20.3 g. (0.1 mole) of 1-methyl-3-ethyl-4-hydroxy-2-pyridone (V) "ethylmalonylmethylaniline" by procedure C above. The base prepared by sodium carbonate treatment of the hydrochloric acid extract was distilled in a wide-path distilling apparatus, discarding a little lower boiling material and collecting 30.17 g. of a liquid boiling at 181–208° (0.005 mm.). This solidified and had m.p. 73–76°, after one recrystallization from hexane. It was converted to its hydrochloride in ethanol, and recrystallized from ethanol–ether for analysis (m.p. 244–246°). It was very hygroscopic especially when wet with solvent. Thirty grams (72%) was obtained.

Anal. Calcd. for $C_{20}H_{31}Cl_2N_3O_2$: C, 57.69; H, 7.51. Found: C, 57.75; H, 7.30.

1-Methyl-3-ethyl-3-bromo-2,4-diketo-1,2,3,4-tetrahydroquinoline (Compound VII) and 1-Methyl-3-ethyl-3,6-dibromo-2,4-diketo-1,2,3,4-tetrahydroquinoline (Compound VIII).—A part solution–part suspension of 40.6 g. (0.2 mole) of finely ground 1-methyl-3-ethyl-4-hydroxy-2-quinolone ("ethylmalonylmethylaniline," Compound V) in 520 ml. of acetone-free methanol was stirred and treated with 37 g. (0.23 mole) of bromine dissolved in 100 ml. of carbon tetrachloride, added in about 30 sec. The initial rapid uptake of bromine slowed near the end of the addition. After 10 min., the solvents were evaporated at the water pump (steam bath). Some bromine was evolved. The residual oil was then dissolved in the minimal amount of boiling ethanol, diluted with ether, and extracted with 0.5 *M* aqueous sodium carbonate. Acidification of the carbonate solution gave 26 g. of precipitated acidic material, m.p. 161–186°. (The starting material had m.p. 184–186°.)

Concentration of the carbonate-extracted ethereal solution left 28.5 g. of a yellow oil, which soon solidified. This was washed with a little hexane, and then had m.p. 123–154°. It was recrystallized from 1.2 l. of hexane, giving 10.8 g. of yellow crystals, m.p. 148–152°. Concentration of the hexane solution to 300 ml. and storage at −14° led to crystallization of 12.2 g. of yellow solid, m.p. 84–88.5°. A third crop of m.p. 69–76° could be obtained by replacement of the hexane by *ca.* 20 ml. of anhydrous ether. The above mentioned second crop was recrystallized twice more from hexane (cooling to −14°) for analysis, m.p. 86–90°. It gave a satisfactory analysis for the mono bromo compound.

Anal. Calcd. for $C_{12}H_{12}BrNO_2$: C, 51.08; H, 4.29. Found: C, 50.80; H, 4.61.

The highest melting first crop above was recrystallized from hexane, cooling to 4°. It had m.p. 152–158°.

Anal. Calcd. for $C_{12}H_{11}Br_2NO_2$: C, 39.91; H, 3.07. Found: C, 40.45; H, 3.17.

1-Methyl-3-dimethylamino-3-ethyl-6-bromo-1,2,3,4-tetrahydroquinoline-2,4-dione (Compound IX).—This was prepared by mixing ethereal solutions of the bromo compound VIII (above) and excess of dimethylamine, and allowing the solution to remain for 2 days. A yield of 85% of the solid base was obtained, m.p. 120–122° after recrystallization from ethanol, and 5% of theory of an acidic material was also obtained. The base was a yellow solid.

Anal. Calcd. for $C_{14}H_{17}BrN_2O_2$: C, 51.70; H, 5.26. Found: C, 51.93; H, 5.11.

Acknowledgment.—We thank Dr. S. Blackman and Mr. C. Marr for the elemental analyses reported here.

1,2,4-Triazoles. VII.[1a] Dimethylformamide in the Synthesis of *s*-Triazoles and a Facile Opening of This Ring System

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Dimethylformamide has been shown to react with benzhydrazide benzenesulfonate yielding 4-benzamido-3-phenyl-*s*-triazolium benzenesulfonate (I), 1-benzoyl-4-formamidobenzhydrazidine (II), and 1-benzoyl-2-formylhydrazine, together with related products formed by self-condensation of benzhydrazide. Treatment with dilute alkali under mild conditions readily effected ring opening of the triazole nucleus of I, forming II; II can be converted into I with benzenesulfonic acid, and into 4-benzamido-3-phenyl-*s*-triazole (IV) with other cyclization agents.

Amides, and especially formamides, have proved particularly useful as a source of a one-carbon fragment bearing hydrogen in the synthesis of various nitrogen-containing heterocycles. It has been shown recently that dimethylformamide is protonated on the oxygen atom by strong acids[2] and that the oxygen atom is also the site of reaction with methyl sulfate,[3] phosphoryl chloride, and thionyl chloride,[4] and that with primary amines substituted amidines are formed. Because the *s*-triazole system may be regarded as incorporating the structural elements of an amidine, these results indicated that dimethylformamide might be a useful reagent for condensation with suitable intermediates in a synthesis of this ring system. This paper describes an application of dimethylformamide in the synthesis of 3,4-disubstituted *s*-triazoles with no substituent on carbon 5; this method is thus complementary to the ring closures of hydrazidines with ortho esters or acidic cyclodehydration agents that yield 1,3-disubstituted and 1,3,5-trisubstituted *s*-triazoles.[5] The usual methods employed in the synthesis of 4-substituted *s*-triazoles lead directly to the *s*-triazole system with substituents in the 3-, 4-, and 5-positions.[6]

Benzhydrazide benzenesulfonate and dimethylformamide at reflux temperature underwent reaction with formation of 4-benzamido-3-phenyl-*s*-triazolium benzenesulfonate (I) and 1-benzoyl-4-formamidobenzhydrazidine (II) as the major products. The addition of concentrated sodium hydroxide solution, followed by mineral acid, was essential for the isolation of I and this isolation procedure probably exerted a salting-out effect on the benzenesulfonate. High temperatures (about 155°) were necessary for the condensation to occur. At 100° the only basic product isolated from the re-

(1) (a) Part VI. P. J. Nelson and K. T. Potts, *J. Org. Chem.*, **27**, 3243 (1962). Part of this material has been published as a Preliminary Communication in *Chem. Ind.* (London), 2049 (1961). (b) Present address.

(2) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

(3) H. H. Bredereck, R. Gompper, H. Rempfer, K. Klemm, and H. Keck, *Chem. Ber.*, **92**, 329 (1959).

(4) (a) H. H. Bosshard and H. Zollinger, *Helv. Chim. Acta*, **42**, 1659 (1959); see also H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *ibid.*, **42**, 1653 (1959); (b) G. Tosolini, *Chem. Ber.*, **94**, 2731 (1961).

(5) A. Pinner, *Ber.*, **27**, 997 (1894); M. R. Atkinson and J. B. Polya, *J. Am. Chem. Soc.*, **75**, 1471 (1953); M. R. Atkinson and J. B. Polya, *Chem. Ind.* (London), 3319 (1954); D. Jerchel and R. Kuhn, *Ann.*, **568**, 185 (1950); W. Reid and F. Muller, *Chem. Ber.*, **85**, 170 (1952).

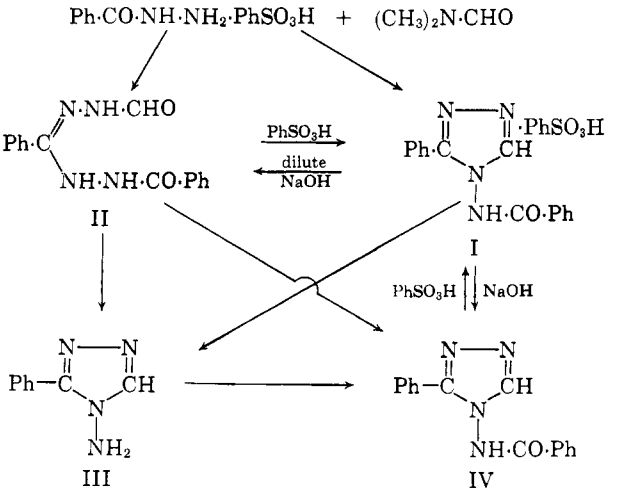
(6) K. T. Potts, *Chem. Rev.*, **61**, 87 (1961).

action mixture was benzhydrazide, obtained as its isopropylidine derivative by condensation with acetone used in the reaction work-up.

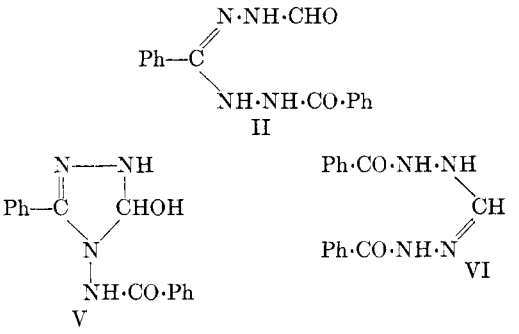
Structures I and II were assigned to these major products on the basis of the following evidence. Analytical data indicated a molecular formula of $C_{21}H_{18}N_4O_4S$ for I. It had typical salt-like properties, behaving as the salt of a strong acid on titration with alkali, and the pattern of a group of bands at 1166, 1122, 1036, 1015, and 998 cm.$^{-1}$ in its infrared spectrum established the anion of the salt as the benzenesulfonate anion.[7] This was verified by a quantitative yield (based on the above molecular formula) of sodium benzenesulfonate being obtained on treatment of I with sodium iodide in methyl cyanide solution. It could not be reduced with hydrogen and catalysts and was also stable to the action of lithium aluminum hydride. The essential nucleus of I was indicated by hydrolysis experiments. With dilute mineral acid, quantitative yields of benzoic acid and 4-amino-3-phenyl-*s*-triazole (III) were obtained. The structure of the latter product was established by comparison with a synthetic specimen (also its *p*-dimethylaminobenzylidene derivative) prepared from benzhydrazide through the reaction sequence: 2-benzoylthiocarbazic acid, ring closure with hydrazine, and removal of the mercapto group from the cyclized product with Raney nickel.[8] Independent verification of the structure of the penultimate mercapto product has recently been published.[9] Mild, dilute alkaline hydrolysis of I converted it into II, which was also obtained by prolonged boiling of I with water. More vigorous alkaline hydrolysis of I gave 4-benzamido-3-phenyl-*s*-triazole (IV), the free base corresponding to I. This does not appear to be a simple neutralization. This reaction most likely proceeded through the hydrazidine (II) as an intermediate, since treatment of the latter under similar conditions also gave IV. Heat alone could not bring about this cyclization, and attempts to prepare IV by neutralization of I resulted in the formation of the hydrazidine (II).

The structure of IV was established by direct comparison with a synthetic specimen obtained by benzoylation of 4-amino-3-phenyl-*s*-triazole with one mole of benzoyl chloride. IV was also obtained directly from benzhydrazide benzenesulfonate and dimethylformamide by a careful choice of experimental conditions, *viz.* a work-up procedure that used dilute reaction conditions. As the isolation of the product was carried out at room temperature (see Experimental), a ring opening–ring closure sequence is probably not involved. In early experiments in which I was treated with sodium borohydride, IV was obtained. This is also regarded as a neutralization of the benzenesulfonic acid by the decomposition products of this reagent in aqueous medium during reaction work-up. The hydroiodide of IV, obtained from I and sodium iodide in methyl cyanide could not be isolated in a pure state. Traces of water very readily effected hydrolysis to II.

The second major product, II, could be converted into I by treatment with benzenesulfonic acid in dimethylformamide under conditions simulating those of the original reaction or, more simply, in alcohol as solvent and precipitation of the salt with dry ether. The use of methanesulfonic acid in this reaction gave the corresponding methanesulfonate salt. Ring closure of II with formic acid or boiling alkali (5 *N* solution) gave the 4-benzamido-3-phenyl-*s*-triazole (IV) and treatment with boiling, dilute mineral acid gave a quantitative yield of benzoic acid and 4-amino-3-phenyl-*s*-triazole (III).

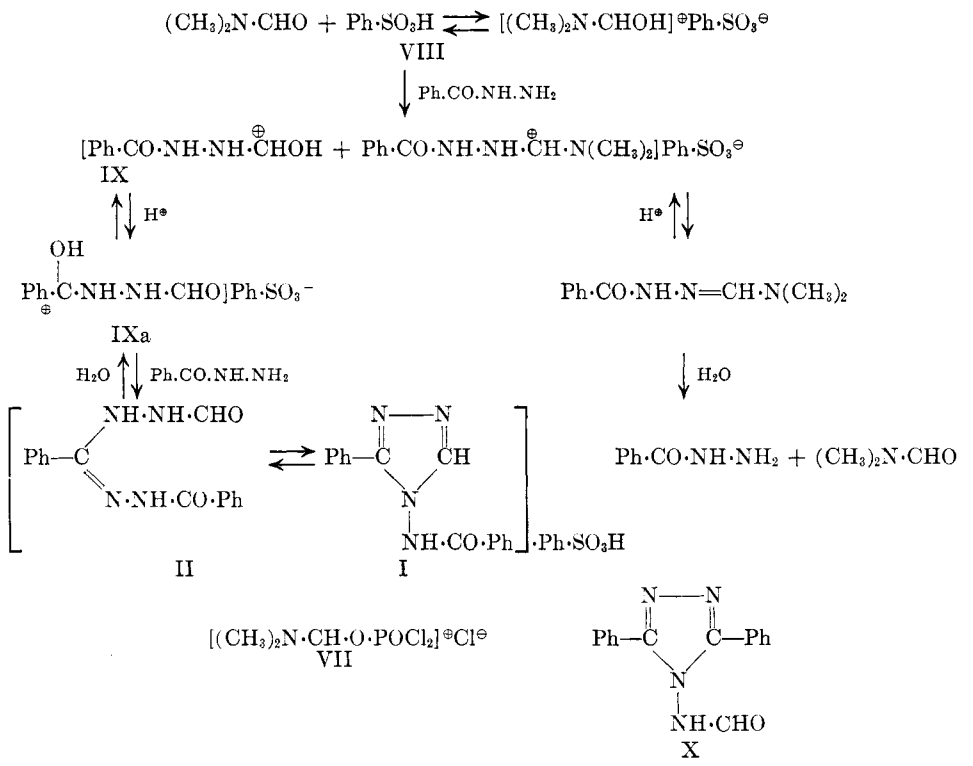


These reactions indicated that II was closely related to the benzenesulfonate (I) and analytical and molecular weight determinations established its formula as $C_{15}H_{14}N_4O_2$. The infrared spectrum of II showed bands at 3484 cm.$^{-1}$ (2.87 μ), a weaker band at 3175 cm.$^{-1}$ (3.15 μ) and an intense carbonyl band at 1698 cm.$^{-1}$ (5.89 μ) with further moderately intense bands to 1099 cm.$^{-1}$ (9.1 μ). These features can be reasonably incorporated in three possible structures, II, V, and VI, with structure II being favored on the basis of the infrared data.



Structure V is most unlikely on chemical grounds. It contains a carbinol–amine grouping that is an intermediate in amidine formation and, as such, would be expected to be extremely unstable and undergo immediate dehydration. Structure VI, 1-benzoyl-4-benzamidoformhydrazidine was eliminated by its synthesis from benzhydrazide and ethyl orthoformate. That this was the product formed and not 2-phenyl-1,3,4-oxadiazole, as described by other workers,[10] was established by analytical and molecular weight data and the presence in the infrared spectrum of absorption bands corresponding to a bonded NH group (3333 and 3226 cm.$^{-1}$), an amide carbonyl (1667 cm.$^{-1}$) and a complex band most likely due to the aromatic —C=C— and the —C=N— absorptions (1626 cm.$^{-1}$). (Ami-

(7) K. T. Potts and D. R. Liljegren, in preparation.
(8) E. Hoggarth, *J. Chem. Soc.*, 4815 (1952).
(9) H. Beyer and C. F. Kröger, *Ann.*, **637**, 135 (1960).
(10) C. Ainsworth, *J. Am. Chem. Soc.*, **77**, 1148 (1955).



dines are reported[11] as having a C=N absorption in the region 1613–1633 cm.$^{-1}$.) The formation of the formamidine was effected in this case by using two moles of the amine and one of the ortho ester in contrast to the excess of ortho ester employed by the other workers.

Confirmatory evidence for the correctness of structure II for the second product isolated from the reaction mixture was obtained from its n.m.r. spectrum.[12] This showed a resonance signal at τ 1.31 (in methanol or deuteriochloroform) and is due to the presence of an aldehydic-type proton. The absence of a hydroxyl proton further argued against structure V. Several model substances were examined (in methanol) to confirm the assignment made to the aldehydic-type proton in II. In N-formylbenzhydrazide a signal at τ 1.93 was assigned to this proton; in N-methylformanilide the signal occurred at τ 1.67 and in dimethylformamide[15] it occurred at τ 2.16.

Further interconversions helped to establish the structure of I. Synthetic 4-amino-3-phenyl-*s*-triazole, on benzoylation, gave 4-benzamido-3-phenyl-*s*-triazole (IV), which with benzenesulfonic acid gave I. Also reaction of I with sodium acetate–acetic acid under anhydrous conditions gave 4-acetamido-3-phenyl-*s*-triazole. This type of amide exchange reaction, or transamination, has been described previously[16] though in this case the equilibrium is probably shifted in the direction of the acetamide because of the large excess of acetic acid–sodium acetate present.

A minor product associated with the benzenesulfonate (I) was 2,5-diphenyl-1,3,4-oxadiazole.[17] This must have arisen by ring closure of the dibenzoylhydrazine[18] present in the reaction mixture. (This latter product was isolated along with II.) This mode of self-condensation of benzhydrazide is well established in the literature.

From the original acidic mother liquors it was possible to isolate benzenesulfonic acid, benzoic acid, and 1-benzoyl-2-formylhydrazine. The isolation of this latter substance raises the interesting question of whether it is the actual intermediate in the formation of I and II.

In its action as a formylation agent, dimethylformamide in the presence of phosphoryl chloride reacts[19–21] through the intermediate VII. Alone, or in the presence of base, it is an effective agent for the N-formylation of amines[22] which, however, form amidines[23] with the intermediate VII. The isolation of N,N′-diphenylformamidine benzenesulfonate from the reaction of aniline benzenesulfonate and dimethylformamide indicates that benzenesulfonic acid must initially act in an analogous fashion to the phosphoryl chloride. However, had the benzhydrazide benzenesulfonate–dimethylformamide reaction followed the same path, a

(11) J. Fabian, M. Legrand, and P. Poirier, *Bull. soc. chim. France*, 1499 (1956); see also ref. 4b and J. C. Grivas and A. Taurins. *Can. J. Chem.*, **37**, 795 (1959).

(12) The assistance of Dr. T. H. Crawford, University of Louisville, in determining these spectra is gratefully acknowledged. They were measured at 60 Mc./sec. using a Varian V-4301 dual purpose spectrometer, equipped with a flux stabilizer and field homogeneity controls. The calibrations were made by the side-band technique[13] and chemical shifts values are reported in τ units[14] (tetramethylsilane as internal reference).

(13) J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(14) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(15) H. Conroy, Nuclear Magnetic Resonance in Structural Organic Chemistry, in "Advances in Organic Chemistry," Vol. II, Interscience Publishers, New York, N. Y., 1960, p. 290.

(16) M. P. Gerchuk, D. A. Lifshits, and S. Z. Taits, *J. Gen. Chem. USSR*, **20**, 924 (1950); N. V. Ridel and M. P. Gerchuk, *ibid.*, **28**, 1365 (1958).

(17) R. Stollé, *J. prakt. Chem.*, **69** [2], 157 (1904).

(18) R. Stollé and A. Benrath, *ibid.*, **70** [2], 268 (1904); F. Arndt, L. Lowe, and L. Ergener, *Rev. Fac. Sci. Univ. Istanbul*, Ser. A, **13**, 116 (1948).

(19) H. H. Brederick, R. Gompper, H. G. v. Schuh, and G. Theilig, *Angew. Chem.*, **71**, 753 (1959).

(20) G. F. Smith, *J. Chem. Soc.*, 3842 (1954).

(21) L. Mangoni, *Ann. Chim.* (Rome), **48**, 930 (1958); *Chem. Abstr.*, **53**, 805 (1959).

(22) G. R. Petit and E. G. Thomas, *J. Org. Chem.*, **24**, 895 (1959); G. R. Petit, M. V. Kalnins, T. M. H. Liu, E. G. Thomas, and K. Parent, *ibid.*, **26**, 2563 (1961); K. T. Potts and S. Shukla, unpublished results.

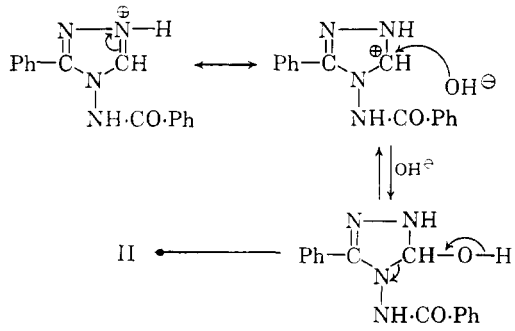
(23) H. H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).

compound having structure VI would have been obtained and attempts to convert VI into the benzenesulfonate I were unsuccessful. The most likely mechanism for this condensation is shown schematically on p. 545.

Assuming VIII to be the initial intermediate, it can react with benzhydrazide in the two ways shown. As IX is a stronger conjugate acid, then IXa is able to react to form II in preference to VI. The cyclization of II to I proceeds through the conjugate acid of the formyl group. If any alternative cyclization *via* the conjugate acid of the benzoyl carbonyl group occurred, it must have been in very small amount since no 3,5-diphenyl-4-formamido-*s*-triazole (X) was isolated.

The evolution of dimethylamine was established by passing the evolved gas into picric acid solution and characterizing it as the picrate. However, there is a possibility that the dimethylamine might have also resulted from the acid-catalyzed decomposition of the dimethylformamide at its boiling point.[24]

The ease of opening the *s*-triazole nucleus of the benzenesulfonate (I) with dilute alkali may be attributed to protonation at N-1 partly destroying the aromatic character of the *s*-triazole nucleus. In this particular molecule, N-1 should be more basic than N-2, which is adjacent to a carbon atom bearing a phenyl group. That protonation occurred exclusively at N-1 was shown by the isolation of only 1-benzoyl-4-formamidobenzhydrazidine (II) and no 1-benzoyl-4-benzamidoformylhydrazidine (VI) from the hydrolysis reaction. The mechanism of the reaction in simple form is shown schematically below and is analogous to that suggested for the hydrolysis of formamidines and acetamidines.[25]



This method of opening the *s*-triazole nucleus is somewhat analogous to the alkali induced ring opening[26] of the pyridine ring of N-isoquinolinium sulfonic acid and offers many advantages over the usual[27] and more tedious process of quaternization with an alkyl halide followed by vigorous treatment with alkali. We are at present investigating the general character and application of this reaction.

In the preparation of the reference compound 4-amino-3-phenyl-*s*-triazole (III), a Raney nickel desulfurization of the corresponding 5-thiol was used. It was found that alkaline Raney nickel W7 brings about deamination as well, with the formation of 3-phenyl-*s*-triazole. This method of deamination is more attractive than the usual nitrous acid method.[28] This hydrogenolysis of nitrogen–nitrogen bonds has been investigated in other systems,[29] and it is noteworthy that more drastic conditions are required in the triazole series where only an exocyclic nitrogen–nitrogen bond is broken.

Experimental[30]

Benzhydrazide benzenesulfonate was prepared as described previously.[31] With the volume of hot ethanol used to dissolve the benzhydrazide at a minimum, a quantitative yield of the pure salt could be precipitated with dry ether.

4-Benzamido-3-phenyl-s-triazolium Benzenesulfonate (I).—Benzhydrazide benzenesulfonate (50 g., 0.19 mole) and a large excess of dimethylformamide (150 ml.) were heated under reflux for 6–7 hr. The excess of dimethylformamide was distilled until a viscous reaction mixture remained; concentrated sodium hydroxide solution (*ca.* 50%) was then added until the reaction mixture was just alkaline. (*Caution:* copious evolution of dimethylamine sometimes occurred, depending on the extent of removal of the dimethylformamide.) With cooling in an ice bath, concentrated hydrochloric acid was added until the reaction mixture was acid to litmus. This caused the precipitation of a white gum which crystallized on standing overnight at 0°. After collection and thorough washing with cold water to remove all traces of hydrochloric acid, the dried material weighed 23.2 g. (64%), m.p. 175–176°. The benzenesulfonate crystallized from alcohol–petroleum ether (b.p. 60–80°) and finally from alcohol as long, white needles, m.p. 188–189°.

Anal. Calcd. for $C_{21}H_{18}N_4O_4S$: C, 59.7; H, 4.3; N, 13.3; S, 7.6. Found: C, 60.0, 59.9; H, 4.5, 4.4; N, 13.0; S, 7.6.

Concentration of the filtrate from the above recrystallization gave a mixture of products. This could be separated with difficulty by fractional crystallization from acetone, then alcohol, into the above benzenesulfonate, 1-benzoyl-4-formamidobenzhydrazidine (II) (see below), and a third product, 2,5-diphenyl-1,3,4-oxadiazole. This last product crystallized from aqueous methanol as small, shiny, white plates, m.p. 138°, alone or on admixture with an authentic specimen[17] with which it also had an identical infrared spectrum.

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.7; H, 4.5; N, 12.6. Found: C, 75.7; H, 4.6; N, 12.7.

This mixture was resolved more simply as follows. Sodium hydroxide solution (15 ml. of 10%) was added and the mixture warmed gently on the water bath for 10 min. The insoluble material was collected, washed, and dried, and found to be the 2,5-diphenyl-1,3,4-oxadiazole, m.p. 138°. Careful neutralization of the filtrate at 0° with acid precipitated the benzhydrazidine (II) which was purified as described below.

The original mother liquor was extracted with chloroform (3 × 25 ml.) and from the extract a pale red oil was obtained. This distilled under reduced pressure as a colorless oil, b.p. 85° (0.001 mm.) (bulb), rapidly crystallizing to low melting, long colorless needles. Infrared analysis indicated that this was a mixture of benzenesulfonic acid and a little benzoic acid.

The aqueous phase was carefully brought to pH 7 and the neutral solution continuously extracted with ether for 48 hr. The ether extract, after work-up in the usual way, yielded a low melting solid that was extracted with boiling chloroform (300 ml.). After concentration to half-bulk, white plates (1.0 g.) of a product, m.p. 159°, were obtained. After further recrystallization from chloroform it formed colorless needles, m.p. 160°. This was identified as 1-benzoyl-2-formylhydrazine by analytical

(24) D. M. F. Product Information, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1954.

(25) R. H. de Wolfe, *J. Am. Chem. Soc.*, **82**, 1585 (1960); R. H. de Wolfe and J. R. Keefe, *J. Org. Chem.*, **27**, 493 (1962).

(26) K. T. Potts, *J. Chem. Soc.*, 1269 (1956).

(27) G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *ibid.*, 3799 (1959).

(28) T. Curtius, A. Darapsky, and E. Müller, *Ber.*, **40**, 836 (1907); E. Hoggarth, *J. Chem. Soc.*, 4815 (1952).

(29) C. Ainsworth, *J. Am. Chem. Soc.*, **76**, 1636 (1956); F. P. Robinson and R. K. Brown, *Can. J. Chem.*, **39**, 1171 (1961).

(30) Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne, Australia. All compounds were identified by their infrared spectra. This was especially necessary in the case of II and IV, which could not be distinguished on the basis of their melting points. II could not be converted into IV simply by heat alone, thus excluding this possibility. However, their infrared spectra were sufficiently distinctive for identity to be established.

(31) K. T. Potts, *J. Chem. Soc.*, 3461 (1954).

data and by comparison of its melting point and infrared spectrum with those of an authentic specimen.[32]

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.5; H, 4.9. Found: C, 58.8; H, 5.1.

Identification of Dimethylamine.—In one of the above condensations, nitrogen was bubbled through the reaction mixture and the exit gases passed into a saturated, ethanolic solution of picric acid. The crystalline precipitate that separated (m.p. 156–157°) crystallized from ethanol as yellow cubes, m.p. 158–159°, not depressed on admixture with an authentic specimen (lit.,[33] m.p. 158–159°).

1-Benzoyl-4-formamidobenzhydrazidine (II).—Benzhydrazide benzenesulfonate (12.0 g., 0.045 mole) and dimethylformamide (50 ml.) were heated under reflux for 4 hr. As much of the dimethylformamide as possible was removed under reduced pressure on the water bath and water then added until precipitation of a white material was complete. After being cooled at 0° for several hours, this material crystallized. It was collected, washed with water, and dried (1.6 g., m.p. 120–125°), and separated into two fractions by recrystallization from water. The product insoluble in hot water, the benzhydrazidine, crystallized from acetone–ether or aqueous methanol as white needles, m.p. 160–161°.

Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.8; H, 5.0; N, 19.9. Found: C, 63.7; H, 5.1; N, 19.9.

The picrate separated from benzene as large, yellow prisms, m.p. 81°.

Anal. Calcd. for $C_{21}H_{17}N_7O_9$: C, 49.3; H, 3.4; N, 19.2. Found: C, 49.2; H, 3.5; N, 19.1.

The product more soluble in water was identified as 1,2-dibenzoylhydrazine and crystallized from benzene as long, fibrous needles, m.p. 240–241°, alone or on admixture with an authentic specimen[18] with which it also had an identical infrared spectrum.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 70.0; H, 5.0. Found: C, 70.4; H, 5.2.

4-Benzamido-5-phenyl-*s*-triazole. A. From Benzhydrazide Benzenesulfonate and Dimethylformamide.—Benzhydrazide benzenesulfonate (12.0 g., 0.045 mole) and dimethylformamide (50 ml.) were heated under reflux for 7 hr., and after most of the excess of dimethylformamide had been removed by distillation, dilute sodium hydroxide solution (0.08 mole) was added. The reaction mixture was cooled in an ice bath and the addition of *dilute* hydrochloric acid precipitated a white oil that crystallized on prolonged rubbing with a glass rod (3.5 g., 54%). This crude material was purified by successive crystallizations from benzene (m.p. 154–155°), sublimation at 155–160° (0.005 mm.), and final crystallization from acetone–ether whence 4-benzamido-5-phenyl-*s*-triazole separated as small, white irregular prisms, m.p. 160–161°.

Anal. Calcd. for $C_{15}H_{12}N_4O$: C, 68.2; H, 4.6; N, 21.2. Found: C, 68.1; H, 4.5; N, 21.1.

B. By the Action of 5 *N* Sodium Hydroxide on the Benzenesulfonate.—The benzenesulfonate (1.0 g.) was heated under reflux for 3 hr. with sodium hydroxide solution (10 ml. of 5 *N*). After cooling in an ice bath, the solution was made just acid with hydrochloric acid (5 *N*) and the precipitate collected, washed well with cold water, and dried (0.63 g., quant.). After sublimation at 160° (0.005 mm.), the 4-benzamido-5-phenyl-*s*-triazole had m.p. 159–160° and crystallized from acetone–ether as white, irregular prisms, m.p. 160–161°. The melting point of a mixture with the product obtained above was 160° and the two samples had identical infrared spectra.

C. By Cyclic Dehydration of 1-Benzoyl-4-formamidobenzhydrazidine with Formic Acid.—The benzhydrazidine (0.28 g.) was heated under reflux overnight in 90% formic acid (10 ml.) and the excess of formic acid then removed under reduced pressure on the water bath. The addition of a small volume of water caused the residual oil to crystallize. This was collected, washed well with cold water, and dried (220 mg., m.p. 153–154°). Final purification to a product with the above constants was achieved by sublimation as above and crystallization from acetone–ether.

D. By Cyclic Dehydration of 1-Benzoyl-4-formamidobenzhydrazidine with 5 *N* Sodium Hydroxide.—The benzhydrazidine (0.50 g.) was heated under reflux for 3 hr. in sodium hydroxide solution (6 ml. of 5 *N*). After cooling in an ice bath, the reaction mixture was made just acid to litmus with concentrated hydrochloric acid and the gum that separated collected and dried. Purification was effected by sublimation at 180–200° (0.01 mm.) and several crystallizations of the sublimate from acetone–ether whence 4-benzamido-5-phenyl-*s*-triazole separated as white, irregular prisms, m.p. 159°. This sample was identical in all respects with those prepared above.

E. By Benzoylation of 4-Amino-3-phenyl-*s*-triazole.—The 4-aminotriazole (1.24 g., 0.0077 mole) in dry pyridine (7 ml.) was cooled to 0° and treated with benzoyl chloride (1.09 g., 0.9 ml., 0.0077 mole) with cooling in an ice bath. After being kept overnight at 0°, the reaction mixture was heated for 6 hr. at 140°, cooled and then poured on to ice. After several hours, the semicrystalline precipitate was collected, washed with water, and dried (600 mg., m.p. 118–120°). This crude material was purified by sublimation at 180–200° (0.01 mm.) and crystallization of the sublimate from acetone–ether, whence 4-benzamido-3-phenyl-*s*-triazole crystallized as white, irregular prisms, m.p. 160–161°. This synthetic material did not depress the melting points of the samples prepared above and its infrared spectrum was identical in all respects with those of the above samples.

F. By Desulfurization of 4-Benzamido-5-mercapto-3-phenyl-*s*-triazole.—The mercaptotriazole (2.0 g.) in ethanol (25 ml.) and neutral Raney nickel (*ca.* 6 g.) were heated on a boiling water bath for 1.5 hr. Filter Cel was added and the reaction mixture filtered, the filter cake being washed with hot alcohol (20 ml.). Evaporation of the solvent left an oily residue which was partly crystalline. This separated from aqueous methanol as a microcrystalline powder and purification as described above gave a product identical with those obtained by the previous methods.

Dilute Acid Hydrolysis of 1-Benzoyl-4-formamidobenzhydrazidine.—The benzhydrazidine (2.1 g.) was heated under reflux for 3 hr. in dilute hydrochloric acid (40 ml. of 5 *N*). After cooling, the crystalline precipitate was filtered off and identified as benzoic acid by its melting point and mixed melting point with an authentic specimen being 121–122°. It had an infrared spectrum identical with that of this authentic specimen. The yield of 0.8 g. corresponded to a recovery of 89% based on the molecular weight of the benzhydrazidine. The filtrate was made strongly alkaline and the solution was continuously extracted with ether for 48 hr. The major portion of the ether was removed by distillation and the white, crystalline residue of 4-amino-3-phenyl-*s*-triazole collected, 1.05 g. (88%), m.p. 84–85°. It crystallized from benzene as white needles, m.p. 85° and did not depress the melting point of a synthetic specimen[8] with which it also had an identical infrared spectrum.

Anal. Calcd. for $C_8H_8N_4 \cdot 1/2H_2O$: C, 56.8; H, 5.4; N, 33.1. Found: C, 57.3; H, 5.3; N, 33.3.

The *p*-dimethylaminobenzylidene derivative separated from aqueous alcohol as lemon, fluffy needles, m.p. 143–144°, the melting point depending on the rate of heating. The infrared spectrum of this product was identical with that of an authentic specimen.[8]

Anal. Calcd. for $C_{17}H_{17}N_5 \cdot 1/2H_2O$: C, 67.95; H, 6.0; N, 23.3. Found: C, 67.94; H, 6.1; N, 23.5.

Acid Hydrolysis of 4-Benzamido-3-phenyl-*s*-triazolium Benzenesulfonate.—The above benzenesulfonate (2.0 g.) was heated under reflux for 3 hr. with dilute hydrochloric acid (40 ml. of 5 *N*). After cooling, the benzoic acid (480 mg., m.p. 121–122°, 83% recovery based on the molecular weight of the benzenesulfonate) was filtered off and identified as above. After making the filtrate strongly alkaline, it was continuously extracted with ether for 48 hr. 4-Amino-3-phenyl-*s*-triazole (0.504 g.) was isolated and its identity established in the same way as in the hydrolysis of 1-benzoyl-4-formamidobenzhydrazidine above.

Conversion of 1-Benzoyl-4-formamidobenzhydrazidine into the Benzenesulfonate. Method A.—The hydrazidine (0.65 g.), benzenesulfonic acid (0.8 g., *ca.* 100% excess), and dimethylformamide (10 ml.) were heated together under reflux for 6 hr. The reaction mixture was then worked up as described in the original preparation and gave 0.9 g., m.p. 174–178°, of crude product. The benzenesulfonate crystallized from alcohol–petroleum ether as large, white needles, m.p. 188°, and did not depress the melting point of a sample prepared from benzhydrazide benzenesulfonate and dimethylformamide. Both products had identical infrared spectra.

Method B.—The benzhydrazidine (0.56 g.) and benzenesulfonic acid (0.32 g., 1 equiv.) in methanol (4 ml.) were warmed gently to effect solution and then dry ether (*ca.* 15–20 ml.) added to precipitate the salt. The yield of material, m.p. 183–184°,

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(33) M. Delepine, *Ann. chim. phys.*, [vii] **8**, 457 (1896); G. Jerusalem *J. Chem. Soc.*, **95**, 1279 (1909).

is 0.85 g. (quant.) and after crystallization from methanol–ether, 4-benzamido-3-phenyl-*s*-triazolium benzenesulfonate was obtained as white needles, m.p. 187–188°. The melting point on admixture with a specimen prepared from benzhydrazide benzenesulfonate and dimethylformamide was 186–187°; these specimens had identical infrared spectra.

Anal. Calcd. for $C_{21}H_{18}N_4O_4S$: C, 59.7; H, 4.3; N, 13.3; S, 7.6. Found: C, 59.5; H, 4.4; N, 13.2; S, 7.5.

Replacement of the benzenesulfonic acid in method B above with an equivalent amount of methanesulfonic acid gave an 89% yield of the corresponding methanesulfonate salt, m.p. 164°. It crystallized from methanol–ether as long, white needles, m.p. 164°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4S$: C, 53.3; H, 4.5; N, 15.5; S, 8.9. Found: C, 53.3; H, 4.4; N, 15.1; S, 9.05.

Alkaline Hydrolysis of 4-Benzamido-3-phenyl-*s*-triazolium Benzenesulfonate.—The benzenesulfonate (3.0 g.) was suspended in water (20 ml.) and after the addition of dilute sodium hydroxide solution (20 ml. of 5 *N*) warmed on the water bath for 30 min. After cooling to 0°, concentrated hydrochloric acid was added until the mixture was just acid to litmus. The gum that separated soon crystallized and was collected and washed well with cold water. 1-Benzoyl-4-formamidobenzhydrazidine crystallized from aqueous methanol as white needles, 1.9 g. (90%), m.p. 160–161°, and did not depress the melting point of a sample prepared from benzhydrazide benzenesulfonate as above. It had an identical infrared spectrum with this sample.

Action of Boiling Water on the Above Benzenesulfonate.—The benzenesulfonate (0.2 g.) was heated under reflux in water (30 ml.) for 24 hr. After cooling to 0°, the crystalline precipitate was collected, washed with a small quantity of cold water, and dried, 35 mg., m.p. 158–159°, It crystallized from acetone–ether as white, irregular prisms, m.p. 161°, and was identical in all respects with 1-benzoyl-4-formamidobenzhydrazidine.

1-Benzoyl-4-benzamidoformhydrazidine.—Benzhydrazide (14.8 g.) and diethyl orthoformate (10 g.) were heated together and the alcohol formed in the reaction slowly distilled. Heating was continued until no more alcohol distilled (temperature of mixture, 85°; volume of alcohol collected, 6 ml.) and the contents of the flask suddenly solidified. This material was collected by filtration and, after drying, was extracted with acetone for 30 hr. in a hot Soxhlet extractor. An analytical sample separated as long, fibrous needles from methanol, m.p. 164°.

Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.8; H, 5.0; N, 19.9; mol. wt., 282.3. Found: C, 63.9; H, 5.2; N, 19.8; mol. wt., 290.

N,N-Diphenylformamidine Benzenesulfonate.—Aniline benzenesulfonate (20 g.) and dimethylformamide (100 ml.) were heated together under reflux overnight. As much as possible of the dimethylformamide was removed by distillation at atmospheric pressure and the residual dark green oil poured onto ice. After standing, the initial gummy product crystallized. The crude material (3 g., 10%) crystallized from acetone (charcoal) and finally from methanol–ether as pale cream needles, m.p. 154°.

Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.4; H, 5.1; S, 9.0. Found: C, 64.5; H, 5.2; S, 8.8.

This product was identical (mixed melting point and infrared spectrum) with a sample of authentic N,N′-diphenylformamidine benzenesulfonate prepared from N,N′-diphenylformamidine[34] and benzenesulfonic acid in methanol–ether solution.

3-Phenyl-*s*-triazole.—4-Amino-5-mercapto-3-phenyl-*s*-triazole (1.5 g.) in ethanol (25 ml.) was heated under reflux with alkaline Raney nickel catalyst (*ca.* 6 g.) for 1.5 hr. Effervescence occurred immediately on adding the catalyst and at room temperature. Filter Cel was added and the reaction mixture filtered, the filter cake being washed with hot ethanol (20 ml.). Evaporation of the solvent under reduced pressure on the water bath left a gummy residue that was extracted several times with boiling ethyl acetate, the extract filtered, and concentrated to small bulk. 3-Phenyl-*s*-triazole separated from this ethyl acetate concentrate and crystallized from water as white needles, m.p. 120° (lit.,[35] m.p. 119.5–120°).

Anal. Calcd. for $C_8H_7N_3$: C, 66.2; H, 4.9; N, 28.95. Found: C, 66.3; H, 4.9; N, 29.1.

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Correlation of Computed Overlap Integrals with Exalted n-π^* Transitions

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An effort is made to correlate computed overlap integrals with exalted n-π^* transitions. The pattern of results is quite encouraging but difficulty is had with data for compounds poorly represented by molecular models.

The abnormally high extinction coefficient exhibited by certain unsaturated, but not conjugated, ketones in the 290 mμ region has received wide attention. Detailed treatment of this phenomenon, particularly with respect to molecules of fixed geometry, has been given by Cookson,[3–5] Labhart and Wagniere,[6] Winstein,[7,8] and Mason.[9]

Part I of this series[10] suggested a simple statistical approach to the problem of predicting exaltations for molecules with free rotation. In a more extensive publication forthcoming,[11] it will be shown that the previously proposed statistical treatment serves well in lengthy series of phenyl- and benzylacetones, connecting the two series in a useful manner. With other compounds, however, the correlation many times fails.

A more uniformly applicable method of predicting these exalted extinction coefficients is currently being sought. Equation I is that presented by Mason[9] and Cookson.[5] Equation II, while never suggested previously in this form, is closely related to an empirical relationship used by Mulliken[12] in a somewhat different context.

$$f_{n-\pi}/f_{ct} = (\nu_{n-\pi}/\nu_{ct})(S_o^2P^2)/(\nu_{ct} - \nu_{n-\pi})^2 \qquad \text{I}$$

$$f_{ct}/f_d = (\nu_{ct}/\nu_d)(S_c^2P'^2)/(\nu_d - \nu_{ct})^2 \qquad \text{II}[13]$$

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(13) In these equations, f is the appropriate oscillator strength of the n-π^* transition, the charge-transfer (ct) transition or the donor (d) transition, P and P' are proportionality constants, S_o is the overlap integral of the nonbonding orbital on oxygen with the orbitals of the donor, S_c is the overlap integral of the orbital on carbon of C=O with the orbital of the donor, and ν is the appropriate frequency, herein always employed in cm.$^{-1}$.