

5.64×10^{-6} c.g.s.-e.m.u., 3.2 B.M.; $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ *tert.* BuBr, 5.37×10^{-6} , 3.4 B.M.; and $(\text{Ph}_3\text{P})_2\text{NiBr}_2(\text{PhBr})_2$, 5.59×10^{-6} , 3.8 B.M. The high magnetic moment of the Ni^{2+} ion in the latter two suggests that distortion from a regular tetrahedral arrangement can be decreased by the presence of crystalline solvent. The distortion in the compounds $(\text{Ph}_3\text{P})_2\text{NiX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and } \text{NO}_3$) seems to be partially due to the steric requirement by the size difference between triphenylphosphine and halide ion. To compensate for such a steric effect in $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ two molecules of bromobenzene may be more suitable than one molecule of *tert.* butyl bromide. The appearance of blue tint in many cases of compounds of the types $(\text{Ph}_3\text{P})_2\text{NiX}_2\text{Y}$ and $(\text{Ph}_3\text{P})_2\text{NiX}_2\text{Y}_2$ may have some correlation with rather small distortion from a regular tetrahedral arrangement.

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1. N. S. GILL, R. S. NYHOLM, and P. PAULING. *Nature*, **182**, 168 (1958).
2. P. W. SELWOOD. *Magnetochemistry*. Interscience Publishers, Inc., New York, 1956. p. 186.
3. J. T. RICHARDSON and W. O. MILLIGAN. *J. Phys. Chem.* **60**, 1223 (1956).
4. F. A. COTTON, E. BANNISTER, R. BARNES, and R. H. HOLM. *Proc. Chem. Soc.* 158 (1959).
5. L. M. VENANZI. *J. Chem. Soc.* 719 (1958).
6. L. M. VENANZI and H. M. POWELL. *Cited in reference 1.*
7. W. REPPE and W. J. SCHWECKENDIEK. *Ann.* **560**, 104 (1948).
8. K. YAMAMOTO. *Bull. Chem. Soc. Japan*, **27**, 501 (1954).

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DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE,
THE UNIVERSITY OF TOKYO,
HONGO, TOKYO, JAPAN.

CRYSTALLINE GLYOXYLIC ACID AND ITS SODIUM-CALCIUM SALT

A. A. EISENBRAUN* AND C. B. PURVES

Early researches on the preparation and properties of glyoxylic acid were extensively reviewed by Debus (1) and by Hendricks (2), who noted that the substance occasionally yielded ill-defined rhombic crystals of a monohydrate when stored over a drying agent. In 1925, Hatcher and Holden (3) used the electrochemical method to reduce oxalic acid, isolated barium glyoxylate, decomposed the latter with sulphuric acid, and prepared anhydrous glyoxylic acid for the first time as monoclinic crystals melting at 98° . This result was questioned by Hendricks (2) because oxalic acid monohydrate, a probable impurity, melted at 99° and occurred as monoclinic crystals, and also because his attempts to repeat the crystallization of glyoxylic acid failed. Later workers oxidized tartaric acid or its esters with a glycol-cleaving agent, periodic acid or a periodate (4, 5, 6), lead tetraacetate (7), or sodium perbismuthate (8, 9), but apparently restricted their interest to the preparation of various esters and metallic salts of glyoxylic acid.

In the present work, tartaric acid was oxidized with aqueous periodic acid, by-product iodic acid was removed as the insoluble lead salt, and, after neutralization with barium hydroxide, crystalline barium glyoxylate dihydrate was recovered in high yield. An ion-exchange resin eliminated the cations from an aqueous solution of this salt, and evaporation of the effluent left glyoxylic acid as a clear syrup which eventually crystallized. The melting point was $104\text{--}107^\circ$, with softening at 94° . The replacement of periodic acid by sodium metaperiodate in the above oxidation, followed by the removal of iodate ion, left

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a solution which was mixed with an equimolar amount of aqueous calcium acetate. A white, crystalline, sodium-calcium salt, $\text{CaNa}_2(\text{C}_2\text{HO}_3)_4 \cdot 4\text{H}_2\text{O}$, promptly separated. This salt was thought to be new.

EXPERIMENTAL

Glyoxylic Acid

An aqueous solution, 300 ml, containing 15 g (0.1 mole) of L-tartaric acid and 25.1 g (0.11 mole) of paraperiodic acid (H_5IO_6) was kept at 23° in the dark for 10 hours, when a titration by the sodium arsenite - iodine method showed that all of the periodic acid had been reduced. The addition of 110 ml of 0.52 M lead acetate (0.114 equivalent) caused the nearly quantitative separation of lead iodate, which was removed by filtration. After residual lead ions were removed as lead sulphide, the clarified liquor was evaporated *in vacuo* to a syrup, by-product acetic and formic acids being incidentally eliminated. The acidity of the syrup was cautiously reduced to pH 8 by the addition of cold 0.3 N barium hydroxide, and partial evaporation of the liquor caused the crystallization of 27.8 g (86.8%) of barium glyoxylate dihydrate. Although the solubility of the salt in water was reported (3) as only 0.005% at 18° and 0.08% at 68°, the present sample could be readily recrystallized from hot water. This recrystallization did not significantly change the composition. Calc. for $\text{Ba}(\text{C}_2\text{HO}_3)_2 \cdot 2\text{H}_2\text{O}$: Ba, 43.0%. Found: Ba, 42.8, 43.0%. Samples, 0.2580 g and 0.2577 g, reduced 32.5, 32.5 ml, respectively, of 0.104 N potassium permanganate (3), the calculated amount being 30.9 ml.

An aqueous solution of 8.0 g of the above salt was freed of barium ions by passage through a column of Amberlite IR-120 cation-exchange resin, and the effluent was evaporated *in vacuo* to a thick syrup. This syrup was dried to nearly constant weight by storage over phosphorus pentoxide in an evacuated desiccator at room temperature. After several months the colorless product, 3.68 g or 99% yield, crystallized solidly. The melting point was 104-107°, with softening at 94°. No solvent suitable for recrystallizing the glyoxylic acid was found.

Sodium - Calcium Glyoxylate Tetrahydrate

Fifteen grams (0.1 mole) of L-tartaric acid dissolved in 300 ml of water was mixed with 200 ml of 0.515 M sodium metaperiodate (0.103 mole). The reduction of the latter was complete after the mixture had been kept in the dark and at room temperature for 36 hours. After iodate ion was removed as the lead salt, the filtrate was evaporated *in vacuo* to 50 ml, and was adjusted to pH 8 with 2 N sodium hydroxide. A concentrated aqueous solution of 17 g (0.1 mole) of calcium acetate monohydrate was then added, and 19.6 g (87.1%) of the sodium-calcium salt separated as white crystals. Calc. for $\text{Na}_2\text{Ca}(\text{C}_2\text{HO}_3)_4 \cdot 4\text{H}_2\text{O}$: Na, 10.2; Ca, 8.3%. Found: Na, 9.65, 9.58; Ca, 9.27, 9.21%. Samples, 0.1338 g, 0.2038 g, and 0.1024 g, reduced 24.6 ml, 37.7 ml, and 19.0 ml of 0.101 N potassium permanganate (3), the calculated volumes being 23.6 ml, 35.9 ml, and 18.1 ml, respectively.

Two recrystallizations from hot water reduced the over-all yield to about 75% but failed to alter the composition significantly. A 0.0365-g sample of the salt when treated with 2,4-dinitrophenylhydrazine yielded 0.0658 g (79%) of crystalline glyoxylic acid 2,4-dinitrophenylhydrazone with the correct (10) melting point of 191-191.5°.

1. H. DEBUS. J. Chem. Soc. **85**, 1382 (1904).
2. R. H. HENDRICKS. Ph.D. Dissertation, St. Louis University, Missouri, Ill. 1935. Univ. Microfilms (Ann Arbor, Mich.) Pub. No. 183; Chem. Abstr. **35**, 2475 (1941).
3. W. H. HATCHER and G. W. HOLDEN. Trans. Roy. Soc. Canada, Section III (3), **19**, 11 (1925).

4. P. FLEURY and G. BON-BERNATETS. *J. Pharm. Chim.* **23**, 85 (1936).
5. A. WEISSBACH and D. B. SPRINSON. *J. Biol. Chem.* **203**, 1023 (1953).
6. D. E. METZLER, J. OLIVARD, and E. E. SNELL. *J. Am. Chem. Soc.* **76**, 644 (1954).
7. F. J. WOLFF and J. WEIJLARD. *Org. Syntheses*, **35**, 18 (1955).
8. W. RIGBY. *J. Chem. Soc.* 1907 (1950).
9. L. J. HEIDT, E. K. GLADDING, and C. B. PURVES. *Paper Trade J.* **121** (9), 81 (1945).
10. O. L. BRADY. *J. Chem. Soc.* 756 (1931).

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DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY,
MCGILL UNIVERSITY AND PULP AND PAPER RESEARCH INSTITUTE OF CANADA,
MONTREAL, QUE.

DIFFERENTIATION BETWEEN SOME 2,3- AND 2,5-DISUBSTITUTED PYRIDINE DERIVATIVES BY INFRARED SPECTROSCOPY

R. A. ABRAMOVITCH, GIAM CHOO SENG, AND A. D. NOTATION

In connection with studies of the orientation in the nucleophilic addition of phenyllithium to 3-substituted pyridines (1, 2) it became necessary to find a simple method of determining whether the attacking phenyl group had entered into the 2- or the 6-position of the pyridine ring, i.e. of distinguishing between 2- and 6-phenyl-3-substituted pyridines. This could be done by examining the N.M.R. spectrum of the compounds (1, 3) but was limited in that these determinations could not be carried out in our own laboratories. We therefore turned to infrared spectroscopy for such a method.

In theory, it should be quite simple to differentiate between 2,3- and 2,5-disubstituted pyridines by an examination of the aromatic C—H out-of-plane deformation region between 830 and 700 cm^{-1} . Infrared spectra - structure correlations have been found for the alkylbenzenes in the 11-15 μ region which are characteristic of the substitution positions in the benzene ring (4, 5). If one then considers that the pyridine ring corresponds to a monosubstituted benzene as far as the aromatic C—H out-of-plane bendings are concerned then a 2,3-disubstituted pyridine derivative should be equivalent to a 1,2,3-trisubstituted benzene whereas a 2,5-disubstituted pyridine derivative should correspond to a 1,2,4-trisubstituted benzene. The 1,2,3-trisubstituted benzenes show absorption in the 810-750 cm^{-1} range with a second band of medium intensity in the 726-680 cm^{-1} region, whereas 1,2,4-trisubstituted benzenes give rise to a strong band in the range 860-800 cm^{-1} (6). A number of 2,3- and 2,5-disubstituted pyridine derivatives have recently been shown to fall in nicely with this pattern (7, 8, 9). In particular, Podall (7) has studied the problem systematically and shown that 2-methyl-5-alkylpyridines exhibited two bands at 828-813 cm^{-1} and 735-724 cm^{-1} , whereas 2-methyl-3-alkylpyridines (1,2,3-trisubstitution) showed two bands at 813-769 cm^{-1} and 752-725 cm^{-1} .

A number of minor discrepancies in the band pattern in this region were observed in the present work. 2-Phenylnicotine exhibited a band at 805 cm^{-1} , quinoline a band at 805 cm^{-1} , and 5,6,7,8-tetrahydroquinoline a band at 827 cm^{-1} (see also (8)). On the other hand, 2-phenyl-3-alkyl- and 2-phenyl-5-alkyl-pyridines exhibited the expected absorptions though the presence of the monosubstituted phenyl-group obscured the assignment of the higher wavelength band. All that could be said was that most 2-phenyl-5-substituted pyridines exhibited a band of medium intensity between 850 and 800 cm^{-1} whereas most 2-phenyl-3-substituted pyridines did not.

A new and quite useful empirical correlation has now been observed in the C=C and