the last small amount of chloroform could be distilled, the substance began to release hydrogen chloride rapidly. Heating was discontinued and the crude chlorothiol added immediately to a solution of 5.0 g. of sodium bicarbonate in 70 ml. of water and shaken until the evolution of carbon dioxide ceased. The mixture was extracted with two 15-ml. portions of ether. The combined extracts were dried with sodium sulfate. The ether was evaporated from a water-bath and the product was distilled at reduced pressure. The fraction boiling at 22–28° at 40 mm. (obviously impure) had a specific rotation of −18.34°. Its infrared spectrum was taken.

Simultaneous Measurements of *p*H and Optical Rotation on the Thiocyanate Reaction.[18]—In a 50-ml. volumetric flask was placed 1.0 g. (1.25 ml.) of the active butene oxide. After dilution to volume with a 50% aqueous ethanolic solution of potassium thiocyanate (0.28 *N*), the flask was shaken rapidly for 10 seconds. A 2-decimeter polarimeter tube was filled, stoppered to prevent evaporation and thermostated at 25.0°. The readings of *p*H and rotation for these samples appear in Table I.

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(18) Edwin C. Mertz assisted in these measurements.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Dinitrogen Tetroxide with Tolane

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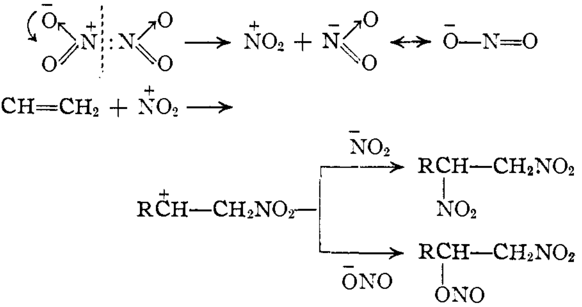
RECEIVED APRIL 18, 1952

Dinitrogen tetroxide has been shown to react with tolane to form *cis*-1,2-dinitrostilbene, *trans*-1,2-dinitrostilbene and 5-nitro-2-phenylisatogen. A free radical mechanism has been proposed to account for the formation of *cis*-1,2-dinitrostilbene, and possible mechanisms for the formation of the isatogen have been discussed.

In recent years several detailed investigations have been carried out, chiefly by Levy, Scaife and their associates[2] on the addition of dinitrogen tetroxide to olefins. In general, two types of addition products have been isolated, the dinitroalkanes and the nitroalkanol nitrite (or nitrate) esters, and the ratio of these two types of products does not appear to be affected by the presence of catalysts or by minor alterations in the experimental conditions. When unsymmetrical olefins are used, the nitroalkyl nitrite obtained has the nitro group attached to the carbon atom carrying the greater number of hydrogen atoms. These results led Levy and Scaife[3] and the Ingolds[4] to postulate an ionic mechanism for the addition.



The object of the present work was to investigate the addition of dinitrogen tetroxide to substituted olefins and to acetylenes, in the hope of isolating the dinitro products for testing as explosives. Although dinitrogen tetroxide reacted readily (at 0° in anhydrous ether) with allyl chloride, methyl vinyl ether, ethyl allyl ether and acrylonitrile, it was not found possible to isolate any homogeneous product as the dark red oils decomposed rapidly at room temperature. Under the same conditions addition of dinitrogen tetroxide to acetylene occurred very slowly, and no definite reaction product could be isolated. Attention was then turned to tolane, in the hope that it would give more stable products.

Schmidt[5] and Wieland and Blumick[6] studied the addition of dinitrogen tetroxide to tolane and obtained as major products the two isomers of 1,2-dinitrostilbene; the *trans* form, m.p. 186–187° and the *cis* form, m.p. 107–108°.[7] They also obtained small amounts of a third compound, which was red, melted at about 234° and which from its empirical formula, $C_{14}H_8N_2O_4$, they considered to be a dinitrotolane. Neither Wieland nor Schmidt found any substance which would correspond to nitronitrite addition. The work of Schmidt and of Wieland was done before the importance of anhydrous conditions and of highly purified dinitrogen tetroxide was recognized, and in view of the experiences of Scaife and others with olefins, it was considered worthwhile to reinvestigate the reaction.

A solution of tolane in anhydrous ether was added to anhydrous, redistilled dinitrogen tetroxide in ether at about 0°, and the mixture was then allowed to stand at 0–25° for varying periods of time. When one mole of N_2O_4 was used per mole of tolane, an appreciable amount of the hydrocarbon was recovered unchanged, so in later work an excess of dinitrogen tetroxide was used. The reaction products were purified by crystallization and by chromatography over alumina and silica gel. The highest yield of crystalline material obtained was about 40% based on the tolane not

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(1) Abstracted from the Ph.D. thesis of John Shavel, Jr., Notre Dame, August, 1951. This work was done in part under contract Nord-10273 between the University of Notre Dame and the Bureau of Naval Ordnance. Presented at the Milwaukee A.C.S. Meeting, April, 1952.

(2) N. Levy and J. D. Rose, *Quart. Rev.*, **1**, 358 (1948); N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948); H. Baldock, N. Levy and C. W. Scaife, *ibid.*, 2627 (1949); E. I. du Pont de Nemours and Co., British Patent 603,344, *C. A.*, **43**, 665 (1949); K. N. Campbell and R. S. Towne, O.S.R.D. Report 3984.

(3) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946).

(4) C. K. Ingold and E. H. Ingold, *Nature*, **159**, 743 (1947).

(5) J. Schmidt, *Ber.*, **34**, 619 (1901).

(6) H. Wieland and E. Blumick, *Ann.*, **424**, 100 (1921).

(7) Schmidt and Wieland showed that the nitro groups were attached to the side chain by reduction to piperazines. They did not, however, establish the geometrical configurations, although Schmidt suggested that the higher-melting form was the *trans*. E. Bergmann, *J. Chem. Soc.*, 402 (1936), confirmed Schmidt's suggestion by showing that the higher melting form had a zero dipole moment.

recovered; the rest of the product was an intractable red oil from which no definite substance could be isolated.

By fractional crystallization and chromatography it was possible to separate the crystalline material into three substances; one of these, m.p. 108–109°, was bright yellow, and corresponded to *cis*-1,2-dinitrostilbene. The second substance also was yellow, and had m.p. 186–187°; it was identical with *trans*-1,2-dinitrostilbene. The relative amounts of these two isomers varied with the experimental conditions used, but strict comparisons are not valid, since the *cis* isomer is much more soluble, and the amounts found are more subject to error than are those of the *trans*.

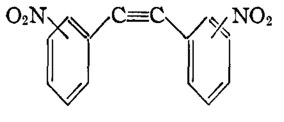
The third crystalline product was a reddish-orange solid, m.p. 238°, which had the empirical formula $C_{14}H_8N_2O_4$, and which appeared to be identical with the "dinitrotolane" obtained by Schmidt and by Wieland as a by-product. The yield of this substance varied, but usually considerably more of it was obtained than was reported by earlier investigators. The yields of the three products under varied experimental conditions are summarized in Table I.

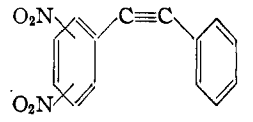
TABLE I

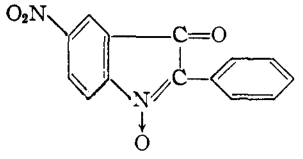
REACTION OF DINITROGEN TETROXIDE WITH TOLANE

Experimental conditions	Tolane, g.	*cis*-cpd., g.	*trans*-cpd., g.	Isatogen, g.
Ether, 0° during addition, 20° for 3 hours	14	5.2	3.9	1.4
Ether, 0° during addition, 30° for 30 minutes	15	3.4	...	2.7
Ether, 0–5° for 30 minutes, 30° for few minutes, 0° for several hours	15	2.7	1.7	5.3
Ether, 0° during addition, 25° (bright sunlight) 30 min.; 0° for 2 hours, 25° for 1 hour	15	0.84	6.24	1.12
Ether, 0° during addition and for 30 hours; 40 hours at room temp. Dark	15	3.27	4.37	0.37
Ether, BF_3 added, dark, 0° 15 min., room temp. 15 min.	15	None	1.8	None
CCl_4, 40°, u.v. light, 1 hour	15	3.6	1.8	0.75
No solvent, 0° 1 hour	15	None	None	None

On the assumption that the compound was a nitrated tolane, it was oxidized with permanganate, but the only isolable product was benzoic acid, which was obtained in quantities accounting for half of the tolane molecule. Catalytic hydrogenation over platinum led to the absorption of five moles of hydrogen and the formation of a product which turned into a black, crystalline material on exposure to air. These results eliminate structures I and II for the red compound, m.p. 238°, for the nitrobenzoic acids and aminodiphenylethanes which would have been obtained from them are easy to isolate and identify.


I


II


III

The dinitrotolane structures I and II are also inconsistent with the high melting point of the compound, and with its color. A more probable structure would seem to be that of a nitrophenylisatogen, III, which would give benzoic acid on oxidation. The isatogens are highly colored, as would be expected from the extended conjugated system, and have high melting points.[8] The keto-nitrone system, $-\underset{\underset{\displaystyle O}{\|}}{C}-C{=}N\rightarrow O$, behaves like an α-diketone or *o*-quinone system, and isatogen reduction products react with unreduced isatogen to form quinhydrones; this explains the black, crystalline material obtained when the red compound, m.p. 238°, was hydrogenated over platinum. Further evidence for the isatogen structure is found in the deep purple color obtained when the red compound is treated with alkali. The ultraviolet spectrum (see Fig. 1) is very different from the spectra of the tolanes and the two 1,2-dinitrostilbenes. There are no literature data on the ultraviolet spectra of isatogens, and hence no direct comparison can be made, but it seems probable that the absorption at 292 mμ is due to the nitrone[9] or indolone[10] structure.

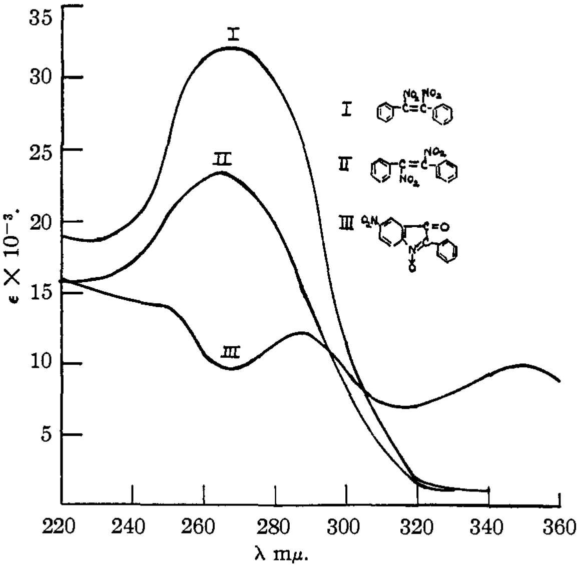


Fig. 1.

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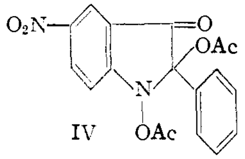
[8] A. A. Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 139; L. I. Smith, *Chem. Revs.*, **23**, 193 (1938); F. Krohnke and M. Meyer-Delius, *Ber.*, **84**, 932 (1951).

[9] G. v. Fodor and P. Csokan, *Ann.*, **535**, 284 (1938).

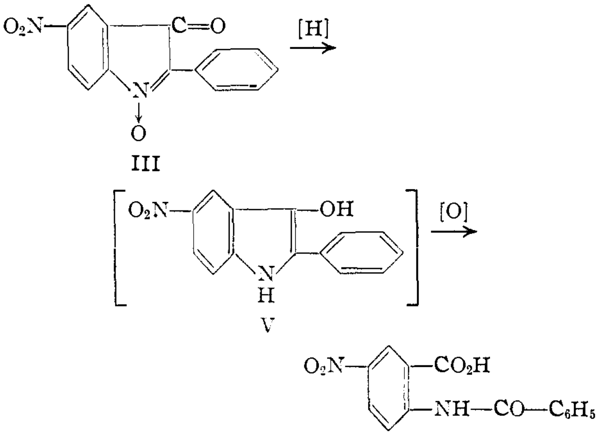
[10] R. G. Ault, E. L. Hirst and R. A. Morton, *J. Chem. Soc.*, 1653 (1935).

Isatogens react with acetic anhydride by addition at the C=N bond[11] to form compounds of the general structure IV. The red compound, m.p. 238°, reacted with acetic anhydride to form a light yellow crystalline product, m.p. 167–168°, which gave an acetyl value in fair agreement with that calculated for 1,2-diacetoxy-2-phenyl-5-nitroindoxyl (IV).



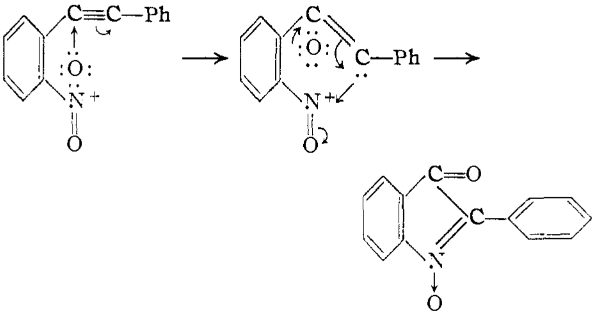
IV

The isatogen structure was confirmed, and the position of the nitro group was established, by reduction with hydrazine to V, followed by oxidation with chromic acid, to give 5-nitro-N-benzoylanthranilic acid (VI), m.p. 256°. 5-Nitro-N-benzoylanthranilic acid has been prepared by Womack, Campbell and Dodds,[12] who reported the m.p. as 257°.[13]



The formation of substantial amounts of *cis*-1,2-dinitrostilbene from tolane and dinitrogen tetroxide is difficult to explain by the ionic mechanism of Levy and Scaife[3] and the Ingolds.[4] While the stereochemical course of addition to acetylenes has not been studied as carefully as in the case of olefins, it appears that in general ionic addition leads to the *trans* adducts.[14] In the present case, the *cis*-1,2-dinitrostilbene does not arise by rearrangement of the *trans* form, as the latter does not isomerize to the *cis* under the conditions of the addition reaction or on prolonged irradiation. It seems to the authors that the addition of dinitrogen tetroxide to an unsaturated center may proceed, in part at least, by a free-radical mechanism.[15] Dinitrogen tetroxide is well known to depolymerize readily to the free radical $\cdot NO_2$. Addition may occur by initial dissociation of dinitrogen tetroxide to the $\cdot NO_2$ radical, followed by addition,[16] and/or by a bimolecular attack of dinitrogen tetroxide on the unsaturated center, followed by homolytic cleavage. Recent work by Shechter and his associates and by Brintzinger and Pfanstiel on the addition of dinitrogen tetroxide[17] and nitryl chloride[18,19] to unsymmetrical terminal olefins, $RCH{=}CH_2$, shows that the product has the structure $O_2N{-}CH_2{-}CH(R)Y$ (Y is Cl or ONO), regardless of the electronic demands of R. These results cannot be explained by an ionic mechanism, and Shechter has, therefore, proposed a homolytic mechanism, with which we concur.

It remains to explain the formation of 5-nitro-2-phenylisatogen from tolane and dinitrogen tetroxide. Two routes appear possible, and at present it is not possible to choose between them. The first route would involve nitration of tolane in the ortho position, followed by rearrangement. *o*-Nitrotolanes are known to rearrange to phenylisatogens under various conditions, but the mechanism of the rearrangement is not clear. It has been suggested[8b,20] that methylene radicals are involved. Molecular models show that the oxygen atom of the nitro group is very close to the first carbon atom of the triple bond, and it appears reasonable to suppose that the rearrangement proceeds through a cyclic intermediate; subsequent nitration of the isatogen would occur in the 5-position to give the observed product. The chief evidence against this route is the absence of *p*-nitrotolane in the reaction products; tolane would be expected to nitrate in both the ortho and para



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[11] P. Ruggli, B. Hegedus and E. Caspar, *Helv. Chim. Acta*, **22**, 411 (1939).

[12] C. R. Womack, N. Campbell and E. C. Dodds, *J. Chem. Soc.*, 1402 (1938).

[13] The most probable alternative structure for III would be that of 6-nitro-2-phenylisatogen. This is ruled out, however, because 6-nitro-2-phenyl-isatogen melts at 206° (P. Pfeiffer, *Ber.*, **45**, 1824 (1912)) and would be converted to 4-nitro-N-benzoylanthranilic acid. This has been prepared by P. Ruggli, A. Zimmerman and O. Schmid, *Helv. Chim. Acta*, **16**, 1249 (1933), and melts at 240-246°.

[14] G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 303-306.

[15] E. A. Shilov and I. V. Smirnov-Zamkov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 32 (1951); *C. A.*, **45**, 7952 (1951), have recently shown that probably the addition of bromine to dimethylacetylene dicarboxylate proceeds by an ionic and a free radical mechanism simultaneously. Ionic addition leads to the *trans* adduct, and free radical addition gives both the *cis* and the *trans*.

[16] The addition of free radicals to an open chain multiple carbon-carbon bond does not seem to be stereospecific. The photochemical halogenation of *trans*-stilbene gives approximately equal amounts of *meso* and racemic α,α'-dichlorobibenzyls (see S. Winstein and D. Seymour, THIS JOURNAL, **68**, 119 (1946)). See also reference 15.

[17] H. Shechter, F. Conrad, A. Daulton and R. B. Kaplan, paper presented at the 121st American Chemical Society Meeting, Milwaukee, April, 1952.

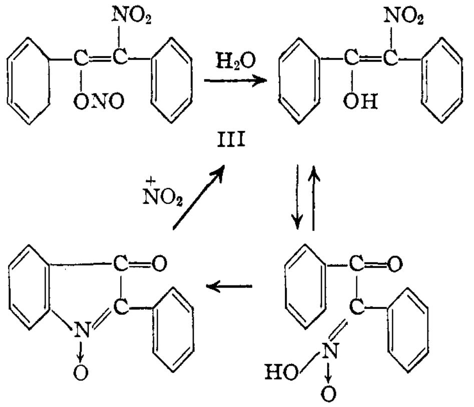
[18] H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, THIS JOURNAL, **74**, 3052 (1952).

[19] H. Brintzinger and K. Pfanstiel, *Z. anorg. Chem.*, **255**, 325 (1948).

[20] P. Ruggli, E. Caspar and B. Hegedus, *Helv. Chim. Acta*, **20**, 250 (1937).

positions, and hence some *p*-nitrotolane should have been found.

Alternatively, the nitro-nitrite type of addition to tolane may occur as it does to ethylene, and the intermediate nitro-nitrite would be very sensitive to traces of moisture. The following sequence of reactions could then occur



Experimental Part[21]

Dinitrogen Tetroxide.—The dinitrogen tetroxide used in this work was obtained from the Matheson Company, and was 99.5% pure. It was distilled twice over phosphorus pentoxide in a stream of oxygen, in an all-glass apparatus, and dissolved oxygen was removed from the distillate by alternate freezing and melting.

Addition of Dinitrogen Tetroxide to Tolane.—A typical run was carried out as follows: A solution of 45 g. of tolane in 250 ml. of dry ether was added rapidly and with shaking to a solution of 50 g. of dinitrogen tetroxide in 250 ml. of ether at 0°. The temperature of the reaction mixture did not rise above 5° at any time during the addition. The mixture was kept in an ice-bath for 30 minutes, and then was allowed to stand at room temperature. At 25° a vigorous reaction set in, and the temperature quickly rose to 30°; the reaction flask was immediately immersed in an ice-bath and kept there overnight while the ice gradually melted.

The next day the red crystalline precipitate was collected (crop A, 16 g., m.p. 209–210°) and the filtrate was evaporated *in vacuo* at 15° to give 75 ml. of a thick oil which contained some crystals. This oil was filtered; the solid obtained weighed 4 g., and melted at 172–174° (crop B). The oily filtrate was concentrated further, taken up in an equal volume of dry ethanol and cooled in Dry Ice. In this way three additional crops of crystals were obtained; crop C, 1.0 g., m.p. 163–166°; crop D, 5.5 g., m.p. 102–105° and crop E, 2.5 g., m.p. 100–102°. The total amount of solid product was 29 g., 42.5%.

Crop A was recrystallized from acetic acid and then from benzene; after purification it formed orange-red crystals, m.p. 238–239°. This is 5-nitro-2-phenylisatogen (III).

Anal. Calcd. for $C_{14}H_8N_2O_4$: C, 62.68; H, 3.01; N, 10.45. Found: C, 62.81; H, 3.31; N, 10.31.

Crops B and C were combined and chromatographed over alumina, using ether as the solvent. The majority of the product formed yellow crystals, m.p. 187–188°, and was identical with Wieland's *trans*-1,2-dinitrostilbene.

Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.48; H, 3.77; N, 9.96.

Crops D and E were essentially *cis*-1,2-dinitrostilbene, and after purification by chromatography over alumina and recrystallization from ethanol melted at 108–109°.

Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.38; H, 3.60; N, 9.90.

In other runs the time of addition and the time which the reaction mixture was allowed to stand were varied, as indicated in Table I.

Identification of the Red Compound, M.p. 238–239°, as 5-Nitro-2-phenyl Isatogen (III). (a) **Physical Properties.**—The analytical sample was recrystallized from glacial acetic acid and then from benzene; it was a deep orange-red, and melted at 238–239°. It was very difficultly soluble in most organic solvents. With alcoholic alkali it gave a deep purple color, which was discharged by the addition of acid.

The ultraviolet absorption spectrum in ethanol showed two peaks; 292 mμ, ϵ_{max} 12,000; 352 mμ, ϵ_{max} 10,000 (see Fig. 1).

A molecular weight determination by the Rast camphor method gave 300; calculated for III, mol. wt., 268.

(b) **Oxidation with Permanganate.**—A mixture of 500 mg. of III, 2 g. of potassium permanganate, 40 ml. of water and 0.15 g. of sodium hydroxide was refluxed for three hours. The solution on decolorization with sulfur dioxide precipitated 53 mg. of unreacted isatogen. Extraction of the aqueous solution with ether and evaporation of the ether yielded 154 mg. of crude benzoic acid, m.p. 119–120°, which did not depress the melting point of an authentic sample. The yield of benzoic acid based on isatogen consumed was 43%.

(c) **Catalytic Hydrogenation.**—A solution of 500 mg. of isatogen in 200 ml. of ethanol and 25 ml. of water containing 100 mg. of sodium hydroxide was shaken with hydrogen at 25° and 40 p.s.i. in the presence of 100 mg. of platinum oxide. At the end of seven hours, five molar equivalents of hydrogen had been taken up. The reaction mixture was greenish-brown in color, and immediately turned black on exposure to air. Evaporation of the solvent gave a black, crystalline material which had no definite melting point and which could not be purified by crystallization or chromatography.

(d) **Acetylation to 1,2-Diacetoxy-2-phenyl-5-nitroindoxyl (IV).**—The isatogen (500 mg.) was added to 3 ml. of acetic anhydride containing 0.1 ml. of concentrated sulfuric acid, and the red solution was kept at 50° for one hour. It was then cooled and poured into 50 ml. of cold water to hydrolyze the unused anhydride. An orange oil precipitated; this was taken up in 25 ml. of methanol and the solution cooled. The first crop of material to precipitate from the methanol was recovered isatogen, orange-red crystals, m.p. 233–235°, weight 5.5 mg. Concentration of the filtrate yielded 207 mg. of buff colored substance, m.p. 147–152°. This was purified by recrystallization from ethanol and then sublimation at 150° and 0.01 mm. The product was obtained as light yellow crystals, m.p. 167–168°.

Anal. Calcd. for $C_{18}H_{14}N_2O_7$ (IV): acetyl, 23.24. Found: acetyl, 23.11.

(e) **Reduction by Hydrazine and Oxidation by Chromic Acid.**—A suspension of 500 mg. of isatogen in 10 ml. of ethanol was treated with 0.75 ml. of hydrazine hydrate. After the vigorous reaction subsided, the mixture was kept at 70° for 30 minutes and then evaporated to dryness. The crude residue was taken up in 8 ml. of hot glacial acetic acid, and 500 mg. of chromic anhydride was added. A vigorous reaction ensued; when it subsided the mixture was diluted to 80 ml. with water and the precipitate was collected. This was washed with water, dissolved in dilute potassium hydroxide and reprecipitated by hydrochloric acid. There was obtained 245 mg. of yellow material, m.p. 198–206°. Two recrystallizations from ethanol raised the m.p. to 245–247°, and sublimation of the recrystallized material yielded light yellow crystals, m.p. 255–256°, of 5-nitro-N-benzoylanthranilic acid (VI).

Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.52; N, 9.79. Found: C, 58.84; H, 3.70; N, 10.5.

Acknowledgment.—This work was supported in part by the Bureau of Naval Ordnance, under a contract with the University of Notre Dame.

NOTRE DAME, INDIANA

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[21] The microanalyses were carried out by the Clark Microanalytical Laboratory, Urbana, Illinois.