in the region 1250–1300 cm^{-1} in RMgH is due to bridging magnesium–hydrogen (MgH_2Mg) stretching.

The NMR spectra of RMgH compounds in THF showed signals due to alkyl groups attached to magnesium (Table II). Unfortunately, the Mg–H signal was not observed, probably due to its masking by the THF solvent. Molecular-association studies in THF showed CH_3MgH and C_2H_5MgH to be dimeric at low concentration and increasing in association with an increase in concentration. However, molecular weight data of PhMgH showed it to be monomeric in infinitely dilute solution (Figure 2).

When $(CH_3)_2Mg$ in THF was added to an active MgH_2 slurry in THF in a 1:3 ratio, about 90% of the initial MgH_2 dissolved. The infrared spectrum of the solution showed a band at 1290 cm^{-1} which shifted to 940 cm^{-1} in the deuterio analogue $CH_3Mg_2D_3$, suggesting that the absorption band is due to the bridging magnesium–hydrogen (MgH_2Mg) band.

$$Me_2Mg + 3MgH_2 \xrightarrow{THF} 2MeMg_2H_3 \qquad (9)$$

When the solvent was removed under vacuum, the resulting solid exhibited x-ray lines due to MgH_2, indicating the disproportion of $CH_3Mg_2H_3$ into CH_3MgH and MgH_2 (eq 10).

$$CH_3Mg_2H_3 \rightarrow CH_3MgH + MgH_2 \qquad (10)$$

When diphenylmagnesium in THF was added to 3 mol equiv of magnesium hydride a clear solution resulted. The elemental analysis of this solution corresponded well to $PhMg_2H_3$. The infrared spectrum (Figure 3) gave a strong band at 1290 cm^{-1} which shifted to 935 cm^{-1} in the deuterio analogue $PhMg_2D_3$, suggesting that the absorption band is due to the bridging magnesium–hydrogen (MgH_2Mg) bond. The molecular weight of $PhMg_2H_3$ could not be determined because it cleaved THF under refluxing conditions producing a THF-insoluble product of emperical formula $PhMg_2(OBu^n)_3$.

The results of vacuum DTA–TGA studies on CH_3MgH, $CH_3Mg_2H_3$, PhMgH, and $PhMg_2H_3$ are given in Table III and Figures 4–7. The product RMgH decomposes at 300 °C with gas evolution. The steps involved in the decomposition of RMgH are shown below.

$$1.\ RMgH{\cdot}THF \rightarrow RMgH + THF \qquad (11)$$

$$2.\ RMgH \rightarrow Mg + RH \qquad (12)$$

The RMg_2H_3 compounds decompose over a wide temperature range centered at 300 °C.

$$RMg_2H_3 \rightarrow Mg + RH + H_2 \qquad (13)$$

Acknowledgment. We are indebted to the Office of Naval Research Contract no. N00014-67-A-0419-005AD, and contract authority no. 093-050/7-11-69(473) for support of this work.

Registry No.—$(CH_3)_2Mg$, 2999-74-8; Ph_2Mg, 555-54-4; MgH_2, 7693-27-8; $(C_2H_5)_2Mg$, 557-18-6; $(i\text{-}C_3H_7)_2Mg$, 3536-97-8; Dicyclopentadienylmagnesium, 1284-72-6.

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Oxidative Cyclodehydrogenation of Aromatic Bis(*o*-aminoanils)

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The two bis-Schiff bases, *N,N'*-terephthalidenebis(*o*-aminoaniline) (**1**) and *N,N'*-dibenzylidene-3,3'-diaminobenzidine (**8**), prepared from the respective aldehyde and amine reactants by low-temperature solution condensation, are converted by molecular oxygen in solution to the benzimidazoles **2** and **9**. The oxidative heteroaromatization, especially when catalyzed with ferric chloride, proceeds readily at temperatures as low as 20–60 °C. The unusually mild conditions required for the oxidative ring closure suggest this experimental approach to be well applicable to the polyconversion of analogous polymeric Schiff bases to the corresponding polybenzimidazoles.

A recent note from this laboratory[1] dealt with the copolymerization of aromatic bis(*o*-diamines) with aromatic dialdehydes and the subsequent cyclodehydrogenation of the resultant polyazomethines, to give polybenzimidazoles. Initial observations in that work led us to conclude that the final aromatization step proceeded in the presence of air, as well as in its absence, in the latter case presumably with elimination of molecular hydrogen. Because of the technological implications of this convenient two-step polycondensation process, it was of prime interest to elaborate more favorable experimental conditions by conducting a study of model reactions leading to well-defined nonpolymeric intermediates and products, in which the progress of the aromatization reaction could be monitored by conventional analytical techniques. It was a particular objective to search for experimental conditions that would favor the primary cyclodehydrogenation step and so would lead to highest possible conversion to benzimidazole structures without concurrently promoting degradation of the amine reactants through oxidative and/or thermal change, or outright elimination, of the sensitive amino groups.

In this communication we present the results of a study

Table I. ^{1}H NMR Resonances of Bisazomethines 1, 8, 3, and 4[a]

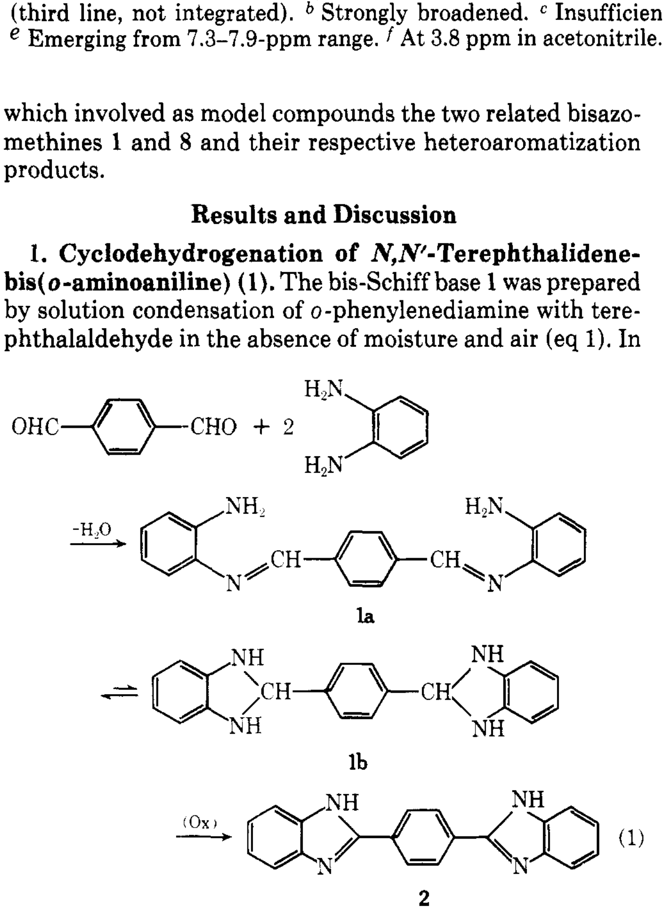
Compd	H (azomethine)	H (amino)	H [ortho, aldehyde ring(s)]	H (all other aromatics)
1	8.59 s (2 H)	5.0 s[b] (4 H)	7.99 s (4 H)	6.3–8.2 m (8 H)
	8.54 s[c]	4.2 s[c]	7.95 s[c]	6.5–7.7 m[c]
	9.1–9.3 m	d	8.4 s	7.7 s[e]
8	8.59 s (2 H)	5.2 s (4 H)	7.8–8.0 m (4 H)	6.7–7.5 m (12 H)
	8.57 s (2 H)	4.2 s[f] (4 H)	7.8–7.95 m (4 H)	6.85–7.6 m (12 H)
	9.1–9.3 m	d	7.0–8.4 m	
3	8.57 s (2 H)		7.95 s (4 H)	7.1–7.4 m[g] 10 H)
	8.4 s (2 H)		7.9 s (4 H)	7.0–7.4 m[g] (10 H)
	9.4–9.5 s		8.55 s	7.4–7.9 m
4	8.58 s (2 H)		7.7–8.0 m (4 H)	7.3–7.6 m (10 H)
	8.4 s (2 H)		7.7–7.9 m (4 H)	7.1–7.5 m (10 H)
	9.3–9.4 s		7.5–8.3 m	

[a] Chemical shifts δ, in parts per million relative to internal Me_4Si. Solvents: Me_2SO-d_6 (first line), $CDCl_3$ (second line), CF_3COOH (third line, not integrated). [b] Strongly broadened. [c] Insufficiently soluble for meaningful integration. [d] Exchange with solvent. [e] Emerging from 7.3–7.9-ppm range. [f] At 3.8 ppm in acetonitrile. [g] Singlet emerging at 7.3 ppm.

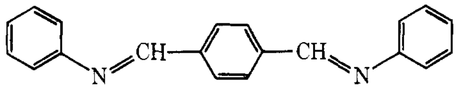
which involved as model compounds the two related bisazomethines 1 and 8 and their respective heteroaromatization products.

Results and Discussion

1. Cyclodehydrogenation of *N,N'*-Terephthalidenebis(*o*-aminoaniline) (1). The bis-Schiff base 1 was prepared by solution condensation of *o*-phenylenediamine with terephthalaldehyde in the absence of moisture and air (eq 1). In an effort to minimize involvement in the condensation process of more than one amino group per diamine molecule, the condensation was performed by adding the highly diluted solution of the aldehyde very slowly to the dissolved amine at low temperatures.[2] Suitable solvents included *N,N*-dimethylacetamide (DMAC), dimethyl sulfoxide (Me_2SO), *N*-methylpyrrolidone, and ethanol.



Aromatic Schiff bases possessing an amino group in the ortho position of the aniline ring are capable of tautomerizing to the corresponding closed-ring imidazoline structures, although the basicity of the ortho substituent disfavors ring closure[3] and thus generally renders the "open-chain", trans-configurated azomethine form the more stable one.[4] For 1, when dissolved in neutral solvents, the azomethine structure **a** is confirmed by spectroscopic data. The IR spectrum ($CHCl_3$) features the moderately strong band of the amino groups' N–H bending mode at 1607 cm^{-1} and the C=N stretching band at 1626 cm^{-1}, the latter in an intensity exceeding that of the benzene bands at 1580–1600 cm^{-1} as similarly observed in the spectrum of the parent compound, terephthalidenedianiline (3). The NMR spectrum (Table I), taken on Me_2SO-d_6 solutions, shows the azomethine 2-proton signal at the position (δ 8.59 ppm) expected for aromatic Schiff bases; both 3 and its isomer 4, *N,N'*-dibenzylidene-*p*-phenylenediamine, give resonances at 8.57–8.58 ppm in this solvent, and signals near this position have been reported for related azomethines.[5] The 4-proton signal of the amino groups emerges at 5.0 ppm (4.6 ppm in the Me_2SO-d_6 spectrum of aniline). The 8-proton resonances of the two outer benzene rings appear as a broad and complex absorption range instead of forming the simple A_2B_2 pattern expected for structure **b**. Solutions in $CDCl_3$ produce very similar shifts, indicating that the reduced solvent polarity has no significant effect, if any, on the ring–chain tautomerism in this system;[6] because of poor solubility in this solvent, however, the spectrum could not be properly integrated. The electronic spectra in various neutral solvents show a band in the vicinity of 300 nm and a slightly more intense one in the range of 415–445 nm (Table II). On the basis of El-Bayoumi's analysis of the benzylideneaniline spectrum[7] and a consequent evaluation of the spectrum of 3, we interpret the 300-nm absorption as resulting from a ($\pi \rightarrow \pi^*$) transition in the planar conjugated $N{=}CC_6H_4C{=}N$ part of the molecule (at about 260 nm in benzylideneaniline),[8] whereas the high-wavelength band may be assigned to an essentially localized ($\pi \rightarrow \pi^*$) excitation in the molecule's noncoplanar[9] anil chromophore (inflection near 310 nm in benzylideneaniline) corresponding to the transition $^1A_{1g} \rightarrow {}^1B_{2u}$ in benzene. In the tautomeric imidazoline structure **b** lacking the conjugated $N{=}CC_6H_4C{=}N$ segment, the 300-nm absorption should be replaced by the only slightly perturbed $^1B_{2u}$ band of the benzene system as shown, for example, by *p*-xylene [λ_{max} (Me_2SO) 270, 276 nm].



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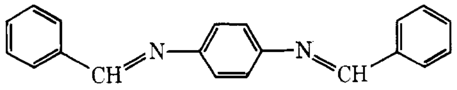

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In the solid state, when isolated by slow and controlled crystallization, the compound likewise exists as the azomethine form **a**. Thus, the electronic spectrum (KBr matrix) exhibits two bands in approximately the same regions (yet as multicomponent systems) as in the solution spectra, and the IR spectrum (KBr), in addition to the nonbonded and bonded N–H stretching bands at 3475 and 3370 cm^{-1}, shows the C=N stretching peak at 1616 cm^{-1}, although now, just as in the

Table II. Electronic Absorption Maxima ($\pi \rightarrow \pi^*$ Transitions) of Bisazomethines 1, 8, 3, and 4 in the 270–500-nm Region[a]

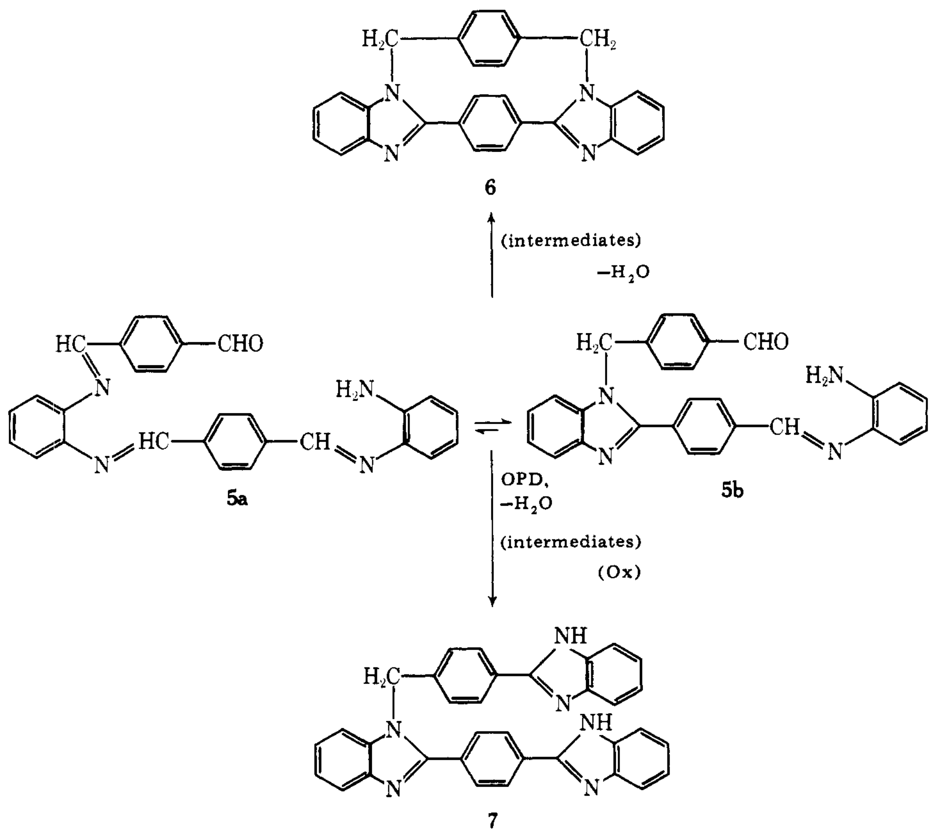
Compd	λ_{max}, nm	$\epsilon \times 10^{-4}$ [b]	λ_{max}, nm	$\epsilon \times 10^{-4}$ [c]
1	300	2.4	445	2.3
	298	2.2	444	2.1
	292	1.8	416[d]	1.7
8	277[e]	3.5[e]	424	2.2
	276[e]	3.5[e]	420	2.4
	265	2.4	402[f]	1.1
3	301	2.4	350	2.4_5
	300	2.2	349	2.3
	298	2.2	348	2.2
4	279	1.9_5	359	2.2_5
	277[e]	2.0	359	2.3
	275	1.9	357	2.0

[a] Solvents: Me_2SO (first line), DMAC (second line), dichloromethane (third line); at ambient temperature. [b] $\pi \rightarrow \pi^*$ transition in $N{=}CC_6H_4C{=}N$ (**1**, **3**) and $C_6H_5C{=}N$ (**8**, **4**) segments. [c] $\pi \rightarrow \pi^*$ transition in amine ring system. [d] At 450 nm in KBr matrix; shoulders at 425 and 490 nm. [e] Value approximate; maximum partly merging with edge absorption of solvent. [f] At 415 nm in KBr matrix; shoulder at 480 nm.

solid-state spectrum of **3** (1617 cm^{-1}), slightly weaker than the adjacent benzene bands.[10]

As a purity check, the 70-eV mass spectra of several crude samples of **1** were examined in the mass number range above the molecular ion peak (*m/e* 314) for the emergence of any peaks due to condensation products involving both amino groups of the phenylenediamine reactant. Indeed, at temperatures of 300 °C and higher, peaks were found invariably at *m/e* 412 and 516 in intensities of 1–5% relative to *m/e* 310 [P^+ (**2**); see subsequent discussion]. These almost certainly represent the cyclophane **6** (no steric preference implied in the structure shown) and the benzyl derivative **7**, both generated from the tris-Schiff base **5a** and its ring tautomer **5b** (eq 2, OPD = *o*-phenylenediamine).[11] From our failure to observe the mass peak of **5** (at inlet temperatures ranging from 150 to 380 °C) or detect aldehydic carbonyl absorption in the IR spectra of the samples investigated, we conclude that tautomers **5**, formed as by-products in the preparation of **1**, under our experimental conditions immediately underwent further reaction involving the formyl function. Self-condensation resulted in the bisimidazole **6** via a macrocyclic pair of Schiff base tautomers (not shown in the scheme), whereas intermolecular condensation (with additional OPD) afforded tautomeric bis- and tetrakis-Schiff bases (not shown; peak at *m/e* 520 not significant because of insufficient volatility below 300 °C), which in turn, at the high inlet temperatures, cyclodehydrogenated spontaneously in the spectrometer to give the trisimidazole **7**. The appearance of the two peaks due to P^+ (**6**) and P^+ (**7**) in the spectra of crude **1** (yet not of rigorously purified compound) shows that the steric accessibility of the primary amino groups in **1** is not sufficiently reduced by the ortho substituent to prevent a minor extent of further condensation even under the strict controls employed in our experiments.

The cyclodehydrogenation of **1** to give the heteroaromatic **2**, 1,4-di(benzimidazol-2-yl)benzene (eq 1), was found to proceed under anaerobic conditions in the melt and, more readily, in the gas phase of the mass spectrometer. Thus,



(2)

Table III. Oxidative Cyclodehydration Reactions (1 → 2; 8 → 9)

Expt[a] no.	Substrate	Substrate concn, mol L^{-1}	Solvent[b]	Temp, °C	Time, h	Method of oxidn[c]
1	1	6.4×10^{-2}	DMAC	60	3[d]	A
2	1	6.4×10^{-2}	DMAC	60	4[d]	B
3[e]	1	6.4×10^{-2}	DMAC[g]	20	50	A
4	1	6.4×10^{-2}	Me_2SO[f]	60	2	B
5	2	5.1×10^{-2}	DMAC[g]	60	3[d]	A
6	2	5.1×10^{-2}	Me_2SO[f]	36	3	A

[a] Crude yields of 2 (expt 1–4) or 9 (expt 5, 6), 89–95%. All experiments conducted in diffuse daylight; no significant changes in yield when conducted either in the dark or under illumination with medium- or high-pressure mercury lamps (quartz vessels). [b] DMAC = *N,N*-dimethylacetamide; Me_2SO = dimethyl sulfoxide. [c] Method A, agitation in air by means of excentrally tumbling stirring bar; method B, air introduced at rate of 120 L/h. [d] Same results after 0.3 h in presence of $FeCl_3$ (6.4×10^{-4} mol L^{-1}). [e] Reaction partially heterogeneous at this temperature. [f] Similar results in absolute ethanolic solution. [g] Similar results in *N*-methylpyrrolidone or tetramethylurea solutions.

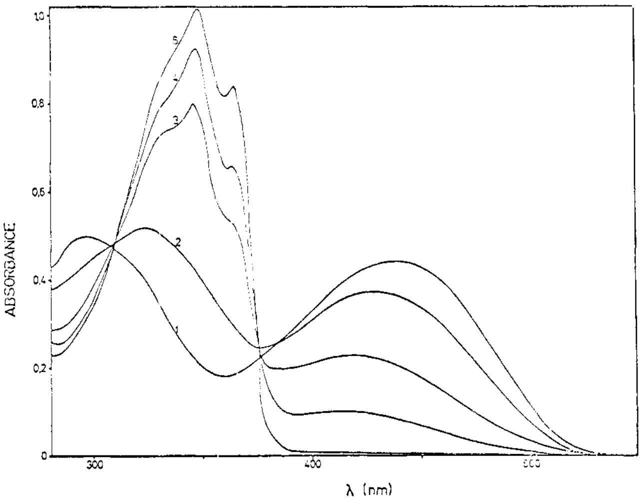


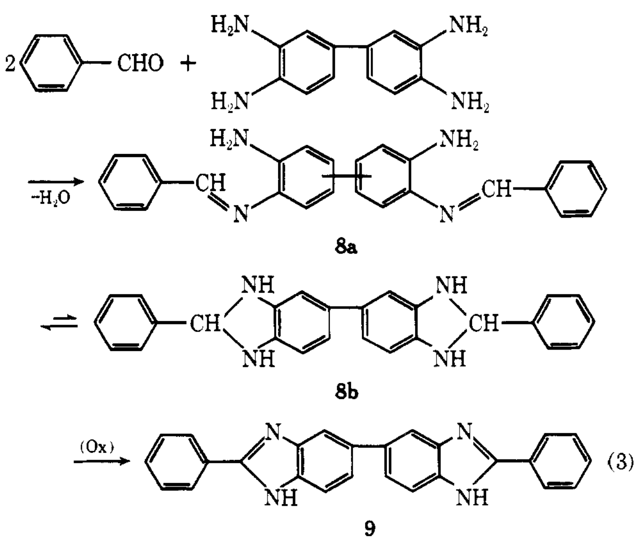
Figure 1. Electronic absorption spectra taken in time intervals on 2.4×10^{-5} M solution of 1 in DMAC during cyclodehydrogenation experiment conducted at 60 °C with excentral stirring (400 rpm) in air. Curve 1, start of experiment; curves 2–5, after respectively 15, 60, 105, and 150 min.

heating the compound above the melting range for 3 h under argon afforded 2 in 40–50% yield (in addition to several degradation products), and a sample volatilized from the probe of the mass spectrometer at inlet temperatures of 250 °C and higher featured the molecular ion peak of **2**, whereas that of 1 predominated at temperatures up to about 200 °C (I_{310}/I_{314} = 4.0 at 260 °C, 0.03 at 170 °C). Surprisingly, however, all attempts to achieve a reasonable extent of cyclodehydrogenation by heating the compound in the dissolved state (60–135 °C) under perfectly anaerobic conditions over periods of time as long as 3 days remained unsuccessful, nor was it possible to accomplish this reaction through photocatalysis by means of medium- or high-pressure mercury lamps as used for the conversion of benzylidene-*o*-aminoaniline to 2-phenylbenzimidazole.[3] In the presence of molecular oxygen, on the other hand, the reaction proceeded smoothly in a number of solvents. For example, the vigorous agitation in air of (or, alternatively, the copious bubbling of air into) a 6.4×10^{-2} M solution in DMAC for 3 h at 60 °C led to more than 90% conversion, and in ethanolic or Me_2SO solutions the same conversion resulted at even lower temperatures. Solute concentration, mode of agitation, and/or rate of air introduction all proved critical variables in these cyclization reactions and had to be controlled carefully for meaningful comparisons of conversion rates. The oxidative ring closure could also be accomplished with ferric chloride or similar oxidants.[12] Catalytic quantities of $FeCl_3$ in the presence of oxygen, preferably in ethanol or Me_2SO media, proved especially efficacious. For example, a low-concentration (6.3×10^{-4} M) run conducted in Me_2SO at 20 ± 2 °C in the presence of $FeCl_3$ (4×10^{-6} M), with air introduced at a rate of 10 L h^{-1}, proceeded to 50% conversion (UV) within 1.5 h, whereas some 48 h was required for the same result in the absence of the iron salt.

The progress of cyclodehydrogenation under the various conditions was conveniently monitored by UV spectroscopy as previously demonstrated by Grellmann and Tauer[3] for similar systems. The multiple-scan electronic absorption spectrum for a typical experiment conducted in DMAC solution is reproduced in Figure 1. Curve 5 practically superimposes upon the spectrum of pure bisimidazole 2[13] recorded at the same molar concentration. Characteristically, as the heteroaromatization proceeds, the 300- and the 445-nm maxima collapse, to be replaced by the typical multicomponent benzazole band with λ_{max} (DMAC) at 348 nm (ϵ 4.1×10^4). The latter, because of the substantially extended chromophore in 2 as compared to the simple 2-phenylbenzimidazole, experiences both hyper- and bathochromic shifts relative to the monoazole, which shows λ_{max} (DMAC) at 306 nm (ϵ 2.7×10^4).

Exemplifying cyclodehydrogenation experiments conducted in DMAC or Me_2SO solutions are summarized in Table III.

2. Cyclodehydrogenation of *N,N'*-Dibenzylidene(3,3'-diaminobenzidine) (8). The solution condensation of 3,3'-diaminobenzidine with benzaldehyde under conditions similar to those leading to 1 afforded the bis-Schiff base 8 (eq 3). For the compound in the dissolved state, the open-chain tautomeric (transoid) structure **a**[14] follows from spectroscopic data, and similar arguments hold as in the case of 1. The IR solution

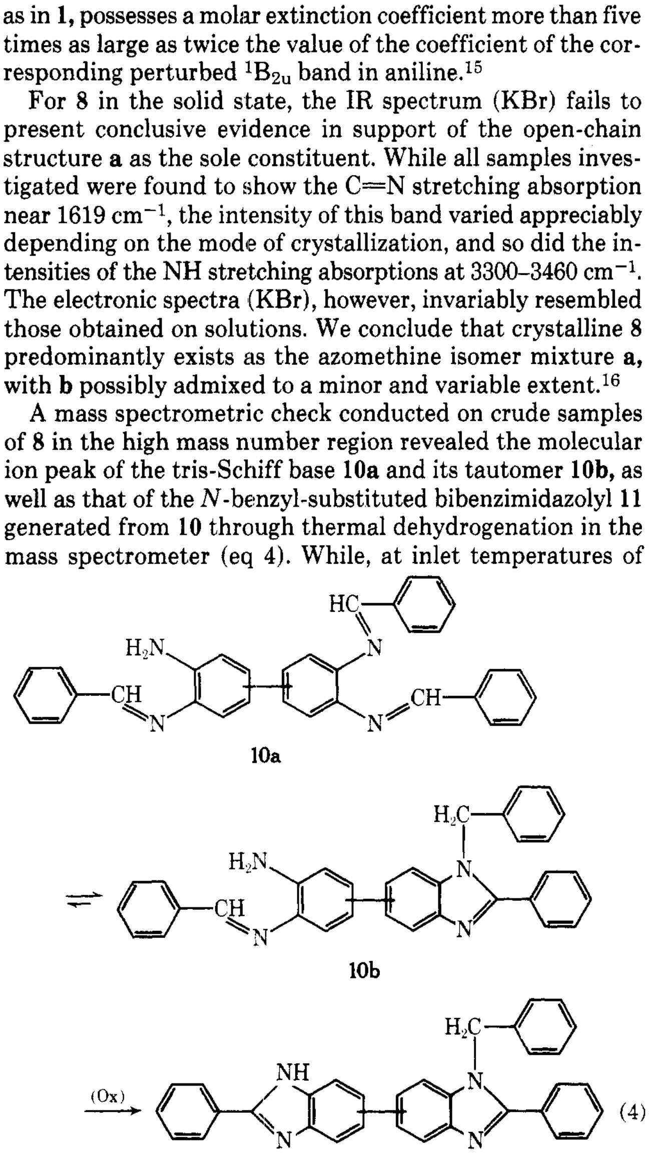


spectrum ($CHCl_3$) shows δ_{N-H} of the amino groups at 1606 cm^{-1}, and $\nu_{C=N}$ appears at 1625 cm^{-1} (1626 cm^{-1} in **4**). In the NMR spectrum (Me_2SO-d_6), the 2-proton peak of the azomethine links is found near 8.6 ppm, the 4-proton resonance of the amino groups appears at 5.2 ppm, and the ortho protons of the two terminal rings, residing in the C=N systems' deshielding zones, give a 4-proton signal at the same position (7.9 ppm) as shown by **3** and **4**, rather than at an upfield position near 7–7.5 ppm expected for a phenyl group in the 2 position of an imidazoline ring. Again, as in **1**, analogous shifts are observed in the $CDCl_3$ and CF_3COOH spectra (Table I).

In the electronic spectrum (Me_2SO) we find the ($\pi \rightarrow \pi^*$) band of the two benzylideneimino segments (each one of these twisted out of the plane of the biphenyl segment) at about 275 nm, and the strong ($\pi \rightarrow \pi^*$) absorption of the two diamine rings emerges with a maximum at about 420 nm. More allowed because of increased perturbation, the last-named band, just as in **1**, possesses a molar extinction coefficient more than five times as large as twice the value of the coefficient of the corresponding perturbed $^1B_{2u}$ band in aniline.[15]

For **8** in the solid state, the IR spectrum (KBr) fails to present conclusive evidence in support of the open-chain structure **a** as the sole constituent. While all samples investigated were found to show the C=N stretching absorption near 1619 cm^{-1}, the intensity of this band varied appreciably depending on the mode of crystallization, and so did the intensities of the NH stretching absorptions at 3300–3460 cm^{-1}. The electronic spectra (KBr), however, invariably resembled those obtained on solutions. We conclude that crystalline **8** predominantly exists as the azomethine isomer mixture **a**, with **b** possibly admixed to a minor and variable extent.[16]

A mass spectrometric check conducted on crude samples of **8** in the high mass number region revealed the molecular ion peak of the tris-Schiff base **10a** and its tautomer **10b**, as well as that of the *N*-benzyl-substituted bibenzimidazolyl **11** generated from **10** through thermal dehydrogenation in the mass spectrometer (eq 4). While, at inlet temperatures of 200–250 °C, the peak due to **10** [*m/e* 478, 3–5% of P^+ (**8**)] predominates over that of **11** [*m/e* 476, ca. 1% of P^+ (**8**)], the latter peak gains intensity and becomes prevalent as the temperature exceeds 300 °C. The appearance of the two peaks in the mass spectra of crude (but not of pure) **8** indicates that the compound, just like **1**, offers sufficient accessibility of the two primary amino groups to allow some trisubstitution despite the rigorous experimental control exercised in our work. The implications of this finding for analogous polymerization studies are obvious.



10a

10b

11

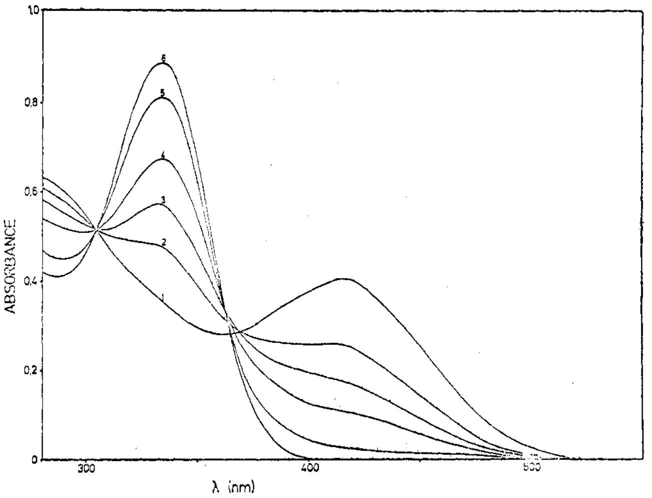


Figure 2. Electronic absorption spectra taken in time intervals on 2.0×10^{-5} M solution of **8** in Me_2SO during cyclodehydrogenation experiment conducted at ambient temperature with excentral stirring (400 rpm) in air. Curve 1, start of experiment; curves 2–6, after respectively 30, 45, 60, 90, and 120 min.

The formation of bisimidazole **9** by cyclodehydrogenation of **8** (eq 3) under anaerobic conditions was brought about both in the melt and in the gas phase of the mass spectrometer at temperatures above 300 °C. On the other hand, just as in the case of **1**, only minimal anaerobic dehydrogenation was observable in the dissolved state within reasonable periods of time, whereas reaction with O_2 proceeded smoothly in ethanolic solution as well as in aprotic solvents. Representative cyclodehydrogenation experiments are summarized in Table III. Progress of the reaction, as before, was monitored by UV spectroscopy (Figure 2); the absorption pattern progressively approached that of authentic[13,17] 2,2′-diphenyl-5,5′-bibenzimidazolyl (**9**),[18] which shows a maximum (DMAC) at 338 nm (ϵ 4.2×10^4). In none of the experiments, conducted either with **1** or with **8**, were we able to isolate and/or identify any by-products that could have resulted from oxidative removal (or involvement in other oxidative side reactions) of the reactants' primary amino groups.

The results of this investigation demonstrate that polynuclear aromatic azomethines derived from *o*-aminoanilines undergo smooth and practically quantitative oxidative cyclodehydrogenation in solution at low temperatures, the experimental conditions being mild enough to preclude thermooxidative degradation or elimination of the reactants' primary amino groups in the course of heteroaromatization. In addition, the aprotic media used in this work belong to the class of neutral solvents most frequently employed in heterocyclic polymer chemistry. The study thus provides conditions suitable for polycyclodehydrogenation of polymeric azomethines comprising a combination of segmental structures of both **1** and **8**, although the observed side reactions involving the tris-Schiff bases and other products require attention. Further work on such macromolecular aspects of the cyclodehydrogenation reaction will be reported elsewhere.

Experimental Section[19]

Solvents and Reagents. All solvents, predried with molecular sieves, type 4A (5A for ethanol), were distilled from suitable dehydrating agents (reduced pressure for DMAC and *N*-methylpyrrolidone). Me_2SO, dried with molecular sieves, was used without redistillation. For use in the preparation of Schiff bases or anaerobic cyclodehydrogenation experiments, solvents were thoroughly degassed and saturated with deoxygenated argon. Benzaldehyde was freshly distilled prior to use. *o*-Phenylenediamine, mp 101 °C, and terephthaldehyde, mp 115–116 °C, were recrystallized from 96% ethanol. 3,3′-Diaminobenzidine (Burdick & Jackson) was purified by repeated recrystallization under Ar from degassed water (pinch of sodium dithionite added) and, ultimately, methanol, mp 176–178 °C. *N,N′*-Terephthalidenedianiline (3) and *N,N′*-dibenzylidene-*p*-phenylenediamine (4), both obtained in ca. 90% yield by condensation of the respective aldehydic and amine reactants in boiling absolute ethanol (1 h) under N_2 and solvent removal under reduced pressure, were recrystallized twice from degassed absolute ethanol, mp 157–159 °C (lit.[20] 166 °C) and 137–138 °C (lit.[21] 138 °C), respectively. 2-Phenylbenzimidazole was prepared by low-temperature condensation of benzaldehyde (0.1 M) with *o*-phenylenediamine (0.1 M) (5 h at −10 °C, 12 h at 20 °C) in degassed absolute ethanol and cyclodehydrogenation of the intermediary *N*-benzylidene-*o*-aminoaniline by stirring the solution for 8 h at 60 °C in the presence of air. Solvent removal and recrystallization from ethanol/benzene furnished the imidazole in 80% yield, mp 291–293 °C (lit.[22] 291, 298–300 °C).

***N,N′*-Terephthalidenebis(*o*-aminoaniline) (1).** To a rapidly stirred and argon-purged solution of *o*-phenylenediamine (1.08 g, 10 mmol) in 10 mL of DMAC was added dropwise, over a period of 3 H, the solution of terephthalaldehyde (0.67 g, 5 mmol) in 25 mL of DMAC at −15 to −17 °C under Ar. The solution was stirred under Ar in the dark for 12 h at −15 °C, followed by 4 h at 0 °C and 1 h at 22 °C. The Schiff base partially crystallized from the solution during this period. The crystals collected after cooling were washed with benzene (3 × 10 mL). A second fraction of 1 crystallized after partial solvent removal in the absence of air (rotating evaporator, 25 °C), and a small third portion was precipitated on further volume reduction by the addition of excess (80 mL) ice water (rapid washing with ethanol and drying under reduced pressure at 20 °C required to prevent hydrolysis), total crude yield 1.46 g (93%). Recrystallization from DMAC at 40 to −8 °C in the absence of air yielded orange-yellow, TLC-pure (R_f 0.7) crystals, mp 210–212 °C (phase change, no clear melting) (lit.[2] 212–214 °C),[21] mol wt 314 (MS).

Anal. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.11; H, 6.10; N, 17.42.

Experiments conducted as described, yet in other aprotic solvents or ethanol, gave similar yields of 1. Under less rigorous conditions of oxygen preclusion (e.g., employing standard-grade N_2 for blanketing), use of ethanol solvent resulted in slightly enhanced intensity of the peak at *m/e* 310 in the mass spectra of all crude fractions.

In several experiments conducted in DMAC, the mother liquor remaining after removal of the second fraction of 1 was evaporated to dryness (rotating evaporator, 25 °C, absence of air). The residual crystalline solids gave mass spectra substantially identical with those of the spontaneously crystallizing fractions except for a slightly increased ratio of I_{310}/I_{314}.

***N,N′*-Dibenzylidene(3,3′-diaminobenzidine) (8).** Under the conditions described for the preparation of 1, a solution of benzaldehyde (1.06 g, 10 mmol) in 25 mL of DMAC was added to 3,3′-diaminobenzidine (1.07 g, 5 mmol) dissolved in 10 mL of MDAC, and the mixture was treated as before. Cooling the red solution to −15 °C produced a minor crystalline fraction of 8 (0.40 g). The main portion of the base, 1.43 g, precipitated upon volume reduction to 15 mL (rotating evaporator, 25 °C) and addition of ice water (100 mL), bringing the total crude yield to 94%. Rapid filtration, washing (ethanol, hexane), and drying (reduced pressure, 20 °C) of the precipitated portion was required to avoid hydrolysis. Recrystallization from DMAC as described for 1 afforded yellow, TLC-pure (R_f 0.7) crystals, mp 164–166 °C (phase change, no clear melting), mol wt 390 (MS).

Anal. Calcd for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; N, 14.35. Found: C, 79.79; H, 5.70; N, 14.31.

Similar yields of 8 resulted from use of other aprotic reaction media or ethanol in place of DMAC. A slight increase in abundance of the peaks at *m/e* 386, 476, and 478 was observed in experiments conducted in ethanol, and the final fractions of product isolated in such experiments tended to be contained with minute quantities of several unknown compounds (TLC).

1,4-Di(benzimidazol-2-yl)benzene (2) from 1. In a typical oxidative cyclodehydrogenation experiment (Table III, expt 1), the solution of 1 (0.200 g, 0.64 mmol) in 10 mL of DMAC was vigorously agitated in air for 3 h at 60 °C by means of an excentrally tumbling (400 rpm) magnetic stirring bar (method A). Predried glassware was used, and the exit neck was fitted with a drying tube. The solution was allowed to stand for 15 h at −15 °C, whereupon 0.07 g of 2 crystallized. Another 0.06 g of crystalline product separated after volume reduction to 5 mL and cooling to −5 °C. A third portion of 2 was precipitated from the filtrate by the addition of water (50 mL), bringing the total crude yield to 0.185 g (93%). The cream-colored compound was recrystallized from DMAC, to give almost colorless fine crystals, TLC pure (R_f 0.2), infusible up to 300 °C (lit.[13] 472 °C), mol wt 310 (MS).

Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.35; H, 4.76; N, 17.98.

In a similar manner, reactions were conducted in other aprotic solvents, as well as in absolute ethanol (Table III). In ferric chloride catalyzed experiments, $FeCl_3$ (1.0 mol % of 1) was added from a 0.05 M stock solution in the same solvent in which the reactions were performed. In a number of experiments, oxidation was accomplished by introducing a rapid stream of predried air (120 L/h) into the solutions of 1 (method B) under otherwise unchanged conditions. In several runs conducted in DMAC or ethanol, the final mother liquors were evaporated to dryness under reduced pressure. The residues, 5–10 mg, constituted 2 contaminated with 4-(benzimidazol-2-yl)-benzaldehyde (R_f 0.4, *m/e* 222);[23] no TLC spots or mass peaks were found that would indicate the presence of compounds resulting either from elimination of NH_2 or from oxidative coupling (formation of –N=N–).

2,2′-Diphenyl-5,5′-bibenzimidazolyl (9) from 8. The following procedure, describing expt 5, Table III, exemplifies the oxidative cyclodehydrogenation of 8. The solution of 8 (0.200 g, 0.51 mmol) in 10 mL of DMAC was agitated in air for 3 h at 60 °C as described for expt 1. The clear solution was reduced in volume to 5 mL, and water (80 mL) was added. The precipitated, grayish-white product, washed with water and dried (0.175 g, 89%), was recrystallized from ethanol/water. The TLC-pure (R_f 0.3) 9 was infusible up to 300 °C (lit. typically[13] 337 °C), mol wt 386 (MS).

Anal. Calcd for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.40; H, 4.91; N., 14.25.

Other experiments were conducted as summarized in Table III. As before, the use of method B involved passing dry air through the solution at a rate of 120 L/h, and in the ferric chloride catalyzed reactions the catalyst was added from a 0.05 M stock solution.

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Registry No.—**1a**, 61990-56-5; **2**, 1047-63-8; **3**, 61990-57-6; **4**, 61990-58-7; **8a**, 62045-63-0; **9**, 15179-41-6; *o*-phenylenediamine, 95-54-5; terephthaldehyde, 623-27-8; benzaldehyde, 100-52-7; 3,3′-diaminobenzidine, 91-95-2.

References and Notes

(1) E. W. Neuse, *Chem. Ind. (London)*, 315 (1975).

(2) (a) The compound was first prepared[2b] from the two components in boiling ethanol (95% yield). In our hands, this procedure afforded the base appreciably contaminated with cyclodehydrogenated material in addition to trisubstituted products **5** and successor species. See text. (b) F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 1722 (1950).

(3) K. H. Grellmann and E. Tauer, *J. Am. Chem. Soc.*, **95**, 3104 (1973); *Tetrahedron Lett.*, 1909 (1967).

(4) (a) Contrasting with the *o*-aminoanils, the corresponding anils possessing the more acidic mercapto group as an ortho substituent generally exist as the ring-tautomeric thiazoline isomers.[3,4b–e] (b) R. G. Charles and H. Freiser, *J. Org. Chem.*, **18**, 422 (1953). (c) P. E. Miller, G. L. Oliver, J. R. Dann, and J. W. Gates, Jr., *ibid.*, **22**, 664 (1957). (d) L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, **1**, 365 (1967). (e) F. J. Goetz, *J. Heterocycl. Chem.*, **5**, 509 (1968).

(5) (a) A. F. McDonagh and H. E. Smith, *Chem. Commun.*, 374 (1966); (b) A. van Putten and J. W. Pavlik, *Tetrahedron*, **27**, 3007 (1971).

(6) (a) In CF_3COOH solution, the azomethine proton signals of both **1** and **8**, as expected,[6b] emerge at a position shifted downfield by some 0.7 ppm (Table I), yet in intensities 20–30% lower than calculated for structures **a**. Although much of this signal attenuation probably results from hydrolysis (peak intensity slowly decreasing with time), the possibility of partial tautomerization to structures **b**, prompted by the amino nitrogen atom's decreased basicity upon protonation, cannot be ignored. Yet the spectra of both compounds lack conclusive evidence for the presence of **b**, as the signals of the rapidly exchanging protons of the NH_2 (forms **a**) and NH (forms **b**) groups both are expected to vanish in this acidic medium, and the tertiary CH protons in **b**, which should resonate at 7–7.5 ppm, may well give signals submerged in the aromatic resonances in this region. (b) M. Kurihara, H. Saito, K. Nukada, and N. Yoda, *J. Polym. Sci. Part A-1* **7**, 2897 (1969).

(7) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Am. Chem. Soc.*, **93**, 586 (1971); M. El-Aasser, F. Abdel-Halim, and M. A. El-Bayoumi, *ibid.*, **93**, 590 (1971).

(8) El-Bayoumi et al.[7] assigned the 260-nm band in benzylideneaniline to a transition to a charge-transfer state in which the C=N system acts as the electron acceptor and the benzal ring as the donor. LCAO–MO calculations[9d] indicate, however, that negative charge is accumulated on the benzal ring in the excited state; moreover, the band undergoes a pro-

nounced red shift on para substitution of that ring by the withdrawing NO_2 group.[9b] Both findings, coupled with the band's comparative intensitivity to solvent effects observed both in benzylideneaniline[7] and in **1** (Table II), render a charge transfer of the type proposed[7] rather unlikely as the cause of this absorption. We prefer to assign the band to a $\pi \rightarrow \pi^*$ transition originating from the highest occupied π level of the $N{=}CC_6H_4C{=}N$ unit. Such assignment accords with the band's bathochromic (and hyperchromic) shift on achieving coplanarity of the molecule by protonation or ring closure to the imidazole system.[9c]

(9) (a) With respect to noncoplanarity of the outer ("aniline") rings with the $N{=}CHC_6H_4CH{=}N$ segment, the same arguments (conjugation of the aniline rings' π systems with the lone-pair electrons on N)[7,9b] hold as in the case of *N*-benzylideneaniline, in which rotation of the *N*-phenyl ring out of the plane of the benzalimino chromophore has been established.[5b,7,9c–e] It is only on heteroaromatization (process **1** → **2**) that an approximate coplanarity of the molecule's benzene rings can result. (b) V. A. Ismailski and E. A. Smirnov, *Zh. Obshch. Khim.*, **26**, 3389 (1956). (c) P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962). (d) W. F. Smith, *ibid.*, **19**, 445 (1963). (e) H. B. Bürgi and J. D. Dunitz, *Chem. Commun.*, 472 (1969); *Helv. Chim. Acta*, **54**, 1255 (1971).

(10) In the KBr spectra of several crude or too rapidly recrystallized products we found the C=N band in reduced intensity; at the same time, two new nonbonded and bonded N–H stretching peaks appeared at 3440 and 3350 cm^{-1} in addition to the aforementioned two bands of these origins. This suggests that product separating from solution under nonequilibrium conditions may indeed contain some imidazoline tautomers.

(11) The facile formation of *N*-benzyl substituted benzimidazoles (aldehydines) from bis-Schiff bases of aromatic *o*-diamines is on record: J. B. Wright, *Chem. Rev.*, **48**, 397 (19651).

(12) (a) The oxidative heteroaromatization of *o*-aminoanils to benzimidazoles has been achieved in the presence of cupric salts,[12b] lead tetraacetate,[12c] and active MnO_2,[12d] and some mechanistic implications have been discussed.[12e] These methods, however, requiring large quantities of oxidants and inefficient separation techniques for the imidazole products, give inferior yields and are not adaptable to polymerization chemistry. (b) R. Weidenhagen, *Chem. Ber.*, **69**, 2263 (1936); R. Weidenhagen and U. Weedon, *ibid.*, **71**, 2347 (1938); R. Weidenhagen and G. Train, *ibid.*, **75**, 1936 (1942). (c) F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 2971 (1949). (d) I. Bhatnagar and M. V. George, *Tetrahedron*, **24**, 1293 (1968). (e) W. G. Nigh in "Oxidation in Organic Chemistry", W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., 1973, p 59.

(13) R. A. Gaudiana and R. T. Conley, *Polym. Lett.*, **7**, 793 (1969).

(14) (a) The product most likely is a mixture of two positional isomers. Electron density determinations by MO calculations[14b] show the two *m*-amino groups in the tetramine starting compound to be somewhat more basic than the two *p*-amino groups. The calculated difference in electronic charge (1.862 vs. 1.856) is, however, not significant enough to justify a prediction of predominance of the 3,3′-di(benzylideneimino) compound over the 4,4′ isomer. (b) D. A. Bochvar, I. V. Stankevich, V. V. Korshak, and A. L. Rusanov, *Dokl. Akad. Nauk SSSR*, **184**, 95 (1969).

(15) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(16) An attempt to differentiate between solid **a** and **b** by N(1s) x-ray photoelectron spectroscopy failed, only a single, albeit broad (width at half-height 3.0–3.5 eV) band (E_b = 399.5 ± 0.5 eV) being shown by both **1** and **8**. The binding energies of $\mathbf{NH_2}$ and **NH**, on the one hand, and of $CH{=}\mathbf{N}$, on the other, in these compounds obviously are within the experimental error limits of the method. Accordingly, E_b values of 398.9, 399.5, and 399.2 eV were found respectively for **3**, **4**, and *o*-phenylenediamine. 2-Phenylbenzimidazole gave a peak corresponding to E_b = 400.0 eV.

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(18) (a) Although conventionally[13,17] represented by structure **9** comprising a 5,5′ linkage between the two benzimidazole units, the compound in the solid state almost certainly is a mxture of tautomers in which the benzazole groups are connected via 5,5′, 6,6′, and 5,6′ bonds. In (neutral) solutions, however, the NH protons of benzimidazoles are known[18b] to undergo rapid 1,3-exchange, rendering such distinctions meaningless. (b) H. A. Staab and A. Mannschreck, *Tetrahedron Lett.*, 913 (1962).

(19) Melting points, uncorrected, were taken in sealed capillaries. IR spectra were taken on a Perkin-Elmer 521 spectrophotometer. ^{1}H NMR spectra were obtained with a Hitachi Perkin-Elmer R20 NMR spectrometer operating at 60 MHz; chemical shifts, δ, are in parts per million relative to internal Me_4Si. Electronic absorption spectra were recorded on a Unicam SP1800 spectrophotometer. Mass spectra (MS) were scanned with a Varian-MAT CH5 mass spectrometer at 70 eV ionizing voltage. N(1s) x-ray photoelectron spectra (Mg Kα radiation) were obtained at −100 °C with the aid of an AEI Scientific ES200 electron spectrometer; peaks were calibrated by reference against internal NH_4NO_3 [$E_{b(NH_4)}$ = 402.3 eV]; precision, ±0.2 eV. Thin layer chromatography (TLC) was performed on precoated SiO_2 plates, Merck silica gel 60 F_{254}, in 4:5 acetone/hexane. Microanalyses were by Robertson Laboratory, Florham Park, N.J.

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(22) (a) H. Franzen, *Chem. Ber.*, **40**, 903 (1907); (b) W. Wrasidlo and H. H. Levine, *J. Polym. Sci., Part A-2*, 4795 (1964).

(23) A sample isolated from large-scale runs by column chromatography (0.5%) had mp 255–260 °C dec; ν_{CO} (KBr) 1703 cm^{-1}; λ_{max} (DMAC) 341 nm; *m/e* 222 (P^+), 193 ($P^+ - H - CO$). The aldehyde probably resulted from partial hydrolysis of **1** and subsequent cyclodehydrogenation.

Palladium-Catalyzed Reductions of Halo- and Nitroaromatic Compounds with Triethylammonium Formate

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Aromatic halides and nitro compounds are readily reduced at 50–100 °C to hydrocarbons and amines, respectively, with triethylammonium formate in the presence of either palladium on charcoal or a soluble triarylphosphine–palladium acetate catalyst. Aryl halides are reduced to deuterio derivatives with dideuterioformic acid.

The reducing ability of alkylammonium formates in the palladium-catalyzed reductive dimerization of conjugated dienes has been noted by Roffia et al.[1] In subsequent studies we also became interested in this reducing system[2] and now report applications of it to the reduction of aromatic halides and nitro compounds.

Results and Discussion

Aryl Halides. We initially employed a soluble catalyst, a combination of palladium acetate with a triarylphosphine, for the reductions with triethylammonium formate. We later found that palladium on charcoal was often as useful and, of course, had the advantage of being easily removable from the reaction mixture. The results of these experiments with organic halides are shown in Table I.

It appears that aromatic halide groups may be removed with extreme ease by the palladium-catalyzed reduction with triethylammonium formate at 50–100 °C. The other products of the reaction are the triethylamine hydrohalide and carbon dioxide. Other reducible groups such as nitrile and nitro are not reduced as readily as the halo substituent. Double bonds are apparently reduced at rates comparable to those with the chloro group, and mixtures resulted from the reduction of