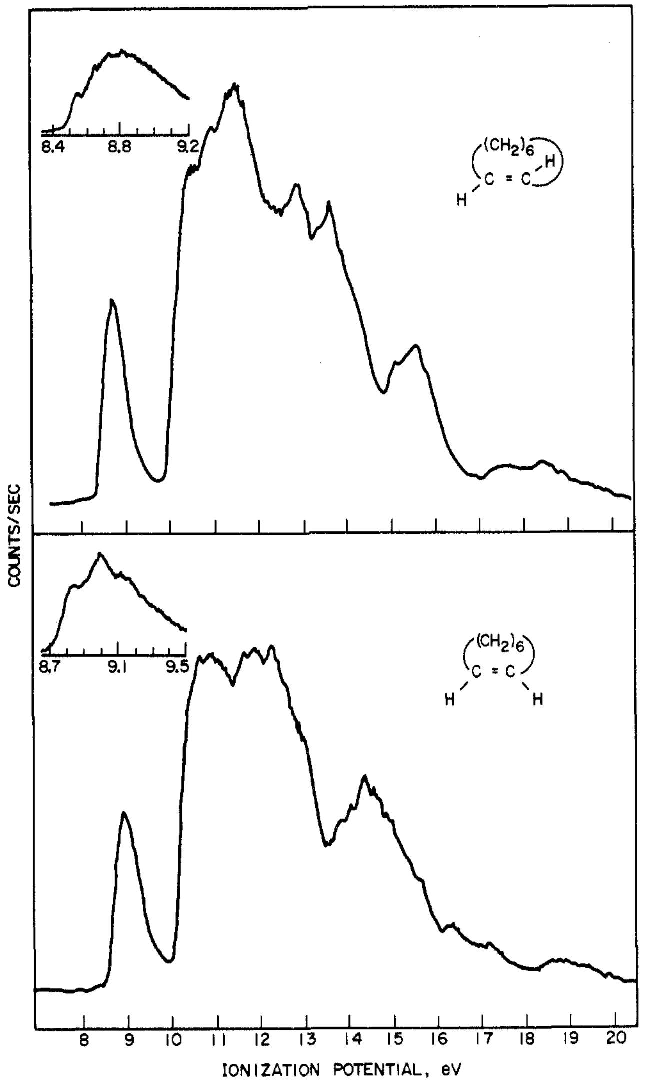

Figure 3.—He(I) photoelectron spectra of *cis*- and *trans*-cyclooctene.

(Figure 3, insert). The ionization potential of the trans isomer is 0.29 eV lower than that of the cis as measured by the positions of the (0,0) bands, and *ca.* 0.2 eV lower as measured by the approximate positions of the band maxima. Using the Mulliken diagram for ethylene and assuming that the 0.29 eV lowering of the trans ionization potential is due solely to twisting, we get a twist angle of 20 ± 3°, which is within the range of previous estimates for this quantity. This result is also in good agreement with the results of a force field calculation[3] in which the angle β between the π atomic orbitals is calculated to be 16.3°.

The present study demonstrates that the strain energies of *cis*-di-*tert*-butylethylene (10.5 kcal/mol)[14] and of *trans*-cyclooctene (9.2 kcal/mol)[15] are not necessarily indicators of the nonplanarity of these olefins. Consequently, any such structural assignments based solely on strain energies are suspect. The conclusions derived from these simple experiments must now be confirmed by more sophisticated measurements. If they are confirmed, and we think they will be, then medium resolution photoelectron spectroscopy will have been shown to be of unsuspected value in the gas phase structure determination of sterically crowded molecules such as olefins, dienes, biphenyls, etc.[16]

Registry No.—*trans*-2-Butene, 624-64-6; *cis*-2-butene, 590-18-1; *trans*-perfluorobutene-2, 1516-64-9; *cis*-perfluorobutene-2, 1516-65-0; *trans*-di-*tert*-butylethylene, 692-48-8; *cis*-di-*tert*-butylethylene, 692-47-7; *trans*-cyclooctene, 22770-27-0; *cis*-cyclooctene, 931-87-3.

Acknowledgment.—It is a pleasure to thank Professors S. H. Bauer, T. T. Tidwell, and L. S. Bartell for several of the samples used in this study.

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[14] J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).

[15] R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

[16] Note Added in Proof.—Professor Bauer has recently informed us that the electron diffraction work of his group on the fluorinated olefins in many cases yielded incorrect structures due to convergence to false minima. In *cis*-perfluorobutene-2, the revised dihedral angle is now quoted as equal to or less than 6°, in agreement with the photoelectron spectra. (S. H. Bauer Third Biannual Conference on Molecular Structure, Austin, Tex., Feb 1972).

2-Imino-4-methyleneoxazolidines from the Reaction of Propargyl Alcohols and Carbodiimides

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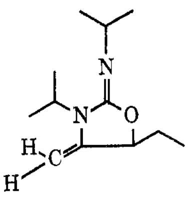
Received July 21, 1972

The formation of pseudoureas from the reaction of alcohols and carbodiimides, catalyzed by cuprous or cupric chloride, is well known.[1] Allyl alcohol and diisopropylcarbodiimide give *O*-allyl-*N*,*N'*-diisopropylpseudourea;[2] an analogous reaction of propargyl alcohol has not been reported. In the course of some earlier studies of propargyl alcohols, we investigated their reaction with carbodiimides.

The reaction of ethylethinylcarbinol with diisopropylcarbodiimide in the presence of cuprous chloride was slightly exothermic. Distillation gave a product which could be assigned structure **1** based on the spectral data. The presence of a terminal methylene group in the nmr spectrum (see Table I) and lack of an NH or C≡CH moiety in infrared or nmr spectra excludes several possible structures which could be written *a priori* except **1** and **2**. The intense uv absorption maximum at 238 mμ, a pK_a of 9.4, and the ability to form salts lend support to structure **1**, 2-isopropylimino-3-isopropyl-4-methylene-5-ethyloxazolidine.



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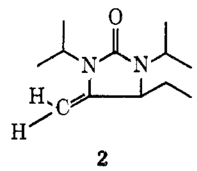

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This facile reaction had thus provided a new entry into the iminooxazolidine class of compounds. Previous syntheses of iminooxazolidines and their deriva-

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[1] F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, **67**, 107 (1967).

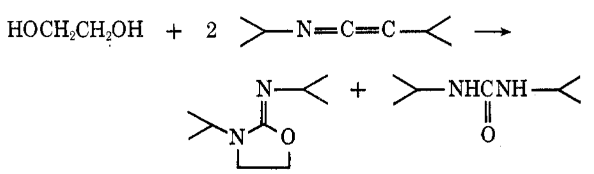
[2] E. Schmidt, E. Däbritz, K. Thulke, and E. Grassmann, *Justus Liebigs Ann. Chem.*, **686**, 161 (1965).

TABLE I

PHYSICAL DATA OF IMINOOXAZOLINE DERIVATIVES **7a–h**[g]

Oxazolidine	R	R_1	R_2	R_3	Mp,[a] °C	Yield, %	ν_{max}, cm^{-1}	λ_{max}, mμ (ϵ)	Nmr, δ, ppm
7a (1)	$(CH_3)_2CH$	H	H	Et	*b*	33	1700, 1660	238 (13,250) 288 (3410)	0.88, (3 H, t, J = 6.5 Hz), 1.03 (6 H, d, J = 6.5 Hz), 1.27 (6 H, d, J = 6.5 Hz), 1.4–1.95 (2 H, m), 3.63 (1 H, t, J = 2 Hz), 3.79 (1 H, septet, J = 6.5 Hz), 3.93 (1 H, t, J = 2 Hz), 4.27 (1 H, septet, J = 6.5 Hz), and 4.68 (1 H, m)
7b (*Z*)	$(CH_3)_2CH$	Ph	H	H	74–76	36.8	1720, 1670	225 (13,500) 284 (15,300)	1.07 (6 H, d, J = 6.5 Hz), 1.29 (6, H, d, J = 6.5 Hz), 3.77 (2 H, m), 4.72 (2 H, d), 5.21 (1 H, t), and 7.20 (5 H, broad singlet)
7c (*E*)	$(CH_3)_2CH$	H	Ph	H	43–44	50[c]	1710, 1645	224 (10,500) 289 (30,500)	1.07 (6 H, d, J = 6 Hz), 1.41 (6 H, d, J = 7 Hz), 3.76 (1 H, septet, J = 7 Hz), 4.52 (1 H, septet, J = 7 Hz), 4.96 (2 H, d, J = 2 Hz), 5.61 (1 H, t, J = 2 Hz), 6.9–7.4 (5 H, m)
7d (*E*)	C_6H_{11}	H	Ph	H	115–116	38.7[d]	1705, 1650	224 (10,750) 291 (32,250)	1.0–2.58 (20 H), 3.3–3.6 (1 H, m), 3.7–4.1 (1 H, m), 5.0 (2 H, d, J = 2 Hz), 5.64 (1 H, t, J = 1 Hz), 6.9–7.4 (5 H, m)
7e (*E*)	$(CH_3)_2CH$	H	*p*-C_6H_4Cl	H	66	63.2[e]	1715, 1650	256 (10,000) 299 (34,000)	1.07 (6 H, d, J = 6.5 Hz), 1.42 (6 H, d, J = 7 Hz), 3.78 (1 H, m J = 6.5 Hz), 4.42 (1 H, m, J = 7 Hz), 4.94 (2 H, d, J = 1 Hz), 5.56 (1 H, t, J = 2 Hz), 6.37 and 7.21 (4 H, A_2B_2 pattern)
7f (*E*)	C_6H_{11}	H	*p*-C_6H_4Cl	H	121–122	35[f]	1715, 1650	225 (10,200) 297 (34,300)	1.2–2.6 (20 H), 3.43 (1 H, m), 4.97 (2 H, d, J = 2 Hz), 6.92 and 7.25 (4 H, A_2B_2 pattern)
7g (*Z*)	$(CH_3)_2CH$	*p*-C_6H_4Br	H	H	88–89	41	1700, 1640	228 (16,000) 295 (16,400)	1.06 (6 H, d, J = 6.5 Hz), 1.30 (6 H, d, J = 6.5 Hz), 3.74 (2 H, 7 lines, J = 6.5 Hz), 4.71 (2 H, d, J = 2 Hz), 5.10 (1 H, broad singlet), 7.05 and 7.37 (4 H, A_2B_2 pattern)
7h (*E*)	$(CH_3)_2CH$	H	*p*-C_6H_4OMe	H	83–84	35	1710, 1660	225 (13,200) 280 (16,800)	1.10 (6 H, d, J = 7.0 Hz), 1.44 (6 H, d, J = 7.0 Hz), 3.76 (1 H, 7 lines, J = 7.0 Hz), 3.76 (3 H, s), 4.46 (1 H, m), 4.96 (2 H, d, J = 2 Hz), 5.61 (1 H, t, J = 2 Hz), 6.88–6.92 (4 H, m)

[a] The crystalline products were recrystallized from pentane. [b] Boiling point 46–48° (0.33 mm). [c] From distillation of **7b** at 125° (0.25 mm). [d] From heating the corresponding *Z* isomer at 90° for 1 hr. [e] From heating the mixture of *E* and *Z* isomers at 80° for 1 hr [f] From heating the mixture of *E* and *Z* isomers at 125° for 1.5 hr. [g] Satisfactory microanalyses were obtained for all of the compounds.



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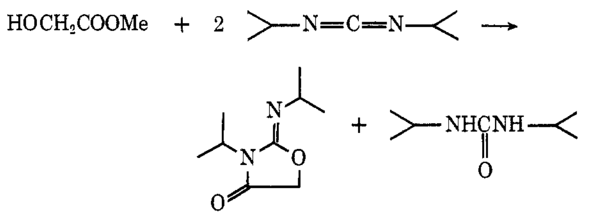

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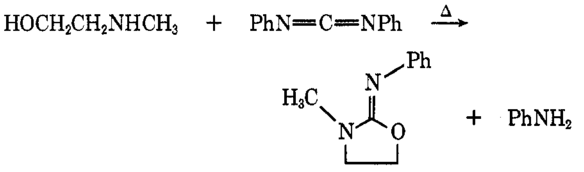

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(3)

tives include the reaction of 2 mol of a carbodiimide and 1 mol of a diol[2] (eq 1), the formation of 2-isopropylimino-3-isopropyloxazolidone-4 (isoelectronic with the basic ring structure of **1**) from 2 mol of diisopropylcarbodiimide and 1 mol of the methyl ester of glycolic acid[3] (eq 2), and the formation of 2-phenylimino-3-methyloxazolidine (**3**) from *N*-methyl-2-hydroxyethylamine and diphenylcarbodiimide[4] (eq 3) or from reaction of the amino alcohol with phenyl isocyanide dichloride.[5] Thermal cyclization of acetylenic ureas has been reported[6] to give 5-methylene-2-iminooxazolidines of the

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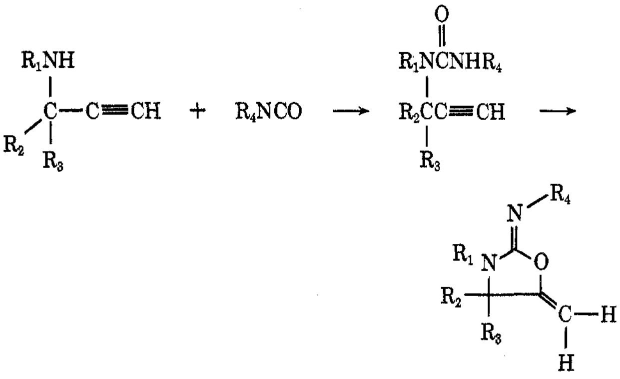
(3) E. Schmidt and W. Carl, *Justus Liebigs Ann. Chem.*, **639**, 24 (1961).

(4) B. Adcock, A. Lawson, and D. H. Miles, *J. Chem. Soc.*, 5120 (1961).

(5) (a) Belgian Patent 632,578 to Farbenfabriken Bayer A. G., May 20, 1963; (b) E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **8**, 20 (1969).

(6) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **29**, 1851 (1964).

general structure **4**, and iminooxazolidine **6** was obtained by allowing the urea **5** to rearrange in ethanol solution.[7]



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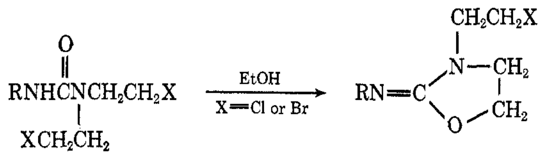
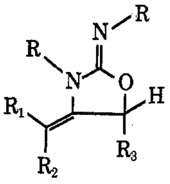


5 **6**

The present reaction provides an entry to the hitherto unknown 2-imino-4-methyleneoxazolidines by a method which permits introduction of a variety of substituents. Several compounds (**7a–h**) analogous to **1**



7a–h

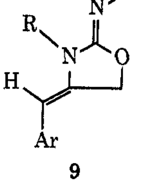
have been prepared and their physical data are given in Table I.

In the reaction of aryl propargyl alcohols of the type **8** with a carbodiimide, two geometrical isomers (*E* and

$ArC{\equiv}CCH_2OH$

8

Z, **9** and **10**, respectively) about the double bond are possible. Pronounced shifts were noted in the nmr and ultraviolet spectra of the isomers **9** and **10**. The first-formed compound **10** undergoes isomerization to the more thermodynamically stable **9**, with relief of the steric crowding between the Ar and R groups of **10**. Thus, the ultraviolet spectra of compounds of the type **9**, in which coplanarity of the entire conjugated system can be achieved, exhibit longer wavelength, higher intensity maxima than those of structure **10**. The shifts to lower field in the nmr signals of **9** are consistent with this change in geometry.



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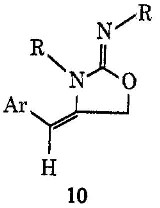
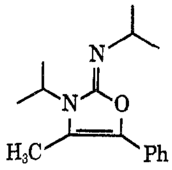


10

The reaction of α-phenylpropargyl alcohol and diisopropylcarbodiimide afforded **11**, an iminooxazoline, in which the double bond had undergone isomerization into the ring.



11

Experimental Section

General.—Melting points were taken on a Kofler hot stage and are uncorrected; boiling points are uncorrected. Infrared spectra were recorded on Beckman Model IR-9 or Perkin-Elmer Models 621 or 337 spectrophotometers; ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Nmr spectra were measured on a Varian Associates HA-100 or A-60 spectrometer or a Jeolco C60H instrument using tetramethylsilane as internal standard. Spectra and analyses were determined by our Physical Chemistry Department.

N,N'-Diisopropyl- and dicyclohexylcarbodiimide and ethylethynylcarbinol were purchased from Aldrich Chemical Co. and were redistilled prior to use. 3-Phenyl-2-propyn-1-ol was purchased from Farchan Research Laboratories; α-phenylpropargyl alcohol was obtained from K & K Laboratories. 3-*p*-Chloro- and 3-*p*-methoxyphenyl-2-propyn-1-ol[8] were prepared from the corresponding aryl acetylenes[9] according to known procedures.[10,11]

Procedure for Compounds 7a–h.—Freshly distilled acetylenic alcohol (0.05 mol) and 0.05 mol of carbodiimide were stirred with 50 mg of cuprous chloride overnight or longer if necessary for completion of the reaction. The product was distilled or recrystallized from the appropriate solvent. Physical data for compounds 7a–h are given in Table I.

3-*p*-Bromophenyl-2-propyn-1-ol.—*p*-Bromophenylacetylene (1.4 g, 7.75 mmol), prepared according to the known procedure[9] from *p*-bromoacetophenone, was treated with equivalent amounts of butyllithium and dry paraformaldehyde as previously described.[11] Upon sublimation, the crude product (72%) afforded colorless crystals, which upon recrystallization from *n*-pentane had mp 68–69°; ν_{max}^{KBr} 3320–3200, 2225, 1480, 1070, 1020, 1010, 950, and 820 cm^{-1}; λ_{max}^{EtOH} 248 mμ (ε 25,080), 258 (23,050), 278 (1160), and 285 (610); nmr ($CDCl_3$) δ 1.52 (OH, broad), 4.43 (2 H, s) and 7.2–7.5 (4 H, m).

Anal. Calcd for C_9H_7BrO: C, 51.32; H, 3.34; Br, 37.61. Found: C, 51.22; H, 3.14; Br, 37.58.

2-Isopropylimino-3-isopropyl-4-methyl-5-phenyloxazoline (11).—A mixture of 6.6 g of α-phenylpropargyl alcohol, 6.3 g of diisopropylcarbodiimide, and 50 mg of cuprous chloride was heated at 70–80° under nitrogen for 4 days. Distillation at 105–109° (0.025 mm) afforded 27.5% yield of oxazoline **11**: $\nu_{max}^{CHCl_3}$ 1680 and 1655 cm^{-1}; λ_{max}^{EtOH} 221 mμ (ε 13,100) and 312 (12,800); pK_a 10.5; nmr ($CDCl_3$) δ 1.15 (6 H, d, J = 7 Hz), 1.41 (6 H, d, J = 7 Hz), 2.25 (3 H, s), 3.87 (1 H, 7 lines, J = 7 Hz), 4.39 (1 H, 7 lines, J = 7 Hz), and 7.2–7.5 (5 H, m).

Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.42; H, 8.52; N, 10.85. Found: C, 73.89; H, 8.49; N, 10.9.

Registry No.—**7a,** 37614-50-9; **7b,** 37681-83-7; **7c,** 37614-51-0; **7d,** 37614-52-1; **7e,** 37614-53-2; **7f,** 37614-54-3; **7g,** 37614-55-4; **7h,** 37614-56-5; **8b,** 1504-

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[7] G. R. Pettit, D. S. Blonda, and R. A. Upham, *Can. J. Chem.*, **43**, 1798 (1965).

[8] F. Bohlmann, R. Enkelmann, and W. Plettner, *Chem. Ber.*, **97**, 2118 (1964).

[9] I. Iwai and Y. Yura, *Takamine Kenkyusho Nempo*, **10**, 30 (1958); *Chem. Abstr.*, **55**, 4400*d* (1961).

[10] H. Gilman and W. E. Catlin, "Organic Syntheses," Collect. Vol. 1, Wiley, New York, N. Y., 1958, p 188.

[11] A. Schaap, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **84**, 1200 (1965).

58-1; **8e,** 37614-57-6; **8g,** 37614-58-7; **8b,** 37614-59-8; **11,** 37614-60-1; dicyclohexylcarbodiimide, 538-75-0; diisopropylcarbodiimide, 693-13-0; *p*-bromophenylacetylene, 766-96-1; α-phenylpropargyl alcohol, 4187-87-5; propargyl alcohol, 107-19-7

Furazans and Furazan Oxides. III.[1] Acenaphtho[1,2-*c*]furazan

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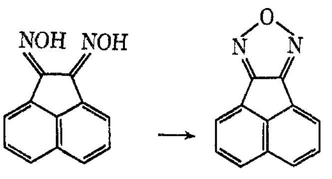
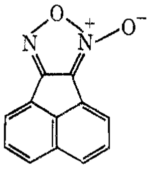
School of Chemical Sciences, University of East Anglia, Norwich, Norfolk, England

Received October 2, 1972

Some years ago, Boyer pointed out[2a] that very few representative furazans and furazan oxides fused to five-membered rings were known, and he also reported[2b] an unsuccessful attempt to prepare the title compound (**1**). Since that date, the number of strained furazan oxides known has increased,[3] but the only strained furazan has remained the rather doubtful example of Ingold and Shoppee.[4] Phosphite deoxygenation of acenaphtho[1,2-*c*]furazan oxide (**2**) has been found to occur under mild conditions, to form 1,8-dicyanonaphthalene (**3**), through the postulated intermediate furazan (**1**).[3] We now report the preparation of **1**, and some of its properties.



4 **1**



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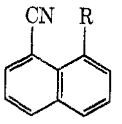
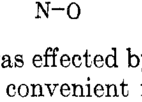


3, R = CN

5, R = CNO

6, R = 

Dehydration of the dioxime **4** was effected by thionyl chloride in methylene chloride, a convenient modification of the method of Tokura, *et al.*,[5] who used sulfur dioxide as solvent. The product **1** was indefinitely stable at room temperature, but slowly decomposed to the nitrile oxide **5** on warming. The decomposition was followed by infrared, at 72° in toluene, and the appearance of two bands was observed, at 2285 (s, CNO) and 2210 cm^{-1} (m, CN). The nitrile oxide band reached a maximum after about 30 min, and then slowly decreased in intensity, falling to about 80% of its maximum after 2 hr. We were unable to isolate the expected furazan oxide dimer of **5**, after prolonged heating, and it is probable that other modes of polymerization had occurred, the product being oily and dark red in color.

The nitrile oxide **5** was not isolated in pure form, but brief (2–3 min) heating of the furazan **1** to 125° gave a product shown by infrared spectroscopy to contain largely the oxide. A number of stable 1-naphthonitrile oxides are known,[6a] although the examples quoted by Grundmann and Grünanger all have a 2 substituent.

The furazan **1** with phenylacetylene gave the adduct **6**, and with trimethyl phosphite formed 1,8-naphthalonitrile (**3**). These results tend to confirm the proposed scheme[3] for the phosphite deoxygenation of strained furazan oxides of type **2**, in that the furazan is now shown to ring open to the dinitrile monoxide under the conditions of the experiment. The finding that the reaction of the furazan oxide **2** with phosphite is rate dependent on phosphite concentration led us to attempt to prepare **1** from **2** using a high concentration of phosphite at temperatures at which **1** is stable. We did indeed isolate the furazan, but in poor yield.[6b]

A recent note[7] has reported that, under more forcing conditions (reflux in tri*phenyl* phosphite), even unstrained furazan oxides can be deoxygenated, with ring cleavage, to nitriles. We have found that 4,5,6,7-tetrahydrobenzofurazan and its oxide are slowly converted into adiponitrile on prolonged reflux in triethyl phosphite.[8] We also observe that the acenaphthofurazan oxide (**2**) is unchanged on heating alone to temperatures 20–30° higher than those at which the furazan **1** is converted into the dinitrile monoxide **5**. We suggest that this apparent greater thermal lability of the furazans, compared with their *N*-oxides, is a result of the greater thermodynamic stability of the nitrile group, compared with the nitrile oxide.[9] The lower energy of formation of the product of ring opening of the furazan oxide, compared with the furazan, is reflected in a slightly increased energy of activation for the ring opening. We have, however, been unable to trap any products of addition of phenylacetylene to 1,8-naphthalonitrile dioxide, which is expected to be formed by this ring opening, although the furazan oxide does decompose spontaneously at temperatures of 100° and above.

Experimental Section

Melting points are corrected. Nmr spectra are of $CDCl_3$ solutions, measured on a Perkin-Elmer R12 60-MHz instrument.

Acenaphtho[1,2-*c*]furazan (1). A.—Acenaphthoquinone dioxime[10] (5.0 g, 0.024 mol) was finely powdered and suspended in dry dichloromethane (20 ml). Thionyl chloride (3.1 g, 0.025 mol) was added, and the mixture was stirred at 20° for 24 hr. It was poured onto ice and extracted with dichloromethane (3 × 25 ml). The extracts were dried ($MgSO_4$) and the solvent was

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[1] Part II: J. Ackrell and A. J. Boulton, *J. Chem. Soc., Perkin Trans. 1,* in press.

[2] J. H. Boyer in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., Wiley, New York and London, 1961, Chapter 6: (a) pp 466, 471; (b) p 508.

[3] J. Ackrell, M. Altaf-ur-Rahman, A. J. Boulton, and R. C. Brown, *J. Chem. Soc., Perkin Trans. 1,* 1587 (1972).

[4] C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.,* **125,** 365 (1928).

[5] N. Tokura, R. Tada, and K. Yokoyama, *Bull. Chem. Soc. Jap.,* **24,** 270 (1961).

[6] (a) C. Grundmann and P. Grünanger, "The Nitrile Oxides", Springer-Verlag, West Berlin and Heidelberg, 1971. (b) The deoxygenation of furazan oxides to furazans by trialkyl phosphites has been observed: C. Grundmann, *Chem. Ber.,* **97,** 575 (1964).

[7] S. M. Katzman and J. Moffat, *J. Org. Chem.,* **37,** 1842 (1972).

[8] A. J. Boulton and S. S. Mathur, unpublished work (1971).

[9] Since we have been unable to locate any references to thermochemical data on nitrile oxides, this must remain an assertion unsupported by other than intuition.

[10] F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.,* **117,** 1344 (1920).