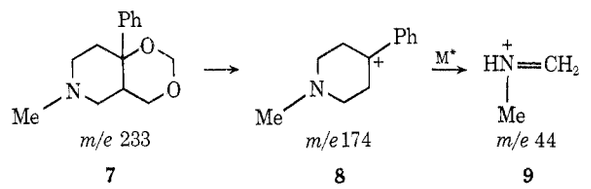
cis derivatives as will also that of the known preference for the "O inside" rather than "O outside" conformation in cis 1,3-dioxadecalanes.[8]

The mass spectral features of **3a** were consistent with the assigned structure; a molecular ion peak was present (*m/e* 233) and prominent lines at *m/e* 44 (base peak) and 174 plus a metastable peak at 11.1 showed the chief fragmentation pathway to be **7** → **8** → **9**.



Experimental Section[12]

Prins Reaction of 1-Methyl-4-phenyl-1,2,3,6-tetrahydropyridine and Analogs.—A mixture of the tetrahydropyridine **1a** (112 g),[13] aqueous formaldehyde (500 ml, 37%), concentrated sulfuric acid (250 ml), and water (to 1-l. total volume) was heated under reflux for 5 hr. The cooled product was made alkaline with aqueous ammonia and extracted with ether which was dried (Na_2SO_4) and evaporated. The residue with excess of ethanolic hydrogen chloride gave the **1,3-dioxane 3a hydrochloride** (81 g): mp 323° dec from ethanol; pmr (base in $CDCl_3$) δ 4.87, 4.80 (2 d, 3-CH_2, ^2J = 6.5 Hz), 3.94, 3.45 (d d, d, 5-CH_2, ^2J = 11.5, ^3J = 2.5 Hz for lower field signal), 2.39 (s, NMe).

Anal. Calcd for $C_{14}H_{20}ClNO_2$: C, 62.32 H, 7.47 N, 5.19. Found: C, 62.05 H, 7.52; N, 5.14.

Similar treatment of **1b**[13] gave the *N*-benzyl analog **3b hydrochloride**: mp 282° dec from ethanol; pmr (base in $CDCl_3$) δ 4.87, 4.71 (2 d, 3-CH_2, ^2J = 6.5 Hz), ~3.78 (d d, one 5-CH_2 proton, ^2J = 11.5, ^3J = 2.0 Hz, higher field signal not resolved), 3.6 (s, NCH_2).

Anal. Calcd for $C_{20}H_{24}ClNO_2$: C, 69.45; H, 7.0; N, 4.0. Found: C, 68.95; H, 7.27; N, 3.93.

Reaction of **1c** gave the ***N-tert*-butyl analog 3c hydrobromide**: mp 297° dec; pmr (base in $CDCl_3$) δ 4.66, 4.58 (2 d, 3-CH_2, ^2J = 6.5 Hz), 3.81, 3.55 (dd, d, 5-CH_2, ^2J = 11.6 Hz, ^3J = 2.5 Hz for lower field signal), 1.12 (s, *t*-Bu).

Anal. Calcd for $C_{17}H_{26}BrNO_2$: C, 57.31; H, 7.36; N, 3.93. Found: C, 57.50; H, 7.38; N, 3.78.

The tetrahydropyridine **1c** was made by treating 1-*tert*-butyl-4-phenyl-4-piperidinol (see below) with a hot mixture of acetic and hydrochloric acids;[14] it formed a **hydrogen oxalate**, mp 224° from acetone–ether.

Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.8; H, 7.46; N, 4.5. Found: C, 66.8; H, 7.59; N, 4.6.

The 4-piperidinol, prepared from 1-*tert*-butyl-4-piperidone[15] and phenyllithium in the usual manner,[14] melted at 112–113° (from ether–ligroin).

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.2; H, 9.93; N, 6.0. Found: C, 77.59; H, 9.93; N, 6.1.

It formed a **hydrogen oxalate**, mp 201–203°.

Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.3. Found: C, 62.98; H, 7.65; N, 4.3.

Registry No.—**1c** hydrogen oxalate, 35116-80-4; **3a** hydrochloride, 35116-81-5; **3b** hydrochloride, 35116-82-6; **3c** hydrobromide, 35116-83-7; 1-*tert*-butyl-4-phenyl-4-piperidinol, 35116-84-8; 1-*tert*-butyl-4-phenyl-4-piperidinol hydrogen oxalate, 35116-85-9.

(12) Melting points were determined in sealed capillary tubes (Gallenkampf apparatus) and are uncorrected. Pmr spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Varian HA-100 instrument.

(13) C. J. Schmidle and R. C. Mansfield, *J. Amer. Chem. Soc.*, **78**, 425 1702.

(14) A. F. Casy, A. H. Beckett, M. A. Iorio, and H. Z. Youssef, *Tetrahedron*, **21**, 3387 (1965).

(15) J. B. Robinson and J. Thomas, *J. Chem. Soc.*, 2270 (1965).

Reactions of 6-Acyl-5*H*-1-pyrindine-5,7(6*H*)-diones with Diamines

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As a continuation of our work on the preparation of 6-acyl-5*H*-1-pyrindine-5,7(6*H*)-diones (**1**) and on their reactions with hydrazine,[1] we now report the results of the reactions of compounds **1** with a variety of other diamines, with emphasis on a new pyridocyclopentadiazepine system.

We found that condensation of 6-acetyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1a**) with ethylenediamine yielded two different types of products depending upon the reaction conditions. Addition of **1a** (1 mol) to a refluxing ethanolic solution of ethylenediamine (1.5 mol) in the presence of formic acid gave 6-[1-(2-aminoethylimino)ethyl]-5*H*-1-pyrindine-5,7(6*H*)-dione (**2**) in good yields. Structure **2** is based on the elemental analyses, on the spectral data, and on the method of preparation which is analogous to that used by Mosher and Piesch to prepare 2-[1-(2-aminoethylimino)alkyl]-1,3-indandiones.[2]

Reverse addition of the reactants, ethylenediamine to a refluxing ethanolic solution of **1a**, and change of their molar ratio yielded the 1:2 product, 6,6′-[ethylenebis(nitriloethylidyne)]di-5*H*-1-pyrindine-5,7(6*H*)-dione (**6**), in very good yields.

When compound **2** was heated for 12 hr in refluxing 1-propanol and in the presence of formic acid, the expected ring closure took place with the formation of only one of the two possible isomers, 2,3-dihydro-5-methylpyrido[2′,3′:4,3]cyclopenta[2,1-*e*][1,4]diazepin-6(1*H*)-one (isomer **4**) or 2,3-dihydro-5-methylpyrido-[2′,3′:3,4]cyclopenta[2,1-*e*][1,4]diazepin-6(1*H*)-one (**3**). Structure **4** was assigned to the isolated isomer on the basis of elemental analyses, spectral data, and its reaction with ferrous ammonium sulfate. A 2:1 complex of pyridocyclopentadiazepinone **4** with ferrous iron as an intense blue-violet product was obtained. The ferrous iron complexes with the nitrogen of pyridine and the oxygen (enol form) of the cyclopentadiazepine moiety. The structurally related 2,3-dihydro-5-methyl-6*H*-indeno[1,2-*e*][1,4]diazepin-6-one[2] did not form a chelate with ferrous ammonium sulfate, indicating that it is not the diazepine ring which complexes with ferrous iron.

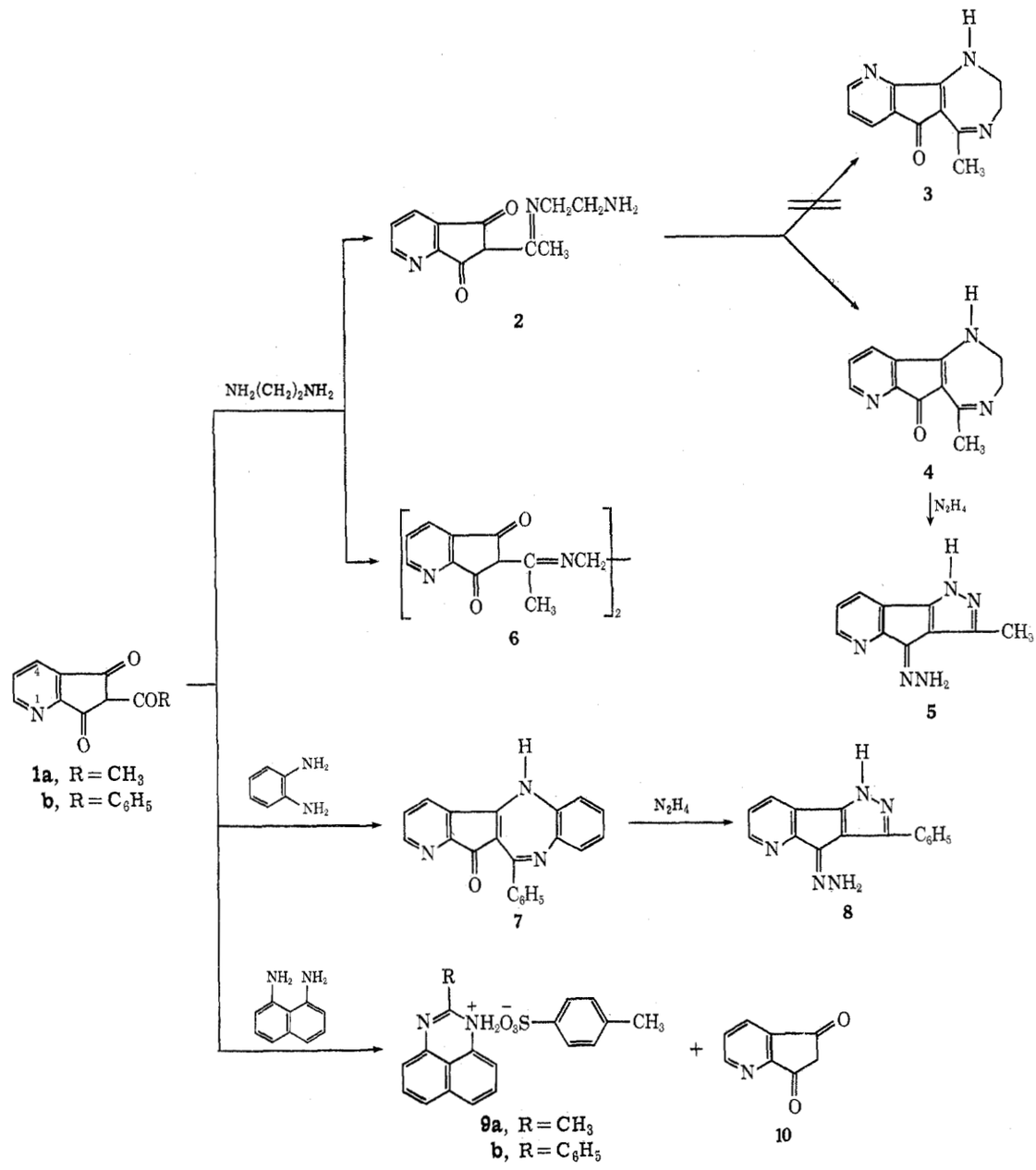
The ring closure of compound **2** to diazepinone **4** is similar to those previously observed in the reactions of 2-acetyl-1,3-indandione with ethylenediamine[2] and of 6-benzoyl-5*H*-1-pyrindine-5,7(6*H*)-dione with hydrazine.[1] Treatment of compound **4** with an excess of hydrazine in ethanolic solution gave the known hydrazone of 3-methylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one (**5**).[1]

Addition of 6-benzoyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1b**) to a refluxing solution of *o*-phenylenediamine in

* Deceased July 23, 1972.

(1) W. A. Mosher, T. El-Zimaity, and D. W. Lipp, *J. Org. Chem.*, **36**, 3890 (1971).

(2) W. A. Mosher and S. Piesch, *ibid.*, **35**, 1026 (1970).



2-propanol and in the presence of formic acid yielded directly 6-phenylbenzo[*b*]pyrido[2′,3′:4,3]cyclopenta-[2,1-*e*][1,4]diazepin-7(12*H*)-one (**7**). As in the above reported ring closure of compound **2** only one isomer was isolated and by analogy structure **7** was assigned. Treatment of compound **7** with excess hydrazine gave the known hydrazone of 3-phenylpyrazolo[3′,4′:3,4]-cyclopenta[1,2-*b*]pyridin-4(1*H*)-one (**8**).[1]

Like the 2-acyl-1,3-indandiones,[3] the acylpyrindinediones **1a** and **1b** reacted with 1,8-naphthalenediamine in the presence of *p*-toluenesulfonic acid to give the known[3] *p*-toluenesulfonates of 2-methyl- and 2-phenylperimidines (**9a** and **9b**), respectively, in good yields. The expected by-product, 5*H*-1-pyrindine-5,7(6*H*)-dione (**10**), was isolated from the reaction mixture. The structure of the new compound **10** is based on elemental analyses and is consistent with the spectral data.

(3) W. A. Mosher and T. E. Banks, *J. Org. Chem.*, **36**, 1477 (1971).

Experimental Section[4]

6-Acetyl- and 6-benzoyl-5*H*-1-pyrindine-5,7-(6*H*)-diones were prepared as described in ref 1 from dimethyl 2,3-pyridinedicarboxylate and the appropriate methyl ketone.

6-[1-(2-Aminoethylimino)ethyl]-5*H*-1-pyrindine-5,7(6*H*)-dione (2).—A solution of 6-acetyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1a**, 1.89 g, 10 mmol) in ethanol (50 ml) was added dropwise over a 2-hr period to a refluxing mixture of formic acid (0.25 ml), ethanol (20 ml), and ethylenediamine (0.90 g, 15 mmol). The mixture was reduced to 1/4th volume *in vacuo*. Water was added (5 ml) with stirring and the mixture was kept at room temperature overnight for complete crystallization. The solid was recrystallized from aqueous ethanol to give 1.36 g (59%) of **2**: mp 245–246°; ir 3340, 3150, 1690 cm^{-1}; mol wt 231 (mass spectrum).

(4) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Ir spectra were recorded on Perkin-Elmer Infracord Models 137 and 237 spectrophotometers, using potassium bromide pellets. Nmr spectra were obtained on a Varian A-60A spectrometer using TMS as an internal standard and solvents as specified. Chemical shifts are reported as δ values (parts per million). Elemental analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium in Max Planck Institute für Kohlenforschung, Mülheim, Germany, and by Micro Analysis Inc., Marshallton, Del.

Anal. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.34; H, 5.63; N, 18.18. Found: C, 62.32; H, 5.70; N, 18.06.

2,3-Dihydro-5-methylpyrido[2′,3′:4,3]cyclopenta[2,1-*e*][1,4]-diazepin-6(1*H*)-one (4).—A solution of **2** (1.15 g, 5 mmol) in 1-propanol (25 ml) and formic acid (1 ml) was heated at reflux for 12 hr. The solution was allowed to stand at room temperature. The formed orange plates of the formic acid salt of the ring-closed compound were treated with dilute NH_4OH in a water–ethanol mixture to yield 0.57 g (52%) of **4** as yellow needles, mp 264–266° (acetone), ir 3300 and 1640 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.61; H, 5.16; N, 19.72. Found: C, 67.58; H, 5.03; N, 19.84.

Reaction of Compound 4 with Ferrous Ammonium Sulfate.—A solution of compound **4** as the formate salt (2.4 g, 10 mmol) in water (5 ml) was added to a solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (1.5 g, 5 mmol) in water. An intense violet colored solution was formed. The dark blue residue obtained after evaporation of the water was crystallized from 1-propanol and dried at 100° in a drying pistol to give a 2:1 complex of pyridocyclopentadiazepinone **4** with ferrous iron, as a blue-violet product of mp 280–281° dec, ir 3300 cm^{-1}. The carbonyl band at 1640 cm^{-1}, observed in compound **4**, was absent.

Anal. Calcd for $C_{24}H_{20}N_6O_2Fe$: C, 59.75; H, 4.56; N, 17.43. Found: C, 59.34; H, 4.40; N, 17.11.

3-Methylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one Hydrazone (5).—A mixture of **4** (1.07 g, 5 mmol), 95% hydrazine (0.5 ml), and ethanol (25 ml) was heated at reflux for 24 hr. The solvent and excess hydrazine were evaporated under reduced pressure and the residue was crystallized from benzene to give 0.81 g (80%) of **5** as yellow crystals of mp 265°, alone and in mixture with an authentic sample synthesized by the literature procedure.[1]

6,6′-[Ethylenebis(nitriloethylidyne)]di-5*H*-1-pyrindine-5,7(6*H*)-dione (6).—A solution of ethylenediamine (0.6 g, 10 mmol) in ethanol (25 ml) was added dropwise to a refluxing solution of 6-acetylpyrindine-5,7-dione (**1a**, 3.80 g, 20 mmol) in ethanol (50 ml) over 1 hr while it stirred. The mixture was refluxed for 12 hr and cooled in an ice bath, and the resulting solid was collected by filtration, washed with cold ethanol, and recrystallized from ethanol to give **6** as yellow crystals (3.9 g, 95%), mp >300°.

Anal. Calcd for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.47; N, 13.93. Found: C, 65.53; H, 4.49; N, 13.77.

6-Phenylbenzo[*b*]pyrido[2′,3′:4,3]cyclopenta[2,1-*e*][1,4]-diazepin-7(12*H*)-one (7).—A solution of 6-benzoyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1b**, 2.7 g, 10 mmol) in 2-propanol (25 ml) was added dropwise over a 1-hr period to a refluxing solution of formic acid (1 ml) and *o*-phenylenediamine (1.5 g, 15 mmol) in 2-propanol (25 ml). The mixture was refluxed for 24 hr and cooled. The dark green solid formed was recrystallized from ethanol to give **7** (47%) as dark green crystals: mp >300°; ir 3300, 1675–1640, 1600 cm^{-1}; mol wt 323 (mass spectrum).

Anal. Calcd for $C_{21}H_{13}N_3O$: C, 78.01; H, 4.01; N, 13.00. Found: C, 77.94; H, 4.00; N, 12.90.

Compound **7** when refluxed with excess hydrazine, as above described for the analogous methyl derivative **4**, gave compound **8**. The identity of this compound with an authentic sample of 3-phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one hydrazone[1] was established by mixture melting point determination and by comparison of the ir spectra.

Reaction of 6-Acyl-5*H*-1-pyrindine-5,7(6*H*)-diones with 1,8-Naphthalenediamine.—To a refluxing solution of 1,8-naphthalenediamine (9.0 g, 5.6 mmol), *p*-toluenesulfonic acid (0.8 g, 4 mmol), and anhydrous 2-propanol (50 ml), was added a solution of **1a** (0.76 g, 4 mmol) in anhydrous 2-propanol (70 ml) over 1 hr. The mixture was heated at reflux for an additional 24 hr, concentrated to 1/4th volume under reduced pressure and cooled. The precipitate was crystallized from 2-propanol to give a 77% yield of **9a**, mp 285–287°, identified by mixture melting point with an authentic sample.[3]

The mother liquor was evaporated to dryness and the residue (0.25 g) was dissolved in chloroform and chromatographed on neutral alumina (elution with chloroform). The compounds isolated from the column in order of elution were 1,8-naphthalenediamine, 5*H*-1-pyrindine-5,7(6*H*)-dione (**10**), and the starting material **1a**. Compound **10** recrystallized from ether–hexane gave yellow crystals: mp 150–151°; nmr ($CDCl_3$) 7.6, 8.0, 8.5 (m, 3 H), 3.2 (s, 2 H).

Anal. Calcd for $C_8H_5NO_2$: C, 65.31; H, 3.40; N, 9.52. Found: C, 65.30; H, 3.48; N, 9.47.

6-Benzoyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1b**) reacted with 1,8-naphthalenediamine as compound **1a** to give a 61% yield of 2-phenylperimidine *p*-toluenesulfonate (**9b**), identified (mixture melting point and ir) with an authentic sample,[3] and the above-cited 5*H*-1-pyrindine-5,7(6*H*)-dione (**10**).

Registry No.—**2**, 35092-40-1; **4**, 35129-61-4; 2:1 **4**–ferrous iron complex, 35085-14-4; **5**, 32111-70-9; **6**, 35092-42-3; **7**, 35092-43-4; **9a**, 28478-03-7; **10**, 35092-45-6.

The Chemistry of Cumulated Double-Bond Compounds. XI. The Reaction of Nitrones with Diphenylcarbodiimide

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The present paper reports a cycloaddition of nitrones to diphenylcarbodiimide, leading to oxadiazolidines. In these reactions, either oxadiazolidine **3** or triazolidinone **4**, which is a rearranged product from the oxadiazolidine **3**, was obtained and an amidine **5** was isolated in some cases. The formation of the amidine **5** may be due to the fragmentation of **3** or **4**. The results of the reactions and the analytical data of the products, **3** and **4**, are given in Tables I and II, respectively.

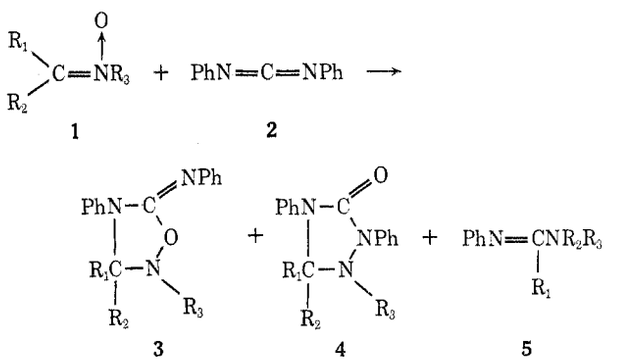

TABLE I

REACTION OF NITRONES WITH DIPHENYLCARBODIIMIDE

Nitrone				Reaction	Yield, %[b]		
Compd	R_1	R_2	R_3	time, hr[a]	**3**	**4**	**5**
1a	Ph	H	*t*-Bu	3	100	0	0
1b	Ph	H	Me	7	64	0	19
1c	Ph	H	Ph	34	0	28	43
1d	$-(CH_2)_5-$		Me	3.5	34	0	0

[a] An equimolar mixture of nitrone and diphenylcarbodiimide was refluxed in benzene under a nitrogen stream until the ir absorption of the N=C=N group disappeared. [b] After chromatography (aluminum oxide–benzene).

The ir spectra of **3a** and **4a** indicated peaks at 1685 and 1715 cm^{-1}, respectively. The former peak was assigned to a C=N stretching vibration and the latter to a C=O stretching vibration. Other spectral data were consistent with structures **3a** and **4a**.