[Contribution from the Department of Chemistry and Radiation Laboratory,
University of California]

THE PHOTOCHEMICAL BEHAVIOR OF SOME *o*-NITROSTILBENES

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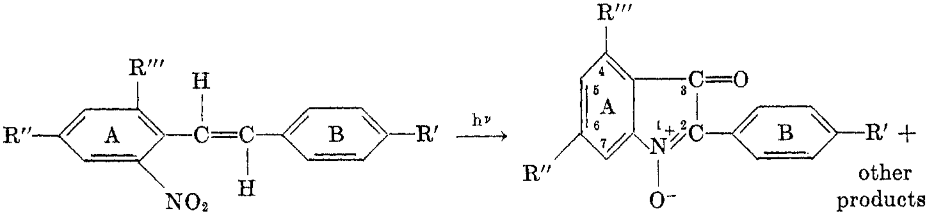
In order to determine the effect of increasing polarity in substituted stilbenes upon the kinetic constants (activation energy and entropy factor) of the *cis-trans* isomerization (1), some 2-nitro-, 2,4-dinitro-, and 2,4,6-trinitro-stilbenes were synthesized. When these were illuminated to obtain the *cis* forms, quite different products resulted, particularly substituted isatogens. The present paper is a report of the examination of these products together with some studies on their possible mode of formation.[1]

Aromatic compounds with nitro groups *ortho* to a side chain have long been known to be photosensitive. The photochemical rearrangements of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid (2–4) and of *o*-nitrotolane to 2-phenylisatogen (5, 6) were among the first to be reported. Substituted isatogens have also been prepared photochemically from *o*-nitro-α-chlorostilbenes and *o*-nitrostilbene dichlorides in pyridine (6), and from 1-(β-hydroxy-*o*-nitro-α-phenylphenethyl) pyridinium bromide in acetic acid (7), as well as by non-photochemical methods (6, 8–10). A 2% yield of 2-phenyl-6-cyanoisatogen was reported from the irradiation of 2-nitro-4-cyanostilbene (11). However, the 2-nitro- and the 2,4-dinitrostilbenes were found to give, on irradiation, the *cis*-isomer and resinous material (11–13).

In this work it was found that *o*-nitrostilbenes, when substituted in Ring B by electron-releasing groups, gave not the *cis*-isomer but mainly substituted isatogens along with other products.



The results summarized in Table I are based on the isolation of products from the irradiation of 100 mg. or more of stilbene in benzene solution.

In the 4'-dimethylaminostilbene series, it appeared qualitatively that the velocity of the reaction was in the order: 2,4,6-trinitro- > 2,4-dinitro- > 2-nitro. In the 2,4-dinitrostilbene series, the velocity was in the order: 4'-dimethylamino > 4'-hydroxy > 4'-methoxy > 4'-acetoxy.

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[1] Since this manuscript was completed, it has come to our attention [Ried and Wilk, *Ann.*, **590**, 111 (1954)] that Dimroth, Bohlman, and Bohlmann, *Angew. Chem.* **A59**, 176 (1947) had reported that *o*-nitrostilbenes which absorb at long wave lengths produce isatogens on irradiation. An example, 2,4,6-trinitro-4'-dimethylaminostilbene, was given, but no experimental work was reported.

TABLE I

PRODUCTS FOUND FROM THE IRRADIATION OF SOME *o*-NITROSTILBENES

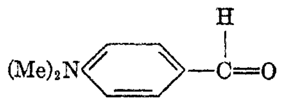
Stilbene	R′	R″	R‴	Isatogen Yield, %	By-products Isolated	Resinous Material Yield, %
Ia....	$N(CH_3)_2$	NO_2	NO_2	IIa, 38	15%, 4,6-Dinitroanthranil (V) 19%, 4-Dimethylaminobenzaldehyde (IV) 13%, 2 (*p*-Dimethylaminophenyl)-4,6-dinitroindoxyl (VI) Trace, 2(*p*-dimethylaminophenyl)-4,6-dinitroindolone (VII)	23
Ib....	$N(CH_3)_2$	NO_2	H	IIb, 44	15%, 2-Amino-4-nitrobenzaldehyde (III)	23
Ic....	$N(CH_3)_2$	H	H	IIc, 24	Could not determine identity	8
Id....	OH	NO_2	H	IId, 40	5%, 2-Amino-4-nitrobenzaldehyde (III)	45
Ie....	OCH_3	NO_2	H	IIe, 22	—	58
If....	$OCOCH_3$	NO_2	H	IIf, 3	—	remainder
Ig....	Cl	NO_2	NO_2	IIg, 16	—	64
Ih....	H	NO_2	NO_2	IIh, 16	—	64
Ii....	H	H	NO_2	IIi, 6	2%, recovered stilbene	remainder
Ij....	NO_2	NO_2	NO_2	—	32%, recovered stilbene	remainder

Of the isatogens reported here four have been prepared before: the 2-(*p*-hydroxyphenyl)-6-nitroisatogen, 2-*p*-methoxyphenyl)-6-nitroisatogen, 2-(*p*-acetoxyphenyl)-6-nitroisatogen, and the 2-phenyl-4-nitroisatogen (6). The first of these was prepared by the hydrolysis of the 2-(*p*-acetoxyphenyl)-6-nitroisatogen, which, in turn, was prepared by the irradiation of the corresponding stilbene dichloride in pyridine. The other three were prepared from the corresponding stilbene dichloride by irradiation in pyridine.

In the irradiation of 2,4-dinitro-4′-dimethylaminostilbene, besides the isatogen there was obtained 2-amino-4-nitrobenzaldehyde (III) and, presumably, 4-dimethylaminobenzaldehyde (IV), although this could not be isolated. The spectrum of the irradiated solution showed a strong absorption in the region of the main absorption band of 4-dimethylaminobenzaldehyde. 2-Amino-4-nitrobenzaldehyde was also obtained in small amount in the irradiation of 2,4-dinitro-4′-hydroxystilbene. In the irradiation of 2,4-dinitro-4′-methoxystilbene, only resinous material could be isolated besides the isatogen. This was found for many of the other stilbenes where the photochemical reaction was slow. The isatogens were, in general, fairly stable towards irradiation.

In the irradiation of 2,4,6-trinitro-4′-dimethylaminostilbene, there was found besides the isatogen, 4-dimethylaminobenzaldehyde (IV), 4,6-dinitroanthranil (V), and 2-(*p*-dimethylaminophenyl)-4,6-dinitroindoxyl (VI). 2-(*p*-Dimethylaminophenyl)-4,6-dinitroindolone (VII) was found in trace amounts.

The 4,6-dinitroanthranil was also isolated when 2,4,6-trinitrobenzaldehyde was reduced with titanium trichloride. This same procedure on 2,4-dinitrobenzaldehyde gave 2-amino-4-nitrobenzaldehyde (14). Depending on the reducing



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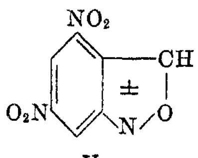

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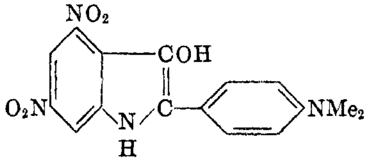

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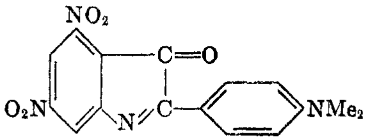


VII

agent, 2-nitrobenzaldehyde is known (15) to give the anthranil, which then can be further reduced to 2-aminobenzaldehyde. So, the 4,6-dinitroanthranil would not be unexpected as a partial reduction product of 2,4,6-trinitrobenzaldehyde. The 4-dimethylaminobenzaldehyde was isolated and converted to its 2,4-dinitrophenylhydrazone. The indoxyl (VI) was prepared by reducing the isatogen with hydrazine hydrate (16). Oxidation of the indoxyl (VI) with benzoyl peroxide in acetone solution gave the indolone (VII). The indoxyl and the indolone were also quite stable to irradiation.

ABSORPTION SPECTRA

The absorption spectra of the stilbenes and the isatogens are shown in Figures 1 to 6. The configuration of the stilbenes is probably *trans*; the method used in the

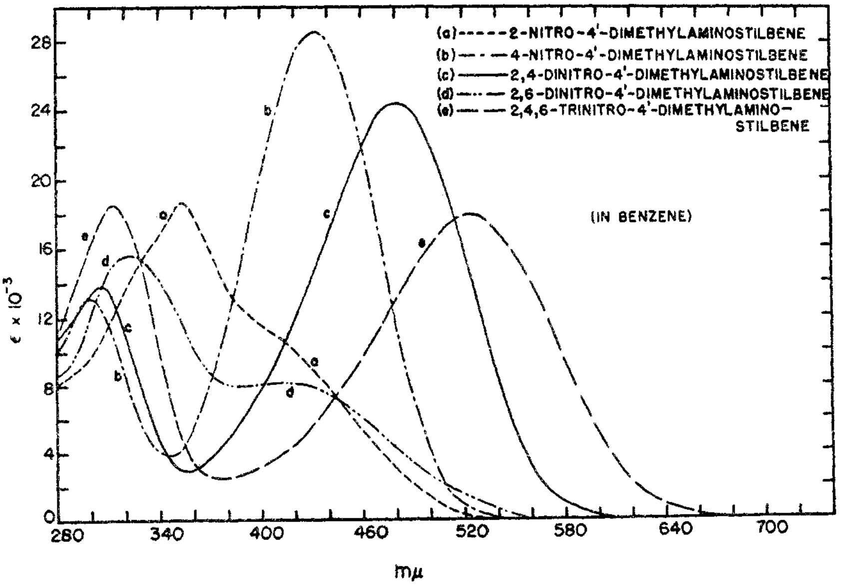
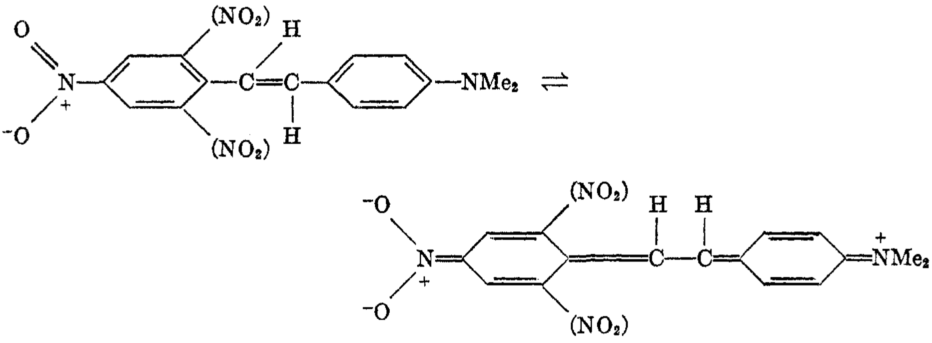


FIG. 1. ABSORPTION SPECTRA OF THE MONO-, DI-, AND TRI-NITRO-4'-DIMETHYLAMINOSTILBENES.

preparation of the stilbenes has been shown (17) to give *trans*-stilbenes. Hargreaves and McGookin (18), however, have reported obtaining one or the other isomer of 2,4-dinitro-4′-hydroxystilbene, depending on whether a solvent was employed in the reaction. Their work could not be duplicated as only one isomer, the *trans*, was obtained in both preparations.

Stilbenes. In the series 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitro-4′-dimethylaminostilbene (Figure 1), the first long wave length band, the transition characteristic of the stilbene chromophore using the valence bond resonance method of representation,



is shifted to longer wave lengths, but with decreasing intensity. Lewis and Calvin (19) and Beale and Roe (20) have observed a reduction in maximum extinction and frequently a hypsochromic shift of the long wave length band when *ortho*-substitution causes steric hindrance to the planarity of the molecule. A comparison of the 2,6-dinitro- compound with the corresponding 2,4-dinitro- compound

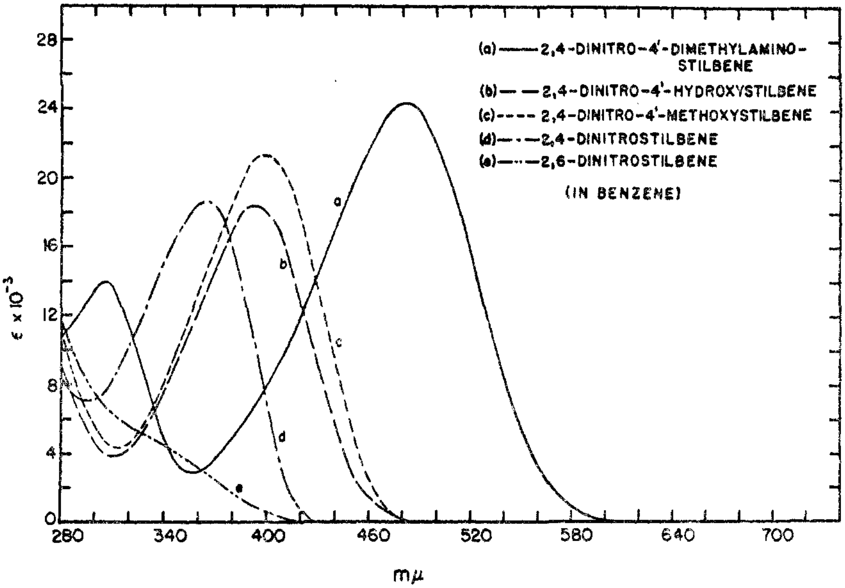
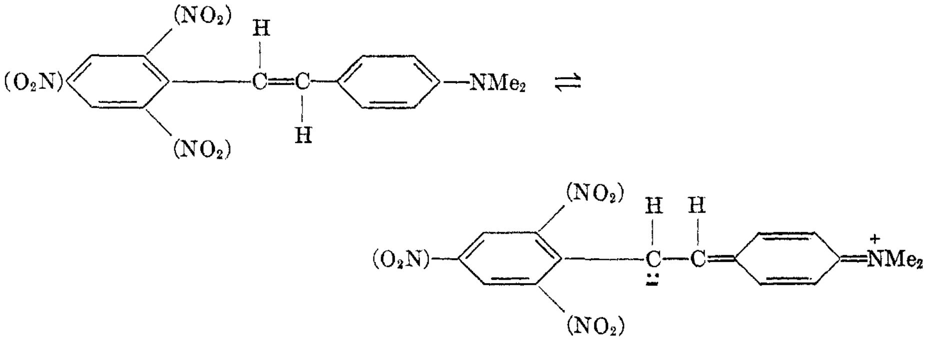


FIG. 2. ABSORPTION SPECTRA OF THE 4′-SUBSTITUTED DINITROSTILBENES

(Figures 1 and 2) shows the marked effect of the double *ortho* steric hindrance in the suppression of intensity as well as the shift to the shorter wave length. In the absence of steric effects in the dimethylaminostilbene series, one would have expected an increase in intensity with added nitro groups and a more marked shift to longer wave lengths, so very likely both effects of the hindrance to planarity are making their appearance here. The second band (~310 mμ) is shifted slightly to longer wave lengths and with increasing intensity. This band is very probably a transition (19, 21) involving only the 4-dimethylaminostyryl part of the molecule, since



this band is common to all three of the stilbenes. The λ_{max} of this band is almost the same as that of the intense long wave length band (~310 mμ) of 4-dimethylamino-2′,4′,6′-trimethylstilbene (20), which is most likely due to its similar partial chromophore because of the hindrance to planarity by the *ortho* methyl groups. The band due to the stilbene chromophore of this molecule (4-dimethylamino-2′,4′-6′-trimethylstilbene) can be seen as a shoulder at about the same wave length as the λ_{max} of 4-dimethylaminostilbene (~350 mμ). Also there is a shoulder (~320 mμ) on the long wave length band of 4-dimethylaminostilbene due probably to the partial chromophore, 4-dimethylaminostyryl. So this entire band may be a composite due to the stilbene chromophore and its styryl partial. In 4-nitro-4′-dimethylaminostilbene and also the 2,4-dinitro- and the 2,4,6-trinitro- compounds, the band due to the stilbene chromophore is at such long wave lengths that one sees a distinct separation of it from that due to its styryl partial chromophore. In this series, as there was a decrease in the intensity of the first band due to the hindrance to planarity, there was an increase in the intensity of the second band and a slight bathochromic shift indicating a greater contribution from the partial styryl chromophore as there was a lesser contribution from the stilbene chromophore. This same sort of effect can also be seen in the spectra of the *cis*- and *trans*-4-nitro-4′-aminostilbenes (17). The band at 354 mμ of the 2-nitro-4′-dimethylaminostilbene is probably one of low intensity superimposed on the other two bands (~320 mμ and ~410 mμ) and much like that found by Beale and Roe (20) at the minimum between the two separated high intensity bands. This weak transition shows some evidence of its presence in all of the spectra.

In the 2,4-dinitro- series of stilbenes (Figure 2) where the 4′-dimethylamino

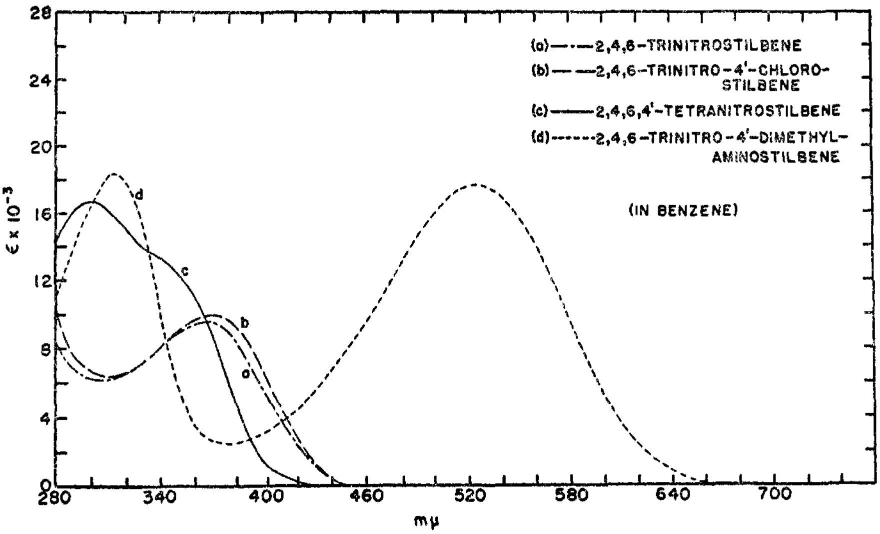


FIG. 3. ABSORPTION SPECTRA OF THE 4'-SUBSTITUTED TRINITROSTILBENES

group is replaced by 4'hydroxy, 4'-methoxy, or H, both the first and second bands are shifted to shorter wave lengths, as the electron-releasing power of the substituent is decreased. The first band should be due to the stilbene chromophore. The methoxy and the hydroxy compounds have about the same λ_{max}, although in the photochemical reaction, the hydroxy appeared to be much the faster reacting. The 2,6-dinitrostilbene as compared to the 2,4-dinitrostilbene is similar to the 2,6-dinitro-4'-dimethylaminostilbene in its relation to the 2,4-dinitro-4'-dimethylaminostilbene (Figure 1). The band due to the stilbene chromophore in the 2,6-dinitrostilbene is so decreased in intensity that it is only a weak shoulder on the rising higher intensity second band which must be due to the partial styryl chromophore.

The trinitro series of stilbenes is shown in Figure 3. In comparison with 2,4-dinitrostilbene (Figure 2), 2,4,6-trinitrostilbene and also the 4'-chloro compound show a greatly decreased intensity of the first band but with λ_{max} about the same. It therefore appears that without the electron-releasing group in the 4' position, the second *ortho* nitro group seems to exert a rather marked steric effect, resulting in a decrease in the coplanarity of the molecule. The band due to the stilbene chromophore of the 2,4,6,4'-tetranitrostilbene is a shoulder on the long wave length side of the higher intensity second band. The λ_{max} of the stilbene band is at shorter wave lengths than that of the 2,4,6-trinitrostilbene, probably as a result of the electron-withdrawing nature of the 4'-nitro group. The second band at 300 mμ would correspond to the 4-nitrostyryl partial chromophore. Its intensity here is almost equal to that of the 4-dimethylaminostyryl partial chromophore of the 2,4,6-trinitro-4'-dimethylaminostilbene.

Isatogens. The absorption spectra of the isatogens (Figures 4–6) are somewhat more complex than those of the stilbenes; however, it seems useful to relate the spectra to transitions described in terms of valence bond resonance formulae. The

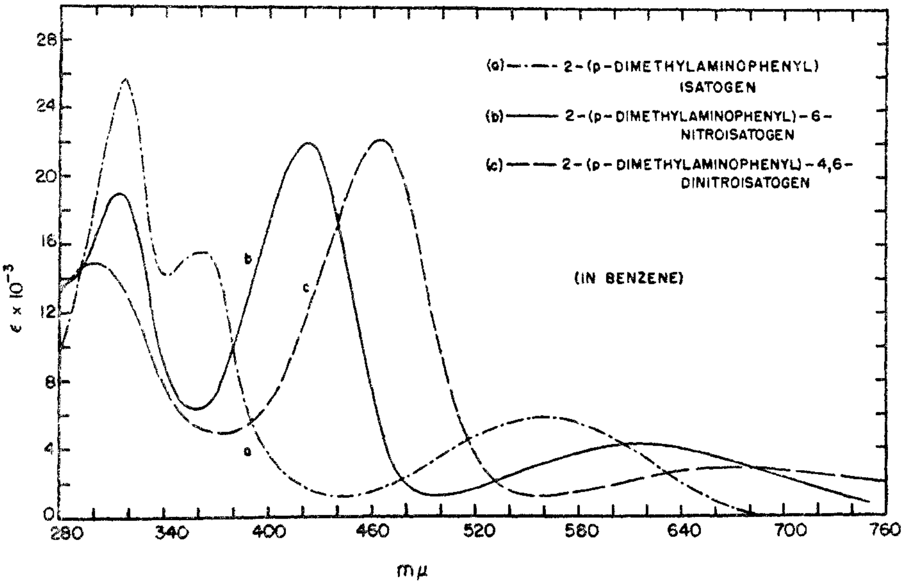


Fig. 4. Absorption Spectra of the 2-(*p*-Dimethylaminophenyl)isatogens

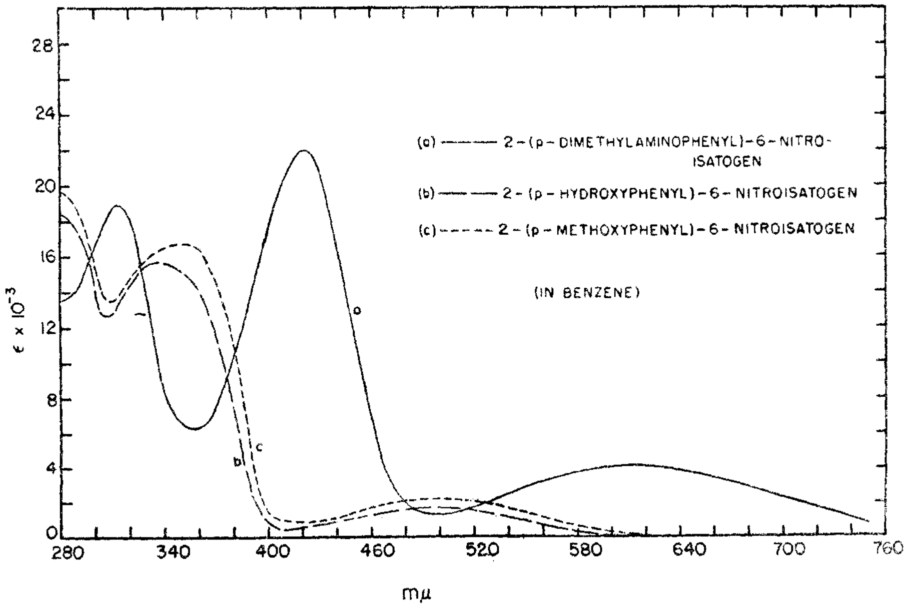


Fig. 5. Absorption Spectra of the Substituted-6-nitroisatogens

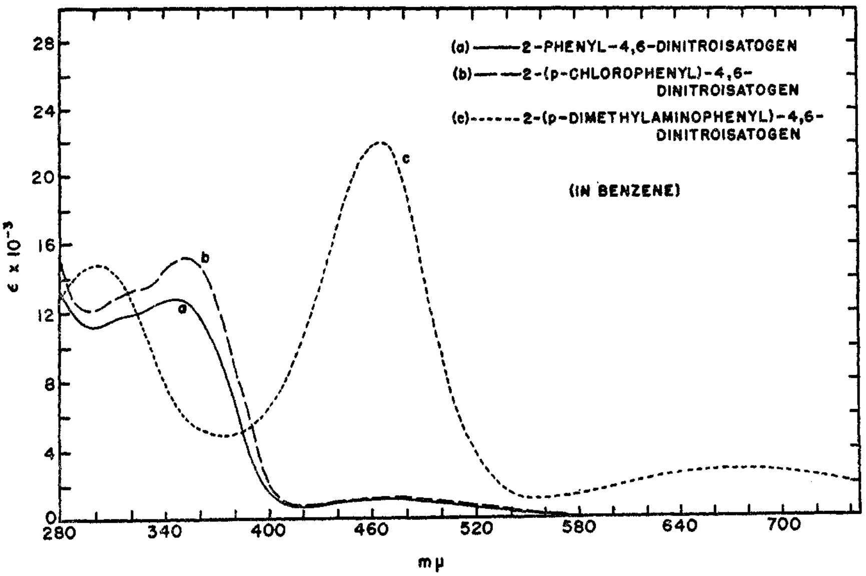
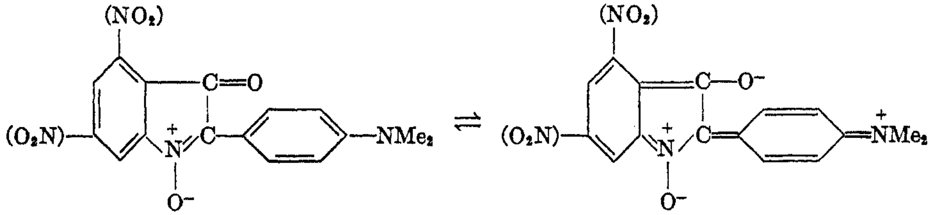
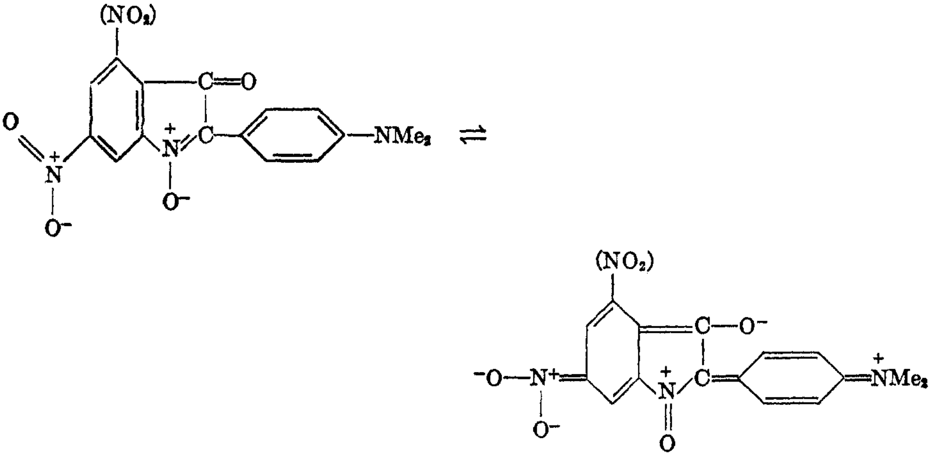


FIG. 6. ABSORPTION SPECTRA OF THE SUBSTITUTED-4,6-DINITROISATOGENS

first band may be associated with the transition,



having a low intensity because of the small transition dipole. The second and third bands which in appearance are similar to those of the stilbenes may be due to transitions, involving the structures,



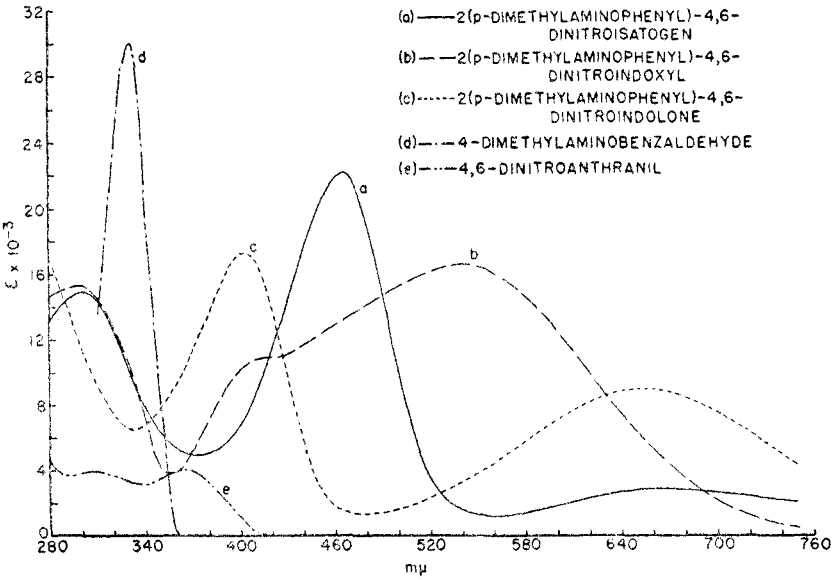
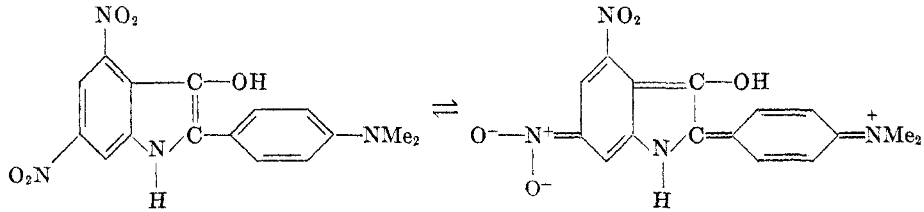


FIG. 7. ABSORPTION SPECTRA OF THE PRODUCTS ISOLATED FROM THE IRRADIATION OF 2,4,6-TRINITRO-4′-DIMETHYLAMINOSTILBENE.

and there seems to be a good correlation between these spectra and those of the corresponding stilbenes, for example, the spectrum of 2-(*p*-dimethylaminophenyl)-4,6-dinitroisatogen compared with that of 2,4-dinitro-4′-dimethylaminostilbene.

Other reaction products. In Figure 7 are shown the spectra of the isolated products of irradiation of 2,4,6-trinitro-4′-dimethylaminostilbene. The long wave length band of the indoxyl (VI) is very broad and with an intensity almost that of the corresponding stilbene. This would indicate that in the ground state the indoxyl is mainly in the enol form, such that the transition might be represented as a stilbene type transition.



The spectrum of the indolone (VII) is somewhat similar to that of the isatogen but all of the bands are shifted to shorter wave lengths. Here the difference would be due to the difference in the character of the N atom in the 5-membered ring. The spectrum of the 4,6-dinitroanthranil (V) shows low intensity bands which are very similar in intensity and λ_{max} to those found in such compounds as *o*-nitroaniline (22) and *o*-aminoacetophenone (23). This would indicate, as already suggested by Baker (24), that the structure of anthranil cannot be represented by a single formula but rather it is a hybrid of many dipolar forms, probably stabilized by resonance to such an extent that it has aromatic stability. It is unlike *o*-quinone in that it is a practically colorless compound.

QUANTUM EFFICIENCY AND KINETIC OBSERVATIONS

When small volumes of very dilute solutions, 10^{-5} M in benzene, were irradiated, it was found in all cases that complete disappearance of the stilbene occurred before very much isatogen had appeared, thus indicating the presence of an intermediate unstable compound. The intermediate had very little absorption at the λ_{max} of the stilbene. When all the stilbene was decomposed and the irradiation was stopped, the isatogen formation proceeded in the dark. It was evident from the spectra of the stilbenes and the corresponding isatogens that at the λ_{max} of the stilbene there was very little absorption by the isatogen so that it was possible to determine the quantum efficiency of the irradiation and to evaluate the kinetics of the stilbene decomposition.

The quantum efficiency as determined here is the ratio of the number of stilbene molecules decomposed, in the range of 0–20% of the total, to the number of quanta of light absorbed by the stilbene. The apparatus used was that described by Seely (25). The number of molecules decomposed was determined spectroscopically at a suitable wave length where products of irradiation would have the minimum absorption. The results are summarized in Table II.

TABLE II

QUANTUM EFFICIENCY OF THE DECOMPOSITION OF VARIOUS STILBENES BY IRRADIATION

Compound	Wave length of irradiating light mμ	Wave length of analyzing light, mμ	Conc. of stilbene solution × 10^{-5} M	Quantum efficiency, %
2,4,6-Trinitro-4′-dimethylaminostilbene (Ia)[a]	365	525	19.4	3.2
	365	525	5.8	2.7
	545 + 576	525	20.5	1.8
	545 + 576	525	5.8	1.1
2,4-Dinitro-4′-dimethylaminostilbene (Ib)	365	480	6.17	1.2
	545 + 576	480	3.49	0.3
2-Nitro-4′-dimethylaminostilbene (Ic)	365	450	9.77	0.9
	365	450	5.63	0.5
2,4-Dinitro-4′-hydroxystilbene (Id)[b]	365	410	22.5	6.5
	365	410	9.05	4.3
	365	410	6.54	3.0
2,4-Dinitro-4′-methoxystilbene (Ie)	365	410	22.3	2.9
	365	410	6.33	2.9

[a] The rate of the photochemical decomposition was the same at 2° as at 24°.

[b] It should be noted for 2,4-dinitro-4′-hydroxystilbene in the range of 0–20% decomposition, the kinetics appeared to be of an order greater than first. In view of this, the quantum yields for this compound should not be compared with those of the dimethylamino series.

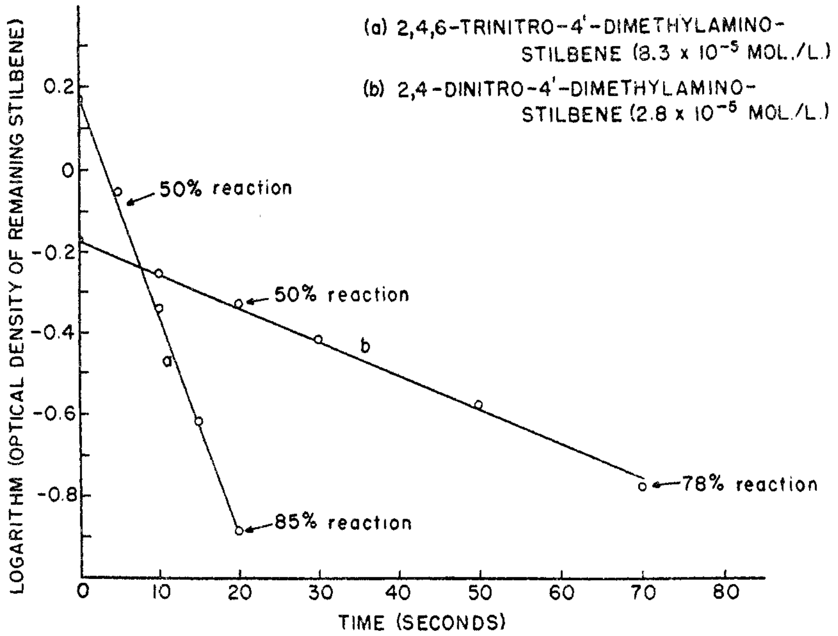


FIG. 8. KINETIC DATA ON THE IRRADIATION OF TWO STILBENES

At about the same concentration and with the same wave length of light, the quantum efficiency of the nitrodimethylaminostilbenes was in the order 2,4,6-trinitro-4'-dimethylaminostilbene > 2,4-dinitro-4'-dimethylaminostilbene > 2-nitro-4'-dimethylaminostilbene. The efficiency was somewhat higher when light of 3650 Å was used instead of 5450 and 5760 Å.

To obtain kinetic data on both the irradiation and the following thermal reaction, 3.5-ml. volumes of benzene (reagent grade) solutions of the stilbenes were irradiated between two photospots (RSP2), the solution being approximately 9 inches from each with a water-jacketed infrared filter for each photospot. For the study of the kinetics of irradiation, samples were irradiated for various periods of time and the amount of stilbene remaining determined spectroscopically at the λ_{max} for the stilbene. A separate sample was used for each determination. The data were plotted as shown in Figure 8. The data fit first order kinetics since log of optical density of remaining stilbene *vs.* time is on a straight line.

Since the quantum efficiencies are very low, the back reaction, k_2,

1. $$S + h\nu \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^*$$

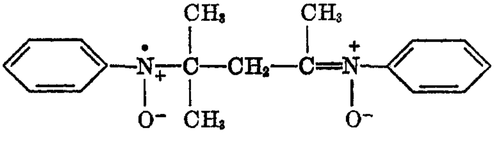
(equation 1) is rapid. Some of the excited stilbene molecules, however, undergo internal rearrangement and it is this process that is a first order reaction (equation 2).

2. $$S^* \xrightarrow{k_3} S_{\text{intermediate}}$$

Assuming that S* reaches a steady state quickly and since the diluted solution was illuminated from both sides so that I (incident intensity) is approximately constant throughout the body of the reaction vessel, the rate law derived from equations 1 and 2 is

$$-\frac{d[S]}{dt} = \left[k_1 - \frac{k_1k_2}{k_2 + k_3}\right][S]I_0 = (\text{constant})\ [S]$$

giving first order kinetics. The addition of the free radical, 2-(phenylnitrogen oxide)-2-methylpentane-4-one oxime N-phenyl ether (26)



VIII

in excess did not change the rate of decomposition of stilbene by irradiation under these conditions. The free radical (VIII) had practically no absorption at the λ_{max} of the two stilbenes.

Figures 9 and 10 show the spectra of the solutions immediately after irradiation and subsequent spectra showing the formation of the isatogen in the dark from the product of irradiation of 2,4-dinitro- and 2,4,6-trinitro-4′-dimethyl-

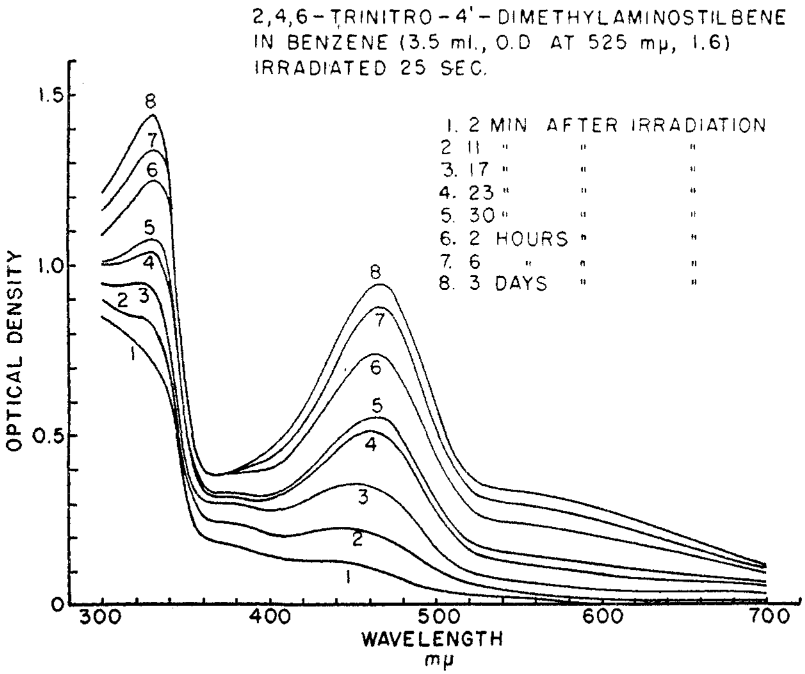


FIG. 9. ABSORPTION SPECTRA FOLLOWING THE IRRADIATION OF 2,4,6-TRINITRO-4′-DIMETHYLAMINOSTILBENE.

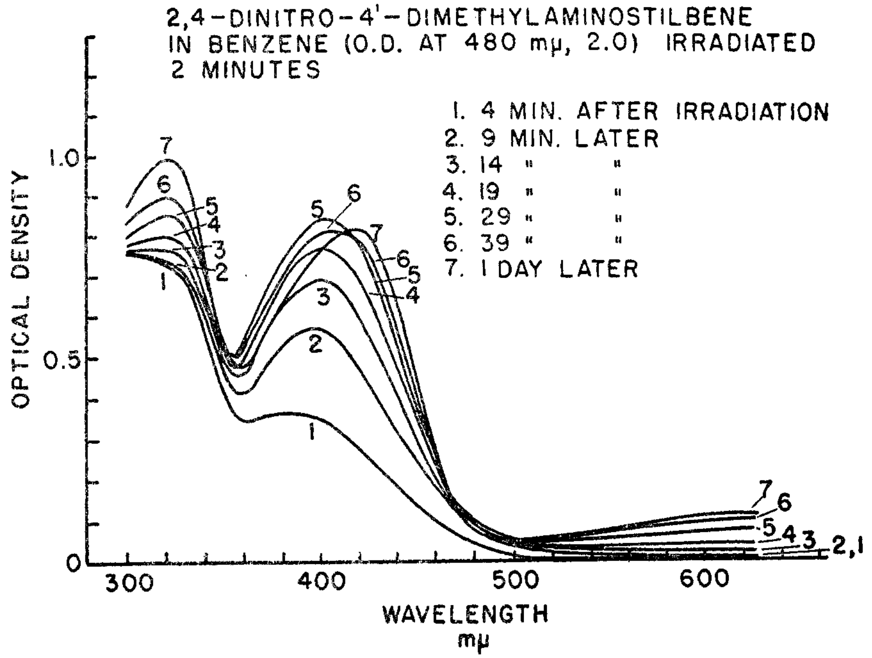


Fig. 10. Absorption Spectra Following the Irradiation of 2,4-Dinitro-4′-dimethylaminostilbene.

aminostilbene. It can be seen that immediately after irradiation practically no isatogen has yet been formed. The rate of isatogen formation from the 2,4-dinitro-4′-dimethylaminostilbene appeared to be slower than that from the 2,4,6-trinitro-4′-dimethylaminostilbene.

The rate of the isatogen formation did not give simple first or second order kinetics. Therefore, the data were plotted as the optical density of the isatogen *vs.* time (Figures 11a, 12a). For Figure 12 the isatogen was estimated from its absorption band at 625 mμ which appeared to be free of interference by any other absorption. For Figure 11, however, there was another absorption band (540 mμ) lying between the two bands (465 mμ and 680 mμ characteristic of the corresponding isatogen. This appeared to be due to indoxyl (see curve b, Figure 7). The optical density of the isatogen at time t was determined by taking the optical density reading at 465 mμ and subtracting from it 73% of the optical density value at 550 mμ as a correction for the indoxyl being formed simultaneously. The failure of the density curves in Figure 11 to extrapolate to zero at zero time (as do those of Figure 12) suggests that an intermediate does indeed have absorption at 465 mμ. Since it was found that faster rates were obtained if the solutions of stilbenes were allowed to stand even for a few hours, all data were taken on freshly prepared solutions, except where indicated. The effect of standing was greater in the more dilute solutions.

The plots are suggestive of autocatalysis, consecutive reactions, or chain reac-

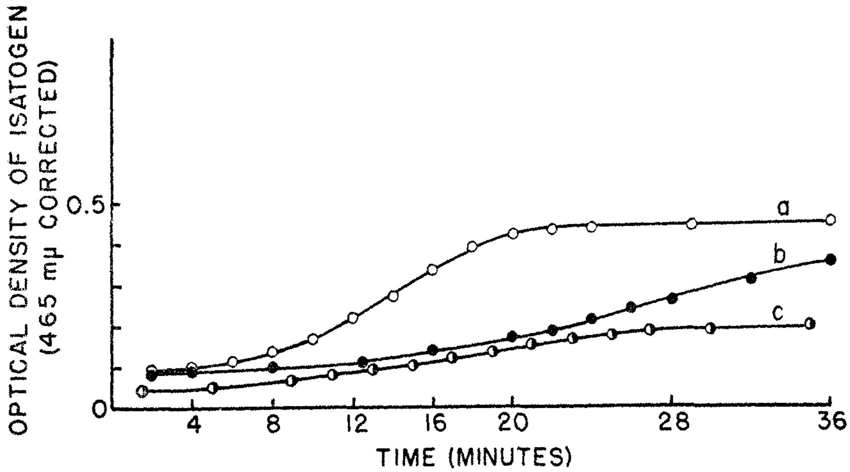


FIG. 11a. KINETIC DATA ON THE FORMATION OF 2-(*p*-DIMETHYLAMINOPHENYL)-4,6-DINITROISATOGEN UNDER VARIOUS CONDITIONS. 2,4,6-Trinitro-4′-dimethylaminostilbene in benzene, 3.5 ml. (a) O.D. at 525 mμ, 1.6 (0.89 × 10^{-4} *M*); irradiated 25 sec.; 25°. (b) O.D. at 525 mμ, 1.6 (0.89 × 10^{-4} *M*); irradiated 25 sec.; 15°. (c) O.D. at 525 mμ, 0.8 (0.445 × 10^{-4} *M*); irradiated 17 sec.; 25°.

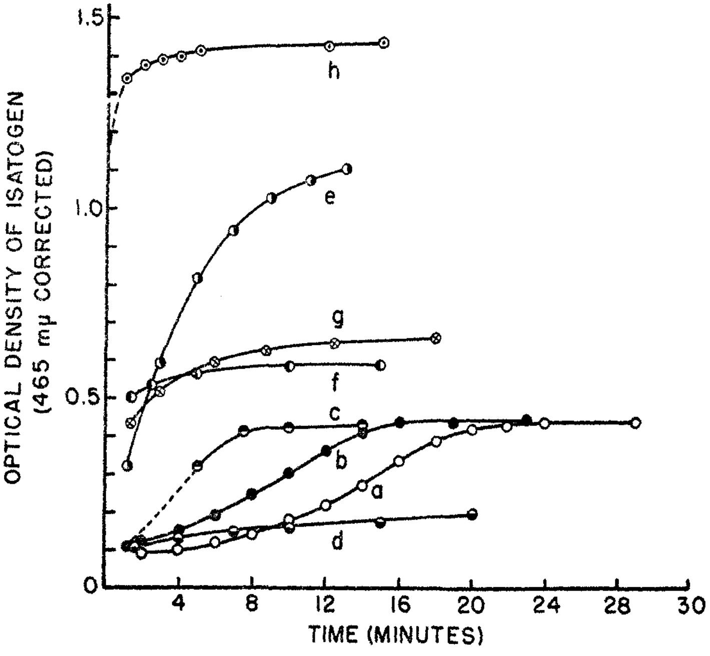


FIGURE 11b. KINETIC DATA ON THE FORMATION OF 2-(*p*-DIMETHYLAMINOPHENYL)-4,6-DINITROISATOGEN UNDER VARIOUS CONDITIONS. 2,4,6-Trinitro-4′-dimethylaminostilbene in benzene, 3.5 ml.; O.D. at 525 mμ, 1.6 (0.89 × 10^{-4} *M*); irradiation time, 25 sec.; 25°. (a) Control; (b) solution aged 3 days before irradiation; (c) irradiation time, 4 minutes; (d) 1 drop of absolute ethanol added before irradiation; (e) 3 moles of VIII added before irradiation; (f) 1 drop of glacial acetic acid added before irradiation; (g) 1 drop of glacial acetic acid added immediately after irradiation; (h) 4 moles of VIII and 1 drop of glacial acetic acid added before irradiation.

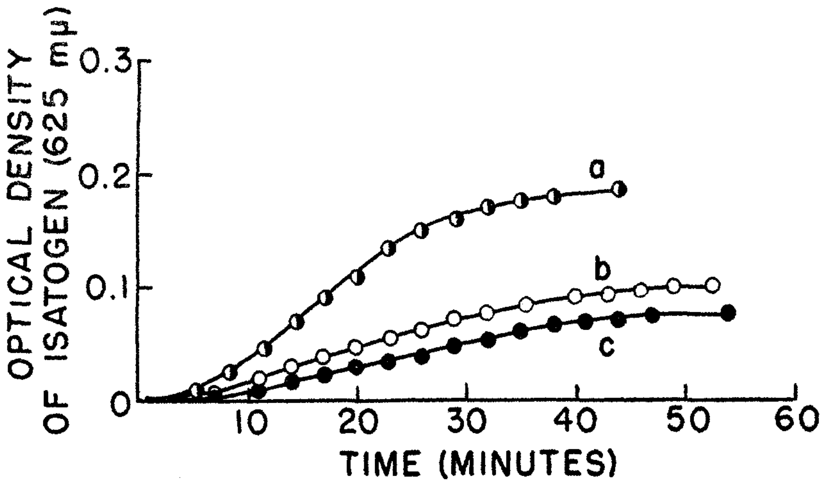


FIGURE 12a. KINETIC DATA ON THE FORMATION OF 2-(*p*-DIMETHYLAMINOPHENYL)-6-NITROISATOGEN UNDER VARIOUS CONDITIONS. 2,4-Dinitro-4'-dimethylaminostilbene in benzene, 3.5 ml. (a) 1.4 × 10^{-4} *M*; irradiated 3.5 minutes; 26°. (b) 1.4 × 10^{-4} *M*; irradiated 3.5 minutes; 15°. (c) 1.4 × 10^{-4} *M*; irradiated 3.5 minutes; then immediately diluted one-half; 26°.

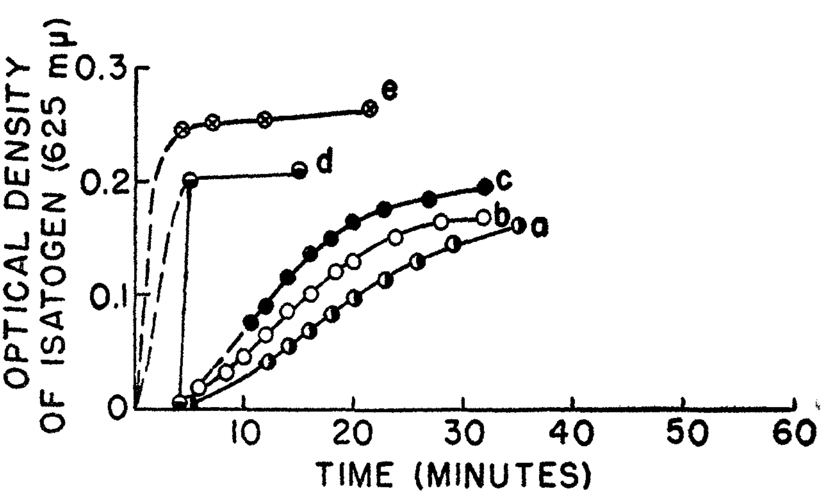


FIGURE 12b. KINETIC DATA ON THE FORMATION OF 2-(*p*-DIMETHYLAMINOPHENYL)-6-NITROISATOGEN UNDER VARIOUS CONDITIONS. 2,4-Dinitro-4'-dimethylaminostilbene in benzene, 3.5 ml.; 1.4 × 10^{-4} *M*; irradiation time, 3.5 minutes; 25°. (a) Control; 1 drop of absolute ethanol added before irradiation; 3 moles of VIII added before irradiation; (b) solution aged 5 days before irradiation; (c) irradiation time, 10 minutes; (d) 1 drop of glacial acetic acid added immediately after irradiation; 1 drop of glacial acetic acid added before irradiation; (e) 4 moles of VIII and 1 drop of glacial acetic acid added before irradiation.

tions. By assuming that the steeper part of the curves represents one reaction with one reaction constant, the activation energy was found to be 15–16 Kcal. for both stilbenes. From second order and first order plots of the data, the activation energy was roughly the same but with a lower value for the formation of isatogen from the 2,4,6-trinitro-4′-dimethylaminostilbene and a higher value from the 2,4-dinitro-4′-dimethylaminostilbene.

In Figures 11b and 12b are shown the effect on the rate of isatogen formation of (a) standing of the solution before irradiation, (b) prolonged irradiation of a freshly prepared solution, and (c) the addition of various substances to the solution. There seemed to be more increase in the rate of isatogen formation from the trinitro- compound than from the dinitro- compound with aging of the solution and with prolonged irradiation. The addition of absolute ethanol caused a greatly decreased rate of isatogen formation from the trinitro- compound, but from the dinitro- compound the rate in the first 40 minutes was nearly the same as the control with the decrease in rate appearing later. When the free radical (VIII) was added in excess (2–3 moles/mole of stilbene) either before or immediately after the irradiation of the trinitro- compound, the rate of isatogen formation was greatly increased. However, when added to the dinitro- compound, the rate in the first 40 minutes was the same as the control but with some decrease in rate appearing later. The molar extinction coefficient of the free radical at 465 mμ was only about 400, so that the correction factor for it at this wave length was small.

The addition of a drop of glacial acetic acid to the benzene solution, either

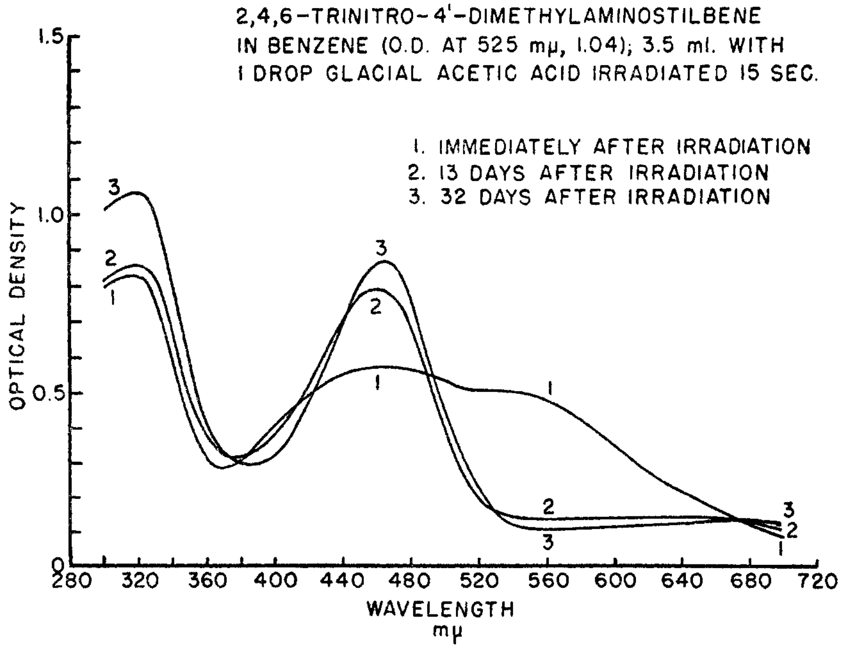


FIGURE 13. ABSORPTION SPECTRA FOLLOWING THE IRRADIATION OF 2,4,6-TRINITRO-4′-DIMETHYLAMINOSTILBENE IN THE PRESENCE OF ACETIC ACID.

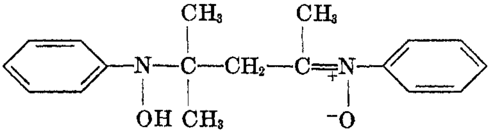
TABLE III

Irradiation of 3.5 ml. of Stilbene Solution Between Two Photospots (9 inches from each)

Stilbene (reagent-grade benzene soln.)	Optical density of stilbene at $\lambda_{\max}$	Added substance	Time of irradiation	Approx. no. of days for completion of the reaction	Isatogen Yield, %	Indoxyl Yield, %	4-Dimethylaminobenzaldehyde Yield, %
Ia	1.57	—	25 sec. (or 4 min.)	14	38–40	21	32
	1.00	EtOH (2 drops) before irrad.	20 sec.	14	27.5	10	49
	1.57	Anthranil (V) (2.5 moles) before irrad.	25 sec.	14	39	19	30?
	1.57	(VIII) (2–3 moles) before or after irrad.	25 sec.	3	60–70	—	40–30?
	.94	(IX) before, excess	20 sec.	14	50	—	Could not determine
	1.52	HOAc (1 drop) before	25 sec.	25	60	—	20–25
	1.53	HOAc (1 drop) after	25 sec.	14	50	—	25
	1.51	HOAc (1 drop) before + (VIII) before (4 moles)	25 sec.	1	75–80	—	Could not determine
	1.00	HOAc (1 drop) before (VIII) after	20 sec.	6	75–80	—	Could not determine
Ib (optical density estimated from a dilution)	3.8	—	3.5 min.	21	50	—	25–35
	3.8	EtOH (1 drop) before	3.5 min.	45	45	—	35
	3.8	(VIII) 4 moles before	3.5 min.	45	40	—	Could not determine
	3.8	HOAc (1 drop) before	3.5 min.	13	50	—	25
	3.8	HOAc (1 drop) after	3.5 min.	19	50	—	25
	3.8	(VIII) 4 moles + HOAc (1 drop) before	3.5 min.	13	50	—	Could not determine

before or after irradiation, caused a greatly increased rate of isatogen formation. When added to the 2,4,6-trinitro-4′-dimethylaminostilbene solution before irradiation, there seemed to be produced a change in mechanism as can be seen from the spectrum immediately after irradiation (Figure 13, curve 1) as compared with Figure 9, curve 1. The amount of isatogen formed was approximately estimated in the same way as for the control, since the intermediate appeared to have a spectrum similar to that of the indoxyl (Figure 7). The formation of isatogen was quite slow after the irradiation, but was catalyzed by further irradiation. When the free radical (VIII) was added even 15 minutes after irradiation to such a solution, the rate of isatogen formation was then greatly increased to an almost instantaneous reaction. When both free radical (VIII) and glacial acetic acid were added before irradiation, isatogen formation was almost instantaneous also. When the glacial acetic acid was added immediately after the irradiation, there was a transient purplish color suggestive of some of the same intermediate as appeared with glacial acetic acid before irradiation.

The yields as reported in Table III were calculated from the composite absorption spectrum taken when the reaction appeared to be completed. The yields of isatogen from the trinitro- compound varied considerably with the addition of various substances. The addition of absolute ethanol resulted in a different proportion of products with the yield of isatogen and indoxyl reduced and that of 4-dimethylaminobenzaldehyde increased. The benzene (drum thiophene-free benzene) that was used in obtaining the data of Table I was found to give approximately the same results as the addition of ethanol to the reagent-grade benzene used to obtain the data of Table III. The yield of 4-dimethylaminobenzaldehyde as reported in Table I was much lower than that calculated from the spectrum when carried out under conditions used in Table III. Very probably, much polymerization occurred during the irradiation of the larger amounts. The addition of the anthranil (V) gave no increase in yield of isatogen. The addition of free radical (VIII) resulted in a greatly increased yield of isatogen (60–70%) and with glacial acetic acid in addition, the yield was even greater (75–80%). The addition of glacial acetic acid alone prevented formation of indoxyl, and the yield of isatogen was greater. With the acetic acid added before irradiation, the yield of isatogen was 60%. This is as yet unexplained and is to be investigated further. With the addition of the product (IX), which, when oxidized, gave the free radical (VIII), the yield of isatogen was only 50%.



IX

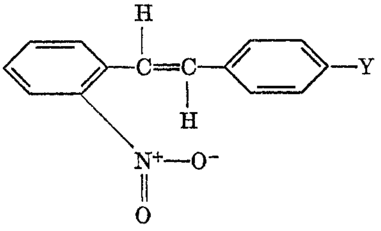
The yields of isatogen from the dinitro- compound did not vary as much. In the two examples, where the yield was less than 50%, the reaction probably was not completed.

DISCUSSION OF MECHANISM

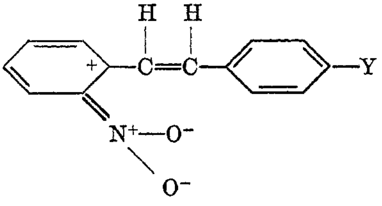
The mechanism of the photochemical rearrangement and oxidation-reduction reaction warrants further investigation. However, it may be of value to indicate now the possible sequence of reactions as deduced from the foregoing results. It seems fairly clear that the rearrangement, or, in particular, the transfer of the oxygen atom from the *o*-nitro group to the α-carbon atom occurs as a direct result of the irradiation and the further oxidation-reduction part of the whole reaction is a thermal dark reaction following the irradiation.

When a molecule of stilbene absorbs radiant energy it is raised to an excited state believed to be more polar than the ground state. If such is the case, then the absorption of light by certain molecules could initiate an ionic type of reaction rather than a radical one if the configuration in space is favorable. In many of the photochemical reactions of *o*-nitro compounds the α-carbon atom in the ground state tends to be electron deficient with respect to groups or atoms attached to it. In the excited state, this deficiency is presumably increased, together with an increase in the electron density on the oxygen atom of the nitro group. In this state a nucleophilic attack on the α-carbon atom by the negative oxygen atom of the nitro group is facilitated. Examples of this are the photochemical reactions of *o*-nitrobenzaldehyde (2), *o*-nitrobenzalaniline (3), *o*-nitrobenzaldehyde diethyl acetal (27), and 1-(β-hydroxy-*o*-nitro-α-phenylphenethyl) pyridinium bromide (7). The *o*-nitro-α-chlorostilbenes and *o*-nitrostilbene dichlorides are similar examples but these and the *o*-nitrotolanes require a basic catalyst for the photochemical reaction to take place (6).

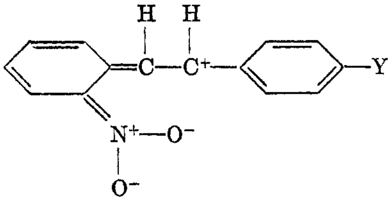
The α-carbon atom in *o*-nitrostilbenes would not be expected to be electron deficient in the ground state, considering the following structures



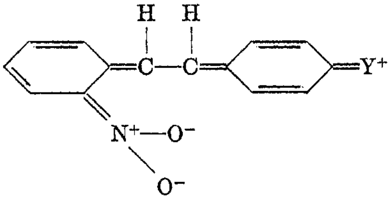
I



I′

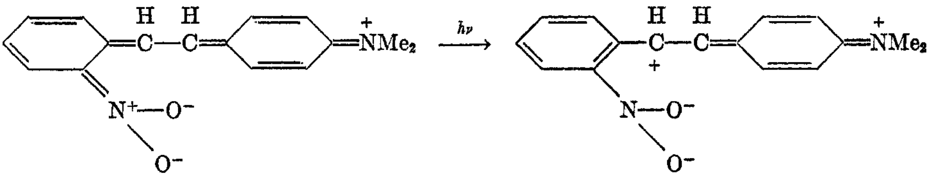


I″



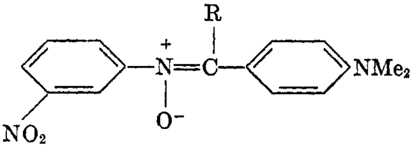
I‴

to be the main contributors to the ground state of the molecule. By a molecular orbital calculation on 4-aminostilbene, Coulson and Jacobs (28) concluded that in the first excited state the greatest electron density is on the carbon atom joined to the ring containing the amino group. Thus one might expect for corresponding reasons that the carbon atom next to the ring containing the nitro group would be electron deficient in the excited state. For the nitrostilbenes in which Y is an electron-releasing group, structure I‴ might be expected to be a major contributor to the electronic structure in the ground state. Then on excitation by light, a further shift of electrons occurs in the nitro half of the molecule, resulting in a deficiency of the electrons on the α-carbon atom. Light of 5450 Å and 5760 Å was found to be active for the 2,4-dinitro- and 2,4,6-trinitro-4′-dimethylaminostilbene, indicating that the lowest excited state of the entire molecule is involved. When the nitro group is in the *p*-position, no further changes occur, excepting *cis*-isomer formation, but with the nitro group in the *o*-position bond formation between a negative oxygen atom of the *o*-nitro group with the α-carbon atom would take place readily. If Y is not an electron-releasing group, then the major contributors to the ground state would be I, I′, and I″. The further shift of electrons would be inhibited because of the adjacent positive charge on the α'-carbon atom in I″. In such a case very little rearrangement would be expected to occur upon absorption of light, *cis*-isomer formation and/or polymerization being the main result. This was found to be true as shown in Table I.[2]

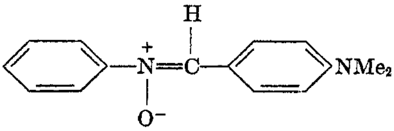


I_c''' I_c^*

From inspection of Figure 10 it appeared that immediately after irradiation of the stilbene, there was little absorption on the long wave length side of 350 mμ. However, there was rapidly formed a substance with λ_{max} about 385 mμ. The buildup of this intermediate took about 30 minutes or longer, during which time isatogen was also forming. The molar extinction coefficient of this intermediate was estimated to be at least 10,000 by subtracting the isatogen component of absorption from curve 7, Figure 10. The amount of isatogen was estimated from the absorption at 625 mμ. There remained a curve similar to curve 1 with a λ_{max} at 385 mμ. This then was considered to be due to an amount of intermediate correspondign to 36% of the initial stilbene since 64% of the final amount of isatogen had formed at this time (curve 7). Such an absorption is about that to be expected from a chromophore of the type



The compound, α-(*p*-dimethylaminophenyl)-N-phenylnitrone (X) was found to have the



X

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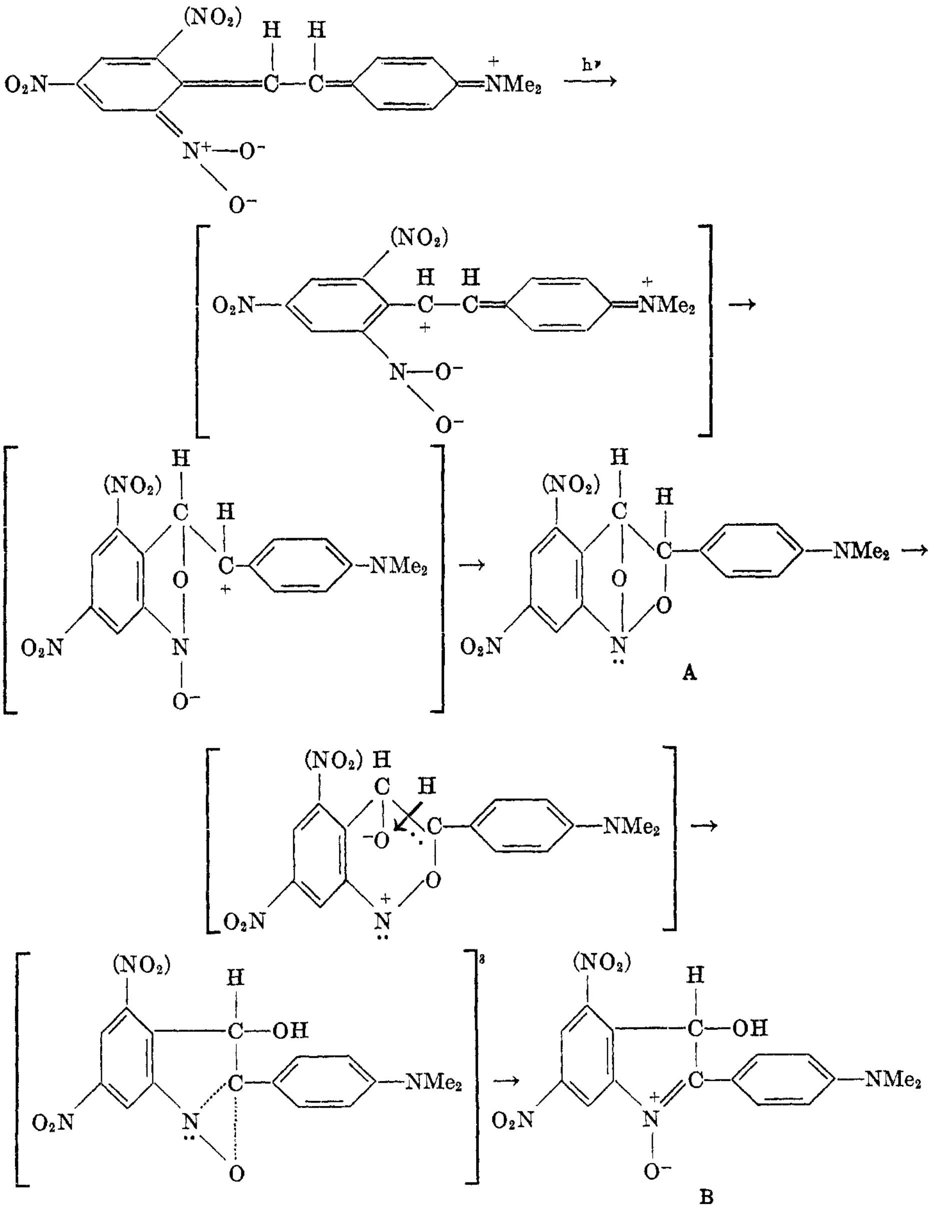
[2] Recently Ried and Wilk [*Ann.*, **590**, 91 (1954)] have found that electron-releasing groups in the 4-position of anils of *o*-nitrobenzaldehyde facilitate the photochemical rearrangement.

λ_{max} at 375 mμ, with ϵ of 30,900 in benzene. If in this intermediate the conjugation between the two benzene rings were through the carbon-carbon bond as in the original stilbene, then the λ_{max} would be close to that of the stilbene, which it is not. So, the mechanism up to this point might be as follows, with intermediate **A** as the direct result of irradiation.



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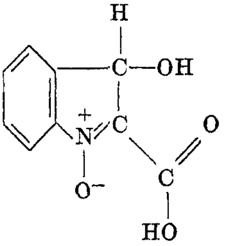
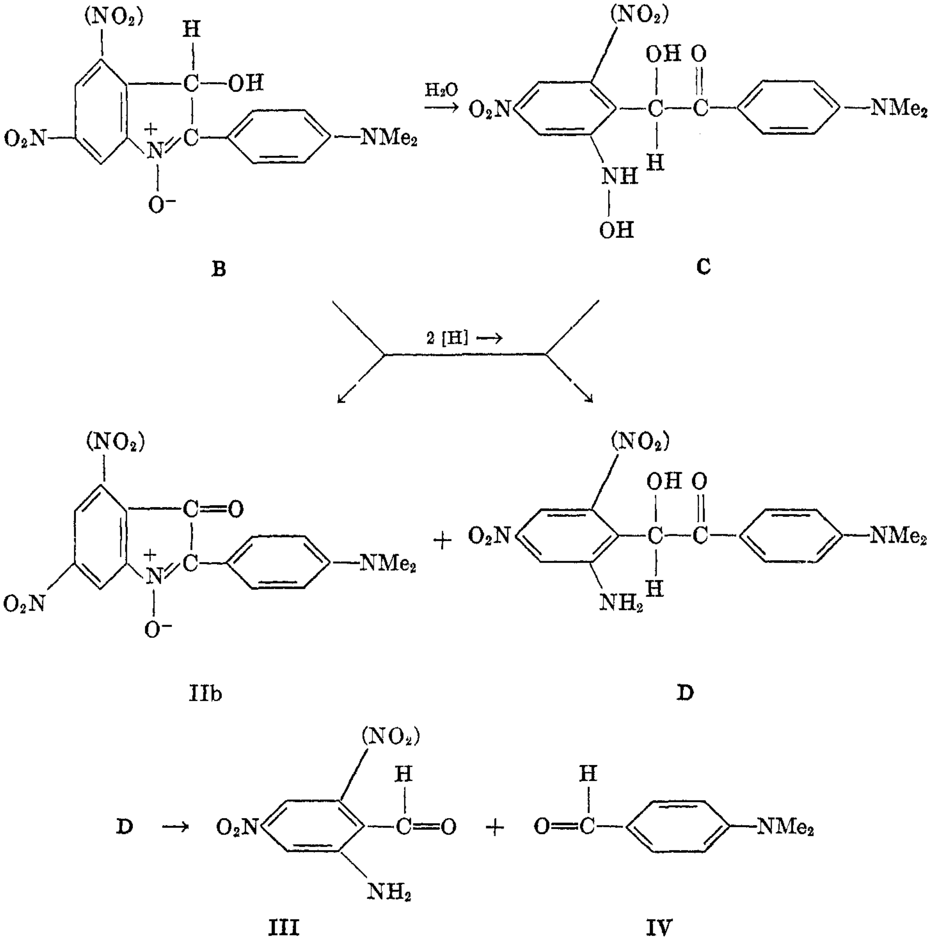
[3] This structure is similar to the structure proposed by Ruggli, *Ber.*, **52**, 1 (1919) for isoisatogens. However, there is some uncertainty about the structure of isoisatogens [Sumpter and Miller, *Heterocyclic Compounds*, Vol. 8, Interscience Publishers, Inc., New York, New York (1954), p. 158].

This colorless intermediate then rapidly rearranges to **B**, with λ_{max} about 385 mμ. The spectrum of the intermediate **B** in the case of the 2,4,6-trinitro- compound (Figure 9) was not so readily ascertained. It probably was more unstable than that from the 2,4-dinitro- compound so that an appreciable build-up of it could not be seen. There has been one report (29) of an isolated compound which was thought to have a structure similar to **B**. 2-Nitrocinnamic acid on irradiation gave an isomer believed to be



The nitrone probably was stabilized to hydrolysis by the carboxyl group as in the case of pyruvic acid semicarbazone (30).



Since aldehyde nitrones hydrolyze readily in the presence of acid (31), intermediate **B** being a ketone nitrone would be expected to hydrolyze even more readily. Ketone semicarbazones have been found to hydrolyze much more easily than aldehyde semicarbazones (30, 32). The amount of water in the benzene was about 100 moles excess over the stilbene used. A trace of acid could have been formed by an oxidation of a stilbene molecule during the irradiation, although the intermediate **B** may not require it for hydrolysis.

For **B** to be converted to isatogen, another molecule must be reduced. As **B** is partially hydrolyzed to **C**, the oxidation-reduction process may take place between **B** and **C**.

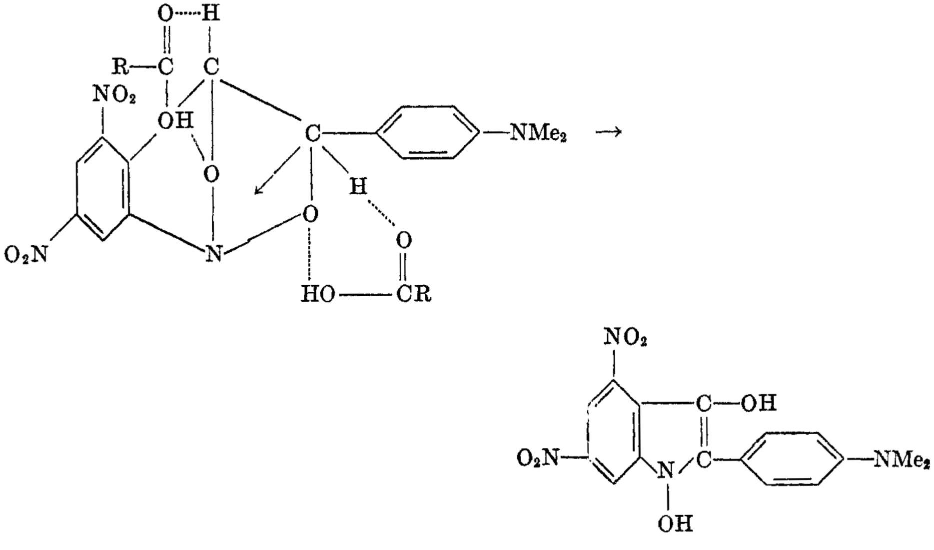
Since the rate of the isatogen formation subsequent to the complete disappearance of stilbene was sensitive to such factors as light, presence of radicals, and the aging of the stilbene solution before irradiation (peroxides?), the oxidation-reduction probably takes place by a radical mechanism. The reaction of **B** with **C** could be considered analogous to the dismutation of phenylhydroxylamine, which is thought to be a chain reaction, easily started by atmosphere oxygen (33). Because of the stability of the isatogen, it is to be expected that in the presence of an oxidizing agent, **B** may be easily oxidized to it. A similar oxidation is that of benzoin to benzil. The benzoin cleavage of **C** or its reduction product **D** may take place at any time. Neither aminobenzaldehydes nor nitrobenzaldehydes form symmetrical benzoins readily, but the aminobenzaldehyde can contribute the carbonyl half of a benzoin (34). It would therefore be likely that the benzoin **D** would not be a stable one and would dissociate to the 4-dimethylaminobenzaldehyde (IV) and the 2-amino-4-nitrobenzaldehyde (III). In the case of the 2,4,6-trinitro- compound, the 4,6-dinitroanthranil (V) and 2-(*p*-dimethylaminophenyl-4,6-dinitroindoxyl (VI) were also formed. The anthranil (V) very probably formed from 2-hydroxylamino-4,6-dinitrobenzaldehyde. In the presence of acid, 2-hydroxylaminobenzaldehyde readily forms anthranil (15). This would indicate that at least some of **C** dissociates to produce a hydroxylaminobenzaldehyde and 4-dimethylaminobenzaldehyde (IV). Since the anthranil is at the same oxidation level as **B** or the stilbene, that amount of intermediate is lost as far as isatogen formation is concerned. The only reduction product isolated was the indoxyl (VI) which could result from reduction of **B** or the isatogen. A trace of the indolone (VII) was also isolated. The yield of indoxyl was not equal to that of the isatogen so presumably some 2-amino-4,6-dinitrobenzaldehyde was formed and polymerized.

The action of the free radical (VIII) in the irradiation of the 2,4,6-trinitro-compound probably was just a dehydrogenation of some of **B**. In the case of the 2,4-dinitro- compound, the free radical did not have this action.

In the presence of absolute ethanol in the benzene solution of the 2,4,6-trinitro- compound, the amount of the anthranil may have been much greater so that the yield of both isatogen and indoxyl were decreased. As seen from Table III, the yield of 4-dimethylaminobenzaldehyde was increased as compared with the control reaction. If the action of the alcohol was simply to increase the rate of **B** → **C** and possibly the rate of the benzoin cleavage of **C** these results would be accounted for.

With the addition of acetic acid to the solution of the 2,4-dinitro- compound, the rate of isatogen formation was greatly increased. The spectrum of **B** disappeared rapidly with the addition of the acetic acid. The acid evidently increased the rate of hydrolysis of **B** to **C**, which, in turn, was then available for the oxidation-reduction step of the reaction.

When the glacial acetic acid was added to the 2,4,6-trinitro-4′-dimethylaminostilbene in benzene before irradiation, the mechanism of the transformations appeared to be different. The spectrum of the solution taken immediately after irradiation (Figure 13) is suggestive of the presence of an intermediate with a spectrum similar to that of the indoxyl. Because of this similarity and the fact that it ultimately is converted to isatogen, its structure may very well be **E**. The presence of the acetic acid might be expected to catalyze the conversion of **A** to **E** by acting as a carboxyl bridge for proton transfer.



E

This intermediate **E** would be expected to be easily dehydrogenated by the free radical (VIII) as was found to be the case. When the acetic acid was added immediately after irradiation, a little of this intermediate appeared to be formed. The mechanism of isatogen formation from **E** is to be investigated further.

EXPERIMENTAL[4]

2,4,6-Trinitro-4′-dimethylaminostilbene (Ia). A solution of 3 g. (0.0132 mole) of 2,4,6-trinitrotoluene, 2 g. (0.0134 mole) of 4-dimethylaminobenzaldehyde, and 3 drops of piperidine in 10 ml. of reagent grade benzene was kept in the dark at room temperature for 24 hours. The dark green crystals were filtered; yield, 2.7 g. (57%); m.p. 227–228° dec. The filtrate was evaporated leaving 1.9 g. of reddish-brown crystals; m.p. 57–62°. These were dissolved in 10 ml. of benzene and 3 drops of piperidine and kept in the dark at room tem-

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[4] The absorption spectra were taken on a Cary Model 11 recording spectrophotometer; microanalyses were performed by the Microchemical Laboratory, University of California; the silicic acid used for chromatography was Baker and Adamson reagent grade.

perature for 3 days. The dark green crystals were filtered; m.p. 227–228° dec., yield, 1.5 g. Total yield was 4.2 g. (89%). After several recrystallizations from xylene, the m.p. was 232–233° dec.

Anal. Calc'd for $C_{16}H_{14}N_4O_6$: C, 53.63; H, 3.94; N, 15.64.

Found: C, 53.63; H, 3.95; N, 15.31.

2-(p-Dimethylaminophenyl)-4,6-dinitroisatogen (IIa). A solution of 100 mg. of 2,4,6-trinitro-4′-dimethylaminostilbene in 300 ml. of thiophene-free benzene in a 500 ml. Pyrex flask was irradiated by placing the flask in direct sunlight for 12 hours. The green-colored solution, with some precipitated solid, was chromatographed on a 15-cm. long column of 40 g. of silicic acid and 20 g. of Supercel packed in a 3 x 50 cm. tube. The chromatogram was developed and eluted with benzene under the vacuum of water aspirator. With addition of 300 ml. of benzene, most of the green layer was collected and then was evaporated; the dark green crystals were washed with 10 ml. of benzene and filtered; yield, 38 mg. (38%); m.p. 206–208° dec. The isatogen was recrystallized from glacial acetic acid, m.p. 210–211° dec.

Anal. Calc'd for $C_{16}H_{12}N_4O_6$: C, 53.93; H, 3.39; N, 15.72.

Found: C, 53.96; H, 3.58; N, 15.40.

Most of the benzene was removed from the column by suction and the dark brown-colored top one-half inch of the column removed. When treated with acetone, filtered and the filtrate evaporated, there was 23 mg. of dark reddish-brown resinous material; m.p. 105–150°. Acetone now was passed through the purplish-colored column until all of the colored products were removed. The acetone solution was evaporated and the crystals of indoxyl (VI) were washed with benzene; yield, 13 mg. (13%); sintered about 250°. This product was quite soluble in acetone but rather insoluble in benzene. Its solution was stable towards light. This compound was identical to that obtained by reduction of the isatogen with hydrazine hydrate. In some cases, there was a bluish-green band between the green isatogen band and the purple indoxyl band. This gave very small amounts of the indolone (VII).

From chromatographing the washings of the isatogen, there was obtained a trace of 2,4,6-trinitrotoluene, which was eluted first. After recrystallization from ethanol, the m.p. was 76–78° and gave no depression when mixed with an authentic sample. Eluted next was 4,6-dinitroanthranil (V) yield, 9 mg. (15%); m.p. 100–115°; after recrystallization from ethanol, m.p. 120–122°. The compound was identified by mixture melting point and comparison of absorption spectrum with that prepared by reduction of 2,4,6-trinitrobenzaldehyde.

When the same amount of irradiated solution of the stilbene was chromatographed on a 1½ x 9 cm. column of magnesium oxide (heavy) without suction, the isatogen, dinitroanthranil, trinitrotoluene, and the indoxyl were adsorbed and the only product not adsorbed was the 4-dimethylaminobenzaldehyde (IV). The yield of this was 8 mg. (19%), calculated from the absorption spectrum. The 2,4-dinitrophenylhydrazone was prepared, m.p. 236° dec., with no depression in melting point when mixed with an authentic sample (35). The absorption spectra in benzene were identical.

4,6-Dinitroanthranil (V). To a solution of 0.5 g. of 2,4,6-trinitrobenzaldehyde in 75 ml. of 95% ethanol was added 13 g. of a 15% aqueous solution of titanium trichloride in portions with stirring. Benzene was added until there were two layers, these were separated, and the benzene layer was evaporated to dryness. The dark resinous solid was extracted with benzene and the extract was evaporated. The light-colored solid was washed with 95% ethanol and then was recrystallized from 95% ethanol; first crop, 45 mg., m.p. 120–122°; second crop, 35 mg., m.p. 115–120°; total yield, 80 mg. (18%). To remove colored impurities, a benzene solution of the product was passed through a column of 10 g. of silicic acid and 5 g. of Supercel. The solid from the evaporation of the benzene solution was recrystallized from 2 ml. of 95% ethanol; m.p. 122–124°; yield, 50 mg. (11%).

Anal. Calc'd for $C_7H_3N_3O_5$: C, 40.20; H, 1.45; N, 20.09; Mol. wt., 209.

Found: C, 40.47; H, 1.61; N, 19.84; Mol. wt., 196.

2-(p-Dimethylaminophenyl)-4,6-dinitroindoxyl (VI). A suspension of 46 mg. of 2-(p-dimethylaminophenyl)-4,6-dinitroisatogen in 20 ml. of 95% ethanol and 0.5 ml. of hydrazine hydrate was heated at just below boiling for one-half hour. The suspension was cooled and filtered and the solid was washed with water. The yield was about 85%. The solid was recrystallized once from glacial acetic acid, giving dark green crystals which sintered about 240°.

Anal. Calc'd for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37.

Found: C, 56.09; H, 4.08; N, 16.01.

2-(p-Dimethylaminophenyl)-4,6-dinitroindolone (VII). A mixture of 49 mg. of 2-(*p*-dimethylaminophenyl)-4,6-dinitroindoxyl and 200 mg. of benzoyl peroxide in 50 ml. of acetone was allowed to stand at room temperature for five hours. Then the mixture was poured into a large evaporating dish and allowed to evaporate to dryness. The residue was powdered and washed with 5 ml. of 95% ethanol to remove the benzoyl peroxide. The ethanol was not in contact with the indolone for more than a few minutes to prevent deterioration of the indolone. The crude indolone then was dissolved in 25 ml. of benzene with heat and the solution was filtered from unreacted indoxyl and other impurities. The filtrate was diluted with 50–75 ml. of ligroin and allowed to stand one hour. The solid was filtered; dark green crystals, m.p. 208–209° dec.; yield, 20–25 mg. (40–50%).

Anal. Calc'd for $C_{16}H_{12}N_4O_5$: C, 56.47; H, 3.55; N, 16.47.

Found: C, 56.40; H, 3.57; N, 16.46.

2-(p-Dimethylaminophenyl)-6-nitroisatogen (IIb). A solution of 500 mg. of 2,4-dinitro-4′-dimethylaminostilbene (36) in 500 ml. of thiophene-free benzene was irradiated in a Pyrex flask in bright sunlight for 25 hours, the color turning from red to green. The solution was chromatographed with suction on a column of 40 g. of silicic acid and 20 g. of Supercel packed in a tube 3 x 50 cm. Benzene was used to develop and elute the bands. The forerun, before the dark green band, was concentrated and rechromatographed into several fractions. The first contained 2,4-dinitrotoluene, obtained by evaporation, dissolving in ethanol and precipitating with water; m.p. 68–70°; mixture m.p. with authentic sample, 68–70°; yield, 2 mg. (0.7%). The other fractions gave 40 mg. (15%) of 2-amino-4-nitrobenzaldehyde (III), which, when recrystallized from water, yielded 10 mg. of yellow crystals, m.p. 120–123°. This was identified by mixture m.p. and comparison of absorption spectra with an authentic sample (14). The main dark green band on the column was eluted and the green solution was evaporated. The residue was washed with a small amount of benzene; yield, 220 mg. (44%) of dark green crystals, the isatogen; m.p. 214.5–215.5° dec. When recrystallized from benzene, the melting point was 215–215.5° dec.

Anal. Calc'd for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50.

Found: C, 61.71; H, 4.29; N, 13.32.

At the top of the column there was a dark brown layer which was removed by acetone. This yielded 115 mg. (23%) of dark brown resinous material, m.p. 100–140°.

When a solution of 100 mg. of the stilbene in 100 ml. of thiophene-free benzene was irradiated 12 hours in sunlight and chromatographed on 10 g. of magnesium oxide (heavy) in a 1.8 x 40 cm. tube, the isatogen was eluted quite rapidly with benzene under suction. The green solution was evaporated and the crystals were washed with 5 ml. of benzene; yield, 43 mg. (43%). From the filtrate there was isolated some 2-amino-4-nitrobenzaldehyde (III) but 4-dimethylaminobenzaldehyde could not be isolated. However, from the spectrum, it was quite likely that this compound was present.

2-Nitro-4′-dimethylaminostilbene (Ic). This was prepared according to the method used for 4-nitro-4′-dimethylaminostilbene (36). A mixture of 0.5 g. of 4-dimethylaminobenzaldehyde, 0.6 g. of 2-nitrophenylacetic acid, and 0.1 ml. of piperidine was heated at 90–92° for 10 hours. A few ml. of benzene was added and the solution was chromatographed on a column of 10 g. of silicic acid and 5 g. of Supercel (1.8 x 13 cm.). The orange band was developed and eluted with benzene. Other colored material remained at the top of the column. The benzene solution was evaporated and the residue was dissolved in about 5–10 ml. of ethanol and 2–5 ml. of distilled water was added until the solution was faintly cloudy. The red crystals which appeared were filtered; m.p. 80–85° dec.; yield, 0.1 g. (11%). This was recrystallized twice from the minimum amount of 95% ethanol; m.p. 87–89° dec.

Anal. Calc'd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44.
Found: C, 71.78; H, 5.87; N, 10.71.

2-(p-Dimethylaminophenyl)isatogen (IIc). It was found that the irradiated solution of 2-nitro-4'-dimethylaminostilbene could not be chromatographed on silicic acid because the isatogen was adsorbed. The solution could be chromatographed on magnesium oxide (heavy) but this was not necessary. A solution of 100 mg. of 2-nitro-4'-dimethylaminostilbene in 100 ml. of thiophene-free benzene in a Pyrex flask was irradiated for 14 hours in direct sunlight and then was evaporated to dryness. About 5 ml. of 95% ethanol was added to the dark blue crystals and the crystals were filtered; yield, 24 mg. (24%); m.p. 201–203° dec. This product was recrystallized from 95% ethanol, m.p. 208–209° dec.

Anal. Calc'd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52.
Found: C, 72.22; H, 5.49; N, 10.62.

There was 2 mg. of resin deposited on the walls of the flask during the irradiation, which was insoluble in benzene but soluble in acetone. When the ethanol washing of the isatogen was evaporated, benzene was added, and the mixture was filtered there was obtained 6 mg. of dark brown solid. The rest of the alcohol and benzene-soluble material had a strong odor of aldehydes but nothing could be identified.

When 3.5 ml. of a dilute solution of the stilbene in benzene (10^{-4} *M*) was irradiated in sunlight with Pyrex filter for 5 minutes, just enough to decompose the stilbene, and the irradiated solution was allowed to stand overnight, the amount of isatogen formed was calculated from the absorption spectrum to be about 37%. It may be that in larger quantity some of the intermediates or the isatogen decomposed during the irradiation so that a lower yield resulted.

2,4-Dinitro-4'-hydroxystilbene (Id). This was prepared according to the procedures of Hargreaves and McGookin (18) from 2,4-dinitrotoluene, 4-hydroxybenzaldehyde, and piperidine. They reported obtaining one isomer, *trans-*, m.p. 186°, by heating the reactants in benzene, the other, *cis-*, m.p. 168° by heating the reactants without a solvent. By both methods only one isomer, the *trans*, was obtained, m.p. 178–180°, with no depression of mixture m.p. and identical absorption spectra.

2-(p-Hydroxyphenyl)-6-nitroisatogen (IId). A solution of 280 mg. of 2,4-dinitro-4'-hydroxystilbene in 500 ml. of thiophene-free benzene in a Pyrex flask was irradiated in direct sunlight for 19 hours. The red solution then was filtered; there resulted a dark brown solid, m.p. 130–150°, yield, 36 mg. (13%). This was probably a polymerization product. The flask was rinsed with acetone and the acetone washing was evaporated, leaving a tan solid; yield, 6 mg. (2%). The filtrate was concentrated to 200 ml., and then was chromatographed on a column of 40 g. of silicic acid and 20 g. of Supercel (3 x 15 cm.). Benzene was used to develop and elute the bands. The first fraction contained about 1 mg., probably 2,4-dinitrotoluene, since its absorption spectrum was similar to that of 2,4-dinitrotoluene. The next fraction was colorless on the column but gave a yellow solution, from which there was obtained 8 mg. (5%) of crude 2-amino-4-nitrobenzaldehyde. This was purified by recrystallization from hot water; m.p. 123–127°; identified as described under preparation of IIb. The next fraction was from the yellow band and was found to be unchanged stilbene. This was re-irradiated and chromatographed. The isatogen band was dark red and gave a red solution. The solutions were evaporated and the solid was washed with a little benzene, m.p. 224–227° dec.; total yield, 110 mg. (40%). After two recrystallizations from glacial acetic acid, the m.p. was 233–235° dec.; the m.p. reported by Pfeiffer (6) for this compound was 235–236°. The mixture m.p. with a sample prepared from the hydrolysis of the 2-(*p*-acetoxy)-6-nitroisatogen, according to Pfeiffer (6), showed no depression and the absorption spectra were identical. There was obtained also 84 mg. (30%) of dark brown resinous material, which was removed from the column with acetone.

When 38 mg. of stilbene in 268 ml. of benzene was irradiated 14 hours, concentrated, and then chromatographed, the isatogen fraction contained 15 mg. of isatogen (39%) according to spectroscopic determination.

2-(p-Methoxyphenyl)-6-nitroisatogen (IIe). A solution of 500 mg. of 2,4-dinitro-4'-

methoxystilbene (18) in 500 ml. of thiophene-free benzene in a Pyrex flask was irradiated for 45 hours by direct sunlight. Then the red solution was concentrated to about 200 ml. and chromatographed on a column of 40 g. of silicic acid and 20 g. of Supercel (3 x 15 cm.). The chromatogram was developed and eluted with benzene. The first fractions (yellow) contained unchanged stilbene plus a little isatogen. The total weight after evaporation was 166 mg. which was re-irradiated in 166 ml. of benzene for 45 hours.

The next fractions (red) were of isatogen. The solution was evaporated to dryness, from which 70 mg. were obtained; yield, 21% based on stilbene decomposed; m.p. 227–237°. This was recrystallized twice from glacial acetic acid, m.p. 256–258°. The mixture m.p. with the isatogen prepared according to Pfeiffer (6) was 255–258°. Both gave the same absorption spectrum in benzene. At the top of the column there was a dark brown layer of which almost all was removed by developing and eluting with acetone. After evaporation of solvent, there was 153 mg. (46%); m.p. 90–150°. This was probably polymeric material. There was also a brown film on walls of the original flask.

The re-irradiated material was concentrated to about 15 ml. and the isatogen was filtered. The filtrate was chromatographed. From the foreruns, it appeared spectroscopically that there was a trace of 2-amino-4-nitrobenzaldehyde. The red band was eluted and the benzene was evaporated. The solid was washed with a small amount of benzene. This, together with the filtered isatogen, was 44 mg.; m.p. 222–228°. The total yield of isatogen was 23% with most of the remainder a dark brown resinous material.

A similar experiment using 100 mg. of stilbene yielded 18 mg. of isatogen, m.p. 233–239°, and 18 mg. of recovered stilbene, determined spectrophotometrically. Based on the stilbene used, the yield of isatogen was 22% and the total resinous material 58%, of which about 10% was deposited on the walls during irradiation.

2-(p-Acetoxyphenyl)-6-nitroisatogen (IIf). A solution of 300 mg. of 2,4-dinitro-4′-acetoxystilbene (6) in 275 ml. of thiophene-free benzene in a Pyrex flask was irradiated in bright sunlight for 80 hours. The solution was concentrated and chromatographed on a column of 8 g. of silicic acid and 4 g. of Supercel (1.8 x 10 cm.). The bands were developed and eluted with benzene. There was a very small amount of recovered stilbene in the first yellow fraction. The next fraction, from the orange band, yielded 9 mg. (3%) of isatogen; m.p. 220–224°; m.p. reported by Pfeiffer (6), 235°. The remainder of the product was resinous.

2-(p-Chlorophenyl)-4,6-dinitroisatogen (IIg). A solution of 500 mg. of 2,4,6-trinitro-4′-chlorostilbene (37) in 500 ml. of thiophene-free benzene in a Pyrex flask was irradiated in sunlight for about 100 hours. The dark brown solid that was deposited on the walls and bottom of the flask weighed 55 mg. The evaporated solution was treated with successive portions of 10 ml. of benzene and the portions were chromatographed on a column of 14 g. of silicic acid and 7 g. of Supercel (1.8 x 18 cm.). The dark solid remaining weighed 10 mg. and was similar to that on the bottom and walls of the flask. The orange-colored isatogen-band on the column was eluted with benzene, the solution was evaporated, and the red solid was washed with a small amount of glacial acetic acid, yield, 95 mg. This was recrystallized from 20 ml. of glacial acetic acid; yield, 54 mg.; m.p. 241–243° dec.

Anal. Calc'd for $C_{14}H_6ClN_3O_6$: C, 48.36; H, 1.74; N, 12.09.

Found: C, 48.32; H, 1.79; N, 11.93.

Additional isatogen, 12 mg., was recovered from the filtrate; by spectrophotometric determination of other crude material, there was 15 mg.; total yield, 81 mg. (16%). There was obtained 22 mg. of gummy material from the forerun which had an odor of aldehydes but from which nothing could be identified. There was obtained 253 mg. of brown resinous material from the column by elution with acetone. Total yield of resinous products was 318 mg. (64%).

2-(Phenyl)-4,6-dinitroisatogen (IIh). A solution of 500 mg. of 2,4,6-trinitrostilbene (38) in 300 ml. of thiophene-free benzene was irradiated for 65 hours in a Pyrex flask in direct sunlight. A dark brown solid on the bottom and sides of the flask was filtered and washed with benzene; the solid did not melt below 230°, yield, 42 mg. The main solution was concentrated to 75 ml. and was chromatographed on a column of 40 g. of silicic acid and 20 g.

of Supercel (3 x 15 cm.). The bands were developed and eluted with benzene. There was 10 mg. of dark brown insoluble material in the concentrated solution. The main orange band after elution and evaporation yielded 210 mg. of crude isatogen, which was washed with a few milliliters of glacial acetic acid, yield, 88 mg. This product was recrystallized from 10 ml. of glacial acetic acid, 64 mg.; m.p. 253–255° dec. By spectrophotometric determination there was an additional 16 mg. of isatogen in the filtrate. The total yield was then 80 mg. (16%).

Anal. Calc'd for $C_{16}H_7N_3O_6$: C, 53.68; H, 2.25; N, 13.42.

Found: C, 53.80; H, 2.34; N, 13.18.

The brownish band at the top of the column was eluted with acetone. This together with resinous material from the crude isatogen was 270 mg., m.p. 100–130° dec. Total resinous material was 322 mg. (64%).

2-(Phenyl)-4-nitroisatogen (IIi). A solution of 100 mg. of 2,6-dinitrostilbene (6) in 100 ml. of thiophene-free benzene in a Pyrex flask was irradiated in sunlight for 60 hours. The dark film on the flask weighed 7 mg. The solution was concentrated by evaporation and then was placed on a column of 10 g. of silicic acid and 5 g. of Supercel (1.8 x 13 cm.). The chromatogram was developed and eluted with benzene. The first fraction before the orange band contained about 2 mg. of stilbene. The orange band, after elution and evaporation of the resultant solution, gave a red solid and resinous material. A few drops of acetic acid were added and the solid was filtered; 12 mg., m.p. 155–175°. This was recrystallized from 2 ml. of 95% ethanol; m.p. 189–190°; yield 6 mg. (6%). Pfeiffer (6) reports this compound melting at 194°. The resinous material extracted from the column with acetone weighed 50 mg.

Irradiation of 2,4,4',6-tetranitrostilbene (Ij). A solution of 50 mg. of 2,4,4',6-tetranitrostilbene (39) in 50 ml. of thiophene-free benzene in a Pyrex flask was irradiated in direct sunlight for 100 hours. A dark brown solid separated during the irradiation. The solution was concentrated and chromatographed on a column of 10 g. of silicic acid and 5 g. of Supercel (1.8 x 13 cm.). The yellow band was eluted and the solution was evaporated; yield, 16 mg. (32%); m.p. 150–155°. This appeared to be recovered stilbene. The remainder of the isolated products was resinous.

α-(p-Dimethylaminophenyl)-N-phenylnitrone (X). To a solution of 1.5 g. (0.01 mole) of 4-dimethylaminobenzaldehyde and 1.1 g. (0.01 mole) of N-phenylhydroxylamine in 10 ml. of 95% ethanol was added distilled water until cloudy. The yellow precipitate which soon appeared was filtered. The solid was dissolved in 95% ethanol and was reprecipitated by the addition of water, m.p. 132–136°; yield, 1.9 g. (79%). A small amount was purified further for analysis, by dissolving in 95% ethanol and precipitating by adding water just to the point of cloudiness; yellow needles, m.p. 136–138°. Exposure to light was avoided as much as possible. In benzene, the λ_{max} was 375 mμ and the molar extinction coefficient was 30,900.

Anal. Calc'd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66.

Found: C, 75.22; H, 6.87; N, 11.69.

SUMMARY

Some *o*-nitrostilbenes were found on irradiation to give substituted isatogens instead of the expected *cis*-isomers, when substituted by electron-releasing groups in the *p*-position of the ring not containing the nitro group.

The absorption spectra of the stilbenes and isatogens are discussed.

The photochemical reaction consisted of two phases: the disappearance of the stilbene by the absorption of light and the following thermal dark reaction. At least two intermediates were apparent by spectroscopic study of the dark reaction. The chemical nature of these intermediates was suggested particularly from their absorption spectra. A study of the kinetics of the reaction and the isolation of products indicated a complex reaction involving both ionic and radical steps.

The light rearrangement and the formation of the two intermediates were thought to take place by an ionic mechanism. The conversion of the second intermediate to the isatogen appeared to be an oxidation-reduction process by a radical mechanism.

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