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Diaziridines. III. Reactions of Some 1-Alkyl- and 1,1-Dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones

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1,1-Dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones isomerize in boiling toluene into 2-(1-alken-1-yl)-4-hydroxy-1(2*H*)-phthalazinones and react with enamines and ynamines to yield derivatives of pyrazolo[1,2-*b*]- and indazolo[1,2-*b*]phthalazinediones.

The thermal conversions of 1-(2,4-dinitrophenyl)-3,3-dialkyl- and 1-(2,4-dinitrophenyl)-2,3,3-trialkyldiaziridines into 2,4-dinitrophenylhydrazones and 2-alkyl-6-nitrobenzotriazole 1-oxides, respectively, and the addition of 3,3-dialkyl- and 1,3,3-trialkyldiaziridines to electrophilic acetylenes have been the subjects of earlier reports in this series.[1,2] In the present paper the synthesis and reactions of 1-alkyl- and 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones (**1–7**) and the related systems **8** and **9** are described. These versatile compounds are thermally isomerized into 2-(1-alken-1-yl)-4-hydroxy-1-(2*H*)phthalazinones and react with ynamines and enamines to give pyrazolo[1,2-*b*]- and indazolo[1,2-*b*]phthalazinediones. Reactions with nitrones are presented in the following paper.

Results

The 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones (**1–5**) were prepared by the addition of phthaloyl chloride to ethereal solutions of 3,3-dialkyldiaziridines containing triethylamine (Scheme I, Table I). The 1-alkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones **6** and **7** were synthesized by generating the 3-alkyldiaziridines *in situ* from the corresponding chloral adducts, $RCHNHNCH(OH)CHCl_3$, in the presence of *o*-phthaloyl chloride. Compounds **8** and **9** were made in much the same manner as **1–5** by employing the appropriate diacid chloride and 3,3-pentamethylenediaziridine.

Scheme I

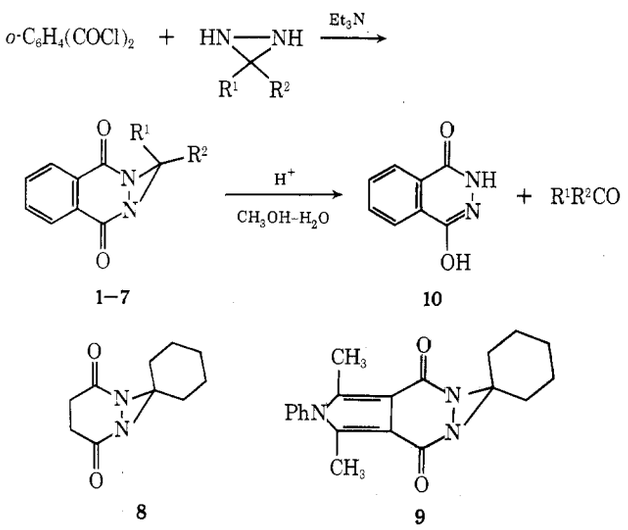
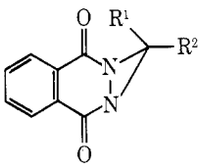


Table I
1-Alkyl- and 1,1-Dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones[a]



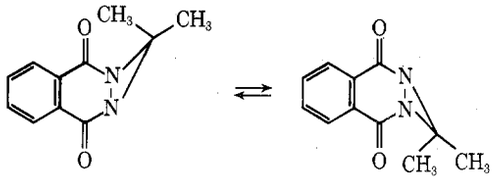
Compd[b]	R^1	R^2	Yield,[c] %	Mp, °C
1	Me	Me	58	98–99
2	Et	Et	35	70–71
3	*n*-Pr	*n*-Pr	47	108–109
4	$-(CH_2)_5-$		75	110–111
5	Me	Et	71	76–77
6	H	*n*-Pr	61	71–72.5
7	H	*t*-Bu	51	110–111

[a] Satisfactory analytical data for C, H, and N were obtained for all compounds listed in the table. Ed. [b] Compounds 1–7 were recrystallized from cyclohexane. [c] Yields are reported on the basis of recrystallized products.

The structures of **1–9** were assigned on the basis of elemental analyses, nmr spectroscopy, and by the hydrolysis of **2**, **4**, and **7** into 4-hydroxy-1(2*H*)-phthalazinone (**10**) and the corresponding carbonyl compounds 3-pentanone, cyclohexanone, and pivalaldehyde, respectively (Scheme I). The nmr spectrum of 1,1-dimethyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-dione (**1**) taken in C_6D_6 shows two peaks at δ 1.45 and 1.25 for the two methyl groups on the diaziridinyl carbon. On heating to about 60° the two peaks coalesce to a broad singlet which on further heating to 75° becomes a sharp singlet at δ 1.55. If the temperature is lowered to 40° the two signals for the methyl groups reappear. The temperature variance of the nmr spectrum of **1** indicates inversions of the nitrogen atoms (Scheme II) and is of some interest, since the *N*-aroyl moieties are perforce cis to

each other. Most equilibration studies of diaziridines have been concerned with those substrates having the N substituents trans to each other.[3,4]

Scheme II

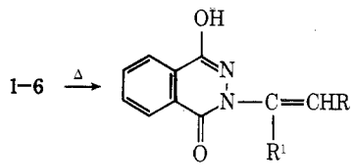


1 1

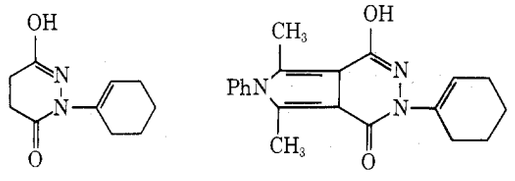
An examination of the nmr spectrum of 1-ethyl-1-methyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-dione (**5**) in C_6D_6 taken at several temperatures also indicated that inversions were taking place at the nitrogens. Thus at 0° two peaks were clearly observed for the methyl group but at 75° these signals became one sharp singlet and the ethyl group exhibited the sharp characteristic quartet–triplet splitting pattern.

Compounds **1–5** in refluxing toluene were converted into 2-(1-alken-1-yl)-4-hydroxyl-1(2*H*)-phthalazinones **11–16**, respectively (Scheme III). In the case of the thermolysis of **5** a 2:1 mixture of **15** and **16** was obtained. It was possible by fractional crystallization to obtain a sample of pure **15**. Thermolysis of **8** and **9** gave the cyclohexene derivatives **17** and **18**, respectively. Compound **9** isomerized with such ease that it was not possible to determine its melting point.

Scheme III



11, R = H; $R^1 = CH_3$
12, R = CH_3; $R^1 = C_2H_5$
13, R = C_2H_5; $R^1 = n\text{-}C_3H_7$
14, R, $R^1 = (CH_2)_4$
15, R = H; $R^1 = C_2H_5$
16, R = $R^1 = CH_3$
19, R = C_2H_5; R^1 = H



17 **18**

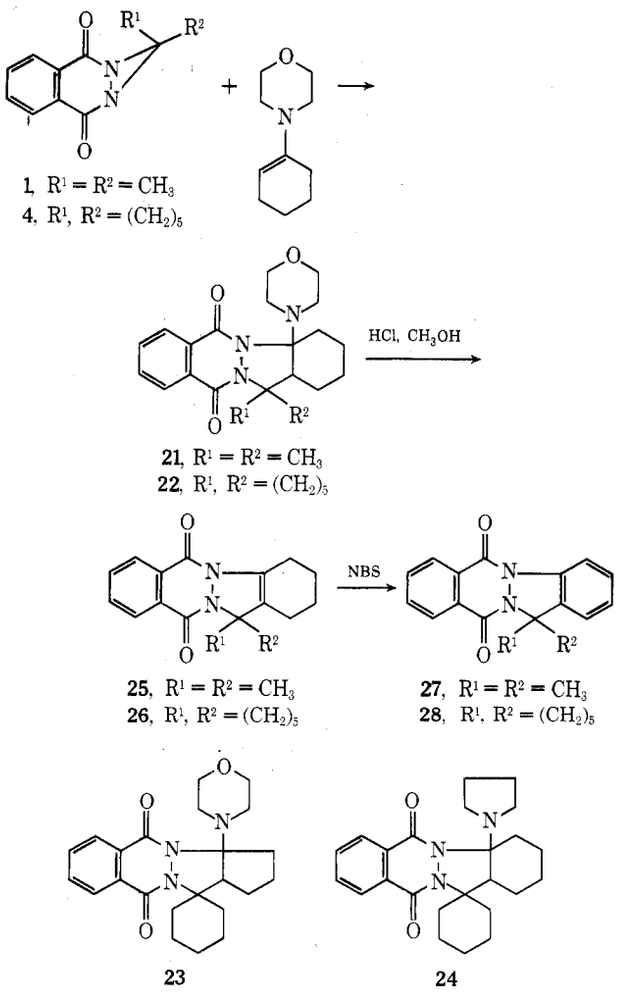
The structures of **11–16** followed from their nmr spectra and elemental analyses. Thus, in $CDCl_3$ the absorption peaks for the vinylic protons of **11–14** appeared at δ 5.32, 5.80, 5.80, and 6.04, respectively, and the absorption peaks for the OH proton appeared at δ 10.00, 10.20, 10.92, and 10.92. That the thermolysis of **5** gave a 2:1 mixture of **15** and **16** was clearly demonstrated by the nmr spectrum of the reaction products. The olefinic protons for **15** gave a broad singlet at δ 5.33 (2 H) and the ethyl group gave the characteristic quartet for the methylene group at δ 2.55 and a triplet for the methyl group at δ 1.14. The vinylic proton of **16** appeared as a quartet at δ 5.78, the methyl group adjacent to the methine hydrogen as a doublet at δ 1.88, and the remaining methyl group as a singlet at δ 2.08. The nmr spectra of **17** and **18** showed the same absorption pattern for the cyclohexenyl protons as **14**.

The assignment of the enamide structure to **12** is further supported by its hydrolysis into 3-pentanone and 4-hydroxy-1(2*H*)-phthalazinone (**10**) (Scheme III). Similarly, hydrolysis of **14** gave cyclohexanone and **10**.

Compounds **6** and **7** did not undergo thermolysis with ease. In the case of **6** reaction times of 7 hr in refluxing *o*-xylene gave ill-defined products from which a small quantity of the anticipated 2-(1-buten-1-yl)-4-hydroxy-1(2*H*)-phthalazinone (**19**) was isolated. However, high yields of **19** were obtained if **6** was refluxed in *o*-xylene containing some triethylamine hydrochloride (Scheme III). Compound **7** after many hours in refluxing *o*-xylene gave a material (**20**) which melted at 210–214°. This substance underwent acid hydrolysis to give **10** and pivalaldehyde. A mass spectrum showed a molecular ion at *m/e* 460 indicating a dimeric structure. The nmr spectrum of **20** did not show any signal in the olefinic region and the aliphatic protons appeared as a complex and broad multiplet extending from δ 0.3 to 1.4. No further work was attempted with this material nor do we feel confident, given the nmr spectrum, to assign a structure to the dimer at this time.

Refluxing the 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones **1** and **4** in benzene with equimolar quantities of the morpholine enamine of cyclohexanone yielded the adducts **21** and **22**, respectively (Scheme IV). Similar

Scheme IV



1, $R^1 = R^2 = CH_3$
4, R^1, $R^2 = (CH_2)_5$

21, $R^1 = R^2 = CH_3$
22, R^1, $R^2 = (CH_2)_5$

25, $R^1 = R^2 = CH_3$
26, R^1, $R^2 = (CH_2)_5$

27, $R^1 = R^2 = CH_3$
28, R^1, $R^2 = (CH_2)_5$

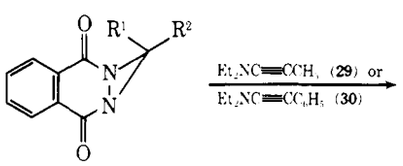
23 **24**

adducts, namely, **23** and **24**, were formed when **4** was treated with 1-*N*-morpholino-1-cyclopentene and 1-*N*-pyrrolidino-1-cyclohexene (Scheme IV).

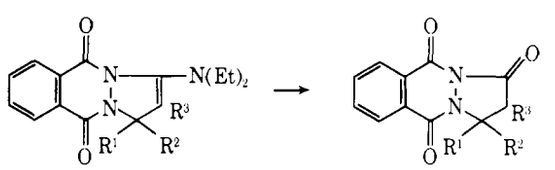
Upon heating in methanol containing a few drops of hydrochloric acid **21** and **22** eliminated morpholine and formed **25** and **26.** Aromatization of the cyclohexene ring of **25** and **26** was achieved by heating them with *N*-bromosuccinimide (Scheme IV).

When **1** and **4** were treated with 1-(*N,N*-diethylamino)propyne (**29**) or phenyl(*N,N*-diethylamino)acetylene (**30**) in refluxing toluene the enamines **31, 32, 35,** and **36** were obtained in good yields (Scheme V). The structures suggested for these products were in accord with their nmr spectra, mass spectra, and elemental analyses. Further evidence for structural assignments was gained by hydrolysis of **31, 32, 35,** and **36** to the 1*H*-pyrazolo[1,2-*b*]phthalazine-1,5,10-triones **33, 34, 37,** and **38,** respectively (Scheme V). Unambiguous proof of structure for **33** rested upon an alternate synthesis involving the reaction of 4-hydroxy-1(2*H*)-phthalazinone (**10**) with 2,3-dimethyl-2-butenoyl chloride in hot nitrobenzene (Scheme V). The preparation of 1*H*-pyrazolo[1,2-*b*]phthalazine-1,5,10-triones by treatment of **10** with α,β-unsaturated acid chlorides has been described.[5]

Scheme V

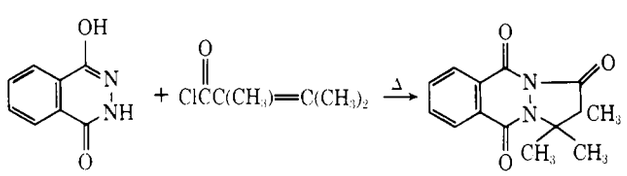


1, $R^1 = R^2 = CH_3$
4, $R^1, R^2 = (CH_2)_5$



31, $R^1 = R^2 = R^3 = CH_3$
32, $R^1 = R^2 = CH_3$; $R^3 = C_6H_5$
35, $R^1, R^2 = (CH_2)_5$; $R^3 = CH_3$
36, $R^1, R^2 = (CH_2)_5$; $R^3 = C_6H_5$

33. $R^1 = R^2 = R^3 = CH_3$
34. $R^1 = R^2 = CH_3$; $R^3 = C_6H_5$
37. $R^1, R^2 = (CH_2)_5$; $R^3 = CH_3$
38. $R^1, R^2 = (CH_2)_5$; $R^3 = C_6H_5$



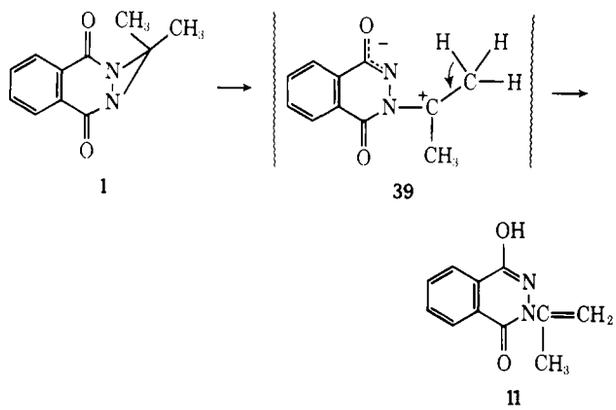
10 **33**

Significantly, compounds **1–5** did not react with electrophilic acetylenes such as diethylacetylene dicarboxylate and dibenzoylacetylene in boiling benzene. The products isolated in these instances were 2-(1-alken-1-yl)-4-hydroxy-1(2*H*)-phthalazinones and unreacted acetylene.

Discussion

The formation of 2-(1-alken-1-yl)-4-hydroxy-1(2*H*)-phthalazinones when 1,1-dialkyl-1*H*-diazirino[1,2-*b*]-phthalazine-3,8-diones are heated (*e.g.*, **1** → **11**) and the formation of cycloadducts when **1** and **4** are heated with enamines and ynamines suggest that these reactions occur through the intermediacy of azomethine imines **39** (Scheme VI). The generation of a dipolar species such as **39** whose anionic charge is delocalized relative to its cationic charge may also explain why 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones react with electron-rich dipolarophiles and fail to react with the electron-poor dipolarophile

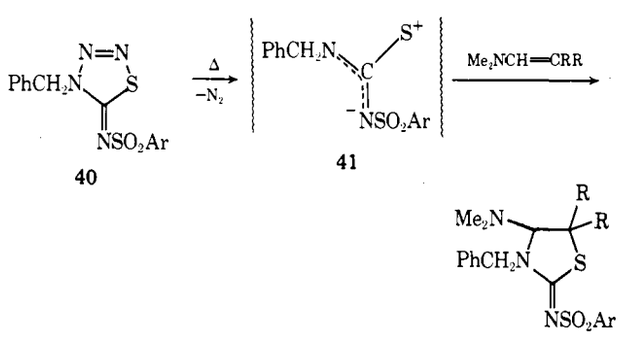
Scheme VI



1 **39** **11**

diethylacetylene dicarboxylate. In this regard the reactions of the 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones appear similar to the thermolysis and reactions of 4-alkyl-5-sulfonylimino-Δ^2-1,2,3,4-thiatriazoline (**40**). Compound **40** upon heating in benzene loses nitrogen to give the dipolar species **41** (also characterized by considerable delocalization of the negative charge relative to the cationic charge). The intermediate **41,** like **39,** undergoes reactions with enamines and ynamines (Scheme VII) and

Scheme VII



40 **41**

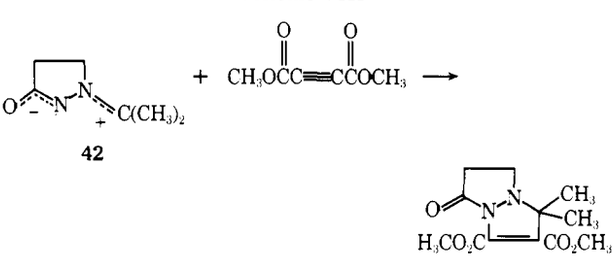
Ar = *p*-$H_3CCC_6H_4$

like **39** does not undergo cycloadditions with diethylacetylene dicarboxylate.[6] It is important to point out that the isolable azomethine imine **42** does form an adduct with dimethylacetylene dicarboxylate[7] (Scheme VIII). However, in this case the cationic charge is delocalized as extensively as the anionic charge.

The reaction of **1** and **4** with enamines and ynamines also may be accounted for by a nucleophilic attack on the diaziridinyl carbon by the electron-rich double bond or triple bond with ring opening followed by ring closure to a pyrazolo[1,2-*b*]- or indazolo[1,2-*b*]phthalazinedione.

The facile acid-catalyzed isomerization of **6** to **19** is probably due to the protonation of the amido moiety of **6** followed by ring opening to a carbonium ion. Loss of a proton from the carbonium ion would give the product **19.**

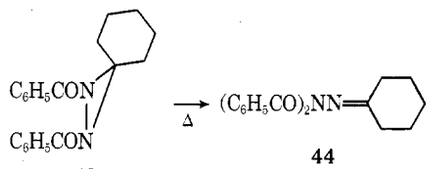
Scheme VIII



42

1,2-Diaroyldiaziridines such as 1,2-dibenzoyl-3,3-pentamethylenediaziridine (**43**), compounds related to but less constrained than **1–7**, have been reported to rearrange in warm ethanol into β,β-diaroylhydrazones (**44**) (Scheme IX).[8] We have observed the same rearrangement of **43** to **44** in boiling benzene. Possibly a dipolar species is involved in this isomerization too.

Scheme IX



43 44

Experimental Section

Materials. 3,3-Dimethyl-, 3,3-diethyl-, 3,3-di-*n*-propyl-, and 3,3-pentamethylenediaziridine were prepared according to known procedures.[9,10] 3-Ethyl-3-methyldiaziridine was purchased from Aldrich.

Syntheses of 1–5. To a mixture of 10 mmol of a 3,3-dialkyldiaziridine in 75 ml of anhydrous ether was added dropwise and with stirring a solution of 10 mmol of *o*-phthaloyl chloride in 75 ml of anhydrous ether. After 0.5 hr the mixture was filtered and the filtrate was evaporated. The residual oily solid was slurried with a small amount of ethanol, filtered, and recrystallized (Table I). The recrystallized **1–5** should be stored in a desiccator and at refrigerator temperatures.

Synthesis of 8. **8** was prepared in the same manner as **1–5** but in 10% yield. It was recrystallized from cyclohexane, mp 119–121°.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.50; H, 7.09; N, 14.21.

Synthesis of 6. A mixture of 1.12 g (4.85 mmol) of 1-(α-hydroxy-β,β,β-trichloroethyl)-3-*n*-propyldiaziridine[11] and 50 ml of 2 *N* NaOH was stirred for 0.5 hr. Several pellets of NaOH were added and the liberated 3-*n*-propyldiaziridine was extracted with five 20-ml portions of Et_2O. The ethereal extracts were dried over $MgSO_4$, filtered, and cooled. Triethylamine (967 mg, 9.4 mmol) was added to the cold ether solution of the diaziridine followed by the dropwise addition of a solution of 785 mg (3.87 mmol) of *o*-phthaloyl chloride in 100 ml of Et_2O. The reaction mixture was filtered and the solvent was evaporated. The residual oil solidified and was immediately recrystallized from cyclohexane to give 509 mg (61%) of **6**. Three recrystallizations from cyclohexane gave **6**, mp 71–72.5°, molecular ion *m/e* 216.

Synthesis of 7. A solution of 20 g of 2,4,6-tri-*tert*-butyl-1,3,5-triazabicyclo[3.1.0]hexane[12] in 50 ml of CH_3OH was added dropwise over a period of 20 min to a mixture of 25 g of chloral hydrate and 250 ml of 2 *N* H_2SO_4 held at 50°. After the addition was complete the pivalaldehyde which had formed by some hydrolysis taking place was removed by means of a flash evaporator. The clear acidic residue was quickly cooled and neutralized with 250 ml of 2 *N* NaOH. The 1-(α-hydroxy-β,β,β-trichloroethyl)-3-*tert*-butyldiaziridine that had precipitated was quickly filtered, washed thoroughly with cold water, and dried under vacuum. The yield of crude product was 19.2 g, mp 149–150°, and it was pure enough for the next step.

To the above chloral derivative (5.7 g) suspended in 50 ml of 2 *N* NaOH was added 4.6 g of *o*-phthaloyl chloride. Heat is liberated in the reaction. After the reaction mixture returned to room temperature the chloroform that was liberated was removed with a flash evaporator. The crude **7** was filtered, washed with water, and vacuum dried. It weighed 2.7 g (51%). Recrystallization from cyclohexane gave **7**, mp 110–111°.

Synthesis of 9. Thionyl chloride (32 g) was added to 2.5 g (10 mmol) of 1-phenyl-2,5-dimethylpyrrole-3,4-dicarboxylic acid.[13] After the initial reaction had subsided the mixture was heated on a steam bath for 2 hr. The excess $SOCl_2$ was removed and the residue was dissolved in dry C_6H_6. This solution was added dropwise and with stirring to a mixture of 1.12 g (10 mmol) of 3,3-pentamethylenediaziridine and 2.02 g of triethylamine in 100 ml of C_6H_6. After 1 hr the reaction mixture was filtered and the benzene filtrate was washed with water and quickly dried over Na_2SO_4. The dried filtrate was filtered and the C_6H_6 was evaporated. The crude **9** (2.5 g, 75%) was recrystallized from a mixture of C_6H_6 and petroleum ether (bp 63–75°). All attempts to determine the melting point of **9** failed, since it isomerized to **18** during heating.

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.60; H, 6.27; N, 12.54. Found: C, 71.25; H, 6.33; N, 12.36.

Hydrolysis of 4. A solution of 242 mg (1 mmol) of **4** in 10 ml of CH_3OH containing 2 drops of concentrated hydrochloric acid was refluxed for 1.5 hr. The solution was cooled and the 4-hydroxy-1(2*H*)-phthalazinone (**10**) was filtered. A solution of 2,4-dinitrophenylhydrazine was added to the filtrate and the cyclohexanone-2,4-dinitrophenylhydrazone was filtered. It weighed 250 mg (89%), mp 157–160°.

Hydrolyses of 2 and 7. The hydrolyses of **2** and **7** were carried out in a similar manner as **4**. In each case **10** was obtained. The 3-pentanone from **2** and the pivalaldehyde from **7** were isolated as 2,4-dinitrophenylhydrazones.

Thermolyses of 1–4, 8, and 9. A solution of 2 mmol of **1–4, 8,** or **9** in 10 ml of anhydrous toluene was refluxed for 3 hr. The solvent was evaporated and the residue was slurried with a small quantity of cold toluene or cold CH_3CN and filtered. The 2-(1-alken-1-yl)-4-hydroxyphthalazinones **11–14** were recrystallized from CH_3CN; **17** was recrystallized from toluene and **18** was recrystallized from ethanol.

Thermolysis of **1** gave **11**, mp 149–152°, in 76% yield.

Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98; N, 13.85. Found: C, 64.96; H, 4.97; N, 13.70.

Thermolysis of **2** gave **12**, mp 129–130°, in 60% yield.

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.77; H, 6.13; N, 12.17. Found: C, 67.73; H, 6.29; N, 12.40.

Thermolysis of **3** gave **13**, mp 128–131°, in 59% yield.

Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.76; H, 7.02; N, 10.84. Found: C, 69.93; H, 7.12; N, 10.69.

Thermolysis of **4** gave **14**, mp 148–150°, in 70% yield.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.15; H, 5.85; N, 11.96.

Thermolysis of **8** gave **17**, mp 167–170°, in 78% yield.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.53; H, 7.25; N, 14.17.

Thermolysis of **9** gave **18**, mp 286–289°, in 78% yield.

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.65; H, 6.27; N, 12.54. Found: C, 71.41; H, 6.32; N, 12.29.

Conversion of 6 into 19. A mixture of 113 mg of **6** and 17 mg of Et_3NHCl in 6 ml of *o*-xylene was refluxed for 1 hr. The mixture was filtered and then was cooled. The crude **19** (94 mg, 83%) was filtered and recrystallized from CH_3CN to give **19**, mp 170–173°, molecular ion *m/e* 216.

Reactions of 4 with Enamines. A mixture of 4 mmol of **4** with equimolar quantities of 1-*N*-morpholino-1-cyclohexene, 1-*N*-morpholino-1-cyclopentene, or 1-*N*-pyrrolidino-1-cyclohexene in 20 ml of dry C_6H_6 was refluxed for 5 hr. The reaction mixture was cooled and the small quantity of **10** that precipitated was filtered. The filtrate was evaporated and the residual oil was slurried with a small quantity of cold CH_3OH and filtered. Purification of **22, 23,** or **24** was achieved by recrystallization from absolute methanol. The crude yields varied from 40 to 70%.

Compound **22** had mp 188–193°.

Anal. Calcd for $C_{24}H_{31}N_3O_3$: C, 70.39; H, 7.63; N, 10.26. Found: C, 70.65; H, 7.76; N, 10.39.

Compound **23** had mp 162–164°.

Anal. Calcd for $C_{23}H_{29}N_3O_3$: C, 69.85; H, 7.39; N, 10.36. Found: C, 69.55; H, 7.52; N, 10.33.

Compound **24** had mp 164–169°.

Anal. Calcd for $C_{24}H_{31}N_3O_2$: C, 73.25; H, 7.94; N, 10.68. Found: C, 73.64; H, 8.00; N, 10.58.

Reaction of 1with 1-*N*-Morpholino-1-cyclohexene. When **1** was treated with 1-*N*-morpholino-1-cyclohexene, compound **21**, mp 191–194°, was obtained in 55% yield.

Anal. Calcd for $C_{21}H_{27}N_3O_3$: C, 68.27; H, 7.36; N, 11.37. Found: C, 68.32; H, 7.42; N, 11.85.

Synthesis of 25. A mixture of 370 mg (1 mmol) of **21**, 10 ml of CH_3OH, and 3 drops of concentrated hydrochloric acid was refluxed for 1 hr. The solvent was evaporated and the residual oily solid was slurried with a small quantity of methanol. The crude **25** (100%) was filtered and then recrystallized from methanol. The purified **25** melted at 198–200°, molecular ion *m/e* 282.

Synthesis of 27. A mixture of 282 mg (1 mmol) of **25** and 356 mg (2 mmol) of *N*-bromosuccinimide in 10 ml of CCl_4 was refluxed for 2 hr. The mixture was cooled and the precipitated succinimide was filtered. The filtrate was evaporated and the crude **27** was slurried with a small quantity of methanol and filtered. The crude yield was quantitative.

Compound **27** was recrystallized from CH_3OH, mp 197–200°.

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.25; H, 5.11; N, 9.83.

Synthesis of 26. Using the same procedure as described for the synthesis of **25**, compound **22** was converted to **26** in quantitative yield. It melted at 173–175° after recrystallization from CH_3OH, molecular ion *m/e* 322.

Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.34; H, 6.90; N, 8.75.

Synthesis of 28. Treatment of **26** with *N*-bromosuccinimide gave **28** in quantitative yield. **28** melted at 140–142° after recrystallization from methanol.

Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.44; H, 5.70; N, 8.80. Found: C, 75.15; H, 5.89; N, 8.98.

Synthesis of 31. A mixture of 277 mg (1.38 mmol) of **1** and 158 mg (1.42 mmol) of $Et_2NC{\equiv}CCH_3$ (**29**) in 5 ml of dry toluene was refluxed for 1 hr. On cooling a small quantity of material precipitated and was filtered. This product melted at 177–179° but it was not **31** as shown by the nmr spectrum. The filtrate was evaporated and the crude **31** was recrystallized from 95% ethanol. A 35% yield of **31**, mp 125–128°, was obtained.

Anal. Calcd for $C_{18}H_{23}N_3O_2$: C, 68.98; H, 7.40; N, 13.41. Found: C, 68.78; H, 7.30; N, 13.54.

Preparation of 32. A mixture of 328 mg (1.62 mmol) of **1** and 291 mg (1.68 mmol) of $Et_2NC{\equiv}CC_6H_5$ in 10 ml of dry toluene was refluxed for 2 hr. The solvent was evaporated and the crystalline residue was recrystallized from 2 ml of absolute ethanol, yielding 307 mg (50.3%) of **32**. Two more recrystallizations gave an analytical sample of **32**, mp 173–175°.

Anal. Calcd for $C_{23}H_{25}N_3O_2$: C, 73.18; H, 7.21; N, 11.13. Found: C, 73.47; H, 6.89; N, 11.07.

Preparation of 33. Method A. To a solution of 235 mg (0.751 mmol) of **31** in 5 ml of 95% ethanol was added 1 ml of H_2O and 20 drops of concentrated hydrochloric acid. The mixture was refluxed for 5 min. Within 2 min the yellow color had disappeared. The solvent was evaporated and the residue was recrystallized from 95% ethanol to give 151 mg (77%) of **33**, mp 201–204°.

Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.33; H, 5.28; N, 10.77.

Preparation of 33. Method B. A mixture of 832 mg (5.13 mmol) of compound **10** and 773 mg (5.82 mmol) of 2,3-dimethyl-2-butenoyl chloride[14] in 2 ml of nitrobenzene was refluxed for 1.5 hr. To the cooled dark solution was added 20 ml of petroleum ether (bp 63–75°). Filtration of this mixture gave 1.24 g (93%) of **33** as a brown powder. Recrystallization from 95% ethanol and activated charcoal gave **33**, mp 200–203°. The nmr and ir spectra of this material were identical with those obtained employing method A. A mixture melting point of samples from methods A and B showed no depression. Method B is a modification of a published procedure for preparing triones such as **33**.[5]

Conversion of 32 into 34. To a solution of 212 mg (0.56 mmol) of **32** in 5.0 ml of 95% ethanol was added 1 ml of water and 20 drops of concentrated hydrochloric acid. The mixture was refluxed for 5 min. The solvent was evaporated and the crystalline residue was recrystallized from methanol to give 110 mg (61%) of **34**, mp 171–173°.

Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.14; H, 5.13; N, 8.81.

Synthesis of 35. A mixture of 1.537 g (6.36 mmol) of **4** and 767 mg (6.90 mmol) of $Et_2NC{\equiv}CCH_3$ in 40 ml of dry toluene was refluxed for 2 hr. The toluene was evaporated and the residual yellow gum was recrystallized from 95% ethanol to give 1.78 g (78%) of **35**, mp 118–122°. Two recrystallizations from methanol gave yellow crystals of **35**, mp 120–123°.

Anal. Calcd for $C_{21}H_{27}N_3O_2$: C, 71.36; H, 7.70; N, 11.89. Found: C, 71.31; H, 7.88; N, 11.70.

Synthesis of 36. A mixture of 242 mg (1.0 mmol) of **4** and 185 mg (1.07 mmol) of $Et_2NC{\equiv}CC_6H_5$ in 10 ml of dry toluene was refluxed for 2 hr. The toluene was evaporated and the crystalline residue was recrystallized from 7 ml of CH_3CN to give 254 mg (63%) of **36**, mp 189–193°. Three more recrystallizations from absolute ethanol gave **36** melting at 191–193°.

Anal. Calcd for $C_{26}H_{29}N_3O_2$: C, 75.15; H, 7.03; N, 10.11. Found: C, 74.97; H, 6.94; N, 9.90.

Conversion of 35 into 37. To a solution of 160 mg (0.454 mmol) of **35** in 9 ml of 95% ethanol was added 2 ml of water and 20 drops of concentrated hydrochloric acid. The mixture was refluxed for 5 min and the solvent was evaporated. The residue was recrystallized from 1 ml of 95% ethanol to give 110 mg (82%) of **37**, mp 162–165°. Two more crystallizations from 95% ethanol gave **37**, mp 165–167°.

Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.45; H, 6.09; N, 9.39. Found: C, 68.36; H, 6.15; N, 9.43.

Conversion of 36 into 38. A mixture of 103 mg (0.257 mmol) of **36**, 6.5 ml of 95% ethanol, 1 ml of H_2O, and 20 drops of concentrated hydrochloric acid was refluxed for 10 min. Evaporation of volatiles and recrystallization of the residue from 95% ethanol gave 83 mg (93%) of **38**, mp 249–252°. Three recrystallizations from CH_3CN gave **38**, mp 250–254°.

Anal. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.46; H, 5.67; N, 7.84.

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