[Contribution from Noyes Chemical Laboratory, University of Illinois]

Conversion of *meso*-Hydrobenzoin with Arylsulfonyl Chlorides and Base to *trans*-Stilbene Oxide and to 1,1-Diphenyl-2-(*p*-toluenesulfonyloxy)ethylene[1]

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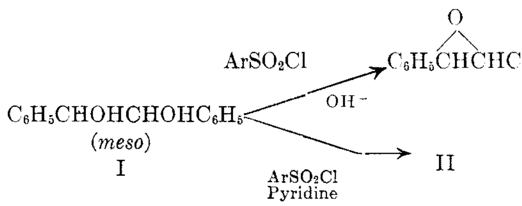
meso-Hydrobenzoin is converted to *trans*-stilbene oxide by treatment with an arylsulfonyl chloride and aqueous sodium hydroxide. With *p*-toluenesulfonyl chloride in pyridine at temperatures below 0° the major product, isolated in 5% yield, is 1,1-diphenyl-2-*p*-toluenesulfonyloxyethylene formed with a rearrangement of the carbon skeleton. The characterization of this product is discussed.

In the course of another investigation[3] it was desired to examine the possibility of preparing stilbene oxides from hydrobenzoins. A number of glycols such as *trans*-cyclopentanediol,[4] *trans*-cyclohexanediol,[5] *trans*-cycloheptanediol,[6] glycerol,[7] and certain polyhydroxy compounds[8] have been converted to the corresponding epoxides by treatment with one mole of *p*-toluenesulfonyl chloride and then reaction of the monotoluenesulfonate with base. In a number of cases the intermediate mono-*p*-toluenesulfonate could be isolated. Eliel and Delmonte[9] have used the reaction to interrelate the configurations of (−)-phenylethane-1,2-diol and (+)-styrene oxide.

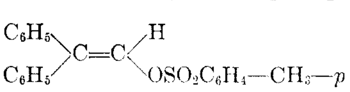
To initiate the present study, *meso*-hydrobenzoin (I) was treated with *p*-bromobenzenesulfonyl chloride in acetone at 0° and aqueous sodium hydroxide was added. A 23% yield of purified *trans*-stilbene oxide was obtained together with 40% of recovered glycol. Similar results were obtained when *meso*-hydrobenzoin was treated with one mole of sodium hydride (to give the mono-sodium salt) and then a mole of *p*-toluenesulfonyl chloride was added and the mixture was treated with sodium ethoxide. In this case 10% of the di-*p*-toluenesulfonate was also formed.

When *meso*-hydrobenzoin (I) was treated with *p*-toluenesulfonyl chloride in pyridine at temperatures below 0°, a 5% yield of a new solid compound, shown below to be 1,1-diphenyl-2-[*p*-toluenesulfonyloxy]-ethylene (II) was obtained together with 35% of recovered glycol. The same compound (II) was obtained in 1.4% yield when I, suspended in ether, was treated successively with 1 mole of butyllithium, 1 mole of *p*-toluenesulfonyl chloride, and then a second mole of butyllithium.

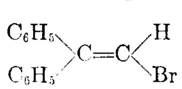
Evidence for the structure (II) is as follows. The infrared spectrum shows no significant absorption in the region between 3200 and 3600 cm.$^{-1}$ from which it is concluded that no hydroxyl group is present. The absence of an absorption maximum between 1640 and 2000 cm.$^{-1}$ indicates that no carbonyl group has been introduced. A small band at 1635 cm.$^{-1}$ is consistent with the presence of a carbon-carbon double bond and absorption at 1175, 1185, and 1360 cm.$^{-1}$ indicate clearly that the substance is a sulfonate ester.[10]

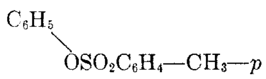


The ultraviolet spectrum of the sulfonate ester (II) provides even more striking evidence. It is seen that the ultraviolet spectrum of II might be approximated by adding together the spectra of



II





a simple *p*-toluenesulfonic ester and a 1,1-diphenylethylene derivative.[11] Phenyl *p*-toluenesulfonate and 2-bromo-1,1-diphenylethylene were chosen and it can be seen in Fig. 1 that the sum of their spectra is quite similar to the spectrum of the product (II).

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[2] American Cyanamid Company Fellow, 1953–1954. We are indebted to E. I. du Pont de Nemours and Company, Inc. for a Grant-in-Aid which supported a part of this work.

[3] Curtin, Bradley, and Hendrickson, *J. Am. Chem. Soc.*, **78**, 4064 (1956).

[4] Owen and Smith, *J. Chem. Soc.*, 4026 (1952).

[5] Criegee and Stanger, *Ber.*, **69**, 2753 (1936); Clark and Owen, *J. Chem. Soc.*, 315 (1949).

[6] Owen and Saharia, *J. Chem. Soc.*, 2582 (1953).

[7] Sowden and Fischer, *J. Am. Chem. Soc.*, **64**, 1291 (1942).

[8] Peat and Wiggin, *J. Chem. Soc.*, 1088 (1938).

[9] Eliel and Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

[10] R. S. Tipson, *J. Am. Chem. Soc.*, **74**, 1354 (1952).

[11] See R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth Edition, John Wiley and Sons, New York, 1956, pp. 185–188, for a discussion of the additivity of ultraviolet spectra in this way.

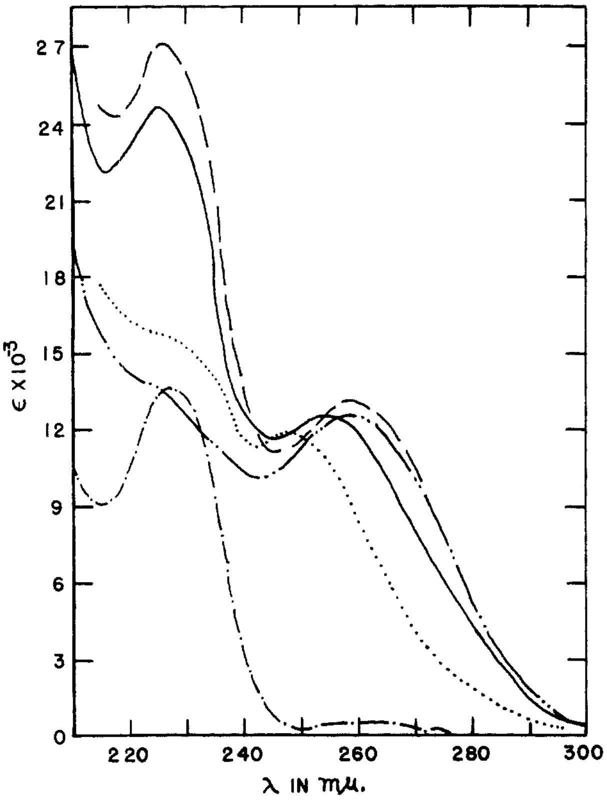
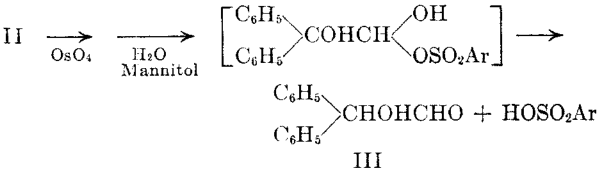


FIG. 1.—ULTRAVIOLET SPECTRA of 1,1-diphenyl-2-[*p*-toluenesulfonyloxy]ethylene (II) (———); 1,1-diphenylethylene in 95% ethanol (......); 1,1-diphenyl-2-bromoethylene (—··—··—); phenyl *p*-toluenesulfonate in 95% ethanol (—·—·—·); and the sum of the curves of phenyl *p*-toluenesulfonate and 1,1-diphenyl-2-bromoethylene (— — — —).

Comparison of the spectrum with those of *cis*- and *trans*-stilbene rules out the possibility of a 1,2-diphenylethylene skeleton since such structures have absorption maxima at 280–320 mμ.

Chemical evidence confirming the assigned structure for II was obtained by oxidation with osmium tetroxide. An osmate ester was obtained which, when hydrolyzed in the presence of mannitol gave an oil which was apparently a mixture of the expected product, β,β-diphenyl-α-hydroxypropionaldehyde (III) with benzophenone obtained by further oxidation of III. Infrared absorption at 3500, 2860, and 1725 cm.$^{-1}$ corresponds to that to be expected of such hydroxy aldehyde.[12]

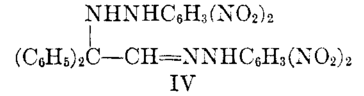
The presence of benzophenone as a major reaction product was indicated both by a band at 1660 cm.$^{-1}$ in the infrared spectrum of the reaction mixture and by isolation of its 2,4-dinitrophenylhydrazone on treatment of the mixture with dinitrophenylhydrazine. The formation of benzophenone provides strong supporting evidence for the presence of the 1,1-diphenylethylene carbon skeleton in II. While the possibility of a phenyl migration during the osmium tetroxide oxidation must be considered, oxidations with this reagent are, in general, notable for their freedom from such abnormalities.[13]



$$\mathrm{II} \xrightarrow[\mathrm{OsO_4}]{} \xrightarrow[\text{Mannitol}]{\mathrm{H_2O}} \left[\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{C_6H_5}\end{matrix}\!>\!\mathrm{COHCH}\!<\!\begin{matrix}\mathrm{OH}\\ \mathrm{OSO_2Ar}\end{matrix}\right] \longrightarrow \underset{\mathrm{III}}{\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{C_6H_5}\end{matrix}\!>\!\mathrm{CHOHCHO}} + \mathrm{HOSO_2Ar}$$

The presence of benzophenone is not surprising since Danilow found that the hydroxyaldehyde (III) gave this ketone even on treatment with boiling ethanol.[14]

The oily reaction mixture containing (III) gave on treatment with 2,4-dinitrophenylhydrazine (in addition to the 2,4-dinitrophenylhydrazone discussed above), a product believed to have the structure IV. The principal evidence is that from the ultraviolet spectrum (Fig. 2) which is very



$$\mathrm{(C_6H_5)_2}\overset{\mathrm{NHNHC_6H_3(NO_2)_2}}{\overset{|}{\mathrm{C}}}\mathrm{-CH{=}NNHC_6H_3(NO_2)_2}$$

IV

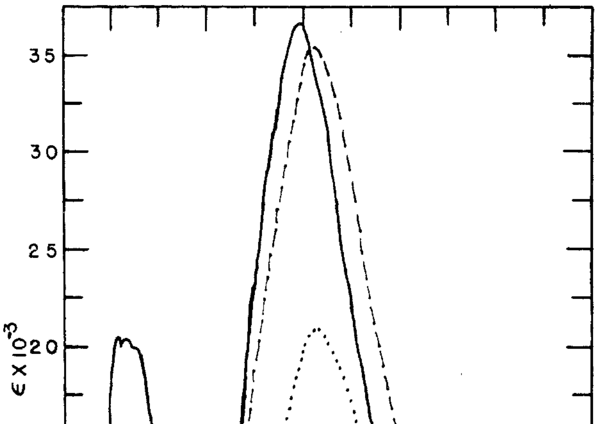


FIG. 2.—ULTRAVIOLET SPECTRA of the 2,4-dinitrophenylhydrazine derivative of the hydroxyaldehyde III in ethyl acetate solution (———); acetaldehyde 2,4-dinitrophenylhydrazone in 95% ethanol (......); 2,4-dinitrophenylhydrazine in 95% ethanol (—··—··—··); the sum of the curves for 2,4-dinitrophenylhydrazine and acetaldehyde 2,4-dinitrophenylhydrazone (— — — —).

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[12] S. Pinchas, *Anal. Chem.*, **27**, 2 (1955).

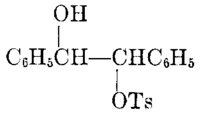
[13] R. Criegee. *Ann.*, **522**, 75 (1936); R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942); M. Mugdan and D. Young, *J. Chem. Soc.*, 2997 (1949).

[14] S. Danilow, *Ber.*, **60**, 2390 (1927).

similar to the sum of the spectra of 2,4-dinitrophenylhydrazine and acetaldehyde 2,4-dinitrophenylhydrazone. While the hydroxyaldehyde (III) has been reported[14] to form a semicarbazone and an oxime in the normal manner, the replacement of the hydroxyl group by a second mole of dinitrophenylhydrazine is not entirely unexpected since the presence of the two phenyl rings might be expected to cause unusual reactivity toward this type of replacement.

It was hoped that it might be possible to hydrolyze the enol tosylate (II) to diphenylacetaldehyde with acid but the starting material (76%) was recovered even after 3 hours of treatment with 40% (by volume) sulfuric acid. The tosylate (II) did react slowly with cold concentrated sulfuric acid but no product precipitated when the solution was diluted with water.

The course of the formation of the enol tosylate (II) from hydrobenzoin is of particular interest. It is possible that it involves a base-catalyzed rearrangement of the glycol monotosylate (V), analo-



$$C_6H_5\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—}\underset{\underset{\text{OTs}}{|}}{\text{CH}}C_6H_5$$

V

gous to the formation of methyl cyclopentyl ketone from *cis*-2-chloro-1-methylcyclohexanol on treatment with base.[15] There appears to be no authentic example of such a rearrangement of a group from one carbon atom to another in an acyclic system although the benzilic acid rearrangement and base-catalyzed α-hydroxy ketone rearrangements[16] are related. An alternative which cannot be excluded is that the ditosylate of glycol I is an intermediate in the rearrangement.

EXPERIMENTAL[17]

Preparation of trans-stilbene oxide. To a mixture of 2.14 g. (0.0100 mole) of *meso*-hydrobenzoin I, m.p. 136–138°, and 2.56 g. (0.0100 mole) of *p*-bromobenzenesulfonyl chloride, m.p. 74.5–76°, at 0° was added with stirring over a period of 10 minutes a solution of 10 g. of sodium hydroxide in 50 ml. of water and then 30 ml. of acetone. The mixture was stirred for 1 hour and poured into 200 ml. of crushed ice and water. A white solid (1.67 g., m.p. 88–112°) separated and, on recrystallization from ethanol gave 0.68 g. (31%) of crude recovered I, m.p. 123–129°, and from the filtrate as a second fraction 0.46 g. (23%) of *trans*-stilbene oxide, m.p. 66.5–68°, mixture m.p. with an authentic sample, 66.5–68°. The infrared spectrum of this substance was identical with that of authentic *trans*-oxide.

An experiment in which twice the above amount of *p*-bromobenzenesulfonyl chloride was employed gave 14% of *trans*-stilbene oxide, m.p. 65–66.5°. Reaction mixtures prepared as above but without the acetone gave no epoxide at 0° or 100°. An attempt to carry out the reaction in dioxane at room temperature also yielded none of the desired product.

An alternative method was somewhat less satisfactory. The glycol (I) (5.35 g., 0.025 mole), m.p. 136–138°, was converted to its sodium salt by treatment with 0.62 g. (0.026 mole) of sodium hydride in 100 ml. of anhydrous ether for 24 hours under reflux and with stirring. The stirred slurry was cooled to −25° and a solution of 4.75 g. (0.025 mole) of *p*-toluenesulfonyl chloride, [m.p. 69–70.5°, b.p. 144–146° (15 mm.)] in 100 ml. of dry ether was added. The reaction mixture was stirred for 1 hour at −25° to −18°, 1 hour at −18° to −7°, and 1.5 hours at room temperature. Sodium ethoxide free from ethanol[18] was added and the slurry resulting was stirred for 7.5 hours at room temperature. The reaction mixture was filtered and the precipitate was extracted with ether. The extracts were washed with some water and dried over sodium sulfate. Evaporation of the ether left 3.55 g. of yellow oil which was dissolved in 30 ml. of 95% ethanol (except for 0.19 g. of insoluble oil which was discarded). Water was added to the warm ethanolic solution until it became cloudy after which the solution, on cooling, gave 1.1 g. (22%) of crude *trans*-stilbene oxide, m.p. 64–67°. Recrystallization from 200 ml. of 70% aqueous ethanol gave 0.61 g. (12%) of epoxide, m.p. 68.5–69.5°, mixture m.p. with authentic epoxide, 68–69°. The solid not extracted by the ether in the original extraction was washed with 500 ml. of water and was collected by filtration to give 2.08 g. of solid, m.p. 151–151.5°. Recrystallization from 40% chloroform in carbon tetrachloride gave 9.8% of crude *meso-hydrobenzoin di-p-toluenesulfonate* as a fraction of 0.48 g., m.p. 145–145.5° (dec.), and 0.80 g., m.p. 140° (dec.). Starting material (I), (0.59 g., m.p. 128–138°) was also obtained. Several recrystallizations of the di-*p*-toluenesulfonate from 30% benzene in hexane gave white needles, m.p. 145.5° (dec.).

Anal. Calc'd for $C_{28}H_{26}O_6S_2$: C, 62.9; H, 5.0; S, 12.3. Found: C, 63.0; H, 5.3; S, 11.7.

An infrared spectrum of this substance in a Nujol mull showed no absorption above 3100 cm.$^{-1}$ nor between 1625 and 2000 cm.$^{-1}$.

Conversion of I to 1,1-diphenyl-2-p-toluenesulfonyloxyethylene (II). To *meso*-hydrobenzoin, m.p. 136.5–137.5°, (8.56 g., 0.0400 mole) in 100 ml. of pyridine at 0 to −3° was added a solution of 6.74 g. (0.0400 mole) of *p*-toluenesulfonyl chloride in 50 ml. of pyridine over a period of 1 hour. After 10 hours of stirring with cooling, the pyridine was removed by distillation under a vacuum and the residue was extracted with 200 ml. of water and of ether. Evaporation of the ether gave a brown jelly-like residue which was dissolved in warm 80% aqueous ethanol, decolorized with charcoal, and concentrated to yield, first, 0.12 g. of a solid, m.p. 145.5° (dec.), probably the di-*p*-toluenesulfonate of glycol (I). Further concentration of the filtrate yielded 1.10 g. of crude 1,1-diphenyl-2-*p*-toluenesulfonyloxyethylene (II), m.p. 106–107°. Further concentration gave 2.56 g. of impure I, m.p. 121.5–133°. Additional I (0.39 g., m.p. 133.5–138°) was obtained by recrystallization from chloroform a small amount of solid which had been insoluble in the original water and ethanol extractions. The total amount of recovered I was thus 35%.

Recrystallization of the crude enol *p*-toluenesulfonate(II) from 85% aqueous ethanol gave 0.69 g. (5%) of white plates of II, m.p. 111–111.5°.

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(15) P. D. Bartlett and R. B. White, *J. Am. Chem. Soc.*, **56**, 2785 (1934).

(16) See R. B. Turner, *J. Am. Chem. Soc.*, **75**, 3484 (1953) for references.

(17) All melting points are corrected. Microanalyses were carried out by Mr. Josef Nemeth, Mrs. Katherine Pih, Mrs. Esther Fett, Mrs. Lucy Chang, Mr. Rollo Nesset, Mrs. Doreen Mosier, and Mrs. Marie Benassi of the University of Illinois Microanalytical Laboratory and by the Clark Microanalytical Laboratory, Urbana, Illinois. Infrared spectra were measured by Miss Helen Miklas, Mrs. Rosemary Hill, and Mr. James Brader. Ultraviolet spectra were obtained by Mrs. Barbara Burnett, Mrs. Rosemary Hill, and Miss Gerardine Meerman.

(18) Koelsch, *J. Am. Chem. Soc.*, **54**, 2487 (1932).

Anal. Calc'd for $C_{21}H_{18}O_3S$: C, 72.0; H, 5.2; S, 9.1. Found: C, 71.6; H, 5.5; S, 9.0.

The infrared spectrum showed strong bands at 1385, 1360, 1196, 1185, and 1068 cm.$^{-1}$ and moderate bands at 1638, 1605, 1504, 1453, 1036, 950, and at 915 cm.$^{-1}$ when measured in chloroform as a 5% solution in an 0.1-mm. cell.

Alternatively, 8.56 g. (0.040 mole) of I, m.p. 136.5–137.5° in 150 ml. of dry ether cooled in an ice-salt bath was treated over a period of 0.5 hours with an ethereal solution containing 0.04 mole of butyllithium in 25 ml. of ether. A gas was evolved and the alcohol went into solution on the addition of the butyllithium. After 0.5 hour, 8.20 g. (0.043 mole) of *p*-toluenesulfonyl chloride in 80 ml. of dry ether was added in two portions over a period of 2.25 hours. Another portion of butyllithium solution equal to that above then was added after which a white precipitate appeared. After standing overnight, the mixture was filtered, the filtrate concentrated, and the residue dissolved in 70 ml. of hot 95% ethanol and water was added until the solution became cloudy. Cooling and concentration gave 2.47 g. of solid, m.p. 62–74°, which when recrystallized from 25 ml. of 95% ethanol (with enough water added to make the solution cloudy when hot) gave 1.73 g. of the enol *p*-toluenesulfonate (II), m.p. 85–95°. Recrystallization of this solid from 50% ligroin-50% hexane gave 1.00 g. (7%) of white needles of II, m.p. 112–114°, mixture m.p. with a sample from the reaction described above, 112–112.5°. A total of 18% of I was recovered by concentration of the first ethanol filtrate. In addition, 0.11 g. (1.4%) of *trans*-stilbene oxide, m.p. 68.5–70°, was obtained.

Another experiment in which two moles of butyllithium were added before the *p*-toluenesulfonyl chloride gave similar results.

Osmium tetroxide oxidation of 1,1-diphenyl-2-[p-toluenesulfonyloxy]ethylene (II). To a solution of 0.69 g. (0.0020 mole) of II, m.p. 112.8–114°, in 15 ml. of dry ether and 2 ml. of dry pyridine was added 0.50 g. (0.0020 mole) of osmium tetroxide dissolved in 15 ml. of dry ether. A yellow-brown precipitate began to form within 1 minute. The mixture was allowed to stand for 14 hours and the precipitate was filtered and washed with cold ether (25 ml.) to yield 1.62 g. of crude osmate ester. The ester was dissolved in 20 ml. of redistilled chloroform and the red solution was shaken for 70 minutes with a solution of 0.5 g. (0.009 mole) of potassium hydroxide and 2.0 g. (0.011 mole) of mannitol, m.p. 167.5–170° in 40 ml. of water. Extraction with water, acidification of the aqueous layer with 10 ml. of concentrated hydrochloric acid, extraction with ether and removal of the ether gave a dark red oil. Concentration of the chloroform layer also gave an oil. The two oils were combined and dried to leave 149 mg. of dark red oil of which the infrared spectrum was measured in a 5% chloroform solution in a 0.1-mm. cell. There was slight absorption at 3500 cm.$^{-1}$. A medium band at 2840 cm.$^{-1}$ and a band at 1725 cm.$^{-1}$ (with a shoulder at 1735 cm.$^{-1}$) were attributed to the desired hydroxyaldehyde (III). A stronger carbonyl band at 1658 cm.$^{-1}$ is attributed to benzophenone. Other strong bands appear at 1454, 1283, and 1322, 945, and 921, and 695 cm.$^{-1}$.

The oil was converted to the mixture of 2,4-dinitrophenylhydrazones by treatment of 137 mg. in 20 ml. of 95% ethanol with 0.40 g. of 2,4-dinitrophenylhydrazine dissolved in a solution of 2 ml. of concentrated sulfuric acid, 3 ml. of water, and 10 ml. of 95% ethanol for 6 days. Filtration gave 210 mg. of red-orange solid, m.p. 202–221°. Two recrystallizations from 50% ethyl acetate-50% ethanol gave 88 mg. of red-orange benzophenone 2,4-dinitrophenylhydrazone, m.p. 242.5–244°, mixture m.p. with an authentic sample, 243–244°. A second fraction after two recrystallizations from ethyl acetate–ethanol was obtained as 40 mg. of golden yellow solid, m.p. 200° (dec.). Two additional recrystallizations of this fraction from 25% nitromethane–75% ethanol gave 14 mg. of yellow solid believed to be the dinitrophenylhydrazone (IV).

Anal. Calc'd for $C_{26}H_{20}N_8O_8$: C, 54.6; H, 3.5. Calc'd for $C_{26}H_{18}N_8O_8$: C, 54.7; H, 3.2. Found: C, 54.3; H, 3.7.

The ultraviolet spectrum of this solid is shown in Fig. 2.

Attempt to hydrolyze the enol tosylate (II). The toluenesulfonate (II), (200 mg.) was refluxed for 3 hours with 10 ml. of concentrated sulfuric acid and 15 ml. of water. Cooling gave 152 mg. (76%) of starting material, m.p. 111.5–112.5°, mixture m.p. with starting material, 112–113°.

The enol sulfonate (II) was only slowly soluble in cold concentrated sulfuric acid, but dissolved more rapidly on heating to give a solution which, when poured into ice-water, gave no precipitate.

When 10 mg. of II, dissolved in 1 ml. of warm acetic acid, was treated with 10 mg. of 2,4-dinitrophenylhydrazine and 1 ml. of acetic acid containing a few drops of concentrated sulfuric acid, under reflux, and allowed to stand for several hours no precipitate formed.

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