Reactions of 3-Acetyltropolone and Its Methyl Ethers with 1,2-Ethanediamines

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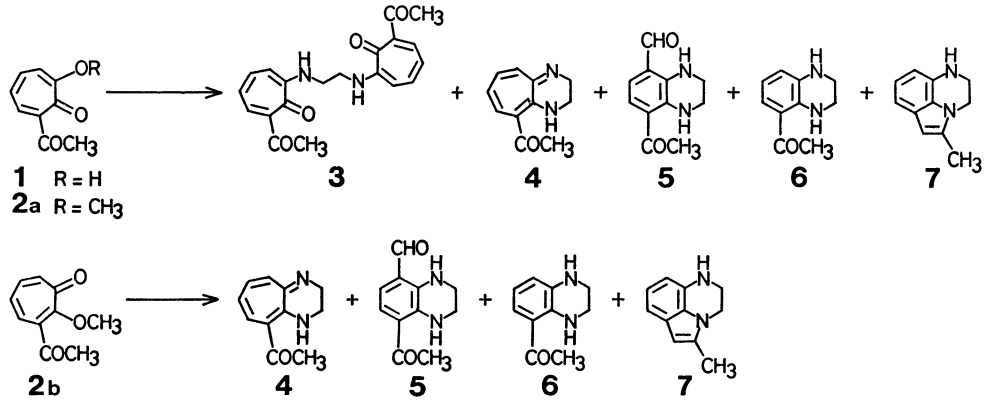
3-Acetyltropolone reacted with 1,2-ethanediamine to give *N,N'*-bis(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-1,2-ethanediamine (**3**) and 5-acetyl-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**4**), along with a small amount of by-products, which were 8-acetyl-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**5**), 5-acetyl-1,2,3,4-tetrahydroquinoxaline (**6**), and 2-methyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**7**). The minor products (**5**—**7**) resulted from the contraction of the seven-membered ring of the compound **4**. 2-Acetyl-7-methoxytropone (**2a**) also reacted with 1,2-ethanediamine to give the same products (**3**—**7**) in higher yields. On the other hand, the same reaction of 3-acetyl-2-methoxytropone (**2b**) readily gave **4**—**7**. The reaction of **2a** with *N*-methyl-1,2-ethanediamine gave *N*-(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-*N'*-methyl-1,2-ethanediamine (**14**), 5-acetyl-1-methyl-2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**15**), 8-acetyl-4-methyl-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**16**), 5-acetyl-1-methyl-1,2,3,4-tetrahydroquinoxaline (**17**), and 2,6-dimethyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**18**). The same reaction of **2b** also gave the products (**15**—**18**). The several reactions of these products are also described.

Recently, we found that 3-acetyltropolone and its methyl ethers reacted with a variety of nucleophilic reagents having two functional groups, such as amino and hydroxyl groups, to give heterocycle-fused troponoid compounds.[1] Amines[2] and *o*-aminophenol[3] reacted at the tropone carbonyl carbon atom and the adjacent carbon atom having the methoxyl group, while hydrazines[4-6] and hydroxylamine[7] reacted at the acetyl group and the adjacent carbonyl carbon atom or carbon atom having the methoxyl group. Furthermore, guanidine,[8] amidines,[8] and *o*-phenylenediamine[9] reacted in the former and in the latter forms to give two types of heterocycle-fused compounds. On the other hand, it was reported that the reactions of 5-nitroso- and 5-phenylazotropolones with 1,2-ethanediamine gave respectively oxime and phenylhydrazone of 7*H*-cyclohepta[*b*]pyrazin-7-one by dehydrogenation in the dihydropyrazine ring.[10] It was also found that 4,5-benzotropolone reacted with 1,2-ethanediamine to give benzo[4,5]cyclohepta[1,2-*b*]pyrazine.[11]

We now describe the reactions of 3-acetyltropolone (**1**) and its two isomeric methyl ethers——2-acetyl-7-methoxytropone (**2a**) and 3-acetyl-2-methoxytropone (**2b**)——with 1,2-ethanediamine and *N*-methyl-1,2-ethanediamine.

Results and Discussion

Reactions with 1,2-Ethanediamine. When 3-acetyltropolone (**1**) and 1,2-ethanediamine were refluxed for 2 h in methanol, *N,N'*-bis(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-1,2-ethanediamine (**3**) and 5-acetyl-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**4**) were isolated in 1 and 3% yields, respectively. Their structures were determined by the elemental analyses and spectral data. The IR, UV, and ^{1}H NMR spectra of the compound **3** are very similar to those of 2-acetyl-7-ethylaminotropone.[2] The ^{13}C NMR spectrum of the compound **4** shows a signal at δ=202.13, which is assigned to the acetyl carbonyl carbon atom. On the other hand, the acetyl carbonyl absorption in the IR spectrum is remarkably shifted to lower frequency region (1600 cm^{-1}) because of hydrogen-bonding with the 4-NH proton. The dehydrogenation reaction of **4** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) failed.



Scheme 1.

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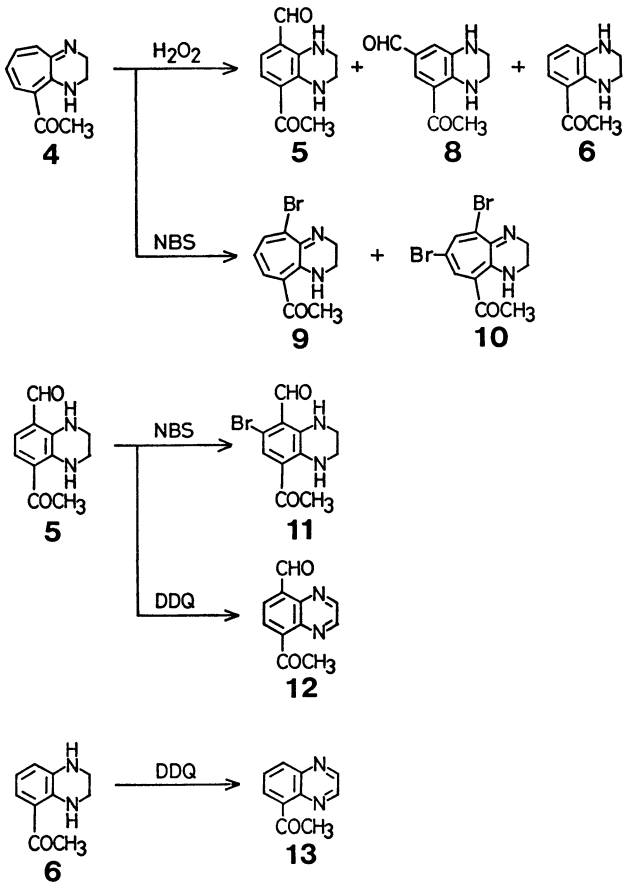
Prolonged reaction (24 h) of **1** with 1,2-ethanediamine afforded **3** and **4** in 4 and 6% yields, respectively, together with traces of 8-acetyl-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**5**) (1%), 5-acetyl-1,2,3,4-tetrahydroquinoxaline (**6**) (trace), and 2-methyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**7**) (1%). The products (**5**—**7**) were assigned on the basis of their elemental analyses and spectral data. Bromination of **4** with *N*-bromosuccinimide (NBS) gave 5-acetyl-9-bromo- (**9**) and 5-acetyl-7,9-dibromo-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**10**). The IR spectrum of the compound **5** shows the characteristic absorptions at 2840 and 2740 cm^{-1} for the formyl group and a broad absorption at 1670—1640 cm^{-1} for the acetyl and formyl groups which exhibited hydrogen-bonding with the NH protons at 1- and 4-positions, respectively. The ^1H NMR spectrum shows two doublets at δ=6.70 and 6.96 (J=9 Hz) for the two protons in the benzene ring. The ^{13}C NMR spectrum shows two peaks at δ=193.86 and 201.03, which are assigned to the formyl and acetyl carbonyl carbon atoms, respectively. The compound **5** reacted with NBS to afford 8-acetyl-6-bromo-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**11**) and was dehydrogenated with DDQ to afford 8-acetyl-5-quinoxalinecarbaldehyde (**12**). For the compound **6**, the IR spectrum shows an absorption at 1635 cm^{-1} for the hydrogen-bonded acetyl group. In the ^1H NMR spectrum, the ABX pattern is observed at δ=6.35, 6.51, and 7.08 (J= 7, 7, and 3 Hz) for the three protons in the benzene ring. This compound **6** was also dehydrogenated with DDQ to afford 5-acetylquinoxaline (**13**). The compound **7** was very unstable on exposure to air. Difference in the UV spectra in methanol and in 6 M sulfuric acid (1 M=1 mol dm^{-3}) is very similar to behavior in spectra of indoles.[12] The ^1H NMR spectrum shows an ABX pattern for the three protons in the benzene ring at δ=6.23, 6.77, and 6.90 (J= 8, 6.5, and 2 Hz) and 1-H proton at δ=6.08 which exhibited a long-range coupling with the methyl protons (J=1 Hz). These compounds (**5**—**7**) were revealed to be secondary products from **4** by time dependence of the yields and conversion of **4** with base—1,2-ethanediamine. In addition, the compound **4** was treated with hydrogen peroxide to afford **5** and **6**, together with 8-acetyl-1,2,3,4-tetrahydro-6-quinoxalinecarbaldehyde (**8**). Although the compound **8** was very unstable, the assignment of the structure is based on the spectral evidences.



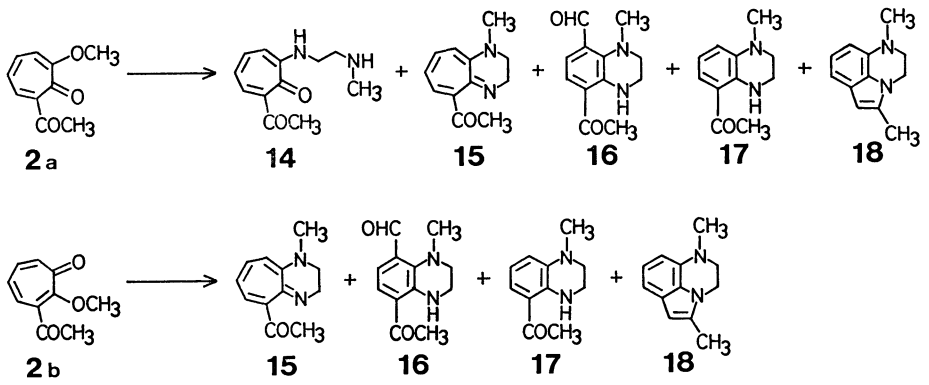
Scheme 2.

The reaction of 2-acetyl-7-methoxytropone (**2a**) with 1,2-ethanediamine also gave the five same products (**3**—**7**), as shown in Table 1. On the other hand, 3-acetyl-2-methoxytropone (**2b**) reacted with 1,2-ethanediamine to give the four products (**4**—**7**). The yield of the product (**4**) decreased, while the yields of the products (**5**—**7**) increased with reaction time.

Reactions with N-*Methyl-1,2-ethanediamine.* As shown in Table 2, 2-acetyl-7-methoxytropone (**2a**) reacted with *N*-methyl-1,2-ethanediamine to afford *N*-(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-*N'*-methyl-1,2-ethanediamine (**14**), 5-acetyl-1-methyl-2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**15**), 8-acetyl-4-methyl-1,2,3,4-

Table 1. Reactions with 1,2-ethanediamine

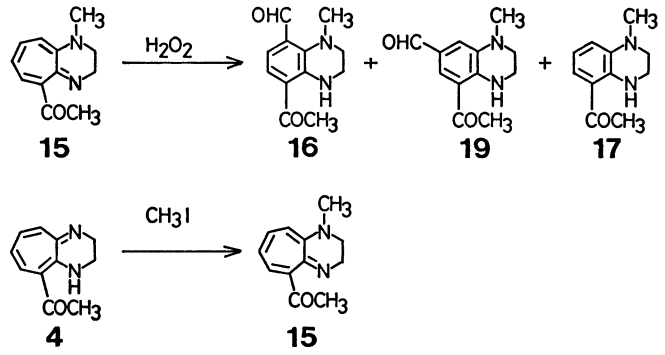
Substrate	Temperature	Reaction time / h	Yield/% 3	4	5	6	7
2a	Reflux	2	2	37	Trace	Trace	Trace
	Reflux	8	4	26	4	2	3
	Reflux	24	2	7	7	3	8
2b	R.t.	2		61	—	—	—
	R.t.	4.5		65	—	—	—
	Reflux	0.5		82	2	Trace	2
	Reflux	2		48	4	3	5
	Reflux	8		2	11	7	12



Scheme 3.

Table 2. Reactions with *N*-methyl-1,2-ethanediamine

Substrate	Temperature	Reaction time / h	Yield/% 14	15	16	17	18
2a	R.t.	2	74	—	—	—	—
	Reflux	2	38	13	—	Trace	Trace
	Reflux	24	4	27	2	2	9
2b	R.t.	2		58	—	—	—
	Reflux	2		26	Trace	8	10
	Reflux	24		—	Trace	11	19



Scheme 4.

tetrahydro-5-quinoxalinecarbaldehyde (**16**), 5-acetyl-1-methyl-1,2,3,4-tetrahydroquinoxaline (**17**), and 2,6-dimethyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**18**).

Their structures were assigned in comparison of the spectral data with those of the corresponding products from the reactions with 1,2-ethanediamine. The compound **15** was also obtained by methylation of **4** with methyl iodide and converted to the compounds (**16**—**18**) by heating in the presence of *N*-methyl-1,2-ethanediamine. Furthermore, the oxidation with hydrogen peroxide gave 8-acetyl-4-methyl-1,2,3,4-tetrahydro-6-quinoxalinecarbaldehyde (**19**), together with **16** and **17**. On the other hand, the reaction of 3-acetyl-2-methoxytropone (**2b**) with *N*-methyl-1,2-ethanediamine similarly gave the products (**15**—**18**).

Experimental

Measurements. The melting points were determined with a Yanagimoto MP-S2 apparatus and are uncorrected. The IR spectra were taken on a JASCO IRA-1 spectrophotometer, and the UV spectra on a Hitachi EPS-3T spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a Hitachi R-24 (60 MHz) and a JEOL JNM-FX-100 spectrometer (100 MHz), respectively. The mass spectra were obtained with a JEOL JMS-01SG-2 and JMS-DX-300 spectrometers.

*Reactions of 3-Acetyltropolone (**1**) with 1,2-Ethanediamine.* *(a)*: A mixture of 3-acetyltropolone (**1**) (164 mg, 1.0 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed for 2 h on a water bath. After removal of the solvent, the residue was twice chromatographed on a Wakogel B-10 plate (30×30 cm²) with ethyl acetate. The upper fraction was recrystallized from ethanol to give 4 mg (1%) of *N,N'*-bis(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-1,2-ethanediamine (**3**) as yellowish brown needles; mp 214—215 °C (decomp); IR ($CHCl_3$) 3240 (NH), 1700 ($COCH_3$), and 1600 cm^{-1} (C=O); UV (CH_3OH) 248 (log ε 4.44), 354 (4.03), and 430 nm (4.22); ^1H NMR [$(CD_3)_2SO$] δ=2.41 (s, 6H, $CH_3\times2$), 3.6—3.9 (m, 4H, $CH_2\times2$), 6.4—6.9 (m, 4H, arom-H), 7.1—7.6 (m, 4H, arom-H), and 8.5 (br, 2H, NH×2). Found: C, 67.93; H, 5.59; N, 7.97%. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95%. The lower fraction was recrystallized from diethyl ether to give 6 mg (3%) of 5-acetyl-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**4**) as light brown prisms; mp 73—74 °C; IR ($CHCl_3$) 3180 (NH) and 1600 cm^{-1} ($COCH_3$); UV (CH_3OH) 254 (log ε 4.25), 303 (3.61), 386 (3.77), and 458 nm (3.97); ^1H NMR ($CDCl_3$) δ=2.48 (s, 3H, CH_3), 3.2—3.5 (m, 2H, CH_2), 3.7—3.9 (m, 2H, CH_2), 5.91 (ddd, 1H, *J*=12, 7, and 2 Hz, H-7), 6.41 (dd, 1H, *J*=12 and 2 Hz, H-6), 12.2 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ=29.88 (CH_3), 38.69 (C-3), 49.90 (C-2), 108.26 (C-5), 116.77, 128.63, 131.16, 132.62, 149.71 (C-4a), 159.69 (C-9a), and 202.13 (C=O). Picrate: mp 216—218 °C. Found: C, 48.85; H, 3.67; N, 16.50%. Calcd for $C_{17}H_{15}N_5O_8$: C, 48.92; H, 3.62; N, 16.78%.

(b): A mixture of **1** (164 mg, 1.0 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed

for 8 h. After removal of the solvent, the residue was thrice chromatographed on a Wakogel B-10 plate (30×30 cm²) with chloroform. The first fraction was recrystallized from methanol–water to give 0.5 mg of 8-acetyl-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**5**) as red needles; mp 132—133 °C; IR ($CHCl_3$) 3300 (NH), 2840 (CHO), 2740 (CHO), and 1670—1640 cm^{-1} (br, CHO and $COCH_3$); UV (CH_3OH) 214 (log ε 4.21), 240 (4.26), 277 (4.00), 328 (4.07), and 490 nm (3.74); ^1H NMR ($CDCl_3$) δ= 2.54 (s, 3H, CH_3), 3.50 (m, 4H, $CH_2\times2$), 6.70 (d, 1H, J=9 Hz, H-6), 6.96 (d, 1H, J=9 Hz, H-7), 8.57 (br, 1H, 4-NH), 9.05 (br, 1H, 1-NH), and 9.75 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ=28.47 (CH_3), 38.28 (C-2 or -3), 38.57 (C-2 or -3), 116.36 (C-4a or -8a), 116.48 (C-4a or -8a), 116.83 (C-6), 118.95 (C-7), 139.03 (C-5 or -8), 139.55 (C-5 or -8), 193.86 (CHO), and 201.03 (acetyl C=O). Found: C, 64.42; H, 6.07; N, 13.72 %. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72%. The second fraction was recrystallized from hexane to give 1 mg of 2-methyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**7**) as colorless needles; mp 64—65 °C; IR ($CHCl_3$) 3380 cm^{-1} (NH); UV (CH_3OH) 226 (log ε 4.44) and 282 nm (3.89); ^1H NMR ($CDCl_3$) δ=2.29 (d, 3H, J=1 Hz, CH_3), 3.3—3.5 (m, 2H, CH_2), 3.58 (br, 1H, NH), 3.9—4.1 (m, 2H, CH_2), 6.08 (q, 1H, J=1 Hz, H-1), 6.23 (dd, 1H, J= 6.5 and 2 Hz, H-7), 6.81 (dd, 1H, J=8 and 6.5 Hz, H-8), and 6.90 (dd, 1H, J=8 and 2 Hz, H-9); ^{13}C NMR ($CDCl_3$) δ=11.57 (CH_3), 41.45 (C-4 or 5-), 41.98 (C-4 or -5), 99.16 (C-1), 102.27 (C-7), 110.02 (C-9), 119.94 (C-8), 125.87 (C-6a or -9a), 126.40 (C-6a or -9a), 132.16 (C-2 or -9b), and 134.33 (C-2 or -9b); MS *m/e* 172 (M^+). Found: C, 76.68; H, 7.11; N, 16.31%. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27%. The third fraction was recrystallized from hexane to give 0.5 mg of 5-acetyl-1,2,3,4-tetrahydroquinoxaline (**6**) as yellow needles; mp 78—79 °C; IR ($CHCl_3$) 3310 (NH) and 1635 cm^{-1} ($COCH_3$); UV (CH_3OH) 215 (log ε 4.34), 262 (4.06), and 419 nm (3.72); ^1H NMR ($CDCl_3$) δ=2.49 (s, 3H, CH_3), 3.2—3.7 (m, 4H, $CH_2\times2$), 3.7 (br, 1H, 1-NH), 6.33 (dd, 1H, J=7 and 7 Hz, H-7), 6.49 (dd, 1H, J=7 and 3 Hz, H-8), 7.08 (dd, 1H, J=7 and 3 Hz, H-6), and 8.7 (br, 1H, 4-NH); MS *m/e* 176 (M^+). Found: C, 68.19; H, 6.93; N, 15.96%. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.96%. The fourth fraction was rechromatographed on a Wakogel B-10 plate (30×30 cm²) with ethyl acetate to afford **3** (3 mg, 1%) and **4** (10 mg, 5%).

(c): A mixture of **1** (164 mg, 1.0 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed for 24 h and worked up, as mentioned above, to give **3** (17 mg, 5%), **4** (12 mg, 6%), **5** (2 mg, 1%), **6** (0.2 mg, trace), and **7** (2 mg, 1%).

*Reaction of 2-Acetyl-7-methoxytropone (**2a**) with 1,2-Ethanediamine.* A mixture of 2-acetyl-7-methoxytropone (**2a**) (178 mg, 1.0 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed and worked up, as mentioned above, to give the following results: (i) Reaction time, 2 h: **3** (8 mg, 2%), **4** (67 mg, 37%), **5** (0.2 mg), **6** (0.6 mg), and **7** (0.6 mg); (ii) Reaction time, 8 h: **3** (14 mg, 4%), **4** (48 mg, 26%), **5** (9 mg, 4%), **6** (3 mg, 2%), and **7** (4 mg, 3%); (iii) Reaction time, 24 h: **3** (8 mg, 2%), **4** (14 mg, 7%), **5** (14 mg, 7%), **6** (5 mg, 3%), and **7** (14 mg, 8%).

*Reaction of 3-Acetyl-2-methoxytropone (**2b**) with 1,2-Ethanediamine. (a)*: A solution of 3-acetyl-2-methoxytropone (**2b**) (357 mg, 2.0 mmol) and 1,2-ethanediamine (0.2 ml, 3.0 mmol) in methanol (10 ml) was allowed to stand for 2 h at room temperature. The reaction mixture was diluted with water and extracted with diethyl ether. After removal of the solvent, the residue was column-chromatographed on a Wakogel C-100 column (30 g) and recrystallized from diethyl ether to afford **4** (229 mg, 61%). Reaction time, 4.5 h: **4** (246 mg, 65%).

(b): A mixture of **2b** (178 mg, 1.0 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed and worked up, as mentioned above, to give the following results: (i) Reaction time, 30 min: **4** (152 mg, 82%), **5** (4 mg, 2%), **6** (1 mg), and **7** (3 mg, 2%); (ii) Reaction time, 2 h: **4** (91 mg, 48%), **5** (7 mg, 4%), **6** (5 mg, 3%), and **7** (8 mg, 5%); (iii) Reaction time, 8 h, **4** (3 mg, 2%), **5** (22 mg, 11%), **6** (12 mg, 7%), and **7** (20 mg, 11%).

*Treatment of the Compound (**4**) with 1,2-Ethanediamine.* A solution of the compound (**4**) (177 mg, 0.9 mmol) and 1,2-ethanediamine (0.1 ml, 1.5 mmol) in methanol (10 ml) was refluxed for 4 h. After evaporation of the solvent, the residue was thrice chromatographed on a Wakogel B-10 plate (30×30 cm²) with chloroform. The first fraction gave **5**. The second fraction was collected and rechromatographed on a Wakogel B-10 plate (30×30 cm²) with chloroform to give **5** and **7**. The third fraction gave **6**. Yields: **5** (23 mg, 12%), **6** (10 mg, 6%), and **7** (20 mg, 12%).

*Oxidation of the Compound (**4**) with Hydrogen Peroxide.* To a solution of **4** (98 mg, 0.5 mmol) in methanol (10 ml) was added 30% hydrogen peroxide aqueous solution (2 ml). The mixture was allowed to stand for 8 h at room temperature, diluted with water, and extracted with chloroform. After removal of the solvent, the residue was chromatographed on a Wakogel B-10 plate (30×30 cm²) with ethyl acetate to give **5** (3 mg, 3%), **6** (3 mg, 3%), and 8-acetyl-1,2,3,4-tetrahydro-6-quinoxalinecarbaldehyde (**8**) as semisolid (2 mg, 2%); IR ($CHCl_3$) 3390 (NH), 3270 (NH), 1690 (CHO), and 1630 cm^{-1} ($COCH_3$); ^1H NMR ($CDCl_3$) δ=2.57 (s, 3H, CH_3), 3.2—3.8 (m, 4H, $CH_2\times2$), 4.1 (br, 1H, 4-NH), 6.96 (d, 1H, J=1.5 Hz, H-5), 7.55 (d, 1H, J=1.5 Hz, H-7), 9.5 (br, 1H, 1-NH), and 9.52 (s, 1H, CHO).

*Bromination of the Compound (**4**) with NBS.* A mixture of **4** (95 mg, 0.5 mmol) and NBS (90 mg, 0.5 mmol) in benzene (10 ml) was refluxed for 30 min in the presence of benzoyl peroxide (catalytic amount). After removal of the solvent, the residue was twice chromatographed on a Wakogel B-10 plate (30×30 cm²) with ethyl acetate. The lower fraction was collected and recrystallized from benzene–hexane to afford 10 mg (7%) of 5-acetyl-9-bromo-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**9**) as brown plates; mp 102.5—103.5 °C; IR ($CHCl_3$) 1600 cm^{-1} (C=O); UV (CH_3OH) 245 (log ε 4.06), 252 (4.06), 270 (sh, 4.04), 380 (3.64), and 449 nm (3.82); ^1H NMR ($CDCl_3$) δ=2.45 (s, 3H, CH_3), 3.3—3.6 (m, 2H, CH_2), 3.8—4.1 (m, 2H, CH_2), 5.72 (dd, 1H, J= 10 and 8 Hz, H-7), 6.98 (d, 1H, J=10 Hz, H-8), 7.33 (d, 1H, J=8 Hz, H-6), and 10.8 (br, 1H, NH). Picrate: mp 206.5—207.5 °C (decomp). Found: C, 41.10; H, 2.90; N, 14.17%. Calcd for $C_{17}H_{14}N_5O_8Br$: C, 41.15; H, 2.84; N, 14.11%. The upper fraction was worked up, as mentioned above, to afford 11 mg (6%) of 5-acetyl-7,9-dibromo-3,4-dihydro-2*H*-cyclohepta[*b*]pyrazine (**10**) as brown prisms; mp 128 °C (decomp); IR ($CHCl_3$) 1620 cm^{-1} (C=O); UV (CH_3OH) 233 (log ε 4.13), 270 (4.07), 386 (3.75), and 461 nm (3.80); ^1H NMR ($CDCl_3$) δ=2.44 (s, 3H, CH_3), 3.2—3.5 (m, 2H, CH_2), 3.8—4.1 (m, 2H, CH_2), 7.31 (d, 1H, J= 1.5 Hz, H-8), 7.51 (d, 1H, J=1.5 Hz, H-6), and 12.1 (br, 1H, NH). Picrate: mp 154—155 °C (decomp). Found: C, 35.78; H, 2.34; N, 12.21%. Calcd for $C_{17}H_{13}N_5O_8Br_2$: C, 35.50; H, 2.28; N, 12.18%.

*Bromination of the Compound (**5**) with NBS.* A mixture of **5** (103 mg, 0.5 mmol) and NBS (89 mg, 0.5 mmol) in benzene (10 ml) was refluxed for 3 h in the presence of ben-

zoyl peroxide (catalytic amount), worked up, and twice chromatographed, as mentioned above. The upper fraction was collected and recrystallized from methanol to afford 16 mg (11%) of 8-acetyl-6-bromo-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehdye (**11**) as red needles; mp 162—163 °C; IR ($CHCl_3$) 3270 (NH), 2870 (CHO), 2770 (CHO), 1645 cm^{-1} (CHO and $COCH_3$); UV (CH_3OH) 232 (log ε 4.24), 280 (3.81), 331 (3.98), 493 (3.74), and 515 nm (sh, 3.70); ^1H NMR ($CDCl_3$) δ=2.50 (s, 3H, CH_3), 3.5—3.7 (m, 4H, $CH_2\times2$), 7.11 (s, 1H, H-7), 9.2 (br, 1H, 4-NH), 9.6 (br, 1H, 1-NH), and 10.15 (s, 1H, CHO). Found: C, 46.88; H, 3.99; N, 9.86%. Calcd for $C_{11}H_{11}N_2O_2Br$: C, 46.67; H, 3.92; N, 9.90%. The starting material (**5**) (13 mg, 17%) was recovered from the lower fraction.

*Dehydrogenation of the Compound (**5**) with DDQ.* A mixture of **5** (76 mg, 0.4 mmol) and DDQ (85 mg, 0.4 mmol) in dry benzene (15 ml) was refluxed for 8 h. After removal of the solvent, the residue was twice chromatographed on a Wakogel B-10 plate (30×30 cm^2) with chloroform. The lower fraction was recrystallized from benzene to give 13 mg (17%) of 8-acetyl-5-quinoxalinecarbaldehyde (**12**) as pale yellow needles; mp 177 °C (decomp); IR ($CHCl_3$) 1710 cm^{-1} (CHO and $COCH_3$); UV (CH_3OH) 218 (log ε 4.28), 239 (4.05), 313 (3.72), and 322 nm (sh, 3.70); ^1H NMR ($CDCl_3$) δ=2.87 (s, 3H, CH_3), 8.08 (d, 1H, J=7 Hz, H-6), 8.36 (d, 1H, J=7 Hz, H-7), 8.97 (s, 2H, H-2,3), and 11.25 (s, 1H, CHO). Found: C, 66.12; H, 4.09; N, 13.99%. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99%. The compound **5** (22 mg, 29%) was recovered from the upper fraction.

*Dehydrogenation of the Compound (**6**) with DDQ.* A mixture of **6** (94 mg, 0.5 mmol) and DDQ (228 mg, 1.0 mmol) in dry benzene (10 ml) was refluxed for 1 h and chromatographed, as mentioned above, to give 14 mg (15%) of 5-acetylquinoxaline (**13**) as pale yellow plates; mp 75—76 °C; IR ($CHCl_3$) 1700 cm^{-1} (C=O); UV (CH_3OH) 214 (log ε 4.11), 238 (3.83), 315 (sh, 3.45), and 322 nm (3.46); ^1H NMR ($CDCl_3$) δ=2.91 (s, 3H, CH_3), 7.88 (dd, 1H, J=7 and 2 Hz, H-7), 8.06 (dd, 1H, J=7 and 2 Hz, H-8), 8.22 (dd, 1H, J=7 and 2 Hz, H-6), and 8.87 (s, 2H, H-2,3). Found: C, 69.68; H, 4.73; N, 16.30%. Calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27%.

*Reaction of 2-Acetyl-7-methoxytropone (**2a**) with N-Methyl-1,2-ethanediamine. (a)*: A solution of **2a** (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was allowed to stand for 2 h at room temperature. The mixture was diluted with water and extracted with chloroform. After removal of the solvent, the residue was four-times chromatographed on two Kieselguhr G plates (30×30 cm^2) with hexane to give 163 mg (74%) of *N*-(3-acetyl-2-oxo-3,5,7-cycloheptatrienyl)-*N'*-methyl-1,2-ethanediamine (**14**) as a yellow oil; IR ($CHCl_3$) 3280 (NH), 1690 ($COCH_3$), and 1600 cm^{-1} (C=O); UV (CH_3OH) 247 (log ε 4.17), 349 (3.80), and 421 nm (3.96); ^1H NMR ($CDCl_3$) δ=1.7 (br, 1H, NH), 2.44 (br.s, 3H, *N*-CH_3), 2.55 (s, 3H, $COCH_3$), 2.7—3.1 (m, 2H, CH_2), 3.2—3.6 (m, 2H, CH_2), 6.4—6.8 (m, 2H, arom-H), 7.1—7.7 (m, 2H, arom-H), and 8.0 (br, 1H, NH). Picrate: mp 176 °C (decomp). Found: C, 47.89; H, 4.11; N, 15.27%. Calcd for $C_{18}H_{19}N_5O_9$: C, 48.11; H, 4.11; N, 15.58%.

(b): A mixture of **2a** (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was refluxed for 2 h. After removal of the solvent, the residue was four-times chromatographed on two Kieselguhr G plates (30×30 cm^2) with hexane. The lower fraction gave **14** (84 mg, 38%). The upper fraction was collected and twice rechromatographed on a Wakogel B-10 plate (30×30 cm^2) with chloroform. The first fraction gave 1 mg of 2,6-dimethyl-5,6-dihydro-4*H*-pyrrolo[1,2,3-*de*]quinoxaline (**18**) as a colorless oil; UV (CH_3OH) 223 (log ε 4.32) and 284 nm (3.84); ^1H NMR ($CDCl_3$) δ=2.19 (s, 3H, CH_3), 2.73 (s, 3H, *N*-CH_3), 2.9—3.2 (m, 2H, CH_2), 3.7—4.0 (m, 2H, CH_2), 5.89 (s, 1H, H-1), 6.03 (dd, 1H, J=4.5 and 3 Hz, H-7), 6.64 (dd, 1H, J=7 and 4.5 Hz, H-8), 6.72 (dd, 1H, J=7 and 3 Hz, H-9). Found: MS *m/e* 186.1181 (M^+). Calcd for $C_{12}H_{14}N_2$: M^+ 186.1156. The second fraction was recrystallized from hexane to give 0.6 mg of 5-acetyl-1-methyl-1,2,3,4-tetrahydroquinoxaline (**17**) as yellow needles; mp 77—78 °C; IR ($CHCl_3$) 3300 (NH) and 1630 cm^{-1} (C=O); UV (CH_3OH) 212 (log ε 4.31), 268 (3.93), and 418 nm (3.67); ^1H NMR ($CDCl_3$) δ=2.49 (s, 3H, $COCH_3$), 2.78 (s, 3H, *N*-CH_3), 3.0—3.2 (m, 2H, CH_2), 3.4—3.7 (m, 2H, CH_2), 6.47 (dd, 1H, J=7 and 6 Hz, H-7), 6.56 (dd, 1H, J=7 and 3 Hz, H-8), 7.08 (dd, 1H, J=6 and 3 Hz, H-6), and 9.1 (br, 1H, NH). Found: C, 69.45; H, 7.39; N, 14.44%. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72%. The third fraction was recrystallized from benzene–hexane to afford 25 mg (13%) of 5-acetyl-1-methyl-2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**15**) as orange prisms; mp 134—134.5 °C; IR ($CHCl_3$) 1680 cm^{-1} (C=O); UV (CH_3OH) 259 (log ε 4.18), 379 (3.75), and 466 nm (3.93); ^1H NMR ($CDCl_3$) δ=2.35 (s, 3H, $COCH_3$), 3.12 (s, 3H, *N*-CH_3), 3.3—3.5 (m, 2H, CH_2), 3.7—4.0 (m, 2H, CH_2), 5.79 (d, 1H, J=9.5 Hz, H-9), 6.06 (dd, 1H, J=10.5 and 8.5 Hz, H-7), 6.66 (ddd, 1H, J=10.5, 9.5, and 1.5 Hz, H-8), and 7.24 (dd, 1H, J=9.5 and 1.5 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ=28.53 (*CO*-CH_3), 39.81 (*N*-CH_3), 50.37 (C-2), 51.96 (C-3), 101.86, 116.80, 132.86, 134.33, 134.97 (C-5), 147.83 (C-4a), and 202.49 (C=O). Picrate: mp 151—153 °C (decomp). Found: C, 50.31; H, 3.82; N, 15.92%. Calcd for $C_{18}H_{17}N_5O_7$: C, 50.12; H, 3.97; N, 16.24%.

(c): A mixture of **2a** (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was refluxed for 24 h. The reaction mixture was worked up, as mentioned above, to give **14** (9 mg, 4%), **15** (54 mg, 27%), **17** (12 mg, 6%), **18** (17 mg, 9%), and 8-acetyl-4-methyl-1,2,3,4-tetrahydro-5-quinoxalinecarbaldehyde (**16**) (4 mg, 2%) as a red oil; IR ($CHCl_3$) 3300 (NH), 1695 (CHO), and 1640 cm^{-1} ($COCH_3$); UV (CH_3OH) 245 (log ε 4.30), 322 (3.62), and 467 nm (3.66); ^1H NMR ($CDCl_3$) δ=2.52 (s, 3H, $COCH_3$), 2.90 (s, 3H, *N*-CH_3), 3.3—3.7 (m, 4H, $CH_2\times2$), 6.94 (d, 1H, J=9 Hz, H-6), 7.40 (d, 1H, J=9 Hz, H-7), 9.1 (br, 1H, NH), and 10.25 (s, 1H, CHO). Found: MS *m/e* 218.0953 (M^+). Calcd for $C_{12}H_{14}N_2O_2$: M^+ 218.1055.

*Reaction of 3-Acetyl-2-methoxytropone (**2b**) with N-Methyl-1,2-ethanediamine. (a)*: A solution of 3-acetyl-2-methoxytropone (**2b**) (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was allowed to stand for 2 h at room temperature. The mixture was diluted with water and extracted with chloroform. After removal of the solvent, the residue was twice chromatographed on two Wakogel B-10 plates (30×30 cm^2) with ethyl acetate to afford **15** (117 mg, 58%).

(b): A mixture of **2b** (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was refluxed for 2 h. After removal of the solvent, the residue was twice chromatographed on two Wakogel B-10 plates (30×30 cm^2) with chloroform. The first, second, third, and fourth fractions gave **18** (20 mg, 10%), **17** (14 mg, 8%), **16** (2 mg), and **15** (52 mg, 26%), respectively.

(c): A mixture of **2b** (178 mg, 1.0 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml)

was refluxed for 24 h. The mixture was worked up, as mentioned above, to give **16** (2 mg), **17** (20 mg, 11%), and **18** (35 mg, 19%).

*Treatment of the Compound (**15**) with* N-*Methyl-1,2-ethanediamine.* A solution of **15** (181 mg, 0.9 mmol) and *N*-methyl-1,2-ethanediamine (0.1 ml, 1.4 mmol) in methanol (10 ml) was refluxed for 7 h. After removal of the solvent, the residue was twice chromatographed on a Wakogel B-10 plate (30×30 cm^2) with chloroform to give **16** (19 mg, 10%), **17** (32 mg, 19%), and **18** (10 mg, 6%).

*Oxidation of the Compound (**15**) with Hydrogen Peroxide.* A mixture of **15** (66 mg, 0.3 mmol) and 30% hydrogen peroxide aqueous solution (1 ml) in methanol (5 ml) was allowed to stand for 6 h at room temperature, diluted with water, and extracted with chloroform. After removal of the solvent, the residue was chromatographed on a Wakogel B-10 plate (30×30 cm^2) with ethyl acetate to give **16** (9 mg, 12%), **17** (3 mg, 5%), and 8-acetyl-4-methyl-1,2,3,4-tetrahydro-6-quinoxalinecarbaldehyde (**19**) (6 mg, 9%) as a semisolid; IR ($CHCl_3$) 3240 (NH), 1680 (CHO), and 1625 cm^{-1} ($COCH_3$); ^{1}H NMR ($CDCl_3$) $\delta=2.60$ (s, 3H, $COCH_3$), 2.95 (s, 3H, *N*-CH_3), 3.0—3.4 (m, 2H, CH_2), 3.5—3.9 (m, 2H, CH_2), 7.02 (m, 1H, H-5), 7.65 (d, 1H, $J=1.5$ Hz, H-7), and 9.65 (s, 1H, CHO).

*Methylation of the Compound (**4**) with Methyl Iodide.* A solution of **4** (188 mg, 1.0 mmol) and methyl iodide (0.2 ml, 3.0 mmol) in dry acetone (20 ml) was allowed to stand for 6 h in the presence of silver oxide (695 mg, 3.0 mmol). The mixture was filtered, concentrated, and thrice chromatographed on a Wakogel B-10 plate (30×30 cm^2) with ethyl acetate to give **15** (26 mg, 13%). The starting material (**4**) was recovered in 35% yield.

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