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.

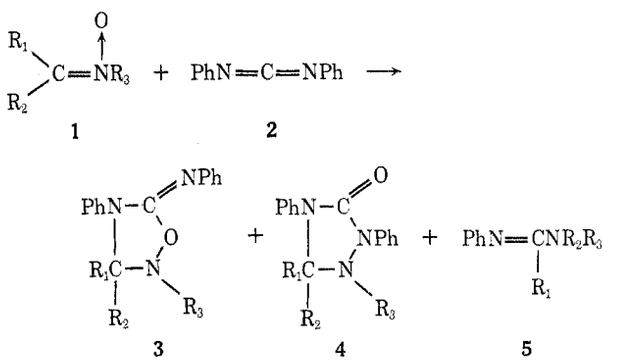


TABLE I

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).

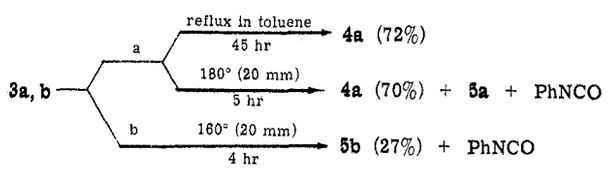
The ir spectra of **3a** and **4a** indicated peaks at 1685 and 1715 cm^{-1}, respectively. The former peak was assigned to a C=N stretching vibration and the latter to a C=O stretching vibration. Other spectral data were consistent with structures **3a** and **4a**.

TABLE II

PROPERTIES OF 3 AND 4[a]

Compd	Mp, °C	Ir (Nujol), cm^{-1}	Nmr ($CDCl_3$), τ	Mass spectrum (70 eV), *m/e*
3a	122–122.5	1685 (C=N)	2.4~3.4 (m, 15, 3 Ph) 4.30 (s, 1, CH) 8.85 (s, 9, *t*-Bu)	371 (M^+) 252 (M^+ − PhNCO) 194 ($PhNCNPh^+$) 180 ($PhN{=}CPh^+$)
3b	108.5–109.5	1675 (C=N)	2.3~3.2 (m, 15, 3 Ph) 4.44 (s, 1, CH) 7.02 (s, 3, CH_3)	329 (M^+) 210 (M^+ − PhNCO) 194 ($PhNCNPh^+$)
3d	115–116	1675 (C=N)	2.5~3.3 (m, 10, 2 Ph) 7.16 (s, 3, CH_3) 7.7~9.1 (m, 10, $(CH_2)_5$)	321 (M^+) 202 (M^+ − PhNCO) 194 ($PhNCNPh^+$)
4a	137–138.5	1715 (C=O)	2.4~3.3 (m, 15, 3 Ph) 4.14 (s, 1, CH) 8.80 (s, 9, *t*-Bu)	371 (M^+) 314 (M^+ − *t*-Bu) 195 (314 − PhNCO)
4c	142–143.5	1710 (C=O)		391 (M^+) 271 (M^+ − PhNCO) 180 ($PhN{=}CPh^+$)

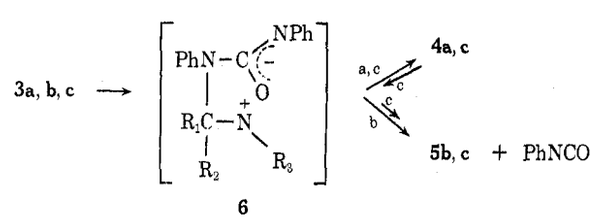
[a] Satisfactory analytical data (±0.2% for C, H, N) are reported for all compounds: Ed.



In the reaction of the nitrone **1a**, the oxadiazolidine **3a** was quantitatively obtained. The compound **3a** underwent thermal rearrangement to **4a** and fragmentation to the amidine **5a** and phenyl isocyanate under severe conditions. Although the reaction of the nitrone **1b** was carried out under mild conditions, the triazolidinone **4b** was not observed, but a considerable amount of the fragmentation product **5b** was isolated. The rearrangement of **3d** to **4d** was not observed under similar conditions. The low yield of **3d** may be ascribed to the hygroscopic property and instability of the nitrone **1d**.

The thermal rearrangement of **3a** to **4a** implies that a triazolidinone **4** is more stable than an oxadiazolidine **3**. The electron-donating ability of substituents, R_3, is considered to be the dominant effect on the stability of **3**. A steric effect of R_3 is inconsistent with the stability order **3a** > **3b** > **3c**.

The rearrangement and fragmentation of **3** can be accounted for by the assumption of the intermediate **6**.



6

Unless the positive nitrogen atom has an effective electron-donating substituent, hydride shift occurs immediately to give amidine **5** and phenyl isocyanate. Therefore, **4b** was not formed. The fact that a large amount of **5c** was obtained in the reaction of **1c** can be accounted for by the reverse reaction, **4c** to **6**, due to the instability of **4c**.

Experimental Section

Materials.—α-Phenyl-*N*-*tert*-butylnitrone (**1a**),[1,2] α-phenyl-*N*-methylnitrone (**1b**),[3] α,*N*-diphenylnitrone (**1c**),[4] and α,α-pentamethylene-*N*-methylnitrone (**1d**)[5] were prepared from 2-*tert*-butyl-3-phenyloxaziridine, benzaldehyde and *N*-methylhydroxylamine, benzaldehyde and *N*-phenylhydroxylamine, and cyclohexanone and *N*-methylhydroxylamine according to the reported procedures, respectively: **1a**, mp 74–75° (lit.[2] mp 75°); **1b**, mp 80–81° (lit.[3] mp 82°;) **1c**, mp 112–113.5° (lit.[4] mp 113–114°); **1d**, bp 101–106° (2 mm) [lit.[5] bp 96° (1 mm)].

Diphenylcarbodiimide was prepared from phenyl isocyanate according to the same procedure as reported previously:[6] bp 170° (7 mm).

Reaction of Nitrone 1a.—A solution of nitrone **1a** (0.026 mol) in benzene (20 ml) was added dropwise to diphenylcarbodiimide (0.026 mol), and the mixture was refluxed under nitrogen stream for 3 hr until the characteristic ir absorption of the N=C=N group (2140 cm^{-1}) disappeared. After the mixture cooled, 9.55 g (100%) of the crude product was filtered off and recrystallized (benzene–hexane) to give pure 2-*tert*-butyl-3,4-diphenyl-5-phenylimino-1,2,4-oxadiazolidine (**3a**), colorless granules.

Reaction of Nitrone 1b.—The reaction between 0.033 mol of nitrone **1b** and 0.033 mol of diphenylcarbodiimide was carried out by the same procedure as above. After refluxing for 7 hr, the reaction mixture was chromatographed (aluminum oxide–benzene) to give 7.0 g (64%) of 2-methyl-3,4-diphenyl-5-phenylimino-1,2,4-oxadiazolidine (**3b**), 1.3 g (19%) of N^1-methyl-N^2-phenylbenzamidine (**5b**), and 0.9 g of *N*,*N*′-diphenylurea.

Oxadiazolidine **3b** was recrystallized (benzene–hexane), colorless needles.

Amidine **5b** was recrystallized (benzene–hexane): colorless needles; mp 136.5–138°; ir (Nujol mull) 3240 (NH), 1605 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* 210 (M^+, calcd 210), 180 (M^+ − $NHCH_3$), 133 (M^+ − Ph).

The ir spectrum of *N*,*N*′-diphenylurea was identical with that of an authentic sample.

Reaction of Nitrone 1c.—The reaction between 0.025 mol of nitrone **1c** and 0.025 mol of diphenylcarbodiimide was carried out by the same procedure as above. Ir spectra indicated the formation of product **4c** in the initial course of the reaction which slowly increased. After refluxing for 34 hr, the reaction mixture was chromatographed (aluminum oxide–benzene) to

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give 2.7 g (28%) of 1,2,3,4-tetraphenyl-1,2,4-triazolidin-5-one (**4c**), 2.9 g (43%) of *N,N'*-diphenylbenzamidine (**5c**), and 2.8 g of *N,N'*-diphenylurea.

Triazolidinone **4c** was recrystallized (benzene–hexane), colorless needles.

Amidine **5c** was recrystallized (EtOH) to give colorless needles, whose spectral data and melting point were identical with those of the authentic sample:[7] mmp 148.5–149.5°.

Reaction of Nitrone 1d.—Nitrone **1d** (0.088 mol) and diphenylcarbodiimide (0.084 mol) were treated by the same procedure as above to give 9.1 g (34%) of 2-methyl-3,3-pentamethylene-4-phenyl-5-phenylimino-1,2,4-oxadiazolidine (**3d**). Compound **3d** was recrystallized (petroleum ether), colorless plates.

Thermal Treatment of Oxadiazolidine 3a. A.—A solution of oxadiazolidine **3a** (0.50 g) in toluene (20 ml) was refluxed for 45 hr. The ir spectrum of the solution indicated that almost all of **3a** had changed. The solvent was removed and then the residue was chromatographed (aluminum oxide–benzene) to give 0.36 g (72%) of 2-*tert*-butyl-1,3,4-triphenyl-1,2,4-triazolidin-5-one (**4a**), which was recrystallized (benzene–hexane) to afford colorless granules.

B.—Oxadiazolidine **3a** (1.0 g) was heated at 180° for 5 hr under reduced pressure (20 mm), and a small amount of phenyl isocyanate was trapped (−70°). The residue was chromatographed (aluminum oxide–benzene) to give 0.70 g (70%) of triazolidinone **4a** and a small amount of N^1-*tert*-butyl-N^2-phenylbenzamidine (**5a**): ir (Nujol mull) 3420 (NH), 1622 cm^{-1} (C=N). The oxadiazolidine was not recovered.

Thermal Treatment of Oxadiazoldine 3b.—Employing the same procedure as above, 0.60 g of **3b** was heated at 160° for 4 hr (20 mm). Phenyl isocyanate (0.11 g, 52%) was trapped and the residue was chromatographed (aluminum oxide–benzene) to give 0.10 g (27%) of amidine **5b**. Compounds **3b** and **4b** were not obtained.

Registry No.—**3a**, 35105-50-1; **3b**, 35105-51-2; **3d**, 35105-52-3; **4a**, 35105-53-4; **4c**, 35105-54-5; **5b**, 2397-29-7; diphenylcarbodiimide, 622-16-2.

Acknowledgment.—The authors thank Mr. Tetsuya Taguchi and Mr. Akio Baba for their help in the experiments.

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3-Oxo-5-cyanopentanamide. A Novel β-Keto Amide from *meso*-Butadiene Diepoxide

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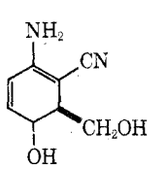
In 1964 Johnson and Heeschen[1] reported the isolation of compound I from the reaction of unbuffered sodium cyanide solution (pH 11.5–12.5) with epichlorohydrin. More recently Moppett, Johnson, and Dix[2] reported the analogous reaction of 2-methylepichlorohydrin which led to an entirely different structural type, namely compound II.



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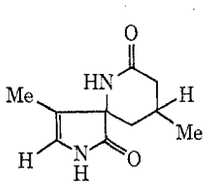
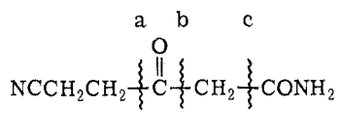


II

In continuation of these studies we now find that *meso*-butadiene diepoxide (III) on treatment with potassium cyanide in the presence of magnesium sulfate (pH ~9.5) leads to 3-oxo-5-cyanopentanamide (IV), and not *meso*-1,4-dicyano-2,3-dihydroxybutane (V). Under conditions of high pH IV not unexpectedly undergoes further transformation, and, when the reaction is conducted in the absence of magnesium sulfate (pH 11.5–12.5), little or none of the β-keto amide IV is obtained.

3-Oxo-5-cyanopentanamide (IV) is a water-soluble, white crystalline solid whose ir spectrum displayed characteristic bands at 3400 and 3170 (NH), 2245 (CN), 1720 (C=O), and 1650 ($CONH_2$) cm^{-1}. It gives with ferric chloride solution an intense violet coloration diagnostic for a β-dicarbonyl system. The nmr spectrum of IV possesses two diffuse singlets at δ 7.0 (one NH proton) and 7.4 (one NH proton) which are readily exchanged with deuterium oxide. The remaining six protons are present as a complex multiplet in the region of δ 2.2–3.2.

The most prominent peaks of the mass spectrum of IV arise from α cleavages. Cleavage at a, b, and c



IV

leads to the ions $C_3H_4NO_2$, C_4H_4NO, and C_5H_6NO, respectively. The parent ion and the fragment $C_3H_4NO_2$ eliminate ammonia.

Oxidation of IV by treatment with concentrated nitric acid followed by methylation of the acidic crystalline residue with diazomethane led to dimethyl oxalate and dimethyl succinate. Base-catalyzed hydrolysis of IV gave succinic acid, further identified as its dimethyl ester. The sodium salt of IV was generated by the use of dimsyl sodium.[3] On treatment with *meta*-chlorobenzyl bromide it afforded the mono-*meta*-chlorobenzyl derivative (VI) and the bis(*meta*-chlorobenzyl) derivative (VII).

We propose the reaction sequence of Scheme I for the mechansim of transformation of *meso*-butadiene diepoxide (III) into 3-oxo-5-cyanopentanamide (IV). The first step of our proposed scheme embraces nucleophilic substitution by cyanide ion on the primary carbon atoms of III leading us to V, whereupon interaction of one of the secondary hydroxyl groupings with a nitrile moiety (1,3 relationship) affords the cyclic intermediate VIII. Base-catalyzed rearrangement of VIII in the fashion indicated by Scheme I would then generate IX or X depending on which of its two diastereotopic protons are abstracted by base. The latter now has available to it by a series of conventional steps a mechanism for passage into IV by virtue of the cis relationship of its secondary hydroxyl and nitrile groupings.

We were able to isolate from the mother liquors from the crystallization of IV a crystalline compound which we formulate as *trans*-3-hydroxy-5-cyanopent-4-enamide (IX). Its nmr spectrum is uniquely consistent

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