

hold for both the prepolymer fractions and the linear high polymers, indicated that typical  $[\eta]$ 's of 0.14, 0.20, and 0.28 dl./g. corresponded to  $\bar{M}_w$ 's of 28,000, 41,000, and 60,000, respectively. Osmotic measurements on a specimen of  $[\eta]$  0.20 showed  $\bar{M}_n$  30,000, indicating  $\bar{M}_w/\bar{M}_n = 1.37$ . This polydispersity corresponds to the 1.4 value found in prepolymer specimens fractionated from a mixture having a "most probable" distribution by a single precipitation from a 10% solution in acetone.

Estimates of OH and OEt contents were made from absorption intensities in the regions corresponding to the strongest SiOH and SiOEt group modes,<sup>11</sup> using the crystalline phenyl-T<sub>3</sub>(OH)<sub>2</sub>(OEt)<sub>2</sub>, m.p. 55–57°,<sup>5</sup> as the reference standard. A more sensitive measure of silanol plus silanolate was achieved by treating the polymer in benzene solution with trimethylchlorosilane and pyridine, whereby these groups were converted to SiOSiMe<sub>3</sub> groups, which were determined in the reprecipitated polymer from the intensity of the very strong band at 844 cm.<sup>-1</sup>. The results on the material of crop 1 were

| Group                   | No. per 1000 Ph-T | Method              |
|-------------------------|-------------------|---------------------|
| SiO <sup>-</sup>        | 4 ± 2             | Titration           |
| SiOH                    | 10 ± 10           | Infrared            |
| SiO <sup>-</sup> + SiOH | 15 ± 3            | Trimethylsilylation |
| SiOEt                   | 0 ± 30            | Infrared            |

Since the observed  $[\eta]$  and the usual  $\bar{M}_w/\bar{M}_n$  ratio indicated an  $\bar{M}_n$  of 20,400, or an average molecular size of 158 phenyl-T units for this specimen, and since it appears likely that SiOEt is 0.5–1.0 the content of SiOH, it would appear that the total content of silanol, silanolate, and alkoxy silane groups was 3–4 per molecule.

When a solution of this same specimen (1.00 g. in 10 ml. of benzene) was allowed to stand, precipitation of phenyl-T<sub>3</sub> occurred as previously reported,<sup>5</sup> and at about the same rate; the conversion was 79% after 2 months, 92% after 6 months. However, when a similar solution which also contained a drop of acetic acid to neutralize the silanolate was allowed to stand, only the trace of phenyl-T<sub>3</sub> which had been originally present in the polymer crystallized out. No further rearrangement to T<sub>3</sub> occurred, and the intrinsic viscosity was unchanged after standing for 4 months.

A small sample of the phenylsilsesquioxane mixture remaining in acetone solution after the separation of crop 1A was recovered by precipitation into dilute aqueous HCl, followed by reprecipitation from acetone into water, drying overnight under vacuum at 35°, and for 0.2 hr. at 110°. Its infrared spectrum showed  $\nu_{\text{SiOSi}}$ 's centered near 1135 and 1057 cm.<sup>-1</sup>, and indicated OH and OEt contents of 1.8 and 2.3%, respectively, which are comparable to those reported previously for a similar product.<sup>5</sup> Presumably, a quarter of this OH represented silanolate prior to neutralization, and some additional portion of it represented ethoxy hydrolyzed during the precipitation.

**Kinetic Studies.**—One-tenth gram samples of phenylsilsesquioxane were weighed into tared 13 × 100 mm. test tubes, fol-

lowed by phenyl-T<sub>3</sub> or -T<sub>12</sub> seed crystals; the solvent was 0.42 or 0.84 ml. of tetrahydrofuran or benzene, and 0.36 ml. of an ethanol-water-base solution (usually containing  $6.05 \times 10^{-5}$  mole of KOH). The stoppered tubes were placed in a 63° constant temperature bath for the desired reaction times, and then cooled to 0°. After 80 min. at room temperature to ensure completion of precipitation, the precipitates were centrifuged down, rinsed with two 1-ml. portions of solvent, dried at 200°, and weighed. The identities of the products were reconfirmed by their X-ray patterns in a number of cases. In general, the measurements of conversion as a function of time were reproducible, but fractions from different prepolymer preparations appeared to be converted to T<sub>12</sub> at different rates. Agitation of the reacting mixtures had no effect upon the precipitation rates. Higher rates of conversion to T<sub>12</sub> were observed in solutions containing both ethanol and water than in those that contained just one of these hydroxylic species. As the base, KOH gave faster conversion rates than NaOH or Me<sub>4</sub>NOH; however, doubling its concentration from 0.078 mole/mole of phenyl-T to 0.156 mole/mole markedly reduced the rate of T<sub>12</sub> formation. In all cases, the conversions to T<sub>3</sub> or T<sub>12</sub> followed sigmoidal curves; representative examples are shown in Fig. 1.

In order to follow the changes occurring in the soluble fraction during the conversions of prepolymer to phenyl-T<sub>12</sub> in tetrahydrofuran, the dissolved phenylsilsesquioxanes were recovered by precipitation into dilute aqueous HCl, and their spectra determined. Representative examples are shown in Fig. 2. The material remaining in solution after the completion of T<sub>12</sub> precipitation was a low-melting, amorphous resin, contained about 2.5% each of OH and OEt groups, and showed an infrared spectrum (third curve on Fig. 2) that was unlike that of any of the fractions obtained after equilibrations in toluene or diglyme, but not inconsistent with that expected for a mixture of cage-like and very short-chain linear polycyclics.

The increase in cage-like structure during the course of this equilibration was followed by measuring the base-line absorbancy of the 1135 cm.<sup>-1</sup> C<sub>6</sub>H<sub>5</sub>Si group peak (which is superimposed upon the broader 1127 cm.<sup>-1</sup>  $\nu_{\text{SiOSi}}$  mode) relative to that of the virtually invariant 697 cm.<sup>-1</sup> peak. This ratio,  $A(1135)/A(697)$ , was 2.9 in the ladder polymer, 4.0 in the lowest prepolymer fractions, 4.4 in the noncrystalline T<sub>9</sub>-T<sub>12</sub> mixtures, 4.5 in T<sub>3</sub>, 5.6 in T<sub>12</sub>, and 5.7 in T<sub>10</sub>. During the course of T<sub>12</sub> formation from unfractionated prepolymer ( $[\eta]$  0.085, prepared in toluene) the ratio went from 3.54 to 3.79 in 48 hr. (dotted line on Fig. 1), and was apparently approaching a final value of 3.80 as in a first-order reaction with a half-time of 10.5 hr.

**Acknowledgment.**—The authors wish to thank Mrs. Nancy R. Young for technical assistance during the early part of this investigation, Mr. H. W. Middleton for the analyses, Miss Dorothea V. McClung for the infrared spectra, and Dr. M. M. Sprung for the phenyl-T<sub>3</sub>(OH)<sub>2</sub>(OEt)<sub>2</sub> specimens. The procedure for synthesizing prepolymer by equilibration in toluene was supplied by Dr. K. W. Krantz.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

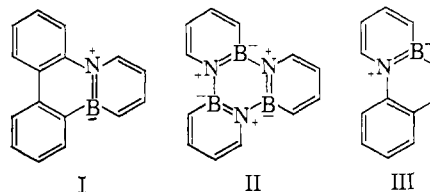
## New Heteroaromatic Compounds. XXIII.<sup>1</sup> Two Analogs of Triphenylene and a Possible Route to Borazarene<sup>2</sup>

By GERALD C. CULLING,<sup>3</sup> MICHAEL J. S. DEWAR,<sup>4</sup> AND PETER A. MARR<sup>4</sup>

RECEIVED OCTOBER 15, 1963

We have prepared two boron-containing analogs of triphenylene, 14,13-borazarotriphenylene and 14,16,18-tribora-13,15,17-triazarotriphenylene. Hydrolysis of the latter with cold dilute alkali probably gives 2-hydroxy-borazarene.

Previous papers of this series have described a wide range of novel heteroaromatic compounds, derived from normal aromatic systems by replacing pairs of adjacent carbon atoms by boron and nitrogen. Here we report the preparation and properties of two further compounds of this type, 14,13-borazarotriphenylene (I) and 14,16,18-tribora-13,15,17-triazarotriphenylene (II).



The synthesis of I followed the route used previously<sup>5</sup> to prepare 12,11-borazarophenanthrene (III). Con-

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(5) M. J. S. Dewar, C. Kaneko, and M. K. Bhattacharjee, *J. Am. Chem. Soc.*, **84**, 4884 (1962).

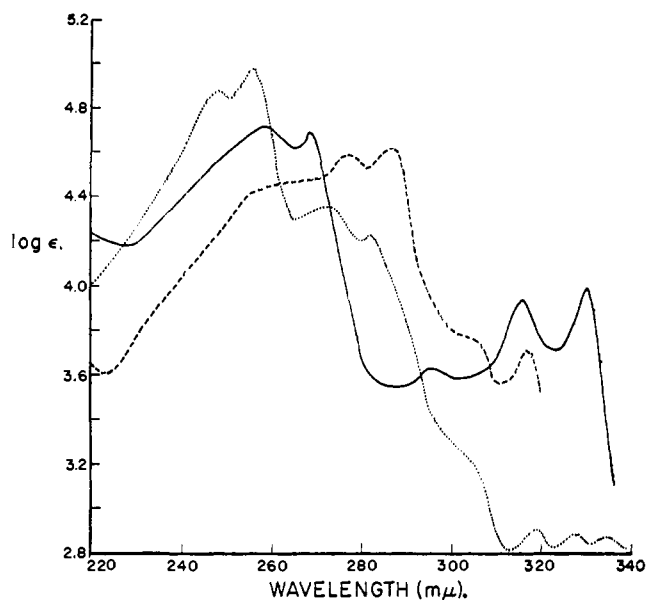
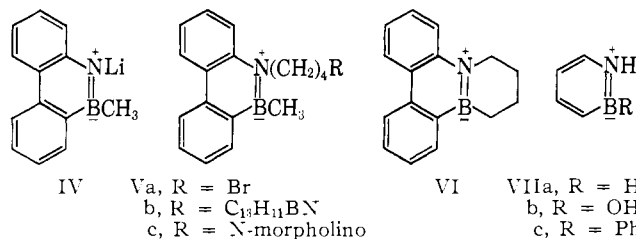


Fig. 1.—Ultraviolet absorption spectra in ethanol of I (—), II (---), and triphenylene (· · ·).

condensation of 9-lithio-10-methyl-10,9-borazarophenanthrene (IV)<sup>6</sup> with 1,4-dibromobutane gave 9-(4-bromo-1-butyl)-10-methyl-10,9-borazarophenanthrene (Va), together with some 1,4-bis-(10-methyl-10,9-borazaro-9-phenanthryl)-butane (Vb). Since Va could not easily be freed from traces of impurities, it was further characterized by conversion to 1-(10-methyl-10,9-borazaro-9-phenanthryl)-4-(N-morpholino)-butane (Vc). On treatment with magnesium, Va underwent cyclization to 1,2,3,4-tetrahydro-14,13-borazarotriphenylene (VI). Dehydrogenation of VI with sulfur gave 14,13-borazarotriphenylene (I) in good yield.



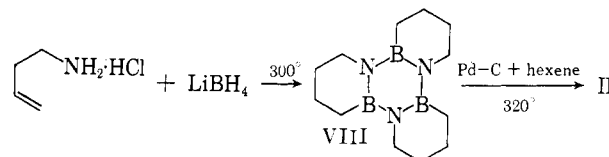
The properties of I indicated it to be a remarkably stable aromatic system. Not only was it unaffected by prolonged exposure to air or treatment with strong acid or alkali, but it also resisted attack by maleic anhydride. This indicates that the peripheral boron-containing ring is highly resonance stabilized. The 1,4-paralocalization energy in I must be much greater than the values for the many typical aromatic hydrocarbons that undergo Diels-Alder reactions with maleic anhydride (*e.g.*, anthracene).

Clar<sup>7</sup> has emphasized that triphenylene behaves very much as though it consisted of three weakly perturbed benzene rings linked together. On this basis, Compound I should likewise behave much as though it contained two benzene units and one of borazarene (VIIa). The stability of I therefore indicates that borazarene itself should be a highly resonance stabilized aromatic system.

We have indeed found<sup>8</sup> that a derivative of VIIa showed considerable hydrolytic stability toward acid or alkali, indicating the borazarene ring to be aromatic.

These conclusions suggested that 14,16,18-tribora-13,15,17-triazarotriphenylene (II) might behave as an aggregate of three weakly perturbed borazarene units, and that the central ring might undergo hydrolytic fission very readily with acid or alkali to give three molecules of 2-hydroxyborazarene (VIIb).

Preliminary attempts to prepare II from trichloroborazine, by reaction with metal derivatives of ethoxyvinylacetylene followed by treatment with ammonia, failed. We finally obtained II by the route



Hydroboration of 4-amino-1-hexene, followed by heating under pressure in an autoclave, gave a moderate yield of tristramethyleneborazine (VIII). The structure followed from elemental analysis and a determination of molecular weight, from the absence of any absorption in the ultraviolet region above 200 mμ in isoctane solution, and from the n.m.r. spectrum which showed peaks at 6.89, 8.44, and 9.03 τ in the ratio 1:2:1. The infrared spectrum was also consistent with the structure VIII.

Dehydrogenation of VIII over palladized charcoal in hexene as hydrogen acceptor in an autoclave at 320° gave, again in poor yield, 14,16,18-tribora-13,15,17-triazarotriphenylene (II). The structure of II was indicated by elemental analysis, by mass spectral determination of its molecular weight,<sup>9</sup> and by the close similarity between the ultraviolet spectra of I, II, and triphenylene (Fig. 1).

When II was treated with cold dilute ethanolic alkali, it underwent rapid hydrolysis. The characteristic spectrum (Fig. 1) disappeared, leaving end absorption. Since the borazarene ring appears to be stable to cold dilute alkali, it seems almost certain that II must have undergone hydrolysis to three molecules of 2-hydroxyborazarene (VIIb). The amount of material was, however, insufficient for isolation and we are repeating the preparation on a large scale. The work is being reported at this stage since White<sup>10</sup> has independently prepared 2-phenylborazarene (VIIc) by a similar route, by condensation of 4-amino-1-butene with diborane followed by dehydrogenation. He found VIIc to be fairly stable, although it was easily destroyed by treatment with acid or alkali. A preliminary account of our work was given at the Symposium on Boron-Nitrogen Chemistry, Durham, N. C., April, 1963.

## Experimental

**9-(4-Bromo-1-butyl)-10-methyl-10,9-borazarophenanthrene (Va).**—A solution of 10-methyl-10,9-borazarophenanthrene<sup>11</sup> (44.75 g., 0.232 mole) in dry benzene (250 ml.) was treated<sup>6</sup> with methyl lithium (0.25 mole) in dry ether (200 ml.) under nitrogen and the resulting solution added dropwise to one of freshly distilled 1,4-dibromobutane (500 ml., 2.3 moles) in dry benzene (400 ml.) at room temperature. When addition was complete (30 min.), the mixture was boiled under reflux for 15 hr. and then cooled. Hydrochloric acid (200 ml. of 2 N) was added and the organic layer extracted with chloroform (3 × 400 ml.). The chloroform layer was washed with dilute hydrochloric acid, then water, dried (MgSO<sub>4</sub>), and evaporated *in vacuo* until no material distilled at 100° (0.45 mm.). The residue was extracted with ether (3 × 200 ml.). Evaporation gave crude 9-(4-bromo-1-butyl)-10-methyl-10,9-borazarophenanthrene (67.0 g., 88%)

(9) We are very grateful to Dr. S. Meyerson, of the American Oil Co., for this determination.

(10) D. G. White, *J. Am. Chem. Soc.*, **85**, 3634 (1963). We are very grateful to Professor White for sending us a preprint of his paper.

(11) M. J. S. Dewar, R. Dietz, V. P. Kubba, and A. R. Lepley, *ibid.*, **83**, 1754 (1961).

(6) M. J. S. Dewar and P. M. Maitlis, *J. Am. Chem. Soc.*, **83**, 187 (1961).

(7) E. Clar, *Tetrahedron*, **6**, 355 (1959); **9**, 202 (1960).

(8) M. J. S. Dewar and P. A. Marr, *J. Am. Chem. Soc.*, **84**, 3782 (1962).

which was used without further purification in the synthesis of VI.

**1,4-Bis-(10-methyl-10,9-borazaro-9-phenanthryl)butane (Vb).**—The residue from the final ether extraction in the preparation of Va crystallized from acetone, giving the **bisborazarophenanthrylbutane (Vb)** as colorless prisms (2.2 g.), m.p. 198–199°.

*Anal.* Calcd. for  $C_{30}H_{30}B_2N_2$ : C, 81.1; H, 6.8; N, 6.4. Found: C, 81.1; H, 6.7; N, 6.3.

**9-(4-Morpholino-1-butyl)-10-methyl-10,9-borazarophenanthrene (Vc).**—Crude Va (1 g.) was heated with morpholine (2 g.) in ethanol (25 ml.) under reflux for 12 hr. The solution was then evaporated *in vacuo*, water, ether, and sodium hydroxide solution (10 ml. of 20%) were added, and the ethereal layer was washed, dried, ( $MgSO_4$ ), and evaporated. The residue crystallized from ethanol in colorless needles (0.75 g., 72%) of the **morpholino-butylborazarophenanthrene (Vc)**, m.p. 111–112°.

*Anal.* Calcd. for  $C_{21}H_{27}BN_2O$ : C, 75.5; H, 8.1; N, 8.4. Found: C, 75.3; H, 8.0; N, 8.3.

**1,2,3,4-Tetrahydro-14,13-borazarotriphenylene (VI).**—A solution of crude Va (67.0 g., 0.2 mole) in dry ether (250 ml.) was added dropwise to magnesium turnings (5 g., 0.21 g.-atom) over 1 hr. and the mixture then boiled overnight under reflux. Carbon dioxide was then bubbled into the solution at such a rate that it continued to boil gently. When the reaction had subsided, the passage of carbon dioxide was continued for a further 15 min. The product was then isolated with ether and chromatographed from petroleum ether (b.p. 60–68°) on alumina (grade IV,  $30 \times 5$  cm.), giving **1,2,3,4-tetrahydro-14,13-borazarotriphenylene** which crystallized from petroleum ether (b.p. 60–68°) in colorless prisms (37.3 g., 80%), m.p. 112–114°, raised by sublimation at 90° (0.1 mm.) to 117°.

*Anal.* Calcd. for  $C_{16}H_{16}BN$ : C, 82.5; H, 6.9; N, 6.0. Found: C, 82.5; H, 7.0; N, 5.9.

**14,13-Borazarotriphenylene (I).**—A mixture of VI (5 g., 0.0215 mole) and sulfur (1.44 g., 0.045 mole) was heated 1 hr. at 250–260°. The residue was extracted with hot benzene and the extract evaporated to 20 ml. An equal volume of petroleum ether (b.p. 60–68°) was added, the solution filtered, and the filtrate chromatographed on alumina (Grade IV,  $20 \times 3$  cm.), eluting with petroleum ether. After a forerun of unchanged VI, the main fraction gave on evaporation **14,13-borazarotriphenylene (I)** which crystallized from petroleum ether (b.p. 60–68°) in colorless needles (2.45 g., 48%), m.p. 185–186°; ultraviolet spectrum in ethanol,  $\lambda_{max}$  in  $m\mu$  ( $\log \epsilon$ ): 258 (4.71), 269 (4.69), 295 (3.62), 316 (3.93), 330 (3.97).

*Anal.* Calcd. for  $C_{16}H_{12}BN$ : C, 83.9; H, 5.3; N, 6.1. Found: C, 84.0; H, 5.3; N, 6.0.

**Attempted Reaction of I with Maleic Anhydride.**—A mixture of I (0.58 g., 2.5 mmoles) and maleic anhydride (0.25 g., 2.5 mmoles)

in dry benzene (20 ml.) was heated under reflux for 3 hr. and then evaporated until crystallization began. The crystals were collected and found to be pure I (0.42 g.). Further I (0.12 g.) was recovered from the mother liquors; total recovery, 0.54 g. (94%) of material with m.p. and mixture m.p. 184–185°.

**Tristetramethyleneborazine (VIII).**—4-Amino-1-butene<sup>12</sup> hydrochloride (100 g.) was added slowly and cautiously to a stirred suspension of lithium borohydride (27 g.) in dry ether (200 ml.) contained in the glass liner of a 1-l. autoclave under nitrogen in a drybox. The volume was maintained by periodic addition of ether and the whole operation took 2 hr. Ether (200 ml.) was then added and the mixture left 60 hr. in the drybox. The liner and contents were then transferred to the autoclave (which had been purged overnight with dry nitrogen), heated to 150°, held there for 2 hr., then heated as rapidly as possible to 300° and held 20 min. at 300–310°. The autoclave was then cooled and vented in a hood, and the contents triturated 1 hr. with ether and water. The ether layer was separated and the aqueous layer extracted with ether. The combined ethereal extracts were washed with 10% sodium hydroxide solution, water, 10% hydrochloric acid, and water, dried ( $MgSO_4$ ), and evaporated. The yellow residue (23 g.) was heated at 50–60° (0.005 mm.) to remove low boiling material and then sublimed at 120° (0.005 mm.). The sublimate crystallized from acetone giving **tristetramethyleneborazine (VIII)** as colorless plates (18 g., 26%), m.p. 184–186°.

*Anal.* Calcd. for  $C_{12}H_{24}B_3N_3$ : C, 59.4; H, 10.0; B, 13.4; N, 17.3; mol. wt., 243. Found: C, 59.1; H, 9.9; B, 13.6; N, 17.0; mol. wt. (Rast), 266.

**14,16,18-Tribora-13,15,17-triazarotriphenylene (II).**—A mixture of VIII (1 g.), palladized charcoal (Matheson, 0.5 g. of 10%), and mixed 1-and-2-hexenes (Phillips, 5 ml.) was heated 18 hr. in a Carius tube in an autoclave at 320°. The contents of the tube were then filtered and the solid washed with hot chloroform. The combined filtrates were evaporated and the residue chromatographed on neutral alumina (Woelm activity grade 1), first with petroleum ether (b.p. 60–68°) until all unchanged starting materials had been eluted (130 ml. of eluate), then with petroleum ether-chloroform (9:1) to elute the **triboratriazarotriphenylene (II)**, 100 mg., 10% which after crystallization from petroleum ether (b.p. 60–68°) and sublimation at 85° (0.005 mm.) had m.p. 193–195°.

*Anal.* Calcd. for  $C_{12}H_{12}B_3N_3$ : C, 62.5; H, 5.2; N, 18.2. Found: C, 62.9; H, 5.4; N, 17.8.

When II was dissolved in cold dilute ethanolic solutions of hydrochloric acid, sodium hydroxide, or sodium ethoxide, the characteristic ultraviolet absorption band rapidly disappeared, indicating hydrolysis.

(12) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH DEPARTMENT, AGRICULTURAL DIVISION, AMERICAN CYANAMID CO., PRINCETON, N. J.]

## The Mechanism of the Rearrangement of *p*-Quinamines to 4-Aminodiphenyl Ethers<sup>1</sup>

BY BERNARD MILLER

RECEIVED SEPTEMBER 18, 1963

The infrared and ultraviolet spectra of the products obtained from reaction of aromatic amines with 4-bromocyclohexadienones confirm the previously proposed quinamine structures (I). Acid-catalyzed rearrangement of a mixture of two quinamines with similar rearrangement rates afforded a mixture of 4-aminodiphenyl ethers containing no cross products from reaction of the two quinamines. The rearrangements are therefore completely intramolecular. The rearrangements are first order in quinamine and first order in hydrogen ion. Electron-withdrawing groups on the cyclohexadienone rings of quinamines increase the rates, while electron-donating groups on the aniline ring increase the rates to a greater extent than can be explained by the expected effects of the substituents on the basicities of quinamines. This suggests that proceeding from the ground state to the transition state increases the positive charge on the anilinium portion of the quinamine and induces a negative charge on the cyclohexadienone portion. The close resemblance between the quinamine and benzidine rearrangement is pointed out, and it is suggested that the two rearrangements proceed through similar mechanisms involving complexes of two roughly parallel aromatic rings.

Some 35 years ago, Fries and his co-workers<sup>2</sup> found that 4-bromocyclohexadienones react with aromatic amines to give yellow, crystalline substitution products, to which they assigned the structures of 4-arylamino-cyclohexadienones (I) and the generic name "quin-

amines." On treatment with hydrochloric acid, quinamines performed a series of remarkable rearrangements which have somehow remained almost unnoticed to this day.

Quinamines with unsubstituted *p*-positions in the aniline rings gave as their principal products 4-aminodiphenyl ethers (II), whose structures were clearly demonstrated by reduction to the halogen-free derivatives (II, X = Y = H), which were independently synthesized.<sup>2b</sup> The aminodiphenyl ethers were usually ob-

(1) This paper is the fourth in a series on "Reactions of Cyclohexadienones." For preceding papers, see (a) B. Miller, *J. Org. Chem.*, **26**, 4781 (1961); (b) B. Miller, *Tetrahedron Letters*, No. 2, 55 (1962); (c) B. Miller, *J. Org. Chem.*, **28**, 345 (1963).

(2) (a) K. Fries and G. Oehmke, *Ann.*, **462**, 1 (1928); (b) K. Fries, R. Boeker, and F. Wallbaum, *ibid.*, **609**, 73 (1934).