none in 50 ml of THF was saturated with NH_3 and stirred overnight at room temperature. The yield of the resulting red precipitate **27**, which turned yellow on drying, was 4.5 g (98%), mp 152–153° [2,5-di-*tert*-butylquinone (**27**) mp 152.5°]. The only other product in this reaction was *o*-quinonedioxime (**25**) which was identified by tlc.

The Reaction of *o*-Aminophenol and Benzofurazan 1-Oxide.—To a solution of 5.0 g (0.045 mol) of *o*-aminophenol and 2.4 g (0.045 mol) of NaOMe in 5.0 ml of MeOH was added 6.1 g (0.045 mol) of benzofurazan 1-oxide. After stirring at room temperature for 2.5 hr, 2.7 g (0.045 mol) of AcOH was added and the resulting slurry was filtered to give 3.0 g (62%) of 2-amino-3*H*-phenoxazin-3-one (**28**) which melted after recrystallization at 254–255°.

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.9; H, 3.78; N, 13.2. Found: C, 67.79; H, 3.85; N, 13.45.

The addition of H_2O to the filtrate resulted in the isolation of 5.0 g (82%) of *o*-quinonedioxime (**25**) which was identified by tlc and a mixture melting point test.

2-Phenozinol 5,10-Dioxide (**1**).—A solution of 0.9 g (0.0065 mol) of *o*-quinonedioxime (**25**) and 0.7 g (0.0065 mol) of *p*-quinone in 10 ml of THF after standing overnight at room temperature was filtered to give 0.5 g (34%) of a red solid which was identical in every respect with an authentic sample of 2-phenazinol 5,10-dioxide (**1**).

5-Hydroxybenzo[*a*]phenazinol 7,12-Dioxide (**14**).—A solution of 1.0 g (0.0063 mol) of 1,4-naphthoquinone and 0.88 g (0.0063 mol) of *o*-quinonedioxime (**25**) in 20 ml of THF was allowed to stand at room temperature for 1 day. Filtration gave 0.050 g (3%) of a red solid, mp 230–235°. The filtrate was allowed to sit for 2 more days and filtered again to give 0.45 g (25.6%), mp 233–235°. Finally the filtrate was allowed to stand 7 more days the solution was filtered again to give 0.7 g (40%) of a brown solid, mp 236–238°.

The three solids were combined and recrystallized from AcOH–trifluoroacetic acid to give 1.0 g of **14** (57%) which melted at 242° dec. This compound was identical in every respect with an authentic sample.

Registry No.—**1**, 303-80-0; **2**, 32839-15-9; **3**, 32839-16-0; **4**, 26390-70-5; **5**, 24890-65-1; **6**, 25629-71-4; **7**, 32846-85-8; **8**, 26390-41-0; **8** dimethoxy derivative, 32866-02-7; **9**, 25629-68-9; **10**, 303-78-6; **11**, 25629-70-3; **11** diacetate, 32861-63-5; **12**, 25629-67-8; **13**, 25629-69-0; **14**, 26390-71-6; **15**, 18636-88-9; **16**, 32861-68-0; **17**, 32861-69-1; **18**, 32861-70-4; **19**, 25629-73-6; **20**, 32861-72-6; **21**, 32861-73-7; **22**, 243-59-4; **24**, 882-33-7; **27**, 2460-77-7; **28**, 1916-59-2.

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Phenylfurazan Oxide. Chemistry

JOSEPH V. BURAKEVICH,* ROBERT S. BUTLER, AND GERT P. VOLPP

Central Research Department, FMC Corporation, Princeton, New Jersey 08540

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The facile stepwise transformation of 4-phenylfurazan 2-oxide (**1**) under a variety of conditions into α-hydroxyimino-*anti*-phenylacetonitrile oxide (**2a**), α-hydroxyiminophenylacethydroxamic acid (**3**), and 3-phenyl-1,2,4-oxadiazol-5-one (**7**), as proposed in the early literature, has been confirmed. Comparison samples of compounds **3** and **7** were synthesized by independent routes. The same α-hydroxyiminophenylacethydroximoyl chloride (**6**) was obtained by the addition of hydrogen chloride to the nitrile oxide **2a**, by chlorination of *anti*-phenyl-*amphi*-glyoxime (**5**), and by reaction of α-ketophenylacethydroximoyl chloride (**9**) with hydroxylamine hydrochloride; dehydrohalogenation of this yielded the nitrile oxide isomer opposite to **2a**. 4-Phenylfurazan 2-oxide could not be methylated by methyl iodide nor by dimethyl sulfate. No reaction occurred when 4-phenylfurazan 2-oxide was irradiated with uv light. A 1:1 adduct of 4-phenylfurazan 2-oxide (or of α-hydroxyimino-*anti*-phenylacetonitrile oxide) with mesityl oxide was isolated.

4-Phenylfurazan 2-oxide (**1**) is a compound with a long history and most investigations of it preceded the arrival of instrumental techniques. In our investigation of this area of chemistry, we have shown that three isomers of phenylglyoxime, *anti*-phenyl-*amphi*-glyoxime, phenyl-*anti*-glyoxime, and phenyl-*syn*-glyoxime are present in the conventional synthesis of this precursor to phenylfurazan oxide.[1] Further, oxidation of each isomer by dinitrogen tetroxide yielded only 4-phenylfurazan 2-oxide (**1**).[2] These results contrasted with the conclusions of previous investigators who described the oxidations of only two isomers into two different phenylfurazan oxides, 3-phenylfurazan 2-oxide and 4-phenylfurazan 2-oxide.[3] In view of these discrepancies between our results and those of former researchers and considering the interesting rearrangements described for phenylfurazan oxide,[4] a reexamination of 4-phenylfurazan 2-oxide chemistry, using modern instrumentation, appeared justified.

It had been reported that phenylfurazan oxide will rearrange into α-hydroxyiminophenylacetonitrile oxide (**2**) completely in base or to the extent of 2–5% in solvents such as benzene or ether.[4,5] We have found that most handlings of 4-phenylfurazan 2-oxide result in significant or complete rearrangement into α-hydroxyimino-*anti*-phenylacetonitrile oxide (**2a**). Thus dissolution of **1** in some solvents, *e.g.*, acetone, alcohol–water, contact with alumina or treatment with a basic buffer, or heating with activated charcoal have all caused this rearrangement. This transformation was not observed when 4-phenylfurazan 2-oxide was dissolved in chloroform, *m*-xylene, or in solvents acidified with hydrogen chloride. The conversion was readily monitored by infrared spectral measurement, by observing the appearance of the strong nitrile oxide absorbance at 2288 cm^{-1} and the disappearance of the strong double bond absorbance associated with the furazan oxide ring at 1610 cm^{-1}. In the very early literature, the product from the rearrangement of phenylfurazan oxide in base was incorrectly described

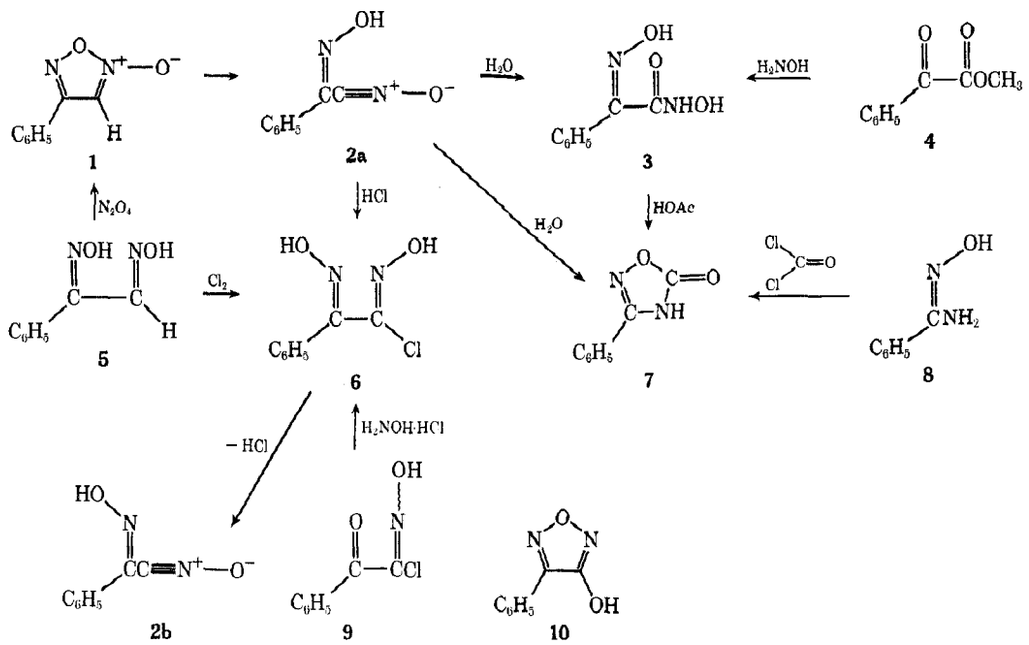
(1) J. V. Burakevich, A. M. Lore, and G. P. Volpp, *J. Org. Chem.*, **36**, 1 (1971).

(2) J. V. Burakevich, A. M. Lore, and G. P. Volpp, *ibid.*, **36**, 5 (1971).

(3) For a discussion and references, see the publications cited in footnotes 1 and 2.

(4) For reviews, see J. H. Boyer in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley & Sons, New York, N. Y., 1961, pp 499–503; L. C. Behr in "The Chemistry of Heterocyclic Compounds, Five- and Six-Membered Compounds with Nitrogen and Oxygen," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1962, pp 287, 298.

(5) (a) G. Ponzio, *Gazz. Chim. Ital.*, **66**, 127 (1936); (b) G. Ponzio, *ibid.*, **66**, 119 (1936).



as 3-hydroxy-4-phenylfurazan (**10**);[4] infrared spectral measurement leaves no doubt as to the correctness of the nitrile oxide structure. Solid α-hydroxyimino-*anti*-phenylacetonitrile oxide (**2a**) was unstable at room temperature and decomposed into a complex mixture on standing. It could be stored at low temperature.

Solutions of **2a** in the presence of moisture yielded mixtures of α-hydroxyiminophenylacethydroxamic acid (**3**) and 3-phenyl-1,2,4-oxadiazol-5-one (**7**) as proposed;[4,5b] acetic acid catalyzes the reaction. Both structures were confirmed by comparison of physical constants with samples obtained by independent syntheses. Compound **3** was synthesized from methyl phenylglyoxylate (**4**) and hydroxylamine in base[6] and compound **7** was synthesized from benzamidoxime (**8**) and phosgene. Product **7** can arise from **3** by a Lossen rearrangement with internal cyclization and this conversion has been effected by acetic acid, alone or in the presence of acetic anhydride to aid in dehydration. Since the oxadiazolone **7** is isomeric with the nitrile oxide **2a**, only a trace of water is required for the transformation of **2a** into **7** through the hydroxamic acid **3**; thus, it is often encountered in various handlings and on storage of the furazan oxide **1**. The characteristic ir band at 1764 cm^{-1} signals its presence. Alternatively, the heterocycle **7** can be formed directly from **2a** by rearrangement of the nitrile oxide function into an isocyanate followed by cyclization.[7]

Configuration **2a** was assigned to the isomer resulting from the rearrangement of 4-phenylfurazan 2-oxide on the basis of the following experiments. The same α-hydroxyiminophenylacethydroximoyl chloride (**6**) was obtained by the addition of hydrogen chloride to the nitrile oxide **2a**,[5a] by chlorination of *anti*-phenyl-*amphi*-glyoxime (**5**) and by reaction of α-ketophenylacethydroximoyl chloride (**9**) with hydroxylamine hydrochloride. The hydrogen chloride introduced or produced during these reactions caused isomerization to the *anti*-glyoxime structure as indicated by the formation of a red nickelous complex.[1,8] Dehydrohalogenation of **6** under basic, neutral, or acidic conditions did not yield the original nitrile oxide **2a** but an isomer which dimerized spontaneously when the isolation of a solid product was attempted, in contrast to the easily obtainable solid **2a**. Since sterically unhindered nitrile oxides readily dimerize to furazan oxides and sterically hindered nitrile oxides can be isolated as solids with indefinite stability,[7] the solid nitrile oxide rearrangement product of 4-phenylfurazan 2-oxide must have configuration **2a**.

Unchanged 4-phenylfurazan 2-oxide was isolated from methylation attempts by refluxing it in neat methyl iodide and from neat dimethyl sulfate treatment at 100°. No reactions were observed when a solution of 4-phenylfurazan 2-oxide in ether was treated with hydrogen chloride or when irradiated with ultraviolet light.

After long standing, a solution of 4-phenylfurazan 2-oxide in mesityl oxide yielded a 1:1 adduct between solvent and solute. Presumably this product arises from slow decomposition of the 4-phenylfurazan 2-oxide into the nitrile oxide **2a** which then adds to the double bond in a 1,3-dipolar addition reaction characteristic of nitrile oxides.[7]

Experimental Section[9]

4-Phenylfurazan 2-Oxide (**1**).—This compound was obtained by oxidation of phenylglyoxime with dinitrogen tetroxide as previously described.[2] 4-Phenylfurazan 2-oxide has the fol-

(6) "Beilstein's Handbuch der Organischen Chemie," 4th ed, Vol. X, 2nd suppl, F. Richter, Ed., Springer Verlag, Berlin, 1949, pp 458–460.

(7) C. Grundmann, *Fortschr. Chem. Forsch.*, **7**, 62 (1966); C. Grundmann in "Methoden der Organischen Chemie (Houben-Weyl)," Vol. X/3, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, pp 841–870; C. Grundmann and P. Kochs, *Angew. Chem., Int. Ed. Engl.*, **9**, 635 (1970), C. Grundmann and S. K. Datta, *J. Org. Chem.*, **34**, 2016 (1969); A. Quilico, *Experientia*, **26**, 1169 (1970).

(8) L. L. Meritt, Jr., *Anal. Chem.*, **25**, 718 (1953); L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953); R. C. Voter, C. V. Banks, V. A. Fassel, and P. W. Kehres, *Anal. Chem.*, **23**, 1730 (1951).

(9) The melting points were determined with a Mettler FP1 melting point apparatus equipped with a Bausch and Lomb VOM 5 recorder except where noted. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. A Varian A-60 spectrometer was used to obtain the nmr spectra and tetramethylsilane was used as the internal standard. The mass spectra were determined on a Consolidated Electrodynamics Corporation Model 21-103C spectrometer.

lowing physical properties: mp 108–110°; ir ($CHCl_3$) 3165 (w), 1610 (s), 1603 (m), 1471 (w), 1451 (m), 1399 (m), 1182 (w), 1000 (w), 985 (w), and 935 cm^{-1} (w); nmr ($CDCl_3$) δ 7.26 (s, 1, –CH=N) and 7.60 ppm (m, 5, phenyl); mass spectrum (70 eV) *m/e* (rel intensity) 162 (15), 146 (6), 145 (2), 132 (14), 103 (44), 102 (100).

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.41; H, 4.01; N, 17.02.

α-Hydroxyimino-*anti*-phenylacetonitrile Oxide (2a).—A solution of 300 mg of 4-phenylfurazan 2-oxide (1) in 50 ml of chloroform was stirred at room temperature for 17 hr with 50 ml of a pH 8.0 buffer solution (Fisher Catalog No. SO-B-112, monobasic potassium phosphate–sodium hydroxide). The chloroform layer was removed and was washed twice with distilled water. The chloroform solution was dried azeotropically by first passing it through phase-separating paper (Whatman 1 PS) followed by removal of the solvent on a rotary evaporator. The crystalline residue was washed with a small amount of benzene. Recrystallization was accomplished by adding petroleum ether (bp 30–60°) to a chloroform solution of the nitrile oxide at room temperature to about the cloud point followed by slow cooling to below 0°. The crystals were collected by filtration and were washed with chloroform–petroleum ether (bp 30–60°): yield 63 mg; mp 101–102° dec (lit.[5a] mp 112–113° dec); ir ($CHCl_3$) 3584 (oxime –OH) and 2288 cm^{-1} ($C{\equiv}N^+{-}O^-$); nmr ($CDCl_3$) δ 8.56 (s, 1, –OH) and 7.22–8.00 ppm (m, 5, phenyl); mass spectrum (70 eV) *m/e* (rel intensity) 162 (42), 132 (38), 115 (12), 103 (38), 102 (100), 77 (28). The nitrile oxide can be stored for three months at −25° with practically no decomposition. During the same period at room temperature, a sample showed massive decomposition (11 spots on tlc) with a prominent carbonyl absorption at 1739 cm^{-1}.

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.26; H, 3.96; N, 17.15.

Comparison of the furazan oxide absorption at 1610 cm^{-1} *vs.* the nitrile oxide absorption at 2288 cm^{-1} was used to observe the conversion of the furazan oxide 1 into the nitrile oxide **2a** in many varied handlings of 4-phenylfurazan 2-oxide. In the present work, this conversion has been observed upon simple dissolution of the heterocycle 1 in acetone or ethanol–water, and by treatment with activated carbon, alumina, or silica gel G.[4,5] Concentration can make a difference; for example, the transformation of 1 into **2a** proceeds rapidly in dilute solutions in acetone but not in concentrated solutions. The furazan oxide can be recovered unchanged from solutions in chloroform, *m*-xylene, ethanol, and organic solvents acidified with hydrogen chloride gas. Infrared monitoring must be employed during any experimentation with 4-phenylfurazan 2-oxide.

α-Hydroxyiminophenylacethydroxamic Acid (3) and 3-Phenyl-1,2,4-oxadiazol-5-one (7) from α-Hydroxyimino-*anti*-phenylacetonitrile Oxide (2a).—A 10-g sample of α-hydroxyimino-*anti*-phenylacetonitrile oxide (**2a**) (synthesized by dissolution of 4-phenylfurazan 2-oxide in acetone followed by evaporation of the solvent) was refluxed for 1 hr in 200 ml of acetic acid. The addition of 600 ml of water caused a precipitate to form which was discarded after filtration. The evaporation of the filtrate to dryness yielded a mixture of **3** and **7**. Since the hydroxamic acid **3** is chloroform insoluble, chloroform was used to extract the oxadiazolone **7** from the mixture.

The solid residue left after the chloroform extraction (1.2 g) required several recrystallizations before an analytically pure sample was obtained even though the infrared spectrum of the crude product was virtually superimposable upon that of the pure sample. Water, ethyl acetate–petroleum ether (bp 30–60°), and ethyl acetate–chloroform were used as the recrystallization solvents. The analytically pure α-hydroxyiminophenylacethydroxamic acid (**3**) melted at 173.5–175.5° (lit.[5] mp 187–188°) and its ir spectrum was superimposable upon that of a sample synthesized from methyl phenylglyoxylate (see below): ir (KBr) 3311 (s), 1650 (s), 1616 (m), 1513 (w), 1418 (s), 1305 (w), 1008 (s), 858 (m), 716 (m), and 689 cm^{-1} (m).

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.17; H, 4.64; N, 15.21.

The chloroform was evaporated from the extraction solution leaving a residue (3.0 g) whose ir spectrum showed it to be mainly the oxadiazolone **7**. Several recrystallizations from water were required to obtain an analytically pure sample of 3-phenyl-1,2,4-oxadiazol-5-one (**7**) whose ir spectrum was superimposable upon that of a sample of the compound obtained from benzamidoxime and phosgene (see below). The analytically pure sample (1.3 g) melted at 203–205° (lit.[5] mp 202–203°) and no depression in melting point was observed in a 1:1 mixture of the product and that from benzamidoxime and phosgene: ir ($CHCl_3$) 3125 (w), 1764 (s), 1616 (w), 1567 (w), 1464 (w), 997 (w), 953 (m), and 893 cm^{-1} (w).

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.47; H, 4.02; N, 17.15.

3-Phenyl-1,2,4-oxadiazol-5-one (7) from α-Hydroxyiminophenylacethydroxamic Acid (3).—A mixture of 200 mg of α-hydroxyiminophenylacethydroxamic acid, 113 mg of acetic anhydride, and 10 ml of acetic acid was refluxed for 1 hr. The solvent was then removed under reduced pressure and the infrared spectrum of the residue showed a strong carbamate band at 1773 cm^{-1} and the disappearance of the bands associated with the hydroxamic acid. Several recrystallizations, first from water and then from chloroform–petroleum ether (bp 30–60°), were required to raise the melting point to 202–203.5° (capillary, oil bath). The product gave the same ir spectrum as that described above for this compound.

α-Hydroxyiminophenylacethydroxamic Acid (3) from Methyl Phenylglyoxylate (4).[6]—A solution of 10.2 g of potassium hydroxide in 25 ml of methanol at 40° was added to a solution of 8.5 g of hydroxylamine hydrochloride in 44 ml of methanol also at 40°. The resulting mixture was cooled to 0° and 5 g of methyl phenylglyoxylate was added and the mixture was filtered immediately. The filtrate was allowed to stand for four days whereupon it was acidified by a solution of 2 ml of acetic acid in 16 ml of water. The mixture was heated until a clear solution resulted. The product was extracted with ether and the ether was evaporated to give a residue which yielded 1.4 g of crystals upon trituration with chloroform. Recrystallization from water yielded analytically pure α-hydroxyiminophenylacethydroxamic acid: mp 173.5–175.5°; ir, same as described above for this compound; nmr (DMSO-d_6) δ 7.15–7.80 (m, 5, phenyl), 9.12 (s, 1, –NH), 11.04 (s, 1, –OH), and 11.80 ppm (s, 1, –OH).

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.33; H, 4.48. Found: C, 53.41; H, 4.65.

3-Phenyl-1,2,4-oxadiazol-5-one (7) from Benzamidoxime (8) and Phosgene.—A solution of 2 g of benzamidoxime[10] and 4 g of triethylamine in 180 ml of benzene was cooled to 5° while phosgene was passed in until about 20 ml was collected. The mixture was allowed to stand in an unstoppered flask for 40 hr and was then washed with 100 ml of water. The water wash was then extracted with benzene. The combined benzene solutions were dried over magnesium sulfate. Evaporation of the solvent left a residue (1.2 g) whose ir spectrum was virtually the same as that of the pure compound but for a small amount of a nitrile impurity. Several recrystallizations from water and chloroform–petroleum ether (bp 30–60°) yielded analytically pure material: mp 203.5–205.5°; ir the same as that described for the compound above.

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.09; H, 4.00; N, 17.02.

α-Hydroxyiminophenylacethydroximoyl Chloride (6) from α-Hydroxyimino-*anti*-phenylacetonitrile Oxide (2a).[5a]—A solution of 150 mg of the nitrile oxide **2a** (prepared by the buffer treatment of 4-phenylfurazan 2-oxide) in 50 ml of absolute ethanol was cooled in ice while it was being saturated with hydrogen chloride gas. The mixture was stirred at room temperature for 2 hr. The solvent was removed on a rotary evaporator and the crystalline residue was triturated with chloroform and was collected by filtration: yield 80 mg; mp 186–188° dec (lit.[5a] 199–200° dec); ir (KBr) 3322, 1399, 1143, 982, 867, 767, 714, and 690 cm^{-1}.

Anal. Calcd for $C_8H_7ClN_2O_2$: C, 48.38; H, 3.55; N, 14.11. Found: C, 48.13; H, 3.68; N, 13.97.

α-Hydroxyiminophenylacethydroximoyl Chloride (6) from *anti*-Phenyl-*amphi*-glyoxime (5).[11]—A solution of 10 g of *anti*-phenyl-*amphi*-glyoxime[1] in 185 ml of glacial acetic acid was cooled to about the freezing point while chlorine gas was passed in for 0.5 hr, and then the mixture was allowed to come to room temperature while chlorination was continued. The solvent was removed on a rotary evaporator under high vacuum. The residue

(10) "Beilstein's Handbuch der Organischen Chemie," 4th ed, Vol. IX, B. Prager, P. Jacobson, P. Schmidt, and D. Stern, Ed., Springer Verlag, Berlin, 1926, pp 304–306.

(11) J. Armand, P. Souchay, and F. Valentini, *Bull. Soc. Chim. Fr.*, 4585 (1968), and references therein.

was extracted with petroleum ether (bp 30–60°) and the crude product was removed by filtration. Recrystallization was accomplished from ethyl acetate–petroleum ether (bp 30–60°): yield 2.2 g; mp 187–188.5°; ir the same as that described for the compound above; molecular weight by mass spectrometry, 198 (calcd 198); nmr (DMSO-d_6) δ 7.37 (s, 5, phenyl), 12.12 (s, 1, –OH) and 12.54 ppm (s, 1, –OH). The product gave a red complex with nickelous acetate, indicating an *anti*-glyoxime structure.[8]

Anal. Calcd for $C_8H_7ClN_2O_2$: C, 48.38; H, 3.55; N, 14.11. Found: C, 48.12; H, 3.43; N, 13.82.

α-Hydroxyiminophenylacethydroximoyl Chloride (6) from α-Ketophenylacethydroximoyl Chloride (9).[11]—The procedure appearing in the literature[11] for reacting α-ketophenylacethydroximoyl chloride (9) and hydroxylamine hydrochloride without base yielded α-hydroxyiminophenylacethydroximoyl chloride melting at 187–189° dec and having an ir spectrum superimposable upon that of the sample obtained by hydrogen chloride addition to the nitrile oxide **2a**.

Dehydrohalogenation of α-Hydroxyiminophenylacethydroximoyl Chloride (6).[5a]—When a suspension of α-hydroxyiminophenylacethydroximoyl chloride in chloroform was shaken with neutral or pH 4.0 buffered solutions, or sodium bicarbonate solutions, dehydrohalogenation was effected smoothly.[5a] The chloroform solutions were then dried azeotropically by first passage through phase-separating paper (Whatman 1 PS) followed by concentration under vacuum. The prominent band in the ir spectrum of these solutions is the nitrile oxide. Removal of the remaining solvent caused spontaneous dimerization of the nitrile oxide to a furazan oxide[5a] as shown by the disappearance of the nitrile oxide band (2288 cm^{-1}) in the ir and the appearance of strong double bond absorption associated with the furazan oxide ring (1600 cm^{-1}).[7,12] The dimer structure was also confirmed by mass spectrometry which showed a molecular ion at *m/e* 324. When the nitrile oxide was generated by simply shaking the hydroximoyl chloride **6** in chloroform–water,[13] the chloroform solution, after drying and concentration as above, showed a strong nitrile oxide absorption in its ir spectrum, but again dimerization occurred when all of the solvent was removed.

Attempted Methylations of 4-Phenylfurazan 2-Oxide.—Samples of 4-phenylfurazan 2-oxide were recovered unchanged after dissolution and refluxing in methyl iodide for 1 hr, or after dissolution in dimethyl sulfate with heating at 100° for 1 hr. Evaporation of the reactants under high vacuum and comparison of the ir spectra and melting points after recrystallization of the residues established that no reaction had occurred.

Irradiation of 4-Phenylfurazan 2-Oxide.—A 1% ethereal solution of 4-phenylfurazan 2-oxide in a quartz flask was subjected to 7 hr irradiation at 253 nm from 16 75-watt low pressure mercury vapor lamps at 35–40°. Ir analyses showed no decomposition of the starting material when the experiment was performed either under a nitrogen atmosphere or with air bubbling through the solution.

1:1 Adduct between 4-Phenylfurazan 2-Oxide (or α-Hydroxyimino-*anti*-phenylacetonitrile Oxide) and Mesityl Oxide.—A solution of 1 g of 4-phenylfurazan 2-oxide in 10 ml of mesityl oxide was allowed to stand for 20 days. Evaporation of the solvent left 1.7 g of a solid residue which was recrystallized from chloroform–petroleum ether (bp 30–60°). The melting point was erratic between 150 and 166°, perhaps indicating a mixture of the two possible isomers although the compound was homogeneous on tlc; ir ($CHCl_3$) 3571, 1709, 1370, and 1353 cm^{-1}; mass spectral molecular weight 260 (calcd 260).

Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.41; H, 6.13; N, 10.39.

Registry No.—**1**, 7707-64-4; **2a**, 32971-22-5; **3**, 32971-23-6; **6**, 33021-14-6; **7**, 1456-22-0; 1:1 adduct of **1** and mesityl oxide, 33015-59-7.

(12) J. H. Boyer, D. I. McCane, W. J. McCarville, and A. T. Tweedie, *J. Amer. Chem. Soc.*, **75**, 5298 (1953); N. E. Boyer, G. M. Czerniak, H. S. Gutowski, and H. R. Snyder, *ibid.*, **77**, 4238 (1955).

(13) In solution there is the following equilibrium: RC(=NOH)C(=NOH)Cl ⇄ RC(=NOH)C≡N^+—O^- + HCl.[11] Since the hydroximoyl chloride is insoluble in chloroform in contrast to the nitrile oxide which is soluble, simply shaking the hydroximoyl chloride with chloroform–water yields a chloroform solution of the nitrile oxide.

Synthesis of 1-Aza-2-silacyclopentane Compounds

TSU-TZU TSAI* AND C. J. MARSHALL, JR.

The Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433

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Ethoxy derivatives of the 1-aza-2-silacyclopentane[1a] ring system were prepared and their reactions investigated. Cyclotri(2-ethoxy-1-aza-2-silacyclopentane) reacted with ethanol to form 3-aminopropyltriethoxysilane and with ethyllithium and phenyllithium to form cyclotri[2-ethyl- (or phenyl-) 1-aza-2-silacyclopentane].

In our previous note,[1b] we have reported the synthesis of 1-(trimethylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane. The ring structure in this compound showed remarkable stability toward cleavage either on standing (which resulted in cleavage of its oxygen analogs)[2-5] or in Grignard reactions in which the two side ethoxy groups were replaced. Since the 1-aza-2-silacyclopentane ring system has received little attention, we extended our study to the synthesis of additional derivatives of this rather stable silazane structure.

Hexaphenyldisilazane and 3-aminopropyltriethoxysilane were allowed to react as indicated in eq 1. Fifty

$$(C_2H_5O)_3SiC_3H_6NH_2 + (C_6H_5)_3SiNHSi(C_6H_5)_3 \xrightarrow[\Delta]{NH_4^+\ salt} (C_2H_5O)_2SiC_3H_6NSi(C_6H_5)_2 + (C_6H_5)_3SiOC_2H_5 \quad (1)$$

A

per cent of the theoretical amount of ammonia was evolved after heating the reaction mixture for 4 days and a small amount of 1-(triphenylsilyl)-2,2-diethoxy-1-aza-2-silacyclopentane (A) was obtained upon work-up. The silazane was found to have been primarily converted into ethoxytriphenylsilane. Since steric effect[6-8] from bulky substituents on nitrogen atoms has been claimed as a main factor in preventing amine

(1) (a) In order to conform to the IUPAC nomenclature system, the name of the ring system, -1-sila-2-azacyclopentane used in our previous report,[1b] was changed to 1-aza-2-silacyclopentane. (b) T. T. Tsai and C. J. Marshall, Jr., *J. Org. Chem.*, **34**, 3676 (1969).

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