could be induced to solidify by cooling for benzyl hydrodisulfide, or to give solid for benzhydryl series. Recrystallization of each solid from alcohol gave pale yellow crystals, 2.3 g (74%), of dibenzyl tetrasulfide, mp 52.5–53°, and 3.9 g (84%) of dibenzhydryl tetrasulfide, mp 82.5–83°. The amount of ferrous ion formed and the pH change in the reaction of benzyl hydrodisulfide or benzhydryl hydrodisulfide were determined as follows. (Data for the latter are shown in parentheses.) By using an aliquot of the aqueous layer, ferrous ion was analyzed colorimetrically by *o*-phenanthroline, indicating that the amount was 19 mg-ion (18.5 mg-ion). The remaining aqueous layer was diluted with water to 200 ml (100 ml). The pH of the solution was 1.20 (0.42). Before the reaction, the corresponding pH was 1.65 (1.06). This pH difference was found by titration to correspond to *ca.* 20 mmol (17 mmol) of sodium hydroxide, *i.e.*, *ca.* 20 mg-ion (17 mg-ion) of proton.

For experiment 3, 2.7 g (10 mmol) of powdered ferric chloride hexahydrate in 20 ml of dioxane was added to a solution of 2.3 g (10 mmol) of benzhydryl hydrodisulfide in 20 ml of dioxane and the mixture was stirred under a nitrogen atmosphere. At once the solution became pale yellow and a precipitate was formed. The precipitate (ferrous salt, 8.4 mmol) and the remaining organic solution (86% of dibenzhydryl tetrasulfide) were treated in a manner similar to that mentioned above.

For experiment 4, atmospheric oxygen was bubbled into the benzyl hydrodisulfide solution in the flask described above. Only one drop (2×10^{-4} mol or 0.01 mol/1 mol of hydrodisulfide) of the solution of ferric chloride hexahydrate from the dropping funnel was added. Vigorous evolution of hydrogen sulfide was observed. Since it appeared that hydrogen sulfide was coming out sparingly after effervescence ceased, the bubbling was continued for 2 days. (Hydrogen sulfide was not swept out smoothly, probably because the reaction mixture was not so acidic as in the case mentioned above.) The amount of hydrogen sulfide was determined, and then the reaction mixture was extracted with benzene. To an aliquot of the dried extract was added an excess of 0.1 *N* ethanolic iodine solution. The amount of thiol was determined by titrating the solution with 0.1 *N* aqueous sodium thiosulfate. Analytical procedure for polysulfides in the remaining benzene extract was identical with that reported elsewhere.[9]

Procedure for the Reaction with Ferrous Sulfate or Other Inorganic Salts.—In the same apparatus as mentioned above, equimolar or 0.005 *M* ferrous sulfate in 10 ml of water was added to a stirred solution of 10 mmol of hydrodisulfide in 30 ml of dioxane under nitrogen atmosphere at room temperature. Hydrogen sulfide evolved slowly for *ca.* 24 hr. The hydrogen sulfide was analyzed and the reaction mixture was extracted with benzene. The amount of thiol was determined by using an aliquot of the benzene extract, and the remainder was oxidized with ethanolic iodine solution. The excess of iodine was removed by washing with aqueous sodium thiosulfate solution followed by water, and was dried. The solvent was evaporated *in vacuo* and yellow viscous oil was obtained. The quantity of polysulfides in the oil was determined by using nmr spectra with 1,1,2,2-tetrachloroethane as another internal standard for integral purpose only. [CH peaks for authentic dibenzhydryl di-, tri-, tetra-, and pentasulfides were τ 5.27, 4.79, 4.45, and 4.40, respectively (s, 7 w/w in CCl_4).]

The reaction of hydrodisulfide with inorganic salts was carried out in the same way as described above. Long periods (20 hr or more) were required to complete each reaction, judging from the evolution of hydrogen sulfide.

Procedure for the Decomposition of Hydrodisulfides in Dioxane–Water or Dioxane Alone.—To a stirred solution of 1.5 g (9.5 mmol) of benzyl hydrodisulfide or 1.2 g (5.2 mmol) of benzhydryl hydrodisulfide in 30 ml of dioxane was added 10 ml of water under nitrogen atmosphere at room temperature. After 24 hr, the dioxane and water were removed *in vacuo*. Yellow oil obtained was subjected to nmr analysis, by which the amounts of thiol,[1] polysulfide,[1] and remaining hydrodisulfide [$C_6H_5CH_2SSH$, τ 7.26; $(C_6H_5)_2CHSSH$, τ 7.28 (both s, 7 w/w in CCl_4)] were estimated. Experiments with dioxane alone were run similarly to that described above.

Registry No.—Dibenzyl tetrasulfide, 4816-54-0; dibenzhydryl tetrasulfide, 21367-78-2.

(9) S. Kawamura, Y. Otsuji, T. Nakabayashi, T. Kitao, and J. Tsurugi, *J. Org. Chem.*, **30**, 2711 (1965).

Chemistry of 4-Pyridineglyoxylonitrile Oxime and Methyl 4-Pyridineglyoxylate Oxime Ethers

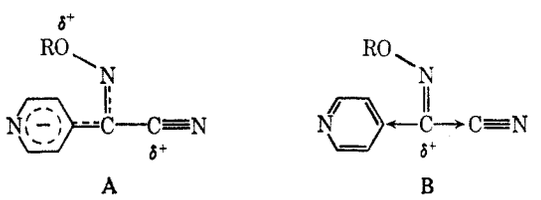
BRUCE C. TYSON, JR.,[1] EDWARD J. POZIOMEK,[2] AND E. RUTH DANIELSON

Physical Research Laboratory, Edgewood Arsenal, Maryland 21010, and Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received January 20, 1969

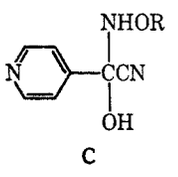
An investigation was made of the reaction of 4-pyridineglyoxylonitrile oxime O-methyl (and benzyl) ethers (**3** and **4**) with hydroxide. Reaction of both **3** and **4** with methanolic potassium hydroxide occurred readily to give the corresponding amides **7** and **8**. Hydrolysis of the methiodide of **4** (**11**) also led to the formation of amide **12** (Scheme I). Compounds **9**, **10**, and **13**, which are geometrical isomers of **8**, **7**, and **12**, were prepared from methyl 4-pyridineglyoxylate oxime (**2**) as illustrated in Scheme I. Isomerization of **8** to **9** was achieved by using sulfuric acid. Synthetic details are given in the Experimental Section.

Electrophilic Character of the Oximino Carbon.—Our finding that the nitrile group in **3**, **4**, and **11** is attacked preferentially to the oximino carbon was interesting. The marked stability of the oximino carbon to attack by hydroxide was illustrated through an experiment in which both **8** and **9** were recovered unchanged after being refluxed in methanolic potassium hydroxide. If attack by hydroxide had occurred, then isomerization would have been evident. The apparent low electrophilic character of the oximino carbon (relative to that of the nitrile carbon) can be rationalized on the basis of a distribution of electron density throughout the conjugated system as represented in structure A. Inductive effects (structure B),



A B

which would increase the electrophilicity of the oximino carbon, must be less important. Nevertheless, it is expected that compounds such as α-hydroxy-α-(O-alkyl)hydroxylamino-4-pyridineacetonitriles (C) if formed would be stable enough for isolation because of the strong electron-withdrawing influence of both the cyano and the 4-pyridyl moieties. Analogy can



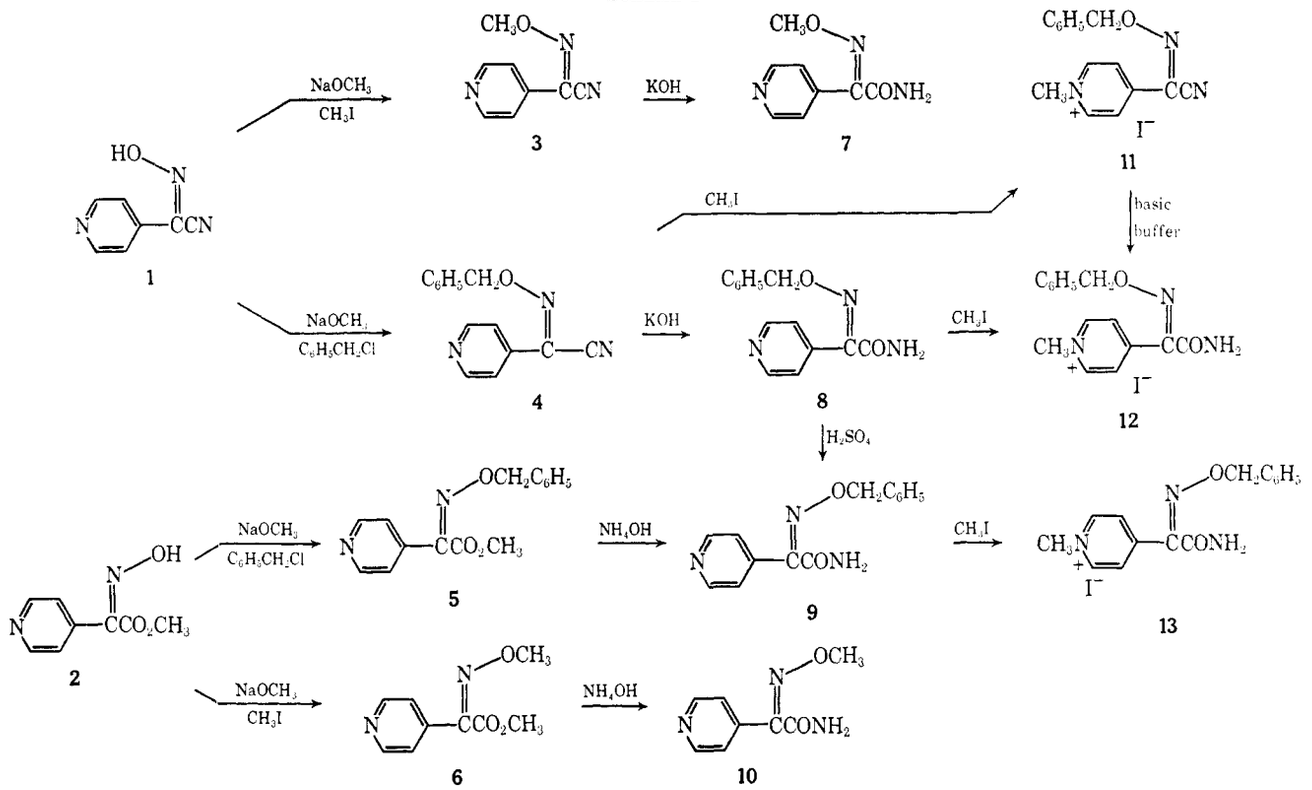
C

be drawn from the previous isolation of carbinolamine intermediates in the formation of pyridinium aldoximes

(1) Taken in part from the Ph.D. thesis of B. C. T., University of Delaware, June 1969.

(2) To whom reprint requests should be addressed at Edgewood Arsenal.

SCHEME I



and hydrazones[3] and the isolation of pyridinium *gem*-glycols and hemiacetals from pyridinium carboxaldehydes in water and alcohol, respectively.[4]

Structural Considerations.—The possibility that compounds **7**, **8**, and **12** are not amides but analogs of C was eliminated on the basis of the strong C=O absorption in the infrared.

It was previously found that alkylation of heterocyclic oximes can lead to N alkylation of the oximino group.[5,6] Buehler[7] showed that alkylation of the sodium salt of *syn*-benzaldoxime leads to both N and O alkylation. In the present study methoxyl analyses for **7** and **10** substantiate O substitution. This does not mean that only O ethers were formed. The synthesis of **3**–**6** involved extraction with ether which did not allow the isolation of the more polar N ethers.

Configurational Analyses.—Nuclear magnetic spectra of **1**–**10** are summarized in Table I. In each case the signals of the α (to the 4 substituent) and β protons of the pyridine ring were observed basically as doublets ($J_{\alpha\beta}$ = 4.5 ± 0.3 cps). Evidence for cross-ring coupling is evident in both doublets. Such behavior is typical of 4-substituted pyridine derivatives.[8a]

Each of the amide derivatives showed nmr behavior consistent with that of primary amides. The amide proton signals occurred as two broad singlets, not a doublet, apparently arising from nonequivalency of the protons due to restricted rotation about the amide C–N bond.[9] Amide proton signals are broadened by N_{14} coupling.[9] They frequently appear as one broad peak, but numerous spectra may be cited[8b] in which two broad peaks occur. The amide proton chemical shifts (δ values) of compounds **7**–**10** are large (downfield) compared with those of most primary amides but are similar to those of 2,2,3-trichloropropionamide,[8c] δ 6.87 and 7.55, and that of fluoroacetamide,[8d] δ 7.56, which also have electron-withdrawing groups adjacent to the carbamido group.

The nmr spectra of the amides obtained by two synthetic routes were consistent with those expected for geometrical isomers of an oxime ether. The two members of each pair gave essentially identical chemical

TABLE I

CHEMICAL SHIFTS OF 4-PYRIDINEGLYOXYLONITRILE AND METHYL 4-PYRIDINEGLYOXYLATE OXIME DERIVATIVES[a]

Compound	δ Values: H_β	H_α[b]	Other
		Z Configuration	
2	8.67	7.42	3.80 (CO_2CH_3), 3.5 (OH, broad)
5	8.67	7.41	3.80 (CO_2CH_3), 5.32 ($CH_2C_6H_5$), 7.37 (C_6H_5)
6	8.67	7.38	3.80 (CO_2CH_3), 3.98 (=$NOCH_3$)
10	8.63	7.34	3.96 (=$NOCH_3$), ~7.3–7.8 (NH_2, very broad)
9	8.62	7.35	5.23 ($CH_2C_6H_5$), 7.6, 7.75 (NH_2, broad), 7.35 (C_6H_5)
		E Configuration	
1	8.75	7.68	3–4 (OH, very broad)
3	8.74	7.66	4.27 (=$NOCH_3$)
4	8.75	7.64	5.55 ($CH_2C_6H_5$), 7.47 (C_6H_5)
7	8.64	7.50	3.98 (=$NOCH_3$), 7.95, 8.18 (NH_2, broad)
8	8.63	7.48	5.26 ($CH_2C_6H_5$), 7.38 (C_6H_5), 7.96, 8.18 (NH_2, broad)

[a] Measured downfield from tetramethylsilane (internal standard) in DMSO-d_6. [b] Ring proton α to 4 substituent.

(3) E. J. Poziomek, D. N. Kramer, B. W. Fromm, and W. A. Mosher, *J. Org. Chem.*, **26**, 423 (1961).

(4) G. M. Steinberg, E. J. Poziomek, and B. E. Hackley, Jr., *ibid.*, **26**, 368 (1961).

(5) B. E. Hackley, Jr., E. J. Poziomek, and G. M. Steinberg, *ibid.*, **27**, 4220 (1962).

(6) E. J. Poziomek, R. H. Poirier, R. D. Morin, and T. F. Page, Jr., *ibid.*, **28**, 1411 (1963).

(7) E. Buehler, *ibid.*, **32**, 262 (1967).

(8) Sadtler Research Laboratories, Inc., Nuclear Magnetic Resonance Spectra: (a) 1344M, 2344M, 2347M, 2350M; (b) 442M, 3486–3450M; (c) 412M; (d) 2180M.

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N.Y., 1959.

shifts for the H_β pyridine protons (Table I). The members of a pair, however, gave different chemical shifts for the protons *ortho* (H_α) to the oximino group. Using a well-established principle[7,10] [that, in the isomer having the oximino oxygen *cis* to the ring, the *ortho* proton (H_α) resonates further downfield], compounds **7–10** were assigned the *Z* or *E* configuration. The recently adopted (*E*–*Z*) system of nomenclature[11] for double-bond stereoisomers is used in this paper. For compounds of the general formula 4-PyC(R′)=NOR, the R′ groups CN, $CONH_2$, and $COOCH_3$ (but not H) have priority[12] over the 4-Py group. Derivatives in Table I with R′ and OR *trans* to each other are termed *E*. Those with R′ and OR *cis* to each other are termed *Z*.

Configurational assignments were also made for the precursors (**1–6**) of the amides (**7–10**) on the basis of the position of the H_α resonance in each case. These assignments are reasonable but must remain tentative until both isomers of each pair are available. That no change in configuration occurred during the O alkylation of either **1** or **2** was evident by comparing the nmr spectrum of each oxime with those of its ethers **3** and **4** or **5** and **6**, respectively. In each case, the H_α and H_β pyridine proton chemical shifts of the ethers are the same as those of the parent oxime.

Synthesis of Geometrical Isomers.—The *E* configuration deduced for **1** is surprising in view of Stevens' assignment of the *Z* configuration to the predominant form of phenylglyoxylonitrile oxime.[13] The *E* form of phenylglyoxylonitrile oxime is formed in small yield during the preparation of the *Z* form by the base-catalyzed isonitrosation of phenylacetonitrile. Only one form of **1** was obtained through either base-catalyzed isonitrosation of 4-pyridineacetonitrile or through the reaction of cyanide with isonicotinohydroxamoyl chloride.[14]

Since Brady and Klein[15] have reported the acid-catalyzed isomerization of O-alkyl benzaldoximes, attempts were made to isomerize the *E* O-alkyl ethers of **1**. These attempts lead only to the recovery of starting material. As mentioned previously, treatment of (*E*)-O-benzyl 4-pyridineglyoxylamide oxime (**8**) with 50% sulfuric acid yielded the *Z* isomer (**9**) also prepared by a different route from **2**.

Polarography.—Polarographic behavior of millimolar solutions of **12** and **13** in pH 9.8 carbonate buffer containing 0.06% gelatin is summarized in Table II. The two samples of *E* configuration gave results identical within experimental error. The *Z* form gave a first wave at slightly more negative values, but the half-wave potentials of the second waves, which are due to further reduction of the *same* amine produced in all cases during the first waves, were the same for all three samples.

TABLE II

POLAROGRAPHIC BEHAVIOR OF GLYOXYLAMIDE OXIME O-ALKYL ETHERS

Compound	$E_{1/2}$,[a] V 1st wave	2nd wave
12[b]	−0.758	−1.441
12	−0.756	−1.437
13	−0.768	−1.438

[a] *Vs.* standard calomel electrode. [b] Formed from the *in situ* hydrolysis of **11**.

(10) E. J. Poziomek, D. N. Kramer, W. A. Mosher, and H. O. Michel, *J. Amer. Chem. Soc.*, **83**, 3916 (1961).

(11) J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *ibid.*, **90**, 509 (1968).

(12) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

(13) T. E. Stevens, *J. Org. Chem.*, **32**, 670 (1967).

(14) E. J. Poziomek and A. R. Melvin, *ibid.*, **26**, 3769 (1961).

(15) O. L. Brady and L. Klein, *J. Chem. Soc.*, 874 (1927).

Experimental Section

(*E*)-4-Pyridineglyoxylonitrile Oxime (1).—The procedure for preparing this compound was previously described:[14] mp 276–278°.

(*Z*)-Methyl 4-Pyridineglyoxylate Oxime (2).—This compound was prepared in 96% yield by the acid-catalyzed isonitrosation of methyl 4-pyridineacetate according to the method reported for the preparation of ethyl 2-pyridineglyoxylate oxime:[16] mp 192–194° dec (from methanol).

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.3; H, 4.5; N, 26.6. Found: C, 53.3; H, 4.5; N, 26.7.

2 Hydrochloride.—This compound had mp 195–196°.

Anal. Calcd for $C_8H_9ClN_2O_3$: C, 44.4; H, 4.2; Cl, 16.4. Found: C, 44.1; H, 4.0; Cl, 16.3.

2 Methyl Iodide.—This compound had mp 160–161° dec.

Anal. Calcd for $C_9H_{11}IN_2O_3$: C, 33.6; H, 3.4; I, 39.4. Found: C, 33.7; H, 3.7; I, 39.2.

(*E*)-O-Methyl 4-Pyridineglyoxylonitrile Oxime (3).—To 200 ml of methanol in which 3.9 g (0.17 g-atom) of sodium had been dissolved were added 25.0 g (0.17 mol) of **1** and 24.1 g (0.17 mol) of methyl iodide. The solution was refluxed for 12 hr and poured into 200 ml of water. The solution was extracted eight times with 100-ml portions of ether. The combined extract was treated with charcoal and anhydrous sodium sulfate. The ether was evaporated to give a pale green solid, which was again dissolved in ether and treated with charcoal and sodium sulfate. Evaporation yielded 6.5 g (24%) of cream-colored crystals, mp 64–67°. A portion was recrystallized from water to yield colorless crystals, mp 66–67°; ir (KBr) 4.49 (vw, C≡N), 5.96 (vw, C=N?), 6.28 and 6.34 μ (m, pyridine).

Anal. Calcd for $C_8H_7N_3O$: C, 59.6; H, 4.5. Found: C, 59.6; H, 4.5.

(*E*)-O-Benzyl 4-Pyridineglyoxylonitrile Oxime (4).—Essentially the same procedure was used as that used for **3** except that benzyl chloride was the alkylating agent: mp 69–72° from methanol–water; yield 39%. A portion was recrystallized from ether to yield colorless crystals: mp 72–73°; ir (KBr) 4.49 (vw, C≡N), 5.91 (vw, C=N?), 6.28 (m) and 6.35 μ (w, pyridine).

Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.9; H, 4.7; N, 17.7. Found: C, 71.1; H, 4.7; N, 17.4.

4 Perchlorate.—This compound had mp 178–179° dec.

Anal. Calcd for $C_{14}H_{12}ClN_3O_5$: C, 49.8; H, 3.6. Found: C, 49.2; H, 3.7.

4 Methyl Iodide (11).—This compound had mp 148–150° dec.

Anal. Calcd for $C_{15}H_{14}IN_3O$: C, 47.5; H, 3.7. Found: C, 47.5; H, 3.7.

(*Z*)-O-Benzyl Methyl 4-Pyridineglyoxylate Oxime (5).—To 200 ml of methanol was added 2.3 g of sodium followed by 18.0 g (0.10 mol) of **2**. To the resulting yellow solution was added 12.7 g (0.10 mol) of benzyl chloride. The solution was allowed to react at room temperature for 24 hr and then was added to 400 ml of water. The product was extracted with several portions of ether which were combined and evaporated to give a brown oil. The oil was redissolved in ether and treated with charcoal. Evaporation yielded 4.7 g (17%) of a pale tan solid: mp 74–76°; ir (KBr) 5.81 (s, C=O), 6.29 μ (m, pyridine).

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.7; H, 5.2. Found: C, 66.7; H, 5.3.

(*Z*)-O-Methyl Methyl 4-Pyridineglyoxylate Oxime (6).—Essentially the same procedure was used as that used for **5** except that the alkylating agent was methyl iodide: fluffy white solid; yield 8.2%; mp 91–93°; ir (KBr) 5.80 (s, C=O), 6.29 μ (m, pyridine).

Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.7; H, 5.2. Found: C, 55.7; H, 5.3.

(16) G. Van Zyl, D. L. DeVries, R. H. Decker, and E. T. Niles, *J. Org. Chem.*, **26**, 3373 (1961).

(*E*)-**O-Methyl 4-Pyridineglyoxylamide Oxime** (**7**).—A 0.80-g (5.0×10^{-3} mol) portion of **3** was dissolved in 5.0 ml of methanol. To this was added 5.0 ml of water containing 0.56 g (1.0×10^{-2} mol) of potassium hydroxide. The mixture was heated in a water bath for 90 min at 60°, cooled, and neutralized to pH 7 with glacial acetic acid. Cooling in an ice bath yielded a white solid which was recrystallized from 10 ml of water to give 0.25 g (25%) of fine white needles: mp 149–152° (softening at 100°); ir (KBr) 3.01 and 3.16 (s, NH_2), 5.98 (s, C=O), 6.27 μ (m, pyridine).

Anal. Calcd for $C_8H_9N_3O_2 \cdot H_2O$: C, 48.7; H, 5.6; N, 21.3; O, 24.3; H_2O, 9.1; CH_3O, 15.7. Found: C, 48.6; H, 5.7; N, 21.6; O, 24.1; H_2O, 9.3; CH_3O, 15.3.[17]

(*E*)-**O-Benzyl 4-Pyridineglyoxylamide Oxime** (**8**).—Compound **4** (5.0 g, 0.02 mol) was dissolved in 100 ml of methanol. Water was added to the point of cloudiness; then 5.0 g of potassium hydroxide was added. The solution was heated on a steam bath for 15 min. Water was added to precipitate 5.5 g (96%) of **8** hydrate, cream-colored crystals. These were dissolved in a minimum amount of methanol and the solution was treated with charcoal. Addition of water gave 4.2 g (73.5%) of colorless crystals, mp 140–142° (softening at 100°).

Anal. Calcd for $C_{14}H_{13}N_3O_2 \cdot H_2O$: C, 61.5; H, 5.5; N, 15.4; O, 17.6; H_2O, 6.6. Found: C, 61.7; H, 5.6; N, 15.6; O, 16.8; H_2O, 6.9.[17]

A 0.5110-g sample of **8** hydrate was heated at 100° for 1 day under vacuum. The weight loss, 0.0367 g, corresponded to 7.2% water content (calcd, 6.6%). The resulting compound, mp 142–144°, gave an ir spectrum very similar to that of **8** hydrate: ir 2.99 and 3.19 (m, NH_2), 5.97 (s, C=O), 6.13 (m), 6.22 (m, pyridine).

Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5; O, 12.54. Found: C, 65.8; H, 5.3; N, 16.4; O, 12.5.

8 Methyl Iodide (**12**).—This compound was prepared by reaction of methyl iodide with **8** in acetone–water (2.5:1): mp 82–85°.

Anal. Calcd for $C_{15}H_{16}IN_3O_2 \cdot H_2O$: C, 43.4; H, 4.4; I, 30.6; N, 10.1; O, 11.6. Found: C, 43.3; H, 4.6; I, 30.6; N, 9.7; O, 12.4.

(*Z*)-**O-Benzyl 4-Pyridineglyoxylamide Oxime** (**9**).—To a 1.5-g (5.6×10^{-3} mol) portion of **5** in 25 ml of methanol was added 25 ml of concentrated ammonium hydroxide. The solution was boiled 10 min and then cooled. Addition of water precipitated 1.0 g (62%) of colorless microcrystalline material: mp 166–167°; ir 2.99 and 3.16 (m, NH), 5.91 (s, C=O), 6.28 μ (m, pyridine).

Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.9; H, 5.1; N, 16.5; O, 12.5. Found: C, 66.1; H, 5.2; N, 16.2; O, 12.4.

9 Methyl Iodide (**13**).—This compound was obtained as pale yellow crystals, mp 218–219° dec.

Anal. Calcd for $C_{15}H_{16}I_1N_3O_2$: C, 45.5; H, 4.1; N, 10.6; O, 8.1. Found: C, 45.5; H, 4.1; N, 10.3; O, 8.4.

(*Z*)-**O-Methyl 4-Pyridineglyoxylamide Oxime** (**10**).—A 0.58-g (3.8×10^{-3} mol) portion of **6** was heated in 10 ml of concentrated ammonium hydroxide. A clear solution was obtained momentarily; then product began to precipitate. On cooling 0.46 g (71%) of colorless solid, mp 170°, was obtained: ir 3.01 and 3.15 (m, NH), 5.89 (s, C=O), 6.27 μ (m, pyridine).

Anal. Calcd for $C_8H_9N_3O_2$: C, 53.6; H, 5.1; N, 23.5; O, 17.9. Found: C, 53.9; H, 5.3; N, 23.3; O, 17.8.

When the product was allowed to stand for 6 months, hydration occurred.

Anal. Calcd for $C_8H_9N_3O_2 \cdot H_2O$: C, 48.7; H, 5.6; N, 21.3; O, 24.3; CH_3O, 15.7. Found: C, 49.3; H, 5.2; N, 23.0; O, 23.0; CH_3O, 16.2.

Isomerization of 8 to 9.—A 0.65-g sample of **8** was dissolved in 50 ml of 50% H_2SO_4 and allowed to stand overnight. A tan solid (0.45 g) precipitated when the solution was neutralized with sodium bicarbonate. The product was dissolved in methanol, treated with charcoal, and filtered. Addition of water precipitated 0.1 g of colorless solid, mp 150–160°, the ir spectrum of which corresponded exactly to that of **9**.

Registry No.—**1**, 21372-44-1; **2**, 21372-45-2; **2** hydrochloride, 21372-46-3; **2** methyl iodide, 21372-47-4; **3**, 21372-48-5; **4**, 21372-49-6; **4** perchlorate, 21372-50-9; **4** methyl iodide, 21449-74-1; **5**, 21449-75-2; **6**, 21449-76-3; **7**, 21449-77-4; **8**, 21449-78-5; **8** methyl iodide, 21449-79-6; **9**, 21449-80-9; **9** methyl iodide, 21449-81-0; **10**, 21449-82-1.

Acknowledgment.—The elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratories Edgewood Arsenal, Md.

(17) The Karl Fischer procedure was used for the H_2O analysis.

Ionization State of *p*-Toluenesulfonic Acid in Acetic Acid

MICHAEL L. SINNOTT[1]

Department of Organic Chemistry, The University, Bristol 8, BS8 1TS, England

Received January 6, 1969

Recently, Goering and Fickes,[2] because of very accurate experimental data, were able to detect the upward drift of the acetolysis rate of a *p*-toluenesulfonate ester, and they ascribed this to a *p*-toluenesulfonic acid salt effect; such salt effects had been reported previously.[3] However, Bruckenstein and Kolthoff[4] had estimated a dissociation constant of $10^{-8.5}$ for *p*-toluenesulfonic acid in glacial acetic acid on the basis of emf measurements. This result means that either the substrate is not ionized in this solvent, or that if it is, the ionized form exists very largely as ion pairs. To distinguish between these two possibilities, a uv spectroscopic investigation was made of *p*-toluenesulfonic acid derivatives in acetic acid.

Spectra were examined in acetic acid 0.1% (v/v) in water and 2.5% (v/v) in acetic anhydride. In the former solvent, the spectrum of *p*-toluenesulfonic acid qualitatively resembled that of its methyl ester and was unchanged in 3.5×10^{-2} *M* perchloric acid, but was qualitatively and quantitatively changed in 4.2×10^{-2} *M* potassium acetate. Of special interest was the longest wavelength vibrational sub-band (Table I).

TABLE I
LONGEST WAVELENGTH VIBRATIONAL SUB-BAND IN ACETIC ACID 0.1% IN WATER

Solute at 1.49×10^{-2} *M*	λ_{max}, mμ	$\epsilon \times 10^2$	Other solute
MeOTs	273.1	5.0	...
HOTs	272.6	3.3	...
HOTs	272.6	3.3	3.5×10^{-2} *M* $HClO_4$
HOTs	272.2	1.7	4.2×10^{-2} *M* KOAc

A similar situation held with spectra examined in acetic acid 2.5% in acetic anhydride, except that addition of perchloric acid caused a marked change in the spectrum, possibly due to its catalysis of mixed anhydride formation (Table II).

In the more polar, more basic of the two solvents examined (0.1% in water), the addition of the very

(1) The author thanks Professor M. O. Whiting and Dr. D. J. MacGregor for their advice, and the Science Research Council of Great Britain for a maintenance grant.

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