this method in a yield of 51%, using a molar ratio of pyridine to **1** of one. Since the crude product was contaminated by pyridinium trinitromethide (**3**) the use of a base weaker than pyridine seemed desirable.[4] As expected the use of 4-nitropyridine or pyridine 1-oxide in place of pyridine eliminated **3** and increased the yield of **2** to 59 and 72%, respectively. Increasing the molar ratio of pyridine to **1** was found to cause nucleophilic attack of pyridine on **1** and resulted in the formation of a new compound, **4**, with the structure $[(C_6H_5N^+{-}CH_2O{-})_2C{=}O][(NO_2)_3C^-]_2$ (see Experimental Section).

Experimental Section

All chemicals were reagent grade except the phosgene gas (99%, The Matheson Co.) and the pyridine 1-oxide (technical grade, Reilly Tar and Chemical Co.). 4-Nitropyridine was made by deoxygenating 4-nitropyridine[5] 1-oxide with PCl_3.[6] The citation in ref 4 gives the methods for preparing 2,2,2-trinitroethanol and trinitromethane. The following instruments were used: a Varian HR-100 nmr spectrometer, a Bendix time-of-flight mass spectrometer, Beckman DU, Beckman IR-4, and Cary Model 14 spectrophotometers. The Cary was used for the CH_2O equivalent weight.

Bis(2,2,2-trinitroethyl) Carbonate (**2**).—Following the method of Kissinger,[3] 10.0 g of 2,2,2-trinitroethanol (0.0552 mol) was dissolved in 6 ml of methylene chloride and 13 ml of chloroform; 4.44 g of pyridine (0.0561 mol) was added; and phosgene was bubbled into the stirred solution at 18 cc/min until 40% excess had been introduced, keeping the temperature near 27°. The reaction mixture was allowed to stand for 1 hr at ambient temperature. The crude product was precipitated by the addition of *n*-hexane and was then stirred with water for 16 hr to remove **3**,[7] collected and air dried. The yield of **2**, mp 113–115°, was 5.44 g (51%). Two recrystallizations from chloroform raised the mp to 116–117°. A mull of **2** showed the expected absorption: a C=O doublet at *1783*[8] and *1795* cm^{-1}, C—O stretching at 1235 cm^{-1},[9] asymmetric and symmetric NO_2 stretching in nonsalt *gem*-dinitro compounds at 1595 and 1345 cm^{-1}, respectively, and C—H stretching at *2882* and *2967* cm^{-1}.

Using this procedure, with a reduction of the stirring period to 1 hr, 6.96 g of 4-nitropyridine (0.0561 mol) in place of the pyridine gave 6.29 g (59%) of **2**, and 5.34 g of pyridine 1-oxide in place of the pyridine gave 7.68 g (72%) of **2**.

Anal. Calcd for $C_5H_4N_6O_{15}$: C, 15.47; H, 1.04; N, 21.65. Found: C, 15.45, 15.50; H, 1.28, 1.41; N, 21.48, 21.54.

Pyridinium Trinitromethide (**3**).—Reaction of equimolar quantities of pyridine and trinitromethane in chloroform gave a yellow precipitate which had the absorption, as a mull, expected for **3**: 1900 and 2400 cm^{-1} for $C{=}N^+H$ of the pyridinium ion, 1613 and 1640 cm^{-1} for C=C, C=N stretching, 1050 and 1203 cm^{-1} for C—H deformation, and 3060 cm^{-1} for C—H stretching of the pyridine ring, 737, 787, 870, 1128, 1260, 1410, and 1544 cm^{-1} for a carbanion of the type $Z(NO_2)_2C^-$.[10]

Anal. Calcd for $C_6H_6N_4O_6$: C, 31.31; H, 2.63; N, 24.35. Found: C, 31.49, 31.32; H, 2.77, 2.83; N, 23.91, 24.17.

Compound 4, $[(C_5H_5N^+{-}CH_2O{-})_2C{=}O][(NO_2)_3C^-]_2$, **Data. A. Preparation.**—Phosgene (0.11 mol) was bubbled at 18 cc/min into a stirred solution of 4.00 g of **1** (0.020 mol) in a mixture of 20 ml of pyridine and 0.40 ml of water, keeping the temperature of the solution near 27°. Stirring the reaction mixture into 80 ml of ice–water caused the precipitation of a yellow solid which was collected, washed with 35 ml of ice–water, and air dried. The yield was 3.85 g of **4** (64%). The analytical sample, made by recrystallizing the crude product twice from acetonitrile, decomposed over a wide range (*ca.* 130–175°).

Anal. Calcd for $C_{15}H_{14}N_8O_{15}$: C, 32.97; H, 2.58; N, 20.51. Found: C, 32.29, 32.83; H, 2.58, 2.45; N, 20.31, 20.60.

B. Spectral Measurements.—A mull of **4** showed the absorption expected: *3106*,[8] *3067*, and *3053* cm^{-1} for C—H stretching of the pyridine ring; *2924* and *2841* cm^{-1} for the methylene C—H stretching; *1773* cm^{-1} for C=O stretching of a carbonate; 1640, 1632, and 1540 cm^{-1} for C=C, C=N stretching of the pyridine ring (1-methylpyridinium iodide used for comparison); 1247 cm^{-1} for C—O stretching in a carbonate;[3,9] 778, 1054, and 1210 cm^{-1} for C—H deformation of the pyridine ring; 737, 785, 870, 1155, 1265, 1414, and 1540 cm^{-1} for a carbanion of the type $Z(NO_2)C^-$.

Strong evidence that **4** contains the quaternized pyridine ring was obtained from the pmr spectrum. τ values in parts per million and relative intensities for **4** in acetone were 0.88 (2), 1.72 (2), 1.19 (1), and −0.10 (2).[11] For comparison, 1-methylpyridinium iodide in acetone-d_6 gave 0.70 (2), 1.72 (2), and 1.27 (1) for the 2-, 3-, and 4-ring H, and 5.23 (3) for the methyl H.

C. Equivalent Weights.—Aqueous solutions of **4** were analyzed spectrophotometrically for $(NO_2)_3C^-$, using ϵ 14,418,[12] and for formaldehyde, using the method developed by Nash,[13] ϵ based on a sulfite-standardized[14] CH_2O solution and an optical density corrected for absorption by $(NO_2)_3C^-$. The amount of pyridine distilled from a basic solution of **4** was determined spectrophotometrically,[15] and the amount of gas generated by the acidification of a basic degassed solution of **4** was determined in a volume-calibrated system by the ideal gas law. Mass spectrographic analysis of the gas generated showed it to be at least 99.9% CO_2. The equivalent weights thus determined were $(NO_2)_3C^-$, 276; pyridine, 273; CH_2O, 283, CO_2, 543.

A single crystal of **4** was shown to have a density of 1.70 g/cc, a unit cell volume of 1097 Å,[3] and a unit cell molecular weight of 1123. These data required that the molecular weight of **4** be 281 or 562. A molecular weight of 562, the molecular weight required by the empirical formula $C_{15}H_{14}N_8O_{15}$ (546), in addition to the spectral data and equivalent weights justify the structure given for **4**.

Registry No.—**1**, 918-54-7; phosgene, 75-44-5; **2**, 17943-76-9; **3**, 17943-77-0; **4**, 17943-78-1.

Acknowledgments.—Grateful appreciation is expressed to Dr. J. R. Holden for determining the molecular weight of the unit cell; Dr. J. R. Holden and Mr. C. W. Dickinson for the X-ray powder diffraction measurements; Dr. W. B. Moniz and Dr. F. E. Saalfeld, of the U. S. Naval Research Laboratory, Washington, D. C., for the nmr and mass spectrographic analysis, respectively; Professor M. A. Aldridge, American University, Washington, D. C., for the microanalyses.

---

(4) Increasing the basicity of the solvent increases the extent to which **1** is dissociated into $(NO_2)_3C^-$ and CH_2O. See T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

(5) Made by nitrating pyridine 1-oxide according to E. Ochiai, *ibid.*, **18**, 534 (1953).

(6) M. Hamana and H. Yoshimira, *J. Pharm. Soc. Jap.*, **72**, 1051 (1952).

(7) Shown to be present by X-ray powder diffraction.

(8) A LiF prism assembly was used for the italicized frequencies and a NaCl prism assembly for the frequencies not italicized.

(9) J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957).

(10) M. J. Kamlet, R. E. Oesterling, and H. A. Adolph, *ibid.*, 5838 (1965).

(11) A value of −0.10 for the methylene protons is unusual, but not unreasonable, for **4** if one considers that both oxygen and positively charged nitrogen are strongly deshielding.

(12) See footnote *c*, Table I, in citation of ref 4.

(13) T. Nash, *Biochem. J.*, **55**, 416 (1953).

(14) J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1964, p 486.

(15) H. D. LeRosen and J. T. Wiley, *Anal. Chem.*, **21**, 1175 (1949).

Conformations of *cis*- and *trans*-2,5-Diphenyl-1,4-dioxanes

JACOB SCHAEFER

Central Research Department, Monsanto Company,
St. Louis, Missouri 63166

Received June 13, 1968

Bryan, Smedley, and Summerbell[1] obtained two compounds melting at 122 (I) and 173° (II) from the

---

(1) L. A. Bryan, W. M. Smedley, and R. K. Summerbell, *J. Amer. Chem. Soc.*, **77**, 2206 (1950).

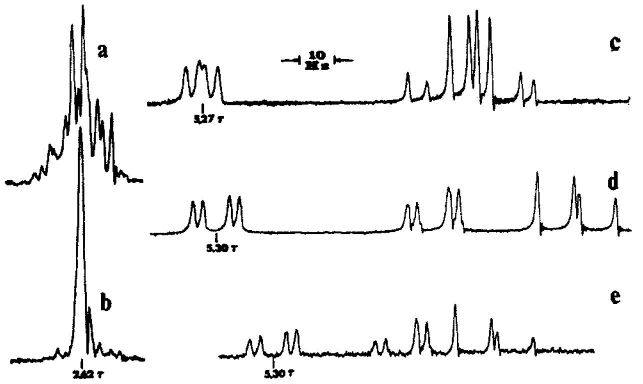

Figure 1.—The 60-MHz aromatic proton spectra of (a) I and (b) II. The 100-MHz ring-proton spectra of (c) I and (d) II. The 60-MHz ring-proton spectra of (e) II. Magnetic field increases left to right. All sweep scales are equal.

reaction of phenylmagnesium bromide with 2,5-dichloro-1,4-dioxane. (These same two compounds can be obtained using styrene oxide as a starting material and anhydrous stannic chloride as catalyst.[2]) They identified the compounds as the two isomeric 2,5-diphenyl-1,4-dioxanes and, on the basis of the melting points, assigned the *cis* structure to I and the *trans* structure to II.

The 60- and 100-MHz proton spectra of I and II as their 10% solutions in $CDCl_3$ are shown in Figure 1. The aromatic region of I at 60 MHz is a broad, complicated multiplet while that of II is much narrower and simpler (Figures 1a and b) indicating the phenyl rings in I may be more hindered that in II, although neither spectrum was temperature dependent. The ring protons of I at 60 MHz form an ABC system which has been analyzed in detail to yield the two vicinal coupling constants of 5.8 and 3.1 Hz and a geminal coupling constant of -11.9 Hz.[3] These values are consistent with the 100-MHz spectrum shown in Figure 1c. The ring protons of II form an ABX system (by comparison of 100- and 60-MHz spectra in Figures 1d and e) with vicinal coupling constants of 10.4 and 2.9 Hz and a geminal coupling constant of -11.5 Hz (the choice of signs being made by analogy to the assignments for I). The values for the vicinal coupling constants obtained from ring-proton spectra of I and II in dimethyl sulfoxide at 30 and 140° are the same.

Making the reasonable assumption of a chair geometry for both I and II[4] and using the fact that for vicinal coupling constants in these kinds of rings $J_{ea} \sim J_{ae} \sim J_{ee} < J_{aa}$,[5] the observed nmr data are consistent with the assignment of *cis* (Ph_e, $Ph_a \rightleftarrows Ph_a$, Ph_e) to I and *trans* (Ph_e, Ph_e) to II, so that the vicinal coupling constants are given by $(J_{aa} + J_{ee})/2 = 5.8$ Hz and $(J_{ea} + J_{ae})/2 = 3.1$ Hz in I, and $J_{aa} = 10.4$ Hz and $J_{ea} = 2.9$ Hz in II. The only other way to assign chair conformations to the isomers consistent with the nmr data involves the unreasonable assumption of a rigid *cis* structure and a rapidly interconvering *trans* structure.

There is little possibility that the bulky phenyl groups cause the *cis* isomer to assume twist–boat conformations[6] in which both phenyls are exclusively in equitorial orientations with respect to the ring. If this were the case, the *cis* isomer would display a large vicinal coupling constant. However, only one vicinal coupling constant greater than 6 Hz is observed so that if a twist–boat conformation is adopted for the *cis* isomer, the *trans* structure must be either in a twist–boat conformation itself or undergoing rapid chair interconversions. Either situation is unlikely. Furthermore, any room-temperature dynamic equilibrium involving substantial amounts of boat and chair forms is unlikely since the spectra of both isomers are unchanged at higher temperatures.

Thus, the original structural assignments given by Summerbell are correct and the *cis*- and *trans*-2,5-diphenyl-1,4-dioxanes are, in fact, an example of the higher melting of two geometrical isomers being the one with the greater molecular symmetry.

Registry No.—I, 13217-26-0; II, 5888-95-9.

---

[2] R. K. Summerbell and M. J. Kland-English, *J. Amer. Chem. Soc.*, **77**, 5095 (1955).

[3] C. Altona and E. Havinga, *Tetrahedron*, **22**, 2275 (1966).

[4] G. Gatti, A. L. Segre, and C. Morandi, *ibid.*, **23**, 4385 (1967).

[5] See, for example, E. L. Eliel and C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

[6] R. D. Stolow and M. N. Bonaventura, *ibid.*, **85**, 3636 (1963); E. W Garbisch, Jr., and D. B. Patterson, *ibid.*, **85**, 3228 (1963); H. Booth and E. O. Gidley, *Tetrahedron Lett.*, 1449 (1964). These authors discuss this possibility for cyclohexane derivatives with large *cis* substituents at C-1 and C-4.

Ionization Constants of Squaric Acid[1]

David J. MacDonald[2]

Department of Chemistry, University of Nevada,
Reno, Nevada 89507

Received June 28, 1968

Squaric acid, $C_4H_2O_4$ (1,2-dihydroxycyclobutenedione), is an unusually strong organic acid, so strong that its first ionization constant cannot be easily measured, and until now there seems not to have been any serious attempt to do so. Its second ionization constant has been variously reported as $pK_2 = 2.2$[3] and as $pK_2 = 3.0$.[4] The availability of a digital-computer program[5] designed for the precise evaluation of the p*K* values of a dibasic acid from experimental titration data made it feasible to do an accurate determination of the p*K* values of squaric acid, the results of which are reported in this communication.

Experimental Section

The experimental data (shown in Table I) were obtained by measuring with a Radiometer pH meter (using a type G202B glass electrode and a type K401 calomel reference electrode) the pH of a 0.173 *F* aqueous solution of squaric acid (squaric acid supplied by Chemische Werke Hüls, A.G., and used after drying for 1 hr at 110°) thermostated to 25.0 ± 0.1° as successive increments of 2.00 *N* KOH were added to it from a micrometer syringe buret. The pH meter and electrodes were calibrated

---

[1] This work was sponsored by the Air Force Office of Scientific Research, AFOSR (SRC)-OAR, USAF, under Grant No. AF-AFOSR-994-66.

[2] Address correspondence to U. S. Bureau of Mines, Reno Metallurgy Research Center, Reno, Nev. 89505.

[3] S. Cohen, J. R. Lacher, and J. D. Park, *J. Amer. Chem. Soc.*, **81**, 3480 (1959).

[4] J. D. Park, S. Cohen, and J. R. Lacher, *ibid.*, **84**, 2919 (1962).

[5] A copy of the program, written in FORTRAN II, with a description of how it works, will be sent on request to interested individuals.