Tetrahedron, 1966, Vol. 22, pp. 1309 to 1316. Pergamon Press Ltd. Printed in Northern Ireland

REASSIGNMENT OF STRUCTURES OF THE DIHYDRO-v-TETRAZINES.—II

MECHANISM OF OXIDATION OF DIACYLHYDRAZONES[1]

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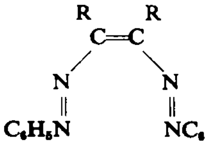
(*Received* 8 *June* 1965; *in revised form* 4 *October* 1965)

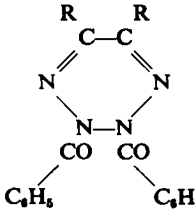
Abstract—Oxidation of biacetyl-bis-mesitoylhydrazone (VA) gives acetonitrile and azodimesitoyl (VII). Oxidation of bis-mesitoyl- and bis-(2,4-dichlorobenzoyl)-hydrazones (VB, VC, VD) gives, instead of the expected 1-amino-1,2,3-triazole enol benzoate (III), 1-amino-1,2,3-triazole derivative (VIII), formed by cleavage of one of the acyl groups. These data show that "tetrazines" are formed only when acyl migration is not sterically retarded and therefore argue against the possibility of the zwitterionic structure IV. On the other hand oxidation of mixed osazones (IXA, IXB), gives the expected bis-azo-ethylene (I).

There is spectral evidence that the oxidation of the disilver salt of the hydrazone (VB) gives initially an azoethylene analogous to VI, with subsequent formation of the triazole derivative (VIII); an analogous path is proposed for the formation of the enol benzoates III.

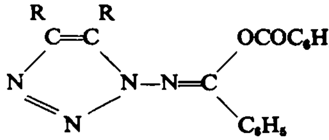
The oxidation of diphenylosazones has long been known to give colored bis-azo-ethylenes (I).[3,4] The oxidation of certain analogous bis-benzoylhydrazones gives colorless products which had originally been assigned the dihydro-v-tetrazine structure (II). This structure has been revised[4] to the benzoylaminotriazole enol benzoate



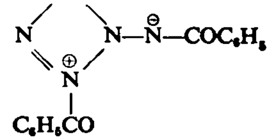
I



II



III



IV

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[1] This work was supported by a grant (G-14,480) from the National Science Foundation for which we express our appreciation.

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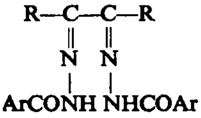
[3] See E. Hoggorth, *Chemistry of Carbon Compounds* (Edited by E. H. Rodd) Vol. IVC; p. 1576 ff. Elsevier, Amsterdam (1960).

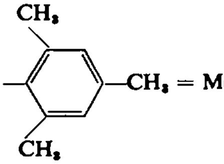
[4] D. Y. Curtin and N. E. Alexandrou, *Tetrahedron* **19**, 1697 (1963).

structure (III) with the zwitterion structure (IV) proposed[5] as an alternative. In this paper additional evidence for the structure III is offered and studies bearing on the mechanism of its formation discussed.

If the reasonable assumption is made that the oxidation of the bis-benzoylhydrazones (V) begins with a reaction analogous to the oxidation of the osazones it might be expected that an intermediate (VI) analogous to I could be isolated or detected by spectral means. Biacetyl-bis-mesitoylhydrazone appeared to offer particular advantage since the steric effect of the *ortho*-methyl groups could help to stabilize the suspected intermediate (VI; Ar = mesitoyl). The zwitterion (IV) should also be stabilized (with respect to acyl migration) by the introduction of the mesitoyl groups.

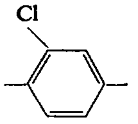


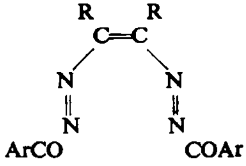
V

VA: $R = -CH_3$, Ar =

= Mes.

VB: $R = -C_6H_5$, Ar = Mes.

VC: $R = -C_6H_4\text{-Cl-p}$, Ar = Mes.

VD: $R = -C_6H_5$, Ar =




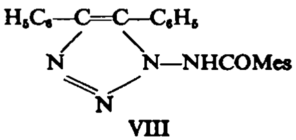
VI

The oxidation of the biacetyl-bis-mesitoylhydrazone (VA) with mercuric oxide and iodine by a method analogous to that of Stolle[6] or with alkaline aqueous potassium ferricyanide[7] led to decomposition of the molecule, with the formation of acetonitrile and azodimesitoyl (VII).

MesCO—N=N—COMes

VII

On the other hand oxidation of the benzil- and *p,p'*-bis-chlorobenzil-bis-mesitoylhydrazones (VB and VC) with mercuric oxide and iodine gave 1-mesitoyl amino-4,5-diphenyl-1,2,3-triazole (VIII) and the corresponding dichloro derivative, formed by cleavage of one mesitoyl group. The same results were obtained in the oxidation of the hydrazone (VD). Products analogous to VIII are obtained from the enol benzoates (III) by reduction with LAH,[4] or by treating the same products with hydrochloric acid.[6,7]



VIII

It is concluded from these results that "tetrazines" now believed to be III are formed only in the case where acyl migration is possible; when this migration is

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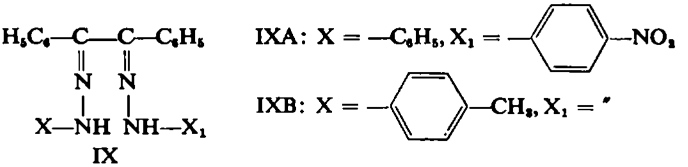
[5] A. R. Katritzky, private communication.

[6] R. Stollé, *Ber. Dtsch. Chem. Ges.* **59**, 1743 (1926).

[7] H. von Pechmann and W. Bauer, *Ber. Dtsch. Chem. Ges.* **33**, 644 (1900); **42**, 659 (1909).

prevented, because of steric hindrance, cleavage of one acyl group or decomposition of the hydrazone takes place with the formation of 1-amino-1,2,3-triazole derivatives or diacylazo derivatives. This observation argues against the zwitterionic structure IV.

Oxidation of mixed osazones (IXA and IXB) with silver oxide in ether, led to the formation of colored products with the bis-azoethylenic structure (I), although the substituents in this case might be considered to favor formation of the zwitterionic product (IV).



IX

It was also of interest to study the oxidation of some mixed diacylhydrazones, but attempts to prepare such compounds were unsuccessful.

Oxidation of the hydrazone (VB) with silver oxide in ether, gave a yellow product, m.p. 244–245° (dec), whose analysis showed that it contained two silver atoms per molecule. This compound is presumed to be the disilver salt of the hydrazone (VB) because the IR spectrum in carbon disulfide shows no absorption attributable to an N—H group and only weak carbonyl absorption at 1675 cm^{-1}.

Treatment of this disilver salt with the calculated amount of iodine in carbon disulfide gave as the main product the hydrazone (VB) in ~55 % yield and 1-amino-1,2,3-triazole derivative (VIII) in ~ 6 % yield. The yield of the silver iodide was 80–90 %. When the reaction time was very short (~5 min) and the reaction product was kept in Dry Ice, the IR spectrum showed a peak at 1750 cm^{-1} (m), which disappeared, together with some other changes of the spectrum, when the sample stood at room temperature. The same behavior was also observed in the visible spectrum with a transient shoulder at 480 mμ. The appearance and disappearance of the bands at 1750 cm^{-1} in the IR and at 480 mμ in the visible spectrum, are attributed to an unstable intermediate with a bis-azoethylenic structure. The rate of disappearance of this product is greatly increased by traces of water. This bis-azoethylenic intermediate, if actually formed, should show a high carbonyl frequency in the IR spectrum, as was observed in the case of azodibenzoyl,[8] which shows a maximum at 1730 cm^{-1} and in the case of the product VII (absorption at 1740 cm^{-1}) and in the visible spectrum an absorption at ~480 mμ, as happens in many other derivatives[9–11] with similar structure. Many attempts to isolate this intermediate by chromatography or crystallization were unsuccessful. It must be notified that neither the starting materials or the products of this reaction show any absorption in these two areas and furthermore the visible spectrum of a mixture of hydrazone (VB), of triazole derivative (VIII) and of iodine showed a maximum, in the same place where the iodine absorbs, at 510 mμ.

Treatment of the disilver salt of the hydrazone (VB) with bromine gave in the IR spectrum a strong peak at 1790 cm^{-1}, although the reaction time was only 1 min.

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[8] D. Y. Curtin and T. C. Miller, *J. Org. Chem.* **25**, 885 (1960).

[9] S. Bodforss, *Svensk. Kem. Tidskr.* **53**, 183 (1941).

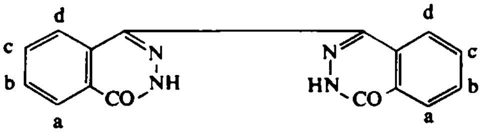
[10] P. Grammaticakis, *C.R. Acad. Sci., Paris*, **224**, 1509 (1947).

[11] D. Y. Curtin, R. J. Crawfort and D. K. Wedegaertner, *J. Org. Chem.* **27**, 4300 (1962).

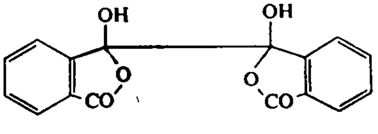
In this case the reaction follows a different course and the peak at 1790 cm^{-1} is attributed to the formation of mesitoyl bromide.

When the hydrazones (VA, VC, VD) were treated with silver oxide, attempts to isolate the corresponding disilver salts, or any other product, were unsuccessful.

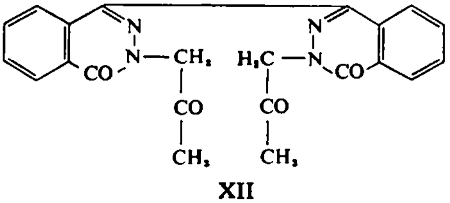
Special interest attaches to the oxidation of 4-bis-(1H,2H-benzo-e-pyridazone-1) (X), because in this system neither migration nor cleavage is possible and the oxidation product was expected to be a bis-azoethylene derivative analogous to VI. The compound X was prepared by treatment of the diphthalyl acid (XI) with hydrazine 85% in ethanol. Analysis, the IR spectrum, which showed peaks at 3170 (NH) and 1660 cm^{-1} (CO) and the NMR spectrum in solution of potassium hydroxide in deuterium oxide (multiplets at 2·40 and 1·80 for b- and c-protons, doublets at 3·00 and 1·15 τ for d- and a-protons) support the above structure. However, many attempts to oxidize X with a great variety of oxidizing agents were unsuccessful and in all cases the starting material was recovered unchanged in 85–95% yield, except when the dipotassium salt of X was oxidized with t-butyl hypochlorite in acetone; in this case there was formed a colorless solid m.p. 261–264° with the formula $C_{22}H_{18}N_4O_4$, of which the IR spectrum showed absorption at 1720 and 1655 cm^{-1} and the NMR of a 7% solution in deuterochloroform peaks at 7·80 and 4·90 τ (singlets), with relative areas 3 : 2 and at 2·30 and 1·70 τ (multiplets). In this oxidation the exchange of potassium atoms with —CH_2COCH_3 group took place with the formation of the product XII.



X

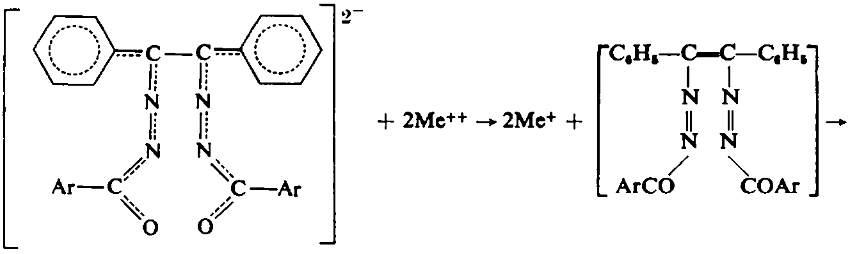


XI



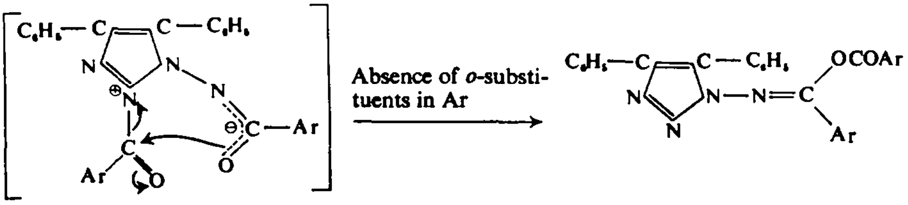
XII

For the mechanism of the oxidation of the diacyl hydrazones the following scheme can be proposed, in accordance with the present experimental data.

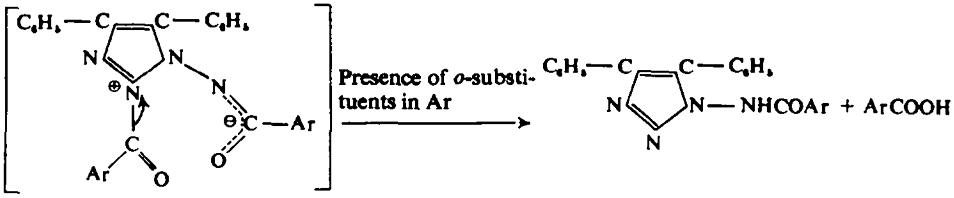


XIII XIV

where Me = meta



XV



XV

The formation of the dianion (XIII) can occur since the oxidation always takes place in basic medium. The evidence for the existence of the intermediate (XIV) is the peak at 1750 cm^{-1} in the IR spectrum and the shoulder at 480 mμ in the visible, when the disilver salt of the hydrazone (VB) was oxidized with iodine. The peak at 1750 cm^{-1} could be also attributed to the intermediate (XV), but this product cannot explain the absorption at 480 mμ in the visible spectrum. In the zwitterionic intermediate (XV) when there is no steric hindrance in the group Ar migration of one acyl group takes place with the formation of the enol benzoate. If this migration is prevented, because of steric hindrance, cleavage of one acyl group is observed, with the formation of 1-amino-1,2,3-triazole derivative. In the case of the oxidation of the hydrazone (VA) decomposition of the molecule is observed, probably because of the decreased stabilization of the dianion (XIII) with the formation of azodimesitoyl (VII).

In conclusion, although the present data seem more compatible with the structure III they do not rigorously exclude the possibility of the zwitterionic structure IV and additional work is required to rule out completely this possibility.

EXPERIMENTAL[11]

Preparation of biacetyl-bis-mesitoylhydrazone (VA). Mesitoylhydrazine, m.p. 149–152°, 6 g, prepared from mesitoyl chloride and hydrazine hydrate 85% by a method analogous to the preparation of benzoylhydrazine,[12] and 1 g biacetyl were refluxed in 20 ml n-propanol for 6 hr. After cooling the mixture was filtered and the precipitate washed with EtOH and ether to give an 85% yield of the

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[11] All m.ps are corrected and were determined with a Reichart hot stage apparatus. IR spectra were measured with a Perkin–Elmer model 21 or 521 spectrophotometer and NMR spectra reported in τ units (G. V. D. Tiers, *J. Phys. Chem.* **62**, 1151 (1958)) with a Varian Associates A-60 spectrophotometer at 60 Mc with tetramethylsilane as an internal standard. I am indebted to Mr. O. Norton and Mr. D. Johnson and their associates for these spectra. UV and visible spectra were measured with a Bausch and Lomb Spectronic 505 double beam spectrophotometer using 1-cm quartz cells. Microanalyses were obtained in the Microanalytical Laboratory at the University of Illinois under the direction of Mr. J. Nemeth and mol. wts. were determined with a Mechrolab Vapor Pressure Osmometer, model 301A. "Petroleum ether" refers to the hydrocarbon fraction b.p. 30–60°.

[12] C. Naegeli and G. Stefanovitsch, *Helv. Chim. Acta.* **11**, 636 (1928).

hydrazone m.p. >350°. It was insoluble in common organic solvents. The IR spectrum in Nujol showed peaks at 3160, 1660, 850 cm^{-1}. (Found: C, 70·2; H, 7·5; N, 13·5. $C_{24}H_{30}N_4O_2$ requires: C, 70·9; H, 7·4; N, 13·8%.)

Oxidation of hydrazone (VA) *to azodimesitoyl* (VII). The oxidation was carried out by a method analogous to Stolle[6] by treating 4 g of VA with 6 g yellow HgO, 0·6 g MgO and 3 g I_2 in 80 ml dry ether. The mixture was shaken at room temp for 18 hr. It was filtered and the filtrate washed with a solution of KI, $Na_2S_2O_3$, water and then dried over Na_2SO_4. After evaporation of the solvent there was obtained in 34% yield the azodimesitoyl as an orange colored solid m.p. 122–125° (dec). The yield is based on the 47% of starting material unrecovered. After recrystallization from EtOH the m.p. was 126–128° (dec). The IR spectrum in chloroform showed peaks at 1740, 1610, 850 cm^{-1} and the NMR of a 10% solution in CS_2 a doublet at 7·75 (area 5) and a singlet at 3·15 τ (area 1). The UV had a peak with $\lambda_{\max}^{\mathrm{EtOH}}$ 247 mμ (ε 11,700) and the visible a shoulder with $\lambda^{\mathrm{CHCl_3}}$ 445 mμ (ε 80). (Found: C, 74·1; H, 6·8; N, 8·6; mol. wt. 313 (in benzene). $C_{20}H_{22}N_2O_2$ requires: C, 74·5; H, 6·9; N, 8·7%; mol. wt. 322.) A part of the ether solution, after filtration to remove insoluble inorganic material, was submitted to VPC analysis through an 8-ft column packed with carbowax on chromosorb W at 65° and gave a peak with retention time 14·1 min, while the retention time of an authentic sample of acetonitrile was 14 min. Azodimesitoyl was also found, but in lower yield, when the hydrazone VA was oxidized with an alkaline solution of potassium ferricyanide.

Preparation of benzil-bis-mesitoylhydrazone (VB). This product was prepared in 90% yield, following the method of preparation of benzil-bis-benzoylhydrazone,[14] m.p. 251–253·5°. The IR spectrum in Nujol showed peaks at 3140 (w), 1675, 1650, 850, 760, 680 cm^{-1}. (Found: C, 76·6; H, 6·5; N, 10·3. $C_{34}H_{34}N_4O_2$ requires: C, 76·9; H, 6·5; N, 10·6%.)

Oxidation of hydrazone (VB) *to* 1-*mesitoylamino*-4,5-*diphenyl*-1,2,3-*triazole* (VIII). The oxidation was carried out with HgO and I_2 in ether as described previously. After evaporation of the solvent an oily product was obtained, which was submitted to chromatographic analysis on alumina. By using MeOH as eluent a solid was received m.p. 150–180°. It was recrystallized twice from ether–pet. ether to give VIII in 18% yield, m.p. 253–255°. The UV spectrum in EtOH had a peak with $\lambda_{\max}$ 242 mμ (ε 22,000), while the IR in Nujol had absorption at 3130 (w), 1712, 1610, 845, 725, 690 cm^{-1}. The NMR of a 10% solution in $CDCl_3$ showed singlets at 8·15, 7·80, 3·30 τ for the mesitylene group and at 2·75 (unresolved multiplet) and 2·65 τ (singlet) for the phenyl groups. (Found: C, 75·4; H, 5·8; N, 14·6. $C_{24}H_{22}N_4O$ requires: C, 75·4, H, 5·8; N, 14·6%.)

Oxidation of hydrazone (VB) *with silver oxide*. Hydrazone VB, 2 g and 5 g Ag_2O in 70 ml abs ether were refluxed with stirring for 30 hr. The reaction product was filtered and the precipitate washed many times with benzene. A yellow solution was obtained which on removal of the solvent with a stream of N_2 left 1·8 g of a yellow amorphous solid m.p. 244–245° (dec). It was soluble in CS_2, $CHCl_3$ and benzene. The IR spectrum of a 2% solution in CS_2 in 0·5-mm cells showed peaks at 1675 and 1590 cm^{-1} but it did not show any peak for >NH. (Found: C, 55·2; H, 4·4; N, 7·6; Ag (as residue) 27·6. $C_{34}H_{32}N_4O_2Ag_2$ requires: C, 54·9; H, 4·3; N, 7·5; Ag, 29.) The analytical sample was dried in air in the dark; in vacuum it was unstable.

Treatment of disilver salt of the benzil-bis-mesitoylhydrazone with iodine. To a solution of 0·25 g of the disilver salt in 8 ml dry CS_2, precooled at 0°, 0·084 g I_2 in 4 ml CS_2 was added and the mixture was shaken for a period of 5–7 min. At the end of this time the reaction product was cooled in Dry Ice, filtered and the filtrate was also kept in Dry Ice. The yield in AgI was 80–90%. The IR spectrum of this solution in 0·5-mm cells showed a peak at 1750 cm^{-1} (m) and another one at 1680 cm^{-1} (s), which is attributed to VB. By leaving the sample at room temp the peak at 1750 cm^{-1} slowly disappeared and, in addition, the following differences between the spectrum of a sample left 3 hr at room temp and the spectrum measured immediately after the reaction were observed: the peak at 1150 cm^{-1} decreased, another one increased at 1160 cm^{-1} and the peaks at 995 and 650 cm^{-1} disappeared. The spectrum of a sample which remained 24 hr in Dry Ice did not show any significant change. On the other hand the visible spectrum of this solution showed a shoulder at 480 mμ which also decreased by leaving the sample at room temp. Before the measurement solid sodium thiosulfate was added to the sample to remove any I_2 present. The addition of this reagent does not seem to have any immediate influence on the decomposition of this intermediate, because there was no change in the IR spectrum before and immediately after the addition of $Na_2S_2O_3$ to the solution and furthermore there was no

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[14] T. Curtius and G. Struve, *J. Prak. Chem.* **50**, 295 (1884).

change in the visible spectrum of a solution of azodimesitoyl, which was allowed to stand at room temp for 30 min with $Na_2S_2O_3$. However, it must be noticed, that the rate of disappearance of the peak at 1750 cm^{-1} and at 480 mμ is not constant and traces of moisture greatly increase the rate of decomposition of the intermediate. For this reason attempts to isolate the intermediate product by TLC on silica gel (solvent benzene), or by crystallization were unsuccessful.

In this reaction none of the products showed any absorption at 1750 cm^{-1} or at 480 mμ and the visible spectrum of a mixture containing 50% VB, 36% VIII and 14% I_2 in CS_2, showed a peak at 510 mμ, in the same region where the I_2 itself absorbs.

When the solvent remaining after the reaction with I_2 was removed with a stream of N_2 an oily product was obtained which on addition of ether and pet. ether gave a solid m.p. 245–248°, of which the UV spectrum in EtOH and the IR spectrum (KBr disc) were identical with those of VB; the yield of VB was 56%. Besides VB another white solid m.p. 246–249° was obtained, of which both IR and UV spectra were identical with those of VIII; the yield was ~6%.

The product of the reaction of the disilver salt of VB with the calculated amount of Br_2 in CS_2 at 0°, showed in the IR spectrum a strong absorption at 1790 cm^{-1} and another one at 1680 cm^{-1}. The first peak is probably due to the mesitoyl bromide and was present, even when the reaction time was only 1 min.

Preparation of p,p′-*bis-chlorobenzil-bis-mesitoylhydrazone* (VC) *and oxidation to* 1-*mesitoylamino*-4,5-*bis*-(p-*chloro-phenyl*)-1,2,3-*triazole*. *p*-Chlorobenzil m.p. 196–197°, 3·1 g, and 4 g mesitoylhydrazine were heated in a sealed tube at 200° for 10 hr. The VC was obtained as white powder m.p. 276–277·5°, in 76% yield. The IR spectrum (KBr disk) showed peaks at 3160, 1670, 850, 815, 710, 545 cm^{-1}. (Found: C, 67·7; H, 5·3; N, 9·2; $C_{34}H_{32}Cl_2N_4O_2$ requires: C, 68·1; H, 5·4; N, 9·3%.)

The oxidation of VC was carried out with HgO and I_2 in ether, according to the previously described method. The reaction product was chromatographed on alumina to give as first fraction a solid m.p. 120–140° which was impure mesitoic acid as shown by its IR spectrum and as second fraction the triazole derivative (eluent $CHCl_3$ containing 10% MeOH) in 4·5% yield, m.p. 314–315°. The IR spectrum (KBr disc) showed peaks at 3150, 1715, 1610, 835 cm^{-1}. (Found: C, 63·5; H, 4·5; N, 12·5. $C_{24}H_{20}Cl_2N_4O$ requires: C, 63·9; H, 4·5; N, 12·4%.)

Oxidation of VC with Ag_2O was carried out as with VB, but evaporation of the solvent did not leave any product. However, the precipitate which was assumed to be a mixture of Ag_2O, of VC and of disilver salt of VC, was suspended in CS_2 and under cooling a solution of I_2 in the same solvent was added dropwise, until the solvent became red. The IR spectrum of the filtrate showed a very weak absorption at 1740 cm^{-1} and another stronger one at 1700 cm^{-1}.

Preparation of benzil-bis-(2,4-*dichlorobenzoylhydrazone*) (VD) *and oxidation to* 1-(2′,4′-*dichlorobenzoylamino*)-4,5-*diphenyl*-1,2,3-*triazole*. Compound VD was prepared by heating 1 mole benzil with 2 moles 2,4-dichlorobenzoylhydrazine,[15] in a sealed tube at 140° for 12 hr; yield 90%, m.p. 215–217°. IR spectrum (KBr disc) showed peaks at 3300, 1690, 1590, 695 cm^{-1}. (Found: C, 57·6; H, 3·2; N, 9·5. $C_{28}H_{18}Cl_4N_4O_2$ requires: C, 57·5; H, 3·1; N, 9·6%.)

Oxidation of VD with HgO and I_2, gave the triazole derivative after chromatographic analysis on alumina, in 4·5% yield, m.p. 211–213°. The IR spectrum (KBr disc) gave peaks at 3150, 1718, 1590, 690 cm^{-1}. (Found: C, 61·4; H, 3·4; N, 13·7. $C_{21}H_{14}Cl_2N_4O$ requires: C, 61·6; H, 3·4; N, 13·7%.) Attempted oxidation of VD with Ag_2O was unsuccessful.

Preparation of benzil-phenyl-p-*nitrophenyl-osazone* (IXA) *and oxidation to a-phenylazo*-a′,p-*nitrophenylazo-stilbene*. Benzil monophenylhydrazone,[16] 3 g, and 1·53 g *p*-nitrophenylhydrazine were heated, without any solvent, at 150° for 2 hr. By cooling and adding acetic acid the osazone IXA was separated in 64% yield, m.p. 220–225°. Recrystallized from boiling acetic acid it had m.p. 223–225°; (lit.[17] 255°). The IR spectrum in $CHCl_3$ showed peaks at 3320, 1605, 1550, 1525, 1335, 842, 690 cm^{-1}, while the NMR of a 10% solution in $CDCl_3$ gave two multiplets at 2·70 and 2·30 τ and a doublet at 1·90 τ. (Found: C, 71·3; H, 4·8; N, 15·8. $C_{26}H_{21}N_5O_2$ requires: C, 71·7; H, 4·9; N, 16·1%.)

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[15] H. L. Yale, K. Losee, J. Martins, M. Holsing, F. M. Perry and J. Bernstein, *J. Amer. Chem. Soc.* **75**, 1933 (1953).

[16] C. Bulow, *Liebigs Ann.* **236**, 197 (1886).

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The oxidation was carried out by heating 1 g of IXA with 2 g Ag_2O in 20 ml ether and 20 ml benzene, under stirring for 17 hr. After filtration and evaporation of the solvent a red oily product remained, which was submitted to chromatographic analysis on aluminum oxide. By using as eluent chloroform and methylene chloride (2:1) a red oily product was again obtained. It was diluted with ether containing a small amount of pet. ether and cooled in Dry Ice, to give 0·4 g of an amorphous orange solid, m.p. 89–91°. The IR spectrum in chloroform showed peaks at 1610, 1590, 1510, 1330, 690 cm^{-1} and the NMR of a 10% solution in $CDCl_3$ gave a doublet at 3·85 and a multiplet at 2·50 τ. On the other hand the UV had two maxima at 240 $m\mu$ (ε 31,800) and 297 $m\mu$ (ε 17,300) and the visible at 420 $m\mu$ (ε 20,300) in ethanolic solution. (Found: C, 71·2; H, 4·6; N, 15·9. $C_{26}H_{19}N_5O_2$ requires: C, 72·0; H, 4·4; N, 16·2%.)

*Preparation of benzil-*p*-tolyl-*p'*-nitrophenyl-osazone* (IXB) *and oxidation to* a,p-*tolylazo-*a'p'*-nitrophenylazo-stilbene.* Benzil, 10 g and 7·55 g *p*-tolylhydrazine hydrochloride (Aldrich Chemicals), m.p. 210–220°,[18] in 65 ml EtOH were refluxed with 7·2 g *p*-nitrophenylhydrazine in 60 ml EtOH for 2 hr. An orange solid (18 g) m.p. 190–215° was obtained. It was extracted with ether in a Soxhlet apparatus to give 8·5 g IXB, m.p. 215–216·5°, after crystallization from a mixture EtOH–$CHCl_3$. The IR spectrum in $CHCl_3$ showed peaks at 3320, 1605, 1550, 1520, 1330, 840, 687 cm^{-1} and the NMR of a 10% solution in $CDCl_3$ gave singlets at 7·75 and 2·95, a doublet at 1·90 and multiplets at 2·55 and 2·30 τ. (Found: C, 71·1; H, 5·2; N, 15·7. $C_{27}H_{23}N_5O_2$ requires: C, 72·1; H, 5·2; N, 15·6%.)

The oxidation of IXB was carried out with Ag_2O as described previously. The bis-azostilbene derivative was obtained in 30% yield as an oily product, which after cooling in Dry Ice gave an amorphous orange solid m.p. 98–100°. Both bis-azostilbene derivatives have the tendency to give oily products. The NMR spectrum of a 7% solution in $CDCl_3$ gave a singlet at 7·65, a doublet at 3·85 and a multiplet at 2·50 τ. The IR in $CHCl_3$ had peaks at 1595, 1578, 1510, 1320, 690 cm^{-1}, while the UV had at 241 $m\mu$ (ε 33,400) and 297 $m\mu$ (ε 21,300) and the visible at 420 $m\mu$ (ε 22,300). (Found: C, 72·1; H, 5·0; N, 15·5. $C_{27}H_{21}N_5O_2$ requires: C, 72·5; H, 4·7; N, 15·6%.)

Preparation of 4-*bis*-(1H,2H-*benzo-e-pyridazone*-1) X. Diphthalyl acid[20] (XI), 1 g, prepared by treating biphthalyl[21] with an alkaline solution of bromine, 2 ml hydrazine hydrate 85% and 30 ml EtOH were refluxed with stirring for 4 hr. The precipitate formed (0·53 g) was filtered and washed with acidified water, then with EtOH and ether. The compound X as an amorphous white solid was obtained, m.p. >350°; it is insoluble in organic solvents, but soluble in alkali, from which it is reprecipitated by adding acid. The IR spectrum (KBr disc) showed peaks at 3170, 1660 cm^{-1}, while the NMR in a solution of KOH in D_2O (with TMS as external standard) gave multiplets at 2·40 and 1·80 and doublets at 3·00 and 1·15 τ. All the peaks had the same area. (Found: C, 65·7; H, 3·4; N, 19·1. $C_{16}H_{10}N_4O_2$ requires: C, 66·2; H, 3·5; N, 19·3%.)

Many attempts to oxidize X with a variety of oxidizing agents, namely with HgO and I_2, Ag_2O, alkaline solution of K_3FeCN_6, Br_2 in the presence of NaOH, $KMnO_4$ and $K_2Cr_2O_7$ in the presence of acetic acid, were unsuccessful. In all cases the starting material was recovering in 85–95% yield.

Reaction of X *with t-butyl hypochlorite in the presence of acetone.* This reaction was carried out by a method analogous to that of Kealy.[22] To 0·65 g dipotassium salt of X (prepared by dissolving X in the calculated amount of a conc KOHaq, removing the water on a water-bath and drying in the oven at 120°) in 5 ml of reagent acetone, 0·25 ml t-butyl hypochlorite[23] was added and the mixture was stirred at room temp for 17 hr. After filtration and evaporation of the solvent 30 mg of a white solid, m.p. 256–264°, was obtained. After recrystallization twice from acetone it had m.p. 261–264°. The IR spectrum (KBr disc) showed two strong peaks at 1720 and 1655 cm^{-1} and the NMR of a 7% solution in $CDCl_3$ showed singlets at 7·80 (CH_3) and 4·90 (CH_2) τ with areas approximately 3:2 and multiplets at 2·30 and 1·70 τ. (Found: C, 65·3; H, 4·4; N, 13·6. $C_{22}H_{18}N_4O_4$ requires: C, 65·7; H, 4·5; N, 13·9%.) These data argue with the structure of XII.

When the reaction was carried out in ether or in CS_2 no reaction took place and the starting material was recovered unchanged. The reaction of monopotassium salt of X with t-butyl hypochlorite in acetone, led to the formation of the same product obtained from the dipotassium salt.

Acknowledgment—I am very much indebted to Professor David Y. Curtin for his advice and encouragment during the course of this work and for his assistance with the preparation of this manuscript.

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