3H, brt, J =1.2 Hz, MeC-4), 5.12 [1H, brquint, J =1.5 Hz, (E)-HC=C-4], 5.17 [1H, brs, (Z)-

HC=C-4], 5.17 (1H, brs, NH-1'), 6.81 (2H, brd, $J_{2,3}$ = $J_{5',6'}$ =8.5 Hz, H-2',6'), 6.81 (1H, brd, $J_{5,6}$ =9.5 Hz, H-5), 6.92 (1H, brt, $J_{3',4'}=J_{4',5'}$ =7.5 Hz, H-4'), 7.14 (1H, dd, $J_{6,7}$ =11.5, $J_{5,7}$ =1.0 Hz, H-7), 7.25 (2H, brdd, H-3',5'), 7.28 (1H, d, $J_{3,5}$ =1.5 Hz, H-3), 7.30 (1H, dd, H-6), and 8.30 (1H, brs, NH-2); MS m/z 252 (M⁺; 72.8), 161 (11), 93 (100), and 77 (33).

Found: m/z 252.1271. Calcd for C₁₆H₁₈N₂O: M, 252.1263.

4-Isopropenyl-2-[2-(*o*-tolyl)hydrazino]tropone (7r): Yellow needles (by Procedure B); mp 141–142 °C (from ether); ¹H NMR (200-MHz) δ =2.05 (3H, brt, J =1.2 Hz, MeC-4), 2.29 (3H, s, Me-2'), 5.12 [1H, brquint, J =1.2 Hz, (E)-HC=C-4], 5.17 [1H, brs, (Z)-HC=C-4], 5.64 (1H, brs, NH-1'), 6.75 (1H, brd, $J_{5',6'}$ =8.0 Hz, H-6'), 6.86 (1H, brd, $J_{5,6}$ =9.5 Hz, H-5), 6.87 (1H, td, $J_{3',4'}=J_{4',5'}$ =7.5, $J_{4',6'}$ =1.0 Hz, H-4'), 7.11 (1H, brt, H-5'), 7.14 (1H, brd, H-3'), 7.14 (1H, d, $J_{6,7}$ =11.5 Hz, H-7), 7.28 (1H, d, $J_{3,4}$ =1.5 Hz, H-3), 7.32 (1H, dd, H-6), and 8.28 (1H, brs, NH-2); MS m/z 266 (M⁺; 52.5), 161 (8), 145 (4), 133 (13), 107 (100), 106 (55), and 91 (16).

Found: m/z 266.1397. Calcd for C₁₇H₁₈N₂O: M, 266.1419.

4-Isopropenyl-2-[2-(*m*-tolyl)hydrazino]tropone (7s): Yellow needles (by Procedure B); mp 165–167 °C (from ether); ¹H NMR (200-MHz) δ =2.05 (3H, brt, J =1.2 Hz, MeC-4), 2.27 (3H, s, Me-3'), 5.13 [1H, qd, J =1.5, 1.0 Hz, (E)-HC=C-4], 5.19 [1H, brs, (Z)-HC=C-4], 5.65 (1H, brs, NH-1'), 6.62 (1H, brd, $J_{4',5'}$ =8.5 Hz, H-4'), 6.64 (1H, brs, H-2'), 6.74 (1H, brd, $J_{5',6'}$ =7.5 Hz, H-6'), 6.86 (1H, brd, $J_{5,6}$ =9.5 Hz, H-5), 7.15 (1H, brdd, H-5'), 7.16 (1H, brdd, $J_{6,7}$ =11.5, $J_{5,7}$ =1.0 Hz, H-7), 7.26 (1H, brd, $J_{3,5}$ =1.5 Hz, H-3), 7.31 (1H, dd, H-6), and 8.28 (1H, brs, NH-2); MS m/z 266 (M⁺; 43.1), 223 (5), 161 (4), 145 (6), 133 (15), 132 (12), 107 (100), and 91 (20).

Found: m/z 266.1432. Calcd for C₁₇H₁₈N₂O: M, 266.1419.

4-Isopropenyl-2-[2-(2-methoxyphenyl)hydrazino]tropone (7t): Yellow needles (by Procedure B); mp 122–123.5 °C (from ether–light petroleum); ¹H NMR (500-MHz) δ =2.05 (3H, brd, J =1.5 Hz, MeC-4), 3.92 (3H, s, MeO-2'), 5.11 [1H, brquint, J =1.5 Hz, (E)-HC=C-4], 5.17 [1H, brs, (Z)-HC=C-4], 6.24 (1H, brm, NH-1'), 6.74 (1H, brd, $J_{3',4'}$ =7.4 Hz, H-3'), 6.84 (1H, brd, $J_{5,6}$ =9.5 Hz, H-5), 6.83–6.88 (3H, m, H-5',4',6'), 7.12 (1H, brd, $J_{6,7}$ =11.7 Hz, H-7), 7.26 (1H, brd, $J_{3,5}$ =1.5 Hz, H-3), 7.29 (1H, dd, H-6), and 8.22 (1H, brm, NH-2); MS m/z 282 (M⁺; 69.2), 161 (10), 132 (21), 123 (100), 122 (42), 108 (42), 94 (97), and 80 (43).

Found: m/z 282.1364. Calcd for C₁₇H₁₈N₂O₂: M, 282.1368.

4-Isopropenyl-2-[2-(3-methoxyphenyl)hydrazino]tropone (7u): Yellow needles (by Procedure B); mp 165–166 °C (from ether); ¹H NMR (200-MHz) δ =2.03 (3H, brd, J =1.5 Hz, MeC-4), 3.71 (3H, s, MeO-3'), 5.08 [1H, brq, J =1.5 Hz, (E)-HC=C-4], 5.13 [1H, brs, (Z)-HC=C-4], 5.65 (1H, brs, NH-1'), 6.30 (1H, t, $J_{2',4'}$ = $J_{2',6'}$ =2.0 Hz, H-2'), 6.35 (1H, ddd, $J_{4',5'}$ =8.0, $J_{4',6'}$ =1 Hz, H-4'), 6.40 (1H, dd, $J_{5',6'}$ =8.0 Hz, H-6'), 6.79 (1H, ddd, $J_{5,6}$ =9.5, $J_{3,5}$ =1.5, $J_{5,7}$ =1.0 Hz, H-5), 7.05 (1H, dd, $J_{6,7}$ =12.0 Hz, H-7), 7.07 (1H, t, H-5'), 7.19 (1H, d, H-3), 7.23 (1H, dd, H-6), and 8.19 (1H, brs, NH-2); MS m/z 282 (M⁺; 53.3), 161 (8), 132 (18), 123 (100), 122 (43), 108 (38), 94 (82), and 80 (50).

Found: m/z 282.1365. Calcd for C₁₇H₁₈N₂O₂: M, 282.1368.

4-Isopropenyl-2-[2-(2,3-dimethoxyphenyl)hydrazino]tropone (7v): A yellow oil (by Procedure B); ¹H NMR (200-MHz) δ =2.02 (3H, dd, J =1.5, 1.0 Hz, MeC-4), 3.85 (3H, s, MeO-3'), 3.90 (3H, s, MeO-2'), 5.09 [1H, qd, J =1.5, 1.0 Hz, (E)-HC=C-4], 5.16 [1H, quint, J =1.0 Hz, (Z)-HC=C-4], 6.27 (1H, brs, NH-1'), 6.36 (1H, dd, $J_{4',5'}$ =8.0, $J_{4',6'}$ =1.5 Hz, H-4'), 6.40 (1H, dd, $J_{5',6'}$ =8.0 Hz, H-6'), 6.82 (1H, ddd, $J_{5,6}$ =9.5,

$J_{3,5}=1.5$, $J_{5,7}=1$ Hz, H-5), 6.87 (1H, t, H-5'), 7.09 (1H, dd, $J_{6,7}=12.0$ Hz, H-7), 7.22 (1H, d, H-3), 7.27 (1H, dd, H-6), and 8.17 (1H, brs, NH-2); MS m/z 312 (M^+ ; 3), 153 (72), and 138 (100).

Found: m/z 312.1470. Calcd for $C_{18}H_{20}N_2O_3$: M , 312.1474.

4-Isopropenyl-2-[2-(2,3-dimethoxy-5-methylphenyl)hydrazino]tropone (7w): A yellow oil (by Procedure B); 1H NMR (200-MHz) $\delta=2.07$ (3H, brs, MeC-4), 2.19 (3H, s, Me-5'), 3.85 (3H, s, MeO-3'), 3.88 (3H, s, MeO-2'), 5.12, 5.20 (1H each, both brs, $H_2C=C-4$), 6.21 (1H, brd, $J_{4',6'}=1.5$ Hz, H-4'), 6.24 (1H, brs, NH-1'), 6.30 (1H, brd, H-6'), 6.84 (1H, ddd, $J_{5,6}=9.5$, $J_{3,5}=1.5$, $J_{5,7}=0.5$ Hz, H-5), 7.13 (1H, d, $J_{6,7}=12.0$ Hz, H-7), 7.28 (1H, d, H-3), 7.29 (1H, dd, H-6), and 8.18 (1H, brs, NH-2); MS m/z 326 (M^+ ; 90), 331 (8), 295 (5), 175 (14), 167 (100), 161 (48), 152 (97), 136 (84), and 91 (57).

Found: m/z 326.1611. Calcd for $C_{19}H_{22}N_2O_3$: M , 326.1630.

4-(1-Acetamidoethyl)-2-[2-(2-methoxyphenyl)hydrazino]tropone (7x): A pale amber syrup (by Procedure B); 1H NMR $\delta=1.41$ (3H, d, $J=7.5$ Hz, MeC-4), 1.88 (3H, s, AcN), 3.97 (3H, s, MeO-2'), 4.87 (1H, brquint, $J=7.5$ Hz, HC-4), 5.6 (1H, brd, $J=6.5$ Hz, HNC-4), 6.3 (1H, brs, NH-1'), 6.65—7.40 (8H, m, aromatic H), and 8.10 (1H, brs, NH-2); MS m/z 327 (M^+ ; 81), 268 (42), 124 (100), and 107 (91).

Found: m/z 327.1556. Calcd for $C_{18}H_{21}N_3O_3$: M , 327.1583.

4-(1-Acetamidoethyl)-2-[2-(3-methoxyphenyl)hydrazino]tropone (7y): A yellow oil (by Procedure B); 1H NMR (200-MHz) $\delta=1.34$ (3H, d, $J=7.0$ Hz, MeC-4), 1.86 (3H, s, AcN), 3.72 (3H, s, MeO-3'), 4.80 (1H, brquint, $J=7$ Hz, HC-4), 5.77 (1H, brd, $J=6.5$ Hz, HNC-4), 5.83 (1H, brs, NH-1'), 6.28 (1H, brt, $J_{2',4'}=J_{4',6'}=2.0$ Hz, H-2'), 6.33 (1H, brdt, $J_{4',5'}=8.0$, $J_{4',6'}=2$ Hz, H-4'), 6.40 (1H, brdd, $J_{5',6'}=8.0$ Hz, H-6'), 6.71 (1H, brd, $J_{5,6}=9.5$ Hz, H-5), 6.99 (1H, brd, $J_{3,5}=1$ Hz, H-3), 7.05 (1H, brd, $J_{6,7}=12.0$ Hz, H-7), 7.08 (1H, t, H-5'), 7.22 (1H, dd, H-6), and 8.21 (1H, brs, NH-2); MS m/z 327 (M^+ ; 92), 268 (63), 124 (100), and 107 (88).

Found: m/z 327.1565. Calcd for $C_{18}H_{21}N_3O_3$: M , 327.1583.

4-(1-Acetamidoethyl)-2-[2-(2,3-dimethoxyphenyl)hydrazino]tropone (7z): A yellow oil (by Procedure B); 1H NMR (200-MHz) $\delta=1.33$ (3H, d, $J=7.0$ Hz, MeC-4), 1.87 (3H, s, AcN), 3.88 (3H, s, MeO-3'), 3.95 (3H, s, MeO-2'), 4.83 (1H, brquint, $J=7$ Hz, HC-4), 5.72 (1H, brd, $J=6.5$ Hz, HNC-4), 6.30 (1H, brs, NH-1'), 6.37 (1H, brdd, $J_{4',5'}=8.0$, $J_{4',6'}=1.5$ Hz, H-4'), 6.49 (1H, brdd, H-6'), 6.76 (1H, brd, $J_{5,6}=9.5$ Hz, H-5), 6.89 (1H, t, $J_{5',6'}=8.0$ Hz, H-5'), 6.96 (1H, brd, $J_{3,5}=1.5$ Hz, H-3), 7.10 (1H, brdd, $J_{6,7}=11.5$, $J_{5,7}=1.0$ Hz, H-7), 7.26 (1H, dd, H-6), and 8.22 (1H, brs, NH-2); MS m/z 357 (M^+ ; 69), 298 (39), 206 (28), 163 (32), 153 (100), and 138 (49).

Found: m/z 357.1736. Calcd for $C_{19}H_{23}N_3O_4$: M , 357.1689.

4-(2,5,5-Trimethyl-1,3-dioxan-2-yl)-2-[2-(2-methoxyphenyl)hydrazino]tropone (7z'): Yellow needles (by Procedure B); mp 145—146.5 °C (from ether-light petroleum); IR (KBr) 3320 (NH) and 1598 cm^{-1} (C=O); 1H NMR $\delta=0.54$ [3H, s, (Z)-Me-5"], 1.20 [3H, s, (E)-Me-5"], 1.47 (3H, s, Me-2"), 3.19 (4H, brs, 2H-4",6"), 3.92 (3H, s, MeO-2'), 6.27 (1H, m, NH-1'), 6.80 (1H, d, $J_{5,6}=9.5$ Hz, H-5), 6.55—7.0 (4H, m, H-3',4',5',6'), 7.16 (1H, brd, $J_{6,7}=11$ Hz, H-7), 7.23 (1H, brs, H-3), 7.30 (1H, brdd, H-6), and 8.29 (1H, m, HN-2); MS m/z 370 (M^+ ; 100), 355 (14), 129 (30), 123 (50), 108 (17), 69 (13), and 43 (18).

Found: m/z 370.1892. Calcd for $C_{21}H_{26}N_2O_4$: M , 370.1893.

6,6'-Bis(phenylhydrazono)-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8a): Bright yellow needles (by Procedure A); mp 183—184 °C decomp (from benzene); IR 3350 (NH) and

1635 cm^{-1} (C=O); 1H NMR (100-MHz) $\delta=3.82$ (2H, brt, $J_{1,2}=3.0$, $J_{1,3}=2.5$ Hz, H-1,1'), 5.48 (2H, brddd, $J_{2,3}=9.0$, $J_{2,4}=2.5$ Hz, H-2,2'), 6.33 (2H, m, $J_{4,5}=11.0$, $J_{3,5}=2.0$ Hz, H-5,5'), 6.34 (2H, m, $J_{3,4}=2.5$ Hz, H-3,3'), 6.66 (2H, brdt, H-4,4'), 6.9—7.4 (10H, m, 2Ph), and 13.6 (2H, brm, NH-6,6'); ^{13}C NMR $\delta=50.3$ (C-1), 115.5, 123.4, 124.2, 124.8, 129.2, 129.4, 129.9, 135.0 (C-1'), 142.4 (C-6), and 187.6 (C-7); MS m/z 212 (41), 210 (97), 193 (24), 182 (19), 181 (22), 154 (26), 119 (38), and 91 (100).

Anal. ($C_{26}H_{22}N_4O_2$) C, H, N.

6,6'-Bis[(*o*-tolyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8b): Bright yellow needles (by Procedure A); mp 161—162 °C decomp (from benzene); IR 3450 (NH) and 1635 cm^{-1} (C=O); 1H NMR $\delta=1.95$ (6H, s, 2 Me-2"), 3.8—3.95 (2H, m, H-1,1'), 5.3—5.7 (2H, m, H-2,2'), 6.15—7.8 (14H, m, aromatic H), and 13.9 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_2$) C, H, N.

6,6'-Bis[(*m*-tolyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8c): Bright yellow needles (by Procedure A); mp 179—181 °C decomp (from benzene); IR 3410 (NH) and 1630 cm^{-1} (C=O); 1H NMR $\delta=2.22$ (6H, s, 2 Me-3"), 3.65—3.85 (2H, m, H-1,1'), 5.2—5.6 (2H, m, H-2,2'), 6.1—7.2 (14H, m, aromatic H), and 14.4 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_2$) C, H, N.

6,6'-Bis[(*p*-tolyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8d): Bright yellow needles (by Procedure A); mp 174—175 °C decomp (from benzene); IR 3450 (NH) and 1630 cm^{-1} (C=O); 1H NMR $\delta=2.30$ (6H, s, 2 Me-4"), 3.65—3.9 (2H, m, H-1,1'), 5.3—5.7 (2H, m, H-2,2'), 6.15—7.3 (6H, m, H-3,3',4,4',5,5'), 7.20 (8H, m, 2H-2",3",5",6"), and 13.8 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_2$) C, H, N.

6,6'-Bis[(2-methoxyphenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8e): Bright yellow needles (by Procedure A); mp 174—176 °C decomp (from benzene); IR 3400 (NH) and 1640 cm^{-1} (C=O); 1H NMR $\delta=3.40$ (6H, s, 2 MeO-2"), 3.90 (2H, m, H-1,1'), 5.3—5.6 (2H, m, H-2,2'), 6.2—7.8 (14H, m, aromatic H), and 13.4 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_4$) C, H, N.

6,6'-Bis[(3-methoxyphenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8f): Bright yellow needles (by Procedure A); mp 162—163 °C decomp (from benzene); IR 3390 (NH) and 1635 cm^{-1} (C=O); 1H NMR $\delta=3.65$ —3.85 (2H, m, H-1,1'), 3.70 (6H, s, 2 MeO-3"), 5.3—5.6 (2H, m, H-2,2'), 6.1—7.3 (14H, m, aromatic H), and 13.75 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_4$) C, H, N.

6,6'-Bis[(4-methoxyphenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8g): Bright yellow needles (by Procedure A); mp 158—160 °C decomp (from benzene); IR 3200 (NH) and 1630 cm^{-1} (C=O); 1H NMR $\delta=3.7$ —3.8 (2H, m, H-1,1'), 3.71 (6H, s, 2 MeO-4"), 5.25—5.6 (2H, m, H-2,2'), 6.15—7.35 (6H, m, H-3,3',4,4',5,5'), 6.73 (4H, brd, $J=8.5$ Hz, 2H-3",5"), 7.11 (4H, brd, $J=8.5$ Hz, 2H-2",6"), and 14.0 (2H, brm, NH-6,6').

Anal. ($C_{28}H_{26}N_4O_4$) C, H, N.

6,6'-Bis[(2-chlorophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8j): Bright yellow needles (by Procedure A); mp 173—175 °C decomp (from benzene); IR 3450 (NH) and 1635 cm^{-1} (C=O); 1H NMR $\delta=3.9$ —4.05 (2H, m, H-1,1'), 5.15—5.55 (2H, m, H-2,2'), 6.1—7.7 (14H, m, aromatic H), and 13.6 (2H, brm, NH-6,6').

Anal. ($C_{26}H_{20}Cl_2N_4O_2$) C, H, N.

6,6'-Bis[(3-chlorophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8k): Bright yellow needles (by Procedure A); mp 180–181 °C decomp (from benzene); IR 3415 (NH) and 1630 cm⁻¹ (C=O); ¹H NMR δ =3.85–3.95 (2H, m, H-1,1'), 5.45–5.8 (2H, m, H-2,2'), 6.3–7.75 (14H, m, aromatic H), and 13.6 (2H, brm, NH-6,6').

Anal. (C₂₆H₂₀Cl₂N₄O₂) C, H, N.

6,6'-Bis[(4-chlorophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8l): Bright yellow needles (by Procedure A); mp 175–176 °C decomp (from benzene); IR 3410 (NH) and 1630 cm⁻¹ (C=O); ¹H NMR δ =3.7–3.95 (2H, m, H-1,1'), 5.4–5.75 (2H, m, H-2,2'), 6.3–7.0 (6H, m, H-3,3',4,4',5,5'), 7.35 (8H, s, 2H-2'',3'',5'',6''), and 14.1 (2H, brm, NH-6,6').

Anal. (C₂₆H₂₀Cl₂N₄O₂) C, H, N.

6,6'-Bis[(2-nitrophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8m): Bright yellow needles (by Procedure A); mp 182–184 °C decomp (from ethyl acetate); IR 3390 (NH) and 1655 cm⁻¹ (C=O); ¹H NMR almost insoluble for the measurement.

Anal. (C₂₆H₂₀N₆O₆) C, H, N.

6,6'-Bis[(3-nitrophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8n): Bright yellow needles (by Procedure A); mp 180–182 °C decomp (from ethyl acetate); IR 3420 (NH) and 1640 cm⁻¹ (C=O); ¹H NMR δ =3.65–3.75 (2H, m, H-1,1'), 5.25–5.45 (2H, m, H-2,2'), 6.2–8.4 (14H, m, aromatic H), and 13.85 (2H, brm, NH-6,6').

Anal. (C₂₆H₂₀N₆O₆) C, H, N.

6,6'-Bis[(4-nitrophenyl)hydrazono]-1,1'-bi(2,4-cycloheptadiene)-7,7'-dione (8o): Bright yellow needles (by Procedure A); mp 189–191 °C decomp (from ethyl acetate); IR 3450 (NH) and 1640 cm⁻¹ (C=O); ¹H NMR δ =3.65–3.8 (2H, m, H-1,1'), 5.2–5.6 (2H, m, H-2,2'), 6.2–8.4 (14H, m, aromatic H), and 13.85 (2H, brm, NH-6,6').

Anal. (C₂₆H₂₀N₆O₆) C, H, N.

3-[2-Phenylhydrazino]tropone (9a): Pale yellow crystals; mp 140–142 °C (from benzene); IR 3250 (NH) and 1600 cm⁻¹ (C=O); UV $\lambda_{\max}$ 248 (log ϵ 4.19), 305 (4.06), and 354 nm (4.39); ¹H NMR δ =6.6–7.6 (9H, m, aromatic H), 7.35 (1H, brm, NH-1'), 7.63 (1H, s, H-2), and 10.82 (1H, brm, NH-3).

Anal. (C₁₃H₁₂N₂O) C, H, N.

3-[2-(4-Chlorophenyl)hydrazino]tropone (9l): Brownish yellow crystals; mp 168–170 °C (from benzene); IR 3320 (NH) and 1600 cm⁻¹ (C=O); UV $\lambda_{\max}$ 242 (log ϵ 4.15), 316 (4.21), and 355 nm (4.40); ¹H NMR δ =6.7–7.8 (8H, m, aromatic H), 8.24 (1H, s, H-2), and 10.25 (2H, brm, NH-3, NH-1'); MS m/z 248 (M⁺; 29), 246 (M⁺; 100), 127 (94), and 126 (53).

Found: m/z 246.0546. Calcd for C₁₃H₁₁ClN₂O: M, 246.0560.

2-(N-Amino-4-methoxyanilino)tropone (10): Reddish orange prisms; mp 105–107 °C (from hexane); IR 3350 (NH) and 1615 cm⁻¹ (C=O); UV $\lambda_{\max}$ 250 (log ϵ 4.22), 285 sh (3.94), 368 (3.83), and 428 nm (3.93); ¹H NMR δ =3.80 (3H, s, MeO-4'), 4.8 (2H, brm, NH₂), 6.5–7.5 (5H, m, aromatic H), 6.82 (2H, brd, J =9.0 Hz, H-3',5'), and 7.16 (2H, brd, J =9.0 Hz, H-2',6').

Anal. (C₁₄H₁₄N₂O₂) C, H, N.

2-(4-Methoxyanilino)tropone (11): Yellow prisms; mp 74–75 °C (from light petroleum); IR 3300 (NH) and 1605 cm⁻¹ (C=O); UV $\lambda_{\max}$ 246 (log ϵ 4.39), 284 sh (3.85), 350 (4.02), and 4.11 nm (4.19); ¹H NMR δ =3.81 (3H, s, MeO-4'), 6.4–7.3 (5H, m, H-3–7), 6.97 (2H, brd, J =9.5 Hz, H-3',5'),

7.19 (2H, brd, J =9.5 Hz, H-2',6'), and 8.6 (1H, brm, NH).

Anal. (C₁₄H₁₃NO₂) C, H, N.

3-Amino-2-(3-methoxyanilino)tropone (12): Orange needles; mp 145–147 °C (from benzene); IR 3450, 3375, 3275 (NH), and 1600 cm⁻¹ (C=O); UV $\lambda_{\max}$ 242 (log ϵ 4.41), 250 sh (4.38), 346 (3.91), and 413 nm (4.16); ¹H NMR δ =3.82 (3H, s, MeO), 3.9 (2H, brm, NH₂), 6.5–6.9 (4H, m, H-4–7), and 8.6 (1H, brm, NH-2).

Anal. (C₁₄H₁₄N₂O₂) C, H, N.

3-[2-(3-Chlorophenyl)-2-methylhydrazino]tropone (13): Red needles; mp 118–120 °C (from benzene); IR 3350 (NH) and 1600 cm⁻¹ (C=O); UV $\lambda_{\max}$ 269 (log ϵ 3.76) and 363 (4.10); ¹H NMR δ =3.86 (3H, s, MeN), 5.6–7.5 (9H, m, aromatic H), and 7.59 (1H, brm, NH); MS m/z 262 (M⁺; 34), 260 (M⁺; 100), 247 (15), 245 (46), 134 (40), 111 (64), and 91 (35).

Found: m/z 260.0729. Calcd for C₁₄H₁₃ClN₂O: M, 260.0716.

Conversion of 10 to 11. A solution of 10 (33 mg) in methanol (5 cm³) containing concd HCl (0.2 cm³, 2 equiv) was refluxed for 8 h, diluted with water, neutralized with a saturated aq NaHCO₃, and extracted with chloroform. The combined organic layers were washed with water, dried (Na₂SO₄), and evaporated in vacuo. The residue was purified by preparative TLC with chloroform to give 11 (4 mg, 13%) and the recovered 10 (36%).

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