[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Bromine-containing and Sulfur-containing Aromatic Boronic Acids

BY LUDOVICO SANTUCCI AND HENRY GILMAN

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A number of new aromatic boronic acids have been synthesized for testing in brain tumor therapy. Some observations are reported on difficulties in the determination of melting point and purification and on the influence of the solvent used for recrystallization upon the transition: acid $\rightleftarrows$ anhydride. A tentative characterization of the aromatic boronic acids by infrared absorption is proposed. The treatment with *n*-butyllithium of a brominated boronic acid was found to produce an unusual cleavage of the C–B bond.

This work was carried out under a project for the synthesis of boronic acids intended for testing in tumor therapy, reference to which has been made previously.[1]

All the compounds herein reported were prepared by boronation of aryllithium compounds with tri-*n*-butyl borate at a low temperature. This proved to be a very convenient and direct way of obtaining these boronic acids. The yields were usually somewhat lower than the yields of the corresponding carboxylic acids obtained by carbonation of the aryllithium compounds.

The melting points of the benzeneboronic acids were 10 to 25° higher than those of the corresponding carboxylic acids. The heterocyclic compounds containing a boronic acid group melted definitely lower than the carboxy analogs. While a similar relationship usually holds for the few other known compounds of the latter series, no generally valid correlation can be drawn from the literature data for the benzene series.

As it has been frequently pointed out in the literature,[1,2] the determination of accurate melting points of boronic acids usually presents much difficulty. This is probably due to the fact that, in many cases, rather than true melting points they can be considered dehydration or decomposition points, with the additional complication that decomposition of some kind may occur before the material passes into the liquid form. In the case of compounds of the acid type, there is usually observed a first fusion or effervescence corresponding to the loss of water, followed by resolidification and melting of the resulting anhydride at a higher temperature. However, the dehydration point may be lost if the sample is heated too long below the dehydration temperature to go directly to the anhydride melting point. Conversely, resolidification of the dehydrated sample may not occur, especially if it is not very pure. Except for a few cases, when decomposition accompanied the fusion of either the acids or the anhydrides,[3] the process was very slow and, moreover, the temperature at which these phenomena would occur depended upon the time of heating. Under such circumstances, in order to obtain reproducible results in the determination of these melting points, special precautions, which are outlined in the Experimental, had to be taken.

The boronic acids reported herein and some others which were studied seemed to have different tendencies toward dehydration. Usually either form, but more frequently the acid, is stable under normal conditions of temperature and pressure, although the infrared spectra and neutralization equivalent of *p*-bromobenzeneboronic acid anhydride[4] often indicated the presence of some acid. Both the boronic acid and anhydride of benzene can be obtained easily while *o*-hydroxybenzene- and *p*-trimethylsilylbenzeneboronic acids[4] are stable in the dehydrated form. It is noteworthy that the introduction into the former of a bromine atom *para* to the phenolic hydroxyl and the replacement of the methyl with phenyl groups in the latter[4] stabilized the acid, the changes corresponding to a withdrawal of electrons from the system. Such gain of stability in the case of the above-mentioned 2-hydroxy-5-bromobenzeneboronic acid was somewhat decreased in the 2-methoxy analog. The methoxy compound readily lost water at 50–60°, although it was hydrated again upon exposure to a moist atmosphere at room temperature. The phenolic compound was practically unaffected by such moderate heating.

The choice of solvent for recrystallization greatly affected the water content of the products. Acids usually were obtained from aqueous solutions, the exceptions being compounds which for other reasons form anhydrides of high stability, while from non-polar solvents like ethylene dichloride the formation of the anhydrides was favored. These include benzeneboronic,[5] *p*-bromobenzeneboronic, *p*-dimethylaminobenzeneboronic,[5] 2-thianthreneboronic and, apparently, 2-hydroxy-6-methoxybenzeneboronic acid. Similarly benzene, although to a lesser extent, showed some dehydrating power. Since the temperature at which these recrystallizations are carried out is not very high, such occurrence might be due to the non-polar solvents favoring a kind of association possible between anhydride molecules. As a matter of fact, molecular weight determinations of *o*-hydroxybenzeneboronic acid anhydride[1] seem to indicate a certain degree of association.

By the examination of the infrared spectra of 25 aromatic boronic acids and anhydrides, we have made the following observations: (1) Absorption at 8.35–8.5μ, present in boric acid, was consistently found throughout the series. This can be interpreted as a B–O bond absorption. *o*- and *p*-hydroxybenzeneboronic acids[1] are slightly out of

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[1] H. Gilman, L. Santucci, D. R. Swayampati and R. O. Ranck, THIS JOURNAL, **79**, 2898 (1957); **79**, 3077 (1957).

[2] Also see for example H. G. Kuivila and A. R. Hendrickson, *ibid.*, **74**, 5068 (1952).

[3] A very definite proof of such occurrence was obtained in the case of the 2-thianthrene compound, where a sublimate of thianthrene was isolated and identified.

[4] B. J. Gaj, unpublished studies.

[5] R. O. Ranck, unpublished studies.

this range, with absorption at 8.2 and 8.55μ, respectively. (2) A band at 9.7–9.8μ (9.95μ for *p*-hydroxybenzeneboronic acid), present in all of the acids, invariably disappeared from the anhydrides. (3) Both acids and anhydrides show a band at 9.1–9.2μ which is not present in boric acid. This is believed to be the C–B absorption band. None of the bands mentioned above are present in non-boron analogs of the compounds examined.

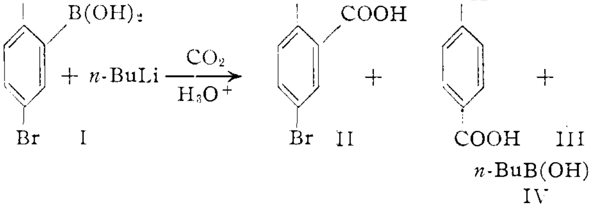
The purification of these compounds is a matter of great care, especially owing to the ease of the transition: acid $\rightleftarrows$ anhydride. In this respect, however, once the more stable form of the compound has been determined, much of the trouble can be overcome by a proper choice of solvent for the recrystallization. One remaining difficulty is the lack of information which can be obtained about the purity of the compound from its melting point, due to the poor reproducibility of these determinations, as already pointed out. Neutralization equivalents provide a better criterion.

The proof of structure always relied upon characterization of the corresponding aryllithium compounds. Infrared spectra provided additional information.

2-Hydroxy-6-methoxybenzeneboronic acid remained insufficiently characterized because a pure sample could not be obtained. Furthermore, it was found that, upon standing in the open, the product spontaneously decomposes into boric acid and an unidentified oil, presumably *m*-methoxyphenol. This reaction was an attempt to prepare a compound possibly more reactive toward coupling with diazonium salts than *o*-hydroxybenzeneboronic acid. It is perhaps noteworthy that the only other reported attempt to obtain an hydroxy-methoxybenzeneboronic acid[6] was also unsuccessful.

The sulfur-containing boronic acids were prepared in order to provide sulfur analogs of some known oxygenated boronic acids and some more recently prepared by other workers in this Laboratory. This will allow a comparison of chemical, physical and therapeutical properties of these two series.

Several attempts were made to obtain a halogen–metal interconversion in bromo-substituted benzeneboronic acids. This would have provided many possibilities for new syntheses. *p*-Bromobenzeneboronic acid, 2-hydroxy-5-bromobenzeneboronic acid and the reaction mixtures for their preparations prior to their hydrolysis were used as starting materials under a variety of conditions. All attempts were unsuccessful, but an interesting reaction, as shown in the reaction sequence, was observed when 2-hydroxy-5-bromobenzeneboronic acid (I) was treated with *n*-butyllithium under the conditions that give a halogen–metal interconversion for *p*-bromophenol.[7] Cleavage of the C–B bond by an organolithium reagent has not been reported previously in the literature. Apparently in this case it occurred by two different mechanisms. In the formation of 5-bromosalicylic acid (II), the cleavage seems to have been effected directly by *n*-butyllithium, since *n*-butaneboronic acid (IV) was among the reaction products. The isolation of *p*-hydroxybenzoic acid (III) shows that halogen–metal interconversion also took place, but there is no evidence that it did prior to the C–B bond cleavage, since when the reaction mixture was carbonated after a short time no III was obtained.



The products II and III were identified by mixed melting points and infrared spectra and IV by infrared spectrum only, since the difficulty in determining its melting point precluded obtaining a sufficiently definite datum.[8]

The available data do not allow a complete explanation of the reaction mechanism. Also, for the original purpose of the experiment, an excess of *n*-butyllithium was used. No further investigation was carried on, since this was not concerned directly with the present project.

Experimental

The melting points are uncorrected. The reported values were obtained with a pre-heated bath, where the starting temperature was determined by successive approximations and the final sample heated at almost constant temperature until it was completely liquefied, the heating period being carefully timed. The use of a Maquenne block may be helpful. All reactions were carried out under a dry, oxygen-free nitrogen atmosphere and employed ether dried over sodium. The end of the reaction between the aryllithium compound and tri-*n*-butyl borate was always checked by Color Test I.[9] For the neutralization equivalent, the sample, dried at room temperature in a flow of dry nitrogen, was dissolved in 50% ethanol containing twenty times the sample weight of D-mannitol, and the titration was carried out with standard sodium hydroxide using phenolphthalein to detect the end-point.

2-Hydroxy-5-bromobenzeneboronic Acid.—To a stirred solution of 15 g. (0.06 mole) of tri-*n*-butyl borate in 15 ml. of ether, the mixture from the metalation with phenyllithium of the 2-tetrahydropyranyl acetal of *p*-bromophenol (containing a theoretical 0.06 mole of 2-tetrahydropyranoxy-5-bromophenyllithium)[10] was added slowly while cooling at −70°. The resulting reaction mixture was stirred at the low temperature for 12 hr. and then allowed to warm up to about 0° and hydrolyzed with cold 10% hydrochloric acid. The ether layer was separated from the aqueous layer, the latter being washed twice with fresh ether, and the combined ether layers being extracted repeatedly with 10% sodium hydroxide. The chilled alkaline extract was acidified with 10% hydrochloric acid, and 9.5 g. (73.5%) of material melting over the range of 149–157° was obtained.

The crude product was extracted twice with hot acetone, a charcoal treatment being employed, and warm water was added to the hot extract until turbidity resulted. Upon cooling there was obtained 4.98 g. (38.7%) of crystals melting at 185–186°. These gave a violet color with ferric chloride. The infrared analysis supported the expected structure.

The analytical sample was recrystallized again from benzene and then from acetone and water to give a product melting at 190° with resolidification. The optimum pro-

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(6) F. R. Bean and J. R. Johnson, THIS JOURNAL, **54**, 4415 (1932).

(7) H. Gilman and F. J. Webb, *J. Org. Chem.*, **10**, 374 (1945).

(8) We are indebted to Dr. R. O. Ranck for preparing an authentic sample of *n*-butaneboronic acid and matching its spectrum against that of the product IV from the above reaction.

(9) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(10) L. Santucci and H. Gilman, *J. Org. Chem.*, in press.

portions of solvents were found to be 11 ml. of acetone and 36 ml. of water per gram of product.

Anal. Calcd. for $C_6H_6BBrO_3$: Br, 36.85; neut. equiv., 216.87. Found: Br, 36.77, 36.49; neut. equiv., 218.5.

A sample twice recrystallized from benzene gave a boron analysis and a neutralization equivalent closer to the calculated values for the anhydride. Also, the infrared spectrum differed from the spectrum of the acid in that the B–O bands were altered and the one at 9.7 μ was absent.

Alkaline extraction with 10% sodium carbonate was also tried. A purer crude product was obtained, melting at about 174°, but the extraction was very time consuming and incomplete.

This compound also was prepared by reaction of the acetal with *n*-butyllithium[10] in molar ratios of 1:1 and 1:0.5 followed by reaction with tri-*n*-butyl borate as described above. The best pure yields, 31 and 28.3%, were obtained for the longest time of reaction (11 hr.) between the acetal and *n*-butyllithium that was tried. The reaction with 0.5 equivalent of *n*-butyllithium, in which 20% sodium hydroxide was used for the alkaline extraction, yielded the purest crude product of all (m.p. 187.5–190°).

2-Methoxy-5-bromobenzeneboronic Acid.—To a stirred solution of 46.0 g. (0.2 mole) of tri-*n*-butyl borate in 60 ml. of ether, 0.15 mole of 2-methoxy-5-bromophenyllithium[11] in 165 ml. of ether was added slowly while cooling at −70°, then the reaction mixture was stirred overnight at the low temperature and subsequently hydrolyzed with 10% hydrochloric acid. The ether layer was extracted four times with 10% sodium hydroxide, additional water being added to dissolve the abundant solid which precipitated during this treatment. The combined alkaline extracts were acidified with 10% hydrochloric acid to give 21.4 g. (62%) of white crystals melting at 128–128.7°. One recrystallization from 75 ml. of acetone and 100 ml. of water yielded 19.6 g. (57%) of product melting at 130.5–131° with resolidification. This compound gave no color with ferric chloride. The infrared analysis supported the expected structure. Another run gave essentially similar results.

Anal. Calcd. for $C_7H_8BBrO_3$: B, 4.68; Br, 34.62; neut. equiv., 230.89. Found: B, 4.48; Br, 34.56, 34.84; neut. equiv., 231.8.

2-Hydroxy-6-methoxybenzeneboronic Acid.—To a stirred solution of 18.5 g. (0.08 mole) of tri-*n*-butyl borate in 25 ml. of ether, 0.04 mole of 2-hydroxy-6-methoxyphenyllithium[10] in 75 ml. of ether was added slowly while cooling at −70°, then the reaction mixture was stirred for 3 hr. at the low temperature and hydrolyzed with 10% hydrochloric acid. The ether layer was extracted five times with 10% sodium carbonate, and the combined alkaline extracts were acidified to a *p*H of 2 with 10% hydrochloric acid. An oil, which solidified on cooling, separated, yielding 0.85 g. (12.7%) of crystals melting at 91–92.5°. This was recrystallized from ethylene dichloride to give 0.17 g. of material melting at 100–101° and giving a violet color with ferric chloride. A neutralization equivalent of 162 was obtained, the calculated value for the acid being 168.01 and for the anhydride, 150.00. The infrared spectrum indicated a boronic acid of the expected structure.

Another run where the reaction mixture was stirred overnight at −70° and was hydrolyzed with saturated ammonium chloride did not give any better results. Also, additional alkaline extraction with 10% sodium hydroxide did not yield any more product.

The product could not be purified further. After a few days of standing in the open an increase of weight was observed and an oily material had separated from the solid. The residual solid was found to be boric acid by infrared analysis and mixed m.p.

***p*-Methylmercaptobenzeneboronic Acid.**—To a stirred solution of 13.83 g. (0.06 mole) of tri-*n*-butyl borate in 35 ml. of ether 0.03 mole of *p*-methylmercaptophenyllithium[12] in 165 ml. of ether was added slowly while cooling at −70°; then the reaction mixture was stirred overnight at the low temperature and hydrolyzed with 10% hydrochloric acid. The ether layer was extracted five times with 10% sodium hydroxide, and the combined alkaline extracts were poured slowly into a stirred excess of saturated ammonium chloride solution to give 3.59 g. of white product melting at 194–203°. By acidification of the mother liquor to a *p*H of 2 with 10% hydrochloric acid, another 0.66 g. of product melting at 197–198° was collected. The total crude yield was 84%. The crude product was recrystallized from water to give 2.35 g. (46.5%) of plate-like crystals melting at 204–206°. Another recrystallization yielded 2.16 g. (43%) melting at 209–209.5°. The infrared analysis supported the expected structure.

Anal. Calcd. for $C_7H_9BO_2S$: B, 6.47; S, 19.09; neut. equiv., 167.91. Found: B, 6.79, 6.74; S, 18.43, 18.60; neut. equiv., 167.5, 169.1.

Another similar experiment gave a 53% yield of product melting at 208.5–209.5° after one recrystallization.

2-Thianthreneboronic Acid.—To a stirred solution of 4.63 g. (0.02 mole) of tri-*n*-butyl borate in 10 ml. of ether, 0.01 mole of 2-thianthrenyllithium[13] in 48 ml. of ether was added slowly while cooling at −70°; then the reaction mixture was stirred overnight at the low temperature and hydrolyzed with 10% hydrochloric acid. The ether layer was extracted eight times with 10% sodium hydroxide, more water being added to dissolve the abundant solid which precipitated during this treatment. This extract was acidified with 10% hydrochloric acid. A yield of 1.71 g. (70.7%) of a white microcrystalline product melting at 200–210° was obtained.

Seven-tenths gram of the crude product was recrystallized from 15 ml. of acetone and 20 ml. of water to give 0.55 g. (63.4%) of plate-like crystals melting at 214.5–215.3° with dehydration occurring at 169°. Another recrystallization from acetone and water gave a quantitative yield of product melting at 215–216° with dehydration occurring at 170°. This product showed O–H bands by the infrared analysis and had a neutralization equivalent of 282.3. The calculated equivalent for the acid is 260.13.

Another 0.60 g. of crude product was recrystallized from acetone and water and then from ethylene dichloride to give 0.32 g. (37.5%) of minute white crystals melting at 226° without an intermediate dehydration point. Further recrystallization from dry ethylene dichloride did not affect the melting point. This sample did not show O–H absorption bands in the infrared spectrum and had the neutral equivalent calculated for the anhydride.

Anal. Calcd. for $C_{12}H_7BOS_2$: neut. equiv., 242.12. Found: neut. equiv., 242.0.

4-Phenoxathiinboronic Acid.—To a stirred solution of 23.1 g. (0.10 mole) of tri-*n*-butyl borate in 20 ml. of ether, 0.05 mole of 4-phenoxathiinyllithium[14] in 180 ml. of ether was added slowly while cooling at −70°; then the reaction mixture was stirred at the low temperature for 7 hr. and hydrolyzed with 10% hydrochloric acid. The ether layer was extracted with 10% sodium carbonate and then with 10% sodium hydroxide. The first extraction, acidified with 10% hydrochloric acid, produced 0.60 g. of a boron-containing organic material melting at about 270°, possibly a diboronic acid. During the second extraction, some product precipitated. This could not be dissolved completely by the addition of water, so that it was collected apárt, to yield 5.00 g. of product melting at 155–157° upon acidification of its water suspension. The filtered alkaline extracts were poured slowly into a stirred excess of saturated ammonium chloride solution to give 2.30 g. of material melting at 148–153°. Another 0.37 g. of solid melting at 153–153.5° was obtained by further acidification of the mother liquor with 10% hydrochloric acid. The total crude yield was 65.5%.

One and fifteen-hundredths grams of the crude product was recrystallized from 15 ml. of acetone and 10 ml. of water to give 0.46 g. (26.3%) of needles melting at 155.5–157.5° with resolidification occurring at 159.5°. Another recrystallization from acetone and water yielded 0.25 g. of product melting at 156.8–157.5° with resolidification at 158.7°.

Anal. Calcd. for $C_{12}H_9BO_3S$: B, 4.44; S, 13.14; neut. equiv., 244.07. Found: B, 4.67, 4.77; S, 13.33, 13.23; neut. equiv., 246.0, 246.8.

Cleavage of 2-Hydroxy-5-bromobenzeneboronic Acid.—To a stirred solution of 2.17 g. (0.01 mole) of 2-hydroxy-5-bromobenzeneboronic acid in 13 ml. of ether, 38 ml. of 1.3 *N* *n*-butyllithium (0.05 mole) was added at room tempera-

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[11] G. Wittig, U. Pockels and H. Dröge, *Ber.*, **71**, 1903 (1938).

[12] H. Gilman and F. J. Webb, THIS JOURNAL, **71**, 4062 (1949).

[13] H. Gilman and D. R. Swayampati, *ibid.*, **79**, 208 (1957).

[14] H. Gilman and S. H. Eidt, *ibid.*, **78**, 2633 (1956).

ture over a period of 10 minutes. The reaction mixture was refluxed for 1.5 hr., then carbonated by pouring into a stirred slurry of Dry Ice and ether and subsequently hydrolyzed with 10% hydrochloric acid. The ether layer from the hydrolysis, combined with two ether washings of the aqueous layer, was extracted with 8% sodium bicarbonate and 5% sodium hydroxide.

The sodium bicarbonate extract was made strongly acidic to give 0.83 g. (38%) of 5-bromosalicylic acid (II) having a melting point of 165.5–167.5°, identified by a mixed melting point and infrared analysis. After concentration of the acid mother liquor, 0.16 g. (12%) of impure *p*-hydroxybenzoic acid (III) melting at 197.5–199° separated. An infrared analysis identified the material beyond doubt.

The sodium hydroxide extract yielded, upon acidification, 0.10 g. of boron-containing crystals melting at 85–87°. The product was recrystallized from ethylene dichloride, but the material obtained decomposed before any test could be effected. The crude product gave no color with ferric chloride, and its infrared analysis showed the presence of an alkyl group, borono group and hydroxyl group and the absence of a phenyl ring and a carboxy group. This spectrum was identical to that of an authentic specimen of *n*-butaneboronic acid. The reported melting point for *n*-butaneboronic acid is 92–94°. The yield, calculated for this compound, is 10%.

When the mixture was carbonated 18 minutes after the addition, there was obtained 30% of II and 10% of *n*-butaneboronic acid. No III was isolated.

Acknowledgment.—We wish to thank Mr. Robert McCord and Mr. E. Miller Layton of the Ames Laboratory of the Atomic Energy Commission for the infrared spectra.

We also wish to acknowledge the support of the Division of Biology and Medicine of the United States Atomic Energy Commission who have helped make this work possible. The results of the biological testing of these compounds will be reported by Dr. Otho D. Easterday of the Brookhaven National Laboratory.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

α-Ketoethers. I. The Reaction of α-Phenoxyacetophenone with Sodium and with Sodium Amide[1]

BY PETER YATES, DONALD G. FARNUM AND GEORGE H. STOUT[2]

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The orange product from the reaction of α-phenoxyacetophenone with sodium in xylene or with sodium amide in ether and methanol is shown to be 1,2,3-tribenzoylpropene (II). The equilibrium between II and its enol IIa is discussed on the basis of infrared and ultraviolet spectral data. The reaction of II with hydrazine is shown to yield the hydrazone of 4-phenacyl-3,6-diphenylpyridazine (V). The mechanism of the formation of II is discussed.

Kostanecki and Tambor,[3] in an attempted synthesis of 3-hydroxyflavone, reacted α-phenoxyacetophenone (I) with ethyl *o*-ethoxybenzoate in the presence of sodium; they obtained, in unreported yield, an orange compound, $(C_8H_6O)_x$, m.p. 120°, which they subsequently showed could also be obtained by the action of sodium in warm xylene on α-phenoxyacetophenone alone.[4] This product was found to be soluble in aqueous sodium hydroxide, from which it was precipitated by passage of carbon dioxide. Reduction with zinc and acetic acid gave a white compound, m.p. 118°, for which no analysis was reported. The only conclusion drawn by these authors was that the orange compound was neither *trans*- nor *cis*-dibenzoylethylene. As part of a general study of the chemistry of α-ketoethers, we have investigated further the nature of this product.

Treatment of I in xylene solution with sodium at 40 to 50° for 40 hr. yielded an orange compound, II, corresponding in properties to Kostanecki's compound. The yield of II, however, was only 7.5% and was improved only slightly by the use of refluxing ether as solvent. It was later found that the same product could be obtained in 48% yield by the reaction of I with sodium amide in ether containing a small amount of methanol at 10° under nitrogen. Several recrystallizations from ethanol gave II as fine, orange needles. On the basis of analysis and titration it was assigned the formula $C_{24}H_{18}O_3$.[6] Its infrared and ultraviolet spectra are characterized by their striking solvent dependence (see Table I). This was early attributed to a mobile tautomeric equilibrium whose operation was also evidenced by the small, but distinct, variations in the melting points of samples with different histories: while all samples normally melted sharply at temperatures between 118° and 123°, it was found that a sample stirred in a slowly heated mineral oil-bath did not melt until the bath temperature reached 138°. Similar phenomena

TABLE I

INFRARED AND ULTRAVIOLET SPECTRA OF II IN VARIOUS SOLVENTS

Solvent	λ_{max}, mμ	log ε	Solvent	λ_{max}, μ
Isoöctane	243	4.45	Carbon tetrachloride	5.93(s)
	248	4.40		6.01(s)
Ethanol	254	4.26		6.20(w)
	406	4.28	Nujol mull	3.10(m)
Ethanolic NaOH (0.5%)	258	4.34		6.14(m)
	487	4.61		6.52(vs)
			Chloroform	5.93(s)[a]
				6.00(s)
				6.18(w)
				6.48(m)

[a] Shoulder.

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(1) A preliminary account of this work has appeared in *Chemistry & Industry*, 821 (1956).

(2) National Science Foundation Pre-doctoral Fellow, 1953–1955.

(3) St. v. Kostanecki and J. Tambor, *Ber.*, **35**, 1679 (1902).

(4) Stoermer and Atenstädt[5] have also treated I with sodium but reported only that no steam-volatile product was formed.

(5) R. Stoermer and P. Atenstädt, *Ber.*, **35**, 3560 (1902).

(6) Since II is a very weak acid the titration values were approximate only; this molecular formula was corroborated by the formulas of the transformation products discussed below.