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.

(7) A. C. Hontz, and E. C. Wagner, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1955, p 258.

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

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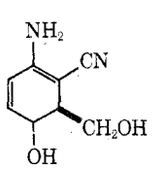
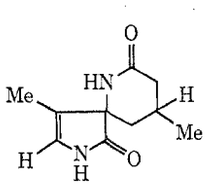
Received March 31, 1972

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.



I

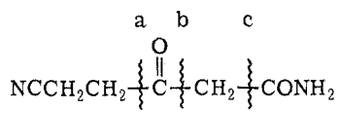


II

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.

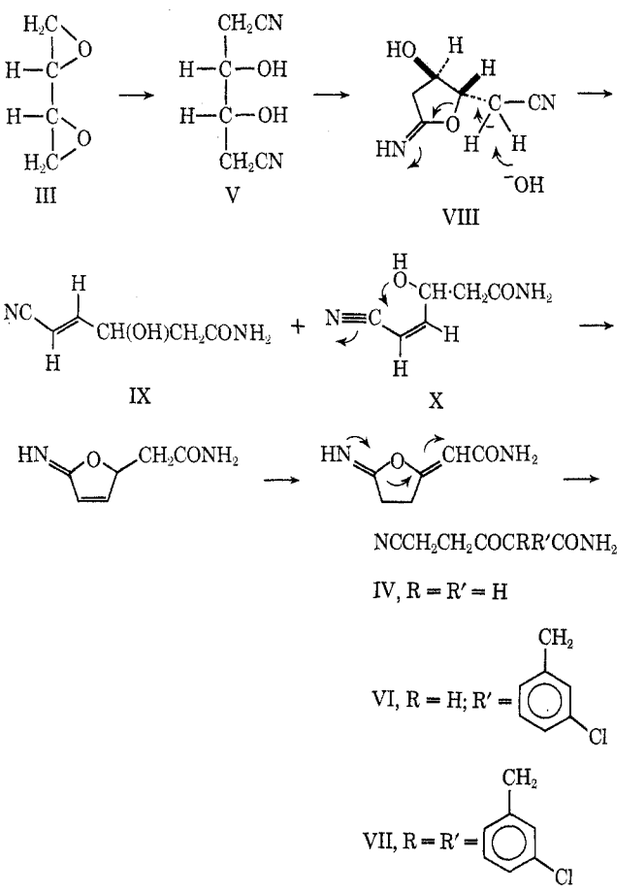
We were able to isolate from the mother liquors from the crystallization of IV a crystalline compound which we formulate as *trans*-3-hydroxy-5-cyanopent-4-enamide (IX). Its nmr spectrum is uniquely consistent

(1) F. Johnson and J. P. Heeschen, *J. Org. Chem.*, **29**, 3252 (1964).

(2) C. E. Moppett, F. Johnson, and D. T. Dix, *Chem. Commun.*, 1560 (1971).

(3) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

SCHEME I



with the assigned structure. The trans stereochemistry follows quite clearly from the magnitude of the couplings constants for the vinylic protons at C-4 (δ 6.8, doublet of doublets, J = 16 and 3.5 Hz) and C-5 (5.7, doublet of doublets, J = 16 and 1.5 Hz). The downfield position of the proton at C-4 reflects the deshielding characteristics[4,5] of the cyano grouping at C-5. The additional 3.5-Hz coupling for this proton arises from its spin-spin interaction with the proton at C-3. There are three exchangeable protons at δ 5.4, 6.8, and 7.3, respectively, and a two-proton doublet at 2.28 attributable to the methylene grouping at C-2, and the single proton at C-3 appears as a multiplet at 4.45.

We were unable to bring about the transformation of IX into V under the conditions of the reaction. Our inability to bring about this change is consistent with the mechanism outlined in Scheme I for the formation of IV and IX from *meso*-butadiene diepoxide (III) and cyanide ion.

Experimental Section

Melting points were taken on an Arthur H. Thomas hot stage apparatus and are uncorrected. Nmr spectra were taken at ambient temperature (31.5°) on a Varian A-56-60 spectrometer. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Ir spectra were taken as Nujol mulls on a Perkin-Elmer Model 337 spectrometer. Mass spectra were obtained on a CEC 21-110B mass spectrometer. Samples were admitted *via* a direct insertion probe at ion source temperatures of ~200°. Metastable transitions were determined by the defocussing technique. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Denmark.

3-Oxo-5-cyanopentanamide (IV).—To an ice-cooled, vigorously stirred solution of 28 g (0.4 mol) of potassium cyanide and 48 g (0.4 mol) of magnesium sulfate in 150 ml of water was added dropwise over 30 min 17.2 g (0.2 mol) of *meso*-butadiene diepoxide. The reaction mixture was allowed to come to room temperature and then left to stand for 18 hr. Continuous extraction with ethyl acetate gave a gummy residue which on tritration with ethanol afforded 5.9 g (21%) of IV: mp 76–77°[6] (from ethanol); ir 3400, 3170, 2245, 1720, 1650 cm^{-1}; nmr (DMSO-d_6) δ 2.2–3.2 (m, 6), 7.0 (br s, NH), and 7.4 (br s, NH); high-resolution mass measurements [empirical formula, experimental (calculated)], $C_6H_8N_2O_2$, 140.0619 (140.0585), $C_6H_6NO_2$, 123.0336 (123.0320), C_3H_6NO, 96.0447 (96.0449), $C_3H_4NO_2$, 86.0250 (86.0242), C_4H_4NO, 82.0298 (82.0293), C_3HO_2, 68.9953 (68.9977); metastables $140^+ \rightarrow 96^+ + 44$, $140^+ \rightarrow 86^+ + 54$, $86^+ \rightarrow 69^+ + 17$.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.45; H, 5.76; N, 20.01. Found: C, 51.40; H, 5.87; N, 19.77.

It proved possible to isolate from the mother liquors from the crystallization of IV by chromatography on silica gel *trans*-3-hydroxy-5-cyanopent-4-enamide (IX) (12%): mp 122–123° (from methanol); ir 3500–2400 (NH and OH), 2230 (C≡N), 1670 ($CONH_2$), 1630 (C=C) cm^{-1}; nmr (DMSO-d_6) δ 2.28 (d, 2, J = 6 Hz, C-2), 4.45 (m, 1, C-3), 5.4 (s, 1), 5.7 (dd, 1, J = 16.0 and 1.5 Hz, C-5), 6.8 (dd, 1, J = 16.0 and 3.5 Hz, C-4), 6.8 (s, 1), and 7.3 (s, 1); high-resolution mass measurements [empirical formula, experimental (calculated)], $C_6H_8N_2O_2$, 140.0558 (140.0585); C_5H_6NO, 96.0440 (96.0449), $C_3H_6NO_2$ 88.0393, (88.0397); metastable $140^+ \rightarrow 96^+ + 44$.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.45; H, 5.76; N, 20.01. Found: C, 51.37; H, 5.82; N, 20.17.

Nitric Acid Oxidation of IV.—3-Oxo-5-cyanopentanamide (IV, 77 mg) and 1 ml of concentrated nitric acid were heated on the steam bath for 1 hr—vigorous evolution of brown fumes. The reaction mixture was evaporated *in vacuo* and the white, crystalline residue was treated with a small volume of water. This too was removed *in vacuo* and this procedure was repeated. A methanolic solution of the above was treated with an excess of an ethereal solution of diazomethane. Evaporation of the organic solvents left dimethyl oxalate and dimethyl succinate—identified by gas–liquid chromatography on a Hewlett-Packard 5750 instrument.[7]

Base-Catalyzed Hydrolysis of IV.—3-Oxo-5-cyanopentanamide (IV, 100 mg) and 5 ml of 25% aqueous potassium hydroxide were heated under reflux overnight—strong smell of ammonia. After cooling to room temperature the reaction mixture was acidified with concentrated hydrochloric acid and continuously extracted with ether to give succinic acid, mp 189–190°, mmp 189–190°.

A small portion was methylated with an ethereal solution of diazomethane to yield dimethyl succinate—identified by comparison with an authentic sample.

2-*meta*-Chlorobenzyl-3-oxo-5-cyanopentanamide (VI) and 2,2-Bis(*meta*-chlorobenzyl)-3-oxo-5-cyanopentanamide (VII).—A solution of 140 mg (0.001 mol) of IV in 2 ml of dimethyl sulfoxide (distilled from calcium hydride) was added to a vigorously stirred, ice-cold solution of dimsyl sodium (0.002 mol)—generated[8] from 94 mg (0.002 mol, 51.3% dispersion) of sodium hydride and 3 ml of dimethyl sulfoxide. After ~30 min a solution of 388 mg (0.002 mol) of *meta*-chlorobenzylbromide in 2 ml of dimethyl sulfoxide was added and the reaction mixture was left to stir overnight at room temperature.

Dilution with water was followed by extraction with methylene chloride to give after removal of the organic solvents *in vacuo* 381 mg of a gummy residue.

Examination of the latter by tlc (silica gel PF_{254}, 90:10% v/v CH_2Cl_2–MeOH) indicated the presence of two compounds which were successfully separated by preparative tlc (two 20 × 20 cm plates, silica gel PF_{254}, 95:5% v/v CH_2Cl_2–MeOH, two elutions).

(4) G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961).

(5) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

(6) When first obtained this compound had mp 67–68°. All subsequent preparations, however, gave only the form of mp 76–77°. The two forms which were separately characterized had identical ir (in solution) and mass spectra and identical tlc behavior. The two forms had mmp 76–77°.

(7) Both dimethyl succinate and dimethyl oxalate were identified by comparison with authentic samples. Separation was achieved on an Hewlett-Packard 5750 instrument, injector 370°, detector 360°, column 150°, flow 85 ml/min. The column was 12 ft, 0.25 in., 10% QF-1 on 60/80 Chromosorb W.

The upper band afforded 144 mg of VII: mp 128–130° (from ethanol); ir 3400, 2250, 1710, 1690, and 1670 cm^{-1}; nmr ($CDCl_3$) δ 2.2–3.0 (m, 4), 3.19 (s, 2), 3.32 (s, 2), 6.7–7.3 (m, 8), and the two exchangeable NH protons; mass spectrum m/e 388 (M^+ $C_{20}H_{18}{}^{35}Cl_2N_2O_2$).

Anal. Calcd for $C_{20}H_{18}Cl_2N_2O_2$: C, 61.72; H, 4.66; Cl, 18.22; N, 7.20. Found: C, 61.51; H, 4.75; Cl, 18.36; N, 7.14.

From the lower band there was obtained 74 mg of VI: mp 121° (from ethanol); ir 3475, 3370, 2250, 1710, 1660, and 1605 cm^{-1}; mass spectrum m/e 264 (M^+ $C_{13}H_{13}{}^{35}ClN_2O_2$).

Anal. Calcd for $C_{13}H_{13}ClN_2O_2$: C, 58.99; H, 4.95; Cl, 13.4; N, 10.59. Found: C, 58.86; H, 4.98; Cl, 13.25; N, 10.52.

Registry No.—III, 564-00-1; IV, 35159-06-9; VI, 35159-07-0; VII, 35159-08-1; IX, 35159-09-2.

Acknowledgment.—We thank Dr. L. Shadoff for the high-resolution mass spectral measurements and Dr. F. Johnson and Mr. A. A. Carlson for the initial isolation of IX.

Synthesis and Reactivity of Adamantane-1-carbonitrile *N*-Oxide

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Received March 10, 1972

The functionalization of adamantane has received considerable attention in recent years and several 1-substituted and some 2-substituted derivatives have been prepared.[1] Although most of the available data pertains to the unusual properties of adamantanes in polar and free-radical reactions involving the bridged ring system,[1,2] considerable interest on the internal reactivity of functional groups linked to the adamantyl moiety has arisen.[3]

We wish to report the first preparation of an adamantylfulmide and to describe some typical reactions at the CNO function in this compound. The present work enlarges the number of adamantane derivatives and provides information on the reactions of nitrile oxides[4] in general. We are currently investigating the chemistry of nitrile oxides.[5]

Adamantane-1-carbonitrile *N*-oxide (**1**) was prepared in good yield from adamantane-1-carboxaldehyde oxime (**1a**) and *N*-bromosuccinimide as outlined by Grundmann[6] for other nitrile oxides. Nitrile oxide **1** was practically unchanged after several days at room temperature, but in carbon tetrachloride solution at 50° it readily dimerized to di[adamantyl-(1)]furazan *N*-oxide (**2**) (*ca.* 80% yield). The structure of **2** is supported by the mass spectrum. Compound **2** gives the parent peak at m/e 354 (M^+) and on electron impact behaves in the characteristic manner[7] of furazan *N*-oxides, giving $(M - O)^+$, $(M - N_2O_2)^+$, $(AdCN)^+$, and $(AdCNO)^+$ as the major fragments ions. The peaks at m/e 338, corresponding to the loss of one oxygen, and at m/e 294, from the loss of N_2O_2, and the absence of absorption corresponding to $(AdCO)^+$ at m/e 163 are compatible only with the furoxan structure **2** and rule out other possible five- or six-membered isomers.

When heated at reflux in carbon tetrachloride, nitrile oxide **1** yielded, in addition to dimer **2**, the isomer 1-adamantylisocyanate (**3**) in variable amounts depending on the time of heating. Typically, after 8 hr of reflux **3** was only present in small amounts with respect to furoxan **2**, but, when heating was prolonged to 10 days, the ratio **2**:**3** was *ca.* 1:2. In the latter experiment, the infrared spectrum of the reaction mixture, taken at intervals, showed that, after the complete disappearance of the 2285- (CN) and 1335-cm^{-1} (NO) bands[8] of **1**, the absorption of the NCO group[9] at 2255 cm^{-1} gradually increased. These facts suggest that on prolonged heating the isocyanate **3** was the major reaction product because a part of it could possibly form from the furazan *N*-oxide **2** *via* a retrocycloaddition to **1** (Scheme I). The formation of isocyanate **3** and trapping of the transient nitrile oxide **1** by cycloaddition with styrene from a sample of **2** heated at reflux in carbon tetrachloride indicate that this possibility is real. Therefore, in spite of the initial formation of **2**, the isomerization of **1** to **3** can still occur directly *via* the mechanism outlined by Grundmann and Kochs.[10] However, it must be noted that an alternative route from the furazan *N*-oxide **2**, in equilibrium with the nitrile oxide **1**, is also conceivable.[11]

(1) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); *Advan. Alicycl. Chem.*, **1**, 283 (1966).

(2) Recent references include Z. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 5731 (1970); I. Tabushi, Z. Yoshida, and N. Takahashi, *ibid.*, **92**, 6670 (1970); C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970); J. K. Chakrabarti and A. Todd, *Chem. Commun.*, 556 (1971); M. O. Luke and J. G. Atkinson, *Tetrahedron Lett.*, 117 (1971).

(3) J. Strating, A. H. Alberts, and H. Wynberg, *Chem. Commun.*, 818 (1970); J. Scharp, H. Wynberg, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 18, 23 (1970); W. V. Curran and R. B. Angier, *J. Org. Chem.*, **34**, 3668 (1969); A. Kreutzberger and H.-H. Schroders, *Tetrahedron Lett.*, 4921 (1970); H. Stetter and E. Smulders, *Chem. Ber.*, **104**, 917 (1971).

(4) Reviews: (a) C. Grundmann, *Synthesis*, 344 (1970); (b) A. Quilico, *Chim. Ind. (Milan)*, **53**, 157 (1971); (c) C. Grundmann and P. Grünanger, "The Nitrile Oxides," Springer-Verlag, Berlin, Heidelberg, New York, 1971.

(5) G. Barbaro, A. Battaglia, and A. Dondoni, *J. Chem. Soc. B*, 588 (1970); A. Battaglia, A. Dondoni, and A. Mangini, *ibid.*, 554 (1971); A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, *ibid.*, 2096 (1971).

(6) C. Grundmann and R. Richter, *J. Org. Chem.*, **33**, 476 (1968).

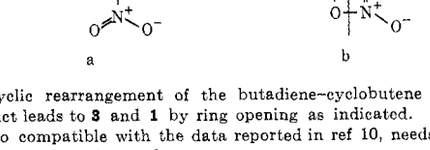
(7) (a) C. Grundmann, H.-D. Frommeld, K. Flory, and S. K. Datta, *ibid.*, **33**, 1464 (1968); (b) A. J. Boulton, P. Hadjimihalakis, A. R. Katritzky, and A. Majid Hamid, *J. Chem. Soc. C*, 1901 (1969).

(8) A. Battaglia, A. Dondoni, G. Galloni, and S. Ghersetti, *Spectrosc. Lett.*, **3**, 207 (1970).

(9) W. H. T. Davidson, *J. Chem. Soc.*, 3712 (1953). For the reliability of the 2290- and 2255-cm^{-1} bands to distinguish nitrile oxides from isocyanates, see also R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

(10) C. Grundmann and P. Kochs, *Angew. Chem., Int. Ed. Engl.*, **9**, 635 (1970).

(11) A referee has drawn our attention to a variant of Scheme I, *i.e.*, **1** $\leftrightarrows$ **2** $\rightarrow$ **3** + **1**. The ring opening of **2** can take place *via* initial migration of the adamantyl group onto the imino nitrogen to give the open-chain intermediate **a** which in turn forms the four-membered ring compound **b** by



a **b**

an electrocyclic rearrangement of the butadiene–cyclobutene type. The latter product leads to **3** and **1** by ring opening as indicated. This route, which is also compatible with the data reported in ref 10, needs to be considered in a more extensive study.