(8) Solvay et Cie, French Demande 2 009 634 (Feb 6, 1970); *Chem. Abstr.*, **74**, 3600j (1971).
(9) A. Nabeya, Y. Tamura, T. Kodama, and Y. Iwakura, *J. Org. Chem.*, **38**, 3758 (1973).
(10) H. W. Heine, R. Henrie, II, L. Heitz, and S. R. Kovvali, *J. Org. Chem.*, **39**, 3187 (1974).
(11) E. Schmitz, *Chem. Ber.*, **95**, 688 (1962).
(12) A. T. Nielsen, R. L. Atkins, J. DiPol, and D. W. Moore, *J. Org. Chem.*, **39**, 1349 (1974).
(13) A. T. Nielsen, R. L. Atkins, D. W. Moore, R. Scott, D. Mallory, and J. M. LaBerge, *J. Org. Chem.*, **38**, 3288 (1973).
(14) The structure of trans-exo **4a** (**3a**, R = CH_3) has been established by x-ray crystallography: G. B. Ansell, forthcoming publication, this laboratory.
(15) R. L. Cook and T. B. Malloy, Jr., *J. Am. Chem. Soc.*, **96**, 1703 (1974).
(16) H.-P. Koopmann and P. Rademacher, *Spectrochim. Acta, Part A*, **32**, 157 (1976).
(17) A. T. Nielsen, *J. Org. Chem.*, **30**, 3650 (1965).
(18) S. A. Giller, A. V. Eremeev, M. Yu. Lidak, V. A. Kholodnikov, and V. A. Pestunovich, *Khim. Geterotsikl. Soedin.*, 607 (1971).
(19) (a) M. J. Cook, R. A. Y. Jones, A. R. Katritzky, M. Moreno Mañas, A. C. Richards, A. J. Sparrow, and D. L. Trepanier, *J. Chem. Soc., Perkin Trans. 2*, 325 (1973); (b) I. D. Blackburne, R. P. Duke, R. A. Y. Jones, A. R. Katritzky, and K. A. F. Record, *ibid.*, 332 (1973); (c) R. A. Y. Jones, A. R. Katritzky, D. L. Nicol, and R. Scattergood, *ibid.*, 337 (1973).
(20) E. L. Eliel, *Acc. Chem. Res.*, **3**, 1 (1970).
(21) R. P. Duke, R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *J. Chem. Soc., Perkin Trans. 2*, 2109 (1973).
(22) E. Breuer and D. Melumad, *J. Org. Chem.*, **38**, 1601 (1973).
(23) Infrared spectra were determined on a Perkin-Elmer Model 137, ^1H NMR spectra on a Varian A-60 or XL-100, and ^{13}C NMR spectra on a Varian XL-100 spectrometer with Transform Technology TT-100 pulsed Fourier transform system. ^1H and ^{13}C chemical shift measurements were determined at ca. 30 °C and are referenced to tetramethylsilane internal standard. Melting points were determined on a Kofler hot stage and are corrected. Elemental analyses and molecular weights (vapor osmometry) were determined by Galbraith Laboratories, Knoxville, Tenn.

Diaziridines. 5. Reaction of Some 1-Aroyl- and 1,2-Diacyldiaziridines

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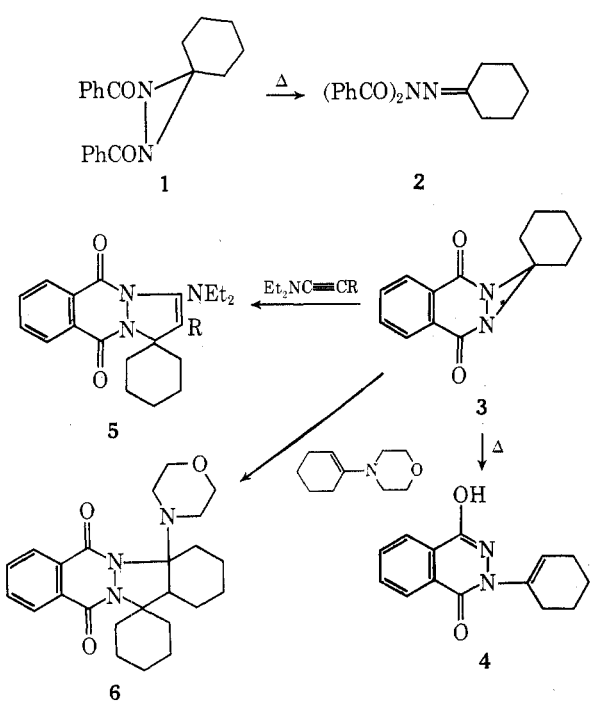
Received April 27, 1976

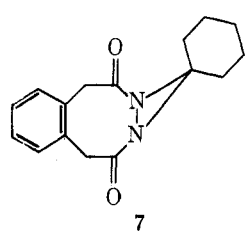
The diaziridine 4′,9′-dihydrospiro[cyclohexane-1,1′(1*H*)-diazirino[1,2-*c*][3,4]benzodiazocine]-3′,10′-dione (**7**) isomerizes in refluxing benzene into 3-(cyclohexylideneamino)-1*H*-3-benzazepine-2,4(3*H*,5*H*)-dione (**8**) and rearranges in refluxing benzene containing triethylamine hydrochloride into 3-(1-cyclohex-1-yl)-1,3,4,6-tetrahydro-3,4-benzodiazocine-2,5-dione (**9**). 1-*p*-Nitrobenzoyl-2,3,3-trialkyldiaziridines isomerize in chloroform or acetonitrile at ambient temperatures into labile 2-aryl-4,5,5-trialkyl-Δ^2-1,3,4-oxadiazolines (**11a–c**). The latter compounds react with both electrophiles and nucleophiles such as aromatic aldehydes and ynamines to give 2,5-diaryl-4-alkyl-Δ^2-1,3,4-oxadiazolines and pyrazoline derivatives, respectively.

Several studies on 1,2-diaroyldiaziridines have appeared recently. Schmitz and co-workers[1] reported the rearrangement of several 1,2-diaroyldiaziridines (**1**) to β,β-diaroylhydrazones (**2**) (Scheme I) and we[2,3] described the reactions of 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones (**3**). The latter compounds isomerize to 2-(1-alken-1-yl)-4-hydroxy-1(2*H*)-phthalazinones (**4**) in refluxing toluene and react with ynamines and enamines to give compounds **5** and **6**, respectively (Scheme I).

Scheme I



The difference in thermal behavior of **1** and **3** prompted us to undertake the preparation and thermolysis of a *N,N′*-diacyldiaziridine similar to **3** but less constrained, namely the benzodiazocine derivative **7**. For purposes of comparison with



7

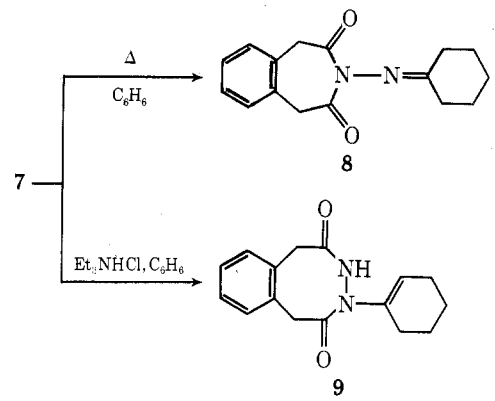
N,N′-diaroyldiaziridines we also prepared several 1-aroyl-2,3,3-trialkyldiaziridines. These substances isomerize in chloroform or acetonitrile to labile 2-aryl-4,5,5-trialkyl-Δ^2-1,3,4-oxadiazolines which react readily with both electrophilic and nucleophilic substrates such as aromatic aldehydes and ynamines.

Results

Compound **7** was synthesized in 41% yield by reacting *o*-phenylenediacetyl chloride with excess 3,3-pentamethylenediaziridine. The NMR spectrum of **7** is consistent with the structure proposed (see Experimental Section). When heated in benzene **7** isomerizes into the benzazepine **8** (Scheme II). The structure of **8** was elucidated by NMR spectroscopy, mass spectroscopy, and elemental analysis. The NMR spectrum taken in $CDCl_3$ consists of two singlets at δ 7.25 and 4.12 for the aromatic and methylene protons, respectively, and two broad multiplets centered at δ 2.50 and 1.70. The two multiplets are characteristic of the cyclohexylidine moiety when bonded to nitrogen and they are observed in the NMR spectra of hydrazone derivatives of cyclohexanone[4] and cyclohexanone oxime. Compound **7** when refluxed in benzene containing

a catalytic amount of triethylamine hydrochloride isomerizes into the benzodiazocine **9** (Scheme II).

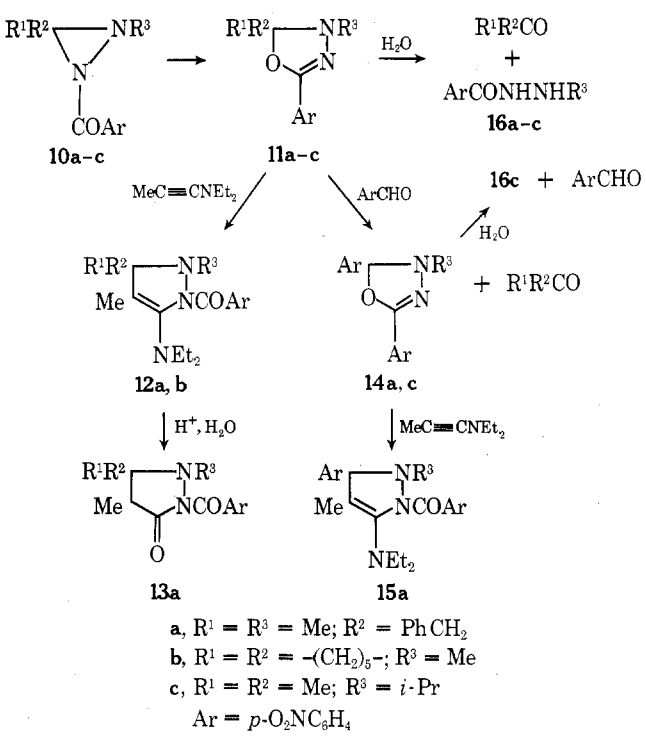
Scheme II



The NMR spectrum of **9** is quite similar to that of **4**. For example, the spectrum shows the presence of a vinylic proton at δ 5.74, an amido proton at δ 8.88, and two broad absorption peaks at δ 2.27 and 1.64 for the aliphatic protons of the cyclohexenyl group. In addition the two nonequivalent methylene groups of the benzodiazocine ring and the aromatic protons appear as multiplets at δ 4.17, 3.47, and 7.18, respectively.

Solutions of 1-aroyl-2,3,3-trialkyldiaziridines **10a–c** in dry methylene chloride, chloroform, or acetonitrile at ambient temperatures gradually change color from pale yellow to red within a few hours. In carbon tetrachloride at 80 °C the change takes place within 10 min. The color change parallels the disappearance of the nuclear magnetic absorption bands of the diaziridines and the appearance of new bands assigned to the 2-aryl-4,5,5-trialkyl-Δ^2-1,3,4-oxadiazolines **11a–c** (Scheme III). Evaporation of the solvent under anhydrous conditions gives solid **11a–c** but exposure of these substnces (or even solutions of these substances) to the atmosphere brings about their immediate hydrolysis to hydrazides **16** and ketones (Scheme III). In only the case of **11a** was it possible to obtain a sample that was stable enough to obtain elemental analyses

Scheme III



a, $R^1 = R^3 = Me$; $R^2 = PhCH_2$
b, $R^1 = R^2 = -(CH_2)_5-$; $R^3 = Me$
c, $R^1 = R^2 = Me$; $R^3 = i\text{-}Pr$
$Ar = p\text{-}O_2NC_6H_4$

although mass spectra for **11a–c** were determined. The hydrolysis of the 2,5-diaryl-4-alkyl-Δ^2-1,3,4-oxadiazolines **14a,c** also occurs rapidly but not as fast as that of the 4,5,5-trialkyl analogues. The hydrolysis of 2,4,5-triaryl-Δ^2-oxadiazolines has been reported to yield hydrazides and aldehydes.[5] The infrared spectra of **11a–c** and **14a,c** and the known 2,4,5-triphenyl-Δ^2-1,3,4-oxadiazolines are quite similar. Significantly there is present an absorption band at 1600 cm^{-1} (Nujol) for the –C=N– moiety and there are no bands attributable to carbonyl absorption.

Addition of 1-(*N,N*-diethylamino)propyne to chloroform solutions of **10a,b** either at the outset of the dissolution of **10a,b** in chloroform or after NMR spectroscopy had revealed the formation of **11a,b** resulted in the formation of the pyrazolines **12a,b** (Scheme III). Analytical and spectral data of **12a,b** together with the hydrolysis of **12a** to the pyrazolone **13a** confirmed their structure. The hydrolysis of 3-diethylamino-3-pyrazolines to pyrazolones is a known reaction.[2] The 2,5-diaryl-Δ^2-1,3,4-oxadiazoline **14a** also reacts with 1-(*N,N*-diethylamino)propyne to give the pyrazoline **15a**.

Treatment of acetonitrile solutions of **10a–c** or **11a–c** with *p*-nitrobenzaldehyde at room temperature gives 2,5-di(*p*-nitrophenyl)-4-alkyl-Δ^2-1,3,4-oxadiazolines **14a,c** and a ketone (Scheme III). Compounds **14a,c** were also prepared by condensing *p*-nitrobenzaldehyde with the appropriate 1-*p*-nitrobenzoyl-2-alkylhydrazine. As mentioned previously **14a,c** hydrolyze to hydrazides **16a,c** and *p*-nitrobenzaldehyde.

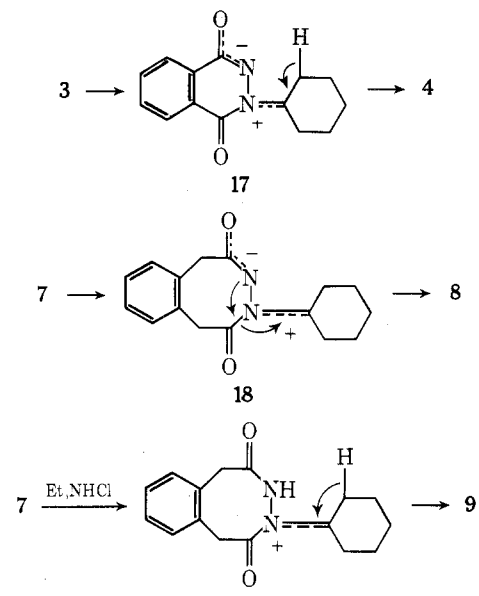
Discussion

One mechanistic scheme to account for the thermal conversions of **3** to **4** and of **7** to **8** involves the intermediacy of the azomethine imides **17** and **18**, respectively. The amido anion of **18** is less encumbered by ring constraint than the corresponding group of **17** and is thus able (unlike **17**) to add to the carbonyl carbon of the other amido group and thereby form **8** (Scheme IV). That this pathway is preferred to the elimination of a proton from the positively charged cyclohexyl group (as is the case with **17**) is borne out by the facile isomerization of the strain-free **1** to **2** via the intermediate $PhCON^+N^-(COPh)C_6H_{11}$.

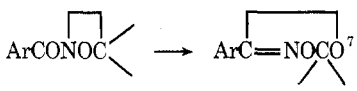
We attribute the conversion of **7** to **9** to the protonation of the amido group, subsequent opening of the diaziridine ring to **19**, followed by an elimination of a proton from **19** (Scheme IV).

The isolation of the labile **11a–c** when the diaziridines

Scheme IV



10a–c were dissolved in acetonitrile or chloroform suggests that **10** ring opened to the azomethine imide **20** which undergoes cyclization to **11** (Scheme V). A 1,3-dipolar species analogous to **20** has been proposed recently to rationalize the isomerization of 1-(anilinoformyl)-2-cyclohexyl-3-phenyl-3-methyldiaziridine to 1-cyclohexyl-4,5-diphenyl-5-methyl-1,2,4-triazolid-3-one.[6] The rearrangement of **10** to **11** bears a close resemblance to the thermal isomerizations of 2-

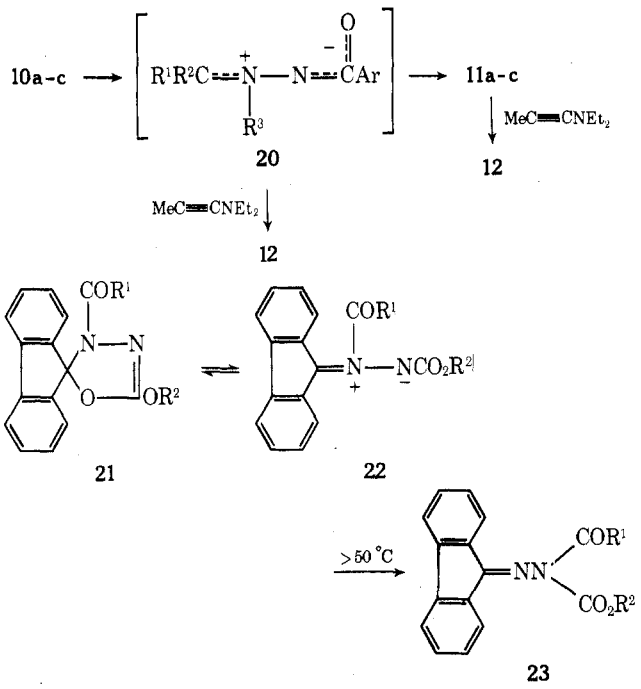


(1)

acyloxaziridines to 1,3,4-dioxazole derivatives and of 1-acylaziridines to Δ^2-oxazolines.[8a,b]

Two mechanisms may be suggested for the formation of the pyrazoline derivatives **12a,b** when **11a,b** reacts with 1-(*N,N*-diethylamino)propyne. One pathway involves an equilibrium between **11** and the azomethine imide **20**. Once formed **20** could undergo a cycloaddition with the ynamine (Scheme V). Such an equilibrium between the Δ^2-1,3,4-oxadiazoline **21** and the azomethine imide **22** has been proposed[9] to explain the rearrangement of **21** to **23** (Scheme V). An alternate reaction scheme for producing **12** is a nucleophilic attack of the ynamine on C-5 to **11** severing the carbon–oxygen bond to give a dipolar intermediate which then cyclizes to **12**.

Scheme V



The reactions of Δ^2-1,3,4-oxadiazolines with aldehydes and other electrophilic reagents are currently under investigation in our laboratories and will be reported at a later date.

It seems likely that the alternate synthesis of **14a** involving the reaction of *p*-nitrobenzaldehyde with a 1-*p*-nitrobenzoyl-2-alkylhydrazine also proceeds through the intermediacy of **20**. Thus Dorn and Otto[10] have isolated stable cyclic azomethine imides in 80–90% yields by condensing 3-pyrazolidones and carbonyl compounds and Oppolzer[11] has even isolated the precursor to an azomethine imide, namely, *N*-hydroxymethyl-*N*-methyl-*N'*-phenacetylhydrazine, when he treated *N*-methyl-*N'*-phenacetylhydrazine with formaldehyde.

Experimental Section

Materials. 1,3-Dimethyl-3-benzyldiaziridine,[12] 1-isopropyl-3,3-dimethyldiaziridine,[13] and 3,3-pentamethylene- and 1-methyl-3,3-pentamethylenediaziridines[14] were prepared according to known procedures.

Synthesis of 4',9'-Dihydrospiro[cyclohexane-1,1'(1*H*)-diazirino[1,2-*c*][3,4]benzodiazocine]-3',10'-dione (7). A solution of 4.62 g (20 mmol) of *o*-benzenediacetyl chloride[15] in 500 ml of dry Et_2O and a solution of 6.73 g (60 mmol) of 3,3-pentamethylenediaziridine in 500 ml of dry Et_2O were simultaneously added dropwise over 7.5 h to a stirred mixture of 10 g of anhydrous $MgSO_4$ in 2.5 l. of dry Et_2O at 5 °C. The reaction mixture was stirred for an additional 19 h and then filtered. Removal of the solvent left crude **7** which was recrystallized from anhydrous hexane (2.20 g, 41%), mp 108–109 °C. An analytical sample of **7** melted at 112–114 °C: NMR ($CDCl_3$) δ 7.25 (s, 4), 3.98 (s, 4), 1.70 (broad s, 10 H).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.07; H, 6.73; N, 10.54.

Synthesis of 3-(Cyclohexylideneamino)-1*H*-3-benzazepine-2,4(3*H*,5*H*)-dione (8). A solution of 132 mg of **7** in 10 ml of dry C_6H_6 was refluxed for 2.5 h. Evaporation of the solvent left 130 mg (98.5%) of **8**, mp 140–147 °C. **8** thrice recrystallized from petroleum ether (bp 110–115 °C) melted at 153–157 °C, molecular ion *m/e* 270.

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.42; H, 6.97; N, 10.36.

Synthesis of 3-(1-cyclohexen-1-yl)-1,3,4,6-tetrahydro-3,4-benzodiazocine-2,5-dione (9). A mixture of 500 mg of **7** and 36 mg of triethylamine hydrochloride in 25 ml of dry C_6H_6 was refluxed for 3 h. The mixture was filtered and the solvent evaporated. The crude **9** (493 mg, 98%) was recrystallized from benzene–petroleum ether (bp 65–110 °C) and then from 95% ethanol, mp 212.5–214 °C.

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.11; H, 6.90; N, 10.27.

Syntheses of 10a–c. To a stirred mixture of 5.5 mmol of triethylamine and 5 mmol of the appropriate diaziridine (1,3-dimethyl-3-benzyl-1-isopropyl-3,3-dimethyl- and 1-methyl-3,3-pentamethylenediaziridine) in 250 ml of dry Et_2O was added dropwise over a period of 15 min a solution of 4.9 mmol of *p*-nitrobenzoyl chloride in 50 ml of Et_2O. The mixture was stirred for 1 h and the triethylamine hydrochloride filtered. The solvent was concentrated to approximately 5 ml. The crude **10** was filtered and recrystallized. In this manner were obtained **10a** (85%), mp 102–104 °C; **10b** (90%), mp 78–81 °C; **10c** (69%), mp 90–91 °C. Ether was used to recrystallize **10a** and **10c** and cyclohexane was used to recrystallize **10b**.

10a. Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.59; H, 5.50; N, 13.49. Found: C, 65.35; H, 5.68; N, 13.45.

10b. Anal. Calcd for $C_{14}H_{17}N_3O_3$: C, 61.06; H, 6.22; N, 15.27. Found: C, 61.08; H, 6.25; N, 15.60.

10c. Anal. Calcd for $C_{13}H_{17}N_3O_3$: C, 59.29; H, 6.51; N, 15.96. Found: C, 59.17; H, 6.53; N, 16.04.

Isomerization of 10a–c to 11a–c. A solution of 933 mg of **10a** in 25 ml of dry acetonitrile was stored in a desiccator for 24 h. The diaziridine dissolved very slowly. After several hours red crystals of **11a** precipitated and were filtered under dry nitrogen (**11a** hydrolyzes rapidly in air). The melting point (sealed melting point tube) was 120–122 °C. No yield was recorded; ir (Nujol) 1600, 1500, 1300, 1350, 854, 848 cm^{-1}; NMR ($CDCl_3$) δ 1.42 (s, 3, CCH_3), 2.81 (s, 3, NCH_3), 3.13 (s, 2, CH_2), 7.18 (s, 5, C_6H_5) 7.90 (AB q, 4, *p*-$O_2NC_6H_4$–).

Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.59; H, 5.50; N, 13.49. Found: C, 65.69; H, 5.65; N, 13.13.

In a similar fashion a solution of 825 mg of **10b** in 10 ml of CH_3CN isomerized to **11b** in almost quantitative yield. The crystals of **11b** were red and they melted from 85 to 97 °C. Compound **11b** could only be obtained by the complete evaporation of the solvent under a stream of dry nitrogen. **11b** was extremely sensitive to atmospheric moisture. The NMR spectra revealed that all of **10b** had isomerized to **11b**: molecular ion *m/e* 275; ir (Nujol) 1600, 1500, 848, 850 cm^{-1}; NMR ($CDCl_3$) δ 1.74 (broad s, 10, C_5H_{10}), 2.81 (s, 3 NCH_3), 7.96 (AB q, 4, *p*-$O_2NC_6H_4$–).

Compound 11c was prepared in a similar manner to **11b** except that CCl_4 was employed as the solvent and the reaction mixture was heated for 30 min. **11c** was also very rapidly hydrolyzed when exposed to the atmosphere. It melted at 83–85 °C: molecular ion *m/e* 263; ir (Nujol) 1600, 1500, 1360, 1320, 1225, 1100, 1040, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.28 [d, 6, $CH(CH_3)_2$], 1.55 [s, 6, $C(CH_3)_2$], 3.2 (m, 1, CH), 7.90 (AB q, 4, *p*-$O_2N_6H_4$–).

Preparation of 12a. To a solution of 1.24 g (4 mmol) of **11a** in 20 ml of dry $CHCl_3$ was added 0.44 g (4 mmol) of 1-(*N,N*-diethylamino)propyne. The mixture was kept in a desiccator for 24 h and then the solvent was evaporated. The residue was slurried with a small quantity of 95% ethanol and filtered. The crude **12a** (960 mg, 57%) was filtered and recrystallized from 95% ethanol. The yellow crystals of **12a** melted at 117–119 °C, molecular ion *m/e* 422.

Anal. Calcd for $C_{24}H_{30}N_4O_3$: C, 68.22; H, 7.15; N, 13.26. Found: C, 68.45; H, 7.06; N, 13.06.

Preparation of 12b. To a solution of 550 mg (2 mmol) of **10b** in 10 ml of dry $CHCl_3$ which had been stored in a desiccator for 3 h was added 220 mg of 1-(*N,N*-diethylamino)propyne. After the reaction mixture had stood for an additional 12 h the chloroform was removed by means of a stream of dry nitrogen. The crude **12b** was washed with 1 ml of cold ethanol and filtered to give 400 mg (52%) of crude **12b**, mp 85–91 °C. Recrystallization from 95% ethanol gave 310 mg of **12b**, mp 107.5–109 °C.

Anal. Calcd for $C_{21}H_{30}N_4O_3$: C, 65.25; H, 7.85; N, 14.49. Found: C, 65.62; H, 7.77; N, 14.52.

Conversion of 12a to 13a. To a solution of 350 mg (0.83 mmol) of **12a** in 50 ml of methanol was added 10 ml of 3 N hydrochloric acid. The reaction mixture was heated for 15 min and then neutralized with sodium hydroxide. The solvent was evaporated and the crude **13a** (230 mg, 0.63 mmol, 76%) was filtered. Recrystallization from acetone gave **13a**, mp 234.5–237 °C, molecular ion *m/e* 367.

Anal. Calcd for $C_{20}H_{21}N_3O_4$: C, 65.39; H, 5.76. Found: C, 65.47; H, 5.47.

Conversion of 11a to 14a. A solution of 933 mg (3 mmol) of **10a** in 30 ml of dry acetonitrile was stored in a desiccator overnight. During this time **10a** slowly dissolved and **11a** gradually precipitated. The solution was heated for 5 min to dissolve **11a** and 450 mg (3 mmol) of *p*-nitrobenzaldehyde added. The reaction mixture was kept in a desiccator overnight and then filtered. The crude **14a** (490 mg, 50%) was recrystallized from benzene and melted at 179–181 °C.

Anal. Calcd for $C_{15}H_{12}N_4O_5$: C, 54.85; H, 3.68; N, 17.06. Found: C, 54.85; H, 3.69; N, 16.81.

Alternate Preparation of 14a. In a 50-ml round-bottomed flask equipped with a reflux condenser and a Dean-Stark apparatus was placed a mixture of 390 mg (2.6 mmol) of *p*-nitrobenzaldehyde, 510 mg of 1-*p*-nitrobenzoyl-2-methylhydrazine, and 15 ml of benzene. The reaction mixture was refluxed for 3 h and then cooled. The crude **14a** (750 mg, 88%) was filtered and recrystallized from benzene. It melted at 177–180 °C and was identical in all respects with **14a** prepared by the reaction of **11a** with *p*-nitrobenzaldehyde.

Conversion of 11c to 14c. A tightly stoppered flask containing 262 mg (1 mmol) of **10c** in 5 ml of acetonitrile was kept in a desiccator for 2 days. To this solution was added 151 mg (1 mmol) of *p*-nitrobenzaldehyde and the reaction mixture was allowed to stand for an additional 24 h. The crude **14c** that precipitated during this time was filtered and the volume of the filtrate was concentrated to 2.5 ml and filtered again. The crude **14c** weighed 160 mg (45%) and melted at 146–148 °C. It was purified by partially evaporating the solvent under a stream of dry nitrogen and filtering. The **14a** so obtained melted at 154–156 °C, molecular ion *m/e* 356.

Alternate Preparation of 14c. A mixture of 223 mg (1 mmol) of 1-*p*-nitrobenzoyl-2-isopropylhydrazine, 151 mg (1 mmol) of *p*-nitrobenzaldehyde, and 10 ml of dry chloroform was refluxed overnight. The solvent was evaporated and the residue was slurried with 2 ml of dry ether and was filtered. The **14c** was purified as described above.

Conversion of 14a to 15a. A mixture of 3.28 g (10 mmol) of **14a** and 1.11 g (10 mmol) of 1-(*N,N*-diethylamino)propyne in 50 ml of dry $CHCl_3$ was stored in a desiccator for 12 h. The solvent was evaporated under a stream of dry nitrogen and the crude **15a** (4.24 g, 97%) was recrystallized thrice from absolute ethanol to give **15a**, mp 163–164 °C.

Anal. Calcd for $C_{22}H_{25}N_5O_5$: C, 60.11; H, 5.73; N, 15.93. Found: C, 59.69; H, 5.26; N, 16.15.

Hydrolysis of 11c to 16c. A mixture of 243 mg of **10c** in 10 ml of benzene was refluxed for 40 min during which time it was converted to **11c**. Evaporation of the solvent in the atmosphere gave 204 mg (0.915 mmol, 98%) of **16c**. Recrystallization of **16c** from benzene gave crystals melting at 140–141 °C.

Anal. Calcd for $C_{10}H_{13}N_3O_3$: C, 53.80; H, 5.85; N, 18.82. Found: C, 53.55; H, 5.95; N, 18.60.

Alternate Synthesis of 16c. A mixture of 3 g (17 mmol) of *p*-nitrobenzoylhydrazide and 2.7 g (16 mmol) of 2-iodopropane in 20 ml of Me_2SO was kept in the dark for 48 h. After the addition of water (50 ml) the reaction mixture was saturated with sodium chloride and allowed to stand overnight. The precipitated hydriodide of **16c** was filtered and slurried with 50 ml of cold water and filtered again. The hydriodide of **16c** weighed 2.9 g (51%) and decomposed at 250 °C. The 2.9 g of **16c** was dissolved in 40 ml of absolute methanol to which 800 mg of triethylamine had been added. The mixture was stirred for 15 min and the methanol was evaporated. The residue was heated in benzene and the undissolved triethylamine hydriodide was filtered. Evaporation of the benzene gave 1.7 h (48%) of **16c**, mp 138–140 °C.

Synthesis of 16a. A solution of 202 mg (0.65 mmol) of **10a** in 15 ml of benzene was refluxed for 1 h. Evaporation of the solvent in the atmosphere caused rapid hydrolysis of **11a** to **16a** (126 mg, 100%). Crude **16a** melted at 140–141 °C but **16a** recrystallized from chloroform melted at 148.5–152 °C.

Anal. Calcd for $C_8H_9N_3O_3$: C, 49.22; H, 4.64; N, 21.53. Found: C, 49.10; H, 4.85; N, 21.51.

Acknowledgments. We are indebted to Professor Charles C. Sweeley of Michigan State University and Dr. William VandenHeuvel of Merck and Co. for the mass spectra of many of the compounds described in this paper. We thank Messrs. Andy Kofke and Robert Henrie for preliminary studies on compounds **7** and **8**, and Dr. Kurt L. Loening for help on nomenclature. This work was supported by Grant CA 15880 from the National Cancer Institute.

Registry No.—**7**, 59811-77-7; **8**, 59811-78-8; **9**, 59811-79-9; **10a**, 59811-80-2; **10b**, 59811-81-3; **10c**, 59811-82-4; **11a**, 59811-83-5; **11b**, 59811-84-6; **11c**, 59830-67-0; **12a**, 59811-85-7; **12b**, 59811-86-8; **13a**, 59811-87-9; **14a**, 59811-88-0; **14c**, 59811-89-1; **15a**, 59811-90-4; **16a**, 57676-56-9; **16c**, 59811-91-5; *o*-benzenediacetyl chloride, 21062-19-1; 3,3-pentamethylenediaziridine, 185-79-5; 1,3-dimethyl-3-benzyldiaziridine, 59872-19-4; 1-isopropyl-3,3-dimethyldiaziridine, 17119-93-6; 1-methyl-3,3-pentamethylenediaziridine, 26177-34-4; *p*-nitrobenzoyl chloride, 122-04-3; 1-(*N,N*-diethylamino)propyne, 4231-35-0; *p*-nitrobenzaldehyde, 555-16-8; *p*-nitrobenzoylhydrazide, 636-97-5; 2-iodopropane, 75-30-9.

References and Notes

(1) E. Schmitz, D. Habisch, and C. Grundemann, *Chem. Ber.*, **100**, 142 (1967).
(2) H. W. Heine, R. Henrie, II, L. Heitz, and S. R. Kovvali, *J. Org. Chem.*, **39**, 3189 (1974).
(3) H. W. Heine and L. Heitz, *J. Org. Chem.*, **39**, 3192 (1974).
(4) H. W. Heine, T. R. Hoye, P. G. Williard, and R. C. Hoye, *J. Org. Chem.*, **38**, 2984 (1973).
(5) R. Huisgen, R. Grashey, M. Seidel, H. Knupper, and R. Schmidt, *Justus Liebigs Ann. Chem.*, **658**, 169 (1962).
(6) A. Nabeya, Y. Tamura, T. Kodama, and Y. Iwakura, *J. Org. Chem.*, **38**, 3758 (1973).
(7) E. Schmitz and S. Schramm, *Chem. Ber.*, **100**, 2593 (1967).
(8) (a) H. W. Heine, *Angew. Chem., Int. Ed. Engl.*, **1**, 528 (1962); (b) H. W. Heine and M. S. Kaplan, *J. Org. Chem.*, **32**, 3069 (1967).
(9) E. Fahr, K. Doppert, and F. Scheckenbach, *Angew. Chem., Int. Ed. Engl.*, **2**, 480 (1963).
(10) H. Dorn and A. Otto, *Angew. Chem., Int. Ed. Engl.*, **7**, 214 (1968).
(11) W. Oppolzer, *Tetrahedron Lett.*, 2199 (1970).
(12) C. J. Paget and C. S. Davis, *J. Med. Chem.*, **7**, 626 (1964).
(13) E. Schmitz, *Chem. Ber.*, **95**, 680 (1962).
(14) E. Schmitz and R. Ohme, *Org. Synth.*, **45**, 85 (1965).
(15) A. I. Kiprianov and M. Yu. Kornilov, *Zh. Obshch. Khim.*, **34**, 77 (1964); *Chem. Abstr.*, **60**, 10665*h* (1964).