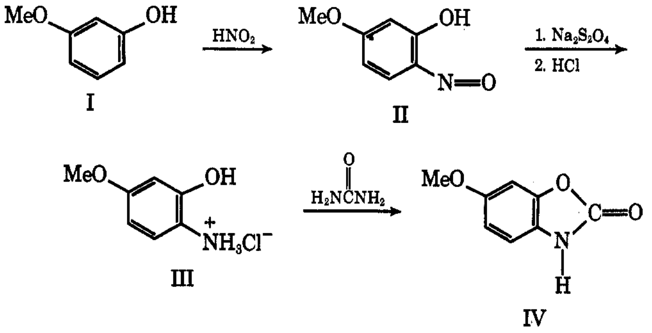
thosporium leaf blight of corn, we attempted to synthesize this compound according to reported methods.[4–6] These methods gave very low yields. One of the procedures was hazardous because phosgene was used.[5]

A shorter method with higher yield was developed. The first objective was to prepare the immediate precursor of IV, 2-amino-5-methoxyphenol hydrochloride (III), in high yield with a minimum number of steps. The orthoaminophenol obtained by reducing 2-nitroso-5-methoxyphenol (II) was not isolated. To maximize the yield of III, neutralization of the reducing solution and other steps including the urea fusion were carried out in the dark or with photographic safety lights. Separatory funnels and flasks were flushed with N_2 gas. The uv, ir, melting point, and derivative data for IV were in good agreement with the literature values.[4–7]



Preparations of the amine hydrochloride which were black, blue, green, purple, or red reduced the yields of IV. Apparently some of the colored substances were partial oxidation products known as Wurster's salts.[8] Usually the white amine hydrochloride samples became grayish white and then blue. These blue preparations were fused with urea to yield about 17% IV when calculated on the basis of the initial starting material, *m*-methoxyphenol (I). This overall yield was about 60 times as great as the yield which we obtained by the use of the method of Klun and Brindley.[6]

Experimental Section[9]

2-Nitroso-5-methoxyphenol (II).—This compound was prepared in yields of 87–93% by the procedure of Hodgson and Clay.[10] The reaction mixture was held at 4° in the dark for 24 hr and the precipitate was isolated by filtration.

Preparation of 2-Amino-5-methoxyphenol Hydrochloride (III) for Fusion with Urea.—2-Nitroso-5-methoxyphenol (5.37 g) was suspended in 300 ml of water. Solid sodium hydrosulfite (18.5 g) was added slowly with continuous rapid stirring.[6,11] The reducing solution (bright yellow) was heated at 50–60° for 15 min, cooled, and neutralized to pH 6 with a saturated aqueous solution of $NaHCO_3$ added slowly by the drop with very rapid stirring. 2-Amino-5-methoxyphenol was extracted from the reducing solution (pH 6) with peroxide-free diethyl ether (eight 100-ml portions). The ether extract was passed through anhydrous Na_2SO_4. The 250-ml round-bottom flask containing the dry ethereal solution of the aminophenol was gently agitated and flushed with dry HCl gas for 1 min. The amine hydrochloride precipitated immediately as a white solid which became gray-white and then blue if water and O_2 were present. The ether was removed by rotatory evaporation *in vacuo* at 20°. The dry amine hydrochloride was mixed with urea (6 g) in a flask fitted with an air condenser, and heated in an oil bath at 170–180° for 2.5 hr.[4] Owing to its extreme instability, the orthoaminophenol was converted without delay to the hydrochloride. Highest yields were obtained when the amine hydrochloride was prepared and fused with urea as a continuous operation in the same flask in the absence of water.

Isolation of 6-Methoxybenzoxazolinone (IV) from the Fusion Mixture.—The fusion mixture was washed with 1.2 *N* HCl. The remaining residue was dissolved in ethyl alcohol, and about 50 ml of 1.2 *N* HCl was added. The alcohol was removed by rotatory evaporation *in vacuo* at 28°. The product (IV) was isolated from the acidic aqueous solutions by continuous extraction with diethyl ether. The wet ether was removed, and the residues were dissolved in a minimum amount of warm dry ether. The ethereal solution of crude IV was loaded on a silica gel (Adsorbosil-1) column which had been pressure packed in diethyl ether–petroleum ether (75:25 v/v) (EPE). The column was developed with EPE under low N_2 pressure and 5-ml fractions were collected (1 ml/min). IV was the first major compound to be eluted from the column and was detected in the fractions by thin layer chromatography on silica gel (microscope slides) developed with EPE (R_f 0.58). All compounds appeared as yellow spots on a purple background when the plates were sprayed with 3% aqueous $KMnO_4$. Fractions containing IV were combined and the solvent was removed. The light pink solid was decolorized with activated charcoal and recrystallized in water to give colorless needles: mp 154–155° (lit.[4] mp 154–155°); uv max (absolute EtOH) 231 mμ (ε 9138), 291 (5230); uv max (water) 230 mμ (ε 10,000), 286 (5380) [lit.[12] uv max (water) 230 mμ (ε 10,000), 287 (4500); lit.[5] uv max (water) 285–286 mμ (ε 5500)]; ir (KBr) 1326 (C—N stretching in ArNHR), 1498 (N—H bending, amide II band), 1620 (C=C aromatic skeletal in plane vibr), 1787 (C=O stretching, carbamate), 3330–3060 cm^{-1} (N—H stretching, multiple amide I band); mass spectrum (70 eV) *m/e* (rel intensity) M + 165.0428 (100%), calcd for $C_8H_7O_3N$ 165.0426. The ir and uv spectra were primarily the same as those reported in the literature.[6,7]

Anal. Calcd for $C_8H_7O_3N$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.96; H, 4.28; N, 8.42.

The benzimide was prepared: mp 165–167° (lit.[4] mp 163–164°); mass spectrum (70 eV) *m/e* (rel intensity) M + 269.0669 (14%), calcd for $C_{15}H_{11}O_4N$ 269.0688.

Registry No.—IV, 532-91-2.

Acknowledgment.—We thank Dr. J. M. Ruth, Entomology Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md., for making mass measurements.

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[4] E. E. Smissman, J. B. LaPidus, and S. D. Beck, *J. Amer. Chem. Soc.*, **79**, 4697 (1957).

[5] P. K. Hietala and O. Wahlroos, *Acta Chem. Scand.*, **10**, 1196 (1956).

[6] J. A. Klun and T. A. Brindley, *J. Econ. Entomol.*, **59**, 711 (1966).

[7] A. I. Virtanen, *Brauwissenschaft*, **14**, 98 (1961).

[8] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, Oxford, 1942, p 97.

[9] Melting points were determined by hot stage microscopy and uncorrected. Mass spectra were measured on a CEC Model 21-110B instrument. Infrared and ultraviolet spectra were recorded, respectively, on Perkin-Elmer Model 621 and Cary Model 15 instruments.

[10] H. H. Hodgson and H. Clay, *J. Chem. Soc.*, 2775 (1929).

[11] H. E. Gahagan and R. O. Mumma, *Phytochemistry*, **6**, 1441 (1967).

[12] E. E. Smissman, J. B. LaPidus, and S. D. Beck, *J. Org. Chem.*, **22**, 220 (1957).

The Mechanism of Formation of Pentaazadecanetetraones in the Reaction of Aryl Isocyanates with *N*,*N*-Dimethylformamide

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Received December 3, 1970

The reaction of aryl isocyanates with *N*,*N*-dimethylformamide gives *N*-dimethyl-*N'*-arylformamidines[1]

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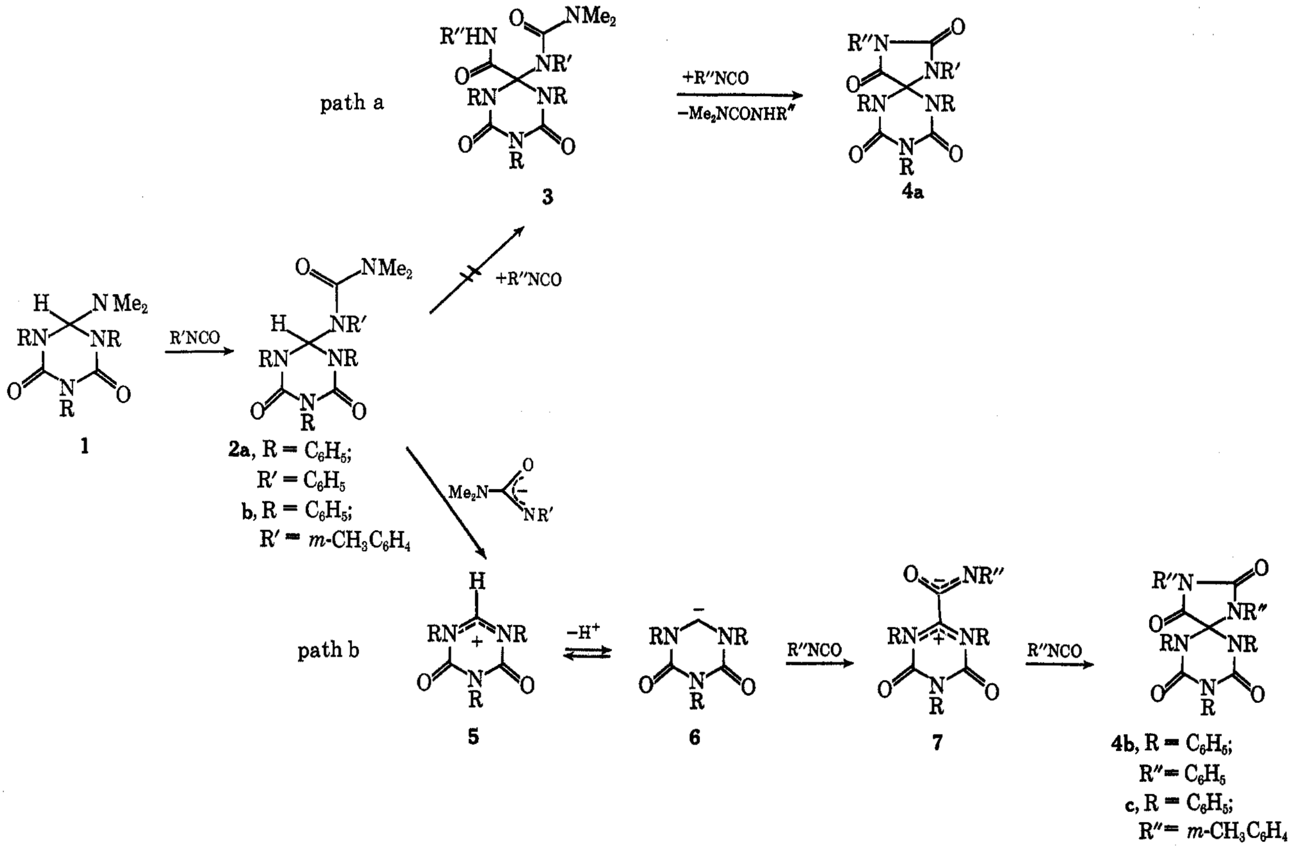
[1] M. L. Weiner, *J. Org. Chem.*, **25**, 2245 (1960).

SCHEME I



which undergo further reaction with aryl isocyanates to yield heterocyclic 2:1 adducts **1**, 3:1 adducts **2**, and spiro compounds **4**.[2–5]

The formation of the ureido-*s*-triazine derivative **2** from its precursor **1** is readily explained by an "insertion reaction" of the heterocumulene into the exocyclic CN single bond in **1**.[6] For the formation of **4**, however, several mechanisms could be visualized. Addition of a second isocyanate molecule to **2**, either by an insertion into the CH bond, as proposed by Dyer, *et al.* (path a, Scheme I), or by a repeated insertion into the exocyclic CN bond could lead to cyclization with formation of **4**. In contrast, an elimination sequence (path b, Scheme I) could give rise to the formation of the heterocarbene intermediate **6**, which would undergo further reaction with two isocyanate molecules to produce **4**. In order to differentiate between an addition (a) and an elimination (b) mechanism, we investigated the reaction of **1** and **2** with different aromatic isocyanates.

In case of an addition sequence a mixed spiro compound **4a** is expected, having one original aryl group (R′) and the new aryl group (R″) attached to the five-membered ring portion of the molecule. In contrast, the elimination sequence would result in the formation of a spiro compound **4b** having two new aryl groups (R″) incorporated into the molecule.

The reaction of **1** (R = C_6H_5) with phenyl isocyanate, following a procedure by Dyer, *et al.*,[4] gives the ureido-*s*-triazinedione **2a** (R = R′ = C_6H_5). By treating **1** with *m*-tolyl isocyanate under similar conditions, the corresponding **2b** (R = C_6H_5; R′ = *m*-$CH_3C_6H_5$) is obtained. Heating of both ureido-*s*-triazinediones **2a**,**b** with excess phenyl isocyanate at 150° gives exclusively the spiro compound **4b** (R = R″ = C_6H_5), identical with **4b** prepared from **1** and phenyl isocyanate. On treatment of **2a** with excess *m*-tolyl isocyanate at 150° the spiro compound **4c** (R = C_6H_5; R″ = *m*-$CH_3C_6H_4$) is formed exclusively, thus proving that in both cases the aryl moiety in the acyclic urea group in **2** is being eliminated. Of course, heating **2b** with excess *m*-tolyl isocyanate also affords **4c**.

A mechanism consistent with the observed facts is shown in Scheme I (b). Elimination of an urea anion in **2** gives **5**, which loses a proton to yield the heterocarbene **6**. Reaction of **6** with aryl isocyanate affords, *via* a delocalized zwitterion **7**, the spiro compound **4b** and **c**.

Heating of **2a** in the absence of aryl isocyanate to 330–340° and under constant removal of volatile decomposition products caused the formation of a solid material, mp >360°, analyzing for $C_{42}H_{30}N_6O_4$. The molecular weight of 682, determined by mass spectroscopy, indicates that the compound may be the dimer **8** of the heterocarbene **6**. Dyer, *et al.*,[4] found also that thermal decomposition of **4b** at 330–360° yields besides 2 mol of phenyl isocyanate a colorless high melting solid which we found to be identical with **8** (by comparison of ir and nmr spectra). Pyrolysis of **4c** also gave only **8**, thus indicating that the imidazolinedione rather than the *s*-triazine ring is cleaved in this reaction.

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(2) R. Richter, *Chem. Ber.*, **101**, 3002 (1968).

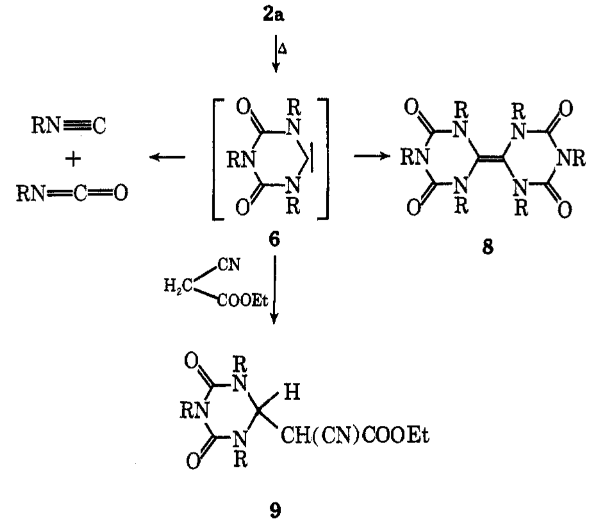
(3) H. Ulrich, B. Tucker, F. A. Stuber, and A. A. R. Sayigh, *J. Org. Chem.*, **33**, 3928 (1968).

(4) E. Dyer, T. E. Majewski, and J. D. Travis, *ibid.*, **33**, 3931 (1968).

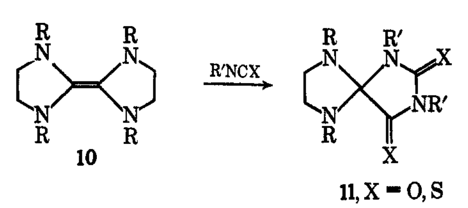
(5) For a discussion of the cycloaddition reaction of imines with heterocumulenes, see R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969); R. Huisgen, *ibid.*, **7**, 321 (1968); and H. Ulrich and R. Richter in "Newer Methods of Preparative Organic Chemistry," Vol. 6, Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(6) For similar reactions, see H. Ulrich and A. A. R. Sayigh, *Angew. Chem., Int. Ed. Engl.*, **5**, 844 (1966).

(The presence of *m*-tolyl groups in **8** could have been easily detected by nmr spectroscopy.) The characteristic odor of isonitriles was also noted in the volatile decomposition products indicating some degradation of **6** into isonitrile and isocyanate. The ir spectrum of **8** (KBr) shows two strong bands of almost equal intensity in the double bond region at 1710 and 1745 cm^{-1}. Similar ir absorptions (1696 and 1731 cm^{-1} in dioxane) were observed for the methyl homolog of **8**, previously obtained by Piskala[7] upon pyrolysis of 2-methoxy-1,3,5-trimethyltriazine-4,6-dione. Attempts to oxidize **8** to triphenyl isocyanurate (with H_2O_2-formic acid, peracetic acid, potassium permanganate in pyridine or acetic acid) were unsucessful; only unreacted starting material was recovered. Insertion of the heterocarbene intermediate **6** into a carbon–hydrogen bond was observed in the reaction of **2a** with ethyl cyanoacetate. Thus heating of **2a** with ethyl cyanoacetate at 140–145° for 1 hr yields the insertion product **9**.



The further reaction of the heterocarbene **6** with isocyanate to produce **4**, as outlined in Scheme I, is quite similar to the reaction of bis(1,3-diphenylimidazolinylidene-2) (**10**) with isocyanates or isothiocyanates, which yields the spiro compound **11**.[8,9]



The dimer **8** in contrast to **10** does not undergo a reverse reaction with aryl isocyanates (*via* the monomer) as evidenced by the fact that refluxing of **8** with excess phenyl or *p*-chlorophenyl isocyanate for 24 hr resulted in complete recovery of the starting material.

Experimental Section[10]

2-[1-(1-*m*-Tolyl-3,3-dimethylureido)]-1,3,5-triphenylhexahydro-1,3,5-triazine-4,6-dione (2b).—A mixture of 5.0 g (0.013 mol) of 2-dimethylamino-1,3,5-triphenylhexahydro-1,3,5-triazine-4,6-dione (**1**) and 25.0 g (0.19 mol) of *m*-tolyl isocyanate was kept at 80–85° for 16 hr. On cooling colorless crystals separated from the reaction solution. Filtration and thorough washing with ether left 3.70 g (53%), mp 205°. Recrystallization from acetone–ether gave tiny white needles: mp 207–210°; ir (KBr) 1715, 1670, 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.15 (s, 3, CH_3C), 2.4 (s, 6, $(CH_3)_2N$), 6.30–6.50 (m, 2, aromatic), 6.8–7.6 (m, 18, aromatic and CH).

Anal. Calcd for $C_{31}H_{29}N_5O_3$: C, 71.66; H, 5.63; N, 13.48. Found: C, 71.63; H, 5.62; N, 13.22.

1,3,6,8,10-Pentaphenyl-1,3,6,8,10-pentaazaspiro[4.5]decane-2,4,7,9-tetraone (4b).—A mixture of 1.0 g (0.0019 mol) of **2b** and 7.0 ml of phenyl isocyanate was kept for 2 hr at 150°. After the reaction the excess isocyanate is removed by vacuum distillation and the residue is treated with ether. This was allowed to stand at room temperature; 0.93 g (81%) of **4b** separated in colorless crystals, mp 228–234°. A mixture with authentic **4b** (prepared according to *loc. cit.*[3,4]) did not give a melting point depression; the material is identical in ir and nmr with authentic **4b**.

1,3-Di-*m*-tolyl-6,8,10-triphenyl-1,3,6,8,10-pentaazaspiro[4.5]-decane-2,4,7,9-tetraone (4c). A. From 2b and *m*-Tolyl Isocyanate.—A mixture of 1.0 g (0.0019 mol) of **2b** and 6.0 g (0.045 mol) of *m*-tolyl isocyanate was treated as described above for the preparation of **4b** yielding 1.0 g (78%) of **4c**: mp 270–273°, after recrystallization from chloroform–ether; ir (KBr) 1790, 1725, 1695 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.2–7.6 (m, 23, aromatic protons), 2.42 (s, 3, CH_3), 2.2 (s, 3, CH_3).

Anal. Calcd for $C_{37}H_{29}N_5O_4$: C, 73.13; H, 4.81; N, 11.53. Found: C, 72.87; H, 4.64; N, 11.34.

B. From 2a and *m*-Tolyl Isocyanate.—A mixture of 5.0 g (0.01 mol) of **2a** and 25 g (0.19 mol) of *m*-tolyl isocyanate was kept for 3 hr at 145–150°. Work-up as described above gave 5.3 g (87%), mp 270–272°, identical in comparison (ir, nmr, mixture melting point) with **4c** prepared under A.

1,1′,3,3′,5,5′-Hexaphenyl[$\Delta^{2,2'(1H,1'H)}$-bis-*s*-triazine]-4,4′,6,6′-(3*H*,3′*H*,5*H*,5′*H*)-tetraone (8). A. From 2a.—A sample of 1.5 g (0.003 mol) of **2a** was placed into a preheated salt bath and kept at 330–340° for 7 min. During the reaction a liquid product was distilled off under reduced pressure (20–30 mm), which on standing solidified partly: 0.32 g; ir (in $CHCl_3$) and nmr ($CDCl_3$) indicated the presence of *N*,*N*-dimethyl-*N*′-phenylurea; no ir bands in the 2000–2500-cm^{-1} region, indicating the absence of isocyanate or isonitrile. The dark brown residue was taken up in acetone, leaving 0.05 g (5%) of **8** undissolved, creamy crystals, mp >360°. A sample was recrystallized for analysis from DMF: ir (KBr) 1740, 1710 cm^{-1} (C=O); nmr (DMSO-d_6) δ 7.36 (s, C_6H_5), 7.46 (s, C_6H_5).

Anal. Calcd for $C_{42}H_{30}N_6O_4$: C, 73.89; H, 4.43; N, 12.31; mol wt, 682. Found: C, 73.70; H, 4.58; N, 12.13; mol wt, 682 (from mass spectral data).

The material is identical (ir) with a sample prepared from **4b** following the procedure of Dyer, *et al.*[4]

B. From 4c.—A sample of 5.0 g (0.008 mol) **4c** was kept for 25 min in a preheated salt bath at 345–350°. Under reduced pressure (20–30 mm) 1.90 g of a yellowish liquid was distilled off [ir ($CHCl_3$) 2220 cm^{-1} (N=C=O)]. The residue was taken up in acetone and the undissolved colorless crystals were filtered off, 0.45 g (16%), mp >360°. The material is identical (ir) with a sample prepared under A.

[2-(1,3,5-Triphenyl-4,6-dioxohexahydro-*s*-triazinyl)]ethyl Cyanoacetate (9).—A mixture of 3.0 g (0.006 mol) of **2a** and 5.0 g (0.048 mol) of ethyl cyanoacetate was kept at 140–145°. After 1 hr the formed clear solution was diluted with ether and kept at room temperature overnight. The formed crystals were filtered off and washed with ether leaving 2.1 g (78%) of **9**: mp 175–179°, after recrystallization from acetone–water; nmr ($CDCl_3$) δ 7.35–7.70 (m, 15, C_6H_5), 6.2 (d, 1, tertiary proton on triazine), 3.98 (d, 1, -CH(CN)COOEt), 3.75 (q, 2, CH_2), 1.0 (t, 3, CH_3).

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[7] A. Piskala, *Tetrahedron Lett.*, 2587 (1964); A. Piskala and J. Gut, *Collect. Czech. Chem. Commun.*, **29**, 2794 (1964).

[8] H. E. Winberg and D. D. Coffman, *J. Amer. Chem. Soc.*, **87**, 2776 (1965).

[9] M. Regitz and J. Hocker, *Synthesis*, 301 (1970).

[10] Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.; ir spectra were taken on a Perkin-Elmer Model 21 spectrophotometer, nmr spectra on a Varian T-60 spectrometer with TMS as internal standard, and mass spectra on a CH-4 mass spectrograph. All melting points (uncorrected) were determined on a Fisher-Johns apparatus.

Anal. Calcd for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.33. Found: C, 68.86; H, 4.99; N, 12.43.

On concentration of the ethereal filtrate 0.4 g (41%) of *N*,*N*-dimethyl-*N'*-phenylurea, mp 134°, was obtained.

Registry No.—**2b**, 29411-17-4; **4b**, 17350-46-8; **4c**, 29411-19-6; **8** (R = Ph), 29411-20-9; **9** (R = Ph), 29520-61-4; *N*,*N*-dimethylformamide, 68-12-2.

Studies of Hydrazine Derivatives. II.[1] The Formation of 1-Phenyl-3-benzoyltriazene by the Base-Catalyzed Condensation of Nitrosobenzene with Benzhydrazide

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Received December 7, 1970

Aromatic nitroso compounds are well known to undergo condensation reactions analogous to those of carbonyl compounds. However, nitrosobenzene (**1**) reacted with a monosubstituted or unsymmetrically disubstituted hydrazine to give a triazene *N*-oxide,[2] and attempted triazene formation in reactions of nitroso compounds with hydrazines have been unsuccessful.[3] In this paper we wish to describe the formation of 1-phenyl-3-benzoyltriazene (**2**) by the base-catalyzed condensation of **1** with benzhydrazide (**3**).

Compound **2** has previously been prepared by the reaction of phenylmagnesium bromide with benzoyl azide.[4]

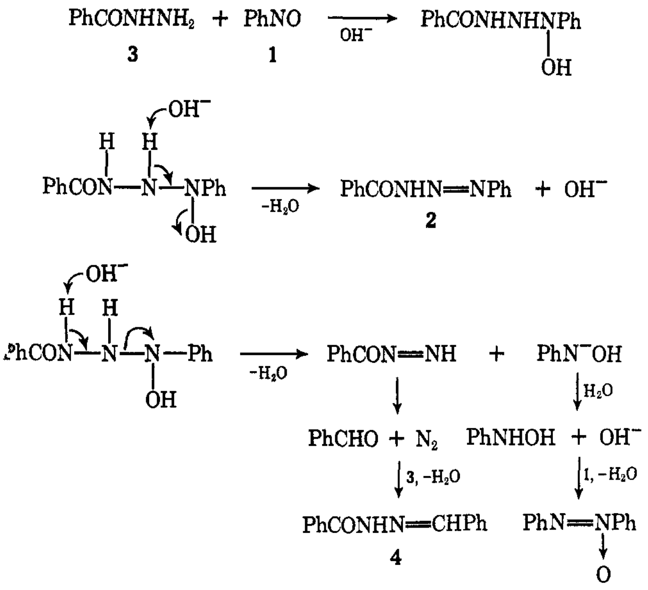
When powdered **1** was added to an aqueous solution of equimolar amounts of **3** and potassium hydroxide at 45–50° with vigorous stirring, a brown oil separated and nitrogen was evolved. After being extracted with ether, compound **2** was separated from the aqueous layer as the silver complex (25%). Benzaldehyde benzoylhydrazone (**4**, 9%), azoxybenzene (24%), benzoic acid (14%), and aniline (4%) were also obtained along with phenyl azide (0.1%) and azobenzene (trace). Either increase or decrease of alkali in the reaction reduced the yield of **2**. Attempted reactions between **1** and **3** in water with sulfuric acid, in *tert*-butyl alcohol with sodium *tert*-butoxide, and in acetic acid did not afford **2** to a significant extent.

As chromatographic treatment on silica gel or alumina brought about the decomposition of **2**, this product could not be obtained quantitatively from the reaction mixture by this technique.

When **2** was treated with dimethylaniline in acetic acid, in hydrochloric acid, or on silica gel in *n*-hexane, *p*-dimethylaminoazobenzene was obtained in 82–84% yield. A diazoaminobenzene-type rearrangement must take place in this process. A solution of the reaction mixture (after being extracted) and dimethylaniline in *n*-hexane was refluxed with a small amount of silica gel for 1 hr and then chromatographed to give *p*-dimethylaminoazobenzene (13%).

The sources of the hydrazone **4** and of azoxybenzene are suggested in Scheme I. Curtius[5] reported that **4** was formed by heating benzhydrazide with alkali, but we were unable to obtain **4** under these conditions in the absence of nitrosobenzene. The formation of aniline was observed by Minato, *et al.*,[6] in the reaction of **1** with hydrazine, though the mechanism has not been well established.

SCHEME I



Experimental Section[7]

Reaction of Nitrosobenzene (1) with Benzhydrazide (3).—To a vigorously stirred solution of 6.8 g (50 mmol) of **3** and 3.2 g (*ca.* 50 mmol) of potassium hydroxide in 75 ml of water was added, over a period of 30 min, 5.4 g (50 mmol) of powdered **1** at 45–50°. The reaction mixture was kept at this temperature for an additional 30 min with stirring. During the reaction, a brown oil separated and gas evolved. The reaction mixture was then cooled, extracted with ether, and separated to an ether layer (a), a water layer (b), and an insoluble solid (c, 1.0 g). The ether layer (a) was washed with aqueous KOH and then with water, dried (Na_2SO_4), and concentrated giving 3.1 g of an oily brown liquid, containing azoxybenzene (2.38 g, 12 mmol, 24%), aniline (0.19 g, 2 mmol, 4%), phenyl azide (0.006 g, 0.05 mmol, 0.1%), and azobenzene (trace), determined by means of column chromatography, vpc, ir, and/or tlc.

The water layer (b), when combined with washings of the ether extract of the reaction mixture, was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and concentrated giving 4.6 g of a brown viscous residue (b′), containing benzoic acid (0.86 g, 7 mmol, 14%) as the methyl ester, determined by means of vpc. Addition of an alcoholic solution of silver nitrate to the ethanol solution of b′ caused precipitation of yellow 1-phenyl-3-benzoyltriazenatosilver (4.15 g, 12.5 mmol, 25%); its ir spectrum was identical with that of an authentic sample.[4] Chromatographic treatment of b′ on silica gel or alumina brought about the decomposition of **2**; by the use of a short column (silica

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[1] Part I of this series: S. Ito and T. Narusawa, *Bull. Chem. Soc. Jap.*, **43**, 2257 (1970).

[2] (a) O. Fischer and L. Wacker, *Ber.*, **22**, 622 (1889); (b) E. Bamberger and A. Stiegelmann, *ibid.*, **32**, 3554 (1899); (c) O. Fischer and W. Johannes, *J. Prakt. Chem.*, **92**, 60 (1915).

[3] For a review about reactions of aromatic nitroso compounds, see J. H. Boyer in "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Interscience, New York, N. Y., 1969, pp 215–299.

[4] A. Bertho, *J. Prakt. Chem.*, **116**, 101 (1927).

[5] T. Curtius, *Ber.*, **33**, 2560 (1900).

[6] H. Minato and T. Fujisawa, *Bull. Chem. Soc. Jap.*, **39**, 1054 (1966).

[7] Melting points were determined in capillary and are uncorrected. The yields of the products are shown in mole percentage based on **1** or **3** used. For the ir spectroscopic determination, a Nihon-Bunko Model DS-301 spectrometer and a Shimadzu gas chromatograph Model GC-2C for the vpc analysis were employed.