the HCl. The acetic acid produced was not purified, but was used directly for the preparation of acetyl chloride-O^{18}.

Preparation of Acetyl Chloride-O^{18}.—Phosphorus trichloride (1.24 g, 0.009 mole) was added to the cooled reaction product from the previous step and the resultant solution was stirred at room temperature for 30 min. To one end of an U-shaped connecting tube with a stopcock attached for evacuation, the reaction flask was affixed and a receiving flask was attached to the other end. After the reactants were frozen in the reaction flask by immersion into liquid nitrogen, the system was throughly outgassed at *ca.* 0.5 mm. After 2 hr, the stopcock to the system was closed and the liquid nitrogen bath was transferred from the reaction flask to the receiving flask. As the reaction mixture warmed to room temperature, the labeled acetyl chloride distilled into the receiving flask, yielding 2.0 g (70%).

Preparation of Mono-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol.—This compound was prepared according to a known procedure.[6] Recrystallization from Skellysolve C–benzene gave a pure sample of the compound with the correct melting point and elemental analysis.

Preparation of 1-O-acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarboxyl-O^{18} (I).—The monotosyl ester (6.3 g, 0.023 mole) was dissolved in 15 ml of dry dichloromethane containing 2.0 ml dry pyridine. The flask was cooled in an ice bath and a solution of 2.0 g of acetyl chloride-O^{18} in 5.0 ml of dry dichloromethane was added dropwise, while the reaction was stirred by means of a magnetic stirrer. After addition of the acetyl chloride-O^{18}, the reaction was left at room temperature for 14 hr. The contents of the flask were poured into 100 ml of 0.5 *M* HCl and the desired product was extracted with 200 ml of diethyl ether. The ethereal solution was washed with 50 ml 10% $NaHCO_3$ solution, then with two 50-ml portions of distilled water, and dried with anhydrous sodium sulfate. Evaporation of the solvent yielded white, granular crystals which were recrystallized from aqueous methanol, yielding 3.8 g (53%), mp 77–78°.

Anal. Calcd for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C, 57.57; H, 6.59; O^{18}, 0.987 atom % excess.

***trans*-1,2-Diacetoxylcyclohexanecarboxyl-O^{18} (III + IV).**—Acetolysis of I (3.0 g) according to procedure of Winstein, *et al.*,[6] yielded 1.5 g (73%) of *trans*-1,2-diacetoxycyclohexanecarboxyl-O^{18}, bp 119–119.5° (12 mm) [lit.[6] bp 120° (11 mm)].

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.96; H, 8.06. Found: C, 59.92; H, 8.16; O^{18}, 1.230 atom % excess (1.238 = 100% retention of O^{18} from I).

***trans*-1,2-Cyclohexanediol-O^{18} (V + VI).**—Saponification of a mixture of diactates (III + IV) by a known procedure[6] yielded *trans*-1,2-cyclohexanediol-O^{18}, which was purified by two recrystallizations from carbon tetrachloride and followed by sublimation, mp 102.8–103.1°.

Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.42. Found. C, 62.18; H, 10.42; O^{18}, 1.22 atom % excess (1.230 = 50% incorporation of O^{18} from III + IV).

Partial Acetolysis of 1-O-Acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarbonyl-O^{18}—The approximate half-life of the reaction was determined by quenching, every 5 min, 1-ml aliquots of the reaction solution. In this experiment, unlabeled 1-O-acetyl-2-O-toluenesulfonyl-*trans*-cyclohexanediol was solvolyzed, according to the procedure of Winstein, *et al.*[6] Each aliquot was shaken in a separatory funnel, along with 5 ml of benzene and 10 ml of 5% aqueous sodium bicarbonate solution. The organic layer was washed twice with 10 ml of water and then dried over anhydrous sodium sulfate. Each benzene solution was spotted consecutively on an 8 × 8 in. thin layer chromatographic plate, which was coated with a 100-μ layer of Absorbosil-3.[7] When all the samples were spotted, the plate was developed twice in ethyl ether–Skellysolve B (2:3, v/v). The spotted materials were located by spraying the plate with 0.5% methanolic iodine solution. Half-life for this reaction was estimated to be *ca.* 12 min by this technique.

Acetolysis of 1-O-acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarbonyl-O^{18} (4.8 g; O^{18}, 1.05 atom % excess) was carried out as previously described, except that the reaction was quenced after 10 min in 150 ml of ice–water. Twenty-five grams of solid sodium bicarbonate was added to neutralize the acetic acid. The organic components were extracted with four 50-ml portions of benzene. The combined benzene extracts were washed with three 50-ml portions of water and dried over anhydrous sodium sulfate. Solvent removal left an oily residue, which crystallized upon addition of aqueous methanol and chilling the solution. After separation of the crystalline material, the mother liquor was subjected to silicic acid column chromatography (3/4 × 9 in.), using Skellysolve B–ethyl ether (2:1, v/v) as the eluent. The combined yield of recovered starting materials by fractional crystallization and chromatography after two crystallizations from aqueous methanol was 1.05 g, mp 78.2–78.8°. It had the proper C–H analysis and the O^{18} enrichment was 1.09 atom %.

Hydrogenolysis of the Recovered 1-O-Acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol-O^{18}.—The recovered O^{18} ester (900 mg, 2.9 mmole; O^{18}, 1.09 atom % excess) from the previous experiment and 25 ml of anhydrous ether were placed in a 100-ml, three-necked flask, affixed with a reflux condenser, an addition funnel, and a magnetic stirrer. Lithium aluminum hydride (120 mg, 3.1 mmoles), dissolved in 25 ml of anhydrous ether and cooled to 0°, was added through the addition funnel at a rate sufficient to maintain gentle reflux; addition time about 1 min. After a total reaction time of 3.5 min, 1 ml of ethanol and 1 ml of water were added to the reaction mixture and heated to reflux for 10 min. The solids were filtered and washed with two 30-ml portions of chloroform. From the combined filtrates, a granular, white solid was obtained, upon solvent removal under reduced pressure. After two recrystallizations from Skellysolve B, 150 mg of pure monotoluenesulfonyl-*trans*-1,2-cyclohexanediol was obtained, mp 97.0–97.8°. This material gave the correct elemental analysis and O^{18} enrichment was 0.28 atom %.

Acknowledgment.—We thank the Arizona State University Grants Committee for partial support of this research and Mr. G. Duane Stone for his able assistance with some of the O^{18} analyses.

---

[6] S. Winstein, H. V. Hess, and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2796 (1942).

[7] A product of Applied Science Laboratories, Inc., State College, Pa.

Nitrile Oxides. VIII. Cyanogen N-Oxide[1]

CHRISTOPH GRUNDMANN AND HANS-DIETER FROMMELD

Mellon Institute, Pittsburgh, Pennsylvania

Received May 17, 1966

The remarkable stability of cyanogen bis-N-oxide (I), $O\leftarrow N\equiv C—C\equiv N\rightarrow O$, at least in dilute solutions, compared with other simple aliphatic nitrile oxides, *e.g.*, acetonitrile oxide,[2] has been attributed to the unusually large number of resonance-hybrid structures which are possible for I.[3] To support this assumption, the investigation of cyanogen N-oxide (II), $NC—C\equiv N\rightarrow O$, seemed of interest, since II, although closely related to I, cannot achieve so high a degree of resonance stabilization as I. For the preparation of II we started with the known cyanoformhydroximic chloride (III),[4] from which we tried to liberate II by reaction with aqueous bases under the various conditions described for the generation of I from oxalobishydroximic chloride (dichloroglyoxime).[3b] Ether extracts obtained from the above reaction at 0° had an intense, aggressive odor, different from III and presumably attributable to II, which, however, disappeared within 1 min. As expected, immediate infrared spectroscopy of these ether solutions did not

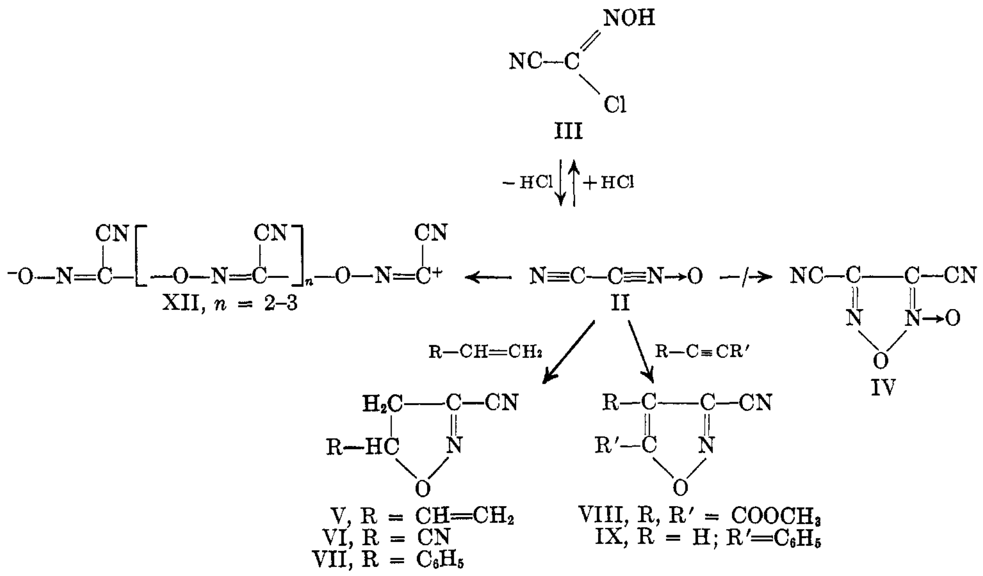
---

[1] Previous communication: C. Grundmann, *Fortschr. Chem. Forschg.*, in press.

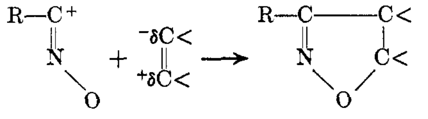
[2] G. Zinner and H. Günther, *Angew. Chem.*, **76**, 440 (1964).

[3] (a) C. Grundmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 260 (1963); (b) C. Grundmann, V. Mini, J. M. Dean, and H.-D. Frommeld, *Ann.*, **687**, 191 (1965).

[4] H. Houben and H. Kauffmann, *Ber.*, **46**, 3821 (1913).



reveal any trace of the characteristic C≡N→O absorption around 2300 cm^{-1}. Compound II does not seem to stabilize itself as most nitrile oxides as the furoxan, since we failed to isolate from such solutions the known dicyanofuroxan (IV).[5] The transient existence of II could be proven by generating it from III with aqueous sodium carbonate in the presence of a suitable dipolarophile, *e.g.*, butadiene, acrylonitrile, dimethyl acetylenedicarboxylate, styrene, or phenylacetylene. The established manner of 1,3-dipolar cycloadditions of nitrile oxides to olefins and acetylenes follows almost invariably eq 1, established by Huisgen and Quilico.[6] Thus, from carbethoxyformoximino chloride, EtOOCC(Cl)=NOH, and styrene or phenylacetylene 3-carbethoxy-5-phenyl-4,5-dihydro-1,2-oxazole[7] and 3-carbethoxy-5-phenyl-1,2-oxazole[8] have been obtained. Therefore, the formulas V–IX of 5-substituted 3-cyano-4,5-dihydro-1,2-oxazoles or 3-cyano-1,2-oxazoles were assigned to the cycloaddition products of II and the above-named dipolarophiles. The structure of VII and IX was proven by hydrolysis of the cyano group, leading to the known 5-phenyl-4,5-dihydro-1,2-oxazole-3-carboxylic acid[7] (X) and 5-phenyl-1,2-oxazole-3-carboxylic acid (XI).[8]



(1)

The first investigators of cyanoformhydroximic chloride (III) had already noted that less than 10% of III reacted with water, even on prolonged contact, forming an insoluble, solid, colorless, halogen-free product, which exploded violently on heating.[4,9] From the aqueous filtrate they could isolate the major part of III unchanged, but, after vacuum distillation, the recovered III again reacted to the same extent with water. They explained this peculiar behavior by assuming that III consisted of an inseparable mixture of the two possible stereoisomers (*syn* and *anti*) of which only one component reacted with water and that subsequent distillation of the remainder restored the original equilibrium mixture.

While we could confirm their observations, the results of our investigation require a different explanation. The solid product is a low polymer of cyanogen N-oxide, its explosive properties suggesting a dipolar structure XII, like that now accepted for the analogous explosive polymers of formo-, aceto- or benzonitrile oxide.[10] The reaction leading from III to XII is a dehydrohalogenation producing first the monomeric II and HCl. The reaction proceeds only to the point where the concentration of the generated HCl stabilizes the equilibrium in favor of III. A solution of III in 2 *N* HCl is definitely stable; in 0.02 *N* HCl traces of XII are formed after several hours. If, on the contrary, the HCl formed is constantly neutralized, maintaining a pH of 6, all of III is consumed and a 42% yield of XII is obtained. The observed properties of cyanogen N-oxide are in good agreement with those reported for other low molecular weight aliphatic nitrile oxides. Like these, II is extremely unstable and experiences no unusual resonance stabilization from the interaction of the neighboring cyano group.

Experimental Section[11]

1,3-Dipolar Cycloadditions of Cyanogen N-Oxide.—Compound III (2.65 g, 25 mmoles) was dissolved together with 50–100 mmoles of the dipolarophile in ether (50 ml), cooled to 0°, and 50 ml of 1 *N* sodium carbonate solution was added dropwise with efficient stirring over a period of 30 min. The organic layer was separated and dried over calcium chloride, the ether was removed

---

[5] H. Wieland, *et al.*, *Ann.*, **444**, 7 (1925).

[6] R. Huisgen, *Proc. Chim. Soc.*, 577 (1961); A. Quilico, "The Chemistry of Heterocyclic Compounds," Vol. XVII, A. Weissberger, Ed., Interscience, Publishers, Inc., New York, N. Y., 1962, pp 1–176.

[7] W. R. Vaughan and J. L. Spencer, *J. Org. Chem.*, **25**, 1160 (1960).

[8] A. Quilico and M. Simonetta, *Gazz. Chim. Ital.*, **77**, 586 (1947).

[9] Houben and Kauffmann had assumed this product to be bisoximinosuccinonitrile, NC⁻(C=NOH)$_2$⁻CN, although this compound was already known and possessed entirely different properties; *cf.* W. Wislicenus and R. Grützner, *Ber.*, **42**, 1938 (1909).

[10] G. Speroni, Abstracts of 14th International Congress for Pure and Applied Chemistry, Zurich 1955, No. 55, p 30; H. Wieland, *Ber.*, **42**, 803, 806 (1909).

[11] Melting points were determined with the Fisher-Johns melting point apparatus and are uncorrected. Microanalyses were by Galbraith Laboratories, Knoxville, Tenn.

followed by the excess dipolarophile, and the reaction product was separated by fractional vacuum distillation. Thus, the following compounds were obtained.

5-Vinyl-3-cyano-4,5-dihydro-1,2-oxazole (V) was obtained as an oil, bp 53° (0.3 mm), $n^{20}\text{D}$ 1.4852, yield 50%. *Anal.* Calcd for $C_6H_6N_2O$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.25; H, 5.07; N, 23.02.

3,5-Dicyano-4,5-dihydro-1,2-oxazole (VI) had bp 87° (0.3 mm), $n^{25}\text{D}$ 1.4920, mp 45–46°,[12] yield 53%. *Anal.* Calcd for $C_5H_3N_3O$: C, 49.59; H, 2.50; N, 34.70. Found: C, 49.43; H, 2.64; N, 34.79.

5-Phenyl-3-cyano-4,5-dihydro-1,2-oxazole (VII) had bp 102–106° (0.1 mm), $n^{24}\text{D}$ 1.5553, mp 40°,[12] yield 61%. *Anal.* Calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27; mol wt, 168. Found: C, 69.94; H, 4.83; N, 16.24; mol wt, 177 (osmometric, acetone).

3-Cyano-4,5-dicarbomethoxy-1,2-oxazole (VIII) had bp 102–106° (0.35 mm), $n^{22}\text{D}$ 1.4797, mp 28°,[12] yield 27%. *Anal.* Calcd for $C_8H_2N_2O_5$: C, 45.72; H, 2.88; N, 13.33. Found. C, 45.59; H, 2.79; N, 13.53.

3-Cyano-5-phenyl-1,2-oxazole (IX) had mp 88–89° [from petroleum ether (bp 35–45°)], yield 40%. *Anal.* Calcd for $C_{10}H_6N_2O$: C, 70.58; H, 3.55; N, 16.46. Found. C, 70.74; H, 3.54; N, 16.29.

When aqueous sodium carbonate was replaced in the above reactions by triethylamine, working at temperatures between −17 and +10° under anhydrous conditions as described by Huisgen,[13] none of the adducts V–IX could be obtained, although III was easily decomposed by the triethylamine.

Polymeric Cyanogen N-Oxide (XII).—Compound III (5.6 g) was dissolved in 100 ml of H_2O and filtered, and the filtrate was diluted with 150 ml of H_2O. After 4 hr at 25–30°, 300 mg of XII was filtered off. Within the next 2 hr saturated sodium bicarbonate solution was added dropwise at a rate to maintain pH 6. After 12 hr an additional amount of the polymeric nitrile oxide XII (1.2 g) was filtered off. The crude XII was apparently amorphous, but could be obtained microcrystalline by precipitation from an acetone solution with water. It could not be dried completely at room temperature; at elevated temperatures violet decomposition occurred. Therefore, the analytical data are not entirely satisfactory, but leave no doubt about the composition of the product.

Anal. Calcd for $(C_2N_2O)_5$: C, 35.31; H, 0.00; N, 41.19; mol wt, 340. Found (for two different preparations). C, 35.50, 35.96; H, 0.30, 0.33; N, 39.43, 39.36; mol wt, 308, 377.

We found our preparations not so explosive as described;[4] when XII was heated in a test tube over the open flame only deflagration occurred; a blow with a hammer did not detonate the polymer. Compound XII is insoluble in water and nonpolar organic solvents, but it is easily soluble in methanol, ethanol, acetone, or ethyl acetate.

5-Phenyl-1,2-oxazolecarboxylic Acid (XI).—The cyano compound IX (333 mg) was refluxed for 30 min with 4 ml of 30% aqueous sodium hydroxide, the solid cake was dissolved by addition of water (20 ml) and ethanol (20 ml), and refluxing was continued for another hour. Ethanol and water were then slowly distilled off until the remaining volume in the flask was reduced to approximately 15 ml. The sodium salt of XI which is little soluble in excess sodium hydroxide separated at this point. After cooling the thick slurry was acidified with concentrated hydrochloric acid. The acid XII was filtered and washed with little cold water, redissolved in 2 *N* ammonia (10 ml), filtered from little insolubles, and reprecipitated by concentrated hydrochloric acid, yield 81%. The product was found identical with an authentic sample[8] by infrared spectrum and mixture melting point (162°).

5-Phenyl-4,5-dihydro-1,2-oxazole-3-carboxylic Acid (X).—The acid X was obtained from the nitrile VIII in an analogous fashion as above and identified by comparison with a specimen prepared according to the literature.[7]

Acknowledgment.—The work reported in this publication was in part supported by Public Health Service Research Grant CA-07272-02 of the National Cancer Institute, Bethesda, Maryland.

---

(12) The substance crystallized only after prolonged storage in the refrigerator.

(13) R. Huisgen and W. Mack, *Tetrahedron Letters*, 583 (1961); R. Huisgen, W. Mack, and E. Anneser, *ibid.*, 587 (1961).

The Enhanced Intensity of the n → π* Transition as Evidence for Orbital Interaction in β-Silyl Ketones[1a]

W. Kenneth Musker and Randolph W. Ashby

Department of Chemistry, University of California,
Davis, California

Received December 20, 1965

The possibility of intramolecular interactions between a trimethylsilyl group and a nonadjacent donor resulting in expanded octet σ bonding of silicon has led previous investigators[1b–4] to search for experimental confirmation. Neither infrared analysis of silicon substituted ketones[1b,2] nor $\text{p}K_\text{A}$ comparisons of silicon containing amines[3] or carboxylic acids[4] with their carbon analogs have yielded evidence for the interaction. Brook[5] reported the spectral properties of some triphenylsilyl substituted ketones, but noted no intramolecular interaction.

Since the enhancement of the extinction coefficient of the n → π* transition in ketones has been attributed to intramolecular orbital interactions, we directed our attention to an ultraviolet study of simple β- and γ-substituted silyl ketones. We found that the ultraviolet absorption spectrum of 1-trimethylsilyl-2-propanone (VIII) and 1-trimethylsilyl-2-butanone (IX) in several solvents exhibited an enhanced extinction coefficient for the n → π* transition, *i.e.*, four to five times greater than values for 2-pentanone (I), 4,4-dimethyl-2-pentanone (II), or 1-methoxy-2-propanone (V) and in the same range as β,γ-unsaturated ketones (see Table I).[6–11]

It should be recalled that ketone carbonyl groups ordinarily exhibit a low intensity ($\epsilon < 30$) absorption between 270 and 310 mμ. The low intensity is attributed to the fact that excitation of a lone pair np oxygen electron to the carbonyl π* orbital is symmetry forbidden.[12,13]

Examination of the intensity of the n → π* transition of related ketones (Table I) suggests that alkyl substitution and steric and inductive effects cannot account for the high intensity absorption of these β-silyl ketones. For example, 4,4-dimethyl-2-pentanone (II) and 2,2,4,4-tetramethyl-3-pentanone (III), compounds for which a steric effect would be expected, have normal extinction coefficients ($\epsilon \sim 20$), and, indeed, comparable with those of 2-pentanone (I). Inductive effects can be similarly

---

(1) (a) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 42-O. (b) L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 12.

(2) R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

(3) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

(4) L. H. Sommer, J. R. Gold, G. Goldberg, and N. S. Marans, *ibid.*, **71**, 1509 (1949).

(5) A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

(6) A. Maroni, *Ann. Chem.*, **2**, 757 (1957).

(7) C. M. R. Rao, G. K. Goldman, and A. Balasubramanian, *Can. J. Chem.*, **38**, 2508 (1960).

(8) S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

(9) H. F. Gray, Jr., R. S. Rasmussen, and D. D. Tunnicliff, *ibid.*, **69**, 1630 (1947).

(10) P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956).

(11) R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962).

(12) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

(13) See J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958), for additional references.