*Shyam Sunder and Norton P. Peet**

Pharmaceutical Research and Development-Medicinal Chemistry, Building 219, The Dow Chemical Company, 9550 Zionsville Road, Indianapolis, IN 46268

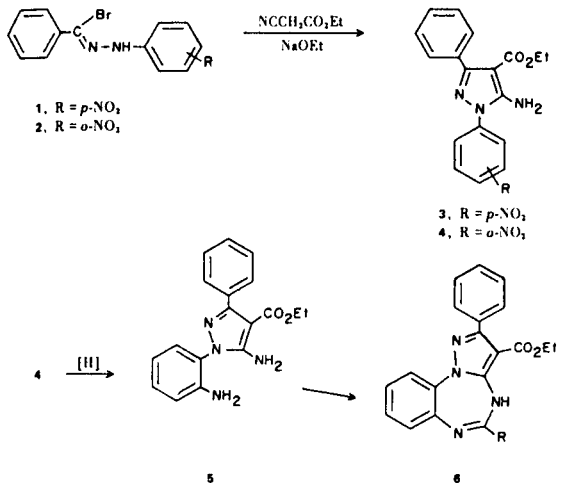
Received May 5, 1978

Benzoyl bromide (2-nitrophenyl)hydrazone (**2**) was treated with sodium ethoxide and ethyl cyanoacetate and two unexpected products were obtained. These products were ultimately shown to be 6-bromo-3-phenyl-1,2,4-benzotriazine (**32**) and 5-bromo-2-phenylbenzoxazole (**38**), by comparison with authentic samples which were synthesized. A mechanism is presented for the formation of these two heterocyclic systems (**32** and **38**) from **2**.

J. Heterocyclic Chem., 16, 33 (1979).

Our interest in the synthesis of benzotriazepines (1) led us to examine a recent report by Shawali, Hassaneen, Sami and Fahham (2). These authors investigated the reactions of ethyl cyanoacetate and cyanoacetanilide with hydrazidic halides to yield 1,3-disubstituted 5-amino-pyrazole-4-carboxylic acid derivatives. A specific reaction is shown in Scheme I, in which ethyl cyanoacetate was

Scheme I

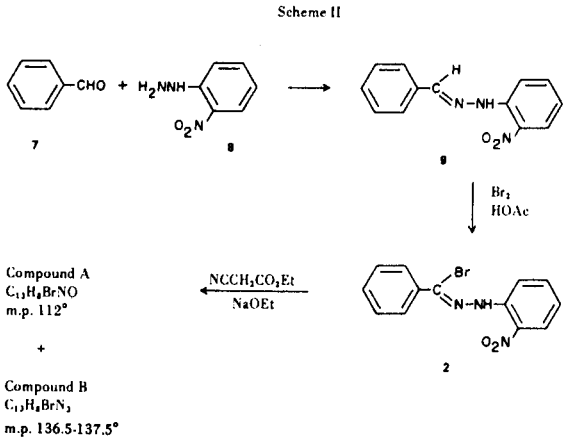


condensed with the hydrazidic bromide **1** to yield pyrazole **3**. We were interested to determine whether the reaction sequence could be employed to produce an isomer of **3**, namely, the *o*-nitrophenylpyrazole **4**. Reduction of **4** should afford aniline **5**. We envisioned the diamino compound **5** as a precursor to 1,3,5-benzotriazepine systems. For example, treatment of **5** with orthoesters or carboxylic acids should afford 1,3,5-benzotriazepines of general structure **6**.

Accordingly, we prepared benzoyl bromide (2-nitrophenyl)hydrazone (**2**) by treating benzaldehyde (2-nitrophenyl)hydrazone (**9**) with bromine in acetic acid according to the procedure of Scott and Aylward (3). Hydrazone **9**, in turn, was simply prepared from benzaldehyde (**7**) and *o*-nitrophenylhydrazine (**8**), as shown in Scheme II.

Treatment of **2** with ethyl cyanoacetate and sodium ethoxide gave a mixture of two products which were

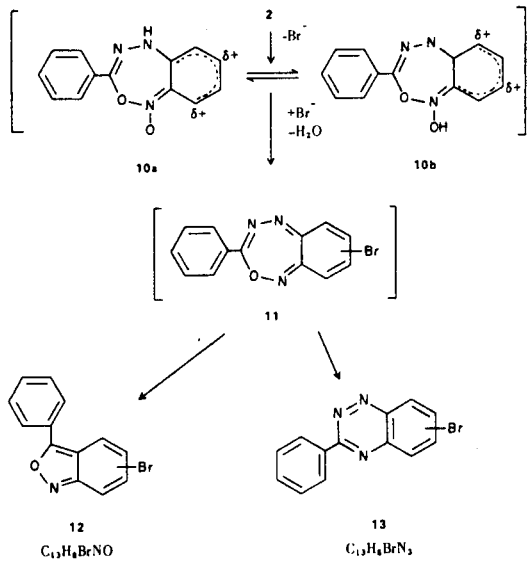
Scheme II



separated by chromatography on silica gel. Mass spectral data and combustion analyses indicated empirical formulas of $C_{13}H_8BrNO$ and $C_{13}H_8BrN_3$ for Compound A and Compound B, respectively (Scheme II). Thus, it was clear that the desired pyrazole **4** had not been produced in the reaction, and that ethyl cyanoacetate had not been a reactant of condensation in the formation of Compound A or Compound B.

Our first considerations for the structures of Compounds A and B were the general structures **13** and **12**, respec-

Scheme III



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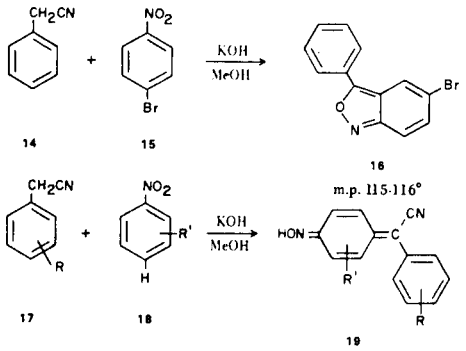
tively, which are shown in Scheme III. A benzotriazine (**13**) and a benzisoxazole (**12**) could arise from the common intermediate **11**, *via* respective extrusions of nitrogen and monoatomic oxygen. Intermediate **11** is depicted as arising from intermediates **10a** and/or **10b**, which could result from displacement of bromide ion by the nitro group. The problem of identifying Compounds A and B intrigued us, and we set out to determine whether our initial supposition (Scheme III) was correct.

One isomer of **12** was known in the literature and its synthesis was straightforward. Treatment of phenylacetonitrile (**14**) and 4-bromonitrobenzene (**15**) with methanolic potassium hydroxide, using the procedure of Davis and Pizzini (4), gave 3-phenyl-5-bromoanthranil (**16**), m.p. 115-116°, in 68% yield (Scheme IV). Although

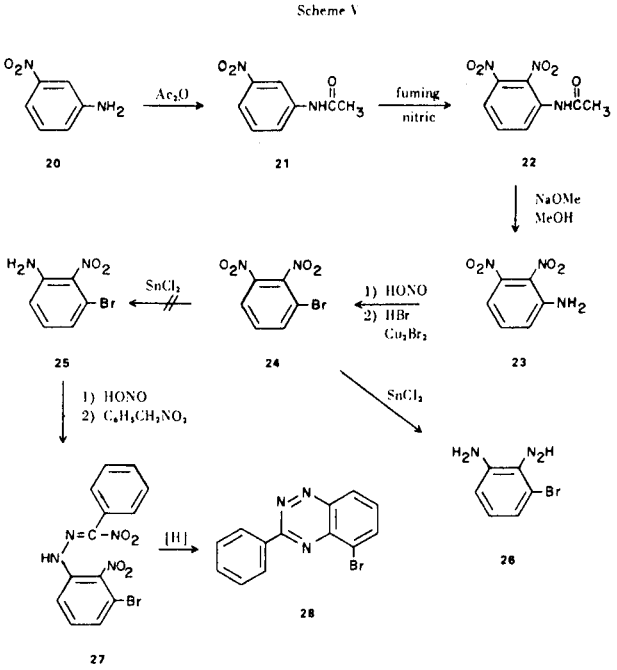
Scheme IV



16 and Compound A co-eluted on tlc (silica gel) and had similar melting points, the compounds were shown to be dissimilar by a mixture melting point determination, which displayed a substantial depression, and by a comparison of infrared and nmr spectra, which were similar but not identical. The synthesis of isomers of **12** other than **16** by the method shown in Scheme IV was not possible. It has been shown by Davis and Pizzini (4a,5) that phenylacetonitriles (**17**) and nitrobenzenes (**18**) unsubstituted at the *para*-position yield phenylcyanomethylene-*p*-benzoquinone oximes of general structure **19** when treated with methanolic potassium hydroxide.

At this point, thinking that Compound A may be an isomer of **12** other than **16**, which would be difficult to prepare (6), we turned our attention to Compound B. We chose to first pursue the synthesis of 5-bromo-3-phenyl-1,2,4-benzotriazine (**28**), because we had a preference for tautomer **10a** over **10b** in Scheme II, and we felt that the 7-bromo isomer of **13** could not be Compound B since **16** was not Compound A. Our attempted synthesis of **28** is shown in Scheme V. Acylation of *m*-nitroaniline (**20**) yielded *m*-nitroacetanilide (**21**), which was treated with fuming nitric acid to yield *N*-(2,3-dinitrophenyl)acetamide (**22**). Hydrolysis of the amide was accomplished with sodium methoxide, and the resulting 2,3-dinitroaniline (**23**) was diazotized and treated with

Scheme V

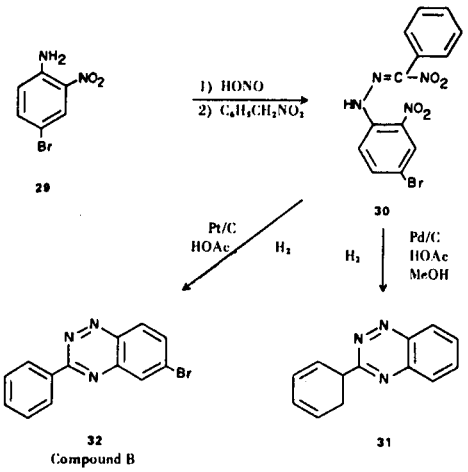


hydrobromic acid and cuprous bromide to yield 1-bromo-2,3-dinitrobenzene (**24**). Tallec (8) reported that 3-bromo-2-nitroaniline (**25**), m.p. 118°, could be prepared by the reduction of **24** with stannous chloride, using the procedure of Burton and Kenner (9) who selectively reduced 2,3-dinitrotoluene to 3-methyl-2-nitroaniline with this reagent. We envisioned the subsequent diazotization of **25** followed by treatment with phenylnitromethane to yield the dinitro compound **27**. Catalytic hydrogenation of **27** should then yield benzotriazine **28** (10). However, when we treated **24** with stannous chloride, our sole isolated product was 3-bromo-1,2-benzenediamine (**26**). Thus, our attempts to produce our proposed Compound B, which would be at least a model compound, had failed.

We next determined to prepare an isomer of **13** whose synthesis was more straightforward. To this end, we treated commercially available 4-bromo-2-nitroaniline (**29**) with nitrous acid followed by phenylnitromethane and obtained the dinitrohydrazone **30**. Catalytic reduction of **30** using palladium as the catalyst produced 3-phenyl-1,2,4-benzotriazine (**31**). It is known that hydrogenolysis of aryl halides may occur with catalytic reduction conditions (11), and that the presence of amino functionality on the ring will facilitate hydrogenolysis (12). A study comparing the effects of catalyst and catalyst support on the rate of dehydrohalogenation of *p*-chloronitrobenzene has been reproted (13), and platinum was found to be a catalyst of choice for minimizing dehydrohalogenation. In fact, several examples (14) illustrate dehydrohalogenation with palladium and halogen retention with platinum in the reduction of nitroaryl substrates. Therefore, we undertook the reductive-cyclization of **30** using platinum

as the catalyst, and obtained the desired 5-bromo-3-phenyl-1,2,4-benzotriazine (**32**). Only a trace of **31** was produced using platinum, as was indicated by tlc (15) (Scheme VI).

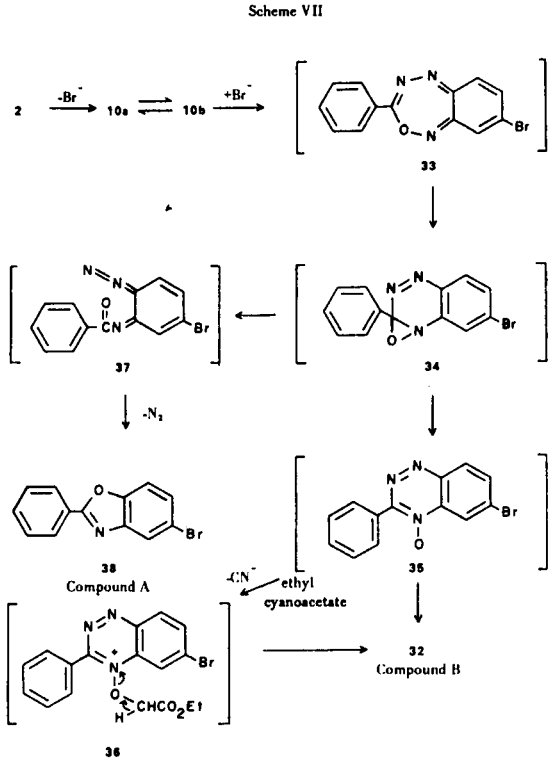
Scheme VI



The synthesis of **32** was a turning point in our efforts to elucidate the structures of our unknown compounds, since a comparison of **32** with Compound B found them to be identical. The structure of Compound B led us to critically examine our initial mechanistic proposal (Scheme I) and the proposed structure for Compound A. We re-examined the ultraviolet spectra of Compound A and **16** and found them to be quite dissimilar, and perhaps indicative of different chromophores. In view of the identity of Compound B (**32**) and the ultraviolet spectrum of Compound A, which was not similar to that of **16**, we proposed the mechanism shown in Scheme VII. Invoking our original intermediates **10a** and **10b**, and **33**, a non-generalized version of intermediate **11**, we proposed **34** as the last common intermediate to Compounds A and B. Rearrangement of **34** to *N*-oxide intermediate **35** followed by reduction of **35** would explain the formation of **32**. In fact, one of our experiments indicated that ethyl cyanoacetate might be involved in the formation of **32**. Treatment of **2** with only sodium ethoxide led to a reaction mixture which, by tlc, indicated the presence of Compound A and the absence of **32** (Compound B). A postulated role for ethyl cyanoacetate in the reduction of proposed intermediate **35** is shown in Scheme VII, where displacement of the cyano group by the *N*-oxide leads to intermediate **36**. Subsequent extrusion of ethyl gloxylate from **36** would then give **32**.

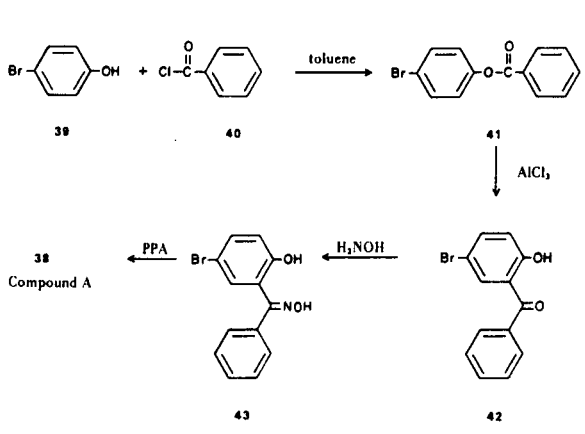
Intermediate **34** could also rearrange to diazoamide intermediate **37**. Loss of nitrogen from **37** would lead to 5-bromo-2-phenylbenzoxazole (**38**). In view of the results heretofore, the mechanism depicted in Scheme VII seemed reasonable. An assessment of its validity, however, awaited the preparation of authentic benzoxazole **38**.

Scheme VII



p-Bromophenyl benzoate (**41**), prepared by acylating *p*-bromophenol (**39**) with benzoyl chloride (**40**) in toluene, was converted to benzoxazole **38** using the procedure of Blatt (16). Rearrangement of benzoate **41** with aluminum chloride gave the benzophenone **42**, which was converted to its oxime (**43**). Beckmann rearrangement of **43** with polyphosphoric acid produced 5-bromo-2-phenylbenzoxazole (**38**), as shown in Scheme VIII, which was identical in all respects with Compound A.

Scheme VIII



Aryl nitro groups are often considered only as site-activating or site-directing groups and not as reactive functional groups. The formation of compounds **32** and **38** from **2**, however, again (17) demonstrates the reactivity of an aryl nitro group in heterocyclic synthesis.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded with a Perkin-Elmer Model 727B Spectrophotometer, nmr spectra with a Varian T-60 spectrometer, and mass spectra with a Finnigan gc/ms Model 3000D (electron impact and chemical ionization) mass spectrometer at 70 eV. Combustion analyses for C, H, and N were performed by Dow Analytical Laboratories.

Materials.

m-Nitroacetanilide (**21**), m.p. 149.5-151.5° [lit. (19) m.p. 154-156°] was prepared in 98% yield from *m*-nitroaniline (**20**) and acetic anhydride in methylene chloride; *N*-(2,3-dinitrophenyl)-acetamide (**22**), m.p. 184-187° [lit. (20) m.p. 186-187°; lit. (21) m.p. 185-186°] and 2,3-dinitroaniline (**23**), m.p. 126-128° [lit. (20) m.p. 126-127°; lit. (21) m.p. 127°] were prepared using the procedure of Vivian, Hartwell and Waterman (20); 1-bromo-2,3-dinitrobenzene (**24**), m.p. 101-102.5° [lit. (22) m.p. 101-102.5°] was prepared using the procedure of Vivian (22); *p*-bromophenyl benzoate (**41**), m.p. 102-103° [lit. (23) m.p. 101-102°; lit. (24) m.p. 99-102°] was prepared in 86% yield by the acylation of *p*-bromophenol (**39**) with benzoyl chloride (**40**) in toluene; (5-bromo-2-hydroxyphenyl)phenylmethanone (**42**), m.p. 111-112° [lit. (16) m.p. 111-112°] and (5-bromo-2-hydroxyphenyl)phenyl-methanone oxime (**43**), m.p. 153-155° [lit. (16) m.p. 155-156°] were prepared using the procedure of Blatt (16).

Benzaldehyde (2-Nitrophenyl)hydrazone (**9**).

A 19.9 g. (0.130 mole) quantity of *o*-nitrophenylhydrazine (Aldrich), 14.3 g. (0.135 mole) of benzaldehyde and 200 ml. of absolute ethanol were heated at reflux for 2 hours. The red solid was collected, washed with ethanol and air-dried to yield 28.7 g. (92%) of **9**: m.p. 184-190° [lit. (25) m.p. 186-187°]; ir (Nujol): 3300 (NH), 1620 (C=N) cm^{-1}; nmr (DMSO-d_6): δ 11.18 (broad s, 1H, NH), 8.50 (s, 1H, aldimine H), 8.30-7.34 (m, 8H, aromatic), 7.11-6.78 (m, 1H, aromatic).

Benzoyl Bromide (2-Nitrophenyl)hydrazone (**2**).

To a vigorously stirring (mechanical) slurry of 4.82 g. (20.0 mmoles) of **9** in 150 ml. of acetic acid was added, dropwise, 6.39 g. (40.0 mmoles) of bromine in 40 ml. of acetic acid, following the general procedure of Scott and Aylward (26). After 5 hours of stirring, the red solid was collected by filtration, washed with ether and air-dried to yield 5.4 g. (84%) of **2**, m.p. 206-211°; m.p. 208-210° (ethanol).

Anal. Calcd. for $C_{13}H_{10}BrN_3O_2$: C, 48.76; H, 3.15; N, 13.12. Found: C, 48.70; H, 3.23; N, 13.31.

Treatment of **2** with Ethyl Cyanoacetate and Sodium Ethoxide.

A 2.26 g. (20.0 mmoles) quantity of ethyl cyanoacetate was added to ethanolic sodium ethoxide, made from 0.460 g. of sodium and 100 ml. of absolute ethanol. A 6.40 g. (20.0 mmoles) quantity of **2** was then added. After 15 hours of stirring, tlc (silica gel, 9:1 chloroform:methanol) indicated only **2**. After 6 hours at reflux, tlc indicated the absence of **2** and two major products. The red solution was concentrated, partitioned between methylene chloride-water, and the organic layer was dried (sodium sulfate) and concentrated. The residue was dissolved in a minimal volume of chloroform and applied to a 150 g. column of Silica Gel 60 (70-230 mesh, EM Reagents) which had been slurry-packed with chloroform. Elution with 1200 ml. of chloroform separated the two components. The first component to elute was Compound A (1.40 g.), m.p. 112° (methanol); ir (Nujol): 1610, 1550, 805, 700, 680 cm^{-1}; nmr (deuteriochloroform): δ 8.33-7.73 (m, 4H, aromatic), 7.60-7.13 (m, 4H, aromatic); uv (ethanol): λ max (ε) 304 (23,400); ms (chemical ionization, methane, 70 eV): m/e 274 (M^+ + 1), 302 (M^+ + 29), 314 (M^+ + 41).

Anal. Calcd. for $C_{13}H_8BrNO$: C, 56.95; H, 2.94; N, 5.11. Found: C, 56.70; H, 3.08; N, 5.41.

The second component to elute was Compound B, m.p. 136-137.5° (methanol); ir (Nujol): 1605, 1515, 1340, 1310, 1020, 700 cm^{-1}; nmr (deuteriochloroform): δ 7.04-6.68 (m, 2H, aromatic), 6.68-6.35 (m, 2H, aromatic), 6.15-5.48 (m, 4H, aromatic); uv (ethanol): λ max (ε) 352 (6,460), 266 (34,700), 214 (25,400); ms (chemical ionization, methane, 70 eV): 286 (M^+ + 1), 314 (M^+ + 29), 326 (M^+ + 41).

Anal. Calcd. for $C_{13}H_8BrN_3$: C, 54.56; H, 2.82; N, 14.68. Found: C, 54.54; H, 2.75; N, 14.61.

3-Phenyl-5-bromoanthranil (**16**).

A solution of 8.10 g. (69.1 mmoles) of phenylacetonitrile and 12.7 g. (62.9 mmoles) of *p*-nitrobromobenzene in 125 ml. of methanol was added dropwise to a solution of 74 g. (1.1 moles) of potassium hydroxide in 150 ml. of methanol, with icebath cooling and vigorous stirring. After 4 hours of stirring at 0°, 400 ml. of water was added. The resulting precipitate was collected and air-dried to yield 11.7 g. (68%) of **16**, m.p. 115-116° (methanol) [lit. (4) m.p. 116-118°]; ir (Nujol): 1620, 810, 765, 740, 720, 680, 650 cm^{-1}; nmr (deuteriochloroform): δ 8.82-8.40 (m, 3H, aromatic), 8.40-7.77 (m, 5H, aromatic); uv (ethanol): 352 (9,850), 257 (14,900), 218 (20,000); ms (chemical ionization, methane, 70 eV): m/e 274 (M^+ + 1), 302 (M^+ + 29), 314 (M^+ + 41).

Treatment of **24** with Stannous Chloride.

A 21.5 g. (0.113 mole) quantity of stannous chloride was dissolved in 100 ml. of ethanol which was previously saturated with dry hydrogen chloride, following the procedure of Burton and Kenner (9). To this solution was added a suspension of 6.11 g. (0.0274 mole) of **24** in 40 ml. of ethanol. The resulting solution was stirred at room temperature for 7 hours, at which time tlc (silica gel, 9:1 chloroform:methanol) indicated the absence of **24** and the presence of two new materials. The solution was concentrated and partitioned between methylene chloride and dilute hydrochloric acid. The aqueous layer was basified (sodium hydroxide), extracted with methylene chloride, and the organic layer, which now contained one material by tlc, was dried (sodium sulfate) and concentrated to leave 1.2 g. of an oil. This oil, which crystallized on standing, was shown to be 3-bromo-1,2-benzene-diamine (**26**), m.p. 52-54° [lit. (27) b.p. 127-128°]; ir (Nujol): 3420 and 3350 (NH_2), 1620, 1675, 1480, 1300, 1240 cm^{-1}; nmr (deuteriochloroform): δ 6.95-6.67 (m, 1H, aromatic), 6.55-6.30 (m, 2H, aromatic), 3.55 (s, 4H, both NH_2 groups); ms (chemical ionization, methane, 70 eV): m/e 187 (M^+ + 1), 215 (M^+ + 29).

Nitrophenylmethanone 2-(4-Bromo-2-nitrophenyl)hydrazone (**30**).

To a slurry of 10.9 g. (50.0 mmoles) of 4-bromo-2-nitroaniline (Fairfield) in 150 ml. of 1*N* hydrochloric acid was gradually added, at 0-5°, 5.18 g. (75.0 mmoles) of sodium nitrite. After a few minutes of stirring, the mixture was filtered directly into another flask containing a cold solution of 6.68 g. (50.0 mmoles) of phenylnitromethane (Pfaltz and Bauer) in 150 ml. of 1*N* sodium hydroxide and 25 ml. of ethanol. The resulting red solution was acidified with acetic acid and extracted with methylene chloride. The organic layer was dried (sodium sulfate) and concentrated to a small volume to yield 5.50 g. (30%) of **30** in two crops, m.p. 149-151°; ir (Nujol): 3275 (NH), 1605 (C=N) cm^{-1}; nmr (DMSO-d_6): δ 8.24-7.20 (m, 8H, aromatic), 3.40 (broad s, 1H, NH); ms (electron impact, 70 eV): m/e 365 (M^+).

Anal. Calcd. for $C_{13}H_9BrN_4O_4$: C, 42.76; H, 2.48; N, 15.34.

Found: C, 42.90; H, 2.71; N, 15.56.

3-Phenyl-1,2,4-benzotriazine (**31**).

A 4.00 g. (10.1 mmoles) quantity of **30** was slurried with 200 ml. of 9:1 methanol:acetic acid and 500 mg. of 5% palladium on carbon was added. The mixture was reduced under 3 atmospheres of hydrogen for 30 minutes. The catalyst was removed by filtration and the filtrate was concentrated. The residue was partitioned between methylene chloride and sodium bicarbonate solution. The organic layer was dried (sodium sulfate) and concentrated to leave 1.89 g. (90%) of crude **31**, which was purified by percolation through a silica gel column with chloroform, m.p. 123.5-124.5° [lit. (28) m.p. 126-127°; lit. (29) m.p. 123-124°]; ir (Nujol): 1610 (C=N), 1515, 1385, 1340, 765 cm^{-1}; nmr (deuteriochloroform): δ 8.67-8.14 (m, 3H, aromatic), 7.94-7.17 (m, 6H, aromatic).

Anal. Calcd. for $C_{13}H_9N_3$: C, 75.34; H, 4.38; N, 20.28. Found: C, 75.40; H, 4.57; N, 20.52.

6-Bromo-3-phenyl-1,2,4-benzotriazine (**32**).

A 1.00 g. (2.74 mmoles) quantity of **30** was mixed with 100 ml. of acetic acid and 200 mg. of 5% platinum on carbon and reduced under 3 atmospheres of hydrogen for 1 hour. The catalyst was removed by filtration and the filtrate was concentrated and treated with aqueous sodium bicarbonate to yield a solid, which, after collection and air-drying afforded 0.64 g. (82%) of crude **32**. Tlc (silica gel, 9:1 chloroform:methanol) indicated the absence of **30**, only a trace of **31**, and one major product spot. Recrystallization from ethanol gave 0.110 g. of pure **32**, m.p. 135-136°, which was spectrally identical with Compound B. A mixture melting point of **32** and Compound B was undepressed.

5-Bromo-2-phenylbenzoxazole (**38**).

A 2.00 g. (6.85 mmoles) quantity of oxime **43** was mixed with 40 g. of polyphosphoric acid and heated on a hotplate at 110°. The mixture became homogeneous after 10 minutes, and after 35 minutes it was poured into cold sodium carbonate solution. The solid was collected, washed with water and air-dried to yield 1.74 g. (93%) of **38**. Recrystallization from methanol gave 1.00 g. of pure **38**, m.p. 111-112°, which was spectrally identical with Compound A. A mixture melting point of **38** with Compound A was undepressed.

Acknowledgement.

The authors wish to thank Professor E. Campaigne of Indiana University for helpful suggestions.

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